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COORDINATION CHEMISTRY REVIEWS

10. Gold 1993

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CONTENTS

INTRODUCTION

This review surveys the coordination chemistry of gold published in 1993, and the format is similar to that of the 1992 review [1]. The literature has been searched by using *Current Contents* and the Cambridge Crystallographic Data Base, implemented through the ETH, Zürich [2]. Although not fully comprehensive, the article does give a representative coverage of new material; 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. Compared to previous years' reviews, 1993 sees a greater proportion of di- and multinuclear complexes, and with it, the difficulty

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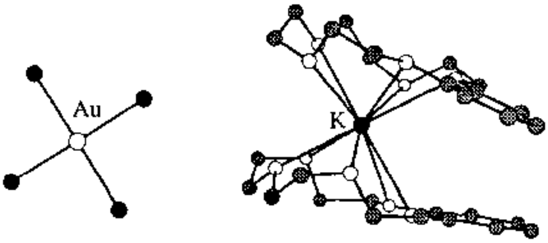
of assigning gold-gold bonding interactions. In sections 10.1 and 10.2, complexes of gold(III) and gold(I) are described, and several di- and multinuclear species are chosen for inclusion mainly on the grounds that there is (or appears to be) no direct Au----Au bonding. In section 10.3, we deal with complexes in which crystallographic data confirm that the gold centres are closer together; these include both homometallic and heterometallic A-frame species. A selected number of gold-containing clusters are described in the last section but transition metal clusters which contain peripheral gold(I) phosphine units have been omitted. Structural figures have been redrawn using atomic coordinates obtained from the Cambridge Crystallographic Data Base [2].

Newkome has reviewed the chemistry of pyridylphosphine ligands and this includes some gold(I) and heterometallic (gold-containing) complexes; extensive tabulation of data helps to make this a valuable source of information (188 references) [3].

10.1 GOLD(III)

10.1.1 Complexes with group 17 ligands

The structure of potassium bis(benzo-15-crown-5) tetrachloroaurate (1) has been determined and the lattice contains discrete $[AuCl_4]^-$ anions [4]. The square planar gold(III) complex $[Ph_3PAuBr_3]$ has also been crystallographically characterized [5], as has the tetrahydrothiophene (L) complex $[LAuCl_3]$ (2) [6]. The $[AuX_4]^-$ anions also appear in the complexes described in the next section [8].



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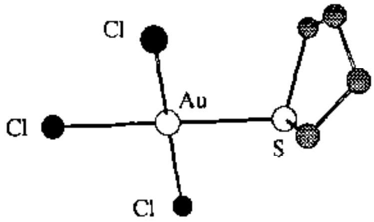


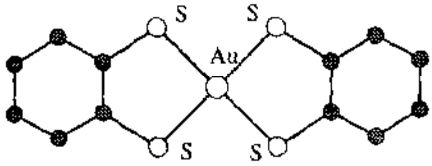
(2)

10.1.2 Complexes with group 16 ligands

The oxo-peroxo-compound $NaBa_4AuO_4(O_2)$ which was previously unknown has been prepared by oxidizing a barium-gold alloy with Na_2O_2 in a closed silver bomb. The formulation of the product has been confirmed by an X-ray diffraction study. The Ba^{2+} ions are in distorted square antiprismatic sites whilst the gold(III) centres are in the expected square planar environments [7].

The complexes $(MAuX_4).4(picH).2H_2O$ (M = Na and X = Cl; M = K and X = Br), $[NaAu(pic)_2X_2].2H_2O$ (X = Cl or I) and $(NaAuCl_4)Na(pic).(picH).2H_2O$ (Hpic = picolinic acid) have been synthesized. Infrared spectroscopy and conductivity measurements have been used to aid complex characterization, and an X-ray diffraction study of $(KAuBr_4).4(picH).2H_2O$ reveals that the compound is correctly formulated as $[K(picH)_2(H_2O)_2][AuBr_4].(picH)_2$. Data for the complexes $[NaAu(pic)_2X_2].2H_2O$ (X = Cl or I) are consistent with the presence of square planar gold(III) centres connected by bridging halide ligands and further interacting weakly in the axial sites with O-donors from the pic^- ligands [8].

Reactions between $[R_3PAuCl]$ (R = Et or Ph) and $1,2\text{-}C_6H_4(SH)_2$ or $1,3\text{-}C_6H_4(SH)_2$ in the presence of Et_3N in thf lead to the formation of the gold(I) complexes $[1,2\text{-}C_6H_4(SAuPR_3)_2]$ (R = Et or Ph) and $[1,3\text{-}C_6H_4(SAuPPh_3)_2]$. When R = Et and the dithiol ligand is $1,2\text{-}C_6H_4(SH)_2$, a byproduct of the reaction is $[Au(PEt_3)_2][Au(1,2\text{-}C_6H_4S_2)_2]$. The square planar gold(III) geometry in the anion (3) has been confirmed crystallographically [9]. The crystal structure of the salt trimethyltellurium bis(4,5-dimercapto-1,3-dithiole-2-thionato)aurate(III) has been determined. Structure (4) shows part of the unit cell and emphasizes the stacking of the gold(III) anions [10].



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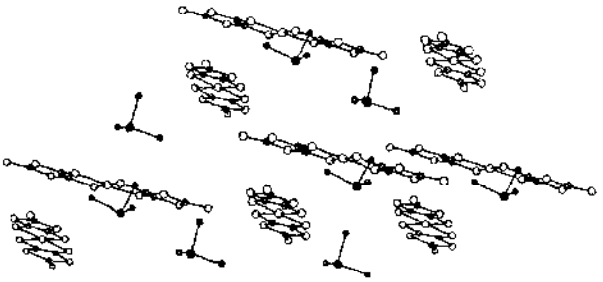
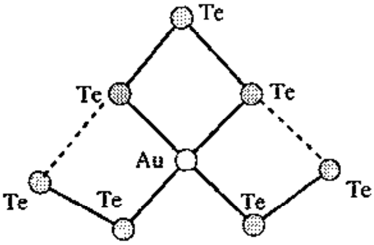


Part of the unit cell

(4)

The reaction between gold(I) cyanide and polytellurides in dmf in the presence of PEt_3 and NH_4Cl gives $[Et_4N]_3[AuTe_7]$ and formation of the anion $[AuTe_7]^{3-}$ (5) contrasts with products in reactions involving the other group 11 metals: $[Te_4M(\mu\text{-}Te_4)MTe_4]^{4-}$ (M = Ag or Cu). In anion (5) the gold(III) centre is square planar and the Au-Te distances lie in the range 2.638-2.664(2)Å with two longer separations (> 3Å). Gold-197 Mössbauer spectroscopy aids in the confirmation of the gold(III) oxidation state [11].



(5)

10.1.3 Complexes with group 15 ligands

The results of ^{197}Au Mössbauer spectroscopic studies of gold(III) and gold(I) complexes with *N*-containing heterocyclic ligands have been reported. Evidence is presented for the presence of two sites in each of the classes of compounds: for gold(III), $AuCl_3N\sim$ and $[AuCl_4]^-[HN\sim]^+$ and for gold(I), $AuClN\sim$ and $[AuCl_2]^-[HN\sim]^+$ where N~ represents the 3-N atom of the cyclic ligand. The ratio of the two sites in each case depends upon a balance of electronic and steric effects [12].

A series of luminescent organogold(III) diimine complexes of the type $[AuLR_2][ClO_4]$ (L = bpy and R = Mes; L = phen and R = CH_2SiMe_3) has been investigated. The synthetic route involves reactions between $[AuLCl_2][ClO_4]$ and MgRX, and both $[Au(bpy)Mes_2][ClO_4]$ and $[Au(phen)(CH_2SiMe_3)_2][ClO_4]$ have been crystallographically characterized. The cations are square planar as expected for gold(III). Their electronic spectra (samples in MeCN) are dominated by intense bands ≈300 nm ($\varepsilon > 10^4$ dm^3 mol^{-1} cm^{-1}) with weaker absorptions in the range 330-380 nm; the former have been assigned to intra-diimine $\pi(a_2) \rightarrow \pi^*(b_2)$ transition. Further discussion of the spectra and the properties of the compounds has been presented [13].

10.2 GOLD(I)

A paper of general importance presents a discussion of the advantages of solvated gold(I) in acetonitrile with a variety of non-coordinating anions as a starting material in gold(I) chemistry; a convenient synthesis is by halide-catalysed electrolysis [14].

