Coordination Chemistry Reviews
193–195 (1999) 837–856

Coordination chemistry of gold(II) complexes

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Received 7 January 1999; accepted 16 April 1999

Contents

Abstract

The number of complexes with gold in a formal oxidation state of two have increased considerably and nowadays this oxidation state can be considered nearly as a common state in gold chemistry. This review covers the evolution of the knowledge of this oxidation state from the first dithiocarbamate derivatives $[Au_2(S_2CNR_2)_2X_2]$, stable only at very low temperature, to the room temperature stable dinuclear gold complexes $[Au_2(L{-}L)_2X_2]$ ($L{-}L = CH_2PPh_2CH_2$, CH_2PPh_2S, $C_5H_4PPh_2$-2; $X =$ halogen). Although a dinuclear structure with a gold(II)–gold(II) bond supported by two equal bridging ligands were the first and most common, this review shows the present diversity as mononuclear, $[Au([9]aneS_3)_2](BF_4)_2$, dinuclear with two different bridging ligands, $[Au_2(S_2CNR_2)(CH_2PPh_2CH_2)X_2]$, with a

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PII: S0010-8545(99)00141-1

non-supported metal–metal bond, $[Au_2(Ph_2PC_8H_6PPh_2)_2Cl_2](PF_6)_2$, and polynuclear gold(II) complexes either with chains of only gold centers or with other metals, such as $[\{(C_6F_3H_2)Au(CH_2PPh_2CH_2)_2Au\}_2Au_2(CH_2PPh_2CH_2)_2]ClO_4$ or $[Au_2Pt(CH_2PPh_2S)_4X_2]$
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Keywords: Dinuclear; Gold; Gold(II); Polynuclear

1. Introduction

The chemistry of gold has increased considerably in recent decades because the theoretical interest of the relativistic and correlation effects which are especially important in this metal and the applications found for new and old gold complexes. Therefore many chemist have focused their work in this golden direction and the number and types of new gold complexes have grown up steadily. Oxidation states which not long ago were denoted as unusual [1] in the chemistry of gold, nowadays are represented by a great variety of structures and stoichiometries. Because of the rapid growth of the field some previous review [1–5] articles soon became obsolete at least in so far as the chemistry of gold(II) is concerned.

The number of gold(II) complexes is very scarce when we compare them with the more common gold(I) and gold(III) derivatives. The energy required to reach [4,5] 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 enough to justify the lack of stability for this oxidation state (II) of gold. There is a strong tendency for disproportionation from Au^{2+} to give Au^{+} and Au^{3+} because the odd electron in d^9 metal complexes is in the $d_{x^2-y^2}$ orbital [1,4,5] (octahedral tetragonally distorted or square planar arrangement) which has a much higher energy compared with copper and can be easily ionised. The formation of a gold–gold bond gives more stable compounds and the Au_2^{4+} core derivatives are the more stable and abundant types of gold(II) complexes.

2. Pseudo-gold(II) compounds

A few derivatives which were believed to be gold(II) complexes by their stoichiometry have been confirmed as gold(I)/gold(III) derivatives in equal proportions as revealed by X-ray diffraction studies. Thus, $[CsAuCl_3]$ [6], $[AuCl_2\{(C_6H_5CH_2)_2S\}]$ [7–9], $[AuCl(dmg)]$ [10] (dmg = dimethylglyoximate), $[AuBr\{(n\text{-}C_4H_9)_2NCS_2\}]$ [11] and $[Au(mnt)(PPh_3)]$ [12] (mnt = malonitriledithiolate) have proved to be $Cs_2[Au^{I}Cl_2][Au^{III}Cl_4]$, $[Au^{I}Cl\{(C_6H_5CH_2)_2S\}][Au^{III}Cl_3\{(C_6H_5CH_2)_2S\}]$, $[Au^{III}\{S_2CN(n\text{-}C_4H_9)_2\}_2][Au^{I}Br_2]$ and $[Au(PPh_3)_2][Au(mnt)_2]$, respectively. Although the binary salt $AuCl_2$, first prepared in the last century [13,14], has been debated extensively, the final result is quite similar. The structure of the black diamagnetic crystals of $AuCl_2$, prepared [15] by reaction of $AuCl_3$ and

[AuCl(CO)], consists of two [$Au^{III}Cl_4$] square planar groups bonded to two linear gold(I) centers [16,17]. It is believed that other binary salts or complexes related to those mentioned above are, in fact, mixed valent complexes of equimolar gold(I) and gold(III) derivatives, such as $AuSO_4$ [18], AuO [19], AuS [20], [$AuX_2\{(C_6H_5CH_2)_2S\}$] (X = Br, I) [21] or [$Au_2Cl_4(nb)_x$] [22] ($x = 1$, 2 and 3, nb = norbornadiene).

There are other complexes whose stoichiometry points to a gold(II) compound but the reported data are not in agreement with this formulation. Thus $(TTF)_2$[$Au(dmit)_2$] seems to be a gold(III) complex with partially oxidised TTF anions [23] as deduced by Raman and EPR data (TTF = tetrathiafulvalene and dmit = 2-thioxo-1,3-dithiole-4,5-dithiolate).

3. Gold(II) compounds as reaction intermediates

Rich and Taube [24] provided kinetic evidence of the transient existence of a gold(II) mononuclear complex in aqueous solution, studying the catalytic activity of iron(II) on the exchange of a radioactive $*Cl^-$ with $[AuCl_4]^-$. They suggested $[AuCl_4]^{2-}$ as the probable species, although the kinetic data do not establish the formula of the intermediate species.

Other gold(II) intermediates have been proposed in oxidation reactions of [$Au(Me)(PMe_3)$] with CF_3I and PhSH, which are thought to proceed by free-radical mechanisms [25,26]. Thus [$Au(Me)(CF_3)(PMe_3)$] and [$Au(Me)(SPh)(PMe_3)$] were postulated, although in all these cases, they are not sufficiently long-lived to be detected by EPR methods. Similarly there are some examples of voltammetry studies of gold(III) derivatives $[Au(2\text{-}PPh_2C_6H_4S)_2]^+$ and $[Au\{PPh_2C(PPh_2Me)C(X)S\}_2]^+$ which show quasi-reversible one electron reduction waves and some gold(II) complexes should be formed. No other data for these complexes are given and reduction of the ligands is not ruled out [27,28].

4. Gold(II) complexes without metal–metal bonds

Mononuclear gold(II) complexes, consistent with a d^9 formulation, 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 real gold(II) mononuclear complexes in addition to their stoichiometry. Thus, is the case of a phthalocyanine gold(II) derivative [$Au(C_{32}H_{16}N_8)$] obtained by heating a mixture of gold(I) bromide and 1,3-diiminoisoindoline in a template synthesis [29]. The EPR spectrum of the complex (77 K, 1-chloronaphtalene) showed a signal with a g value of 2.065 in accordance with the presence of gold(II). A dicarborane gold(II) derivative has been prepared by the sodium amalgam reduction of the corresponding gold(III) derivative. The complex $(NEt_4)[Au\{\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}\}_2]$, which is deep blue–green in color and paramagnetic ($\mu_{eff} = 1.79$ MB), is proposed to have a similar structure to that shown for the Cu(II) complex [30].

