1

The Chemistry of Gold

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1.1

Introduction

1.1.1

History

Gold was discovered as shining yellow nuggets and is undoubtedly the first metal known to early civilizations. The symbol derives from the Latin word *aurum*, which is related to the goddess of dawn, Aurora. Early civilizations equated gold with gods and rulers, and gold was sought in their name and dedicated to their glorification. Humans almost intuitively attribute a high value to gold, associating it with power, beauty, and the cultural elite. And since gold is widely distributed all over the globe, it has been perceived in the same way throughout ancient and modern civilizations everywhere.

Archeological digs suggest gold was first used in the Middle East where the first known civilizations developed. Experts in the study of fossils have observed that pieces of natural gold were found in Spanish caves used by Paleolithic Man in about 40 000 BC. The oldest pieces of gold jewellery were discovered in the tombs of Queen Zer of Egypt and Queen Pu-abi of Ur in Sumeria and date from the third millennium BC. Most Egyptian tombs were raided over the centuries, but the tomb of Tutankhamun was discovered undisturbed by modern archeologists. The largest collection of gold and jewellery in the world included a gold coffin whose quality showed the advanced state of Egyptian craftsmanship and goldworking (second millennium BC). The Persian Empire, in what is now Iran, made frequent use of gold in artwork as part of the religion of Zoroastrianism. Persian goldwork is most famous for its animal art, which was modified after the Arabs conquered the area in the seventh century AD. Gold was first used as money in around 700 BC, when Lydian merchants (western Turkey) produced the first coins. These were simply stamped lumps of a 63% gold and 27% silver mixture known as "electrum."

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Nevertheless, gold as a metal has been omnipresent since the dawn of civilisation and its chemistry has played a minor role in history. Initially, all that was known of its chemistry was its concentration, recovery, and purification. Moreover, compounds, such as tetrachloroauric acid or salts of the anions $[Au(CN)_2]^-$ or $[Au(CN)_4]^-$, were very important because they were intermediates in the recovery of the metal. The chemistry of gold was merely regarded as an art to recover and convert gold metal into all possible forms of ornamental, monetary, anticorrosive or electrical usage. It is therefore no surprise that the chemistry of gold, which is so clearly dominated by the metallic state, remained undeveloped for so long. The associated development of an old handicraft, with all its secrets, into a field of research based on technology is a good example of how gold chemistry has finally matured into an advanced branch of science with a significant bearing on applications in many fields [1].

1.1.2
Chemical and Physical Properties

What is it about gold that makes it so attractive and so useful? Gold is not very hard; a knife can easily scratch pure gold and it is very heavy or even dense for a metallic mineral. Some of the other characteristics of gold are ductility, malleability and sectility, meaning it can be stretched into a wire, pounded into other shapes, and cut into slices. Gold is the most ductile and malleable element on our planet. It is a great metal for jewellery because it never tarnishes.

The color and luster of gold are what make this metal so attractive. Gold is found as the free metal and in tellurides. It is widely distributed and almost always associated with pyrite or quartz. It is found in veins and in alluvial deposits. Gold also occurs in seawater in concentrations of $0.1–2\,\mathrm{mg\,ton^{-1}}$, depending on the location of the sample. In the mass, gold is a yellow-colored metal, although it may be black, ruby, or purple when finely divided. One ounce of gold can be beaten out to $300\,\mathrm{ft^2}$. Gold is a good conductor of electricity and heat. It is not affected by exposure to air or to most reagents. It is inert and a good reflector of infrared radiation. Gold is usually alloyed to increase its strength. Pure gold is measured in troy weight, but when gold is alloyed with other metals the term *karat* is used to express the amount of gold present.

Gold has an electrochemical potential which is the lowest of any metal. This means that gold in any cationic form will accept electrons from virtually any reducing agent to form metallic gold. It is the most electronegative of all metals, which once again confirms its noble character. Moreover, although the electron affinity for metals is not usually included in textbooks for gold; the process from gold(0) to gold(–I) can be easily accomplished, and it has, in fact, been known since 1930.

1.1.3
Theoretical Considerations

The electronic configuration of gold(0) is $5d^{10}6s^1$; for gold(I) it is $5d^{10}6s^0$ and for the gold(–I) anion it is $5d^{10}6s^2$. These configurations would justify the relative stability of gold(I) compounds, with 10 electrons in a closed set of 5d orbitals, or even, to some

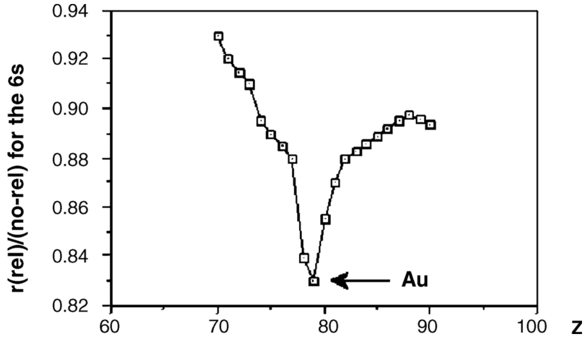


Figure 1.1 Ratio of r(rel)/r(non-rel) versus atomic number for the 6s electrons.

extent, the formation of the aurate anion, but they do not allow us to understand the predominance of the metallic form.

Post-lanthanide elements contain a large number of protons in their atomic nuclei; therefore, the electrons move in a field of very high nuclear charge, which leads to velocities approaching that of light and, consequently, they have to be treated according to Einstein's theories of relativity. This is particularly true for electrons that are in s orbitals, which have wavefunctions that correspond to a finite electron density at the atomic nucleus, but it is less important for electrons in p or d orbitals. Electrons moving at a speed close to the speed of light cannot be treated in terms of classical physics, but they are assigned a relativistic mass that is larger than the mass of the electron at rest. The effect on the 6s electrons, in the post-lanthanide elements, is that the orbital radius is contracted and the distance of the electron from the nucleus is reduced. Figure 1.1 shows a plot where the ratio of the relativistic radius of the valence electrons to their non-relativistic radius is presented as a function of atomic number. It is clear that this ratio strongly deviates from unity as Z increases, and it reaches a pronounced local minimum for gold. Thus, without making any further special assumptions, this theoretical approach leads to the conclusion that gold actually occupies a unique position among the elements.

There are several consequences of this effect in gold chemistry:

1. The color of gold. Gold has an absorption beginning at 2.4 eV, attributed to a transition from the filled 5d band to the Fermi level (essentially the 6s band). It therefore reflects red and yellow light and strongly absorbs blue and violet. The analogous absorption for silver, however, lies in the ultraviolet, at around 3.7 eV.

2. A marked reduction in the lengths of covalent bonds involving gold atoms is often found and the covalent radius of gold is smaller than that of silver. Schmidbaur has recently confirmed this in the isomorphous di-coordinated complexes $[M(PMes_3)_2]BF_4$ (M = Ag, Au; Mes = mesithyl) [2]. The estimated covalent radii for silver and gold are 1.33 and 1.25 Å, respectively, so di-coordinated gold is smaller than silver by about 0.09(1) Å.

3. In gold, more than in silver, both states are now available for bonding. The closed shell $5d^{10}$ is no longer chemically inert and can interact with other elements, that is, with other gold atoms in molecules or clusters. Bonding between two gold(I) centers with equal charge and a closed shell $5d^{10}$ configuration can also be rationalized, and this is a very difficult fact to explain in terms of classical bonding. The metal atoms approach each other to an equilibrium distance of between 2.7 and 3.3 Å. This range includes the distance between gold atoms in gold metal and approaches, or even overlaps with, the range of distances established for the few authentic Au–Au single bonds. Schmidbaur has called this effect *aurophillic attraction* or *aurophilicity* [3].

4. The small difference in energy between the s, p and d orbitals leads to the efficient formation of linear two-coordinate complexes in gold(I). However, silver(I) prefers the formation of three- and four coordinate derivatives.

5. The destabilization of the 5d orbitals allows the easy formation of the oxidation state III in gold to be explained; this is almost absent in silver; and the stabilization of the 6s orbitals explains the formation of the gold(–I), oxidation state, which is unknown in silver.

Theoretical calculations have played a key role in understanding the origin of these differences and also in the development of gold and silver chemistry. Bonding between closed-shell atoms was successfully traced in several early theoretical investigations by extended Hückel quantum chemical calculations [4–7]. Based on the hybridization concept, the nature of the bonding interaction could be qualitatively rationalized in the language of chemists. The introduction of relativistic effects in more advanced calculations has shown that bonding between closed-shell metal atoms or ions may be strongly enhanced by these effects [8–18]. Since relativistic effects have been known to reach a local maximum for gold in particular, aurophilicity was accepted as a logical consequence of these contributions. In fact, aurophilic bonding is considered as an effect based largely on the electron correlation of closed-shell components, somewhat similar to van der Waals interactions but unusually strong [15, 16]. All these studies have consistently shown that calculations will only reproduce the attractive forces between the gold atoms very well if relativistic affects are included.

1.2
Chemistry

Since the early 1980s, the chemistry of gold has undergone continuous expansion; not only well-established areas of research have developed, but also new innovative approaches have enabled great diversification of the fields of research. The metal and its complexes also have special characteristics that make them suitable for several uses. Gold possesses special characteristic features that make it unique, such as high chemical and thermal stability, mechanical softness, high electrical conductivity, and beautiful appearance. All these attributes gave rise to many relevant applications. For example, gold is an essential element for nanoscale electronic devices because it is resistant to oxidation and mechanically robust. The well-known elegant red color in Venetian crystal glass stems from surface plasmon absorption of blue light by gold nanoparticles a few tens of nm in size. Gold compounds have been used successfully for the treatment of rheumatoid arthritis [19–21]. Gold is also an outstanding element for use as a heterogeneous catalyst operating at ambient temperature because it is catalytically active at low temperature (200–350 K compared with Pd and Pt at 400–800 K) [22]; in the last few years several uses in homogeneous catalysis have been reported [23–26].

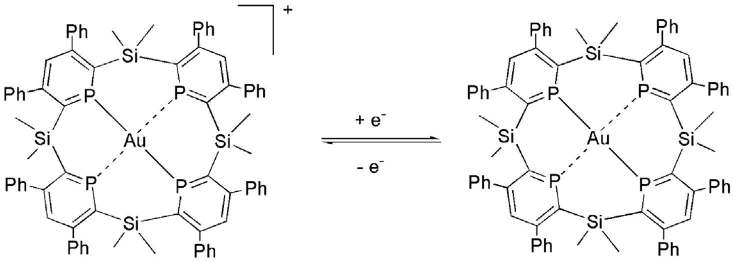
1.2.1
Gold(-I) Compounds

Many of the peculiarities of the chemical and physical properties of gold are due to its relativistic effects, including the high electron affinity which explains the high propensity of gold to adopt the negative oxidation state $-$I. The binary alkali metal aurides RbAu and CsAu have been known for about 50 years [27, 28], but the ternary auride oxides M_3AuO (M = K, Rb, Cs) and the aurideaurates Rb_5Au_3O and M_7Au_5O (M = Rh, Cs) have been discovered only recently [29–32].

The anionic character of gold is also emphasized by its similarities to the heavier halides Br^- and I^-. Using a macroreticular ion exchange resin with a high affinity toward cesium ions in liquid ammonia, it has been possible to exchange cesium for thetramethylammonium and the first compound of negatively-charged gold with a non-metal cation was thus isolated, $NMe_4{}^+Au^-$ [33]. An estimation has been made of the auride radius as 1.9 Å, which is very similar to the bromide anion; in fact, the compound crystallizes isotypically to $(NMe_4)Br$. CsAu dissolves in liquid ammonia forming a yellow solution and, when ammonia is removed, CsAu is not recovered directly. Instead, a new, intense blue solid crystallizes which has the composition $CsAu{\cdot}NH_3$ [34]. The crystal structure exhibits features characteristic of low-dimensional systems. Slabs of overall composition CsAu are separated by single NH_3 layers. The gold atoms are shifted towards one another forming zig-zag chains with Au$\cdots$Au separation of 3.02 Å (4.36 Å in CsAu). This auridophilic attraction takes place between $d^{10}s^2$ anions but surprisingly yields a similar distance to the aurophilic attraction in d^{10} cations. The theoretical nature of this effect is not clear. Both the dispersion effects and the net bonding, resulting from partial oxidation from the top of the 6s band, could play a role. The observed Mössbauer isomer shift at gold (CsAu 7.00 mm S^{-1}, RbAu 6.70 mm S^{-1}, $CsAu{\cdot}NH_3$ 5.96 mm S^{-1}, Au -1.23 mm S^{-1}) does not show a full -1 auride charge and means the latter is still a possibility [35]. Following the concept of similarity between gold(–I) and the halides, since the latter are good acceptors in hydrogen bonding systems, complexes with hydrogen bonds involving Au^- ions as acceptors should be possible. The first complex in which neutral ammonia molecules act as donors and auride anions as acceptors has been found in the complex $[Rb([18]crown\text{-}6)(NH_3)_3]Au{\cdot}NH_3$ [36].

1.2.2
Gold(0) and Gold Clusters

The synthesis of silicalix[n]phosphinines, a new class of macrocycles incorporating sp^2-hybridized phosphorus atoms, has enabled the preparation of gold(0) macrocycles [37]. These ligands have an adequate balance between σ-donating and π-accepting properties and can then act as a macrocyclic equivalent of carbonyl groups. The reaction of these macrocycles with $[AuCl(SMe_2)]$ in the presence of $GaCl_3$ yields the complexes $[AuL][GaCl_4]$. The electrochemical reduction of one of these derivatives enables the synthesis of the gold(0) compound (Equation 1.1).



(1.1)

However, there is an important class of gold compounds in which the formal oxidation state is intermediate between 0 and +1. They can be homo- or heteronuclear compounds and the nuclearity can range from 4 to 39 [38–41]. These compounds are available through several synthetic routes, which are mainly:

1. Reaction of a suitable gold(I) precursor such as $[AuX(PR_3)]$ (X = halide, SCN, NO_3) or $HAuCl_4$ with a reducing agent such as $NaBH_4$, CO, $Ti(\eta\text{-}C_6H_5Me)_2$, and so on, a representative example is given in Equation 1.2 [42]:

$$[Au(NO_3)(PPh_3)]+NaBH_4 \rightarrow [Au_9(PPh_3)_8](NO_3)_3 \quad (1.2)$$

2. Treatment of gold vapor with phosphine ligands (Equation 1.3) [43]:

$$Au(g)+dppm \rightarrow [Au_5(dppm\text{-}H)(dppm)_3](NO_3)_2 \quad (1.3)$$

3. Reactions of gold clusters with other ligands or metal complexes. These types of reactions can progress with or without change in the metal skeleton and in the latter with an increase or decrease in nuclearity (Equations 1.4 and 1.5) [44, 45]:

$$[Au_9(PPh_3)_8]^{3+}+Bu_4\ Nl \rightarrow [Au_8\ l(PPh_3)_6]^{+} \quad (1.4)$$

$$[Au_9(PPh_3)_8]^{3+}+3[Au(C_6F_5)_2]^{-} \rightarrow [Au_{10}(C_6F_5)_4(PPh_3)_5] \quad (1.5)$$

4. Nucleophilic addition, elimination, and substitution reactions in which the cluster core remains intact (Equation 1.6) [46, 47]:

$$[Au_8(PPh_3)_6]^{2+}+2PPh_3 \rightarrow [Au_8(PPh_3)_8]^{2+} \quad (1.6)$$

The bonding in gold cluster molecules has been interpreted using free electron models based on Stone's tensor surface harmonic theory [48, 49]. High similarity has

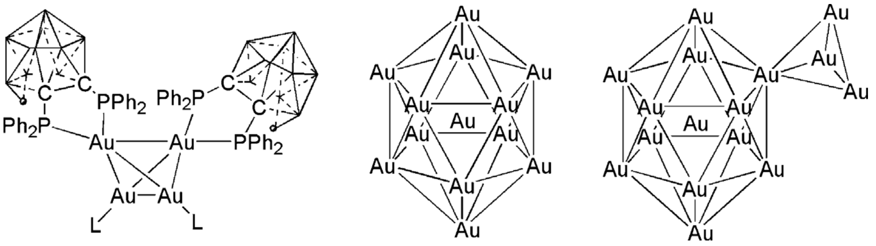


Figure 1.2 Gold clusters representative of Au_4, Au_{13} and Au_{16} cores.

been observed between alkali metals and gold in the spectra of molecular orbitals when they form clusters, and the primary bonding and antibonding interactions result from the overlap of the s valence orbitals. For gold, the 5d orbitals are core-like and only hybridize slightly with the 6s, where the 6p valence orbitals are too high-lying to contribute significantly to the bonding. The geometries have been classified as (i) spherical polyhedral clusters characterized by a total of $12n+8$ valence electrons (n is the number of peripheral gold atoms); and (ii) toroidal or elliptical polyhedral clusters characterized by a total of $12n+6$ valence electrons [50].

All the nuclearities from 4 to 13 gold atoms are known in homonuclear clusters, the latest is a regular icosahedron with a central gold atom [51, 52]. This icosahedron may add in one of the corners three more gold atoms, forming a pendant tetrahedron and thus resulting in a 16-gold-atom cluster [53]. Some representative examples are shown in Figure 1.2.

The largest structurally-characterized gold cluster is $[Au_{39}Cl_6(PPh_3)_{14}]Cl_2$ [54], which has a structure related to a hexagonal packed geometry with 1 : 9 : 9 : 1 : 9 : 9 : 1 individual layers of gold atoms (Figure 1.3).

Several heteronuclear clusters are known and with early transition metals based on carbonyl clusters [55]. With the platinum group metals, the clusters $[M(AuPPh_3)_8]^{2+}$ ($M = Pd$, Pt), synthesized by the reduction of mixtures of $[M(PPh_3)_4]$ and $[Au(NO_3)(PPh_3)]$, have been thoroughly studied [56–58]. They undergo several types of reactions such as nucleophilic additions ranging from 16-electron to 18-electron clusters, which induce a change in the geometry from toroidal to spheroidal, as shown in Figure 1.4 [59, 60].

The most outstanding examples of heteronuclear gold clusters are the series of Au–Ag supraclusters whose metal frameworks are based on vertex-sharing. In the structure of these compounds, the basic building block is the 13-metal atom (Au_7Ag_6) icosahedra. These high nuclearity clusters have been termed “clusters of clusters” and they follow a well-defined growth sequence by successive additions of

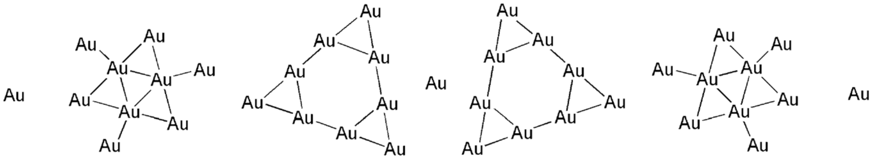
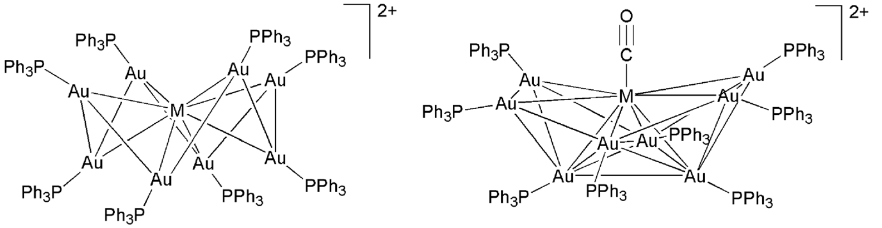


Figure 1.3 Layers of the cluster $[Au_{39}Cl_6(PPh_3)_{14}]Cl_2$.



$[M(AuPPh_3)_8]^{2+}$ M = Pd, Pt $[M(CO)(AuPPh_3)_8]^{2+}$

Figure 1.4 Structure of the 16- and 18-electron clusters.

icosahedral units via vertex sharing. The first member of this vertex-sharing poly-icosahedral cluster series is the 25-metal-atom cluster, $[(Ph_3P)_{19}Au_{13}Ag_{12}Br_8]^+$ [61, 62], whose metal core can be considered as two icosahedra sharing a common vertex (Figure 1.5). They have been obtained by reducing a mixture of $[AuX(PR_3)]$ and $[AgX(PR_3)]$ with $NaBH_4$. The growth sequence by successive additions of icosahedral units via vertex-sharing has been used to obtain the triicosahedral $[(p\text{-TolP})_{12}Au_{18}Ag_{20}Cl_{14}]$ [63], and the tetraicosahedral $[(p\text{-TolP})_{12}Au_{22}Ag_{24}Cl_{10}]$ [64]. The structure of the triicosahedral clusters is three M_{13} atom (Au_7Ag_6) Au-centered icosahedra sharing three Au vertices in a cyclic manner (Figure 1.6).