10.2.1 Complexes with halide and pseudo-halide ligands

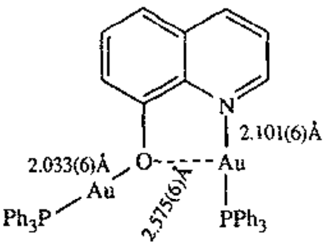
Reactions of $[Au(CN)]_n$ with chloride and bromide ions lead to the anions $[Au(CN)X]^-$, isolated as the $[PPN]^+$ (X = Cl) or $[PPh_4]^+$ (X = Br) salts. The chloride complex $[Au(CN)Cl]^-$ can be converted into the iodide by reaction with I^- ions. Triphenylphosphine reacts with $[Au(CN)X]^-$ (X = Cl or I) to give mixtures of $[Au(PPh_3)_2]X$, $[PPN][Au(CN)_2]$ and $[PPN]X$ [15]. Nitrogen-15 labelled cyanide has been used in reactions with gold(I) thiomalate and gold(I) thioglucose (at pH 7.4) and the system studied by ^{15}N NMR spectroscopy. Resonances at δ +265.94 and 260.3 are assigned to $[Au(C^{15}N)_2]^-$ and $[RSAu(C^{15}N)]^-$ respectively; a line width analysis allows estimates to be made of the approximate lifetimes of the $[RSAu(C^{15}N)]^-$ species [16]. The complex $[\{(Cy_2PCH_2CH_2PCy_2)Au\}_2(\mu\text{-}Cy_2PCH_2CH_2PCy_2)][Au(CN)_2]_2$ has been crystallographically characterized (see section 10.2.6) [17].

In a study of halotetrahydrothiophenegold(I) and halotetrahydroselenophenegold(I) complexes, it has been found that in the solid state $[Au(C_4H_8Se)I]$ exists in the ionic form $[Au(C_4H_8Se)_2][AuI_2]$. The structure consists of infinite zig-zag chains and is supported by Au--Au interactions (Au-Au = 2.987 and 3.001Å, ∠Au-Au-Au = 160.9 and 156.4°) (see also section 10.2.3) [18].

10.2.2 *Complexes with oxygen donor ligands*

The crystal structures of $[Au(NO_3)(PPh_3)]$ and $[Au(OAc)(PPh_3)]$ have been determined and in each complex, the gold(I) centre is in a linear environment [19].

The reaction of PhO^-K^+ with two equivalents of $[R_3PAu][BF_4]$ in thf leads to the salts $[PhO(AuPR_3)_2][BF_4]$ (R = Ph, Et or 2-MeC_6H_4) which have been characterized by NMR spectroscopy, mass spectrometry and elemental analyses. With potassium quinolin-8-olate, two equivalents of $[Ph_3PAu][BF_4]$ react to give the tetrafluoroborate salt of cation (6). In solution this is fluxional but at low temperature, the spectroscopic data are consistent with there being two inequivalent gold(I) centres. This has been confirmed in the solid state by an X-ray diffraction study; the Au---Au separation is well outside the bonding range (4.049(1)Å) [20].



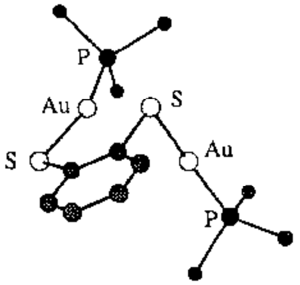
(6)

10.2.3 *Complexes with sulfur donor ligands*

A large number of gold(I) complexes containing linear S-Au-P units have been reported this year; they are described in this section rather than in section 10.2.6.

The reactions of $[Ph_3PAuCl]$ with PhSH or the hindered thiols $(2,4,6\text{-}R_3C_6H_2)SH$ (R = Me, Et or ^iPr) take place in the presence of triethylamine to give the complexes $[Ph_3PAuSR']$ (R' = Ph or $2,4,6\text{-}R_3C_6H_2$). All the products have been crystallographically characterized and all possess linear S-Au-P coordination spheres. The hindered thiolate complexes are monomeric whereas

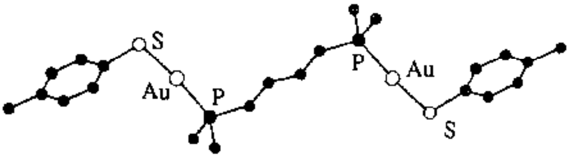
[$Ph_3PAuSPh$] associates in the solid state with an Au-Au separation of 3.135(5)Å. Mossbauer spectroscopic data for the products are discussed [21]. The compound [$Ph_3PAuSC_6Cl_5$] has been prepared from [$(Ph_3PAu)_3O$][BF_4] in a thf solution containing potassium carbonate and C_6Cl_5SH. Structural data confirm a linear gold(I) centre (∠S-Au-P = 171.01(5)°); bond lengths are Au-S = 2.253(1) and Au-P = 2.303(1)Å [22]. Reactions between [R_3PAuCl] (R = Et or Ph) and 1,2-$C_6H_4(SH)_2$ or 1,3-$C_6H_4(SH)_2$ in thf in the presence of Et_3N yield [1,2-$C_6H_4(SAuPR_3)_2$] (R = Et or Ph) or [1,3-$C_6H_4(SAuPPh_3)_2$] respectively. When R = Et and the dithiol ligand is 1,2-$C_6H_4(SH)_2$, [$Au(PEt_3)_2$][Au(1,2-$C_6H_4S_2)_2$] is also formed (see section 10.1.2). The new complexes have been characterized by NMR spectroscopy and by an X-ray diffraction study of [1,2-$C_6H_4(SAuPPh_3)_2$] (7). In (7), the S-Au-P bond angles at the two gold(I) centres are 175.2(1) and 159.5(1)° and some degree of Au-Au interaction is indicated by the distance of 3.145(1)Å [9].



Only ipso-C atoms of Ph groups are shown.
(7)

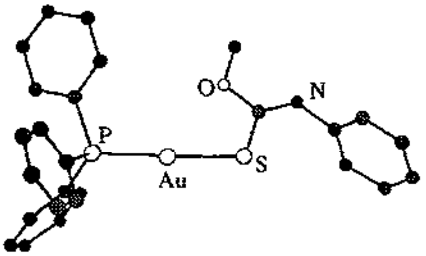
The reactions of the lead(II) thiolates $Pb(SR)_2$ (R = Et, Ph, CH_2Ph, C_6F_5, Mes, ^iPr or ^tBu) with [Ph_3PAuCl] produce complexes of the type [Ph_3PAuSR] in good yield with the elimination of $PbCl_2$. Infrared and multinuclear NMR spectroscopies and mass spectrometry have been used to characterize these compounds [23].

Members of a series of digold compounds have been prepared in which bis(diphosphino)alkane ligands bridge between two {$Au(SC_6H_4$-4-Me)} groups. For the dppb complex (8), crystallographic data confirm that the gold units are remote from each other; similar complexes have been produced in which the bridging ligand is dppm, dppe and dppp. Cyclic species of the general type [$Au_2\{Ph_2P(CH_2)_nPPh_2\}\{S(CH_2)_3S\}$] (n = 2, 3, 4 or 5) have also been formed.



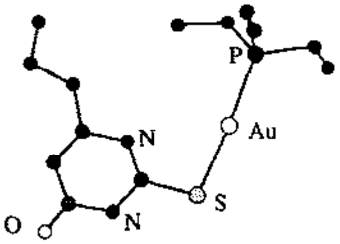
Only ipso-C atoms of Ph groups are shown.
(8)

Electronic and ^1H and ^{31}P NMR spectra have been recorded, and the UV-VIS spectroscopic properties have been discussed in terms of the chain lengths of the ligands. The solution dynamic behaviour of $[Au_2(SC_6H_4\text{-}4\text{-}Me)_2(\mu\text{-}dppm)]$, $[Au_2(dppe)\{S(CH_2)_3S\}]$ and $[Au_2(dppp')\{S(CH_2)_3S\}]$ (dppp' = $Ph_2P(CH_2)_5PPh_2$ has been observed by using VT NMR spectroscopy [24].