More abundant are those gold(II) complexes with polyfuntional thiolate and related ligands. Thus, Vänngard and Åkerström [31] observed a four line EPR spectrum when they dissolved $[Au(S_2CNR_2)_3]$ (S_2CNR_2 = dialkydithiocarbamate, $R = C_2H_5$, i-C_3H_7) in benzene. The observed *g* value of 2.040 provides strong evidence for the existence of a Au(II) complex. The same results were obtained when the gold(I) dithiocarbamate and the corresponding thiuram disulfide were mixed in benzene. Similar reactions involving the *n*-butyldithiocarbamate were studied by Bergendahl and Bergendahl [32] and a four-line EPR spectrum with a g value of 2.039 was obtained, showing that one equilibrium (Eq. 1) should be present. The existence of a corresponding diethyldiselenocarbamate $[Au(Se_2CNEt_2)_2]$ has been confirmed by EPR spectroscopic methods [33].

$$[Au(S_2CNR_2)_3] \rightleftharpoons [Au(S_2CNR_2)_2] + 0.5\,(S_2CNR_2) \qquad (1)$$

R = Et, i-Pr, n-Bu

Waters et all [34,35] reported the preparation of a monomeric gold(II) complex $(n\text{-}Bu_4N)_2[Au(mnt)_2]$ (mnt = malonitriledithiolate) by the borohydride reduction of the corresponding gold(III) derivative. Although obtained initially in low yield it can be obtained in better yield by reaction of $Li_2(mnt)$ with the gold(I)/(III) derivative mentioned above $[AuCl\{(C_6H_5CH_2)_2S\}][AuCl_3\{(C_6H_5CH_2)_2S\}]$. The magnetic moment of $\mu_{eff} = 1.85$ MB and its four equal spaced lines in the EPR spectrum clearly show the gold(II) nature. In addition the cyclovoltammetry results are in accordance with that formulation. Good chemical and structural evidence is also provided [36] for the formation of the anionic complex $[Au(mnt)(S_2CNEt_2)]^-$, by electrochemical reduction of $[Au(mnt)(S_2CNEt_2)]$.

Some $[Au(S_2CNR_2)_2]$ and $[Au(mnt)_2]^{2-}$ complexes have been studied by the EPR of diluted magnetic samples cocrystallized with diamagnetic $[Ni(S_2CNR_2)_2]$ or $(n\text{-}Bu_4N)_2[M(mnt)_2]$ (M = Ni, Pd and Pt), respectively. The dithiocarbamate complexes show some anomalous behaviour indicating that the odd electron is at least in part delocalized through the ligand [37–39]. The malonitrile derivative is best described as an Au(III) complex with a radical-anion ligand [40].

Several gold(II) complexes with the ligand *o*-aminobenzenethiolate (abt) have been reported [37], obtained by reduction of $HAuCl_4{\cdot}3H_2O$ with the ligand in degassed absolute ethanol. Two isomers violet or blue are obtained which show a magnetism of $\mu_{eff} = 2.66$ MB or 2.60 MB, respectively and an EPR spectrum of seven lines. Both data, magnetism and EPR, point to the dinuclear nature of these complexes. A stoichiometry $[Au(abt)_2]_2$ was proposed with no metal–metal bonds. Both complexes dissolve in *N*,*N*-dimethylformamide (dmf) and from these solutions a deep blue $[Au(abt)_2(dmf)_2]$ was obtained. The latter shows a magnetic moment of $\mu_{eff} = 1.76$ MB and a four lined EPR spectrum in accordance with a monomeric formulation [41]. The reaction of these *o*-aminobenzenethiolate gold complexes with SCN^-, $SeCN^-$, NCO^- and CN^- gave new paramagnetic complexes which are postulated to remain as gold(II) derivatives, although they have only been studied by EPR and even their stochiometries are not accurately determined.

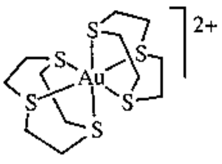


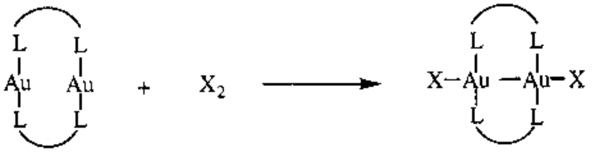
Fig. 1. Schematic structure of the cation of $[Au([9]aneS_3)_2](BF_4)_2$.

More precisely described is the mononuclear gold complex $[Au([9]aneS_3)_2](BF_4)_2$ obtained [42] by reduction of $HAuCl_43H_2O$ with two molar equivalents of $[9]aneS_3$ in refluxing HBF_4 (40%)/MeOH and further extraction with CH_3NO_2. This is the solely mononuclear gold(II) complex studied by X-ray diffraction studies showing an octahedral disposition of six sulfur centres around the gold atom, with a Jahn–Teller distortion (Fig. 1). The apical Au–S distance is 2.839(5) Å and the two different Au–S distances in the plane are 2.462(5) and 2.452(5) Å. The EPR spectrum shows a hyperfine four line EPR signals at $g = 2.010$ and in this case the lone electron belongs predominantly to the gold center and the delocalizarion through the ligand is limited.

5. Dinuclear gold(II) complexes with metal–metal bonds

As mentioned in the introduction, one of the reasons for the poor stability of gold(II) complexes should be the unfavourable energy of the odd electron. The formation of a metal–metal bond in binuclear gold(II) complexes gives an extra stability and avoids a decomposition pathway. Thus, the number of gold(II) complexes containing the Au_2^{4+} core has been increasing in the last two decades and different stoichiometries are known. The more abundant are those containing two equal bridges holding together the gold centers and retaining them in a close proximity giving rise to a diauracycle with a gold–gold bond across the cycle (Tables 1–4). Apart from this class, some dinuclear gold(II) complexes with two different bridges have been synthesized, as well as complexes with only one bridge holding the gold(II) centers, and a Au_2^{4+} complex without any bridge has recently been described [43].

The more usual method of preparation of these complexes is the oxidative addition of halogens to dinuclear gold derivatives. The result is the formation of the gold–gold bond in addition to two gold–halogen bonds *trans* to the former (Eq. 2).



(2)

This method works properly with a great variety of dinuclear gold(I) complexes, such as shown in Fig. 2. These include symmetrically double-bridged diauracycles,

