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4. Gold 1992

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CONTENTS

INTRODUCTION

This review surveys the coordination chemistry of gold which was published in 1992. Its format is similar to that of the 1991 review [1]. The literature has been searched by using *Current Contents* and also by use of the Cambridge Crystallographic Data Base, implemented through the ETH, Zürich [2]. Although not fully comprehensive, the article does give a significant coverage of new material and I apologise to authors whose work has not been included. Organometallic complexes (defined as those with Au-C bonds with the exception of cyanide complexes) have not been included unless there is a feature of particular interest to the coordination chemist.

Complexes have been arranged according to the formal oxidation state of the gold centre and subsections are organized according to the donor atoms of the ligands. In a large number of complexes, the question of gold-gold interactions arises. It is always difficult to assign these as metal-metal bonded species or not. Interested readers should address not only sections 4.4 and 4.5 (di-, tri- and poly-nuclear complexes) but also section 4.3 in which interactions between gold(I)

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centres are mentioned where appropriate. A selected number of clusters have been included with the emphasis being on aggregation of gold atoms; in particular, the use of gold(I) phosphine units as auxilliary cluster units in heterometallic clusters has not been surveyed. A short section has been added which considers the extraction of gold.

4.1 *EXTRACTION*

The extraction of $[Au(CN)_2]^-$ among other metal cyanides by polydiallyl (PDAA) has been investigated. It has been found that cross-linking has a significant influence on anion selectivity. For example, PDAA with a low degree of cross-linking favours the extraction of $[Ni(CN)_4]^{2-}$ over $[Au(CN)_2]^-$, although at high pH, $[Au(CN)_2]^-$ is the favoured species [3]. Related work is reported in an accompanying paper [4]. Two eluent systems have been described for use in the separation and determination of gold and other metal cyano complexes. When the eluent contains NH_3, ionic column selectivity for gold is increased [5]. Two polyamine moderate base resins have been assessed for the extraction of gold from cyanide solutions over a pH range of 5 to 12. The resins show a good selectivity for gold, and exhibit both a good loading capacity and elution properties [6].

4.2 *GOLD(III)*

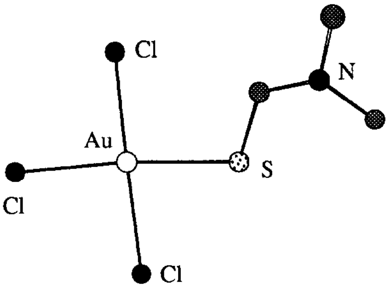
4.2.1 *Complexes with halide and pseudo-halide ligands*

Anions of the type $[AuX_4]^-$ (X = halide) feature in several crystallographic studies. The structure of $K[AuCl_4]$ has been redetermined in the $P2_1/c$ space group; the gold atoms lie on centres of symmetry [7]. In a study which includes the complex formation between gold and *N,N*-diethyl-*N'*-benzoylthioureas, the crystal structure of $[Et_2NCHNHC(O)Ph][AuCl_4]$ has been determined [8]. The preparation and X-ray crystallographic structure of the $[(\text{methylquinaldate})_2H]^+$ salt of $[AuBr_4]^-$ have been reported. The infrared spectral characteristics of the complex have been detailed [9].

The halide complexes $[AuCl_3SCl_4]_n$, $[AuCl_3SeBr_4]_n$, and $[AuBr_3SeBr_4]_n$ have been structurally characterized. They are isostructural and in each, the gold(III) centre is in a square planar environment with the chalcogen atom in a trigonal bipyramidal site. The related complex $[AuCl_3TeCl_4]_n$ has a dimeric structure (*i.e.* n = 2), again with the gold(III) centre in a square planar environment surrounded by four halide ions [10].

4.2.2 *Complexes with sulfur donor ligands*

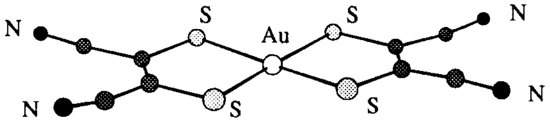
Amongst a series of gold(III) and gold(I) thione complexes to be studied is $[AuCl_3L]$ (**1**) where L = Me_2NCHS. Compound (**1**) has been characterized by ^1H NMR, IR and UV spectroscopies and a structural determination confirms coordination of ligand L through the sulfur donor atom and the square planar environment of the metal centre. Structural data have been compared for gold(I) and gold(III) species [11].



(1)

The crystal structure of the dithiocarbamato complex $[AuL_2][SbF_6]$ ($HL = Et_2NCS_2H$) has been determined. The Au-S bond distances lie in the range 2.318-2.330Å [12].

As one of a series of three related complexes, the complex $[Pt(CNMe)_4][AuL_2]_2.MeCN$ (H_2L = 1,2-$(HS)_2C_2(CN)_2$) has been studied. The crystal structure of $[Pt(CNMe)_4][AuL_2]_2.MeCN$ has been determined and the results show that the lattice is composed of neutral columns made up $[Pt(CNMe)_4]^{2+}$ dications and pairs of $[AuL_2]^-$ (**2**) anions. The two anions that constitute a pair associate with one another through edge-to-edge S---S interactions (S---S = 3.75 to 3.80Å). The packing in this system is compared with those in $[Pt(CNMe)_4][PdL_2].nMeCN$ (n = 0 or 2) [13]. In an accompanying paper, Connelly *et al* also look at related, non-gold containing systems. In independent work, Matsubayashi and Yokozawa have prepared $[Cp^*{}_2Fe][Au(C_3S_5)_2]$ from $[^nBu_4N][Au(C_3S_5)_2]$ and $[Cp^*{}_2Fe][BF_4]$ in dmf and have investigated the structure of the product [14]. Similar edge-to-edge association of pairs of $[Au(C_3S_5)_2]^-$ (**3**) units as was noted in the solid state structure of $[Pt(CNMe)_4][AuL_2]_2.MeCN$ is observed in $[Cp^*{}_2Fe][Au(C_3S_5)_2]$. The complex $[^nBu_4N][Au(C_3S_5)_2]$ may be oxidized electrochemically using $Cp^*{}_2Fe$ or Cp_2Fe in MeCN to yield $[Cp^*{}_2Fe]_{0.33}[Au(C_3S_5)_2]$ or $[Cp_2Fe]_{0.33}[Au(C_3S_5)_2]$, respectively. Measurements of the electrical conductivities, electronic reflectance and X-ray photoelectron spectra of these materials have been carried out [14].



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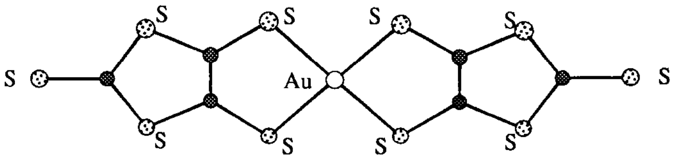
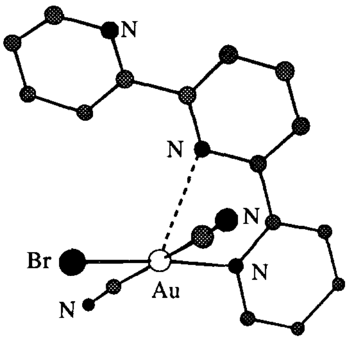


(3)

4.2.3 Complexes with nitrogen donor ligands

The reaction of $HAuCl_4$ with gly-L-his.HCl leads to the gold(III) complex [Au(gly-L-his)Cl]Cl.$3H_2O$ in which the dipeptide ligand is monodeprotonated at the peptide nitrogen atom. Structural characterization of this complex confirms a square planar environment for the gold(III) centre with the chloride ligand *trans* to the peptide nitrogen atom. The $[\text{gly-L-his}]^-$ ligand acts as an *N,N',N''*-donor set. The tetrameric complex $[\{\text{Au(gly-L-his)}\}_4]$ can be obtained from [Au(gly-L-his)Cl]Cl in aqueous solution at pH 6-7; the ligand is now $[\text{gly-L-his}]^{3-}$. A cyclic structure has been confirmed crystallographically for $[\{\text{Au(gly-L-his)}\}_4]$ and each gold(III) centre is coordinated in a square planar fashion by an *N,N',N''*-donor set from one $[\text{gly-L-his}]^{3-}$ ligand and by the remaining hist-*N* donor atom from a second $[\text{gly-L-his}]^{3-}$ ligand. The latter hence functions in a bridging mode. The ring structure of the tetramer is folded to give a saddle-like conformation. ^1H NMR spectroscopic data are also presented [15].