(9)

A set of related structural studies has been carried out on the complexes $[R_3PAuSC(S)OCy]$ (R = Et, Ph or Cy) [25], $[Ph_3PAuSC(S)OPr]$ [26] and $[Cy_3PAuSC(S)OR]$ (R = Et, ^{n}Pr or ^{i}Pr) [27], and a further report deals with the preparation and spectroscopic characterizations of the compounds $[R_3PAuSC(NPh)OR']$ (R = Et, Ph or Cy; R' = Me, Et, ^{n}Pr, ^{i}Pr or Cy). The solid state structure of $[Ph_3PAuSC(NPh)OMe]$ (**9**) has been elucidated; the angle P-Au-S is 177.7(1)° and the Au-S and Au-P bond distances are 2.301(1) and 2.258(1)Å respectively [28]. Another related species is the complex $[Et_3PAuL]$ (**10**) where HL = 6-^{n}propyl-2-thiouracil, the structure of which has been confirmed by X-ray diffraction methods [29]. Pyridine-2-thionate and pyrimidine-2-thionate gold(I) complexes of the general type $[R_3PAuL]$ (R = Et, Ph or Cy) have been synthesized and characterized by IR and ^{1}H and ^{13}C NMR spectroscopies and mass spectrometry. The mononuclear nature of the complexes and the linear gold(I) coordination environment have been confirmed crystallographically for the triphenylphosphine complexes. In $[Ph_3PAuL]$ (**11**) (HL = pyridine-2-thione), ∠P-Au-S = 177.9(1)° and the distances Au-S and Au-P are 2.297(2) and 2.258(1)Å, whilst in $[Ph_3PAuL]$ (HL = pyrimidine-2-thione) ∠P-Au-S = 174.7(1)° and Au-S and Au-P = 2.310(3) and 2.253(2)Å [30].



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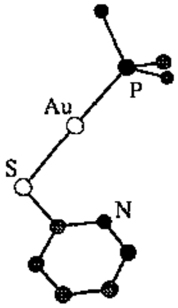
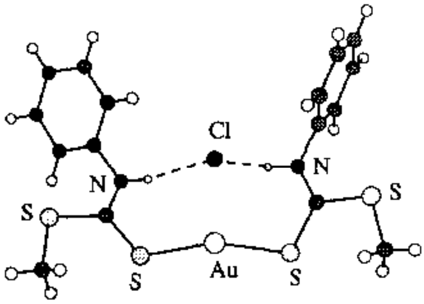


Only ipso-C atoms of Ph groups are shown

(11)

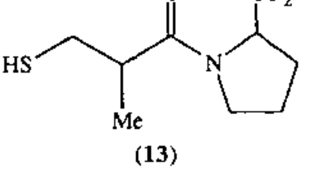
The reaction between chloroauric acid and PhNHC(S)SMe yields the gold(I) complex $[Au\{PhNHC(S)SMe\}_2Cl]$ (**12**). The solid state structure has been confirmed crystallographically; the gold(I) centre is close to being linear (∠S-Au-S =158.2(1)°) but the chloride ion is hydrogen bonded between the two arms of the two ligands and lies 3.218(2)Å away from the gold atom. The Au-S bond lengths are 2.291(1) and 2.300(2)Å [31].



(12)

An investigation of halotetrahydrothiophenegold(I) and halotetrahydroselenophenegold(I) complexes includes [Au(C_4H_8S)Cl], [Au(C_4H_8S)Br] and [Au(C_4H_8Se)I]. Whilst in the solid state the latter exists in the ionic form [Au(C_4H_8Se)$_2$][AuI_2] (see section 10.2.3), the thiophene complexes are monomeric and isostructural. The linear gold(I) coordination sphere is as expected, and the monomers are stacked in a staggered conformation to produce an infinite array supported by Au---Au interactions. The Au-Au distances in the chains of metal atoms are 3.324Å (chloride complex) and 3.353Å (bromide complex) [18].

The interaction of gold(I) thiomalate [AuX], and 2-thiouracil, L, in aqueous solution has been investigated by ^{13}C NMR spectroscopy. At a 1:1 ratio of [AuX]:L, the 2-thiouracil is involved in a slow exchange process but at higher concentrations, a fast exchange process is observed. However, no free X^- is seen in the ^{13}C NMR spectrum. When L-cysteine and cyanide ion are added to a 1:3 mixture of [AuX] and L, the cysteine does not replace the thiomalate ligand, but the cyanide ion coordinates to give $[Au(CN)_2]^-$ releasing both L and X^- [32]. Exchange reactions between the complex [AuL] [HL = captopril (**13**)] and cyanide and thiomalate ions have similarly been studied using ^{13}C NMR spectroscopy. There is evidence that [AuL] forms a high molecular mass polymeric species. Both CN^- and thiomalate ions bind to the [AuL] complex, and the cyanide ion is the more tightly coordinated. Use has been made of labelled $[^{13}CN]^-$ to illustrate the formation of $[LAu(^{13}CN)]^-$ — there are two isomers arising from either a *trans*- or *cis*-arrangement (with respect to the amide bond in HL) and in addition, $[Au(^{13}CN)_2]^-$ forms. It appears that [(*cis*-L)Au(^{13}CN)]$^-$ is more stable than the *trans*-analogue [33].



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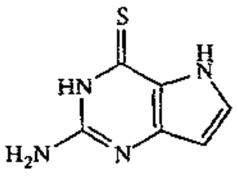

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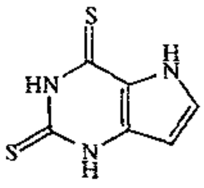

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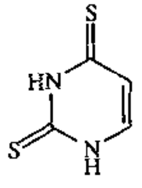

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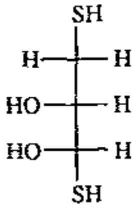
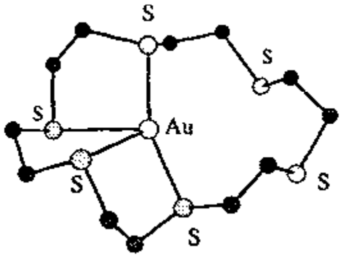


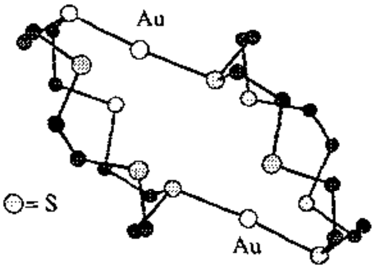
(17)

Complexes of the type $[R_3PAu(HL)]$ and $[R_3PAu(\mu\text{-}L)AuPR_3]$ (R = Et or Ph) where H_2L is one of the ligands (**14**)-(**17**) have been prepared and characterized by use of elemental analyses and ^1H, ^{13}C and ^{31}P NMR spectroscopies. It is proposed that in $[R_3PAu(HL)]$, the ligands are *S*-bonded but act as *S,N*-bridging ligands in $[R_3PAu(\mu\text{-}L)AuPR_3]$ when H_2L is one of (**14**)-(**16**) and as an *S,S'*-bridge when H_2L = (**17**). The authors have discussed the potential of these complexes to function as anti-tumour drugs [34].

A study of complex formation between macrocyclic thioether ligands and gold in its three oxidation states has illustrated two contrasting modes of coordination to gold(I) centres. With 1,4,7,10,13,16-hexathiacyclooctadecane, gold(I) forms a monomeric species (**18**) (isolated as the $[PF_6]^-$ salt) in which the gold centre is in a distorted tetrahedral environment. When the ligand is 1,4,7,10,13-pentathiacyclopentadecane, the dinuclear complex dication (**19**) (isolated as the $[B(C_6F_5)_4]^-$ salt) is produced and here each gold(I) centre is in the normal linear geometry [35].



(18)

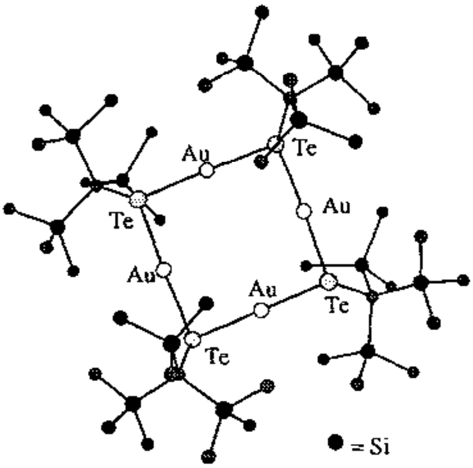


(19)

The complex $[Au_4\{SC(SiMe_3)_3\}_4]$ possesses a cyclic array and is discussed along with Se and Te analogues below [36].

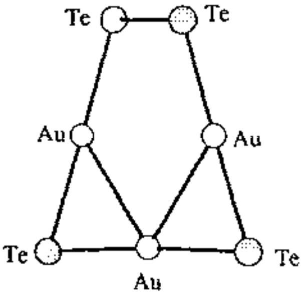
10.2.4 Complexes with selenium and tellurium donor ligands

The reactions of Li(ER) [E = S, Se or Te; R = $C(SiMe_3)_3$, $Si(SiMe_3)_3$ or $Ge(SiMe_3)_3$] with [(tht)AuCl] lead to the formation of the gold(I) complexes [Au(ER)]. Related to these are the compounds $[Ph_3PAu(ER)]$ which form when Li(ER) is treated with $[Ph_3PAuCl]$. In the solid state, aggregation of the [Au(ER)] complexes is observed with the formation of the tetramers $[Au_4\{SC(SiMe_3)_3\}_4]$ and $[Au_4\{TeC(SiMe_3)_3\}_4]$ (**20**). In contrast, cyclization is prevented by the presence of the phosphine ligand in the second group of compounds, but a crystal structure of the complex $[Ph_3PAu\{TeC(SiMe_3)_3\}]$ confirms that there is weak association between pairs of molecules via Au----Au interactions [36].