1.2.3
Gold Nanoparticles and Nanoclusters

One area related to gold clusters is the field of nanoparticles and nanoclusters. These materials have actually been known since ancient times when they were used for their esthetic appeal and also for their therapeutic properties in the form of colloidal gold. In recent decades, the field of nanoparticle research has emerged and in-depth research has dealt with the properties and potential applications of these systems.

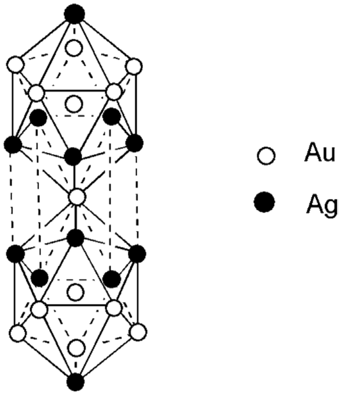


Figure 1.5 Core of $[(Ph_3P)_{19}Au_{13}Ag_{12}Br_8]^+$.

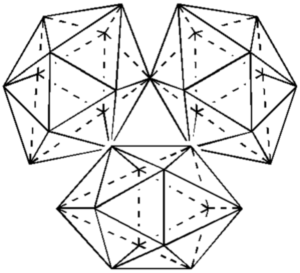
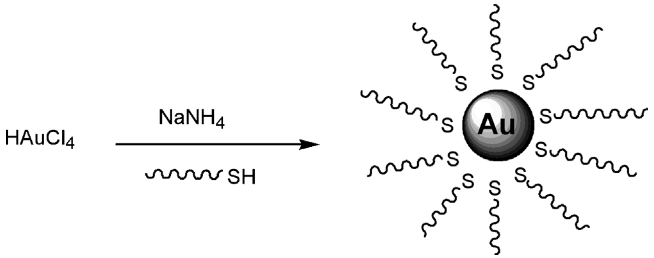


Figure 1.6 Core of the triicosahedral clusters.

Gold nanoparticles have dimensions in the range 1 nm to 1 μm, although there is often no clear demarcation between a nanoparticle and a non-nanoparticle system. For example, the 39-atom gold cluster has dimensions in this range and could therefore be considered to be a nanoparticle. However, a well-defined large-atom aggregate (X-ray characterization) is usually classified as a cluster. The compound $[Au_{55}Cl_6(PPh_3)_{12}]$, synthesized from $[AuCl(PPh_3)]$ by reduction with B_2H_6 [64, 65], is usually referred to as a cluster, although the crystal structure is not available and it can be classified as nanoparticles with dimensions of 1.4 ± 0.4 nm. Many attempts have been made to characterize this gold cluster and its physical properties and reactivity have been widely studied [66].

The synthetic methods used to produce gold nanoparticles range from the reduction of $HAuCl_4$ with citrate in water, reported by Turkkevitch in 1951 [67], to the reduction of Au(III) complexes and stabilization with different ligands from which the thiolates of different chain lengths [68] are the most popular (Equation 1.7), although others such as xanthates, disulfides, phosphines, isocyanide, and so on, have been used. Other techniques such as microemulsion, copolymer micelles, seeding growth, and so on, have also been utilized to synthesize gold nanoparticles [69]. With the discovery of the self-assembled monolayers (SAMs) absorbed onto metal colloids, the surface composition of gold nanoparticles can be modified to contain a variety of functional groups and even mixtures of functional groups.



(1.7)

These Au nanoparticles, protected by a monolayer of thiolated ligands, display interesting properties, such as single-electron charging and molecule-like HOMO–LUMO energy gaps, and can be used in optical and chemical sensing [70, 71]. Their physicochemical properties are closely related to their size and size distribution. Therefore, the ability to synthesize nanoparticles in a size-controlled manner has been one of the goals of materials science. Consequently, new procedures have been developed and one of the most successful synthetic routes consists in the reductive decomposition of polymeric Au(I)-SR complexes [72, 73]. Many clusters of different nuclearities have been obtained by this or other methods, such as Au_{25}(glutathione)$_{18}$ [74], $Au_{38}(SPhX)_{24}$ [75], $Au_{75}(SC_6H_{13})_{40}$ [76] obtained by reduction of $[Au_{55}Cl_6(PPh_3)_{12}]$, or even clusters of higher nuclearity such as the Au_{140} monolayer protected cluster [77].

Much research has also been carried out into determining whether highly ordered clusters with cage-like structures are possible for gold. The closest match to a cage-like cluster is the bimetallic icosahedron W@Au_{12}, which was first predicted by Pyykkö and Runeberg [78] and later synthesized by Li *et al.* [79]. However, the pure icosahedral form of Au_{12} is unstable and must be stabilized by the endohedral W atom. Theoretical studies of gold fullerenes are also scarce [80] but a highly stable icosahedron Au_{32} fullerene was predicted based on DFT calculations [81] and recently an alternative icosahedral Au_{42} fullerene cage has been shown to be competitive energetically [82]. Gold nanotubes are a synthetic reality [83] and platonic gold nanocrystals have also been prepared through careful growth-rate regulation in different crystallographic directions [84]. These nanocrystals have the perfect symmetry for 2D and 3D packing and therefore could enable the rational tuning of their optical, electrical, and catalytic properties.

1.2.4
Gold(I) Complexes

The chemistry of gold(I) species is by far the most developed. Many monoclear, dinuclear or, in general, polynuclear derivatives with several types of ligands have been described. It is difficult to say which type of complexes are more stable and important for gold, those of phosphine or polyphosphine ligands have been studied in depth, as have organometallic gold complexes or species with chalcogenolate or chalcogenide ligands. In this chapter on the chemistry of gold, the most important types of gold(I) complexes for synthetic applications, structural patterns, properties, and so on, will be discussed.

1.2.4.1 Mononuclear [AuXL], $[AuL_2]^+$ or $[AuX_2]^-$ Complexes

The chemistry of gold(I) complexes is dominated by linear two-coordinate complexes of the form [AuXL], which, despite being known for a long time, have returned to prominence because they display short intermolecular gold–gold contacts that associate the monomeric units into dimers, oligomers or even uni- and multidimensional polymers. These aurophilic interactions, together with other secondary bonds such as hydrogen bonds, play a role in determining the solid state arrangement of Au(I) complexes [85]. The tendency of molecules containing an Au$\cdots$Au interaction to crystallize with more than one molecule in the asymmetric unit ($Z' > 1$) has been calculated [86]. This behavior is believed to be related to the size of the differential of the two substituents. If the two ligands have a disparity in size, the $Z' > 1$ is favored, whereas the ligands of equivalent size have a tendency to form structures with $Z' > 1$.

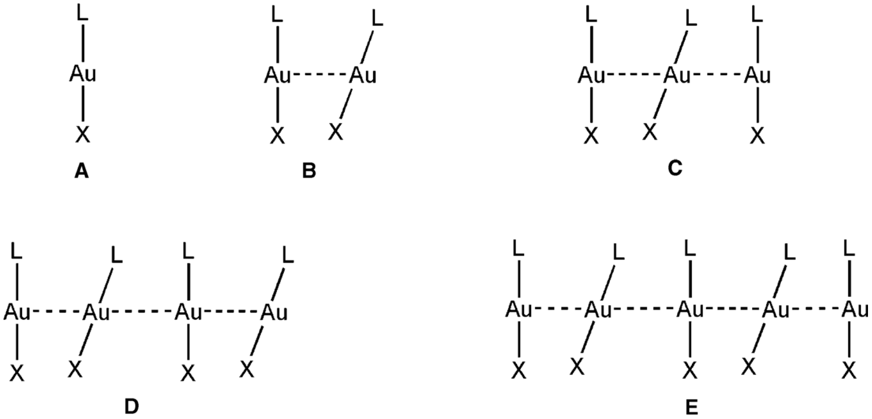


Figure 1.7 Association of [AuXL] complexes in dimers (B), trimers (C), tetramers (D) or chain polymers (E) through short gold–gold contacts.

This fact can be easily seen in neutral complexes of the type [AuXL], which have been prepared for a great variety of donor ligands. The neutral ligand is mainly a phosphine, arsine, isocyanide, carbine, ylide, amine, and so on, and the anionic moiety can be an halide, alkyl or aryl, chalcogenolate, and so on. The complexes with the smallest ligands form the highest-dimensional aggregates and the complexes [AuCl(CO)] [87] or [Au(CN)(CNMe)] [88] form two-dimensional layers, but [AuCl(PMe$_3$)] [89] and [Au(CN)(PMe$_3$)] [90] are chains, and [Au(OCOCF$_3$)(PMe$_3$)] is a trimer [91], and many [AuX(PR$_3$)] complexes with medium-sized ligands are dimers [41]. Figure 1.7 shows the association of these molecules.

A particular case is the gold chloride isocyanide complexes of the type [AuCl(CNR)] ($R = C_nH_{2n+1}$, $n = 1$–11) [92]. The molecules behave like flexible hydrocarbon chains with a rod-like endgroup containing the gold atom. In the solid state the molecules arrange in antiparallel chains formed by aurophilic bonding. This structure is similar to those seen for the ($1 - n$)-alcohols (with hydrogen bonds) and also shows temperature-dependence polymorphism consistent with the formation of rotator phases. This is further proof of the concept that hydrogen bonding and aurophilic bonding are similar in their binding energies and directionality.

In some cases, the complexes [AuXL] may undergo ligand redistribution in solution and crystallize as homoleptic isomeric forms $[AuL_2]^+[AuX_2]^-$. These derivatives also aggregate in the solid state through aurophilic interactions in the form $+-+-+-$, such as for example in [AuIL] (L = tetrahydrothiophene, tetrahydroselenophene) [93]. The sequence of ions in the aggregates may vary against all intuition by placing ions of like charge next to each other, for example, in patterns $-++-$ as in the complex [Au(py)$_2$][AuX$_2$] (X = Cl, Br, I) [94] or $+--+$ in [Au(PPhMe$_2$)$_2$][Au(GeCl$_3$)$_2$] [95] instead of the expected $+-+-$. A novel pattern [+ neutral –] has recently been found in the trimeric compound $[Au(2\text{-}NH_2py)_2]^+$[AuCl(2-NH$_2$py)]$[AuCl_2]^-$ [96] (Figure 1.8).

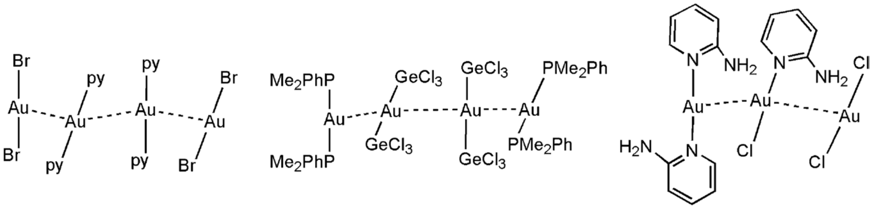


Figure 1.8 Association −++−, +−−+ and + neutral − in [AuXL] complexes.

In other complexes and depending on the ligands present, the formation of aggregates is based on other secondary bonds such as hydrogen bonds or Au···S interactions. The complexes [AuCl(4-$PPh_2C_6H_4CO_2H$)] [97] or [Au($SC_4H_3N_2O_2$)(PPh_3)] [98] associate in pairs through hydrogen bonding and [Au(4-$SC_6H_4CO_2H$)(PPh_3)] forms a supramolecular structure through hydrogen bonding and aurophilic interactions [99]. Some thiolate complexes, such as [Au{SSi(O^iPr)$_3$}(PPh_3)], form dimers through Au···S interactions [100]. Supramolecular structures are also achieved in mononuclear gold(I) complexes such as [Au(O_2CCF_3)(4-$PPh_2C_6H_4CO_2H$)], which crystallizes as infinite polymer chains of "[Au(4-$PPh_2C_6H_4CO_2H$)]$_n$," with a degree of helicity in the chains arising from the propeller-like arrangement of the phenyl groups [97]. The complexes with chiral secondary phosphines [AuX(PHMePh)] (X = Cl, Br, I) show chain-like supramolecular aggregates through aurophilic interactions, the chain contains both enantiomers following the sequence···RSRSRS···[101].

An interesting physical property exhibited by gold(I) compounds with short Au···Au interactions is the visible luminescence observed under UV excitation in the solid state. In the complexes [AuCl(TPA)] (Figure 1.9) and [AuCl(TPA·HCl)] (TPA = 1,3,5-triaza-7-phosphaadamantane), which have a phosphine ligand with a small cone angle that allows short aurophilic interactions, their luminescence spectra are substantially different and are correlated with the change in the Au···Au interaction [102]. At 78 K [AuCl(TPA)] luminesces intensely red (674 nm), while the protonated [AuCl(TPA·HCl)] luminesces yellow (596 nm). The emission bands in both complexes blue-shift as the temperature is increased. The interpretation of the phenomena is supported by extended Hückel MO calculations.

Although the [AuXL] complexes are well represented for many donor L ligands and for many X anionic ligands and have long been used as precursors in gold chemistry, curiously, analogous fluoride complexes [AuFL] have only been observed recently. AuF has long been considered a "non-existent compound"; its existence in the gas phase was theoretically predicted [103] and was later identified and characterized in the gas phase [104]. A series of neutral gold complexes [AuXNg] (Ng = Ar, Kr, Xe; X = F, Cl, Br)

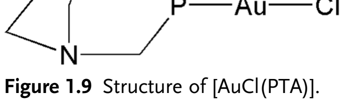


Figure 1.9 Structure of [AuCl(PTA)].

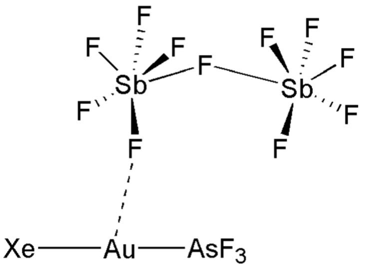


Figure 1.10 Structure of $[AuXe(AsF_3)][Sb_2F_{11}]$.

have been generated by laser ablation of the metal in the presence of a suitable precursor, and stabilized in a supersonic jet of Ar [105]. The complex [AuFXe] has been detected and characterized in the gas phase using microwave rotational spectroscopy. As expected, it is the noble gas–noble metal halide complex more strongly bonded to a very short Au–Xe distance of 2.54 Å [106]. All evidence is consistent with an AuXe covalent bonding in [AuFXe]. The first gold(I) complex with an XeAu bond is the cationic $[AuXe(AsF_3)][Sb_2F_{11}]$ (Figure 1.10), it was prepared by reaction of $[Au(AsF_3)]^+[SbF_6]^-$ with xenon in SbF_5-rich HF/SbF_5 solutions. The cation interacts only weakly with the anion and has an Au–Xe distance of 2.607 Å [107].

Another type of neutral gold(I) complex is $[AuX(PR_3)]$ where X is an anionic oxygen or nitrogen donor ligand such as $[Au\{N(SO_2CF_3)_2\}(PR_3)]$ or $[Au(OR)(PR_3)]$ or even $[Au(OSO_2CF_3)(PR_3)]$, which are relevant as catalytically-active species or catalytic precursors [26, 108].

Gold thiolates of the form $[Au(SR)(PR_3)]$ are important complexes that are known for a great variety of thiolate ligands and also serve as building blocks to obtain polynuclear species [109]. Several applications have been found, for example, in medicine with the commercialization of the antiarthritic drug Auranofin $[Au(SR)(PEt_3)]$ (Figure 1.11). Many other examples with this stoichiometry have been reported, which also have antiarthritic, antitumoral or antimicrobial activity. The structure of another antiarthritic drug, gold thiomalate (myocrysine), has been reported and crystallized as a mixed sodium/cesium salt $Na_2Cs[Au_2L(LH)]$ (Figure 1.12), which is a polymer that consists of two interpenetrating spirals, with approximately fourfold symmetry [110].

Anionic $[AuX_2]^-$ with halide or pseudohalide ligands are well known and have been widely used as a starting materials. The salts $[Au(SCN)_2]^-$ have been structurally characterized showing, for alkaline metals, infinite linear chains with alternating

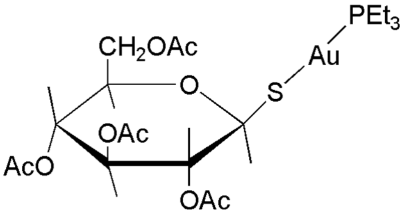


Figure 1.11 Structure of Auranofin.

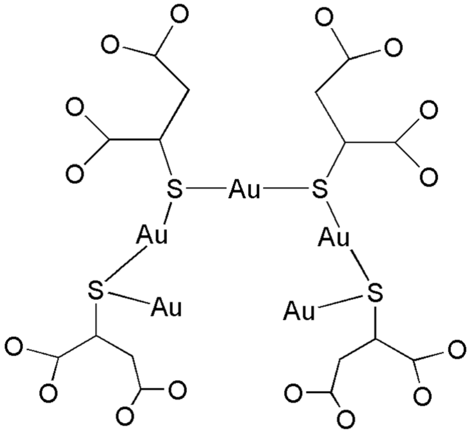


Figure 1.12 Structure of gold thiomalate.

short and long gold–gold distances along the chain, the $[NMe_4]^+$ salt forms a kinked chain of trimers joined at a shared gold atom as the kink, and the $[NBu_4]^+$ salts contain isolated dimers with a short aurophilic interaction [111]. All these complexes with Au–Au interactions are emissive and, as suggested by Fackler and Schmidbaur [102], the emission correlates inversely with distance. The anionic gold(I) thiolates, $Bu_4N[Au(SC_6H_4R)_2]$ show luminescence in the solid state, the emission maxima range from 438 nm (blue) to 529 nm (green), depending on the substituent R [112]. The anionic complexes with the hydrosulfide ligand, $[(PPh_3)_2N][Au(SH)_2]$ and $[AuR(SH)]^-$ are the only gold(I) complexes described with this ligand [113].

1.2.4.2 Gold(I) Complexes with Polydentate Ligands

Polydentate ligands have been widely used as bridging or quelating ligands in gold(I) chemistry. One of the most important types are diphosphines, which give very stable gold(I) complexes with different structural patterns. Dinuclear (chloro)gold(I) complexes with the phosphorus atoms bridged by one to eight carbon atoms, of the type $[Au_2Cl_2\{\mu\text{-}(PPh_2)_2(CH_2)_n\}]$ ($n = 1$–8), have been prepared from [AuCl(CO)] or $[AuCl(SR_2)]$ with the corresponding bidentate phosphine. They can adopt different structural patterns, as a result of the formation of Au–Au bonds (see Figure 1.13). The crystal lattice of the 1,4-bis(diphenylphosphino)butane ($n = 4$) or hexane ($n = 6$) derivatives contain independent molecules (type A) [114, 115], which show no intra- or inter-molecular Au–Au interactions, in contrast with the structures of the related gold complexes with shorter or longer chain diphosphines, where intra- ($n = 1$, type B) [116] and intermolecular metal–metal interactions with the formation of discrete dimers (type C) [117, 118] or polymeric chains (type D) are found [114, 115, 119]. The completely different packing of the monomeric molecules of $[Au_2Cl_2\{\mu\text{-}(PPh_2)_2(CH_2)_4\}]$ and the two polymorphic forms of $[Au_2Cl_2\{\mu\text{-}(PPh_2)_2(CH_2)_2\}]$, where the short Au–Au contacts give rise to dimers or to a polymeric chain structure, are particularly remarkable, since the conformations of the free phosphines show a close relationship. It has been suggested that packing effects, with or without solvent

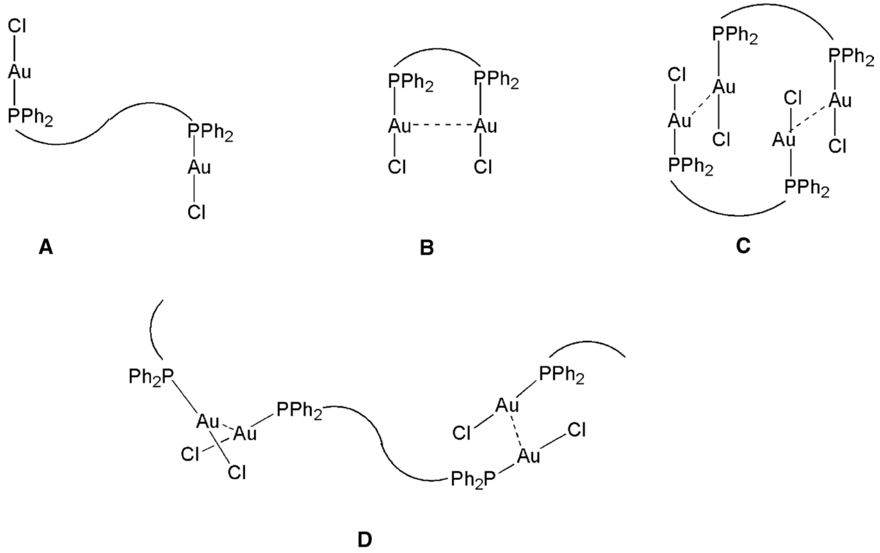


Figure 1.13 Different structural patterns of $[Au_2Cl_2\{\mu\text{-}PPh_2(CH_2)_n\}]$.

molecules, determine the conformation of these molecules; in fact, for $[Au_2Cl_2\{\mu\text{-}(PPh_2)_2(CH_2)_2\}]$ the presence of dichloromethane in the crystal leads to a transformation of the dimeric units present in the solvent-free crystal modification to a polymeric chain. For the $n = 3$ and larger chains, the complexes show monomeric dinuclear molecules connected through intermolecular Au–Au contacts of about 3.30 Å to give polymeric chains.