Coordination of terpyridine to gold(III) is illustrated in the complex $[\text{Au(terpy)Br(CN)}_2]$ (4); the terpy ligand functions in a monodentate fashion as confirmed crystallographically although the nitrogen atom of the central pyridine ring is at a distance of 2.839(5)Å from the gold(III) centre. This distance is less that the sum of the van der Waals radii but greater than the sum of the covalent radii of Au(III) and N. Within the square planar coordination sphere, the cyanide ligands are mutually *trans*; the $\text{Au-N}_{\text{square plane}}$ bond length is 2.078(6)Å [16].



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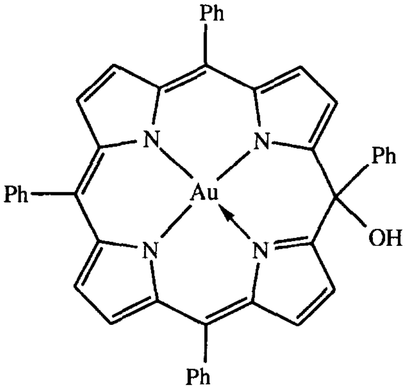
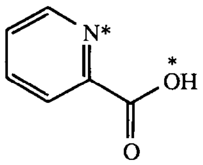


(5)

The first examples of the direct nucleophilic addition of hydroxide ion to a non-oxidized porphyrin ring have been reported. The products are *meso*-saturated adducts with electronic structures which resemble those of phlorins. The reactions reported are those of [Au(TPP)]Cl, [Au(TPPS)]Cl, [Au(TPyP)]Cl and [Au(TCPP)]Cl ($TCPPH_2$ = 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin) with OH^- in dmf or dmso; the sources of OH^- are aqueous NaOH or $^nBu_4NOH$. Complex (5) illustrates the product for the case of the reaction of $[\text{Au(TPP)}]^+$ [17].

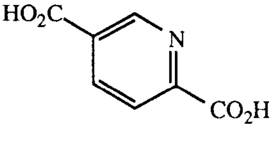
4.2.4 Complexes with mixed donor ligands

Various gold(III) complexes involving *N,O*-donor ligands have been synthesized from reactions of $[AuX_4]^-$ (X = Cl or Br). For the ligands HL = 2-$HOC_6H_4CH{=}NR$ (R = Me, Et, ^{i}Pr, ^{n}Bu, CH_2Ph and *c*-C_6H_{11}) the complexes formed are of the type $[AuL_2][AuCl_4]$, although minor amounts of $AuCl_2L$ accompany their generation. When HL = 2-pyridylmethanol or 2-pyridylethanol, the complexes produced are $[AuX_3(HL)]$; these compounds are formed in the presence of an excess of X^- ion. Other related gold(III) complexes have also been reported and the crystal structures of $[AuBr_2L]$ for HL = (**6**) and $[AuL_2]^-$ for H_2L = (**7**) have been determined. In the former, the two bromide ligands are mutually *cis* in the square planar coordination sphere of the gold(III) centre, and the ligand L^- functions as an *N,O*-donor (see structure (**6**)). In the anion $[AuL_2]^-$ (H_2L = (**7**)), each ligand L^{2-} acts as an *N,O*-donor leaving one carboxyl group free; the two nitrogen (and, it follows, the two oxygen) donor atoms are *trans* to one another [18].

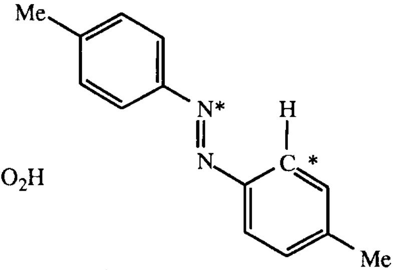


* = coordination site in L^-

(**6**)



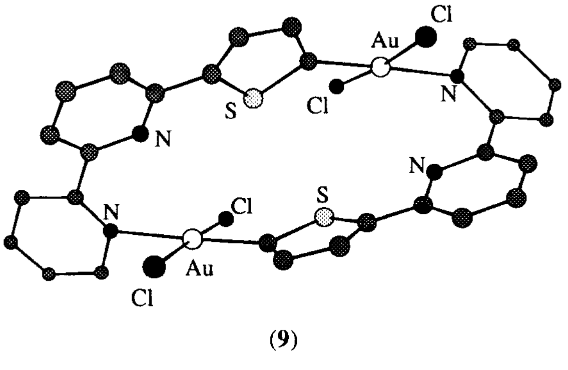
(**7**)



* = coordination site in L^-

(**8**)

Ligand (**8**), HL, undergoes cyclometallation during complex formation with gold(III) to give the compounds $[AuLCl_2]$ and $[AuL(py)(CH_2COMe)](ClO_4)$. Structural data for these two complexes confirm the square planar gold(III) coordination geometry. In both $[AuLCl_2]$ and the cation $[AuL(py)(CH_2COMe)]^+$, L^- acts as an *N,C*-donor with these atoms occupying *cis* positions. In $[AuL(py)(CH_2COMe)]^+$, the pyridine ligand is *trans* to the *C*-donor atom of L^- [19].



(**9**)

The reaction of 6-(2-thienyl)-2,2'-bipyridine (HL') with Na[$AuCl_4$] yields the gold(III) complex [$AuCl_3$(HL')], but on heating, the C-H bond at the 5-position of the thienyl moiety of HL' is activated and the complex that is isolated in the dimeric species (**9**). Complex (**9**) can also be obtained by performing the original reaction at 100°C. The new complexes have been characterized by ^1H NMR and IR spectroscopies, and the solid state structure of (**9**) has been studied crystallographically. The results of these reactions have been compared with parallel palladium and platinum chemistries; significant differences have been observed, in particular as regards the site of metallation [20].

4.3 GOLD(I)

4.3.1 Complexes with halide and pseudo-halide ligands

The gold(I) anion [$AuCl_2$]$^-$ has been generated electrochemically. It is a highly reactive species and complexation with the ligands L-cysteine, D-penicillamine and imidazole has been studied by electrochemical techiniques [21].

Isoelectonic with CN^- is CO; the complex [$Au(CO)_2$][Sb_2F_{11}] has been prepared and a comparison has been made between [$Au(CO)_2$]$^+$ and [$Au(CN)_2$]$^-$ by studying the results of a normal coordinate analysis and general valence force field calculations. Interestingly, attempts to crystallize [$Au(CO)_2$][Sb_2F_{11}] from acetonitrile led instead to crystals of the complex [$Au(NCMe)_2$][SbF_6] (see section 4.3.5) [22]. Structural determinations have been carried out for the complexes [Au(CN)(CN^tBu)] and [(NC)Au($CNCMe_2CH_2CH_2CMe_2NC$)Au(CN)]. Both show, as expected, linear gold(I) environments [23]. The cyano complexes [$Me_3PAu(CN)$] [24] and [$(NC)_xAu(\mu\text{-}L)AuBr_y$] (L = bis(dicyclohexylphosphino)ethane; x + y = 2) [25] have both been the subjects of structural studies and will be discussed in section 4.3.6.

The reader is also directed to section 4.3.5 for complexation involving the two ligands (**19**) and (**20**) that might well have been included as pseudo-halides.

