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COORDINATION CHEMISTRY REVIEWS

Gold 1994

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Contents

1. Introduction

This review covers the coordination chemistry of gold published in 1994 and follows the corresponding 1993 survey [1]. The literature has been searched using *Current Contents* and the Cambridge Structural Data Base, implemented through the ETH, Zürich [2]; most structural diagrams have been drawn using coordinates from the latter with hydrogen atoms omitted for clarity.

Some references from the latter part of 1993 are included in this survey, and some citations from the tail end of 1994 will fall within the remit of the 1995 survey. Although not fully comprehensive, this article gives a significant coverage of papers published; organometallic complexes (defined as those possessing a Au–C bond with

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the exceptions of cyano complexes, orthometallated species, and selected complexes with C_6F_5 substituents) have been excluded.

Complexes are organised according to the oxidation of the gold centre and by the donor-type of the ligand of main interest. A great many gold(I) complexes contain a $Au{-}P_{phosphine}$ link, but other donor atoms (where present) usually take priority for categorisation purposes. In the previous two reviews in this series, multinuclear complexes have been separated out from mononuclear species. However, the number of multinuclear complexes continues to grow and a significant proportion of the gold(I) complexes reported over the last few years have been shown to exhibit intramolecular or intermolecular Au···Au interactions, so much so that the emphasis in this year's review has been placed on the donor-atoms rather than the nuclearity. 'A-frame'-type complexes have been described in a separate section, as have gold-containing clusters; organometallic clusters featuring $AuPR_3$-units have not been included in this survey.

2. Gold(III)

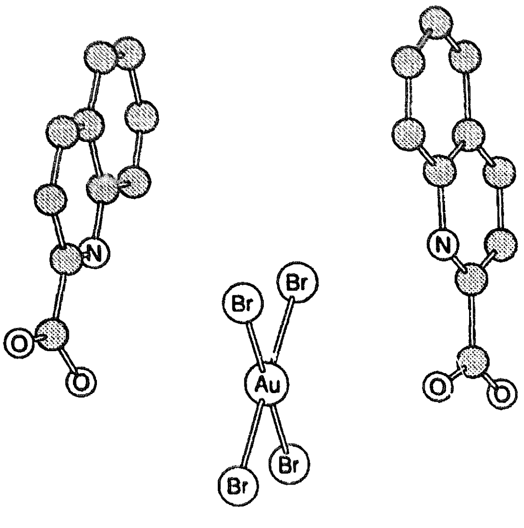
Of general interest is an analytical paper which describes a selective and sensitive spectrophotometric method for the determination of microgram quantities of gold. The ligand is 2,3-dichloro-6-(3-carboxy-2-hydroxy-1-naphthylazo)quinoxaline and its 1:1 complex with gold(III) (in the pH range 3.4 to 7.0) obeys the Beer–Lambert law over a concentration range 0.1 to 6.9 $\mu g\ cm^{-3}$ [3].

2.1. Complexes with halide ligands

The X-ray crystal structure of a bis(3,3'-dimethylene-2,2'-biquinolinium) salt containing both gold(I) and gold(III) counter-ions ($[AuBr_2]^-$ and $[AuBr_4]^-$) has been determined [4]. Complex formation between quinaldic acid (HL) and $HAuCl_4$ or $HAuBr_4$ has been studied; the products include those of the general type $HAuX_4 \cdot 2HL$ and the crystal structure of $HAuBr_4 \cdot 2HL \cdot H_2O$ (**1**) indicates that the complex is better formulated as $[H(HL)_2][AuBr_4] \cdot H_2O$. The coordination environment of the gold(III) centre is described as 'elongated octahedral' but the Au–O distances are extremely long (≈ 340 pm) [5]. When chloroauric acid reacts with Ph_2CN_2, the product is the salt $[Ph_2C{=}N(H)N{=}CPh_2][AuCl_4]$ [6]; see also Section 3.5 for related work.

The salt $[et]_3[AuBr_4]$ where et = bis(ethylenedithio)tetrathiofulvalene has been structurally characterised and compared with its nickel analogue. In the solid state, $[et]_3[AuBr_4]$ possesses a herring-bone stack of bis(ethylenedithio)tetrathiofulvalene moieties. The results of conductivity studies have been correlated with structural data for the compounds. It was found that a band description of the conducting properties of the gold compound were not appropriate and the system was better described as a Mott–Hubbard semiconductor [7].

The gold(I)–gold(III) intervalence charge transfer transitions in the salts



(1)

$Cs_2[Au_2X_6]$ (X = Cl, Br, I) have been investigated and group theory analysis has been used to assign the bands in $Cs_2[Au_2I_6]$ [8].