Analogous structures occur in other diphosphine or diarsine complexes of the type $[AuCl_2\{\mu\text{-}(PPh_2)_2X\}]$ [120–124] where X can be a great variety of bridging moieties; the structure varies from monomeric molecules without Au–Au interactions to dimeric complexes with intramolecular metal–metal contacts or polymeric compounds with intermolecular Au–Au interactions. In the complexes with the diphosphine $PPh_2C(=PMe_3)PPh_2$, the ligands change their ground state syn/anti orientation to a symmetrical syn/syn conformation upon coordination to gold(I). From temperature-dependent NMR studies, the energy of the Au–Au interaction was estimated to be of the order of 29–33 kJ mol^{-1} [120, 121]. Figure 1.14 shows some examples of this type of complex.

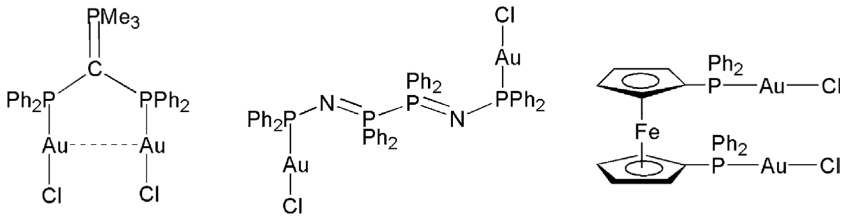


Figure 1.14 Some examples of $[AuCl_2\{\mu\text{-}(PPh_2)_2X\}]$ complexes.

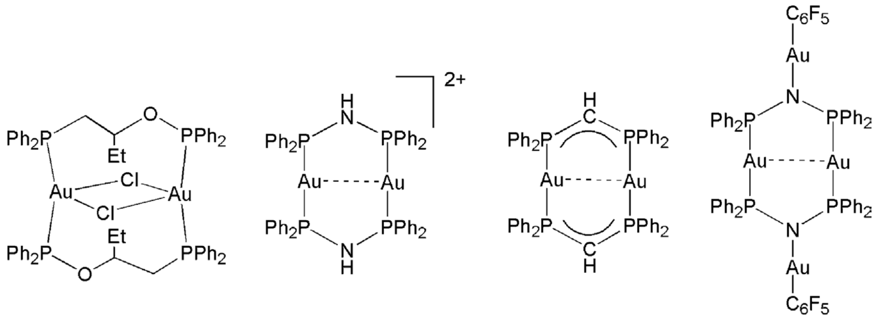


Figure 1.15 Dinuclear diphosphine complexes.

Other types of well-represented dinuclear derivatives with diphosphines have the stoichiometry $[Au_2(\mu\text{-}PP)_2]^{2+}$ and are known for a great variety of diphosphines R_2PXPR_2 (Figure 1.15) where X can vary from the simple methylene CH_2 [125–127], bis(diphenylphosphino)methane (dppm), for which many studies have been carried out, to another hydrocarbon chain [128], to NH [129], and so on. Most of these derivatives are three-coordinate by bonding to the anionic ligand, which may be Cl, Br, I, S_2CNEt_2, or BH_3CN and also by formation of Au–Au interactions with molecules such as $[AuCl(GeCl_3)]^-$. Some of these complexes are luminescent, such as $[Au_2\{(PR_2)_2CH_2\}]^{2+}$ (R = Me, Ph, Cy) for which several studies have been carried out on aurophilic attraction and luminescence [130]. The high luminescent complex $[Au_2\{(PPh_2)_2CH_2\}](OTf)_2$ with a triplet excited state has been postulated to be used in light-emitting diodes [131]. The dinuclear derivatives $[Au_2\{(PR_2)_2X\}]^{2+}$ (X = CH_2, NH) can be easily deprotonated to give the neutral complexes $[Au_2\{(PR_2)_2Y\}]$ (Y = CH, N) [132, 133]. Further coordination of the C or N atoms to other metal complexes gives tetra or hexanuclear derivatives [133, 134].

Most of the dinuclear gold(I) complexes are homobridged diauracycles with the same bridging ligand on each side, but some examples of heterobridged derivatives have been reported. These contain a diphosphine in addition to other bidentate ligands such as bis(ylide) [135, 136], dithiolate [137], dithiocarbamate [136, 138], xantate [139], phosphoniodithioformate [140], dithiophosphinate [141], pyridine-2-thiolate [136], and so on. They can be obtained by reaction of the $[Au_2X_2(\mu\text{-}PP)]$ complexes with the bidentate ligand or by ligand exchange reactions between two different homobridged dinuclear compounds. Examples of these complexes are shown in Figure 1.16.

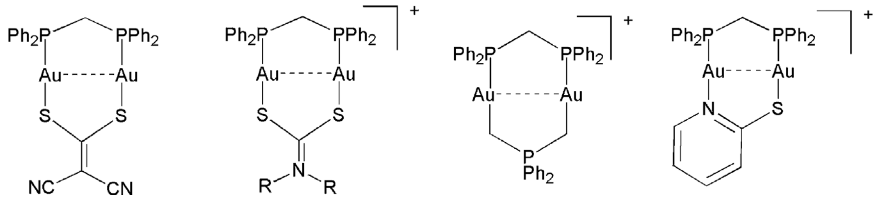


Figure 1.16 Dinuclear heterobridged diphosphine gold(I) complexes.

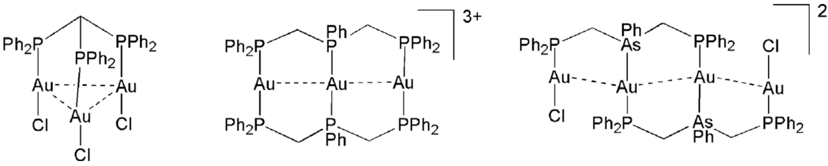


Figure 1.17 Gold(I) complexes with tertiary phosphine or phosphine-arsine ligands.

Triphosphines or mixed phosphine-arsine ligands have also been used as ligands to coordinate gold(I) centers and the structures of the complexes can vary, depending on the structural requirements of the phosphine ligands. Then complexes with stoichiometry $[Au_3Cl_3(\mu\text{-LLL})]$ [142–144], $[Au_3(\mu\text{-LLL})_2]^{3+}$ [145, 146], $[Au_2\{(PPh_2)_2CHPPh_2\}_2]^{2+}$ [143] or $[Au_4Cl_2(\mu\text{-LLL})_2]^{2+}$ [147] have been prepared but sometimes with different structural frameworks such as $[Au_3Cl_3\{(PPh_2)_3CH\}_2]$, which forms a triangle of gold atoms, and $[Au_3(PPh_2CH_2PPhCH_2PPh_2)_2]^{3+}$, for which the gold atoms form a linear chain (Figure 1.17).

With tetraphosphines, the usual stoichiometry is $[Au_4Cl_4(\mu\text{-}P_4)]$, such as those with tetrakis(diphenylphosphine)methane [148], or tetrakis(diphenylphosphine)tetrathiafulvalene, $(PPh_2)_4$TTF, [149] (Figure 1.18), and gold(I) complexes with dentritic polymers containing phosphorus atoms as terminal groups have also been described [150]. Some of these polyphosphine complexes have been used to synthesize heteronuclear complexes, such as bis(diphenylphosphino)methane (dppm) [151], $PPh_2CH_2AsPhCH_2PPh_2$ [152], and so on, which lead to several derivatives with the polydentate ligands bridging two or more metal atoms (Figure 1.19).

Another important class of bidentate ligands in gold chemistry are those composed of sulfur donor ligands such as dithiocarbamates, dithiolates, dithiocarboxylates, dithiophosphinates, dithiophosphates, and so on. The complexes prepared with these ligands are generally of the type $[Au_2(\mu\text{-SS})(PR_3)_2]^{n+}$ or $[Au_2(\mu\text{-SS})(\mu\text{-PP})]$ [153–155], $[Au_2(\mu\text{-SS})_2]^{n-}$ [156, 157] or $[Au_3(\mu\text{-SS})_2(PPh_3)_2]^-$ [158]. All these

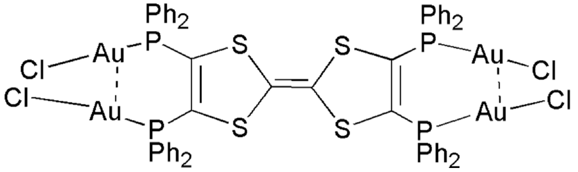


Figure 1.18 Structure of $[Au_4Cl_4\{(PPh_2)_4TTF\}]$.

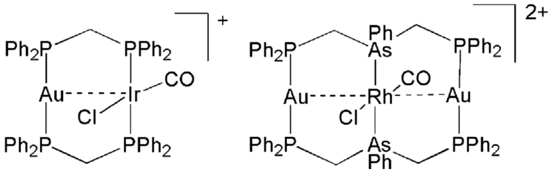


Figure 1.19 Heteronuclear phosphine gold(I) complexes.

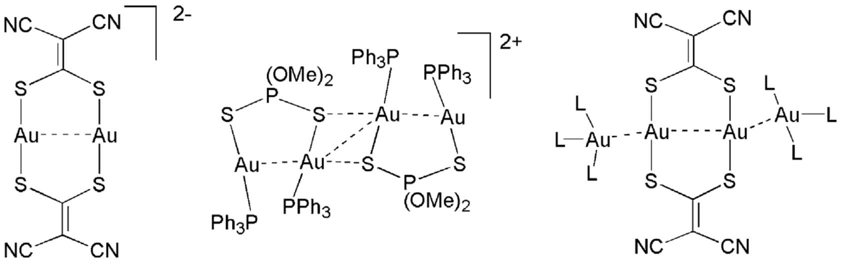


Figure 1.20 Gold(I) complexes with bidentate sulfur ligands.

complexes have intramolecular Au–Au interactions and some of them also present intermolecular contacts. The usual structure for $[Au_2(\mu\text{-}SS)(PR_3)_2]$ complexes is dinuclear but some of them form a supramolecular structure through Au–Au and Au–S interactions such as in $[Au_2\{\mu\text{-}S_2P(OMe_2)\}(PPh_3)_2]^+$. The species $[Au_2(\mu\text{-}SS)_2]^{n-}$ can be discrete dinuclear units with intramolecular gold–gold contacts or linear chains through intermolecular aurophilic interactions. As a consequence of these aurophilic interactions, many of these complexes present luminescence properties. The compound $[Au_4\{\mu\text{-}S_2C_2(CN)_2\}_2(PTA)_2]$ has a dinuclear structure with the "AuPTA" fragment bonded to the gold atom with an unsupported Au–Au interaction and is highly luminescent [159]. A chiral luminescent Au_{16} ring has been reported by reaction of $[Au_2Cl_2(\mu\text{-}dppm)]$ with $K_2(pippzdc)$ (pippzdc = piperazine-1,4-dicarbodithiolate) which gives the tetramer $[Au_4(pippzdc)(dppm)_2]_4$ [160]. Figure 1.20 shows some of these complexes.

Homoleptic dithiocarboxilates can be tetrameric as $[Au_4(S_2CMe)_4]$ [161] or hexameric as in $[Au_6(S_2C_6H_4\text{-}Me\text{-}2)_6]$ [162] (see Figure 1.21). Analogous complexes with selenium ligands are far less developed although some examples have been reported, such as $[Au_2\{\mu\text{-}Se_2C_2(CN)_2\}]^{2-}$ [163] (Figure 1.22).

Substituted phenylene-dithiolate ligands have been thoroughly studied and di-, tri- and tetranuclear complexes of the type $[Au_2(\mu\text{-}S_2C_6H_3R)(PPh_3)_2]$, $[Au_3(\mu\text{-}S_2C_6H_3R)(PPh_3)_3]^+$ or $[Au_4(S_2C_6H_3R)_2L_2]$ have been reported with the *ortho* isomer [137, 153, 164–166]. The *meta* and *para* isomers present different stoichiometries and structures such as $[Au_3(1,3\text{-}S_2C_6H_4)(PPh_3)_3]^+$, which shows a one-dimensional aggregate through head-to-tail aurophilic interactions or the

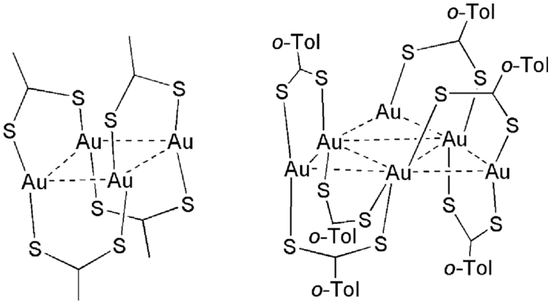


Figure 1.21 Dithiocarboxilate gold(I) complexes.

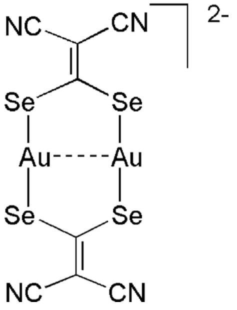


Figure 1.22 Structure of $[Au_2\{\mu\text{-}Se_2C_2(CN)_2\}]^{2-}$.

tetranuclear $[Au_4(1,4\text{-}S_2C_6H_4)(PPh_3)_4]^{2+}$ [167]. Benzenehexatiol reacts with $[AuCl(PPh_3)]$ to give the hexanuclear golden wheel $[Au_6(S_6C_6)(PPh_3)_6]$ [168]. Figure 1.23 shows some of these complexes.

Other complexes with these polydentate ligands include species with diphosphine ligands such as the complex with the 2-thioxo-1,3-dithiole-4,5-dithiolate (dmit) ligand, $[Au_4(dmit)_2(dppm)_2]$ [169] (Figure 1.24a), the tetracoordinated compound with the 1,2-dithiolate-*o*-carborane $[Au_4(S_2C_2B_{10}H_{10})_2\{(PPh_2)_2C_2B_{10}H_{10}\}_2]$ [170] (Figure 1.24b), or the gold complex $[Au_2Cl_2\{Fc(S_2CNEt)_2]$ [171] with the bis(dithiocarbamate)ferrocene ligand in which there are η^2 interactions between the gold(I) atoms and the cyclopentadienyl ligands (Figure 1.24c).

Other types of polydentate ligands are those with different donor atoms that can be of the type P,C or N,C or S,S,C,C or P,N, and so on, [172–175]. Many gold(I) complexes with these heterofunctional ligands have been prepared. Figure 1.25 shows some examples.

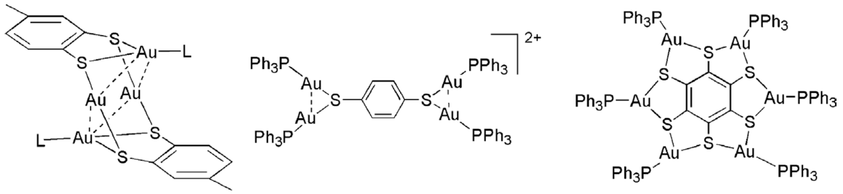


Figure 1.23 Di- and hexa-thiolate gold(I) complexes.

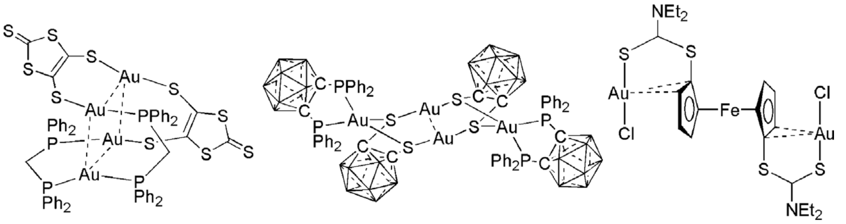


Figure 1.24 Some gold(I) complexes with bidentate sulfur ligands.

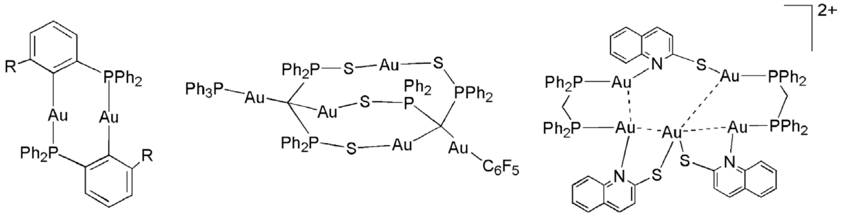


Figure 1.25 Gold(I) complexes with mixed donor ligands.

Gold(I) complexes with polydentate nitrogen ligands are also known, such as with the ferrocenyl-terpyridine ligand (Figure 1.26a) in which the ligand acts as tridentate [176], or the tetranuclear derivative with 2,2′-bibenzimidazolate (Figure 1.26b) [177], or the complexes obtained in the reaction of *trans*-1,2-bis (4-pyridyl)ethylene with $[Au_2(O_2CCF_3)_2\{\mu\text{-}(PPh_2)_2(CH_2)_n\}]$ which gives with $n = 2$ the cyclic compound and with $n = 3$ or 4 one-dimensional linear or U-shaped polymers (Figure 1.26c) [178]. In the same reaction with 4,4′-bipyridine in solution the complexes exist as an equilibrium mixture of linear oligomers and cyclic compounds; when $n = 1$, 3 or 5 they exist as 26-, 30- and 34 membered macrocyclic rings, respectively, and only when $n = 1$ are there significant intramolecular Au–Au contacts. Some of these compounds are strongly emissive at room temperature and in the solid state [179].

1.2.4.3 Three and Four-Coordinate Gold(I) Complexes

High coordinated gold(I) complexes with monodentate phosphines, arsines or stibines have been reported. It was first demonstrated by $^{31}P\{^1H\}$ NMR studies that bis-, tris, and even tetrakis(phosphine)gold(I) complexes exist in solution. Owing to rapid ligand exchange on the NMR time scale the individual complexes can only be observed at low temperature. The linear complexes $[AuX(PR_3)]$ interact with an excess of phosphine to give a series of species including primarily $[AuX(PR_3)_2]$, $[Au(PR_3)_3]X$ or $[Au(PR_3)_4]X$ as components of the equilibria, as shown in Equation 1.8. The

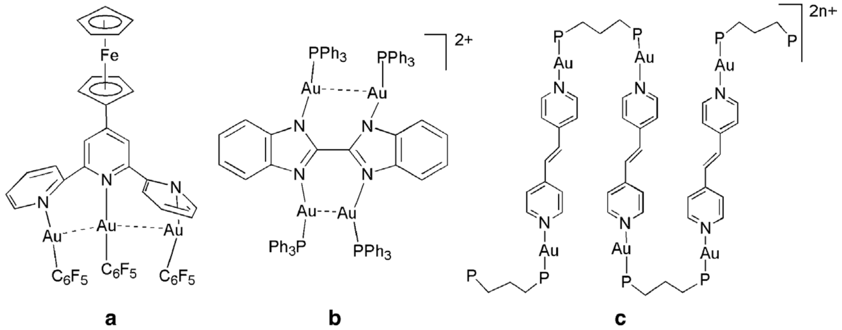


Figure 1.26 Gold(I) derivatives with polydentate nitrogen ligands.

maximum coordination number attainable depends on the particular ligand used. For bulky phosphines, such as $PR_3 = PCy_3$, only the two coordinated cation $[Au(PCy_3)_2]^+$ is accessible, but with $PR_3 = PBu_3$, $P(4\text{-Tol})_3$ or $PPh_2\{CH_2CH_2(2\text{-py})\}$ both $[Au(PR_3)_2]^+$ and $[Au(PR_3)_3]^+$ are detected; for $PR_3 = PEt_3$, PMe_2Ph, $P(OEt)_3$ or $P(OCH_2)_3CEt$ finally the two- three- and four-coordinated species are observed [180–182].

$$[AuX(PR_3)] \overset{PR_3}{\rightleftharpoons} [AuX(PR_3)_2] \rightleftharpoons [Au(PR_3)_2]X \overset{PR_3}{\rightleftharpoons} [Au(PR_3)_3]X \overset{PR_3}{\rightleftharpoons} [Au(PR_3)_4]X \tag{1.8}$$

Three-coordinate complexes of the type $[AuX(PR_3)_2]$ are known and they show Au–P distances longer than those in two-coordinate complexes and P–Au–P angles somewhat wider than 120° [183–185]. Some of these three-coordinate bis(phosphine) gold(I) complexes luminesce in the solid state, as well as in solution. The emission is attributed to the metal-centered pz → ($d_{x2\text{-}y2}$, d_{xy}) transition [184, 186]. The most regular three-coordination is observed in compounds where all the three ligands are identical, as in $[Au(PPh_3)_3]^+$ salts for which several crystal structures with different anions have been reported [187]. The cation of $[Au(PCy_2Ph)_3]ClO_4$, obtained by reaction of $[AuCl(PCy_2Ph)]$ with an excess of PCy_2Ph in the presence of $(NH_4)ClO_4$, has an almost ideal trigonal planar geometry [P–Au–P angles of 119.3(3)°] [188]. The complexes $[Au(TPA)_3]Cl$ and $[Au(TPPTS)_3]^{8-}$ [TPPTS = tris[(3,3′,3″-phosphinidyne-tris(benzenesulfonate)] show luminescence in aqueous solution [189].