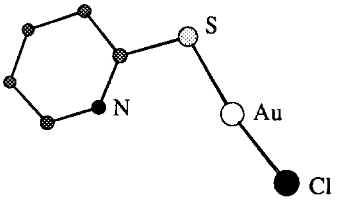
4.3.2 Complexes with oxygen donor ligands

Alkoxide chemistry is represented in this review by the reactions of KOR (R = CH_2CF_3 or $CH(CF_3)_2$) with [LAuCl] where L is a tertiary phosphine ligand, namely PPh_3 or P(*c*-C_6H_{11})$_3$. The products are the highly nucleophilic species [LAu(OR)] [26].

4.3.3 Complexes with sulfur donor ligands

The reaction of HL (2- or 4-pyridine thiol = 2-HL or 4-HL) with [Me_2SAuCl] yields [Au(HL)Cl] in which the ligands are *S*-bound and in the pyridinium thione tautomeric form. In the case of L^-, reaction with [Me_2SAuCl] leads to the oligomeric species [$\{AuL\}_n$]. In [Au(2-HL)Cl] (**10**), the *S*-coordination mode of the ligand has been confirmed crystallographically. The coordination geometry around the gold(I) centre is linear and there is evidence for intermolecular

Au---Au and NH----Cl interactions [27]. The reaction between $[PPN][AuCl_2]$ and Tl(acac) leads to $[PPN][Au(acac)_2]$, a complex that has been successfully utilized in reactions with a series of compounds of type RH in which H is acidic. For example, organometallic complexes such as $[AuR_2]^-$ for RH = $CH_2(CN)_2$ or $Me_3SiC{\equiv}CH$ have been prepared by this method. Of significance to this review though are the reactions of $[PPN][Au(acac)_2]$ with 2-SHpy and $HPPh_2$ to yield $[Au(2\text{-}Spy)_2]^-$ and $[Au(PPh_2)]_n$ respectively [28].



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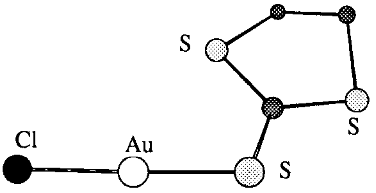
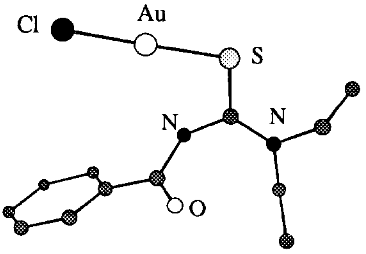


(11)

Various gold(I) thione complexes have been prepared and studied by ^1H NMR, IR and UV spectroscopies. One example involves the heterocycle 1,3-dithiolane-2-thione, L, which coordinates to gold(I) through the thione sulfur donor atom in the complex [LAuCl] (**11**); the crystal structure of this complex has been determined. The gold(I) centre is in the anticipated linear coordination geometry [11].

In work that complements that described in section 4.2.1 [8], complex formation between gold(I) and *N,N*-diethyl-*N'*-benzoylthioureas has led to the isolation and structural characterization of the compound $[Au\{Et_2NC(S)NHC(O)Ph\}Cl]$ (**12**) in which the organic ligand is bonded to the gold(I) centre (a linear geometry) through the sulfur donor atom (Au-S = 2.258(3)Å) [29]. Coordination of thiourea to gold(I) occurs through the sulfur atom in the complex cation $[Au\{(H_2N)_2C{=}S\}_2]^+$ (**13**) which has been isolated and structurally characterized as the bromide salt [30].



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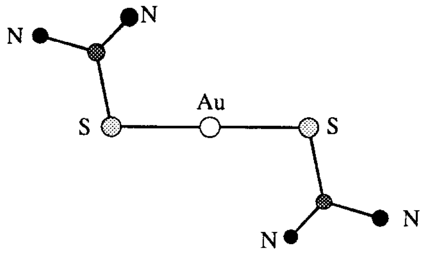
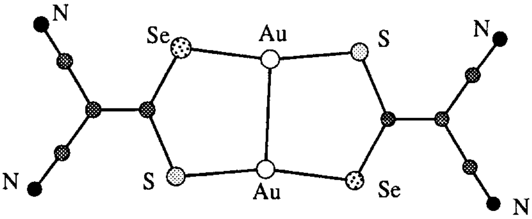


(13)

A single crystal structure analysis of the ethyldithiocarbonate complex $[(Ph_3P)Au(S_2COEt)]$ has been carried out. The $EtOCS_2^-$ ligand is *S*-bonded to the gold(I) centre which is in a linear environment, although there is a relatively close Au---O contact (3.028Å); this cannot be considered to correspond to a significant degree of bonding Au---O character [31]. A series of gold(I) aryldithiocarboxylate complexes has been synthesized. In addition to the compounds $[Au(S_2CPh)]_n$, $[Au(S_2CC_6H_4\text{-}4\text{-}Me)]_n$ and $[Au(S_2CC_6H_4\text{-}2\text{-}Me)]_6$, their 1:1 and 1:2 complexes with triphenylphosphine have been studied. Complex characterization has been by elemental analysis, molecular weight determinations and IR and multinuclear NMR (including variable temperature ^1H and ^{13}C NMR) spectroscopies. The crystal structures of the phosphine complexes $[Au(S_2CPh)(PPh_3)]$ and $[Au(S_2CPh)(PPh_3)_2]$ have been elucidated. In $[Au(S_2CPh)(PPh_3)]$, the gold(I) centre is linearly coordinated to the *P*-donor atom of PPh_3 and one *S*-donor atom of the dithiocarboxylate ligand; the unit cell contains two independent molecules. In $[Au(S_2CPh)(PPh_3)_2]$, the coordination geometry is described as being 'pseudo-tetrahedral', with the dithiocarboxylate ligand functioning as an *S,S'*-donor. Also reported in this work is the structure of the non-stoichiometric complex $[Au_{0.56}Cu_{0.44}(S_2CC_6H_4\text{-}4\text{-}Me)(PPh_3)_2]$ which has similar features to that of $[Au(S_2CPh)(PPh_3)_2]$ [32].

The complex dication $[Au_2\{SSeC{=}C(CN)_2\}_2]^{2+}$ (**14**) is an example of the type of complex referred to in the introduction as difficult to categorize — is there or is there not an Au-Au 'bond'? This complex and its all-selenium analogue have been prepared and structurally characterized; they are isotypic. In (**14**), each gold atom is bonded to one sulfur and one selenium atom; the Au--Au separation is 2.810(1) and *ab initio* Hartree-Fock calculations provide some evidence for an Au-Au bond order > 0 [33].



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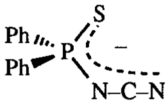


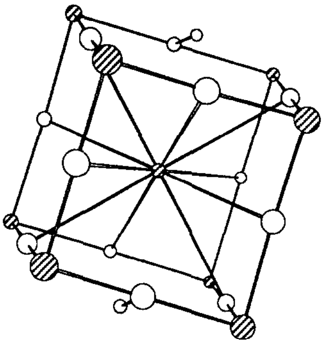
(15)

Anion (**15**) may be classed as a 'pseudo-halide' ligand. However, it is included here because it binds to gold(I) through the sulfur donor atom in the complex $[(Ph_3P)Au(\mathbf{15})]$; this contrasts with the *N*-bonded modes observed for two related ligands which are discussed in section 4.3.5. The gold(I) complex $[(Ph_3P)Au(\mathbf{15})]$ has been synthesized and characterized; a crystal structure determination confirms a linear coordination geometry for the metal atom [34].

A re-determination [7] of the crystal structure of $[(Ph_3P{=}S)AuCl]$ has illustrated a more reasonable value for the Au-S bond distance (2.265(2)Å) than that previously reported (2.555Å).