Table 1
Dinuclear gold(II) complexes characterised by X-ray studies

Complex	Ref.	d(Au–Au)	d(Au–X)	d(Au–R)
[IAu(CH$_2$PMe$_2$CH$_2$)$_2$AuI]	[74–76]	2.654(4)	2.699(8)	–
[(CH$_3$)Au(CH$_2$PMe$_2$CH$_2$)$_2$AuI]	[74,75,86]	2.695(4)	2.894(5)	2.13(5)
[ClAu(CH$_2$PEt$_2$CH$_2$)$_2$AuCl]	[77–79]	2.597(5)	2.359(30)	–
[ClAu(CH$_2$PPh$_2$CH$_2$)$_2$AuCl]	[74,80,81]	2.600(1)	2.388(8)	–
[BrAu(CH$_2$PPh$_2$CH$_2$)$_2$AuBr]	[66,74,84]	2.614(1)	2.516(1)	–
[IAu(CH$_2$PPh$_2$CH$_2$)$_2$AuI]	[52,74,80]	2.650	2.693	–
[PhCO$_2$Au(CH$_2$PPh$_2$CH$_2$)$_2$AuO$_2$CPh]	[82,83]	2.561(2)	2.117(13)	–
[MeCO$_2$Au(CH$_2$PPh$_2$CH$_2$)$_2$AuO$_2$CMe]	[84]	2.592(1)	2.144(12)	–
[Et$_2$NCS$_2$Au(CH$_2$PPh$_2$CH$_2$)$_2$AuS$_2$CNEt$_2$]	[50]	2.647(1)	2.433(2)	–
[ClAu(CH$_2$PPh$_2$CH$_2$)$_2$AuSePh]	[64]	2.636(1)	2476(3)	–
[C$_5$H$_4$NSAu(CH$_2$PPh$_2$CH$_2$)$_2$AuSNC$_5$H$_4$]	[73]	2.669(1)	2.437(3)	–
[(CH$_3$)Au(CH$_2$PPh$_2$CH$_2$)$_2$AuI]	[72,74,86]	2.695(4)	–	–
[(CH$_3$)Au(CH$_2$PPh$_2$CH$_2$)$_2$AuBr]	[72,74,80]	2.674(1)	2.698(3)	2.159(2)
[(CH$_2$Cl)Au(CH$_2$PPh$_2$CH$_2$)$_2$AuI]	[87]	2.681(3)	2.858(4)	2.00(4)
[(CH$_2$CN)Au(CH$_2$PPh$_2$CH$_2$)$_2$AuBr]	[80,87,88]	2.658(1)	2.660(2)	2.120(14)
[(CF$_3$CH$_2$)Au(CH$_2$PPh$_2$CH$_2$)$_2$AuI]	[90]	2.681(1)	2.826(1)	2.082(14)
[(CH$_3$CH$_2$)Au(CH$_2$PPh$_2$CH$_2$)$_2$AuI]	[90]	2.684(4)	2.950(6)	2.054(3)
[(CH$_2$Cl)Au(CH$_2$PPh$_2$CH$_2$)$_2$AuBr]	[91]	2.653(1)	2.587(4)	2.10(3)
[(PhC(O)CH$_2$)Au(CH$_2$PPh$_2$CH$_2$)$_2$AuBr]	[88]	2.688(2)	2.649(5)	2.148(36)
[(CCl$_3$)Au(CH$_2$PPh$_2$CH$_2$)$_2$AuCl]	[51,81]	2.646(1)	2.466(3)	2.120(13)
[NCAu(CH$_2$PPh$_2$CH$_2$)$_2$AuCN]	[47]	2.637(2)	2.046(22)	–
[O$_2$NAu(CH$_2$PPh$_2$CH$_2$)$_2$AuNO$_2$]	[48]	2.596(1)	2.142(11)	–
[(C$_6$F$_5$)Au(CH$_2$PPh$_2$CH$_2$)$_2$Au(C$_6$F$_5$)]	[49]	2.677(1)*	–	2.151(1)*
[(CF$_3$)Au(CH$_2$PPh$_2$CH$_2$)$_2$Au(CF$_3$)]	[49]	2.679(1)	–	2.140(7)
[IAu(CH$_2$PPh$_2$CH$_2$)$_2$Au(CH$_2$PMe$_3$)]I	[61]	2.681(1)	2.822(1)	2.083(8)
[O$_2$NAu(CH$_2$PPh$_2$CH$_2$)$_2$AuNO$_2$]	[48]	2.596(1)	2.142(11)	–
[ClAu(CH$_2$PPh$_2$CH$_2$)$_2$AuSePh]	[64]	2.636(1)	2.476(3)	2.469(2)
[{Au(CH$_2$)$_2$PPh$_2$}$_2${SSC(NPh)(NHPh)}$_2$]	[59]	2.651(1)	2.392(5)	–
[(PPh$_3$)Au(CH$_2$PPh$_2$CH$_2$)$_2$Au(PPh$_3$)](ClO$_4$)$_2$	[66]	2.579(3)	2.384(6)	–
[(tht)Au(CH$_2$PPh$_2$CH$_2$)$_2$Au(tht)](ClO$_4$)$_2$	[51,52]	2.646(1)	2.432(4)	–
[(C$_6$F$_5$)Au(CH$_2$PPh$_2$CH$_2$)$_2$Au(PPh$_3$)]ClO$_4$	[70]	2.661((8)	2.443(3)	2.078(12)
[Me$_2$NCS$_2$Au(CH$_2$PPh$_2$CH$_2$)$_2$AuS$_2$CNMe$_2$]	[97]	2.647(1)	2.433(2)	–
[Au$_2$(CH$_2$PPh$_2$CH$_2$){S$_2$CN(CH$_2$Ph)$_2$}Br$_2$]	[98]	2.565(1)	2.502(1)	–
[Au$_2$(CH$_2$PPh$_2$CH$_2$)(C$_5$H$_4$NS)Br$_2$]	[100]	2.564(4)	2.515(5)	–
[(PPh$_2$Me)Au(CH$_2$PPh$_2$CH$_2$)$_2$Au(OH$_2$)](ClO$_4$)$_2$	[69]	2.601(1)	2.326(2)	2.308(7)
[Au$_2$(CH$_2$PPh$_2$CH$_2$)(S$_2$COMe)Br$_2$]	[99]	2.556(1)	2.510(2)	2.466(6)
[Au$_2$(CH$_2$PMe$_2$CH$_2$)$_2$(CH$_2$P(S)Ph$_2$)$_2$]	[60]	2.694(1)	–	2.13(1)
[Au$_2$(CH$_2$PMe$_2$CH$_2$)$_2$(CH$_2$P(S)Ph$_2$)Br]	[60]	2.661(1)	2.675(3)	2.12(2)
[IAu(SPPh$_2$CH$_2$)$_2$AuI]	[85]	2.609(1)	2.687(2)	–
[ClAu(SPPh$_2$CH$_2$)$_2$AuCl]	[96]	2.553(1)	2.380(4)	–
(NBu$_4$)[BrAu{S$_2$C$_2$(CN)$_2$}$_2$AuBr]	[92,93]	2.570(5)	2.510(8)	–
(AsPh$_4$)[ClAu{S$_2$C$_2$(CN)$_2$}$_2$AuCl]	[92,93]	2.550(1)	2.380(3)	–
[IAu(*o*-C$_6$H$_4$PPh$_2$)$_2$AuI]	[94,95]	2.593(1)	2.669(6)	–
[Cl(C$_6$F$_5$)Au(PPh$_2$NHPPh$_2$)Au(C$_6$F$_5$)Cl]	[63]	2.576(2)	2.341(3)	–
[Au$_2$(dppn)Cl$_2$](PF$_6$)$_2$	[43]	2.611(7)	2.339(4)	–

dinuclear gold(I) derivatives with two different bridges and some monobridge dinuclear complexes. The double bridged complexes are more abundant (Tables 1–4) showing how the bridges have an important role holding the gold centers in close proximity to improve the metal–metal strength and prevent decomposition. The number of known gold(II) complexes containing the bis-ylide $(CH_2PR_2CH_2)^-$ group is large showing the special stability that these ligands confer to this kind of complex. Schmidbaur [44] and Fackler [45] did the seminal work in gold(II) chemistry with these ligands.

This method can be extended to other oxidants such as MeI or other haloalkyl RX. The two gold(II) centers in the final complex are bonded in a different way, one to the halogen X and the other to the alkyl group through a carbon–gold bond. In fact, the first methyliodide oxidative addition across two metal atoms with metal–metal formation was reported by Schmidbaur [46] using $[Au_2(CH_2PPh_2CH_2)_2]$.

Other oxidants have been used to synthesise gold(II) complexes starting from gold(I) diauracycles, such as $[Hg(CN)_2]$ [47], nitroalkanes [48], N_2O_4 [48], $[Tl(C_6F_5)_2Cl]_2$ [49], tetraethylthiuram [50], $[Ag(OClO_3)PPh_3]$ [51,52] and $[Ag(MeCN)_4](PF_6)_4$ [43]. The latter is the oxidant used in the preparation of the only Au_2^{4+}

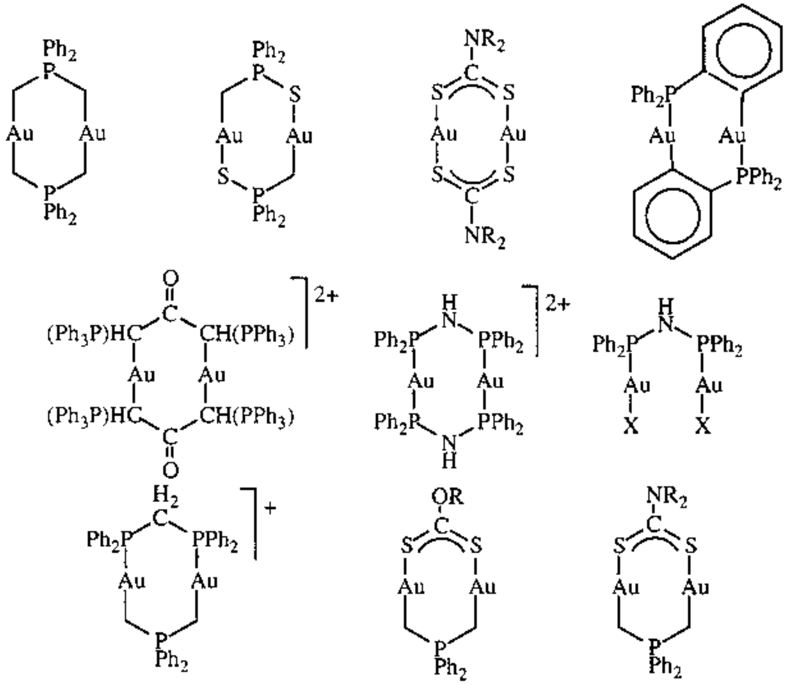


Fig. 2. Dinuclear gold(I) precursors.