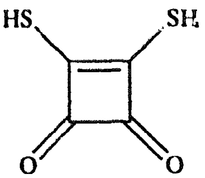
2.2. *Complexes with oxygen-donor ligands*

The synthesis of $Au_2O_3 \cdot 5.2H_2O$ and its use as a precursor to double selenates have been reported; selenates described included $HAu(SeO_4)_2$ and $MAu(SeO_4)_2$ (M = K, Rb or Cs). The results of thermal decomposition studies of the new products have also been presented [9].

2.3. *Complexes with sulfur-donor ligands*

Structural studies of the complex $[Au(PEt_3)_2][(1,2\text{-}S_2C_6H_4)_2Au]$ confirm the expected square planar coordination environment of the gold(III) centre in the complex anion [9a] and the X-ray crystal structure of $[(Ph_3P)_2N][(C_3S_5)_2Au] \cdot 0.5CH_2Cl_2$ has also been reported [10].

The reaction between $K[AuCl_4]$ and $K_2L \cdot H_2O$ [H_2L = (**2**)] with cation exchange has given complexes containing the anions $[AuL_2]^-$ and $[Au_2L_2]^{2-}$. The former gold(III) complex has a square planar coordination sphere and the anions form stacks along the *a* axis. The guanidinium and cyclopropyltriphenylphosphonium salts have been structurally characterised and structure (**3**) shows the twisted nature of the $[Au_2L_2]^{2-}$ anion [11]. The reactions of dithiocarbamates $[RHN{=}C(SMe)S]^-$ (R = 4-MeC_6H_4, 2-MeC_6H_4, 4-$MeOC_6H_4$ or 3,5-$Me_2C_6H_4$) with the gold(I) compound $[C_6F_5Au(tht)]$ or the gold(III) complex $[(C_6F_5)_3Au(OEt_2)]$ have been reported to give a series of complexes in which the dithiocarbamates are *S*-bound to the gold centres. Reactivity studies of the new complexes have been carried out [12].



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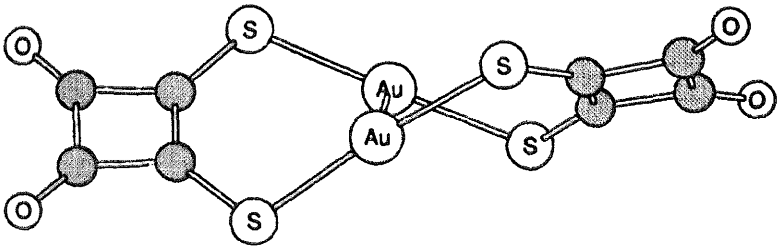

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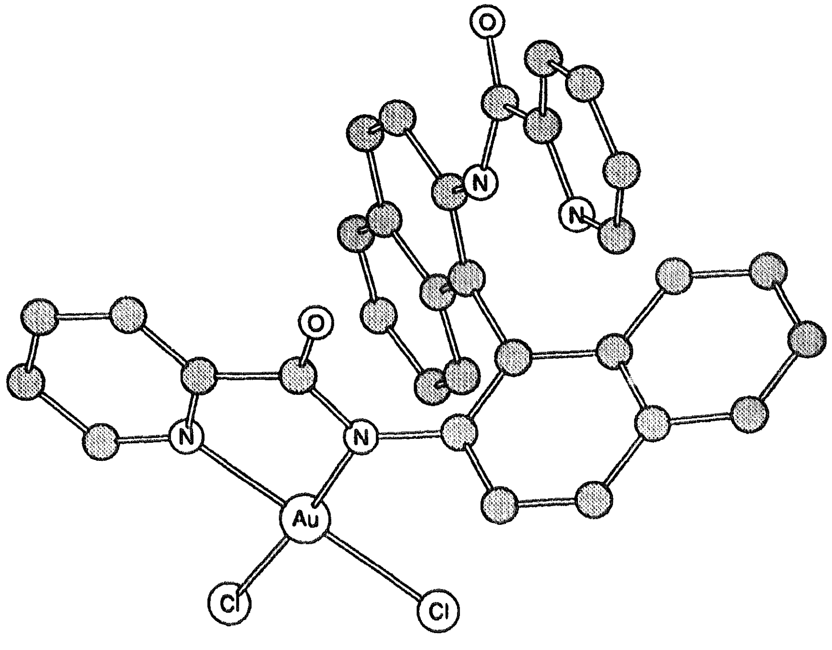
2.4. Complexes with tellurium-donor ligands