Four-coordinate complexes with monodentate ligands $[Au(L)_4]^+$ have been described for PPh_3, PPh_2Me, $AsPh_3$ and $SbPh_3$ [190–193]. For triphenylphosphine the structures of three modifications of the compound have been determined, none of which shows the expected simple tetrahedral geometry, however, the cation of $[Au(PMePh_2)_4]PF_6$, or those with the arsine or stibine ligands, show a nearly regular tetrahedral geometry. Other tetra-coordinate complexes are of the form $[AuX(PR_3)_3]$ [194] and show the presence of a four-coordinate gold atom in a distorted tetrahedral geometry, with rather long Au–P and Au–X distances. The water soluble and luminescent gold(I) complex $[AuI(MeTPA)_3]I_3$ [(MeTPA)I = 1-methyl-1-azonia-3,5-diaza-7-phosphaadamantane iodide] has been obtained by reaction of $[AuCl(SMe_2)]$ with three equivalents of (MeTPA)I [195]. The coordination environment of the gold center is approximately trigonal planar and the iodine is weakly coordinated to the gold atom perpendicular to the AuP_3 plane [Au–I distance 2.936(1) Å]. The solid shows a yellow emission (598 nm) at 77 K and an orange emission (686 nm) at 140 K. $[AuI(MeTPA)_3]I_3$ undergoes an unusual phenyl-transfer reaction in aqueous solution with $NaBPh_4$ to form $[AuPh(MeTPA)_3]BPh_4$.

Three-coordinate gold(I) complexes with functionalized ligands have been used to prepare heteronuclear derivatives. Thus the reaction of 7-diphenylphosphino-2,4-dimethyl-1,8-naphthyridine (dpnapy) with [AuCl(tht)] affords the tricoordinate compound $[Au(dpnapy)_3]^+$ (Figure 1.27a), the latter shows strong affinity towards Cu(I) and Cd(II) (Figure 1.27b) ions [196]. The 2-(diphenylphosphino)-1-methylimidazole (dpim) also forms a three-coordinate Au(I)–Ag(I) dimer, $[AuAg(dpim)_3]^{2+}$ (Figure 1.27c) with a short metal–metal distance, which shows an intense luminescence [197].

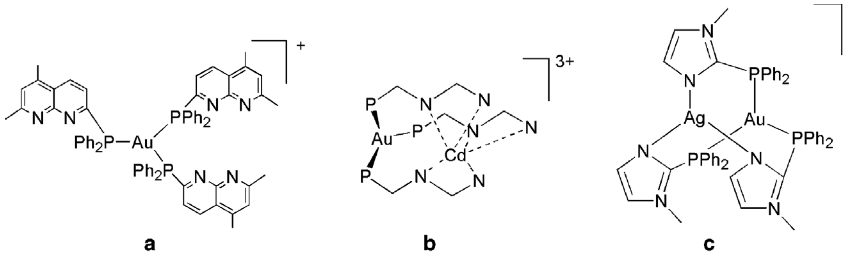


Figure 1.27 Three-coordinate gold(I) complexes with heterofunctional ligands.

Neutral or cationic three-coordinate gold(I) complexes with chelating diphosphines have been synthesized and are of the type [AuX(P–P)], $[AuL(P–P)]^+$ or $[Au_2(\mu\text{-P–P})(P–P)]^{2+}$, which has chelating and bridging diphosphine ligands [198–201]. Many of these complexes are strongly luminescent. Other three-coordinate complexes are those composed only of bridging diphosphines such as $[Au_2(\mu\text{-P-P})_3]^{2+}$, which have been described for $Me_2PCH_2PMe_2$, PPh_2pyPPh_2, PPh_2pzPPh_2, and so on, [202–204]. Better represented are species of the form $[Au_2(\mu\text{-L–L})(\mu\text{-P–P})_2]^{n+}$, where L-L are anionic ligands that can be halogens or pseudohalogens, dithiocarbamate, dithiophosphonate, and so on [205, 206]. Many of these complexes are strongly luminescent. Some examples of these complexes can be seen in Figure 1.28.

Luminescent trigonal gold(I) metallocryptates have been obtained by reaction of 2,9-bis(diphenylphosphino)-1,8-naphthyridine or 2,9-bis(diphenylphosphino)-1,10-phananthroline $PPh_2(phen)PPh_2$ with [AuCl(tht)] (molar ratio 3 : 2) and in the presence of a cation Na^+, Tl^+ or Hg^0, which is encapsulated in the cavity making Au–M interactions [207]. Similar mixed metal metallocryptands with Pd(0) or Pt(0) have been reported (Figure 1.29) [208].

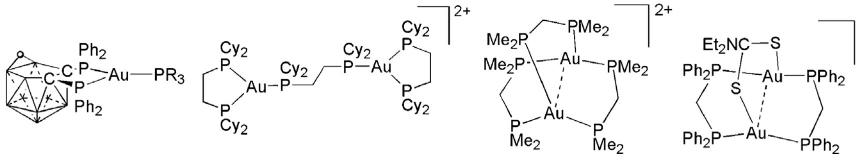


Figure 1.28 Three-coordinate gold(I) complexes with diphosphine ligands.

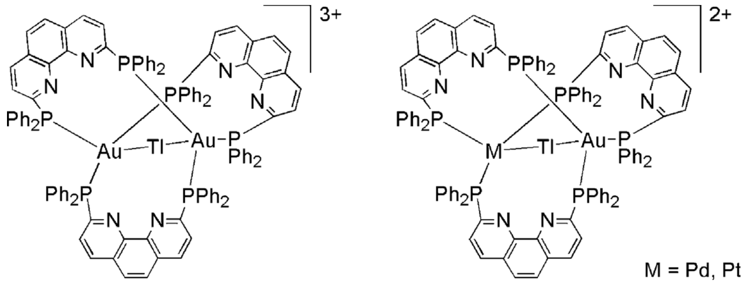


Figure 1.29 Gold(I) and mixed-metal metallocryptands.

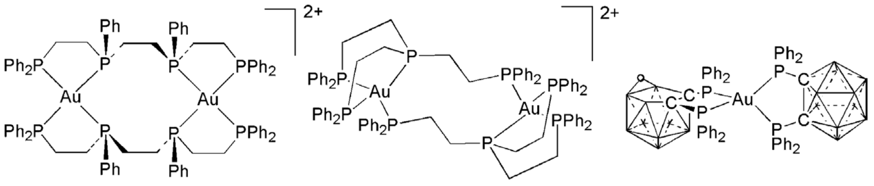


Figure 1.30 Tetra-coordinate gold(I) complexes.

Four-coordinate homoleptic species of thetype $[Au(L–L)_2]^+$, where L–L can be a diphosphine or diarsine, have been obtained for several ligands such as $R_2PCH_2PR_2$ [209], *cis*-$Ph_2PCH=CHPPh_2$ [209], $(PPh_2)_2C_2B_{10}H_{10}$ [210], bis(diphenylphosphino)ferrocene [124], and so on. Some of these tetrahedral diphosphine complexes are cytotoxic and present a broad spectrum of antitumor activity [209]. Dinuclear tetra-coordinate derivatives are achieved with tetradentate phosphines, including tetraphos or tris(2-(diphenylphosphino)ethyl)phosphine [211]. Mixed four-coordinate gold(I) complexes have been prepared with the 1,2-bis(diphenylphosphino)-*o*-carborane ligands and are of the type $[Au\{(PPh_2)_2C_2B_{10}H_{10}\}(P\text{-}P)]^+$ [212] or with one *nido* and one *closo* diphosphine such as $[Au\{(PPh_2)_2C_2B_9H_{10}\}\{(PPh_2)_2C_2B_{10}H_{10}\}]$ [51]. Figure 1.30 shows some of these complexes.

1.2.4.4 **Oligomeric Gold(I) Complexes**

These complexes have the general formula $[AuL]_n$ or $[Au_2(L–L)]_n$ and are obtained with different ligands. The dinuclear complexes with bidentate ligands have been commented previously. Organometallic complexes of the type [AuR] are known, for example for mesityl, the structure of which is a pentamer $[Au_5(Mes)_5]$ (Figure 1.31a). This is a useful starting material to prepare other organometallic derivatives. It also displays unusual reactivity, for example with naked Ag^+ ions to give a complex, $[Au_6Ag(Mes)_6]$, with unsupported Au(I)–Ag(I) interactions (Figure 1.31b) [213]. Alkynyl complexes of the type $[Au(C\equiv CR)]_n$ have been formulated as polymeric but the structure of $[Au(C\equiv C^tBu)]_n$ has been shown to be a "catena" species with two interconnected cyclic hexamers [214].

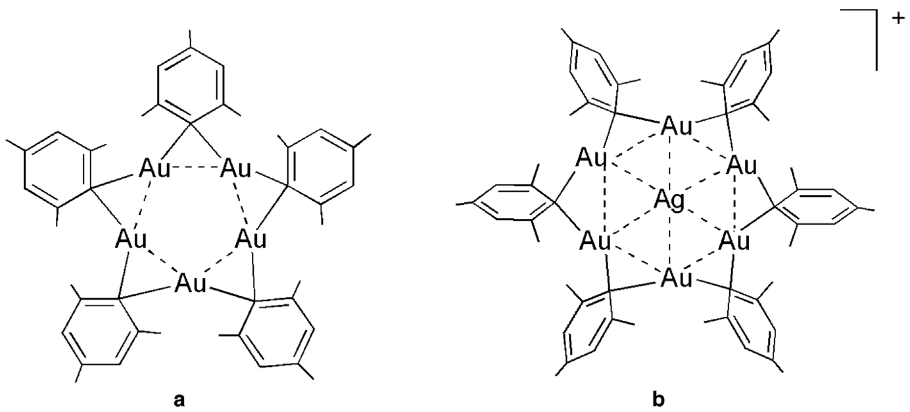


Figure 1.31 Oligomeric gold(I) complexes with carbon donor ligands.

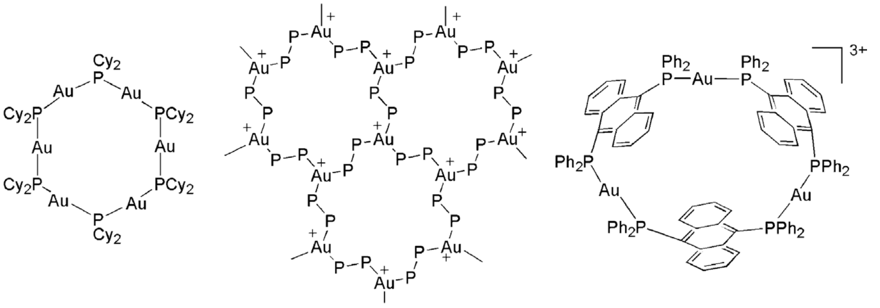


Figure 1.32 Oligomeric gold(I) complexes with phosphide or phosphine ligands.

For phosphorus donor ligands the structures of $[Au(PR_2)_2]_n$ are oligomeric rings of different sizes ($n = 3,4,6$) depending on the phosphide substituents [215]. With diphosphines, the most common stoichiometry for complexes $[Au(P\text{–}P)]^+$ are dimers, as commented above, but other studies of gold(I) cations with empirical formula $[Au\{PPh_2(CH_2)_nPPh_2\}]^+$ show that the complexes crystallize as rings for $n = 3$ or 5 but as a polymer when $n = 4$ (as fused $Au_6(\mu\text{-}P\text{–}P)_6$ rings) [216]. With the diphosphine 9,10-bis(diphenylphosphino)anthracene, the 1 : 1 reaction with [AuCl (SMe_2)] gives the trinuclear complex $[Au_3(\mu\text{-}PP)_3]^{3+}$ [217]. This luminescent gold ring is shown to be an inorganic analog of cyclohexane in terms of structure and solution dynamics. These complexes are presented in Figure 1.32.

Thiolates, selenolates or tellurollates of general formula $[Au(ER)]_n$ are usually insoluble and only a limited number have been characterized structurally as oligomers. Tetramers have been reported, for example, for $[Au_4\{E(SiMe_3)\}_4]$ (E = S, Te) [218], hexamers for $[Au_6\{S(2,4,6\text{-}C_6H_2{}^iPr_3\}_6]$ [219], or the catenanes $[Au_{10}(SC_6H_4\text{-}p\text{-}CMe_3)_{10}]$ and the precursor of the gold(I) drug Auranofin $[Au_{11}(SR)_{11}]$ R = 2,3,4,6-tetra-O-acetyl-β-1-D-thioglucopyranosato [220] (Figure 1.33).

Triangular trigold(I) complexes of the type $[Au_3L_3]$ are formed with pyrazolate, orthometallated pyridine, benzimidazole, and so on; they have been known for a long time but their remarkable chemical reactivity and physical properties have only recently been discovered. The gold trimer with carbeniate ligands $[Au_3(MeN{=}COMe)_3]$ displays the new phenomenon termed solvo-luminescence. After irradiation with near-UV light, crystals of this compound show a long-lived photoluminescence that can be detected by the human eye for tens of seconds after cessation of irradiation. Addition of dichloromethane or chloroform to these previously-irradiated crystals produces a bright burst of light. For this phenomenon the solid state

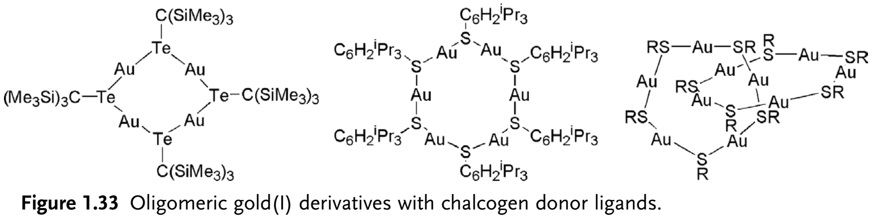


Figure 1.33 Oligomeric gold(I) derivatives with chalcogen donor ligands.

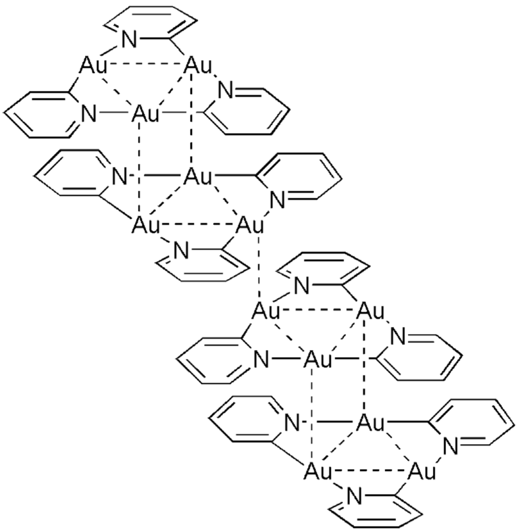


Figure 1.34 Structure of $[Au_3(NC_5H_4)_3]$.

structure is crucial and consists of individual molecules of Au_3L_3 which aggregate to form columnar stacks through Au–Au interactions. It is believed that energy storage involves charge separation within the solid, and this charge separation is facilitated by conduction of electrons along the columnar structure [221]. A similar complex $[Au_3(PhCH_2N=COMe)_3]$ does not associate into a trigonal prismatic array but packs in a stair-step fashion with eight discrete molecules in the asymmetric unit. This compound does not display solvoluminiscence [222]. The structure of the trimer $[Au_3(NC_5H_4)_3]$ has been studied and shows that individual molecules self-associate through aurophilic interactions into two distinct structural motifs that involve both extended chains of molecules connected by pairwise and individual Au–Au contacts, and discrete dimers linked by pairwise Au–Au interactions (Figure 1.34) [223].

The trinuclear derivatives $[Au_3(p\text{-}MeC_6H_4N=OEt)_3]$ and $[Au_3(Bzim)_3]$ (Bzim = 1-benzylimidazolate) are colorless complexes but can produce brightly colored materials by sandwiching Ag^+ or Tl^+ ions and forming linear-chain complexes (Figure 1.35) with interesting luminescence properties such as thermochromism [224]. They also

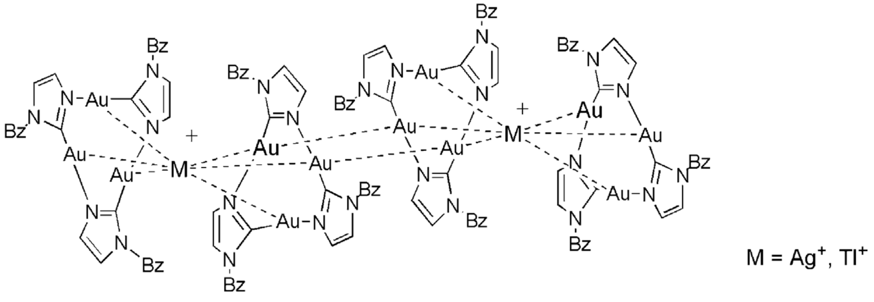


Figure 1.35 Structure of $[Au_3M(benzimidazolate)_3]^+$.

react with the π molecular acid trinuclear Hg^{II} complex $[Hg(\mu\text{-}C_6H_4)_3]$ to give compounds with acid–base stacking among the planar molecules [225].

Other oligomeric complexes are obtained with nitrogen donor ligands including amides, such as $[Au_4\{NSiMe_3)_3\}_4]$ [226], or formamidates such as $[Au_4\{(NPh)_2CH\}_4]$ [227], triazenides, such as $[Au_4\{(NPh)_2N\}_4]$ [228], or pyrazolates, such as the trinuclear species commented above or the hexanuclear $[Au_6(2\text{-}5\text{-}Ph_2pz)_6]$ [229].

1.2.4.5 Single Heteroatom Bridged Gold(I) Complexes

One of the most fascinating areas of gold(I) chemistry has been the discovery that phosphine–gold fragments coordinate around a central heteroatom. The species formed are exciting, not only from an experimental and structural viewpoint but also theoretically and are the clearest example of the "aurophilic power of gold." Thus, interesting hypercoordinated species of clustering of gold(phosphine) fragments around a central heteroatom such as carbon, phosphorus, nitrogen, sulfur, and so on, have been described, in addition to other complexes with more conventional stoichiometry, and all have in common the presence of short gold–gold interactions of about 3 Å. Usually, the chemistry of the first row elements of the p-block is known to follow classical rules of bonding, and only in cases of extreme electron-deficiency has the traditional electron count to be reconsidered in order to account for special types of molecular or solid state structures. Many of the heteroatom-centered complexes are electron deficient and the gold–gold interactions provide a significant contribution to their stability. The type of structure adopted is greatly influenced by the existence of gold–gold interactions.

Polyauration starts from the carbon atom for which the species with four, five and six gold atoms have been prepared. These are available from the reaction of polyborylmethanes with $[AuCl(PR_3)]$ or trimethylsilyl diazomethanes with $[O(AuPR_3)_3]^+$. The tetranuclear derivatives are formed with bulky phosphines and less sterically demanding phosphines enable the synthesis of the hypervalent species [230]. The structures of these complexes are tetrahedral, trigonal bypiramidal and octahedral, respectively (Figure 1.36). Many complexes of the type $[RC(AuPR_3)_4]^+$ [231] have also been synthesized.

Similar complexes have been prepared with nitrogen as a central hereroatom but to date only the tetranuclear and pentanuclear derivatives have been achieved from the reaction of ammonia with the oxonium complexes (Figure 1.37), with a tetrahedral or trigonal bipyramidal geometry, respectively [232]. Auration of polyamines or related

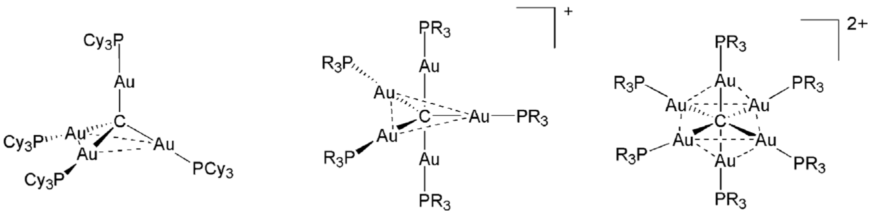


Figure 1.36 Carbon-centered gold(I) complexes.