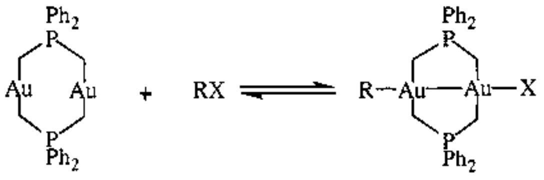
Table 2
Reported $[LAu(CH_2PPh_2CH_2)_2AuL'](A)_n$ complexes

L	L′	$(A)_n$	Ref.	L	L′	$(A)_n$	Ref.
PhC(O)S	PhC(O)S		[82]	$C_6F_3H_2$	$C_6F_3H_2$		[66]
NO_3	NO_3		[65,66]	MeCOO	MeCOO		[66]
NCS	NCS		[66]	$S_2CNC_4H_8$	$S_2CNC_4H_8$		[97]
$S_2NC_7H_4$	$S_2NC_7H_4$		[73]				
$(SiMe_3)CH_2$	I		[74]	$PhCH_2$	Br		[74]
$CHBr_2$	Br		[51]	$CHCl_2$	Br		[102]
C_6F_5	NO_3		[70]	C_6F_5	Cl		[70]
C_6F_5	SCN		[70]	C_6F_5	MeCOO		[70]
C_6F_5	$C_6F_3H_2$		[70]	$C_6F_3H_2$	Cl		[70]
C_6F_5	$OClO_3$		[71]	$C_6F_3H_2$	$OClO_3$		[71]
CH_3	$OClO_3$		[71]	CH_2Cl	Br		[89]
CH_2PPh_3	Br	Br	[61]	CH_2PPh_3	I	I	[61,62]
C_6F_5	tht	ClO_4	[70]	C_6F_5	$PTol_3$	ClO_4	[70]
C_6F_5	$AsPh_3$	ClO_4	[70]	C_6F_5	py′	ClO_4	[70]
Cl	PPh_3	ClO_4	[69]	Cl	PPh_2Me	ClO_4	[69]
$S_2CN(CH_2Ph)_2$	PPh_3	ClO_4	[69]	$OClO_3$	PPh_3	ClO_4	[69]
$OClO_3$	PPh_2Me	ClO_4	[69]				
PPh_3CH_2	PPh_3CH_2	$(ClO_4)_2$	[70]	$AsPh_3$	$AsPh_3)$	$(ClO_4)_2$	[66]
$SbPh_3$	$SbPh_3$	$(ClO_4)_2$	[70]	$PPh_2(CH_2SiMe_3)$	$PPh_2(CH_2SiMe_3)$	$(ClO_4)_2$	[106]
py	py	$(ClO_4)_2$	[65,66]	$S(SMe)CNHR_2$[a]	$S(SMe)CNHR_2$[a]	$(ClO_4)_2$[a]	[97]
PPh_3	tht	$(ClO_4)_2$	[69]	PPh_2Me	tht	$(ClO_4)_2$	[69]
$P(MeOPh)_3$	tht	$(ClO_4)_2$	[69]	PPh_3	py	$(ClO_4)_2$	[69]
PPh_3	$AsPh_3$	$(ClO_4)_2$	[66]	PPh_3	PPh_2Me	$(ClO_4)_2$	[69]
$S(SMe)CNHR_2$	PPh_3	$(ClO_4)_2$	[97]				

[a] R = *p*-MePh, *o*-MePh, *p*-MeOPh, 3,5-Me_2Ph.

complex $[Au_2(dppn)Cl_2](PF_6)_2$, which does not have bridges holding the two gold centers connected by a metal–metal bond. The starting gold(I) derivative was $[Au_2(dppn)Cl_2]$ (dppn = 1,8-bis(diphenylphosphino)naphthalene).

The addition of haloalkyl derivatives to the bis-ylide $[Au_2(CH_2PR_2CH_2)_2]$, has been studied extensively by Fackler and his group showing that the reactivity trend of addition follows the inverted order of dissociation energy of the C–X bond [53]. Eq. 3 is in fact one equilibrium with constants for different RX having been evaluated [54].

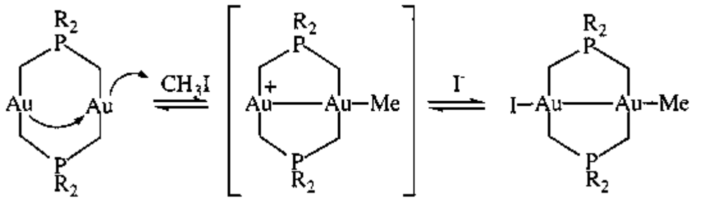


(3)

Table 3
Gold(II) complexes with the symmetrically bridged Au_2^{4+} core

Complex	Ref.	Complex	Ref.
$[ClAu(CH_2PMe_2CH_2)_2AuCl]$	[75,76]	$[BrAu(S_2CNEt_2)_2AuBr]$	[103]
$[BrAu(CH_2PMe_2CH_2)_2AuBr]$	[74–76]	$[IAu(S_2CNEt_2)_2AuI]$	[103]
$[(SiMe_3)CH_2Au(CH_2PMe_2CH_2)_2AuI]$	[74]	$[NCSAu(S_2CNEt_2)_2AuSCN]$	[103]
$[BzAu(CH_2PMe_2CH_2)_2AuBr]$	[74]	$[NCSeAu(S_2CNEt_2)_2AuSeCN]$	[103]
$[BrAu(CH_2PEt_2CH_2)_2AuBr]$	[77–79]	$[NCSAu(S_2CN(Bu)_2)_2AuSCN]$	[103]
$[IAu(CH_2PEt_2CH_2)_2AuI]$	[77]	$(NBu_4)_2[ClAu(S_2C_2(CN)_2)_2AuCl]$	[93]
$[Et_2NCS_2Au(CH_2PEt_2CH_2)_2AuS_2CNEt_2]$	[69]	$(NBu_4)_2[IAu(S_2C_2(CN)_2)_2AuI]$	[93]
$[ClAu\{SPPh_2CH(PPh_2Me)\}_2AuCl](ClO_4)_2$	[101]	$(AsPh_4)_2[BrAu(S_2C_2(CN)_2)_2AuBr]$	[93]
$[PhCO_2Au(SPPh_2CH_2)_2AuO_2CPh]$	[96]	$(AsPh_4)_2[IAu(S_2C_2(CN)_2)_2AuI]$	[93]
$[BrAu(o\text{-}C_6H_4PPh_2)_2AuBr]$	[84]	$[Cl_2Au(PPh_2CMe_2PPh_2)AuCl_2]$	[104]
$[ClAu\{CHRPPh_2CHR\}_2AuCl]$ $R = CO_2Et$	[67]	$[BrClAu(PPh_2CMe_2PPh_2)AuClBr]$	[104]
$[IAu\{CHRPPh_2CHR\}_2AuI]$	[67]	$[Cl_2Au(PPh_2NMePPh_2)AuCl_2]$	[105]
$[ClAu\{CHRPPh_2CHR\}_2AuCl]$ $R = CO_2Me$	[67]	$[Br_2Au(PPh_2NMePPh_2)AuBr_2]$	[105]
$[IAu\{CHRPPh_2CHR\}_2AuI]$	[67]	$[(C_6F_5)_2Au(PPh_2NHPPh_2)Au(C_6F_5)_2]$	[63]
$[pyAu\{CHRPPh_2CHR\}_2Aupy](ClO_4)_2$	[67]	$[Br(C_6F_5)Au(PPh_2NHPPh_2)Au(C_6F_5)Br]$	[63]
$[(Brpy)Au\{CHRPPh_2CHR\}_2Au(Brpy)](ClO_4)_2$	[67]	$[Cl(C_6Cl_5)Au(PPh_2NHPPh_2)Au(C_6Cl_5)Cl]$	[63]
$[(NCpy)Au\{CHRPPh_2CHR\}_2Au(Ncpy)](ClO_4)_2$	[67]	$[Br(C_6Cl_5)Au(PPh_2NHPPh_2)Au(C_6Cl_5)Br]$	[63]
$[(Me_2py)Au\{CHRPPh_2CHR\}_2Au(Me_2py)](ClO_4)_2$	[67]	$[ClAu\{PPh_2NHPPh_2\}_2AuCl](ClO_4)_2$	[63]
$[Ph_3PAu\{CHRPPh_2CHR\}_2AuPPh_3](ClO_4)_2$	[67]	$[BrAu\{PPh_2NHPPh_2\}_2AuBr](ClO_4)_2$	[63]
$[Ph_3AsAu\{CHRPPh_2CHR\}_2AuAsPh_3](ClO_4)_2$	[67]	$[(C_6F_5)Au\{PPh_2NHPPh_2\}_2Au(C_6F_5)](ClO_4)_2$	[63]