4.3.4 Complexes with selenium and tellurium donor ligands

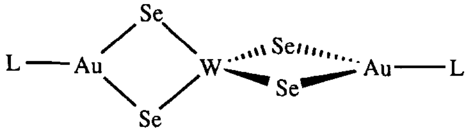
The preparation of the selenide $(Et_4N)_3Na[Au_{12}Se_8]$, perhaps more appropriately considered as $(Et_4N)_3[NaAu_{12}Se_8]$, has been described. Crystallographic characterization of the compound reveals a centred cubic structure; the sodium ion lies at the centre of the $[Au_{12}Se_8]^{4-}$ unit as illustrated in structure (**16**). The system is compared with a range of related structures and infrared spectroscopic data have been analysed [35].



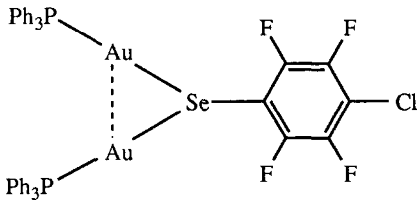
open circle = Au; hatched circle = Se; central hatched circle = Na^+

(16)

The reaction of $[WSe_4]^{2-}$ in acetonitrile with two equivalents of a source of gold(I) in the presence of an excess of PMe_2Ph leads to the formation of the neutral complex $[\{AuL\}(\mu\text{-}WSe_4)]$ **(17)** (L = PMe_2Ph). Analogous systems containing Cu(I) and Ag(I) as the group 11 metal have also been prepared. The PMe_2Ph ligands in $[\{Au(PMe_2Ph)\}(\mu\text{-}WSe_4)]$ can be replaced by $PMePh_2$ and the crystal structure of **(17)** (L = $PMePh_2$) has been determined at 113 K. Each gold(I) centre is in a trigonal planar environment. Structural studies are complemented by multinuclear (including ^{77}Se) NMR spectroscopic investigations [36].



(17)



(18)

The complex dication $[Au_2\{SSeC{=}C(CN)_2\}_2]^{2+}$ **(14)** and its all-selenium analogue were described in the previous section [33]. Another species which exhibits gold atoms in close proximity is the cation $[(Ph_3P)_2Au_2Se(C_6F_4\text{-}4\text{-}Cl)]^+$ **(18)** which has been isolated as the $[SbF_6]^-$ salt. The complex [(**18**)]$[SbF_6]$ results from the reaction of $[(PPh_3P)AuCl]$ with $Se_2(C_6F_4\text{-}4\text{-}Cl)_2$ in the presence of silver hexafluoroantimonate. In its ^{31}P NMR spectrum, [(**18**)]$[SbF_6]$ exhibits one resonance at δ +38.8 and the ^{77}Se NMR spectrum shows a signal at δ +120. The structure of [(**18**)]$[SbF_6]$ has been studied by X-ray diffraction methods. Each gold(I) centre is linear with respect to the P and Se donor atoms. Important distances are Au-Se = 2.458(2) and 2.467(1)Å and Au-P = 2.272(3) and 2.274(2)Å. The Au---Au separation is 3.031(1)Å which is significantly longer than in $[Au_2\{SSeC{=}C(CN)_2\}_2]^{2+}$ mentioned above. The geometry about the selenium atom is distorted with an acute Au-Se-Au angle of 76.0(1)° [37].

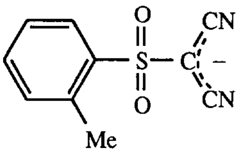
Treatment of gold(I) cyanide with polyselenide (Se_x^{2-}) or polytelluride (Te_x^{2-}) in dmf in the presence of a suitable cation (*e.g.* Ph_4P^+) gives rise to cyclic complex gold(I) chalcogenide anions.

The anions $[Au_2Se_5]^{2-}$ and $[Au_2Se_6]^{2-}$ have similar structures with an Au---Au 'unit' being bridged by an Se_2^{2-} ligand on one side and either an Se_3^{2-} or Se_4^{2-} ligand on the other. The Au---Au separations in $[Au_2Se_5]^{2-}$ and $[Au_2Se_6]^{2-}$ are 3.004Å and 3.132Å respectively. Another product to be structurally characterized is $[Au_4Te_4]^{4-}$. This anion exhibits a distorted square with the tellurium atoms defining the corners and gold(I) centres in linear coordination geometry and located along the edges of the square. The reaction of $AuCl_3$ with Te_x^{2-} has also been reported. The product is $[Au_2Te_4]^{2-}$ and an X-ray diffraction study of this species reveals a structural type similar to those of $[Au_2Se_5]^{2-}$ and $[Au_2Se_6]^{2-}$ involving two Te_2^{2-} ligands [38].

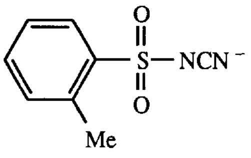
4.3.5 Complexes with nitrogen donor ligands

In section 4.3.1, we mentioned that efforts to crystallize $[Au(CO)_2][Sb_2F_{11}]$ from acetonitrile gave rise instead to crystals of $[Au(NCMe)_2][SbF_6]$. The cation $[Au(NCMe)_2]^+$ has a linear geometry with relatively short Au-N bond distances of 1.97(1)Å [22].

The 'pseudo-halide' ligands (**19**) and (**20**) have, arbitrarily, been assigned to this *N*-donor ligand section rather than to section 4.3.1. Both behave as monodentate ligands, binding to gold(I) through the a nitrogen donor atom in the complexes $[(Ph_3P)AuL]$ where L = (**19**) or (**20**). Spectroscopic data for the new complexes have been presented [34].



(**19**)



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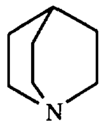

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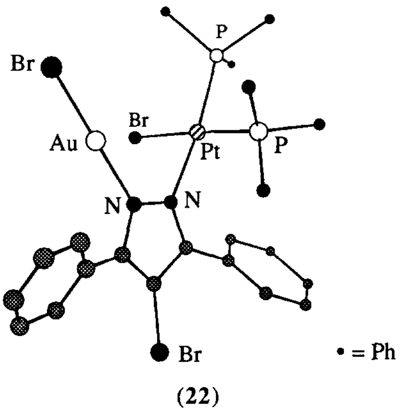


(**22**)

The secondary amd tertiary amines, piperidine (pip) and quinuclidine (**21**), react with $[(Ph_3P)Au](BF_4)$ in thf to give the complexes $[(Ph_3P)Au(pip)](BF_4)$ and $[(Ph_3P)Au(\mathbf{21})](BF_4)$ respectively. These are obtained in good yields and have been characterized by IR and NMR spectroscopies, mass spectrometry and elemental analysis. The crystal structure of

$[(Ph_3P)Au(\mathbf{21})](BF_4)$ has been elucidated. The cations are monomeric and the gold(I) centre is linearly coordinated. The Au-N bond distance of 2.11(1)Å is noted to be longer than in polyaurated ammonium salts studied by the same researchers (see section 4.4) [39].

The platinum(II) complex *cis*-$[Pt(PPh_3)_2Cl(3,5\text{-}Ph_2pz)]$ (Hpz = pyrazole) has been found to form adducts with group 11 metal halides. Amongst a series of new compounds prepared and characterized is the gold(I) complex (**22**) which contains the pyrazole ligand $[3,5\text{-}Ph_2\text{-}4\text{-}Brpz]^-$. A structural study of (**22**) confirms a linear coordination environment for the gold(I) centre with bond distances of Au-N = 2.02(1)Å and Au-Br = 2.351(3)Å. The Au---Pt separation is non-bonding at 3.425(3)Å [40].