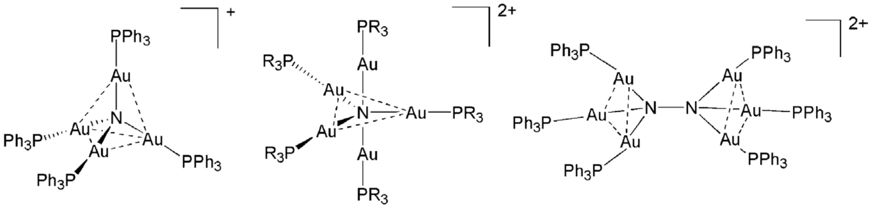


Figure 1.37 Nitrogen-centered gold(I) complexes.

compounds has also been developed and many examples, such as the auration of hydrazine (Figure 1.37), have been reported [233].

Phosphorus and arsenic atoms also act as bridging ligands for several $AuPR_3^+$ fragments. The $[P(AuPR_3)_4]^+$ [234] and the $[As(AuPR_3)_4]^+$ [235] have different geometry because the phosphonium adopts the expected tetrahedral structure, whereas arsonium has a square-pyramidal geometry with the arsenic in the apical position, probably because the radius of the arsenic is too large to allow for metal–metal bonding in a tetrahedral structure (see Figure 1.38). If a lone pair of electrons is allocated to the As apex, then the $AsAu_4$ core has to be described as electron deficient. The $[P(AuPPh_3)_5]^{2+}$ has a square pyramidal arrangement, in contrast to the trigonal bipyramidal structure expected by classical bonding arguments [236]. For the tricationic species $[P(AuPR_3)_6]^{3+}$ an octahedral structure has been proposed [237].

The field of chalcogen-centered gold(I) complexes is well developed. Among the trinuclear derivatives $[E(AuPR_3)_3]^+$ which exist for all the chalcogens, usually as dimers in the solid state, the oxonium cations have displayed the most synthetic applicability, not only in the preparation of other heteroatom centered species but in many organometallic gold(I) complexes. The tetra(oxonium) compounds have been obtained by reaction of $[O(AuPR_3)_3]^+$ with $[Au(BF_4)(PR_3)]$ and have the expected tetrahedral geometry [238]. Heteronuclear complexes with a triply or quadruply oxo ligand have been reported, such as $[Rh_2(dien)_2\{O(AuPPh_3)_2\}_2](BF_4)_2$ obtained from $[O(AuPPh_3)_3]^+$ and $[RhCl(dien)]_2$ [239], or $[O(AuPPh_2py)_3M](BF_4)_2$ (M = Ag, Cu), prepared by reaction of $[O(AuPPh_2py)_3]^+$ with M^+ [240] (Figure 1.39). The latter has also been obtained for the sulfur or selenium atoms. A distinctive feature of these complexes is that they present an extremely bright luminescence. These species exhibit a large variation λ_{em}^{max} as a function of the μ_3-E capping ligand; The energy of

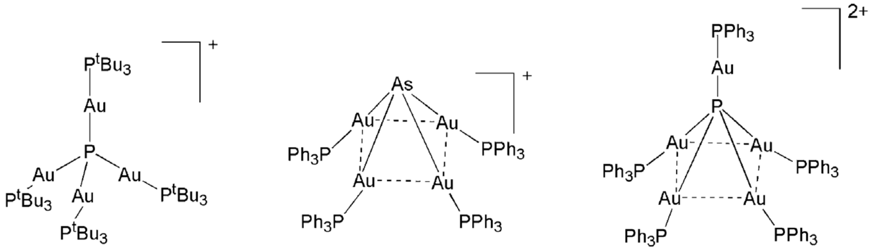


Figure 1.38 Phosphorus and arsenic centered gold(I) complexes.

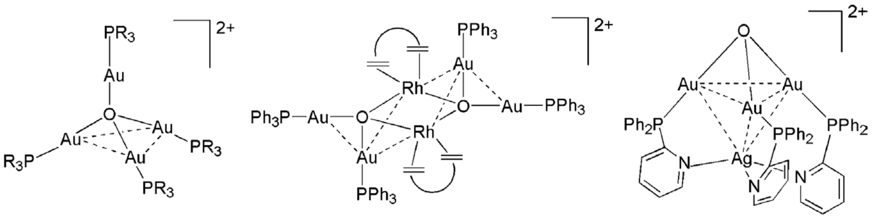


Figure 1.39 Oxo-centered gold(I) complexes.

the emissions decreases on changing from oxygen, significantly at higher energy, to sulfur and to selenium. The large change in λ_{em}^{max} between these complexes clearly indicates involvement of the Group 16 capping atom in the excited state. Since the lone pair orbitals lie lowest in O, next in S, and highest in Se, an assignment consistent with the emission results in a ligand-to-metal–metal charge transfer (^{3}LMMCT).

The tetranuclear sulfur and selenium derivatives $[E(AuPPh_3)_4]^{2+}$ show a square pyramidal geometry with the chalcogen atom in the apical position [241]. These cations dimerize in the solid state through Au···E interactions (Figure 1.40). Further auration of sulfur and selenium to give the penta- and hexa-nuclear species has been achieved and trigonal bipyramidal and octahedral structures have been proposed [242].

Diphosphines have also been used as auxiliary ligands in chalcogen-centered gold chemistry and several complexes with a great variety of structural frameworks have been reported, such as the polynuclear derivatives $[Au_{12}S_4(\mu\text{-dppm})_6]X_4$, $[Au_{10}Se_4(\mu\text{-dppm})_4]^{2+}$ or $[Au_{10}Se_4(\mu\text{-dppf})_4]^{2+}$ shown in Figure 1.41 [242, 243]. Some of these

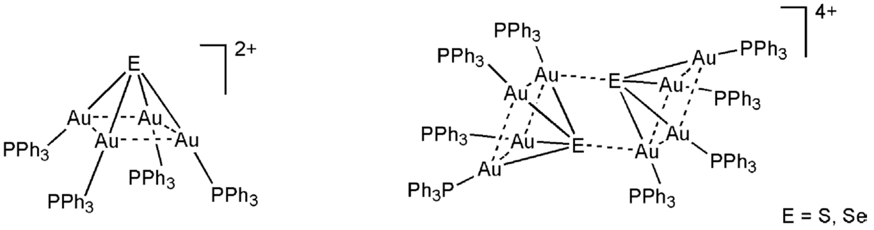


Figure 1.40 Sulfur and selenium-centered gold(I) complexes.

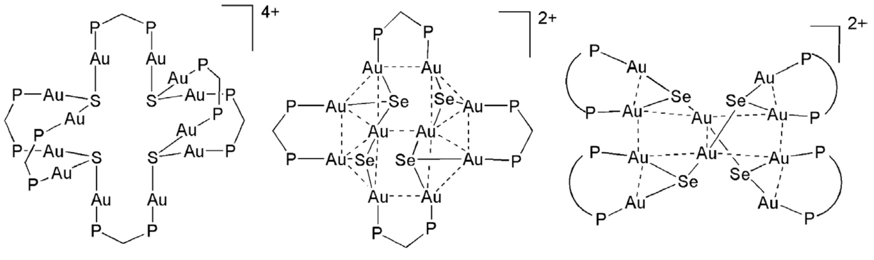


Figure 1.41 Polynuclear gold(I) complexes with bridging chalcogenide ligands.

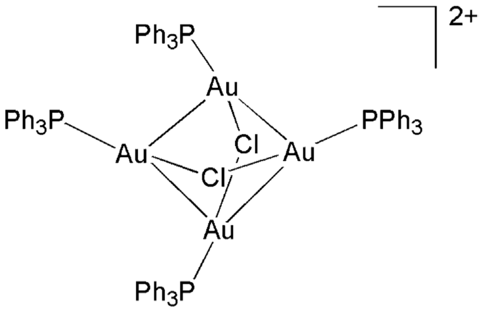


Figure 1.42 Structure of $[\{Cl(AuPPh_3)_2\}_2]^{2+}$.

compounds display rich luminescence properties with intense green and orange emissions.

Halide anions can also act as single bridges between two gold centers in complexes of the type $[X(AuPPh_3)_2]^+$ (X = Cl, Br), which are usually monomers but in SbF_6^- salt the chloronium cations undergo an intimate aggregation; dimerization occurs against electrostatic repulsion, which appears to be offset by the gain in the number of aurophilic interactions (Figure 1.42) [244].

Other examples of polyauration around a single bridging heteroatom are those arising at borides, phosphide or chalcogenolate ligands. Therefore the reaction of the phosphineborane $(Cy_3P)(SiMe_3)BH_2$ with the oxonium salt, $[O(AuPPh_3)_3]BF_4$, gives the tetra-aurated compound $[(Cy_3P)B(AuPPh_3)_4]BF_4$ (Figure 1.43) [245].

Phosphide ligands of the type PR^{2-} or PR_2^- also yield polynuclear derivatives such as $[RP(AuPPh_3)]BF_4$, obtained by reaction of RPH_2 with $[O(AuPPh_3)]BF_4$; this subsequently reacts with $[Au(BF_4)(PPh_3)]$ to afford $[RP(AuPPh_3)_4](BF_4)_2$ [246]. Gold clusters with arsenide (AsR^{2-}) or phosphide (P^{3-} and PR_2^-) have been synthesized from the reaction of $[Au_2Cl_2(\mu\text{-}P\text{–}P)]$ with $RAs(SiMe_3)_2$, or with $RP(SiMe_3)_2$ and $P(SiMe_3)_3$, respectively [247]. They have a varied stoichiometry, such as $[Au_{19}(As^nPr)_8(dppe)_6]Cl_3$, $[Au_{10}(AsPh)_4(dppe)_4]Cl_2$ or $[Au_{18}P_2(PPh)_4(PHPh)(dppm)_6]Cl_3$ (Figure 1.44).

Chalcogenolate gold(I) complexes of the type $[Au(ER)(PR'_3)]$ (E = S, Se, Te) can further aggregate more gold atoms giving di- or trinuclear complexes of the form $[Au_2(\mu\text{–}ER)(PR'_3)_2]^+$ or $[Au_3(\mu\text{–}ER)(PR'_3)_3]^{2+}$ [41]. Similar complexes are

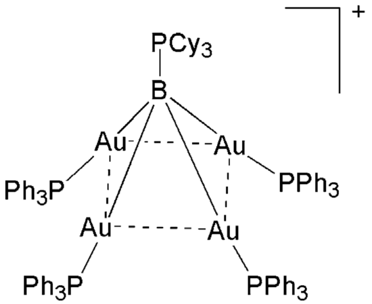


Figure 1.43 Structure of $[(Cy_3P)B(AuPPh_3)_4]BF_4$.

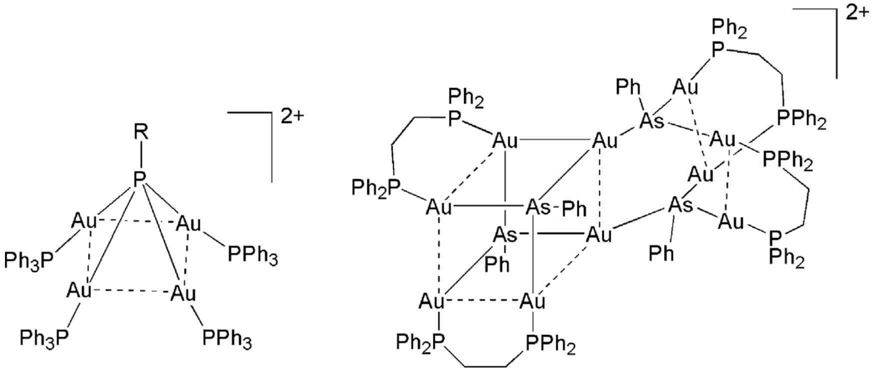


Figure 1.44 Phosphide and arsenide gold(I) complexes.

obtained with diphosphine ligands, for example the oxidation of $[Au_2(SC_6H_4\text{-}4\text{-}Me)_2(\mu\text{-}dppm)]$ with the ferrocenium cation $[FeCp_2]PF_6$ gives the luminescent cluster $[Au_9(\mu\text{-}SR)_6(\mu\text{-}dppm)]^{3+}$ [248]. A dinuclear diphosphine gold(I) thiolate has been functionalized with a macrocycle designed for specific coordination of K^+, the macrocycle encapsulates the ion in a sandwich fashion, bridging the two gold atoms in close proximity which triggers luminescence because of the formation of an Au–Au interaction [249]. The doubly-bridging chalcogenolate complexes are very numerous for sulfur, less for selenium and are not well represented for tellurium; one example is the cluster compounds $[Au_8(TeR)_8(PR'_3)_4]$ prepared by reaction of TeR^- with $[AuCl(PR'_3)]$ in contrast to the expected mononuclear complexes obtained for sulfur and selenium [250]. The triply-bridging species are very scarcely represented and only the sulfur complexes $[MeS(AuPMe_3)_3]^{2+}$ or $[{}^tBuS(AuCl)_3]^-$ have been structurally characterized [251]. Figure 1.45 shows some examples of these chalcogenolate complexes.

1.2.4.6 Organometallic Gold(I) Complexes

Organometallic gold(I) complexes are an important class of complexes in gold chemistry. The Au–C bond is largely covalent and its stability depends largely on the type of ligand. Carbonyl gold(I) complexes are very scarce and unstable, alkyl complexes are not as stable as aryl, and the latter are in turn less stable than ylide or methanide ligands. Other important types of organometallic ligands in gold chemistry are alkynyl and carbene ligands, whose chemistry has recently been developed.

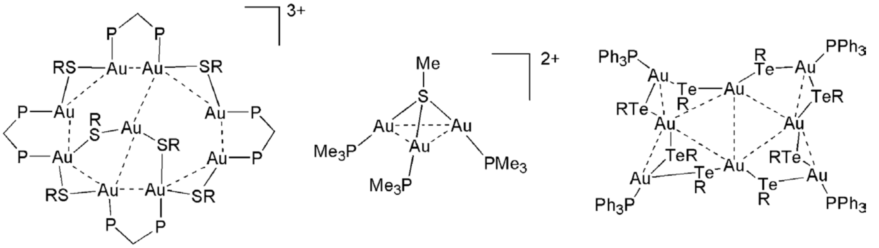


Figure 1.45 Chalcogenolate gold(I) complexes.

Only a few carbonyl complexes have been reported: the long known [AuX(CO)] (C = Cl, Br), [Au(OSO$_2$F)(CO)], [Au(CO)ClAuCl$_3$] and the tris(pyrazolyl)borate [Au{HB(2,5-(CF$_3$)$_2$pz)}$_3$(CO)] [252]. All the compounds exhibit υ(CO) infrared frequencies at higher wavenumbers than free CO, indicating insignificant π-back donation from gold to CO. Alkyl or aryl gold(I) complexes are usually synthesized by reaction of an alkyllithium or a Grignard reagent with a gold(I) compound. Complexes of the type [AuRL] have been reported for a great variety of organic ligands [253], some of them, such as [Au(C$_6$F$_5$)(tht)], with the pentafluorophenyl unit that confers great stability to these complexes, have been widely used as starting material in order to coordinate the "Au(C$_6$F$_5$)" fragment to almost any ligand type [41]. The anionic complexes [AuR$_2$]$^-$, where R is a perhaloalkyl group, have special electronic characteristics that allow them to react as Lewis bases towards many Lewis acid metals such as Ag$^+$, Tl$^+$, Cu$^+$, and so on. With silver, complexes of the type [Au$_2$Ag(C$_6$F$_5$)$_4$(OCMe$_2$)$_2$]$_n$ are obtained; this is a polymeric chain with the tetranuclear units bonded through aurophilic interactions [254]. However, with TlPF$_6$ a chain with unsupported Au–Tl–Au–Tl bonds is formed with [Au(C$_6$Cl$_5$)$_2$]NBu$_4$ [255]. Similar behavior is displayed by the dicyanide salt [Au(CN)$_2$]$^-$, which acts as a building block to synthesize supramolecular coordination polymers [256]. All these complexes show intense luminescence and in some cases reversible vapochromic behavior with several organic solvents. Figure 1.46 shows some of these complexes.

Ylide complexes of gold(I) in which a carbanionic center is σ-bonded to the gold center, are very stable. The ligands are usually phosphonium or sulfonium ylides with tetra-coordinated, positively charged P or S atoms and, consequently, the negative charge should be on the metal center. This is the reason for the excellent donor properties of these ligands. In order to illustrate these donor properties, the complex [Au(CH$_2$PPh$_3$)$_2$]ClO$_4$, in spite of its cationic nature, behaves as a donor towards Ag$^+$ salts giving the tetranuclear derivatives [Au$_2$Ag$_2$(OClO$_3$)$_4$(CH$_2$PPh$_3$)$_4$] (Figure 1.47a) with Au–Ag interactions [257]. Complexes with aurated ylides of the type [Me$_3$PC(AuPPh$_3$)$_3$]$^+$ [258] (Figure 1.47b) or multiaurated [(Me$_2$SO)C(AuPPh$_3$)$_4$]$^{2+}$ [259] (Figure 1.47c) have been reported.

Phosphonium salts of the type Me$_4$P$^+$ or Ph$_2$Me$_2$P$^+$, which has two carbon centers, can, after deprotonation, give the bis(ylide) species and its gold compounds

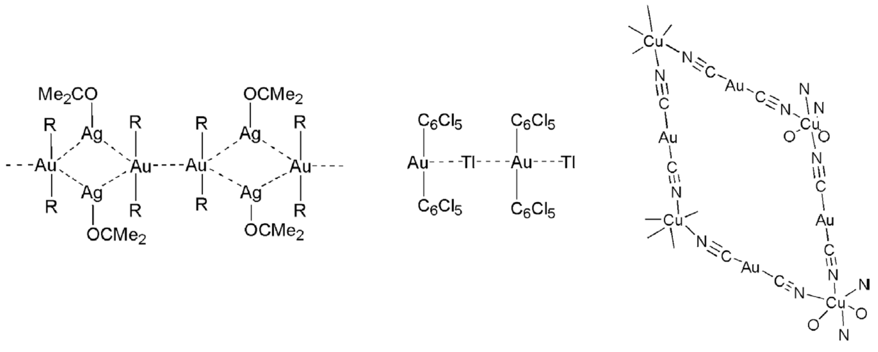


Figure 1.46 Donor–acceptor supramolecular gold(I) complexes.

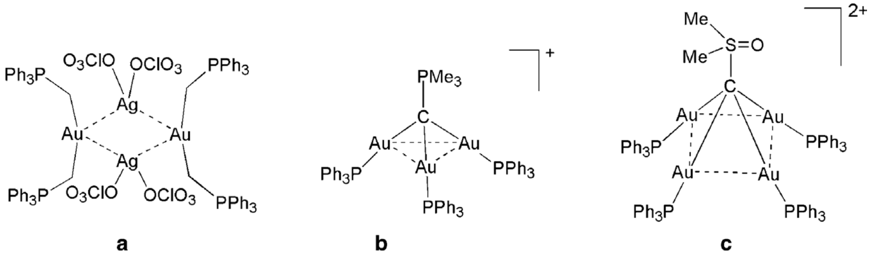


Figure 1.47 Ylide gold(I) complexes.

$[Au_2\{(CH_2)_2PR_2\}_2]$ have remarkable stability and have served as a gateway to a rich chemistry in dinuclear gold(II) ylide complexes [260]. Similar dinuclear complexes have been prepared with the $CH_2PPh_2S^-$ ylide ligand (Figure 1.48) [261]. Ligands related to the ylides are methanides. These are produced after deprotonation of a methylene ligand, usually between two phosphorus atoms. The best example is the dppm ligand which, after deprotonation, gives monoanionic tridentate or dianionic tetradentate ligands as in $[Au_4(CH_2SONMe_2)\{(PPh_2)_2CH\}(dppm)]$ [262] or $[(PPh_3Au)_2C\{(PPh_2)_2Au(PPh_2)_2\}C(AuPPh_3)_2]^{2+}$ [134], respectively, (Figure 1.49).

Carbenes are species with a divalent carbon atom with various substituents and a lone pair of electrons. Classic carbene gold complexes were synthesized in the coordination sphere of the gold atom, addition of amines or alcohols to the coordinated isocyanide ligands. N-Heterocyclic carbenes (Arduengo's carbenes)

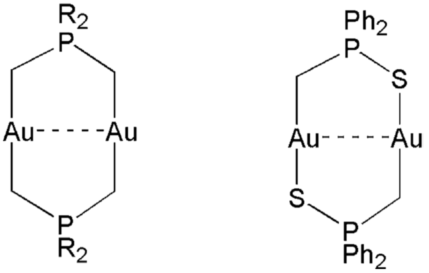


Figure 1.48 Dinuclear gold ylides.