Fackler has discussed in depth [55] the mechanism of these additive oxidations in dinuclear gold(I) complexes, in accordance with the Goddard–Low model [56–58]. He proposed that the first step of the oxidative addition consists of nucleophilic attack by a gold(I) center on the added molecule involving the formation of the metal- metal bond. The second step is the attack on the other gold center by the rest of the added molecule to give the gold(II) final product. There is evidence for the nucleophilic character of the gold(I) center of the diauracycle [52,55]. The donation of electron density from one gold center to the added molecule gives rise to a shortening of the gold–gold distance in the diauracycle, which is close to the proposed intermediate (Eq. 4). On the other hand, there is evidence that the oxidative addition does not first form a mixed-valence Au(I)/Au(III) intermediate [55].



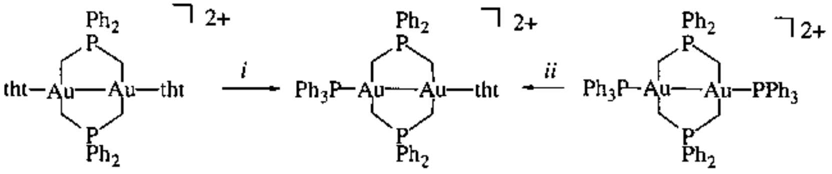
(4)

Other general procedures to prepare gold(II) complexes consist of substitution reactions starting from other gold(II) derivatives, usually halo-gold complexes by

Table 4
Gold(II) complexes with the unsymmetrically bridged Au_2^{4+} core $[LAu(L{-}L)(L'{-}L')AuL'](A)_n$

Complex	Ref.
$[ClAu(CH_2PPh_2CH_2)(Ph_2PCH_2PPh_2)AuCl](ClO_4)$	[98]
$[BrAu(CH_2PPh_2CH_2)(Ph_2PCH_2PPh_2)AuBr](ClO_4)$	[98]
$[IAu(CH_2PPh_2CH_2)(Ph_2PCH_2PPh_2)AuI](ClO_4)$	[98]
$[ClAu(CH_2PPh_2CH_2)(Ph_2PNHPPh_2)AuCl](ClO_4)$	[98]
$[BrAu(CH_2PPh_2CH_2)(Ph_2PNHPPh_2)AuBr](ClO_4)$	[98]
$[IAu(CH_2PPh_2CH_2)(Ph_2PNHPPh_2)AuI](ClO_4)$	[98]
$[ClAu(CH_2PPh_2CH_2)(S_2CNMe_2)AuCl]$	[98]
$[BrAu(CH_2PPh_2CH_2)(S_2CNMe_2)AuBr]$	[98]
$[IAu(CH_2PPh_2CH_2)(S_2CNMe_2)AuI]$	[98]
$[(C_6F_5)Au(CH_2PPh_2CH_2)(S_2CNMe_2)Au(C_6F_5)]$	[98]
$[ClAu(CH_2PPh_2CH_2)(S_2CNEt_2)AuCl]$	[98]
$[BrAu(CH_2PPh_2CH_2)(S_2CNEt_2)AuBr]$	[98]
$[IAu(CH_2PPh_2CH_2)(S_2CNEt_2)AuI]$	[98]
$[ClAu(CH_2PPh_2CH_2)\{S_2CN(CH_2Ph)_2\}AuCl]$	[98]
$[BrAu(CH_2PPh_2CH_2)\{S_2CN(CH_2Ph)_2\}AuBr]$	[98]
$[IAu(CH_2PPh_2CH_2)\{S_2CN(CH_2Ph)_2\}AuI]$	[98]
$[(PPh_3)Au(CH_2PPh_2CH_2)(S_2CNMe_2)Au(PPh_3)](ClO_4)_2$	[98]
$[(PPh_3)Au(CH_2PPh_2CH_2)\{S_2CN(CH_2Ph)_2\}Au(PPh_3)](ClO_4)_2$	[98]
$[ClAu(CH_2PPh_2CH_2)(S_2COMe)AuCl]$	[99]
$[BrAu(CH_2PPh_2CH_2)(S_2COMe)AuBr]$	[99]
$[IAu(CH_2PPh_2CH_2)(S_2COMe)AuI]$	[99]
$[ClAu(CH_2PPh_2CH_2)(S_2COEt)AuCl]$	[99]
$[BrAu(CH_2PPh_2CH_2)(S_2COEt)AuBr]$	[99]
$[IAu(CH_2PPh_2CH_2)(S_2COEt)AuI]$	[99]
$[ClAu(CH_2PPh_2CH_2)(S_2CO^iPr)AuCl]$	[99]
$[BrAu(CH_2PPh_2CH_2)(S_2CO^iPr)AuBr]$	[99]
$[IAu(CH_2PPh_2CH_2)(S_2CO^iPr)AuI]$	[99]
$[ClAu(CH_2PPh_2CH_2)(S_2CPCy_3)AuCl](ClO_4)$	[68]
$[BrAu(CH_2PPh_2CH_2)(S_2CPCy_3)AuBr](ClO_4)$	[68]
$[IAu(CH_2PPh_2CH_2)(S_2CPCy_3)AuI](ClO_4)$	[68]
$[(C_6F_5)Au(CH_2PPh_2CH_2)(S_2CPCy_3)Au(C_6F_5)](ClO_4)$	[68]
$[(PPh_3)Au(CH_2PPh_2CH_2)(S_2CPCy_3)Au(PPh_3)](ClO_4)_3$	[68]
$[\{P(OMePh)_3\}Au(CH_2PPh_2CH_2)(S_2CPCy_3)Au\{P(OMePh)_3\}](ClO_4)_3$	[68]

reaction with different reagents, such as $K\{SC(NPh)(NHPh)\}$[59], $Li\{CH_2P(S)Ph_2\}$[60], CH_2PR_3 [61,62], $Cd(CF_3)_2$ [49], $[Ag(C_6F_5)]_4$ [63], NaSePh [64], $[Ag(OClO_3)(tht)]$ [65] (tht = tetrahydrothiophene), $AgNO_3$ [65], $[Ag(OClO_3)PPh_3]$ [66] or $Ag(OClO_3)$ in the presence of ligands [67], among others. The use of the silver salts is facile because the substitution proceeds under very mild conditions and in this way it was possible to synthesise the first cationic complexes with the bis-ylide ligand, $[Au_2(CH_2PR_2CH_2)_2(PPh_3)_2](ClO_4)_2$ [66], and characterised by X-ray methods. Complexes with very poor ligands such as $[Au_2(CH_2PR_2CH_2)_2(tht)_2](ClO_4)_2$ [51,52], or even tricationic gold(II) complexes as $[Au_2(CH_2PR_2CH_2)(S_2CPCy_3)(PR_3)_2](ClO_4)_3$ [68] could be obtained by these soft methods.