(20)

The gold(III) anion $[AuTe_7]^{3-}$ (**5**) was described in section 10.1.2, and a related species is the anion $[Au_3Te_4]^{3-}$ (**21**) in which the gold centres are formally in an oxidation state of +1. This anion is prepared by the controlled cathodic dissolution of gold-tellurium alloys (i.e. the $AuTe_2$ electrode) and the $[Bu_4N]^+$ salt has been isolated; the crystal structure of $[Bu_4N]_3[Au_3Te_4]$ has been determined. Note however that the course of the reaction is cation-dependent and when the counter-ion is $[Ph_4P]^+$, the product is $[Ph_4P]_3[Au_2Te_4]$. The methodology should find a wider application [37].

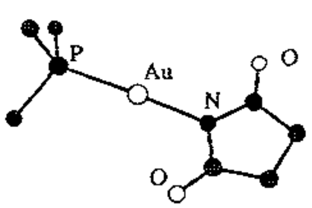


(21)

10.2.5 *Complexes with nitrogen donor ligands*

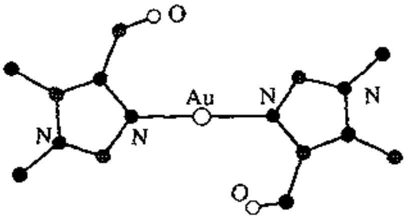
Two gold(I) complexes containing Au-N coordination have already been described: complex (**6**) [20] and the complexes $[R_3PAu(\mu\text{-}L)AuPR_3]$ where H_2L is one of ligands (**14**)-(**16**) [34].

The synthesis and full characterization of the succinimide (L^-) complex $[Ph_3PAuL]$ (22) have been described. This compound reacts with hydrated praseodymium(III) nitrate in MeOH to yield a novel polymeric macrocyclic species of formula $[Pr(Ph_3PAuL)_2(NO_3)_3]_n$. Structural analysis of this compound reveals that the praseodymium centres are linked by succinimide ligands to generate sheets of fused 24-membered Pr_4L_4-rings. The gold(I) phosphine units appear to play a vital role in the assembly of this system since attempts to form such macrocyclic arrays with the succinimide ligand alone (rather than its gold(I) complex) have been unsuccessful [38]. The crystal structure of the complex bis(4-hydroxymethyl-1,5-dimethylimidazole-*N*)gold(I) chloride (23) has been reported [39].



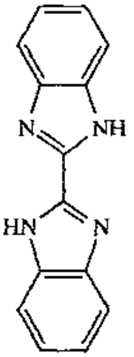
Only ipso-C atoms of Ph groups are shown.

(22)



(23)

The dibenzimidazole ligand (24), H_2L, has been incorporated into two gold(I) complexes. The first is $[Ph_3PAu(\mu\text{-}L)AuPPh_3]$ and in this, one *N*-donor atom of each ring is coordinated to a gold(I) centre such that the two $AuPPh_3$ units are mutually *trans* respect to the ligand; the gold centres are thus remote from each other. The second complex is $[(Ph_3PAu)_2(\mu\text{-}L)(AuPPh_3)_2]^{2+}$ (25) (isolated as the perchlorate salt) and structural data confirm that in the two digold units, the two Au centres are within bonding contact. Excitation of the products at 330 nm gives rise to intense intra-ligand fluorescence and phosphorescence in fluid solution at room temperature [40].



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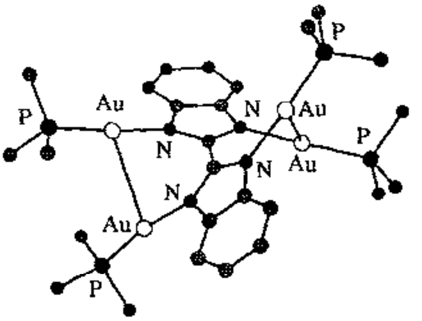


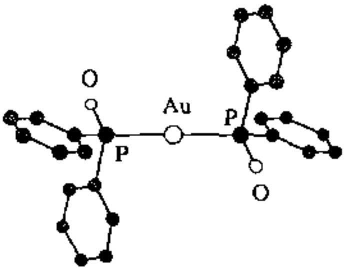
Only ipso-C atoms of Ph groups are shown.

(25)

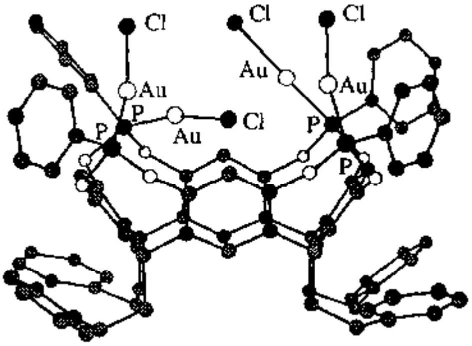
10.2.6 Complexes with phosphorus donor ligands

The dominance of phosphine ligands in gold(I) chemistry means that many are described in other sections in this review. In this section, we look only at those complexes in which the Au-P bond is the principal feature of interest.

Simple complexes of the type [R_3PAuCl] continue to be studied and the crystal structures of [(Mes_3P)AuCl] [41] and [(Me_2PhP)AuCl] [42] have been reported. The reactions of [LAuX] (where L = tetrahydrothiophene, and X = Cl or Br) with Ph_2PH in a 1:1 ratio leads to the formation of [(Ph_2HP)AuX]. The addition of concentrated ammonia to the system alters the route so that the polymer [AuPPh_2]$_n$ is produced. If the ratio of the reactants [LAuX]:Ph_2PH is 1:2 and the reactions are carried out in the presence of sodium perchlorate, the product is [Au(PPh_2H)$_2$][ClO_4]. The polymer [AuPPh_2]$_n$ reacts with [PPN][AuX_2] (X = Cl, Br or I) to give [PPN][(XAu)$_2$(μ-PPh_2)], and if proton sponge (PS) is present when [LAuCl] is treated with diphenylphosphine (2:1 ratio), the complex [HPS][(ClAu)$_2$(μ-PPh_2)] can be isolated. Finally, when [PPN][Au(acac)$_2$] and Ph_2PH react together, and oxidation in the air is permitted to occur, the product is [PPN][Au(PPh_2O)$_2$], which has been structurally characterized. The linear P-Au-P coordination sphere in the cation is shown in structure (**26**) [43].



(26)

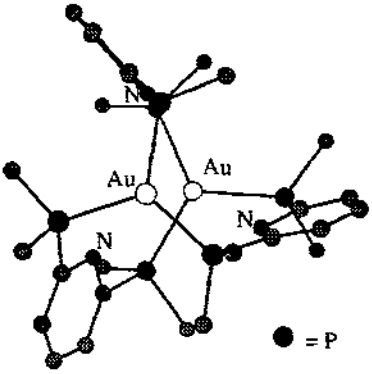


(27)

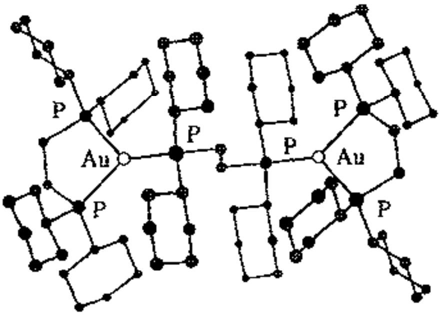
An interesting system is the tetragold(I) calix[4]resorcinarene (**27**), the preparation and crystal structure of which have been reported. Each PPh-unit of the ligand binds one gold(I) chloride moiety and the latter are situated around the open face of the calix[4]arene [44].

Several reports of cations of the type [L_2Au]$^+$ (L = phosphine) have been appeared, and these include the results of a crystallographic study of [(Ph_3P)$_2$Au][PF_6] and [(Ph_3P)$_2$Au][NO_3] [45]. The reactions of [L_2Au][ClO_4] (L = PPh_3, Ph_2MeP, P(C_6H_4-4-Me)$_3$ and P(C_6H_4-4-OMe)$_3$) with Li(tcnq) lead to the formation of the complexes [L_2Au][tcnq]. The packing of the anions and cations in the solid state is obviously of interest, and structural details of [(Ph_3P)$_2$Au][tcnq] have been described [46]. The ligand P(CH_2CH_2CN)$_3$ reacts with [(tht)AuCl] to yield [{($NCCH_2CH_2$)$_3$P}AuCl]. The derivative complex [Au{P(CH_2CH_2CN)$_3$}$_2$]Cl may be synthesized from [($NCCH_2CH_2$)$_3$PAuCl] and excess P(CH_2CH_2CN)$_3$ and has been studied using X-ray diffraction. The gold(I) centre is in a linear P-Au-P environment but is encapsulated by the six cyano-groups such that the cation has S_6 symmetry (Au---N = 3.579(3)Å). Infrared and ^{31}P NMR spectroscopic data are reported [47].