The preparations of the gold(I) complex [(2,4,6-Ph$_3$C$_6$H$_2$)Te(AuPPh$_3$)$_2$][BF$_4$] and its hexafluorophosphate analogue have been reported; see also Section 3.4. Oxidation of [(2,4,6-Ph$_3$C$_6$H$_2$)Te(AuPPh$_3$)$_2$][BF$_4$] by diiodine leads to the formation of [(2,4,6-Ph$_3$C$_6$H$_2$)TeAuI$_2$]$_2$ and an X-ray crystal structure analysis reveals the presence of a rhomboidal Te$_2$Au$_2$ core ($\angle$Au-Te-Au = 99°, $\angle$Te-Au-Te = 81°) and in which each gold(III) centre is additionally bound to two iodine atoms [13]. The synthesis and characterisation of the dark red compound [Et$_4$N]$_4$[Au$_2$Te$_{12}$] have been described. The complex anion consists of two square planar gold(III) centres each coordinated by an η^3-[Te$_5$]$^{4-}$ ligand; the two gold centres are further bridged by an η^2-[Te$_2$]$^{2-}$ ligand [14].

2.5. Complexes with nitrogen-containing ligands

The reaction of K[AuCl$_4$] with 2,2'-bis(2-pyridylcarboxyamide)-1,1'-binapthyl, H$_2$L, yields the gold(III) complex [AuCl$_2$(HL)] (4) in which the chloro ligands are mutually *cis*. The ligand [HL]$^-$ functions in a didentate *N,N'*-manner through one 2-pyridylcarboxyamide substituent. In the solid state, the molecules are paired by virtue of Au···Au contacts of 372 pm. The emission properties of [AuCl$_2$(HL)] have been reported [15]. Che and coworkers have also described the photophysical and photochemical properties of a gold(III) complex of 2,9-diphenyl-1,10-phenanthroline, HL. Cyclometallation occurs to give a *C,N,N'*-bonded species and an X-ray crystal structural analysis has shown that the [AuLCl]$^+$ cations form stacks in the solid state with Au···Au separations of 360 pm. The emission spectra of [AuLCl][ClO$_4$] and [AuLCl][MeC$_6$H$_4$SO$_3$] are not solvent dependent. A reduction potential for the excited state, E^{0*}Au^{III}/Au^{II}, has been estimated as 2.2 V vs. NHE and implies that the complex cation is a strong photooxidant; the ability of $[AuLCl]^+$ to oxidise 1,4-dimethoxybenzene to the corresponding cation radical provides an example of such an oxidation process [16].



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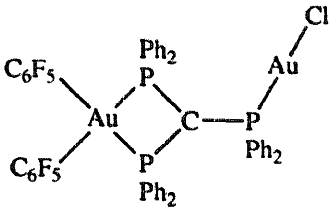
The preparation and characterisation of a series of gold(III) complexes containing the ligands phenylthioacetamide, 2-tolylthioacetamide, 2,5-dimethylthioacetamide, diphenylthioacetamide, 3-thioacetylaminodibenzofuran, 3-thiobenzoylaminodibenzofuran and 3-thiofuroylaminodibenzofuran have been reported. In each case, a square planar gold(III) coordination sphere involving an *N,S*-bound ligand is suggested; data include elemental analyses, UV–VIS and IR spectroscopies, and conductivity measurements [17].

2.6. *Complexes with phosphorus-donor ligands*

The crystal structure of $[Ph_3PAuCl_3]$ (monoclinic) has been described and results confirm the expected square planar coordination environment about the gold(III) centre [18]. The reaction of $[(C_6F_5)_2Au(acac)]$ with $(Ph_2P)_3CH$ yields $[(C_6F_5)_2Au\{(Ph_2P)_2CPPh_2\}]$, the structure of which has been established by X-ray crystallography. Treatment of this complex with $[AuX(tht)]$ ($X = Cl$ or C_6F_5) leads to dinuclear or trinuclear species. Related reactions are also reported and the products have been characterised by elemental analysis, conductivity measurements and multinuclear NMR spectroscopies. A single crystal X-ray analysis of $[(C_6F_5)_2Au\{(Ph_2P)_2CPPh_2\}AuCl]$ confirms structure (5) [19].

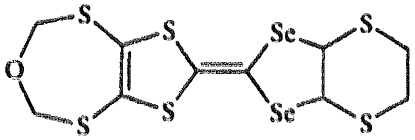


(5)