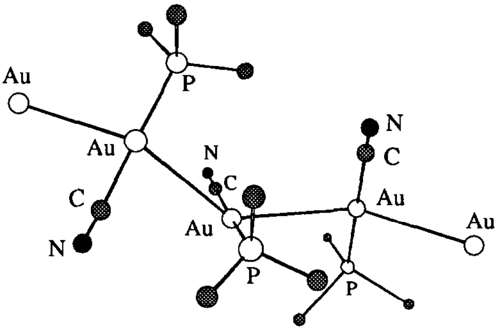
4.3.6 Complexes with phosphorus donor ligands

The chemistry of gold(I) phosphine compounds is always a dominant section of this annual survey, and 1992 in particular seems to have been an active year in the area. A significant quantity of structural data has revealed some interesting aspects of the bonding in the solid state of a range of multidentate phosphine gold(I) derivatives. Some of these systems are categorized under the heading of di- and tri-, and polynuclear complexes (section 4.4).

Neutral mononuclear systems that have received attention include $[(Cl_3P)AuCl]$ [7], $[(F_3P)AuCl]$ [41], $[(Me_3P)Au(CN)]$ [24], $[(^tBuF_2P)AuCl]$ [42], $[\{(Me_2N)PF_2\}AuCl]$ [42], $[\{(Et_2N)PF_2\}AuCl]$ [42], $[\{(2,5\text{-}Me_2C_6H_3)PF_2\}AuCl]$ [42], $[(\{^tBuC(O)\}PF_2)AuCl]$ [42], $[(Ph_2P(Se)CH_2PPh_2)AuCl]$ [43] and $[\{(4\text{-}Me_2NC_6H_4)_xPPh_{3-x}\}AuCl]$ (x = 1, 2 or 3) [44]. In addition are the complexes $[(Ph_3P)Au(OR)]$ and $[\{(c\text{-}C_6H_{11})_3P\}Au(OR)]$ (R = CH_2CF_3 or $CH(CF_3)_2$) [26], $[(Ph_3P)Au(S_2COEt)]$ [31], $[(Ph_3P)_nAu(S_2CPh)]$ (n = 1 or 2), [32], $[(Ph_3P)_nAu(S_2CC_6H_4\text{-}4\text{-}Me)]$ (n = 1 or 2) [32], $[(Ph_3P)_nAu(S_2CC_6H_4\text{-}2\text{-}Me)]$ (n = 1 or 2) [32], $[(Ph_3P)_2Au_{0.56}Cu_{0.44}(S_2CC_6H_4\text{-}4\text{-}Me)]$ [32], $[(Ph_3P)Au(\mathbf{15})]$ [34], $[(Ph_3P)Au(\mathbf{19})]$ [34] and $[(Ph_3P)Au(\mathbf{20})]$ [34], all of which have been discussed in appropriate previous sections.

The crystal structure of $[(Cl_3P)AuCl]$ has been redetermined (at –95°C), and thus provides more precise data than those previously available from the results of a 1962 X-ray analysis. Bond distances to the linear gold(I) centre are Au-P = 2.198(2)Å and Au-Cl = 2.279(2)Å. There are relatively short intermolecular Au----Au contacts which lead to the formation of chains in the solid state lattice [7]. The related complex $[(F_3P)AuCl]$ has been prepared from the reaction of $[Au_2Cl_6]$ and PF_3 in $SOCl_2$. Both PF_3 and CO are good π-acids, but results indicate that $[(F_3P)AuCl]$ is more stable than its carbonyl analogue. The vapour pressure of $[(F_3P)AuCl]$ is ≈ 10^{-4} mbar at room temperature. $[(F_3P)AuCl]$ has been characterized by IR and NMR spectroscopies ($\delta\ ^{31}P = +112.1$ w.r.t. H_3PO_4; quartet, J_{PF}= 1361 Hz) and by mass spectrometry [41]. The ligands (L) $^tBuF_2P$, $(Me_2N)PF_2$, $(Et_2N)PF_2$, $(2,5\text{-}Me_2C_6H_3)PF_2$ and $\{^tBuC(O)\}PF_2$ react with [(tht)AuCl] to give the gold(I) complexes [LAuCl]. A reaction in the same series is that of $F_2POCH_2CH_2OPF_2$ with [(tht)AuCl]. The products have been characterized spectroscopically and the structures of $[\{(Me_2N)PF_2\}AuCl]$ and $[\{(2,5\text{-}Me_2C_6H_3)PF_2\}AuCl]$ have been investigated by X-ray diffraction methods. Once again there is evidence for intermolecular interactions through Au----Au contacts (*e.g.* Au---Au = 3.34Å in $[\{(Me_2N)PF_2\}AuCl]$) [42].

The synthesis and crystal structure of [(Me$_3$P)Au(CN)] have been reported. In the solid state, each gold(I) centre is linearly coordinated within a molecule; stacking of molecules along the crystallographic *a*-axis leads to the formation of an infinite zig-zag array (**23**) with adjacent molecules being staggered with respect to one another [24].



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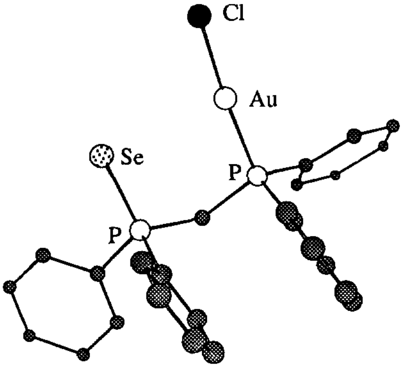

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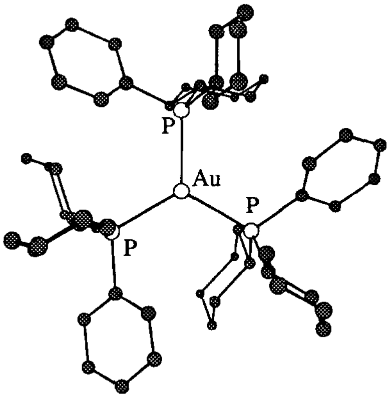

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When the ligand Ph$_2$P(Se)CH$_2$PPh$_2$ bonds to gold(I) in the complex [(Ph$_2$P(Se)CH$_2$PPh$_2$)AuCl] (**24**), the preference is for *P*- rather than *Se*-coordination. The structure of this complex has been confirmed by X-ray crystallography [43].

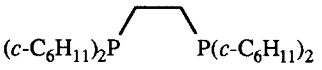
In a study which focuses on a novel hexagold species (see section 4.5), the crystal structures of several of the precursor gold(I) mononuclear complexes are included, namely [{(4-Me$_2$NC$_6$H$_4$)$_x$PPh$_{3-x}$}AuCl] (x = 1, 2 or 3) [44].

Cationic gold(I) species with Au-P bonds include [(Ph$_3$P)Au(pip)]$^+$ and [(Ph$_3$P)Au(**21**)]$^+$ (pip = piperidine) which were described in section 4.3.5 [39]. Here the gold(I) centres were linearly coordinated as is also the case in the cation [Au(PMePh$_2$)$_2$]$^+$ [45]. This cation formed rather unexpectedly as a result of a ligand redistribution in the reaction of [(MePh$_2$P)AuCl] with the ferraborane [PPN][HFe$_4$(CO)$_{12}$BH]. Instead of introducing a gold(I) phosphine fragment to the cluster, Au-P bond cleavage occurred to generate a fused cluster system $[\{HFe_4(CO)_{12}BH\}_2Au]^-$ with $[Au(PMePh_2)_2]^+$ as the counter-ion. Geometries around the gold(I) centre in cations are varied and examples of linear, trigonal planar and tetrahedral AuP_n (n = 2, 3 or 4) environments are all detailed in the 1992 literature. The linear geometry is shown in, for example, $[Au(PMePh_2)_2]^+$ [45]. The trigonal planar geometry features in $[Au\{PPh(c\text{-}C_6H_{11})_2\}_3]^+$ (**25**), the perchlorate salt of which has been crystallographically studied [46]. A rare example of tetrahedral gold(I) is seen in the cation $[Au(cis\text{-}Ph_2PCH{=}CHPPh_2)_2]^+$. This cation (along with its copper(I) analogue) has been isolated as the hexafluorophosphate salt; it exhibits cytotoxic and antitumour activities. $[Au(cis\text{-}Ph_2PCH{=}CHPPh_2)_2](PF_6)$ has been studied by solid state ^{31}P cross-polariztion MAS NMR spectroscopy as well as by crystallography. The restriction imposed by the bite of the chelating ligand causes distortion from a true tetrahedral geometry; angles P-Au-P within the chelate rings are 86.87(5)° and 86.90(5)°. The Au-P bond distances lie in the range 2.377(2) to 2.388(2)Å [47].