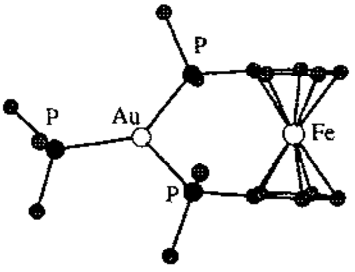
The ligand 2,6-$(PPh_2)_2$py complexes with gold(I) to give the dinuclear cationic species $[Au_2\{2,6\text{-}(PPh_2)_2py\}_3]^{2+}$ (**28**). Each ligand bridges between the two three-coordinate gold centres which are 4.866Å apart. The absorption spectrum of $[Au_2\{2,6\text{-}(PPh_2)_2py\}_3]^{2+}$ (MeCN solution) exhibits an intense, broad band (ε_{max} = 80 300 dm^3 mol^{-1} cm^{-1} at 260 nm, and 31 200 dm^3 mol^{-1} cm^{-1} at 300 nm). The complex is of particular interest in view of its photoluminescent properties [48]. Three-coordinate gold(I) is also observed in the complex dication $[\{(Cy_2PCH_2CH_2PCy_2)Au\}_2(\mu\text{-}Cy_2PCH_2CH_2PCy_2)]^{2+}$ (**29**) which has been isolated as the $[Au(CN)_2]^-$ salt and crystallographically characterized. Each gold(I) centre is bound to one chelating bis(phosphine) ligand and to one *P*-donor atom of the bridging ligand [17]. A similar complex is the dppf derivative $[\{(dppf)Au\}_2(\mu\text{-}dppf)]^{2+}$. This is one of a series of dppf derivatives that has been reported, and amongst the other complexes are further examples of three-coordinate gold(I) — in $[(dppf)AuPPh_3]^+$ (**30**), the gold(I) centre lies 0.066Å out of the plane containing the three *P*-donor atoms (Au-P_{PPh_3} = 2.318(10Å, Au-P_{dppf} = 2.405(1), 2.417(1)Å). The reactions of dppf with [(tht)AuX] (X = Cl or C_6F_5) or $[(tht)AuL][ClO_4]$ (L = CH_2PPh_3, CH_2PMePh_2 and CH_2PMe_2Ph) lead to the complexes $[(dppf)(AuX)_2]$ or $[(dppf)(AuL)_2][ClO_4]_2$ respectively. The chloride ligand in $[(dppf)(AuCl)_2]$ may be displaced by SCN$^-$ or tht to give $[(dppf)(AuSCN)_2]$ or $[(dppf)\{Au(tht)\}_2]^{2+}$ respectively. Other species in this work that have been prepared and characterized include [(dppf)AuCl], $[Au(dppf)_2]^+$ and $[(dppf)AuPMePh_2]^+$ [49].



Ipso-C atoms only of Ph rings are shown.
(28)



(29)



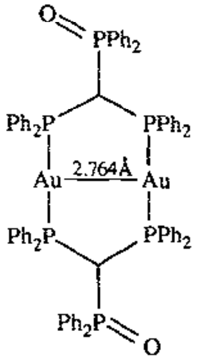
Only ipso-C atoms of Ph groups are shown.
(30)

10.3 DI-, TRI- AND POLYNUCLEAR COMPLEXES EXCLUDING CLUSTERS

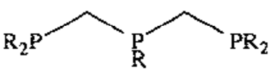
As discussed in the introduction, the complexes that have been chosen for inclusion as "di-, tri- and polynuclear complexes" are those in which the is good evidence for direct metal-metal bonding — either gold-gold bonds or in heterometallic systems. Several di- [9, 17, 20, 24, 34, 37, 38, 40, 43, 48, 49], tri- [37] and tetragold [36, 40, 44] compounds have already been mentioned and in several of these there is the possibity of Au-Au bonding interactions. Additionally, in the solid state, the monomers [$Au(C_4H_8S)Cl$] and [$Au(C_4H_8S)Br$] are stacked in an infinite array supported by Au---Au interactions [18], and association is also observed in the solid state structure of [Ph_3PAuSH] [21]. A survey of 693 gold complexes and which uses data from the Cambridge Crystallographic Data Base has focused on the ranges of bond distances between gold centres; geometrical features of the complexes have been addressed [41].

10.3.1 'A-frame' and related complexes

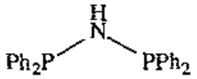
The reactions of $[Au(tht)_2]^+$ or [$Ph_3PAu(acac)$] with $CH(PPh_2)_3$ yield the complexes $[Ph_2PCH\{PPh_2AuPPh_2\}_2CHPPh_2]^{2+}$ or [$Ph_2PC\{PPh_2AuPPh_2\}_2CPPh_2$]. Further treatment with [$Au(tht)X$] ($X = C_6F_5$ or Cl) or $[Ph_3PAu(tht)]^+$ generates tetragold complexes. Elemental analysis, conductance measurements and multinuclear NMR spectroscopies have been used to characterize the products. Oxidation of [$Ph_2PC\{PPh_2AuPPh_2\}_2CPPh_2$] with hydrogen peroxide yields [$Ph_2P(O)C\{PPh_2AuPPh_2\}_2CP(O)Ph_2$] which possesses the A-frame structure shown in (**31**); two modifications of [$Ph_2P(O)C\{PPh_2AuPPh_2\}_2CP(O)Ph_2$].$4CH_2Cl_2$ have been crystallographically characterized [42].



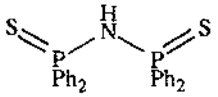
(**31**)



(**32**) R = Me; (**33**) R = Ph



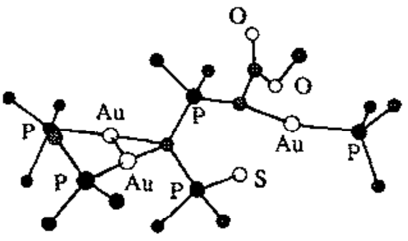
(**34**)



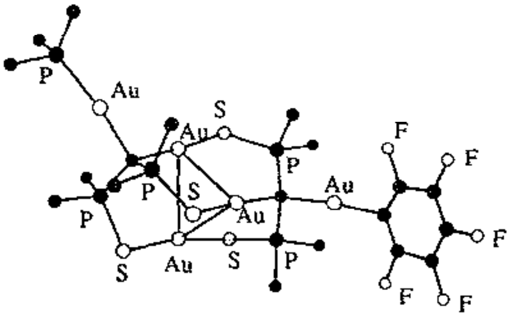
(**35**)

Excess dmmp (**32**) reacts with $[Au_3(dmmp)_2]^{3+}$ (as the perchlorate) in methanol to give $[Au_3(dmmp)_3]^{3+}$. Excitation of this cation (MeCN solution) with light of $\lambda > 350$ nm produces an intense phosphorescence ($\lambda_{emit} = 625$ nm, $\tau_0 = 2.2 \pm 0.2$ μs). The properties of $[Au_3(dmmp)_3]^{3+}$ have been compared with those of $[Au_2(dmpm)_3]^{2+}$; the excited state redox potentials of $[Au_3(dmmp)_3]^{3+*}$ and $[Au_2(dmpm)_3]^{3+*}$ have been measured using an oxidative quenching technique [43]. The tetrachloroaurate ion reacts with 2,2'-thiodiethanol in methanol to give an intermediate species that reacts further with dpmp (**33**) and NaSCN to yield $[Au_3(dpmp)_2]^{3+}$ and $[Au_4(dpmp)_2(SCN)_2]^{2+}$. Crystallographic data for these cations (as the tris(thiocyanate) and the chloride thiocyanate respectively) confirm the presence of double- and triple-A-frame structures respectively; in $[Au_4(dpmp)_2(SCN)_2]^{2+}$, the terminal gold centres are coordinated to one *P*-donor atom and to a thiocyanate ligand. In $[Au_3(dpmp)_2]^{3+}$, the angle Au-Au-Au is 167.21(2)° and Au-Au distances are 3.1037(8) and 3.0049(8)Å, whilst in $[Au_4(dpmp)_2(SCN)_2]^{2+}$ the Au-Au-Au angles are 160.0(1) and 167.2(1)°, and the Au-Au separations are 3.150(1), 3.057(1) and 3.122(1)Å. Both complexes exhibit room temperature photoluminescence [44].