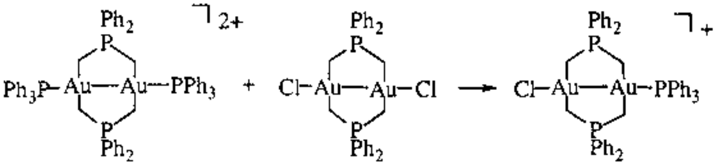


Scheme 1. (i) [Ag(OClO$_3$)PPh$_3$; (ii) [Au(C$_6$F$_5$)(tht)].

In addition to the use of silver salts to prepare gold(II) complexes, starting from halo-gold(II) derivatives, other reagents which very smoothly change the ligands bonded to the gold center were [Au(C$_6$F$_5$)(tht)] and [Ag(OClO$_3$)PPh$_3$]. The former can replace a PPh$_3$ bonded to a gold(II) center by tht and the latter can replace the tht by PPh$_3$ [69] (Scheme 1).

The tetrahydrothiophene (tht) is a weak ligand in gold(I) and gold(III) chemistry and so is its behaviour in gold(II) chemistry. It provides enough stability to some gold(II) complexes although it can be replaced easily by any other anionic or cationic ligand. Therefore gold(II) complexes containing tht were the door to the preparation of a great variety of gold(II) derivatives with different ligands bonded to each gold center: [Au$_2$(CH$_2$PR$_2$CH$_2$)$_2$LL′](ClO$_4$)$_2$, [Au$_2$(CH$_2$PR$_2$CH$_2$)$_2$XL](ClO$_4$)$_2$ or [Au$_2$(CH$_2$PR$_2$CH$_2$)$_2$RL](ClO$_4$)$_2$ (L and L′ = neutral ligands, X = halide, R = polyhaloaryl group) [69–71]. Table 1 collects the complexes with the Au_2^{4+} core whose structures have been resolved by X-ray methods. Table 2 contains those described and characterised by different techniques, but not by X-ray studies, belonging to the general formula [Au$_2$(CH$_2$PPh$_2$CH$_2$)$_2$LL′](A)$_n$, where L and L′ could be equal or different, neutral or anionic ligands and, depending on that, the total complex could possess one or two positive charges. The number of complexes of this general formula shows how the studies have been focused in this particular bis-ylide, CH$_2$PPh$_2$CH$_2$, which confers great stability to this oxidation state of gold. Table 3 collects gold(II) complexes either with a symmetrical double bridge, or those containing only one bridge holding the gold(II) centers. Table 4 contains the gold(II) complexes reported with two different bridges between the metallic centres. Note the presence of the bis-ylide, CH$_2$PPh$_2$CH$_2$ in all the examples reported in Table 4.

The preparation of asymmetrical gold(II) complexes can be achieved by simple mixture of equimolar quantities of the symmetrical derivatives (Eq. 5). When it works, it is very fast and no intermediates can be detected, although in some cases an equilibrium of the three components can be observed [60,69,70].



(5)

There are other synthetic procedures which are not so general as the previous ones. Therefore, an equimolar mixture of the gold(I) $[Au_2(CH_2PPhMeCH_2)_2]$ and the tetrabromo gold(III) derivative $[Au_2(CH_2PPhMeCH_2)_2Br_4]$ leads to the gold(II) complex $[Au_2(CH_2PPhMeCH_2)_2Br_2]$ in a way that can be described as a comproportionation process [72]. The recent preparation of $[Au_2(CH_2PPh_2CH_2)_2(SN)_2]$ (SN = pyridine-2-thiolate or 2-sulfanylbenzothiazole) [73] by the simple reaction of the bis-ylide $[Au_2(CH_2PPh_2CH_2)_2]$ with the protonated ligands HSN, in the presence of oxygen, represents both a rare example of oxidation by oxygen from gold(I) to gold(II) and further evidence for the nucleophilicity of gold(I) diauracycles as required for the mechanism proposed by Fackler [55] on the oxidative addition of gold, mentioned above.

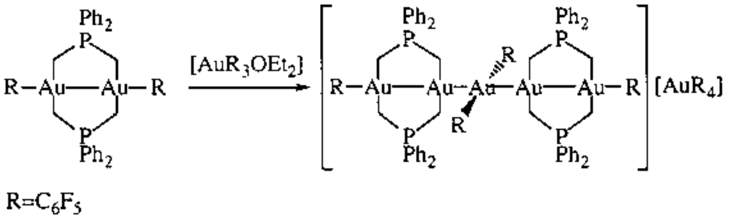
From Table 1 it is possible to see some trends regarding the gold–gold distances, e.g. shortening from iodide to chloride or with the shortest distances corresponding with double bridges containing sulfur donor atoms, such as $S_2C_2(CN)_2$, $SPPh_2CH_2$ or S_2COMe. Murray and Fackler [54,74,86] showed that the different groups attached to gold(II) atoms in $[XAu(CH_2PR_2CH_2)_2AuX']$ complexes do not greatly affect metal–metal bond length but have more influence on the Au–X distances. In addition the lengthening of the Au–X distances (X = halogen) in gold(II) derivatives C-Au–Au–X compared with mononuclear C-Au–X, may reflect the *trans* influence or the 'structural *trans* effect' of the groups bonded and transmitted through the metal–metal bond. This effect should be equally observed when comparing the X-ray structures of symmetrical derivatives $[(C_6F_5)Au(CH_2PPh_2CH_2)_2Au(C_6F_5)]$ and $[(PPh_3)Au(CH_2PPh_2CH_2)_2Au(PPh_3)](ClO_4)_2$ with the unsymmetrical one $[(C_6F_5)Au(CH_2PPh_2CH_2)_2Au(PPh_3)](ClO_4)$ [70]. The structure of $[Au_2(dppn)Cl_2]$-$(PF_6)_2$ (dppn = 1,8-bis(diphenylphosphino)naphthalene) is particularly interesting because it shows two different types of Au-P distances, one *trans* to the Au–Au bond of 2.385(4) and 2.387(3), and the other *cis*, of 2.286(4) and 2.296(4). The lengthening of the *trans* Au-P distance show the higher *trans* effect of this strong Au–Au bond (2.611Å) compared with the chloride [43].

6. Polynuclear gold(II) complexes

The most abundant gold(II) complexes belong to the Au_2^{4+} formulation and have been discussed above. In this section we refer to nuclearity higher than two. This includes complexes with more than two gold atoms in the molecule or with other metals in their composition in addition to the gold centers.

Regarding only gold as metal centers, the first polynuclear complexes appear by substitution reactions. Starting from the dinuclear gold derivative [107] $[ClAu(CH_2PPh_2CH_2)_2AuCl]$ and by reaction with Na_2S_n, the tetranuclear gold(II) complexes $[S_4\{Au(CH_2PPh_2CH_2)_2Au\}_2S_5]$ and $[S_4\{Au(CH_2PPh_2CH_2)_2Au\}_2S_4]$ were obtained. X-ray studies show two diauracycles connected by S_4 and S_5 polysulphide ligands or by two S_4 moieties, respectively. Therefore, the complexes show -S_4-Au–S_4-Au- or -S_4-Au–S_5-Au- diauracycles. In a similar way the reaction of $[(C_6F_5)Au(CH_2PPh_2CH_2)_2Au(tht)](ClO_4)$ with NaS_2CNR_2 affords tetranuclear complexes $[\{(C_6F_5)Au(CH_2PPh_2CH_2)_2Au\}_2(S_2CNR_2)]$. Based on the spectroscopic properties a structure with the dithiocarbamate ligand acting as a bridge between two eight-membered gold(II) diauracycles was proposed [97].

The synthesis of polynuclear gold(II) complexes involving different kinds of gold–gold bonds was achieved by reaction of gold(II) derivatives with the Au_2^{4+} core with either gold(I) or gold(III) compounds. We reported [65] the reaction of $[(C_6F_5)Au(CH_2PPh_2CH_2)_2Au(C_6F_5)]$ with $[Au(C_6F_5)_3(OEt_2)]$ which led serendipitously to the pentanuclear cationic complex $[\{Au_2(CH_2PPh_2CH_2)_2(C_6F_5)\}_2Au(C_6F_5)_2][Au(C_6F_5)_4]$. The structure of the cation is schematically showed in Eq. 6. Its backbone is a linear chain of five gold atoms, all of which have square planar geometry. Two diauracycle units $[(C_6F_5)Au(CH_2PPh_2CH_2)_2Au]$ are bonded to a $Au(C_6F_5)_2$ moiety which lies nearly perpendicular to the two eight membered rings. 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.