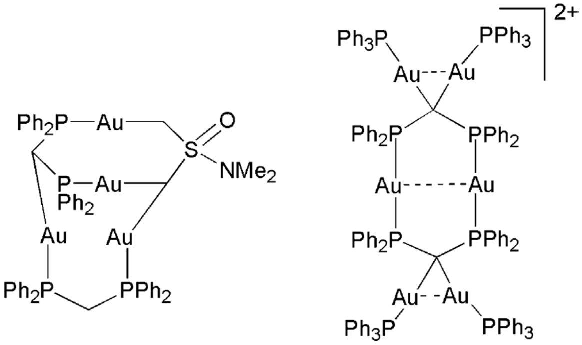


Figure 1.49 Methanide gold(I) complexes.

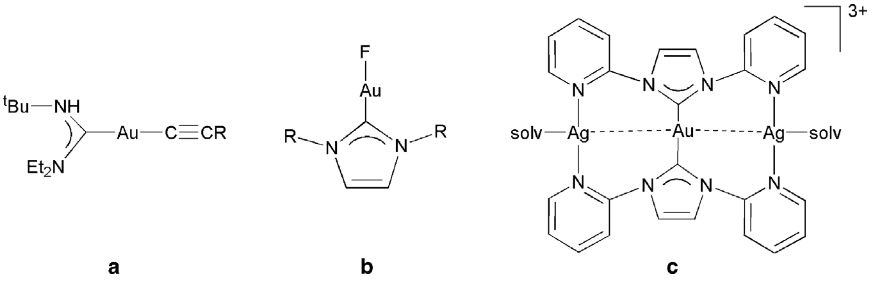


Figure 1.50 Carbene gold(I) complexes.

based on imidazol or benzimidazol have been developed more recently and have been extensively used in the catalysis of organic reactions by gold [26]; these complexes have also been postulated as intermediates in many gold catalyzed reactions (see Chapter 8). Addition of amines to gold(I) isocyanide complexes, including alkynes as auxiliary ligands in gold, gives the carbene derivatives (Figure 1.50a) [263]. Cationic bis(carbene) complexes have been known for a long time but their interesting luminescence properties have only been discovered recently. The complexes $[Au\{C(NHMe)_2\}_2]PF_6$ show structures in which the cations are stacked through aurophilic interactions and hydrogen bonds and are emissive. Frozen solutions are also luminescent with different colors, depending on the solvent, but the solutions are nonluminescent. Since the complex $[Au\{C(NHMe)(NMe_2)\}_2]PF_6$ is a monomer in the solid state, luminescence clearly occurs in the presence of the metallophillic interactions [264]. Many complexes with N-heterocyclic carbene ligands of different stoichiometries have been reported; they are of the type [AuX(carbene)], $[AuL(carbene)]^+$ or $[Au(carbene)_2]^+$ [265]. They derive mainly from imidazol, benzimidazol and benzothiazol salts that, after deprotonation, give the free carbene that can coordinate the gold center. Another route is reaction with the easily available silver carbene complexes. The complexes [AuCl(carbene)] have been successfully used as a catalyst in several organic reactions. A remarkable case is the obtainment of [AuF(carbene)] (Figure 1.50b), which represents the first example of an isolable gold(I) fluoride complex [266]. Theoretical calculations show significant $\pi p/d\pi$ interactions between fluoride and gold(I) and indicate a substantial negative charge on fluorine. Heterofunctional carbene ligands also give heteronuclear species with Au–Ag interactions and luminescence properties (Figure 1.50c) [267].

The chemistry of alkynyl gold(I) complexes has grown in recent years. The preference of gold(I) for a linear coordination, together with the linearity of the $C\equiv C$ bond of the alkyne unit and its π-unsaturated nature, have made the alkynyl gold complexes attractive building blocks for molecular wires and organometallic oligomeric and polymeric materials, which may have unique properties such as optical nonlinearity, liquid crystallinity or luminescence. Alkynyl gold complexes have been postulated as intermediates in many organic reactions catalyzed by gold complexes (see Chapter 8). Complexes of the type $[Au(C\equiv CR)L]$ are well represented and are readily obtained through the reaction of the polymeric $[Au(C\equiv CR)]_n$ species with L or by methathesis of [AuClL] complexes with the

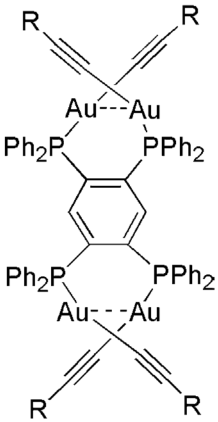
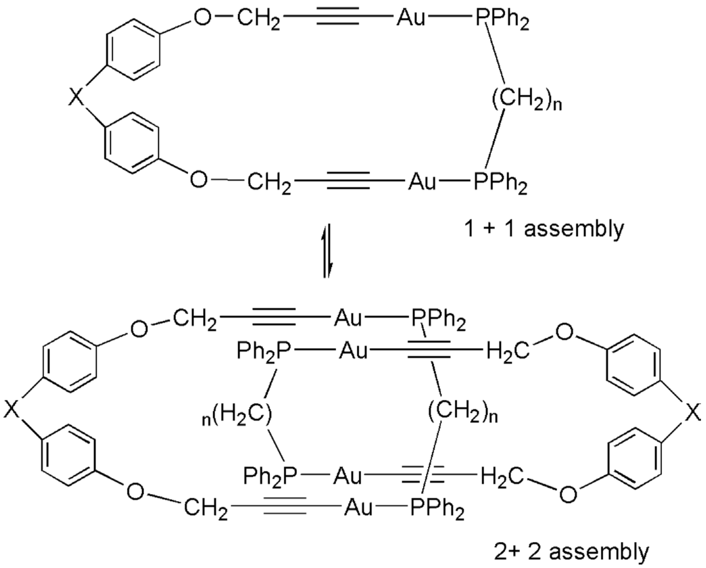


Figure 1.51 Structure of $[Au_4(C{\equiv}CR)_4\{(PPh_2)_4C_6H_2\}]$.

deprotonated alkynyls. The ligand L is usually a tertiary phosphine and bidentate or polydentate phosphines (Figure 1.51) have been used as auxiliary ligands, giving polynuclear complexes not always of the expected nuclearity [41, 268]. These reactions have led to the discovery of organometallic catenanes by self-assembly of an oligomeric digold(I) diacetylide $[\{(AuC{\equiv}CCH_2OC_6H_4)_2X\}_n]$ and a diphosphine ligand $Ph_2P(CH_2)_nPPh_2$. Systematic research of this unusual reaction has revealed that the number of methylene spacer groups n in the diphosphine ligand and the nature of the hinge group X are key factors for determining whether self-assembly will give a simple ring by 1 + 1 assembly, a [2]catenane by 2 + 2 assembly, or a double braided [2]catenane by 4 + 4 asembly (Scheme 1.1) [269].



Scheme 1.1 Catenane gold alkynyl complexes.

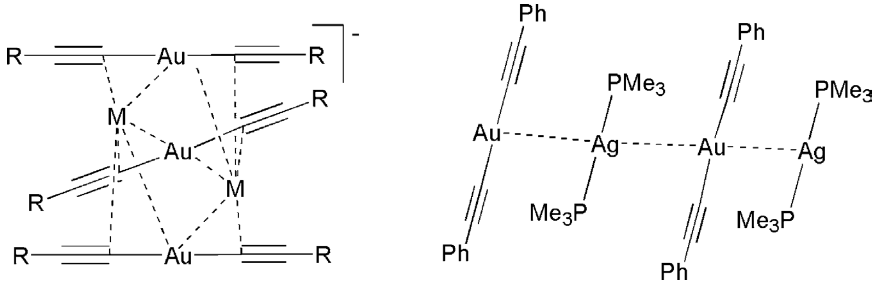


Figure 1.52 Heteronuclear alkynyl gold(I) complexes.

Anionic gold(I) alkynyl complexes of the type $[Au(C{\equiv}CR)_2]^-$ are also known and reactions with metals such as Ag^+, Cu^+ give heteropolynuclear complexes $[Au_3M_2(C{\equiv}CR)_6]^-$ ($M = Cu$, Ag). The complex $[Ag(PMe_3)_2][Au(C{\equiv}CPh)_2]$ forms a chain of alternating cations and anions through Au–Ag interaction [270]. Figure 1.52 collects some of these alkynyl gold(I) complexes.

1.2.5
Gold(II) Complexes

The number of complexes with gold in a formal oxidation state of two have increased considerably and nowadays this oxidation state can almost be considered as a common oxidation state in gold chemistry; however, the number of gold(II) complexes is very scarce if compared with the more common gold(I) or gold(III) derivatives. The energy required to reach Au^{2+} from atomic gold is not very far from that required to form either Cu^{2+} or Ag^{2+} and to attain M^{3+} less energy is required for Au than for Cu and Ag. Therefore, this argument is not sufficient to justify the lack of stability for the oxidation state 2+ in gold. There is a strong tendency for disproportionation to give Au^+ and Au^{3+} because the odd electron in d^9 metal complexes is in a d_{x2-y2} orbital (octahedral tetragonally distorted or square planar arrangement) which has a much higher energy than copper and can be easily ionized. The formation of a gold–gold bond gives more stable compounds and the $Au_2{}^{4+}$ core species are the most stable and abundant types of gold(II) complexes. Mononuclear gold(II) derivatives are not very abundant and, when reported, further study confirmed that they were mixed gold(I)–gold(III) complexes such as the halides $CsAuX_3$ ($=Cs_2Au^IAu^{III}X_6$, $X = Cl$, Br, I) [271].

1.2.5.1 Mononuclear Gold(II) Complexes

Mononuclear gold(II) complexes, consistent with a d^9 configuration, must be paramagnetic ($\mu_{eff} = 1.79$ MB) and show a hyperfine four-line EPR signal, in accordance with the nuclear spin of ^{197}Au ($I = 3/2$). These two properties are evidence of a real gold(II) complex in addition to their stoichiometry.

In 1992 Herring *et al.* gave clear EPR and magnetic evidence for Au^{2+}, as a species present in partially-reduced $Au(SO_3F)_3$ and as a solvated ion in the strong protonic acid HSO_3F [272]. Recently, Bartlet *et al.* prepared and structurally characterized Au(II) fluoro complexes [273]. Gold dissolves at around 20 °C with F_2 in anhydrous HF acidified with SbF_5, to give a red solution from which orange crystals of $Au(SbF_6)_2$ crystallize. Exhaustive fluorination results in total conversion of the gold to an insoluble crystalline red solid, which is $Au^{II}(SbF_6)_2Au^{II}(Au^{III}F_4)_2$. Solvolysis of $Au(SbF_6)_2$ in anhydrous HF results in disproportionation to gold and the mixed-valence fluoride $Au^{II}Au^{III}{}_2F_8$. In $Au(SbF_6)_2$ the gold(II) atom is at the center of an elongated octahedron of F ligands, the fluor atoms of the approximately square AuF_4 unit are at 2.09(2) and 2.15(2) Å × 2, each F provided by a different SbF_6 species. The two long Au–F interatomic distances are at 2.64(2) Å.

Most of the compounds already described were prepared with unsaturated S-donor ligands such as dithiocarbamates, dithiolates, dithiolenes or, in general, ligands able to delocalize the unpaired electron, and can be better described as ligand-radical species [274]. The mononuclear gold(II) complex with the thioether macrocycle 1,4,7-trithiacyclononane ([9]aneS_3), $[Au([9]aneS_3)_2](BF_4)_2$, (Figure 1.53) obtained by reduction of $HAuCl_4{\cdot}3H_2O$ with two equivalents of [9]aneS_3 in refluxing HBF_4 (40%)/MeOH [275] was described as a truly gold(II) complex with an octahedral arrangement of six sulfur atoms around the gold center, with a Jahn–Teller distortion. The EPR spectrum showed a hyperfine four-line EPR signal at $g = 2.010$ and the lone pair of electrons belonged predominantly to the gold center, with limited delocalization through the ligand. However, DFT calculations and EPR simulations coincided and showed that the singly-occupied molecular orbital (SOMO) has about 27–30% Au $5d_{xy}$ character and 62–63% equatorial S 3p character, confirming the non-innocence of thioether ligands in this system [276].

Stable gold(II) complexes with nitrogen- and oxygen-containing ligands such as CO_2, Me_2CO, thf, pyridine, and so on, have been prepared in the gas phase. The successful ligands are characterized by being good σ donor–π acceptor molecules and the most stable are those with large dipole moment and a high ionization energy [277].

Recently, the first metal–xenon compound was obtained by reducing AuF_3 with elemental xenon. In attempts to synthesize the elusive AuF, gold(III) reduction was performed with xenon, which is a very mild reducing and very weakly coordinating agent. Surprisingly, the reaction stopped at the Au^{2+} state and resulted in a completely unexpected complex, the cation $AuXe_4{}^{2+}$, the crystals of which can be

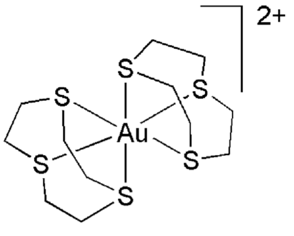


Figure 1.53 Structure of $[Au([9]aneS_3)_2](BF_4)_2$.

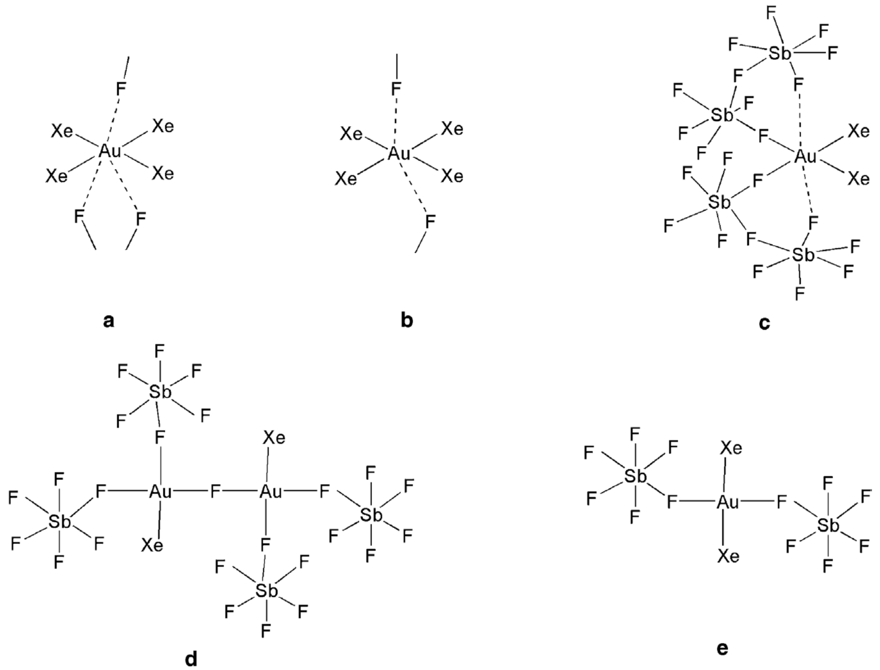


Figure 1.54 (a) triclinic $[AuXe_4]^{2+}$; (b) monoclinic $[AuXe_4]^{2+}$; (c) $[AuXe_2]^{2+}[Sb_2F_{11}]^{2-}$; (d) $[Au_2Xe_2F]^{+}[SbF_6]^{-}$; (e) *trans*-$[AuXe_2]^{+}[SbF_6]^{-}$.

grown at –78 °C. Removal of gaseous xenon under vacuum results in the crystallization of $Au(SbF_6)_2$ [278]. The crystal structure of $(Sb_2F_{11})_2[AuXe_4]$ shows a regular square with Au–Xe bond lengths ranging from 2.728(1) to 2.750(1) Å. Three weak contacts between the cation and the anion complete the coordination sphere around the gold atom with Au–F distances of 2.671 and 3.153 Å (Figure 1.54).

In this complex, xenon functions as a σ-donor toward Au^{2+}. This is reflected in the calculated charge distribution within the cation, where the main part of the positive charge resides in the xenon atoms. Relativity plays a large role in stabilizing this and other predicted Au–Xe compounds; about half of the Au–Xe bonding energy comes from relativistic effects [279].

A further study of this reaction [280] has shown that if the concentration of SbF_5 is fairly high, complex $[AuXe_4][Sb_2F_{11}]_2$ forms as the sole product in two crystallographically-different modifications, the triclinic commented previously and another monoclinic, which has been seldom observed. Both modifications differ only in the cation–anion interactions, with a long Au–F contact of 2.928(7) in the monoclinic form. Through a variation in xenon pressure and the acid strength of the HF/SbF_5 other species have been isolated such as *cis*-$[AuXe_2][Sb_2F_{11}]_2$, *trans*-$[AuXe_2][SbF_6]_2$, $[Au_2Xe_2F][SbF_6]_3$ and the first Au(III)-Xe complex $[AuXe_2F][SbF_6][Sb_2F_{11}]$. Their structures are shown in Figure 1.54.

1.2.5.2 Polynuclear Gold(II) Complexes

As mentioned previously, one of the reasons for the poor stability of gold(II) complexes is the unfavorable energy of the odd electron. The formation of a metal–metal bond in dinuclear gold(II) complexes giving diamagnetic species provides extra stability. Thus, the number of gold(II) complexes containing the Au_2^{4+} core has increased in recent decades and different stoichiometries are known. Most of the dinuclear gold(II) compounds are synthesized from the corresponding gold(I) precursors by oxidative addition of halogen. This method works properly with a great variety of dinuclear gold(I) complexes. These include symmetric and asymmetric doubly bridged compounds, monobridged dinuclear derivatives or compounds without any bridging ligand. The bridging ligands vary from diphosphines, dithiocarbamates and related species, ylide ligands and mixed-donor ligands of the types C,S or C,P. Experimentally it has been confirmed that the oxidation of a dinuclear gold(I) complex to a gold(II) derivative gives more stable complexes when the gold is bonded to carbon donor ligands. This is true in the case of bis-ylide ligands. Although the most commonly used oxidants are halogens, others have been used such as haloalkyl RX, $[Hg(CN)_2]$, nitroalkanes, N_2O_4, $[Tl(C_6F_5)_2Cl]$, tetraethylthiuram disulfide, $[Ag(OClO_3)(PPh_3)]$ or $[Ag(NCMe)_4]PF_6$.

Dinuclear homoleptic gold(II) complexes with a homo-bridged ligand have been described with many ligands such as sulfate [281], ylide [260] dithiocarbamate [282], dithiolate [283], amidinate [284] or with heterofunctional ligands such as $SPPh_2CH_2^-$ [261], $PR_2C_6H_4^-$ [285] (Figure 1.55). The sulfate salt $AuSO_4$ has long been referred to as a mixed-valent compound in many chemistry textbooks, in spite of the lack of information regarding its crystal structure. Recently, the crystal structure has been determined and shows that $AuSO_4$ is the first simple inorganic compound known containing the cation Au_2^{4+}. This cation is coordinated by two chelating sulfate groups and two monodentate SO_4^{2-} ions. The gold–gold distance is 2.49 Å, the shortest known for dinuclear gold(II) complexes.