The reaction of $[PPN][Au(acac)_2]$ (see section 4.3.3) with Ph_2PH leads to the formation of the polymeric complex $[Au(PPh_2)]_n$. This reaction is one of a series of preparations which utilize $[Au(acac)_2]^-$ as the source of gold(I) [28].

Didentate phosphines are of course well established as a means of generating such compounds as A-frame complexes. In these, the metal atoms are held in close proximity and the formation of a metal-metal bond, or at least a weak interaction, is feasible. An example is seen in $[Au_2(dmpm)_2]^{2+}$. The structure of the hexafluorophosphate salt of $[Au_2(dmpm)_2]^{2+}$ has been determined as part of a detailed study of silver and gold dimers which includes a discussion of the relationship between metal-metal force constants and internuclear separations. In $[Au_2(dmpm)_2]^{2+}$, each gold(I) centre is linear (∠P-Au-P = 178.3(1)°) and the dmpm ligands hold the two gold atoms within a distance that is less than the sum of the van der Waals radii (Au----Au = 3.045(1)Å). In the unit cell, the $[Au_2(dmpm)_2]^{2+}$ dications are stacked along the crystallographic *b*-axis but do not exhibit any close inter-cation contacts. The solid state low frequency (40-400 cm^{-1}) vibrational spectra of salts of $[Au_2(dmpm)_2]^{2+}$ and its silver analogue have been analysed. For $[Au_2(dmpm)_2](PF_6)_2$ and $[Au_2(dmpm)_2]Cl_2$ ν_{AuAu} = 68 and 71 cm^{-1}, respectively and the force constant, F_{AuAu} = 0.27 and 0.29 mdyn $Å^{-1}$ respectively [48].

The structure of the digold complex $[(\mathbf{26})Au_2Br_x(CN)_y]$ $(x + y = 2)$ has been determined and shows disordering in the bromide adn cyanide groups. The population of the sites are found to be: Br on Au(1) = 0.532(5) and Br on Au(2) = 0.628(5). This gives a formulation with x:y = 1.16:0.84 [25]. The tripodal ligand (**27**) reacts with $[(Me_2S)AuCl]$ to yield $[(\mathbf{27})Au_3Cl_3]$ which has been characterized by ^1H, ^{13}C and ^{31}P NMR and ^{197}Au Mössbauer spectroscopies as well as X-ray crystallography. In the solid state, the complex adopts a layer-structure and is not a discrete monomer. Of the three phosphorus donor atoms in a molecule of (**27**), two coordinate to two gold(I) centres which then associate together (Au---Au = 3.077(2)Å). These pairs of gold atoms are aligned in chains through the crystal lattice. The third phosphorus donor atom coordinates to a third gold(I) centre which is, in turn, associated with a similar gold centre in another chain (inter-chain Au----Au = 3.179Å). In this way, chains are cross-linked to form layers of $[(\mathbf{27})Au_3Cl_3]$ molecules [49]. Ligand (**28**) is potentially tetradentate. It reacts with $[(Me_2S)AuCl]$ to give $[(\mathbf{28})Au_4Cl_4]$, the crystal structure of which has been determined. Of the four gold(I) centres per molecule, two are in close contact but steric interactions appear to restrict further aggregation. Changes in ligand conformation upon complex formation have been discussed [50].



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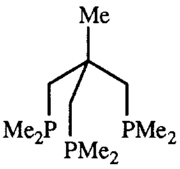

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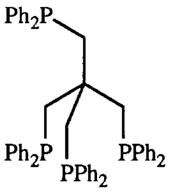
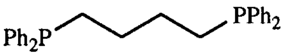


(28)

The reactions of dppb (**29**) and its pentane analogue (**30**) with [{$(HOCH_2CH_2)_2S$}AuCl] produce the complexes [(**29**)Au_2Cl_2] and [(**30**)Au_2Cl_2] respectively. The solid state structures, determined by single crystal X-ray diffraction methods, of these two derivatives of didentate phosphines show some interesting differences. In both cases, the compounds crystallize with dichloromethane solvate. In [(**30**)Au_2Cl_2].CH_2Cl_2, the crystal lattice is composed of monomers which are associated together to form chains (intermolecular Au-----Au = 3.323Å). In contrast, the structure of [(**29**)Au_2Cl_2].CH_2Cl_2 shows isolated monomer units and this is attributed to the particular packing of the solvate molecules [51].



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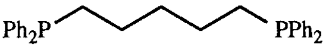
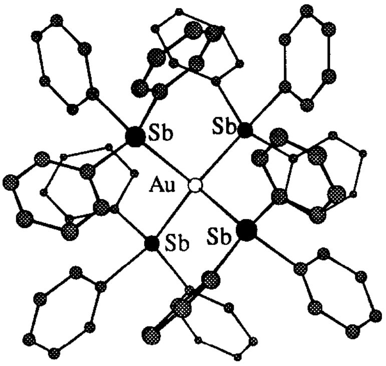


(30)

4.3.7 Complexes with arsenic and antimony donor ligands

The results of extended Hückel molecular orbital calculations have been used to provide some insight into similarlties and differences between the bonding around the gold(I) centre in the carbaborane derivative 1-$MeOCH_2$-2-(Ph_3AsAu)-1,2-*closo*-$C_2B_{10}H_{10}$ and the more simple complex [(Ph_3As)AuMe]. This study forms part of a wider investigation of complexes which are formed in the reactions of LAuCl (L = PPh_3, P(*o*-tolyl)$_3$, P(*c*-hexyl)$_3$, PEt_3, $AsPh_3$) with Li[1-R-1,2-*closo*-$C_2B_{10}H_{10}$] (R = Ph or CH_2OMe) [52].

The crystal structure of [$(Ph_3Sb)_4Au$](ClO_4) has been elucidated. In the cation (**31**), the gold(I) centre is tetrahedrally sited; the Au and one of the Sb atoms lie on a crystallographic 3-fold axis. Selected bond parameters for (**31**) are Au-Sb = 2.658(2) and 2.656(2)Å and ∠Sb-Au-Sb = 108.8(1) and 110.1(1)° [53]. Compare this case to the distortions caused by the chelating nature of the ligands in [Au(*cis*-$Ph_2PCH{=}CHPPh_2$)$_2$]$^+$ discussed in the previous section [47].



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4.3.8 Gold(I)-containing drugs

The papers cited in this section are meant to be exemplary of the field of the inorganic chemistry of gold(I)-containing drugs and are not intended to provide the reader with a comprehensive survey of work published in 1992.

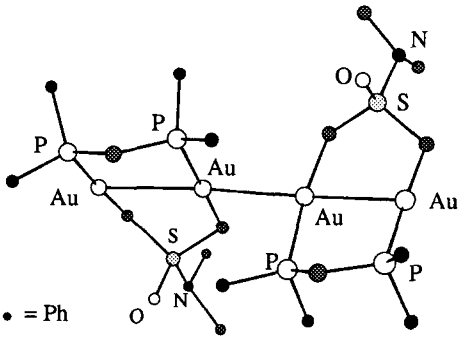
A ^{13}C NMR spectroscopic study has been carried out of the reaction of aurothioglucose (AuTg) with ^{13}C labelled and unlabelled cyanide ion. It was found that labelling was required in order to detect the species formed in the reaction. When the AuTg : $^{13}CN^-$ ratio reached 1:2, the only observed product is $[Au(CN)_2]^-$ [54]. Evidence has been provided for structural changes in bovine serum albumin (BSA) which accompany the binding of the latter to antiarthritic drugs; release of cys from the protein occurs during the complexation. The particular reactions studied were those between the fatty acid-free BSA and aurofin, Et_3PAuTg and $Et_3PAuSATg$ (HSATg = 2,3,4,6-tetraacetato-1-thio-β-D-glucopyranose). The loss of cys is a significant finding and details concerning this observation are discussed [55]. The effects of aurofin, aurothiomalate, aurothioglucose and Et_3PAuTg on the growth of *Pseudomonas putida* have been assessed [56].