3. Gold(I)

3.1. Complexes with halide and pseudo-halide ligands

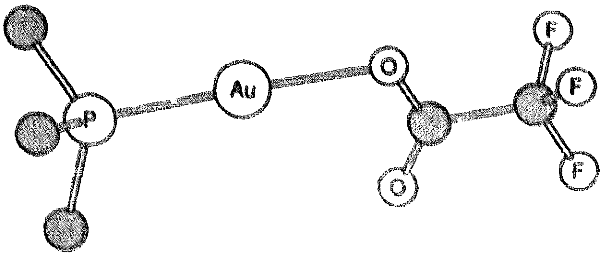
The crystal structure of the 3,5-diphenyl-1,2-dithiolium salt of $[AuI_2]^-$ has been determined [20] and in work that aims to develop organic superconductors, charge transfer salts of ligand (**6**) including those containing the anions $[Au(CN)_2]^-$ and $[AuBr_2]^-$ have been prepared and characterised. The electrical resistivity of the α-type $[(\mathbf{6})][AuBr_2]$ decreases monotonically down to 4 K. The salt $[(\mathbf{6})][Au(CN)_2]$ exists in two morphologies; the first is an insulating phase and has been characterised by X-ray crystallography while the second is metallic to 40 K [21].



(**6**)

3.2. Complexes with oxygen-donor ligands

The gold(I) complex $[Ph_3PAu(O_2CCF_3)]$ (**7**) has been characterised by X-ray diffraction methods. The gold(I) centre is linearly coordinated by the phosphine *P*-donor and one oxygen donor of the trifluoroacetate ligand (Au–O = 207.8 pm) [22].



Only the *ipso*-C atoms of Ph rings are shown.

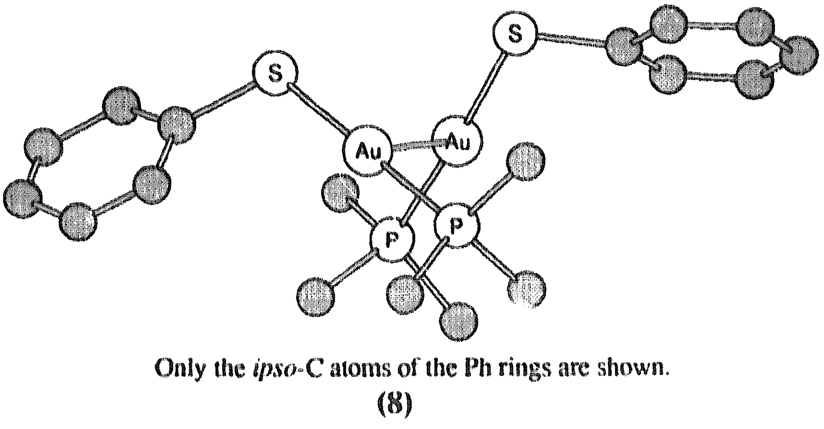
(**7**)

3.3. *Complexes with sulfur-donor ligands*

The reaction of $[(Ph_3P)_2N][Au(acac)_2]$ with H_2S (as a saturated solution in CH_2Cl_2) has given the first homoleptic hydrogensulfido complex of gold(I); $[(Ph_3P)_2N][Au(SH)_2]$ can also be prepared by bubbling H_2S through a solution of $[(Ph_3P)_2N][AuCl_2]$ in Et_2NH. In the ^1H NMR spectrum, a signal at $\delta -1.22$ due to the SH protons was observed, and in the IR spectrum, an absorption at $340\,cm^{-1}$ has been assigned to the ν(Au–S) mode. The solid state structure of $[(Ph_3P)_2N][Au(SH)_2]$ has been determined and confirms a linear S–Au–S unit in the anion [23].

Several papers have been concerned with gold(I) complexes of benzenethiolate and related ligands. The crystal structure of $[\{Ph_3PAu\}_2(\mu\text{-}SC_6H_5)][CF_3SO_3]$ has been determined and reveals a bridging $[PhS]^-$ ligand supporting a digold unit with a Au···Au separation of 317 pm. Each gold(I) centre is in a linear S–Au–P arrangement [24]. The related complex $[Ph_3PAuSC_6H_5]$ (**8**) has also been structurally characterised and is dimeric in the solid state. The Au···Au distance is 315.4 pm and the two PAuS units adopt in a staggered conformation [25]. The related compound $[Ph_3PAuSC_6H_4\text{-}2\text{-}OMe]\cdot 0.25Et_2O$ has also been studied crystallographically but here the Au···Au separation is large (574.1 pm) [26]. The reactions of $[Ph_3AsAuCl]$ with $K_2[1,2\text{-}S_2C_6H_4]$ or $K_2[3,4\text{-}S_2C_6H_3Me]$ have yielded similar complexes of formula $[Au_2L(AsPh_3)]_n$ ($H_2L = 1,2\text{-}(HS)_2C_6H_4$ or $3,4\text{-}(HS)_2C_6H_3Me$), but with $K_2[1,3\text{-}S_2C_6H_4]$, the product was $[Au_2(1,3\text{-}S_2C_6H_4)]_n$. The reactions of these complexes with phosphines have been investigated, and higher nuclearity species have been obtained, for example by treating $[Au_2L(PPh_3)_2]$ with $[Ph_3PAu(Me_2CO)][ClO_4]$. Product characterisation has included X-ray crystallographic studies of representative complexes [27]. The self-assembly of a 'wheel-like' gold(I) complex takes place when benzenehexathiol reacts with $[Ph_3PAuCl]$. The product is $[C_6S_6(AuPPh_3)_6]$ (**9**) and the beautiful nature of this complex has been confirmed from X-ray crystallographic data. The C_6S_6-core is necessarily planar but there is some puckering of the S–Au(P)–S units around the periphery of the S_6-hexagon; there are no bonding interactions between the gold(I) centres [28].