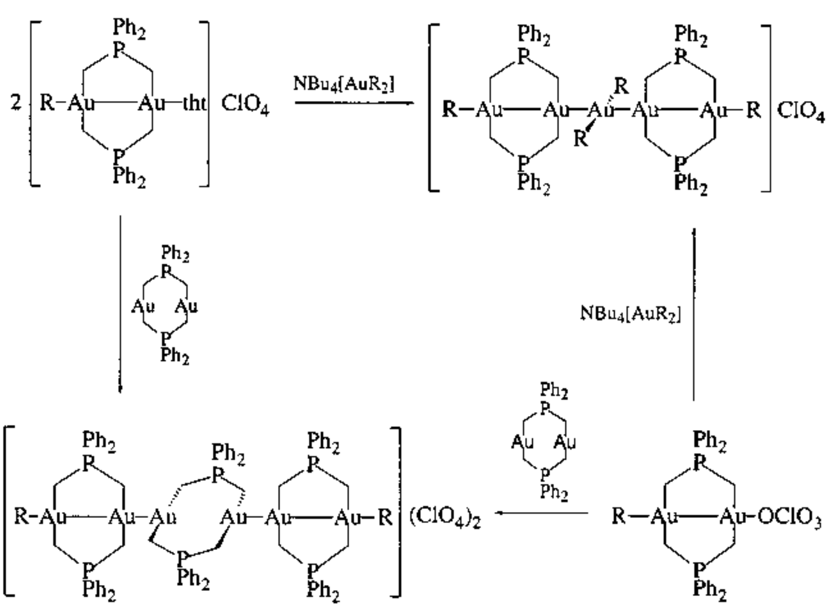


(6)

In accordance with extended Hückel calculations [108,109] the pentanuclear chain can be better described as Au(III)–Au(I)–Au(I)–Au(I)–Au(III), so the central gold can be regarded as part of one $[Au(C_6F_5)_2]^-$ unit which acts as an electron donor to the dinuclear gold cations $[(C_6F_5)Au(CH_2PPh_2CH_2)_2Au]^+$. Complexes containing the organoaurates $[AuR_2]^-$ ($R = C_6F_5$ or 2,4,6-$C_6F_3H_2$) as nucleophilic centers have been described [110,111] and cationic dinuclear gold complexes have been postulated as intermediates in oxidative additions [55] (Eq. 4).

The unit $[RAu(CH_2PPh_2CH_2)_2Au]^+$ was nearly prepared from different gold(II) complexes mentioned above, such as $[RAu(CH_2PPh_2CH_2)_2Au(tht)]ClO_4$ ($R = C_6F_5$ or 2,4,6-$C_6F_3H_2$) and $[RAu(CH_2PPh_2CH_2)_2Au(OClO_3)]$ ($R = C_6F_5$, 2,4,6-$C_6F_3H_2$ or CH_3) The tetrahydrothiophene or perchlorate ligands are easily displaced in gold chemistry, although they are enough to stabilise the gold(II) precursors. The reaction of these gold(II) complexes with either organoaurates $NBu_4[AuR_2]$ ($R = C_6F_5$ or 2,4,6-$C_6F_3H_2$) or the diauracycle $[Au(CH_2PPh_2CH_2)_2Au]$, whose nucleophilic character was repeatedly evident [52,55], is the way to the preparation of these chains of gold centers.

Scheme 2 collects the results of these reactions. The pentanuclear chain of gold atoms is now accessible with ClO_4 as anion. A complex containing the trifluorophenyl group, $[\{(C_6F_3H_2)Au(CH_2PPh_2CH_2)_2Au\}_2Au(C_6F_3H_2)_2]ClO_4$, can be obtained using instead the starting trifluophenyl derivatives. When the diauracycle $[Au(CH_2PPh_2CH_2)_2Au]$ is used as electron donor, hexanuclear complexes



Scheme 2. R = C_6F_5, 2,4,6-$C_6F_3H_2$, Me.

$[\{RAu(CH_2PPh_2CH_2)_2Au\}_2Au_2(CH_2PPh_2CH_2)_2](ClO_4)_2$ (R = C_6F_5, 2,4,6-$C_6F_3H_2$ or CH_3) were obtained. The X-ray structure of the trifluorophenyl derivative has been determined. The whole dication consists of three $Au(CH_2PPh_2CH_2)_2Au$ diauracycles in a nearly perpendicular disposition linked together through two unbridged gold–gold bonds, building up an almost linear six atom gold chain. The gold–gold distances in the pentanuclear and hexanuclear derivatives are very close despite the differences in the aryl group bonded to the ending gold atoms (see Table 5). In accordance with these data the bond in penta-, Au_5^{9+}, and hexa-nuclear, Au_6^{10+}, complexes can be understood as a donation of electron density from the central gold(I) centers to two $[RAu(CH_2PPh_2CH_2)_2Au]^+$ fragments, which were gold(II) in the starting materials. Extended Hückel calculations [109] in the hexanuclear derivative show a better description as Au(III)–Au(I)–Au(I)–Au(I)–Au(I)–Au(III), very close to the description of pentanuclear gold complex and slightly different from the preparative procedures.

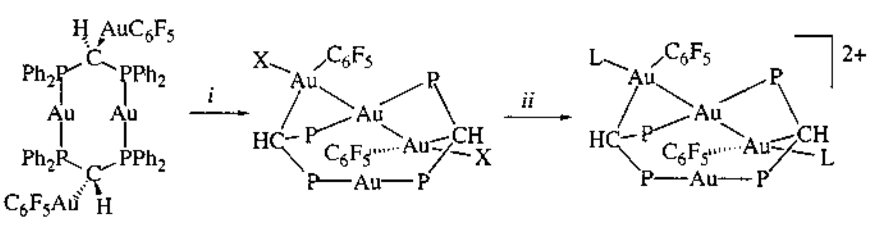
The reaction of the tetranuclear complex $[Au(PPh_2CH\{Au(C_6F_5)\}PPh_2)_2Au]$ [112] with chlorine or bromine does not oxidise the two gold centers of the diauracycle to give the usual gold(II) derivatives with an X-Au–Au–X backbone. Instead, a new type of reaction occurs, probably due to the presence of other gold(I) centers in close proximity [113]. Displacement reactions using silver salts, such as $[Ag(OClO_3)(tht)]$ and $[Ag(OClO_3)PR_3]$ afford cationic complexes. The X-ray structure of the blue PPh_3 derivative, shows a linear chain of three gold atoms in a P–Au–Au–Au–P backbone (Scheme 3). The assignment of oxidation states in the linear chain is not straightforward. Because the sum must equal + 5,