The reactions between $[Ph_3PAu(acac)]$ and a range of diphosphines (HL) proceed via acac$^-$ displacement by L$^-$ (and formation of acacH), loss of PPh_3 and dimerization. For example, dppm or ligand (**34**) react to give the complexes $[Au_2(\mu\text{-dppm–H})_2]$ or $[Au_2(\mu\text{-}(\mathbf{34})\text{–H})_2]$, the H^+ having been removed from the bridgehead C or N atom respectively. Although dppm and (**34**) react in similar ways, $Ph_2P(S)CH_2P(S)Ph_2$ and ligand (**35**) do not — $[Ph_3PAu(acac)]$ reacts with (**35**) to yield $[Au_2\{\mu\text{-}(\mathbf{35}\text{–H})\}_2]$, but when $Ph_2P(S)CH_2P(S)Ph_2$ is used, a mixture of $[Ph_3PAu\{C\text{-}CH(P(S)Ph_2)_2\}]$ and $[(Ph_3PAu)_2\{C\text{-}C(P(S)Ph_2)_2\}]$ is produced. A wide range of related reactions has been studied and detailed spectroscopic results are complemented by crystallographic data. The structures of the complexes $[(Ph_3PAu)_2\{C\text{-}C(P(S)Ph_2)PPh_2CH(CO_2Me)AuPPh_3\}]^+$ (**36**) and of (**37**), (which was prepared by reacting $[(Ph_3PAu)_2\{C\text{-}C(P(S)Ph_2)_2\}]$ with two equivalents of $[(tht)Au(C_6F_5)]$), illustrate the diversity of molecular aggregation that can be achieved starting with ligands that also provide the basic units of 'A-frame' complexes [45].



Only ipso-C atoms of Ph groups are shown.
(**36**)

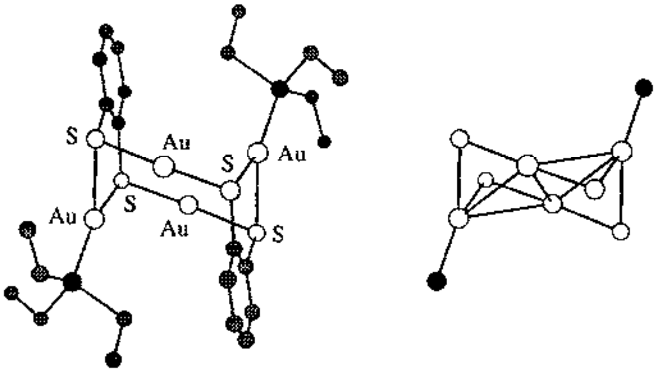


Only ipso-C atoms of Ph groups are shown
(**37**)

Heterometallic 'A-frame' complexes include $[AuRh(\mu\text{-dppm})_2(CN^tBu)_2]^{2+}$ [46] and $[AuPt(\mu\text{-dppm})_2(C{\equiv}CPh)_2]^+$ [47]. The $[AuRh(\mu\text{-dppm})_2(CN^tBu)_2]^{2+}$ dication exhibits an intense band at 455 nm (ε_{max} = 24 000 $dm^3\ mol^{-1}\ cm^{-1}$) assigned to a $^1(d\sigma^* \rightarrow p\sigma)$ transition, and molecular orbital calculations on a model system show that the transition possesses substantial $Rh \rightarrow \pi^*(CN^tBu)$ charge transfer character. The absorption and emission spectra of $[AuPt(\mu\text{-dppm})_2(C{\equiv}CPh)_2]^+$ have been recorded; there is an intense absorption band (λ_{max} = 387 nm; ε_{max} = 11 100 $dm^3\ mol^{-1}\ cm^{-1}$). Extended Hückel MO calculations on model compounds have been used to probe the electronic structure of this and related systems. The crystal structure of $[AuPt(\mu\text{-dppm})_2(C{\equiv}CPh)_2][PF_6]$ has been determined; the Au-Pt bond distance is 2.910(1)Å. The reaction between [Ph_3PAuCl] and *mer*-[Mo(dppm-*P,P'*)(dppm-*P*)$(CO)_3$] has been reinvestigated and is found to be solvent dependent. In benzene, the product is (as previously reported) [Au(μ-dppm)$_2$MoCl$(CO)_3$] and the results of an X-ray diffraction study show that the Mo-Au separation is 3.302Å. When the reaction is carried out in dichloromethane, the product is [$Ph_3PAuMo(CO)_2\{Ph_2PCH_2P(O)Ph_2\}_2$ which contains an unsupported Au-Mo bond (2.709 and 2.691Å for two independent molecules) and a seven-coordinate Mo centre. The complexes have also been characterized by IR and NMR spectroscopies [48].

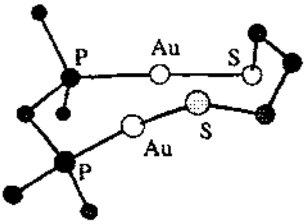
10.3.2 Other multinuclear gold complexes

Two reports of the compound [$Au_4(PEt_3)_2(1,2\text{-}S_2C_6H_4)_2$] (**38**) have appeared. In the first [49], the compound was prepared by treating 1,2-$(SH)_2C_6H_4$ with [Et_3PAuCl] in the presence of a tertiary amine. The mass spectrometric and ^{31}P and ^1H NMR spectroscopic data are complemented by a crystal structure analysis which illustrates that the dithiolate ligands bridge two gold centres in an 'A-frame' type geometry but each is further associated with an $AuPEt_3$ unit. The four gold centres form a rhombus as is shown in the right hand structure in (**38**) with a cross-rhombus distance of 3.114(1)Å and edge lengths of 3.052(1) and 3.129(1)Å. If PPh_3 replaces PEt_3 in the reaction, the product is the digold compound [$Au_2(PPh_3)_2(1,2\text{-}S_2C_6H_4)$] (see below). The second report of compound (**38**) comes as part of a detailed study of a range of thiolate gold(I) phosphine complexes [50]. In addition to this, Fackler and coworkers have fully characterized [Au_2(μ-dppm)(μ-$S(CH_2)_3S$)] (**39**) in which the Au-Au separation is 3.128Å, [$Au_2(PPh_3)_2$(μ-1,2-dicyanoethene-1,2-dithiolate-*S,S'*)], and [$Au_2(PPh_3)_2(1,2\text{-}S_2C_6H_4)$] (**40**).

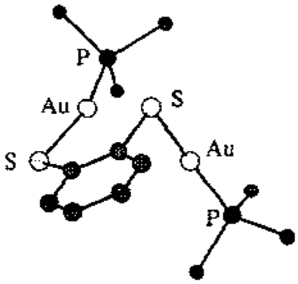


(**38**)

Polymeric systems include [Au(dppf)Cl]$_n$ (compare this to the species discussed in section 10.2.6) which has been produced in a 1:1 reaction of dppf and [$(Me_2S)AuCl$] in CH_2Cl_2. Two crystalline modifications of the polymer exist (monoclinic and orthorhombic forms) [51]. The functionalized ethene-acrylic acid copolymers Primacor 1430 and 5980 (with 9.5% and 20% acrylic acid respectively) have been the basis for the formation of gold/polymer dispersions and gold/polymer ionomers respectively [52].



Only ipso-C atoms of Ph groups are shown.
(39)



Only ipso-C atoms of Ph groups are shown.
(40)

10.4 SELECTED CLUSTERS

10.4.1 p-Block element centred clusters

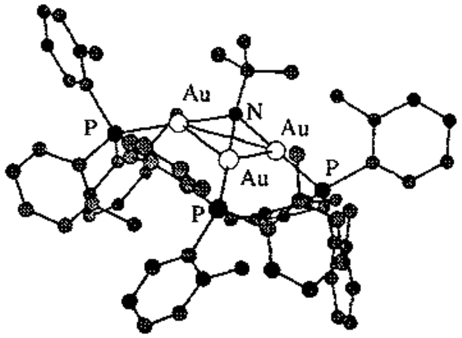
The work of Schmidbaur in developing *p*-block element centred multi-gold species has provided us with an ever increasing and novel area of gold chemistry, and one which Schmidbaur has recently reviewed (39 references) [53]. Since the number of gold atoms ≥3, they are described here as "*p*-block element centred clusters". Quasi-relativistic pseudo-potential methods at the HF and MP2 levels have been applied to some model compounds of the type $[E(AuPH_3)_4]^+$ (E = N, P, As) and the naked clusters $[EAu_4]^+$ and their H and Ag analogues. The optimized geometries have been compared with experimental structures where possible; T_d and C_{4v} symmetries are found for $[N(AuPH_3)_4]^+$ and $[As(AuPH_3)_4]^+$ respectively, and these results agree with experimental findings for the substituted phosphine compounds. It is predicted that the structure of $[P(AuPH_3)_4]^+$ resembles that of $[As(AuPH_3)_4]^+$. Secondary Au-Au interactions are attributed to correlation, and not hybridization, effects [54].