The majority and the most stable compounds have been prepared with bis-ylide ligands. Complexes of the type $[Au_2\{\mu\text{-}(CH_2)_2PR_2\}_2]$ have been useful starting materials for the development of gold(II) chemistry. Their oxidation with several reagents such as halogens, alkyl halides, E_2R_2, $[Hg(CN)_2]$ affords the corresponding gold(II) derivatives (see Scheme 1.2). The addition of haloalkanes to dinuclear gold(I) bis-ylide complexes also affords the gold(II) species. Considerable effort has been expended to elucidate the oxidative addition reaction of haloalkanes, and experimental evidence supports the notion that the order of reactivity of such

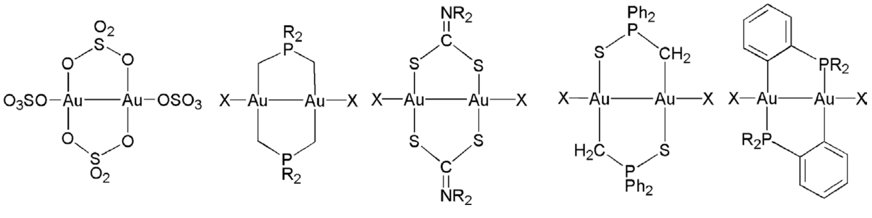
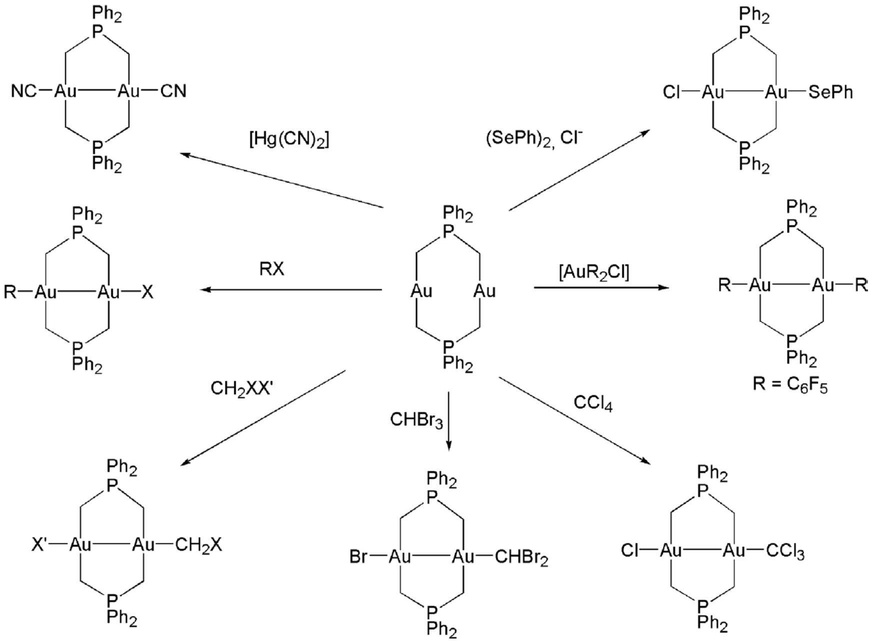


Figure 1.55 Homobridged gold(II) complexes.



Scheme 1.2 Synthesis of bis(ylide) gold(II) complexes.

substrates is inversely proportional to the carbon–halogen bond dissociation energies [286].

Dinuclear gold(II) derivatives with two different bridging ligands have also been synthesized; all of them have the ylide $(CH_2)_2PPh_2^-$ ligand and another bridging ligand that can be diphosphines such as $Ph_2PCH_2PPh_2$ or $Ph_2PNHPPh_2$, dithiocarbamates, xanthate, 2-pyridinethiolate, phosphoniodithioformate, or dithiophosphinate [287] (Figure 1.56).

Another general procedure for preparing gold(II) complexes consists of substitution reactions on gold(II) derivatives. Halide ligands can be substituted by neutral donor ligands such as tetrahydrothiophene, py, ylide, phosphine, and so on, to give the corresponding cationic complexes, or with other anionic ligands such as pseudohalide, carboxylate, dithiocarbamate, thiourea derivatives, and so on, [288]. An interesting class of substitution reactions in these gold(II) derivatives are those where the new

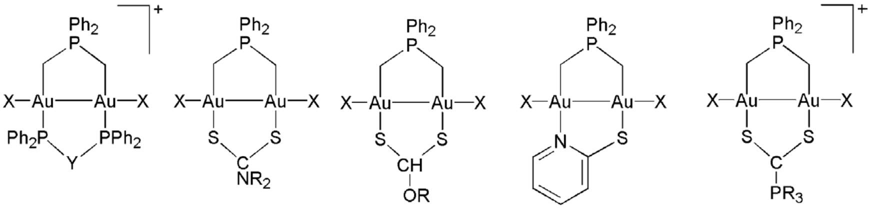
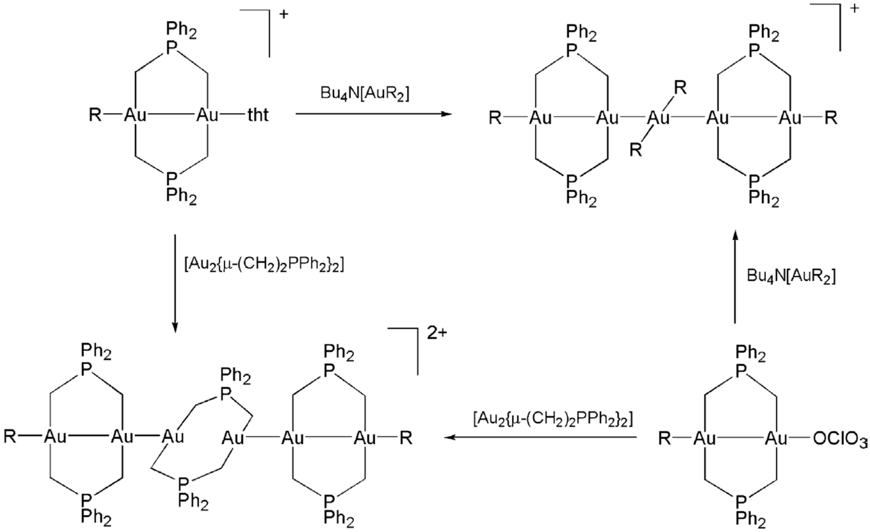


Figure 1.56 Heterobridged gold(II) complexes.



Scheme 1.3 Synthesis of polynuclear gold(II) ylide complexes.

ligands are metal complexes. The reaction of the gold(II) $[Au_2(C_6F_5)_2\{\mu\text{-}(CH_2)_2PR_2\}_2]$ with the gold(III) species $[Au(C_6F_5)_3(OEt)_2]$ gives the pentanuclear complex $[\{Au_2R\{\mu\text{-}(CH_2)_2PR_2\}_2\}_2(AuR_2)][AuR_4]$ ($R = C_6F_5$) [289]. Its backbone is a linear chain of five gold atoms, all of which have square planar geometry. The Au–Au distances of 2.755(1) and 2.640(1) Å are characteristic of metal–metal bonds, the former corresponding to the unsupported gold–gold bond. The unit $[\{Au_2R\{\mu\text{-}(CH_2)_2PR_2\}_2\}_2]^+$ is readily accessible from many complexes such as $[Au_2R(tht)\{\mu\text{-}(CH_2)_2PR_2\}_2]^+$ or $[Au_2R(OClO_3)\{\mu\text{-}(CH_2)_2PR_2\}_2]$ ($R = C_6F_5$, 2,4,6-$C_6F_3H_2$). The reaction of these gold(II) complexes with either organoaurate $Bu_4N[AuR_2]$ or the gold(I) bis-ylide $[Au_2\{\mu\text{-}(CH_2)_2PR_2\}_2]$, both highly nucleophilic compounds, enables the synthesis of gold chain complexes (Scheme 1.3) [290].

Another interesting polynuclear gold(II) complex has been reported with the ylide ligand $SPPh_2CH_2^-$ by oxidation with halogens of the trinuclear species $[Au_2Pt(\mu\text{-}CH_2PPh_2S)_2]$. A Cl–Au–Pt–Au–Cl (Figure 1.57a) is obtained and although an Au^{II}-

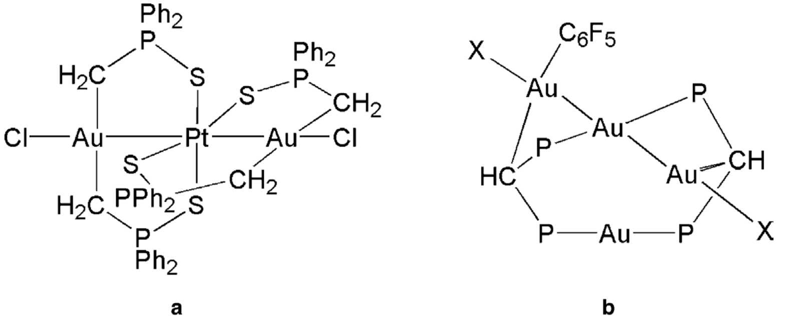


Figure 1.57 Polynuclear gold(II) complexes.

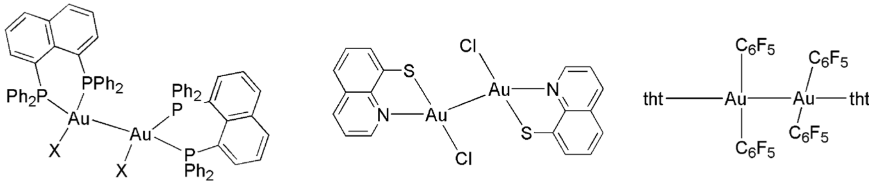


Figure 1.58 Unsupported gold(II) complexes.

Pt^{II}-Au^{II} assignment of the oxidation states can be made, a more correct description, based on Fenske–Hall calculations, is that an $[Au\text{-}Pt\text{-}Au]^{2+}$ moiety is formed [291]. The reaction of the tetranuclear complex $[Au_2\{\mu\text{-}(PPh_2)_2CHAu(C_6F_5)\}_2]$ with chlorine or bromine does not oxidize the two gold centers of the diauracycle to give the usual gold(II) derivatives with an X–Au–Au–X backbone. Instead, a new type of reaction occurs, probably because of the presence of other gold(I) centers in close proximity (Figure 1.57b). The proposed assignment of the oxidation states in the linear chain is Au(II)–Au(I)–Au(II) [292].

Dinuclear gold(II) complexes with unsupported Au^{II}–Au^{II} bonds have been reported for chelating ligands such as 1,8-bis(diphenylphosphino)naphthalene (dppn), obtained by oxidation of $[Au_2X_2(dppn)]$ with $[Ag(NCMe)_4]PF_6$ [293], or bis (quinolin-8-ylthio) [294]. The only one described with no chelating ligands is $[Au_2(C_6F_5)_4(tht)_2]$, which has been prepared by reaction of equimolar amounts of $[Au(C_6F_5)(tht)]$ and $[Au(C_6F_5)_3(tht)]$ [295]. Figure 1.58 shows these unsupported gold (II) complexes.

1.2.6
Gold(III) Complexes

The chemistry of gold(III) complexes is far less developed than the corresponding gold(I) complexes. Gold(III) gives stable complexes with C, N, P, S, or even O-donor ligands. Organometallic chemistry is very important because many compounds have been prepared starting from organometallic gold(III) precursors.

1.2.6.1 Organometallic Gold(III) Complexes

The majority of gold(III) complexes with carbon donor ligands are with alkyl and mainly aryl ligands and several methods exist for their synthesis:

1. Oxidative addition of halogen to the respective gold(I) complex
2. Electrophilic substitution by gold(III) of one aromatic ring (metallation)
3. Transmetallation reaction with HgR_2
4. Substitution reactions on gold(III) derivatives.

Alkyl gold(III) complexes have the general formula $[AuR_4]^-$, $[AuR_3L]$, $[AuR_2X_2]^-$ or $[AuR_2L_2]^+$ where L can be a great variety of donor ligands and R can also be replaced by another anionic ligand such as halogen, giving complexes of the type $[AuR_nX_{3-n}L]$ or with mixed organometallic ligands $[AuRnR'_{3-n}L]$. Some examples are with methyl or trifluoromethyl ligands such as $[Au(CF_3)X_2(PR_3)]$ or $[AuMe_2(P,N)]^+$ [296]

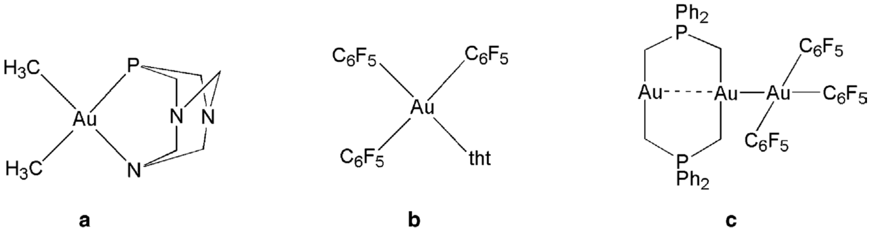


Figure 1.59 Alkyl or aryl gold(III) complexes.

(Figure 1.59a). Aryl gold(III) complexes are more numerous and complexes with perfluoroaryls, such as $[Au(C_6F_5)_3(tht)]$ (Figure 1.59b) obtained by oxidative addition of $[Au(C_6F_5)(tht)]$ with $[Tl(C_6F_5)_2Cl]_2$, have been widely used as a starting material because of their high stability [297]. The compound $[Au(C_6F_5)_3(OEt_2)]$ is a very good acceptor that reacts with the electron-rich bis(ylide) to give the donor–acceptor complex $[Au\{(CH_2)_2PPh_2\}_2Au(C_6F_5)_3]$ (Figure 1.59c) [298]. The complexes $[Au(C_6F_5)_2X_2]^-$ and $[Au(C_6F_5)_2Cl]_2$ are also excellent starting materials for obtaining complexes with the "$Au(C_6F_5)_2$" unit [297]. Arylgold(III) complexes are good catalysts for the addition of nucleophiles to alkynes (see Chapter 8).

The auration of hydrocarbons such as benzene, toluene, and so on, with anhydrous $AuCl_3$ in an inert solvent gives $AuRCl_2$, which, in the presence of ligand L, affords $[AuRCl_2L]$ compounds [299]. The reaction of substituted pyridine ligands (HL) with $[AuCl_4]^-$ gives the complexes $[AuCl_3(HL)]$, which upon heating give the cyclometallated species $[Au(C,N)Cl_2]$ or $[Au(C,N,N)Cl]^+$ [300]. Several gold(III) cyclometallated complexes have shown cytotoxic activity to various cancer cells and sometimes with significant antiproliferative effects and promotion of apoptosis to a greater extent than platinum drugs [301]. Sometimes cyclometallation is difficult to achieve and the use of organomercurials as arylating agents is an appropriate route to $[Au(N,C)Cl_2]$ complexes [302], which has been used with azobenzene, *N*,*N*′-dimethylbenzylamine, and so on. Sequential arylations enable the synthesis of complexes with two different ligands of the type $[Au(C,N)ArCl]$. Upon treatment with phosphine or chloride, some of the N,C quelated diarylgold(III) chloride complexes undergo reductive elimination of the aryl ligands to give biaryls [303]. Figure 1.60 presents some examples of these complexes.

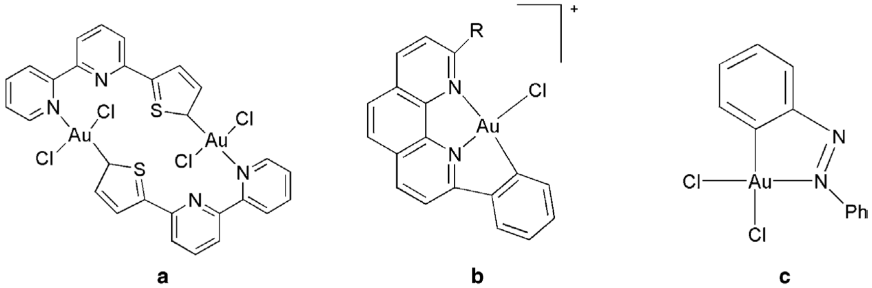


Figure 1.60 Cyclometallated gold(III) complexes.

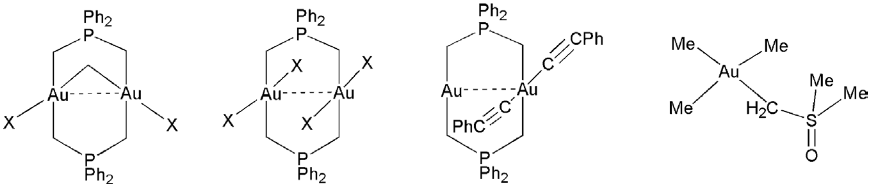


Figure 1.61 Ylide gold(III) complexes.

Ylide gold(III) complexes have been prepared by oxidation of the corresponding gold(I) complexes with CH_2X_2 or with halogens in the bis(ylide) gold(I) complexes $[Au_2\{(PPh_2)_2PR_2\}_2]$ [304], even by disproportionation of the gold(II) derivatives as in $[Au_2\{(PPh_2)_2PR_2\}_2(C{\equiv}CPh)_2]$ [305], and also by substitution reactions in gold(III) complexes of the type $[AuMe_3(PPh_3)]$, or by ylide transfer reactions from ylidegold(I) species [306]. Figure 1.61 shows some of these examples.

With methanide ligands a great amount of work has been carried out starting with complexes of the type $[Au(C_6F_5)_2(\eta^2\text{-L–L})]ClO_4$, $[Au(C_6F_5)_3(\eta^1\text{-L–L})]$, in which L–L represents a ligand such as $PPh_2CH_2PPh_2$, $PPh_2CH_2PPh_2R^+$ or $SPPh_2CH_2PPh_2$, and so on. Substitution by deprotonation with a base or with $[Au(acac)(PPh_3)]$ from one to three protons in one or two methylene groups affords a variety of polynuclear complexes with different coordination modes, as shown in Figure 1.62 [307].

Carbene gold(III) complexes have been developed to a much lesser extent than the corresponding gold(I). The reaction of the gold(III) isocyanide complexes $[Au(C_6F_5)_2(CNR)_2]ClO_4$ with hydrazines gives the double carbene species [308]. Related species have been prepared from $[AuCl_3(tht)]$ and lithiated thiazoline [309] or from the tetra(azide)gold(III) complex with isocyanide [310]. N-Heterocyclic carbenes have been prepared only recently by oxidation of the gold(I) derivatives [311]. Figure 1.63 shows these types of complexes.

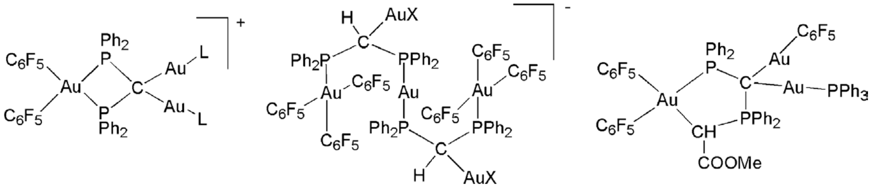


Figure 1.62 Methanide gold(III) complexes.

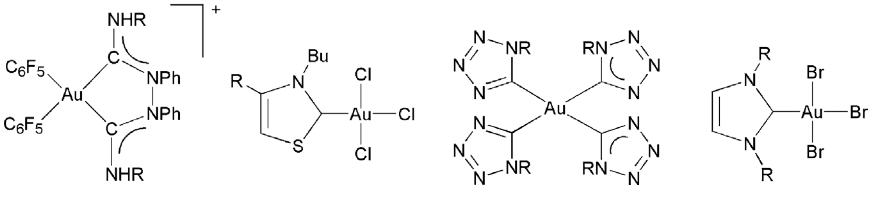


Figure 1.63 Carbene gold(III) complexes.

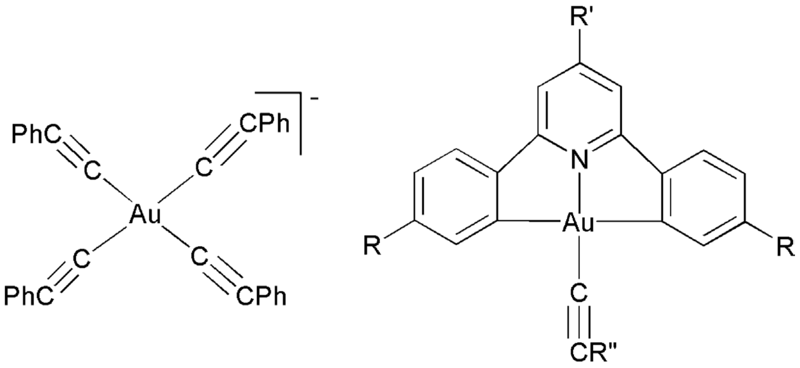


Figure 1.64 Alkynylgold(III) complexes.

Alkynyl gold(III) derivatives are not very numerous and the homoleptic species [Au$(C\equiv CR)_4]^-$ or the neutral $[Au(C\equiv CR)_3L]$ have been prepared, but rapid reduction to dialkynyls or $[Au(C\equiv CR)L]$ complexes occurs [312]. Several alkynylgold(III) complexes, which contain cyclometallated ligands, have been prepared and display rich luminescence. These are of the type $[Au(C\equiv CR)(C,N,C)]$ and the origin of the emission is assigned to a π–π^* intraligand transition of the cyclometallated moiety [313]. Figure 1.64 shows the alkynyl gold complexes. The tetra(cyano)gold(III) derivative $[Au(CN)_4]^-$ also functions as a building block in the synthesis of coordination polymers. It is a weaker ligand than the dicyanoaurate(I) and does not form gold–gold interactions but still yields polymers via M–NC coordinate bonds and also weak Au–NC intermolecular contacts [314] (Figure 1.65).