4.4 DI-, TRI- AND POLYNUCLEAR COMPLEXES EXCLUDING CLUSTERS

For the purposes of this review, a cluster is defined as containing a polyhedral skeleton with four or more metal atoms.

A theoretical paper has addressed the question of relativistic effects in stabilizing Au_x-systems. Calculations at the Hartree-Fock and Møller-Plessert levels have probed the bonding in Au_2 and in $[Au_2(PH_3)_2]$, the latter being a model for the known complex $[Au_2(PPh_3)_2]$. The role of the phosphine ligands is a point of particular interest. The optimized structure of $[Au_2(PH_3)_2]$ turns out to be linear and it is noted that the calculated Au-P distances are in excess of those observed in related experimentally studied systems. Comparisons are made between calculated data for $[Au_2(PH_3)_2]$ and experimental data for $[Au_2(PPh_3)_2]$ [57].

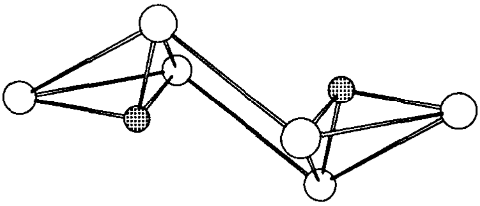
Differing degrees of intramolecular association between gold centres in a range of complexes have already been noted, for example in the complexes $[Au_2\{SSeC{=}C(CN)_2\}_2]^{2+}$ **(14)** [33], $[(Ph_3P)_2Au_2Se(C_6F_4\text{-}4\text{-}Cl)]^+$ **(18)** [37], $[Au_2Se_5]^{2-}$, $[Au_2Se_6]^{2-}$ and $[Au_2Te_4]^{2-}$ [38], $[Au_2(dmpm)_2]^{2+}$ [48], [(**27**)Au_3Cl_3] [49], and [(**28**)Au_4Cl_4] [50]. Examples of intermolecular Au---Au contacts in solid state structures have also been described, for example in $[(Cl_3P)AuCl]$ [7], $[(Me_3P)Au(CN)]$ [24], $[\{(Me_2N)PF_2\}AuCl]$ [42], $[\{(2,5\text{-}Me_2C_6H_3)PF_2\}AuCl]$ [42], [(**27**)Au_3Cl_3] [49] and [(**30**)Au_2Cl_2]$.CH_2Cl_2$ [51]. In the luminescent complex $[Au_2(\mu\text{-dppm})\{\mu\text{-}(CH_2)_2S(O)(NMe_2)\}]^+$, there is an interesting pairing of the cations such that the intermolecular Au---Au distance is *shorter* than the intramolecular separation. This gives rise to the dimeric structure (**32**). This complex and the related tetranuclear cation $[Au_4(\mu\text{-dppm})(\mu_3\text{-}Ph_2PCHPPh_2)\{\mu\text{-}(CH_2)_2S(O)(NMe_2)\}_2]^+$ have been prepared by phase transfer catalytic methods [58].



(32)

Related to the tripodal ligand (**27**) is $MeC(CH_2PPh_2)_3$ (triphos). The iridium complexes $[(triphos)Ir(H)(C_2H_4)]$ and $[(triphos)Ir(H)_2Et]$ react with $[(Ph_3P)Au(thf)]^+$ in the presence of ethene to give the heterometallic complex cation $[(triphos)Ir(H)(C_2H_4)(AuPPh_3)_2]^+$ which has been isolated as the hexafluorophosphate salt. Equal moles of $[(triphos)Ir(H)(C_2H_4)(AuPPh_3)_2]^+$ and $[(Ph_3P)AuCl]$ react to give $[(triphos)Ir(Cl)(\mu\text{-}H)(AuPPh_3)_2]^+$. This cation and its arsine analogue have also been synthesized by direct routes. A detailed NMR spectroscopic study of the new complexes has been carried out and the X-ray crystal structure of $[(triphos)Ir(Cl)(\mu\text{-}H)(AuPPh_3)_2](PF_6)$ has been determined. The two gold atoms are adjacent to each other, forming part of a triangular Au_2Ir-framework [59].

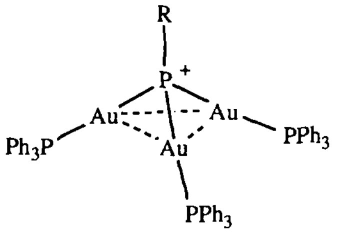
The trigold oxonium ion $[(Ph_3PAu)_3O]^+$ is a well known species and finds application in a range of cluster expansion reactions. A re-determination of the structure of $[(Ph_3PAu)_3O](BF_4)$, this time in the monoclinic form, has yielded some interesting results: the Au_3O-units are associated in pairs, (**33**), through Au---Au interactions. The reactions of $[(Ph_3PAu)_3O]^+$ with Ph_2NNH_2, Me_2NNH_2 and $Ph_2NNH_2.HCl$ have been studied. With the hydrazines, water is eliminated and $[(Ph_3PAu)_3NNR_2]^+$ (R = Me or Ph) is formed, whilst with $Ph_2NNH_2.HCl$, the products are $[(Ph_3PAu)_2HNNPh_2]^+$, H_2O and $[(Ph_3P)AuCl]$. Hydrazine itself reacts with $[(Ph_3PAu)_3O]^+$ to give the hexagold product $[(Ph_3PAu)_3NN(AuPPh_3)_3]^{2+}$. All the hydrazido complexes are stable in the solid state but in thf or dichloromethane solutions, the complexes $[(Ph_3PAu)_3NNR_2]^+$ (R = Me or Ph) decompose to yield $[(Ph_3PAu)_6]^{2+}$. Structures have been proposed for the new complexes and in the cases of $[(Ph_3PAu)_3NNPh_2]^+$ and $[(Ph_3PAu)_2HNNPh_2]^+$ have been confirmed by X-ray crystallographic results [60].



(33)

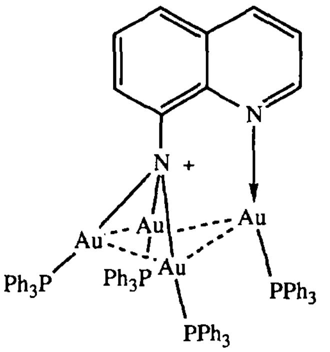
In section 4.3.6, we considered the solid state structure of $[(\mathbf{27})Au_3Cl_3]$ in which (**27**) is a tripodal ligand [49]. The three gold atoms were associated together in a [2+1] fashion and the net result in the crystal lattice was a layer structure. The ligand $HC(PPh_2)_3$ is also tripodal in nature but has shorter chain lengths in each 'arm' than does (**27**). The gold(I) complex $[(Me_2S)AuCl]$ reacts with $HC(PPh_2)_3$ to give $[HC(PPh_2AuCl)_3]$ and this can be converted into the corresponding tribromo-, triiodo- and trimethyl-derivatives through reactions with HBr, KI and MeLi respectively. $[HC(PPh_2AuCl)_3]$ has been investigated by Mössbauer spectroscopy and by single crystal X-ray diffraction. In contrast to the situation in the solid state for $[(\mathbf{27})Au_3Cl_3]$, the structure of $[HC(PPh_2AuCl)_3]$ features a triangular array of gold atoms with the three chlorine atoms held in a *cis* arrangement. Crystals were grown from CH_2Cl_2 at room temperature yielding a cubic form and at –30°C to give a monoclinic form. The structure of each crystal form has been determined and the molecular arrangement is the same in each; the Au---Au separations lie in the range 3.20–3.42Å [61].