In the following discussion, we focus on species with Au_xE-cores and these are described in periodic order of atom E — B, C, N, P, O and S. The association of boron with four gold centres is observed in $[Cy_3PB(AuPPh_3)_4]^+$ which is formed as the tetrafluoroborate salt in the reaction of $Cy_3PCH_2SiMe_3$ with $[(Ph_3PAu)_3O][BF_4]$ in thf at −78°C. The five-coordinate nature of the boron atom has been confirmed crystallographically [55].

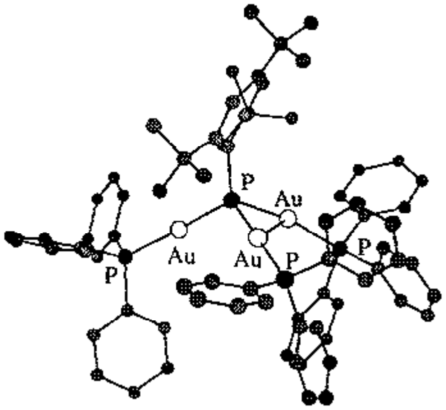
Carbon-centred systems are strictly organometallic complexes since Au-C bonds are principal features, but the following species are included briefly here for the sake of completeness. The preparation and structure of $[(Me_3Si)_2CHAuPPh_3]$ have been described; this complex reacts with $[(Ph_3PAu)_3O][BF_4]$ to give $[(Me_3Si)_2C(AuPPh_3)_2]$ and $[(Me_3Si)_2C(AuPPh_3)_3][BF_4]$. The latter contains a five-coordinate C atom [56]. The reactions of $[R_3PAuCl]$ (R = Ph or Cy) or $[\{1,2\text{-}(Ph_2PCH_2CH_2)_2C_6H_4\}Au_2Cl_2]$ with $MeC(B(OMe)_2)_3$ in the presence of CsF lead to the formation of $[(R_3PAu)_4CMe][BF_4]$ or $[\{1,2\text{-}(Ph_2PCH_2CH_2)_2C_6H_4\}_2Au_4CMe][BF_4]$ respectively. Crystallographic data reveal that in the cations $[(Ph_3PAu)_4CMe]^+$ and $[\{1,2\text{-}(Ph_2PCH_2CH_2)_2\text{-}C_6H_4\}_2Au_4CMe]^+$ the four gold centres form the base of a Au_4C-square-based pyramidal array with Au-Au separations of ≈2.85Å [57]. The reactions of $[R_3PAuCl]$ ($R_3P = Cy_3P$ or Ph_x(2-

$MeC_6H_4)_{3-x}P$) with $C\{B(OMe)_2\}_4$ in the presence of CsF and hmpt yield $[(R_3PAu)_4C]$ and $[(R_3PAu)_5C]^+$ which can be separated by fractional crystallization; however, the nature of PR_3 influences the product distribution [58]. Analogous reactions using $[Et_3PAuCl]$ or $[^iPr_3PAuCl]$ lead to the formation of $[(R_3PAu)_6C]^+$ isolated as the $[BF_4]^-$ salts; the interstitial carbon atom is characterized by a signal in the ^{13}C NMR spectrum at δ +159.0 (R = Et) or +154.6 (R = ^iPr) (J_{CP} $\approx$ 52 Hz) and it is suggested that this means there is little *s* character in the orbitals of the carbon atom used for C-Au bonding. Crystallographic data confirm an octahedral carbon centre. Attempts to make the $^tBu_3P$ analogue have failed and this is attributed to steric effects [59].

The crystal structures of the tetrafluoroborate salts of three new nitrogen-centred gold complexes have been reported — in each of $[4\text{-}MeC_6H_4N(AuPPh_3)_3]^+$, $[RN(AuPPh_3)_3]^+$ (R = 8-quinolinyl) and $[L(AuPPh_3)_3]^+$ (H_2L = 1-(aminoethyl)aziridine) the N atom is four-coordinate [60]. The oxonium salts $[(R_3PAu)_3O][BF_4]$ (R = 2-MeC_6H_4, Mes or Cy) are excellent aurating agents and react with primary amines ($R'NH_2$ with R' = Ph, ^tBu or 8-aminoquinolinyl) to yield $[R'N(AuPR_3)_3][BF_4]$; the complexes with R' = ^tBu and R = 2-MeC_6H_4, [that is, complex cation (**41**)], and with R' = Ph and R = Cy have been studied by X-ray diffraction methods [61]. The primary aryl phosphine $(2,4,6\text{-}^tBu_3C_6H_2)PH_2$ is the precursor to $[(2,4,6\text{-}^tBu_3C_6H_2)P(AuPR_3)_3][BF_4]$ (R = Ph or ^tBu), and the crystal structure of $[(2,4,6\text{-}^tBu_3C_6H_2)P(AuPPh_3)_3][BF_4]$ has been determined. In the cation (**42**), the central phosphorus atom is, as expected, four-coordinate but only one of the three Au---Au separations can be considered to be bonding (3.1546(3)Å vs. 3.6571(3) and 3.9443(3)Å). The compound $[(2,4,6\text{-}^tBu_3C_6H_2)P(AuPPh_3)_3][BF_4]$ reacts with $[Ph_3PAu][BF_4]$ to give $[(2,4,6\text{-}^tBu_3C_6H_2)P(AuPPh_3)_4][BF_4]_2$. The structural data are complemented by NMR spectroscopic and mass spectrometric results [62].

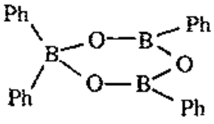


(41)



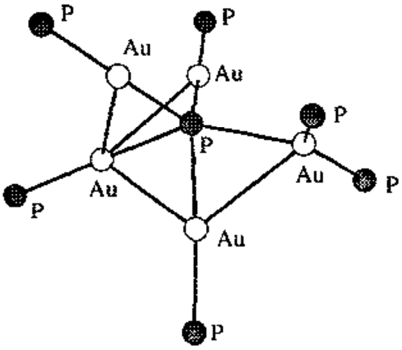
(42)

The phosphonium salt $[(^tBu_3PAu)_4P][BF_4]$ is formed when $[(^tBu_3PAu)_3O][BF_4]$ is treated with $P(SiMe_3)_3$ in thf at −78°C; anion exchange leads to the isolation of the tetraphenylborate salt. However, attempts to crystallize $[(^tBu_3PAu)_4P][BPh_4]$ have lead instead to $[(^tBu_3PAu)_4P]$[**43**]. The central P atom in the complex cation is tetrahedrally sited and the Au---Au separations are quite long, being in the range 3.4395(5) to 4.3314(5)Å [63]. Ligand (**44**) has been synthesized and fully characterized, and its use as a bridging unit between P-centred gold clusters has been demonstrated — **(44)** reacts with $[(R_3PAu)_3O]^+$ (R = Ph or ^tBu) to give $[(R_3PAu)_3(P\text{-}C_6H_4\text{-}P)(AuPR_3)_3]^{2+}$, and with $[(Ph_3PAu)_3O]^+$ in the presence of $[Ph_3PAu][BF_4]$ to yield $[(Ph_3PAu)_4(P\text{-}C_6H_4\text{-}P)(AuPPh_3)_4]^{4+}$. These new complexes have been characterized by multinuclear NMR spectroscopies and mass spectrometry [64].



(43)

(44)



(45)

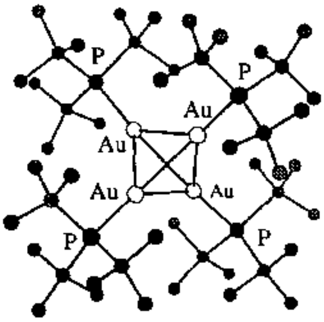
Higher degrees of gold aggregation around phosphorus centres are seen in $[(Ph_3P)_6Au_5P]^{2+}$ [65] and $[(R_3PAu)_6P]^{3+}$ (R = ^iPr or ^tBu) [66]. The former has been prepared by reacting PH_3 with $[(Ph_3PAu)_3O][BF_4]$ and structural data for the cation $[(Ph_3P)_6Au_5P]^{2+}$ **(45)** confirm the presence of one $Au(PPh_3)_2$ unit; the solid state structure is consistent with solution data which suggest that $[(Ph_3P)_6Au_5P]^{2+}$ may be formulated in terms of $[(Ph_3PAu)_4]^+[(Ph_3P)_2Au]^+$. Indeed, the mass spectrum of **(45)** exhibits a fragmentation pattern that is dominated by $[(Ph_3PAu)_4]^+$ and $[(Ph_3P)_2Au]^+$ [65]. The tetrafluoroborate salts of $[(R_3PAu)_6P]^{3+}$ (R = ^iPr or ^tBu) are formed when $[(R_3PAu)_3O][BF_4]$ reacts with $[P(SiMe_3)_3]$ in thf in the presence of KF. The product has been spectroscopically characterized [66].