Table 5
Polynuclear gold(II) complexes

Complex	Ref.	d(Au–Au)
$[S_4\{Au(CH_2PPh_2CH_2)_2Au\}_2S_5]$	[107]	2.649(9)
$[S_4\{Au(CH_2PPh_2CH_2)_2Au\}_2S_4]$	[107]	2.662(1)
$[\{(C_6F_5)Au(CH_2PPh_2CH_2)_2Au\}_2(S_2CNMe_2)]$	[97]	–
$[\{(C_6F_5)Au(CH_2PPh_2CH_2)_2Au\}_2(S_2CNEt_2)]$	[97]	–
$[\{(C_6F_5)Au(CH_2PPh_2CH_2)_2Au\}_2\{S_2CN(CH_2Ph)_2\}]$	[97]	–
$[\{(C_6F_3H_2)Au(CH_2PPh_2CH_2)_2Au\}_2(S_2CNMe_2)]$	[97]	–
$[\{Au_2(CH_2PPh_2CH_2)_2(C_6F_5)\}_2Au(C_6F_5)_2][Au(C_6F_5)_4]$	[65]	2.640(1), 2.755(1)
$[\{Au_2(CH_2PPh_2CH_2)_2(C_6F_5)\}_2Au(C_6F_5)_2](ClO_4)$	[71]	–
$[\{(C_6F_3H_2)Au(CH_2PPh_2CH_2)_2Au\}_2Au(C_6F_3H_2)_2]ClO_4$	[71]	–
$[\{(C_6F_5)Au(CH_2PPh_2CH_2)_2Au\}_2Au_2(CH_2PPh_2CH_2)_2]ClO_4$	[71]	–
$[\{(C_6F_3H_2)Au(CH_2PPh_2CH_2)_2Au\}_2Au_2(CH_2PPh_2CH_2)_2]ClO_4$	[71]	2.654(1), 2.737(1), 2.838(1)
$[\{(CH_3)Au(CH_2PPh_2CH_2)_2Au\}_2Au_2(CH_2PPh_2CH_2)_2]ClO_4$	[71]	–
$[Au_4(C_6F_5)_2\{(PPh_2)_2CH\}_2Cl_2]$	[113]	–
$[Au_4(C_6F_5)_2\{(PPh_2)_2CH\}_2Br_2]$	[113]	–
$[Au_4(C_6F_5)_2\{(PPh_2)_2CH\}_2(tht)_2](ClO_4)_2$	[113]	–
$[Au_4(C_6F_5)_2\{(PPh_2)_2CH\}_2(PPh_3)_2](ClO_4)_2$	[113]	2.730(1), 2.909(2)
$[Au_4(C_6F_5)_2\{(PPh_2)_2CH\}_2(PPh_2Me)_2](ClO_4)_2$	[113]	–
$[Au_4(C_6F_5)_2\{(PPh_2)_2CH\}_2\{P(tol)_3\}_2](ClO_4)_2$	[113]	–
$[Au(CH_2PPh_2CH_2)_2Au]_2(TCNQ)$	[114]	–
$[ClAu(CH_2PPh_2S)_2Pt(CH_2PPh_2S)_2AuCl]$	[115]	–
$[Au_2(CH_2PPh_2CH_2)_2(MeSi\{Me_2SiN(p\text{-tol})\}_3Sn)_2]$	[118]	2.749(1)

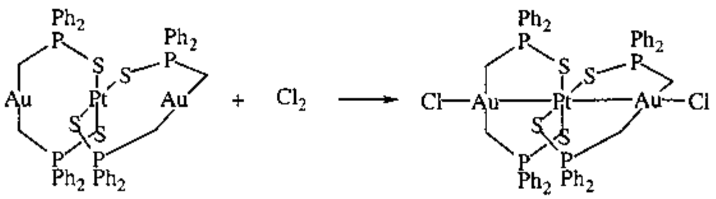
the only two possibilities with integral oxidation states are Au(II)–Au(I)–Au(II) or Au(I)–Au(III)–Au(I) the former being the most appropriate and very close to those heteronuclear gold(II) derivatives Au(II)–Pt(II)–Au(II) reported by Fackler (see below).

Polynuclear gold complexes with partial oxidation states could be present in the charge transfer salts complexes reported by oxidation of $[Au(CH_2PPh_2CH_2)_2Au]$ or $[Au(NC_5H_4S)_2Au]$ with 7,7′,8,8′-tetracyanoquinodimethane (TCNQ) [114]. The complex $[Au(CH_2PPh_2CH_2)_2Au]_2(TCNQ)$ contains radical TCNQ anions, therefore partial oxidation could have happened; the X-ray structure has not yet been reported.



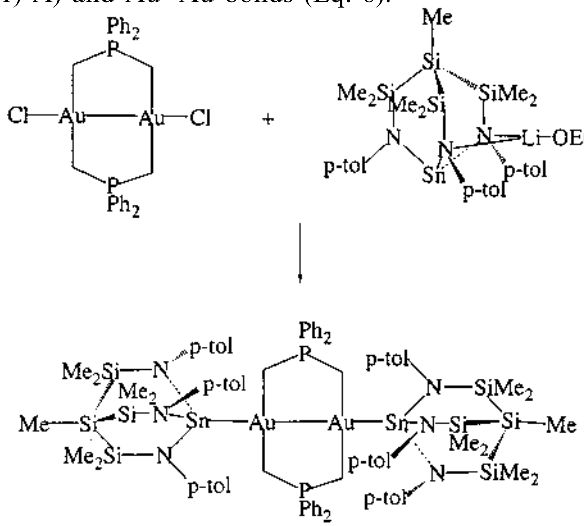
Scheme 3. (i) Cl_2 or Br_2, (ii) $[Ag(OClO_3)L]$ [L = tht, PPh_3, PPh_2Me, $P(Tol)_3$].

The preparation of heteropolynuclear gold(II) complexes containing a linear chain of trinuclear species was achieved by oxidative addition of trinuclear derivatives. Fackler et al. have prepared different trinuclear complexes containing the bridging ligand $SPPh_2CH_2$ which holds two gold(I) centers connected with the other metal in the center of the compound, such as $[Au(CH_2PPh_2S)_2M(CH_2PPh_2S)_2Au]$ ($M = Pt(II)$ [115] or Pb(II)[116]). Whereas the platinum derivative by oxidative addition of chloride or $PhICl_2$ affords the gold(II) derivative with a linear Cl-Au-Pt-Au-Cl backbone (Eq. 7), the Pb analogue does not. The gold-platinum distances are 2.668(1)Å and 2.662(1)Å, clearly in the range of a metal–metal bond. While it is convenient to describe the gold centers as the atoms being oxidised, the more correct description, based on Fenske–Hall calculations, is that a $[Au\text{-}Pt\text{-}Au]^{2+}$ moiety is formed [55,117].



(7)

Other heteropolynuclear gold(II) complexes can be obtained by replacement of halide groups in bis(ylide)gold(II) complexes by other anionic nucleophilic metal complexes, without reduction of the gold precursor. That is the case for the formation [118] of $[Au_2(CH_2PPh_2CH_2)_2(MeSi\{Me_2SiN(p\text{-tol})\}_3Sn)_2]$ by reaction of the triamidostannate $[MeSi\{Me_2SiN(p\text{-tol})\}_3SnLi(Et_2O)]$ with $[Au_2(CH_2PPh_2CH_2)_2Cl_2]$. The tetranuclear gold(II) derivative consists of a gold(II) eight-membered diauracycle with a chair conformation, linked to two tripodal tris(amido)tin fragments. This generates a nearly linear Sn–Au–Au–Sn chain linked by covalent Sn–Au (2.680(1) Å) and Au–Au bonds (Eq. 8).



(8)

7. Conclusion and remarks

The vigorous growth of gold(II) chemistry is due to different reasons but probably the more important one is the use of the bis-ylide $(CH_2PR_2CH_2)^-$ in gold chemistry and mainly the phenyl derivative. Its negative charge ensures that the starting dinuclear material and its posterior derivatives have neither positive nor negative charges which made the complexes accessible to different decomposition pathways. Nevertheless the stability this ligand confers on the gold(II) centres is so strong that complexes with one, two and even three positive charges have been reported. The formation of unsupported gold–gold or gold-metal bonds generating chains of metal centers, also represents an important aspect of this chemistry. In order to prevent these complexes from breaking down the ligands may surround the metal–metal bond. Similar properties should enable the ligands to stabilise mononuclear gold(II) complexes and in fact the one that does, thioether [9]aneS_3 in $[Au([9]aneS_3)_2](BF_4)_2$, nearly wraps up the gold(II) center.

Progress in this field should be expected by implementation of the ligand properties noted above. Ligands able to wrap around the gold center or centers with some preference to those with sulfur donor atoms and with one negative charge should be the most appropriate to develop this chemistry. We agree with Fackler that the combination of different metals, such as rhodium or iridium with the gold centers in the same molecule is another area for development, as a source of heteronuclear chains.

Acknowledgements

We thank the Dirección General de Investigación Científica y Técnica (No. PB95-0140 and PB97-1010-C02-01) for financial support.

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