The novel complex cation $[(2\text{-}MeC_6H_4)P(AuPPh_3)_3]^+$ (**34**) has been synthesized by using $(2\text{-}MeC_6H_4)PH_2$ as the source of the central phosphorus unit. The arsonium analogue has also been prepared. The tetrafluoroborate salt of (**34**) has been crystallographically characterized. The phosphonium centre is tetrahedrally sited and the Au---Au separations are quite long (3.639 to 3.709(1)Å). The reaction of $[(\mathbf{34})](BF_4)$ with $[AuPPh_3](BF_4)$ results in the formation of $[(2\text{-}MeC_6H_4)P(AuPPh_3)_4](BF_4)_2$ in high yield. The crystal structure of this salt has been determined; the dication consists of a square pyramidal PAu_4-core with a PPh_3 group associated with each gold(I) centre. The Au---Au separations are significantly shorter here (2.891 to 3.012(1)Å) than in cation (**34**) [62]. In related work, Schmidbauer *et al.* have also investigated some ammonium complexes, namely $[RN(AuPPh_3)_3]^+$ and $[RN(AuPPh_3)_4]^{2+}$ (**35**) in which R is defined in structure (**35**). The salt $[RN(AuPPh_3)_3](BF_4)$ has been prepared by reacting RNH_2 with $[(Ph_3PAu)_3O](BF_4)$ and the structure of $[RN(AuPPh_3)_3]^+$ resembles that of the phosphonium cation (**34**); the Au-N distances in $[RN(AuPPh_3)_3]^+$ are 2.071(3), 2.040(3) and 2.059(3)Å. Treatment of $[RN(AuPPh_3)_3](BF_4)$ with $[AuPPh_3](BF_4)$ leads to the complex $[(\mathbf{35})](BF_4)_2$. The $\{RN\}^{2-}$ unit bridges across the tetragold framework such that three gold atoms are within bonding contact of the ammonium centre (Au-N = 2.103(6), 2.101(5) and 2.074(6)Å) and one gold centre is bonded to the pyridine *N*-donor atom (Au-N = 2.115(6)Å). The Au---Au separations in the two ammonium cations fall in the range 2.940(1) to 3.207(1)Å [63]. This work has been extended to systems of the type $[(LAu)_6C]^{2+}$ (see section 4.5) [44].



R = 2-MeC_6H_4

(34)



(35)

4.5 SELECTED CLUSTERS

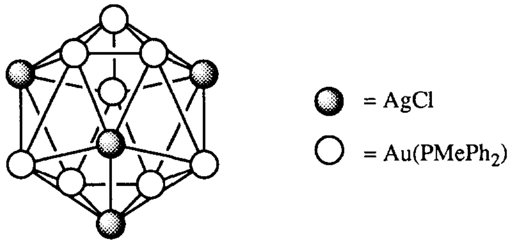
The majority of clusters in this section involve aggregates of gold atoms. One feature of note however, is the reaction of [LAuCl] (*e.g.* L = Me_2PhP or $MePh_2P$) with the cluster $[HFe_4(CO)_{12}BH]^-$. Usually, gold(I) phosphine halides are used as a source of the $\{AuL\}^+$ but in this example, Au-P bond cleavage occurs in conjunction with a ligand distribution to give the products $[\{HFe_4(CO)_{12}BH\}_2Au][AuL_2]$. The gold(I) centre acts as a point of fusion for the two cluster sub-units. Similar results are obtained with ruthenium cluster analogues to give $[\{HRu_4(CO)_{12}BH\}_2Au]^-$ [45]. In related work, the association of the $\{Au_2(dppf)\}^{2+}$ unit with tetraferra- and tetraruthenaborane clusters has been examined. In the case of the reaction of $[HRu_4(CO)_{12}BH]^-$ with $[(dppf)Au_2Cl_2]$, the $\{Au_2(dppf)\}^{2+}$ moiety can act either as a bridging unit in a single cluster or as a unit which links two sub-cluster units together. The products $[\{HRu_4(CO)_{12}BHAu\}_2(\mu\text{-}dppf)]$ and $[HRu_4(CO)_{12}BAu_2(dppf)]$ have been spectroscopically characterized and the X-ray crystal structure of the latter has been determined [64].

Members of the family of hexagold clusters $[(LAu)_6C]^{2+}$ (L = $(4\text{-}XC_6H_4)PPh_2$ with X = Cl, Br, Me, OMe, CO_2H or NMe_2, or $(4\text{-}Me_2NC_6H_4)_2PPh$ or $(4\text{-}Me_2NC_6H_4)_3P$) have been prepared and spectroscopically studied. The data are in accord with the six AuL^+ groups being arranged octahedrally around a central carbon atom [44].

The synthesis of the acetylide-containing cluster $[Au_3Ag_2(C_2Ph)_6]^-$ has been reported [65] and in further work by the same author, the trimetallic cluster $[AuAg_6Cu_6(C_2Ph)_{14}]^-$ is one of two similar systems studied [66].

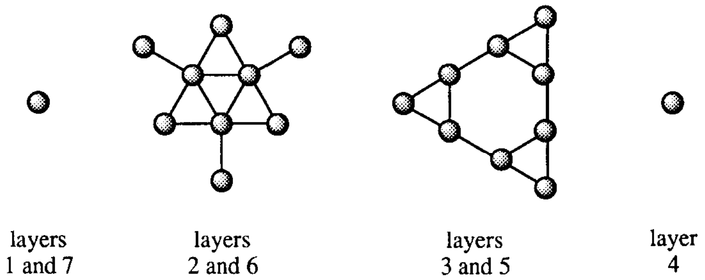
The reaction of four molar equivalents of $[(Ph_2MeP)AuCl]$ with $[Au_{11}(PMePh_2)_{10}]^{3+}$ leads to a silver-for-gold exchange as well as cluster expansion. The products are the cations $[Au_9Ag_4Cl_4(PMePh_2)_8]^+$ and $[Au(PMePh_2)_3]^+$ (in a ratio 1:2). The former cation has been isolated as the carbaborane salt $[Au_9Ag_4Cl_4(PMePh_2)_8][C_2B_9H_{12}]$ and has been structurally characterized.

The group 11 cluster cation features a centred icosahedral core, and the arrangement of the metal atoms in the Au_8Ag_4-skeleton is shown in structure (**36**). In solution, the ^{31}P NMR spectrum shows three signals with relative integrals of 4:2:2 and this pattern is consistent with the same structure as is seen in the solid state [67]. The reaction of the nitrate salt of $[Au_9(PPh_3)_8]^{3+}$ with three equivalents of $[Au(C_6F_5)_2]^-$ leads to the high-yield formation of the neutral complex $[Au_{10}(C_6F_5)_4(PPh_3)_5]$. A single crystal X-ray diffraction study of this compound reveals that the Au_{10}-cluster core has a toroidal geometry. The Au-Au contacts which involve the unique, central gold atom are, in most cases, shorter than Au-Au separations between peripheral gold atoms [68].



(**36**)

The large clusters $[Au_{13}Ag_{12}\{P(4\text{-}MeC_6H_4)_3\}_{10}Cl_8]^+$ [69] and $[Au_{39}(PPh_3)_{14}Cl_6]^{2+}$ [70] have been made and fully characterized. The former possesses a bi-icosahedral metal core, whilst the latter exhibits a 1:9:9:1:9:9:1 layered structure as defined in (**37**) such that a centred hexagonal *antiprism* forms the central unit of the metal stack.



(**37**)

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