Another example of the assembly of a multinuclear species is observed in the



Only the *ipso*-C atoms of the Ph rings are shown.

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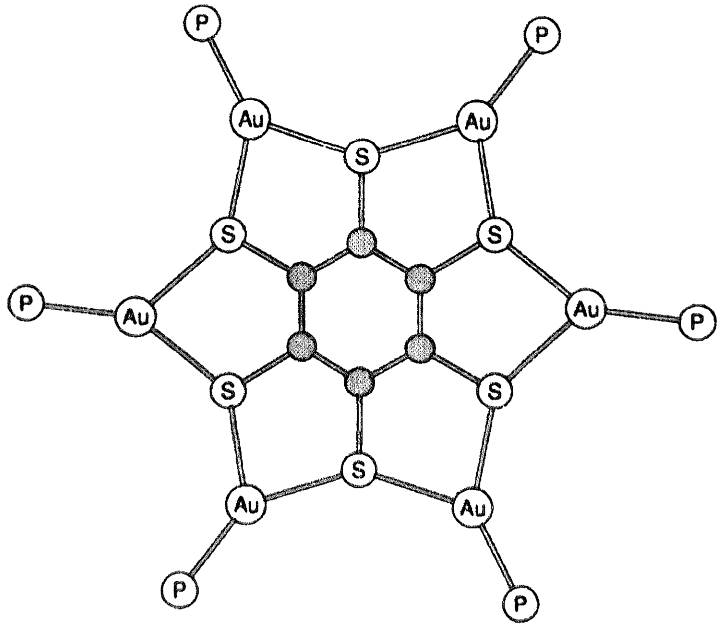
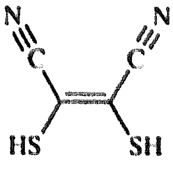


Only P atoms of PPh3 groups are shown.

(9)

reaction of chloroauric acid with $(^tBuO)_3SiSH$ in the presence of triethylamine. This yields the complex $[\{(^tBuO)_3SiSAu\}_4]$ in which the four gold and sulfur centres form a monocycle. The new compound has been characterised by IR, UV–VIS and NMR spectroscopies as well as mass spectrometry and X-ray diffraction methods [29].

The syntheses of the complexes $[Au_2L(PR_3)_2]$, where $H_2L = $ (**10**) and R = Me, OPh, Et or Cy, have been reported. The solid state structure of $[Au_2L(PCy_3)_2]$ reveals that the ligand L^{2-} bridges across the two gold(I) centres but the steric crowding of the cyclohexyl groups prevents there from being any gold–gold interaction. However, for the less bulky phosphines, interaction is possible: e.g. for R = Me, Au···Au = 314.5 pm, 299.1 pm for R = OPh, and 308.4 pm for R = Et. Solution ^{31}P NMR spectroscopic data for the complexes indicate the presence of only one phosphorus environment down to −80°C [30].



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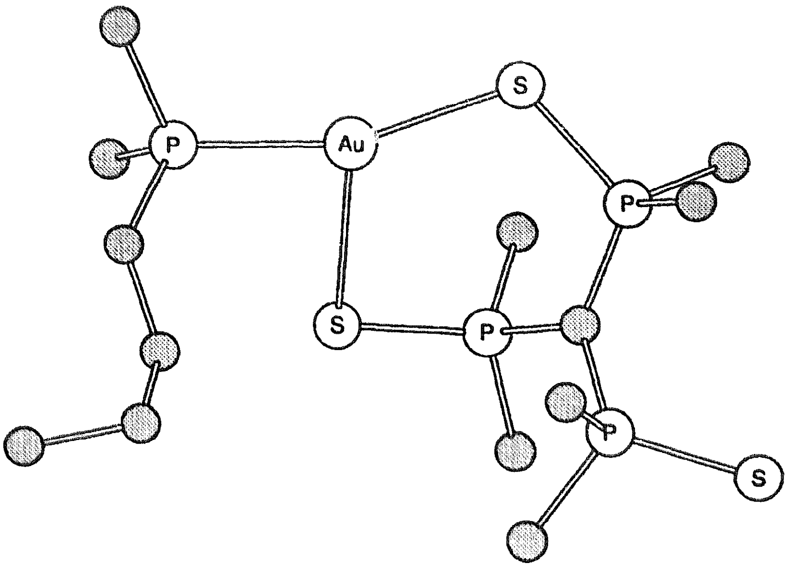
The reactions of $[R_3PAuCl]$ ($R_3 = Ph_3$, $MePh_2$ or Me_2Ph) with selenourea have been investigated and the products have been characterised by elemental analysis and ^1H and ^{31}P NMR spectroscopies. The crystal structure of the related *N,N'*-dimethylthiourea complex $[Ph_3PAu\{SC(NHMe)_2\}]Cl \cdot SC(NHMe)_2$ has been determined and in the cation, the gold(I) centre is in the expected linear coordination