1.2.6.2 **Gold(III) Complexes with Polydentate Ligands**

Gold(III) complexes with nitrogen donor ligands are more stable than the corresponding gold(I) species. Several examples with polydentate amine ligands of different types have been reported. Polypyridines such as phenanthroline, terpyridine, pyrazolate ligands, and so on, form square planar gold(III) complexes such as $[AuCl(terpy)]^{2+}$ [315], $[AuMe_2(py_2CHpy)]^+$ [316] or $[AuCl_2(\mu\text{-}pz)]_2$ or $[Au\{N,N'\text{-}(pz)_3BH\}_2]ClO_4$ [317]. The rigid bidentate ligand phen enables the synthesis of pseudo-pentacoordinate gold(III) derivatives as in $[Au(C_6H_4CH_2NMe_2)(phen)(PPh_3)]^{2+}$ [318]. Complexes with polyamines and triethylenetetramine are known [319]. Figure 1.66 shows several of these complexes with polydentate amine

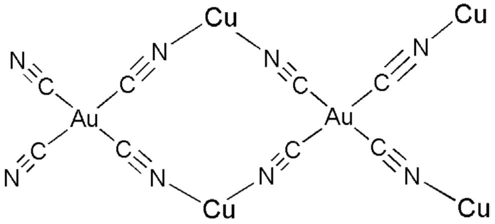


Figure 1.65 1-D chain structure of the cation $[Cu(bipy)(H_2O)_2(Au(CN)_4)_{0.5}][Au(CN)_4]_{1.5}$.

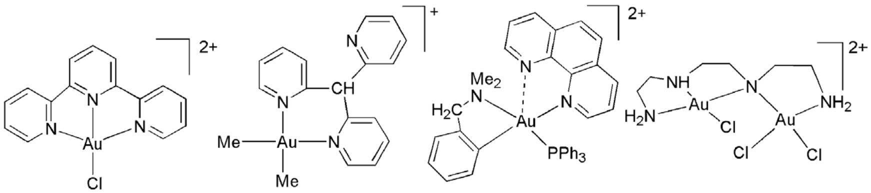


Figure 1.66 Gold(III) complexes with polydentate amine complexes.

complexes. The cytotoxic activity of some of these complexes with polydentate nitrogen ligands has been tested. The complex $[AuCl_2(phen)]Cl$ has shown to be highly cytotoxic toward the A2780 tumor cell line either sensitive or resistant to cisplatin; solution chemistry studies show that the fragment $[Au^{III}phen]^{3+}$ is stable in solution for several hours, even under physiological conditions. The predominant species existing in solution under physiological conditions is likely to be $[Au(OH_2)_2(phen)]^+$ [320].

Gold(III) porphyrins have been used as acceptors in porphyrin diads and triads due to their ability to be easily reduced, either chemically or photochemically. A new method for incorporating gold(III) into porphyrins (Figure 1.67a) has been described and consists of the disproportionation of $[Au(tht)_2]BF_4$ in its reaction with the porphyrin in mild conditions [321]. The metallation of [16]-hexaphyrin with $NaAuCl_4$ yielded the aromatic gold(III) complexes (Figure 1.67b) and the two-electron reduction of the aromatic complexes provided the antiaromatic species [322].

Complexes with diphosphines are numerous and are prepared mainly from substitution reactions in $[Au(C_6F_5)_3(tht)]$ or $[Au(C_6F_5)_2(OEt_2)_2]^+$ and are of the form $[Au(C_6F_5)_3(L\text{-}L)]$, $[Au_2(C_6F_5)_6(\mu\text{-}L\text{-}L)]$, $[Au(C_6F_5)_2Cl(L\text{-}L)]$ or $[Au(C_6F_5)_2(\mu\text{-}L\text{-}L)]^+$ [323]. The complex $[Au(C_6F_5)_2Cl\{PPh_2C(=CH_2)PPh_2\}]$ undergoes Michael-type additions with several nucleophiles, with addition to the terminal carbon of the double bond, giving methanide-type complexes [324]. Gold(III) complexes with triphosphines such as 1,1,1'-tris(diphenylphosphinomethyl)ethane, bis(diphenylphosphinomethyl)phenylphosphine have also been obtained [325]. The 2-(diphenylphosphino)aniline reacts with the $[Au(C_6F_5)_2(acac)]$ to give the depronated $[Au(C_6F_5)_2(PPh_2C_6H_4NH)]$,

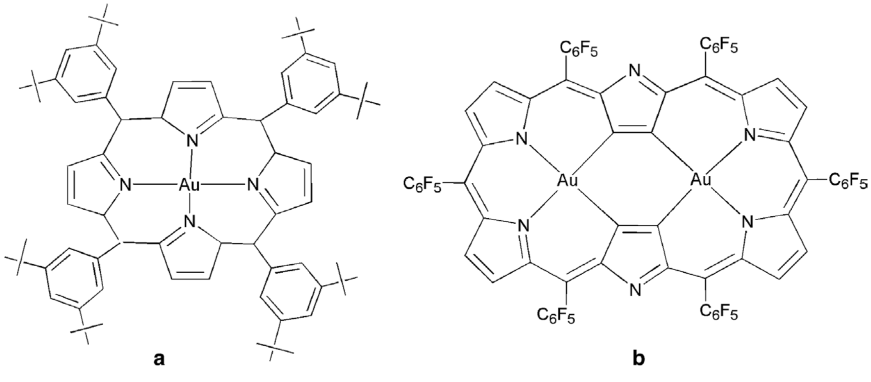


Figure 1.67 Gold(III) porphyrins.

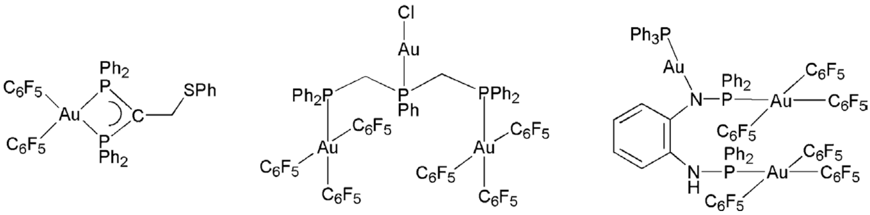


Figure 1.68 Gold(III) complexes with phosphine ligands.

which can be further deprotonated with [Au(acac)(PPh$_3$)] to give the complex [Au(C$_6$F$_5$)$_2${PPh$_2$C$_6$H$_4$N(AuPPh$_3$)$_2$}] [326]. Figure 1.68 shows some of these examples.

The reaction of [Au(C$_6$F$_5$)$_3$(tht)] or [Au(C$_6$F$_5$)$_2$(OEt$_2$)$_2$]ClO$_4$ with diphenylphosphine leads to complexes [Au(C$_6$F$_5$)$_3$(PPh$_2$H)] or [Au(C$_6$F$_5$)$_2$(PPh$_2$H)$_2$]ClO$_4$, which are useful starting materials for preparing polynuclear derivatives with bridging phosphide ligands by reaction with acetylacetonate gold compounds. The treatment of these derivatives with [N(PPh$_3$)$_2$][Au(acac)$_2$] or with salts of Ag$^+$ or Cu$^+$ in the presence of NBu$_4$(acac) gives the complexes shown in Figure 1.69 [327]. When the phosphine is the phenylphosphine PH$_2$Ph, the reaction with [Au(C$_6$F$_5$)$_2$Cl]$_2$ gives the cyclic trinuclear derivative [Au(C$_6$F$_5$)$_2$(μ-PHPh)]$_3$ (Figure 1.69) [328] .

1.2.6.3 Gold(III) Complexes with Chalcogen Ligands

Gold(III) forms very stable complexes with chalcogen donor ligands, mainly with sulfur donor compounds but stable species with Au^{III}–O bonds are known, in contrast to those found in Au(I) where these complexes, with some exceptions, are unstable. Hydroxo and oxo complexes have been reported with bypyridine, terpyridine or cyclometallated ligands. The hydroxo complexes are generally synthesized from the corresponding gold(III) precursor with NaOH or KOH in aqueous solution. The oxo species are mostly obtained, by deprotonation or by condensation of the hydroxo species [329]. Oxo complexes have shown antiproliferative effects and DNA and protein binding properties [330]. Other interesting gold(III) derivatives have been prepared by reaction of AuCl$_3$ with metal oxide polytungstate ligands [331]. These complexes, K$_{15}$H$_2$[Au(O)(OH$_2$)P$_2$W$_{18}$O$_{68}$]·25H$_2$O and K$_7$H$_2$[Au(O)(OH$_2$) P$_2$W$_{20}$O$_{70}$(OH$_2$)$_2$]·27H$_2$O are unique because they are the first examples of terminal Au-oxo complexes that exhibit multiple bonding between gold and oxygen. The gold atom is bonded to six oxygen atoms in an octahedral geometry, the equatorial positions are bridging oxide ligands, distances 1.877(11) Å, and the axial positions are occupied by a terminal Au=O bond, 1.763(17) Å, and an aqua molecular, Au–O 2.29(4) Å (see Figure 1.70).

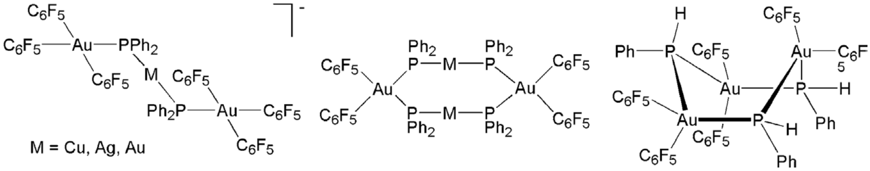


Figure 1.69 Phosphide gold(III) complexes.

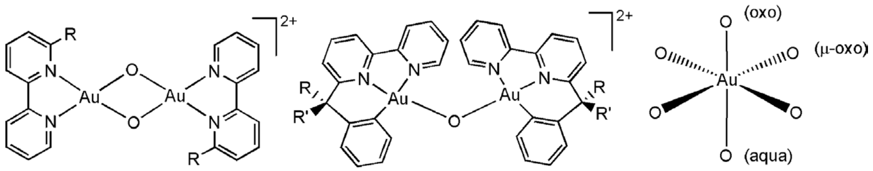


Figure 1.70 Gold(III) complexes with μ-oxo ligands and environment of gold(III) in $K_7H_2[Au(O)(OH_2)P_2W_{20}O_{70}(OH_2)_2]\cdot 27H_2O$.

Gold(III) complexes with sulfur or selenium donor ligands such as thiolates or selenolates, dithiolates, dithiocarbamates or bridging sulfide or selenide ligands are more numerous. They are obtained by oxidation of a gold(I) precursor, such as $[AuCl(CO)]$ with $PhCH_2SSCH_2Ph$ to give the gold(III) species $[Au_2Cl_4(\mu\text{-}SPh)_2]$ [332] or by substitution reactions such as the diethylether ligand in $[Au(C_6F_5)_3(OEt_2)]$ for the thiolate or selenolate metalloligand $[Au_2(\mu\text{-}dppf)(ER)_2]$ [333]. The homoleptic complex $[Au(SR)_4]^-$ has been obtained for the 1-methyl-1,2,3,4-tetrazole-5-thiolate ligand [334]. The gold(III) hydrosulfide complex $NBu_4[Au(C_6F_5)_3(SH)]$ has been prepared by reaction of $NBu_4[Au(C_6F_5)_3Br]$ with Na(SH) [335]. Figure 1.71 shows some of these complexes.

Homoleptic gold(III) derivatives with dithiolate, ligands of the type $[Au(S\text{–}S)_2]^-$ are well known and are usually prepared from $[AuCl_4]^-$ with the dithiol; some examples are with 1,2-benzene dithiolate, maleonitriledithiolate, dmit, and so on, [164, 336]. Similar complexes have been reported for bidentate sulfur ligands such as dithiocarbamates, dithiophosphates, and so on, [41]. Other derivatives as the trinuclear species $[Au(C_6F_5)(S_2C_6H_4)]_3$ [337] or the complex with one *nido* and one *closo*-carborane dithiolate are known [338]. Figure 1.72 collects some of these complexes.

Gold(III) complexes have also been prepared with mixed-donor ligands such as the phosphino thiolates $PhP(C_6H_4SH)_2$ or $P(C_6H_4SH)_3$, which give the dinuclear

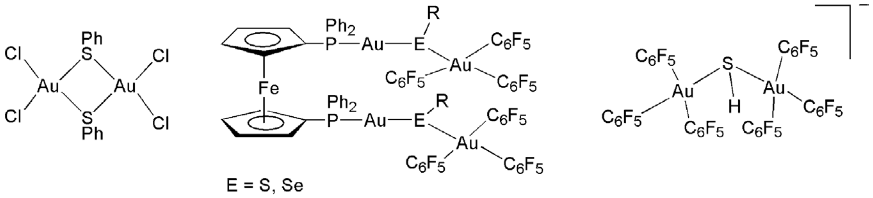


Figure 1.71 Gold(III) complexes with thiolate or selenolate ligands.

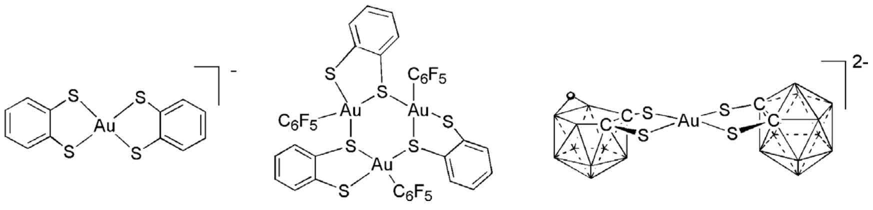


Figure 1.72 Dithiolate gold(III) complexes.

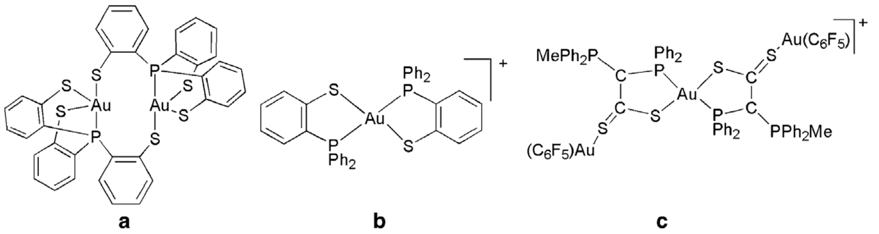


Figure 1.73 Gold(III) complexes with phosphino-thiolate ligands.

$[Au_2\{PPh(C_6H_4S)_2\}_2]$ with gold(I) and gold(III) atoms, or $[Au_2\{P(C_6H_4S)_3\}_2]$ with two gold(III) centers (Figure 1.73a) [339]. The reaction of tetrachloroaurate(III) with two equivalents of 2-(diphenylphosphino)benzenethiol gives a cation that can be precipitated from solution as tetraphenylborate salt, $[Au(2\text{-}PPh_2C_6H_4S)_2]BPh_4$ (Figure 1.73b). Surprisingly, the electrochemical behavior corresponds to a reversible single-electron transfer process and indicates that this gold(III) can be reduced to gold(II) and that the gold(II) state has reasonable stability on the electrochemical time scale [340]. The methanide carbon of $[Au(C_6F_5)(PPh_2CHPPh_2Me)]$ reacts with carbon disulfide affording the gold(III) derivatives $[Au\{PPh_2C(PPh_2Me)C(S)S\}_2]^+$ through a carbon–carbon coupling reaction. The reaction of this complex with 2 equivalents of $[Au(C_6F_5)(tht)]$ gives $[Au\{PPh_2C(PPh_2Me)C(SAuC_6F_5)S\}_2]^+$ (Figure 1.73c), which is a vapochromic material and can be used for the detection of some volatile organic compounds [341]. This material changes color from black to orange in the presence of organic vapors.

Gold(III) complexes with a central sulfur or selenium ligand have been reported. The substitution of the proton in $NBu_4[Au(C_6F_5)_3(SH)]$ by the isolobal fragments $MPPh_3^+$ (M = Au, Ag) affords the compounds $NBu_4[Au(C_6F_5)_3(SMPPh_3)]$ (Figure 1.74a) [335]. The reaction of $[E(AuPPh_3)_2]$ or $[E(Au_2dppf)_2]$ with one or two equivalents of $[Au(C_6F_5)_3(OEt_2)]$ gives the mixed valence complexes $[E(AuPPh_3)_2\{Au(C_6F_5)_3\}]$ and $[E(Au_2dppf)\{Au(C_6F_5)_3\}]$, which have a trigonal pyramidal structure, or $[E(AuPPh_3)_2\{Au(C_6F_5)_3\}_2]$ (Figure 1.74b) and $[E(Au_2dppf)\{Au(C_6F_5)_3\}_2]$, which are tetrahedral in contrast to the quadruply bridging gold(I) complexes, which are square pyramidal [342]. The reaction with $[Au(C_6F_5)_2(OEt)_2]^+$ also gives mixed valence complexes of the type $[\{S(Au_2dppf)\}_2Au(C_6F_5)_2]^+$ (Figure 1.74c) or $[Se(AuPPh_3)Au(C_6F_5)_2]_2$. These complexes show the presence of Au(I)–Au(III) interactions but weaker than the corresponding Au(I)–Au(I) interactions [342].

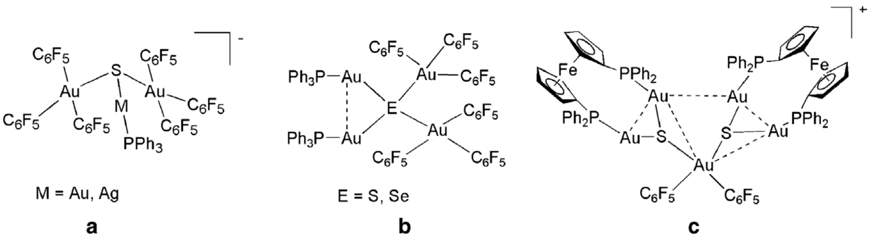


Figure 1.74 Gold(I)–Gold(III) complexes with bridging chalcogen ligands.

1.2.7
Gold in Higher Oxidation States

Complexes with gold in higher oxidation states are known with very electronegative and small ligands such as fluorine. The highest oxidation state that is known beyond doubt is Au^V. It was claimed that the yellow crystalline AuF_7 was prepared by disproportionation of AuF_6, obtained by reaction of AuF_5 with atomic fluorine, and isolated at −196 °C it decomposes into AuF_5 and F_2 at 100 °C [343]. However, so far these results have never been reproduced or confirmed and recent quantum chemical studies show that this is highly improbable. The strongly exothermic elimination of F_2 with a low activation barrier is not consistent with the reported stability of AuF_7 at room temperature, even the homoleptic dissociation of one equatorial Au–F bond is exothermic and has a barrier only from structural rearrangement. Also, and given the extremely high electron affinity of AuF_6, this species is unlikely to exist in most experimental conditions [344]. The pentafluoride AuF_5 is formed by vacuum pyrolysis of either $[KrF][AuF_6]$ (at 60–65 °C) or $[O_2][AuF_6]$ (at 160–200 °C) [345]. An electron diffraction study of AuF_5 has indicated that the vapor phase consists of di- and trimeric molecules with the gold octahedrally coordinated [346]. A recent single-crystal X-ray diffraction study has shown that AuF_5 exists as a dimer in the solid state [347] (Figure 1.75). Salts of $[AuF_6]^-$ with different cations, including Ag^+, are also known [345, 348]. The compound $[Xe_2F_{11}][AuF_6]$ was first prepared by fluorination of AuF_3 with XeF_2 in the presence of XeF_6. In the solid state, gold is octahedrally surrounded by the fluorine atoms and bonded to the dimeric xenon cation by two of the fluorine atoms (Figure 1.75) [349].

Evidence of the existence of oxidation state +IV is not yet convincing. Some complexes with dithiolene or dithiolate systems have been reported, such as [Au(5,6-dihydro-1,4-dithiin-2,3-dithiolate)$_2$] (Figure 1.76) [350], or [Au(2,3-dithiophenedithiolate)$_2$] [351]. They were prepared by chemical or electrochemical oxidation of

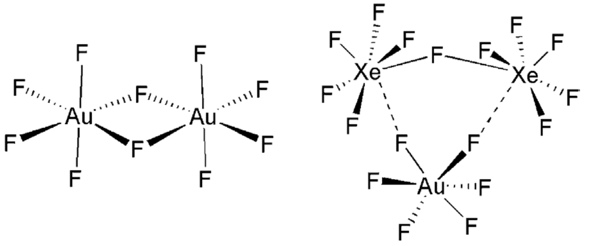


Figure 1.75 Gold(V) fluorocompounds.

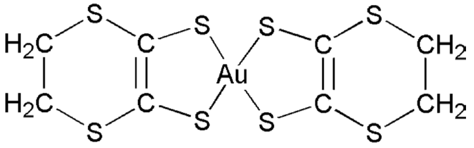


Figure 1.76 Gold(IV) dithiolate species.

the corresponding gold(III) derivatives. The molecular orbital calculations suggest that the metal ions of the molecules are best described as d^8 ions, as expected for a square planar gold(III) compound, and therefore the unpaired electron in each molecule resides largely on the ligands.

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