The syntheses of a series of oxonium salts $[(LAu)_3O][BF_4]$ have been described [L = $PMePh_2$, PMe_2Ph, $PEtPh_2$, P^iPrPh_2, $P(2\text{-}MeC_6H_4)_3$, $P(OEt)Ph_2$ and $P(OMe)_3$] starting from [LAuCl] and Ag_2O. This method is not successful when L = $P(OPh)_3$, $P(OPh)Ph_2$ or $P(4\text{-}ClC_6H_4)_3$, but for the latter phosphine, an alternative route is to react [LAuCl] with $AgBF_4$ followed by NaOH. Multinuclear (^{31}P, ^1H and ^{17}O) NMR spectroscopic data have been recorded and the reaction of $[LAuCl]/AgBF_4/NaOH$ has been found to be useful in preparing ^{17}O labelled compounds. Structural data have illustrated that the oxonium cations are dimers for L = $PMePh_2$ and PPh_3 but a monomer for L = $P(2\text{-}MeC_6H_4)_3$, a difference that is attributed to steric effects [67]. Related, but independent work, reports that when KOH reacts with three molar equivalents of

$[Et_3PAuBF_4]$, the product is $[(Et_3PAu)_3O][BF_4]$, and that $[(^tBu_3PAu)_3O][BF_4]$ may be synthesised by treating $[^tBu_3PAuCl]$ with Ag_2O in the presence of $NaBF_4$ in thf. These compounds are the first examples of oxonium salts with *alkyl* phosphine derivatives and they are shown to be good aurating agents some examples of which were described above [68]. Schmidbaur has also reported the reaction of $[(Ph_3PAu)_3O][BF_4]$ with $(Me_3Si)_2S$ which gives $[(Ph_3PAu)_3S][BF_4]$. A crystallographic study of this salt confirms that the cations are monomeric in the solid state and exhibit significant Au–Au interactions (3.156 to 3.1910Å). The Au-S distances fall in the range 2.309-2.328Å [68].

10.4.2 Other clusters

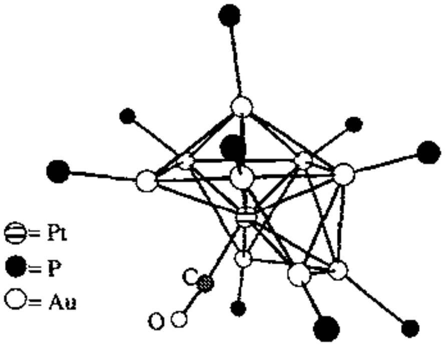
The tetrahedral cluster $[(^tBu_3P)_4Au_4]^{2+}$ (46) has been prepared as the tetrafluoroborate salt by reacting $[(^tBu_3PAu)_3O][BF_4]$ with $(Me_3Si)_3P$. In the ^{31}P NMR spectrum there is a single resonance and the cluster geometry has been confirmed by the results of an X-ray diffraction study. The Au-Au distances lie in the range 2.7031 to 2.7302Å and all the Au-Au-Au bond angles are ca. 60°. The bonding in this cluster has been addressed in the light of earlier MO investigations [69].



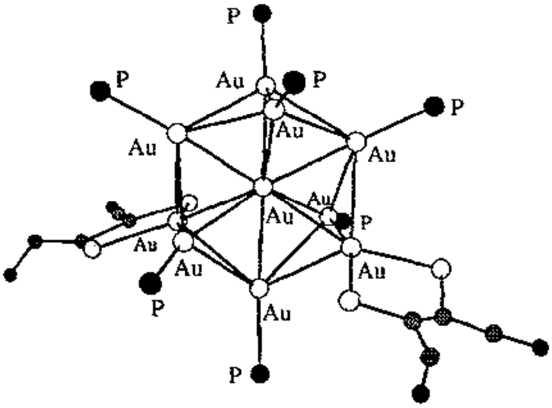
(46)

Further to work reported in previous surveys in this series, mixed gold-group 10 clusters in which gold predominates have been described. The compound $[Pt(AuPPh_3)_8][NO_3]_2$ reacts rapidly and reversibly with dihydrogen under ambient conditions both in the solid state and in solution. The oxidative addition has been monitored for the solution reaction by using ^{31}P, ^1H and ^{195}Pt NMR and UV-VIS spectroscopies. The product $[Pt(H)_2(AuPPh_3)_8]^{2+}$ shows a signal in its ^{195}Pt NMR spectrum at δ –5994 with couplings of J_{PtP} 380 Hz (nonet) and J_{PtH} 645 Hz (triplet). Voltammetric studies have also been carried out. Further, the oxidative addition of D_2 has been studied. Some attention has been given to the catalytic applications of this reaction, for example, with respect to the conversion of ethene to ethane [70]. When treated with halide or cyanide ions, the compound $[Pd(AuPPh_3)_8][NO_3]_2$ gives $[PdI(AuPPh_3)_7(AuI)_2]$, $[Pd(AuPPh_3)_7(AuBr)_3]^+$, $[Pd(AuPPh_3)_8(AuCl)_3]$ (or $[Pd(AuPPh_3)_7(AuCl)_3]^+$ in the presence of extra acid) and $[Pd(AuPPh_3)_8(AuCN)_3]$. The iodide ligand in $[PdI(AuPPh_3)_7(AuI)_2]$ can be replaced by CO, and the cations $[Pd(AuPPh_3)_7(AuBr)_3]^+$ and $[Pd(AuPPh_3)_7(AuCl)_3]^+$ react with CO forming adducts.

In contrast, CO does not react with $[Pd(AuPPh_3)_8(AuCl)_3]$ or $[Pd(AuPPh_3)_8(AuCN)_3]$. The crystal structure of $[PdI(AuPPh_3)_7(AuI)_2]$ has been determined and the cluster skeleton is a Pd-centred fragment of an icosahedron [71]. The photolysis of a mixture of $[Ph_3PAuN_3]$, $[Ph_3PAuCl]$ and $[(Ph_3P)_2Pt(N_3)_2]$ in thf produces the cluster $[Pt(CO)(AuPPh_3)_6(AuCl)_3]$ and structure **(47)** illustrates the Pt-centred icosahedral fragment that is present. Reaction between $[Pt(dppe)Co_2(CO)_7]$ and an excess of $[Ph_3PAuN_3]$ under photolytic conditions leads to the formation of the cationic species $[Pt(dppe)(AuPPh_3)_4]^{2+}$ for which a trigonal bipyramidal cluster core with the Pt atom in an equatorial site is observed. A second product of this reaction is $[Co_2(CO)_6Au(AuPPh_3)_6]^+$ [72].



Phenyl groups are not shown.
(47)



Phenyl groups are not shown.
(48)

The preparation and structural analysis of the compound $[Au_{10}(PPh_3)_7\{S_2C_2(CN)_2\}_2]$ using monochromatic synchrotron radiation have been reported. Three edge-sharing trigonal bipyramidal Au_5 groups share a common gold centre [73].

The results of theoretical and spectroscopic investigations of the cluster cations $[LMH_2(AuPPh_3)_3]^{2+}$ (M = Rh or Ir) and $[LRuH_3(AuPPh_3)_3]^{2+}$ in which L is $MeC(CH_2PPh_2)_3$ have been reported. The work focuses upon ^{31}P CP-MAS , ^{197}Mössbauer and incoherent inelastic neutron and IR spectroscopic studies in addition to extended Hückel MO calculations. The theoretical and experimental data are consistent and proposals have been put forward in regard of the hydrogen locations and respective bonding modes [74]. Related work reports the preparations of $[LRuH_3(AuPR_3)_3]^{2+}$ and $[L'RuH_3(AuPR_3)_3]^{2+}$ (R = Ph, Et or ^{i}Pr; L = $MeC(CH_2PPh_2)_3$, L' = $MeC(CH_2AsPh_2)_3$) as well as related species. Proton and ^{31}P NMR spectroscopic data are presented in addition to the crystal structure of $[LRuH_3(AuPPh_3)_3][PF_6]_2$; $RuAu_2$-face capping hydride ligand sites are found, and in solution the complexes are highly fluxional [75].

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