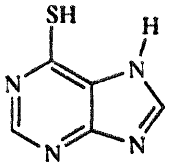


Only the *ipso*-C atoms of the Ph rings are shown.

(11)

environment [31]. The coordination of the conjugate base of $HC\{P(S)Ph_2\}_3$, HL, to the gold(I) centre in $[(^nBuPh_2P)AuL]$ (**11**) takes place through two of the sulfur-atoms with an S–Au–S angle of 104.5° within the chelate ring [32]. Compounds of the type $[(Ph_2P(CH_2)_nPPh_2)(AuS_2CNR_2)_2]$ where $n=1$, 2 or 3 and R = Et or Cy have been prepared and characterised spectroscopically. The dithiocarbamate ligands bind to the gold(I) centres in a monodentate fashion and this has been confirmed by an X-ray diffraction study of $[(dppe)(AuS_2CNR_2)_2]$ in which the dppe ligand is in an extended conformation supporting the gold(I) centres at significant separation [33]. Complexes of the general type $[(R_3P)_2AuS_2COR']$ where R = Ph or C_2H_4CN have been prepared and, for R′ = Et, characterised by X-ray diffraction methods; the gold(I) centre in each is in a distorted tetrahedral coordination sphere and for $R = C_2H_4$, the P–Au–P angle is 145.2° while angle S–Au–S is 63.2°. The electronic structure of these systems has been probed by use of extended Hückel and Fenske-Hall SCF MO calculations and results indicate that bending at the gold(I) centre activates it towards reactions with nucleophiles. The UV–VIS spectra of the complexes $[(R_3P)_2AuS_2COR']$ exhibit a relatively intense absorption at 306 nm ($\epsilon = 1.5-3.0 \times 10^4$ M^{-1} cm^{-1}) and a weak absorption at 390 nm ($\epsilon = 100$ M^{-1} cm^{-1}) and changes in the electronic spectra as a function of R′ have been discussed. It has been proposed that the luminescent properties of the complexes (in solution and the solid state) arise from ligand excitation ($n \rightarrow \pi^*$) [33a].

A number of gold(I) complexes containing sulfur-containing heterocyclic ligands were reported during 1994. The monohydrate of bis(1,3-thiazolidine-2-thione)gold(i) chloride has been structurally characterised; in the cation, the two thione ligands are *S*-coordinated with an S–Au–S angle of 176.4°. The electronic structure of the cation has been investigated at the extended Hückel level and the structural consequences of hydrogen-bonding in this and related systems have been explored [34]. The conjugate base of ligand HL (**12**) features in a series of gold(I) complexes of the type $[R_3PAuL]$ ($R=Ph$, Et, Cy, $2\text{-}MeC_6H_4$, $3\text{-}MeC_6H_4$ or $4\text{-}MeC_6H_4$, or $R_3=PhMe_2$), [ClAu(dppe)AuL], [ClAu(dppp)AuL], [(dppm)-Au_2L_2], [(dppe)Au_2L_2] and [(dppp)Au_2L_2]. Their syntheses and IR and NMR spectroscopic properties have been described, and a crystallographic investigation of $[Ph_3PAuL]\cdot EtOH$ has been carried out. The ligand L^- binds to gold(I) through the thiolate moiety and the coordination geometry is linear as expected. The compounds have been tested in rats for their anti-arthritic activity and the results are encouraging [35].



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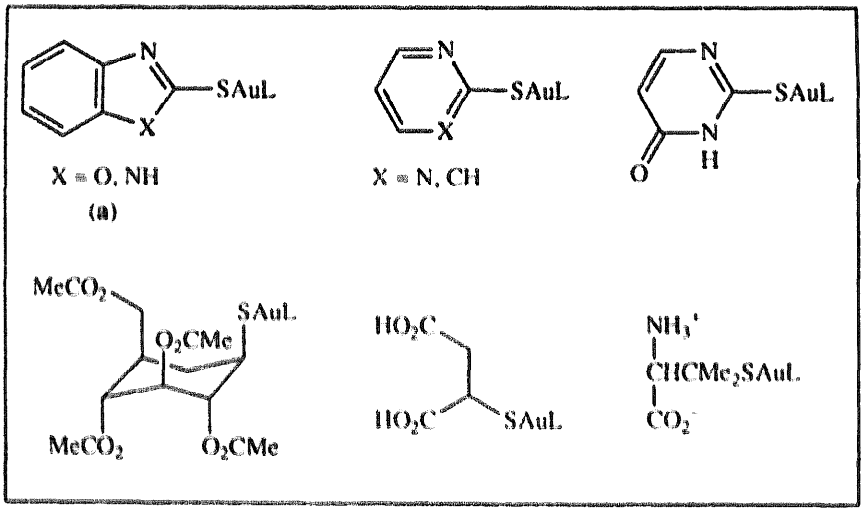

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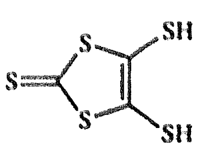

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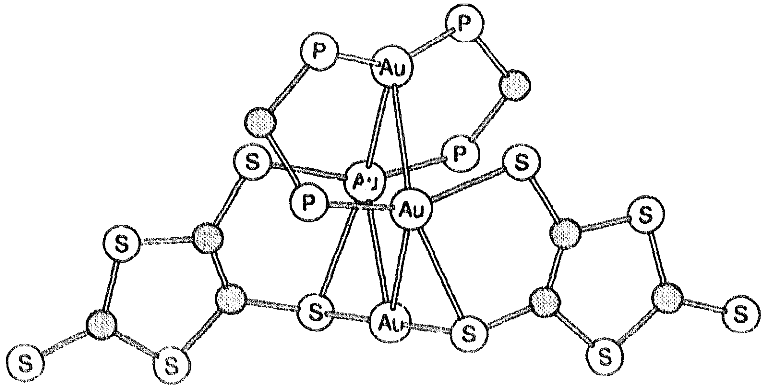
Mass spectrometric data for complexes formed between $[Ph_3AsAuCl]$ or $[Ph_3PAuCl]$ and the anions of 2-mercaptopyridine or thiophene have been analysed as well as those for complexes involving furan and derivatives of pyrazole; evidence for multinuclear species has been presented [36]. The reactions between $[(Ph_3P)_2N][Au(acac)_2]$ and the ligands HL lead to the formation of complexes

$[(Ph_3P)_2N][AuL_2]$ where HL is $HOCH_2CH_2SH$ or is as defined in structures (**13**) in which the anions $[AuL_2]^-$ are shown. The anticipated linear S–Au–S coordination sphere has been confirmed for complex (**13a**) with X = O by the results of an X-ray diffraction study [37]. The reaction of $[Ph_3PAuCl]$ with $[Et_4N]_2[ZnL_2]$ in which H_2L = (**14**) has been reported to yield the digold complex $[(Ph_3PAu)_2L]$ in which the two gold(I) moieties are bound to the two thiolate groups. This complex may also be prepared by adding 2 equivalents of PPh_3 to $[(Ph_3As)Au_2L]$, itself made by treating $[Et_4N]_2[ZnL_2]$ with $[Ph_3AsAuCl]$. A means of increasing the nuclearity of the complex is found in the reaction of $[(Ph_3PAu)_2L]$ with $[Ph_3PAu][ClO_4]$ which yields $[(Ph_3PAu)_3L][ClO_4]$ in which ligand L^{2-} forms S–Au bonds through the two thiolate sulfur donors and the thione group. A tetragold complex (**15**) is formed when $[Et_4N]_2[ZnL_2]$ reacts with $[dppm(AuCl)_2]$ and the structures of the tri- and tetragold products have been confirmed by X-ray diffraction studies. All complexes have been characterised from spectroscopic and mass spectrometric data [38].



Only the PCP-backbone of each dppm ligand is shown.

(**15**)

3.4. Complexes with selenium- or tellurium-donor ligands

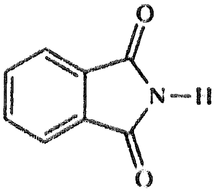
Gold(I) phosphine chlorides ($PR_3 = PPh_3$, $PMePh_2$ or PMe_2Ph) have been reacted with R'_2Se_2 ($R' = CH_2Ph$, Ph, naphthyl, $C_6H_4NH_2$-4 or C_6H_4Cl-4) and silver hexafluoroantimonate to give the salts $[(R_3P)_2Au(SeR')][SbF_6]$ for which ^1H and ^{31}P NMR spectroscopic and mass spectrometric data have been reported. The reaction of $PhSeSiMe_3$ with $[dppe(AuCl)_2]$ has given the complex $[dppe(AuSePh)_2]$ and for this species, the ^{77}Se NMR spectrum has been recorded. Representative complexes have been structurally characterised and in each, short Au···Au contacts have been observed [39]. Tellurium-containing complexes have been prepared by the reaction of $[\{(2,4,6\text{-}Ph_3C_6H_2)Te\}_2]$ with a source of $[Ph_3PAu]^+$ and subsequent oxidation with I_2; see also Section 2.4. The first gold(I) complex $[(2,4,6\text{-}Ph_3C_6H_2)Te(AuPPh_3)_2]^+$ has been isolated as the $[PF_6]^-$ salt and a crystallographic investigation has revealed a pyramidal tellurium centre (Te–Au = 259.1 and 257.8 pm) and gold atoms that are within bonding contact (295.3 pm) [13].

3.5. Complexes with nitrogen- or N,C-donor ligands

The high-yield synthesis of the complex $[Au(NCPh)_2][BF_4]$ has been detailed; the method involves the reaction of metallic gold with $[NO][BF_4]$ in PhCN under reflux. The synthetic utility of $[Au(NCPh)_2]^+$ lies in the labile nature of the benzonitrile ligands and its applications have been exemplified [40]. The preparation and crystal structure of the azine complex $[(C_6F_5)Au(Ph_2C{=}NN{=}CPh_2)]$ have been reported; the gold(I) environment is linear as expected with the azine ligand acting in a monodentate fashion. The precursor to $[(C_6F_5)Au(Ph_2C{=}NN{=}CPh_2)]$ was $[(C_6F_5)Au(SC_4H_8)]$, and further reactions of this complex with diazoalkanes have also been investigated [6].

The gold(I) complex $[Ph_3PAuL]$ where HL = (**16**) has been prepared by using $[\{Ph_3PAu\}_3O][BF_4]$ as the aurating agent. Characterisation of $[Ph_3PAuL]$ has included structural determinations of this and the solvate $[Ph_3PAuL]\cdot CHCl_3$. Linear gold(I) coordination spheres are observed with Au–N distances in the range previously reported for electron-withdrawing RR′N-substituents [41]. The single crystal structure of $[Ph_3PAuL]$ [HL = (**16**)] has been independently determined by Kuz'mina [42].

Members of a series of complexes of the type $[\{LAuX\}_2]$ [L = (**17**); X = Cl, Br]



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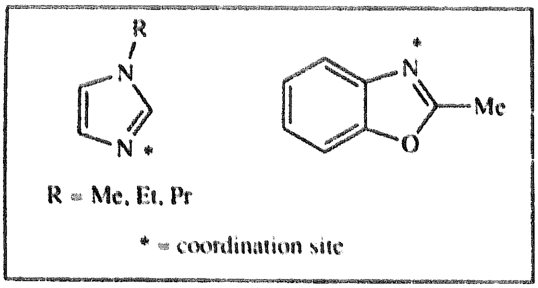

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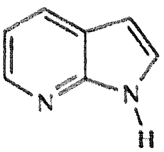
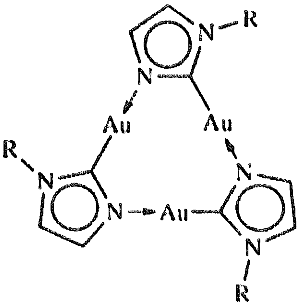


(18)

have been prepared from [$(Me_2S)AuCl$]. The products have been characterised by elemental analyses and IR, Raman and ^1H NMR spectroscopies; the ligands bind through a single nitrogen donor atom [43]. The synthesis of the complex [Ph_3PAuL] for which HL is (**18**) has been described along with its spectroscopic (UV–VIS, ^1H NMR and emission) characterisation. Photoluminescence was observed for this gold(I) species and also for the heterometallic complex [$Ph_3PAu(\mu\text{-}L)Cu(\mu\text{-}L)_2Cu(\mu\text{-}L)AuPPh_3$]. The crystal structures of both complexes have been determined and linear coordination geometries for the gold(I) centres have been confirmed; in the mixed metal compound, each copper(I) centre is 3-coordinate and each L^- ligand is in an *N*,*N'*-bridging mode [44]. Gold-197 Mössbauer spectroscopy has been used to investigate the reactivity of complex (**19**). With reagents which may undergo oxidative addition, (**19**) gave either gold(III) or mixed compounds or gold(I) carbene species; the work also includes an X-ray diffraction study of a gold(I)/gold(III) species formed by the addition of an equivalent of I_2 to (**19**) [45].



R = benzyl

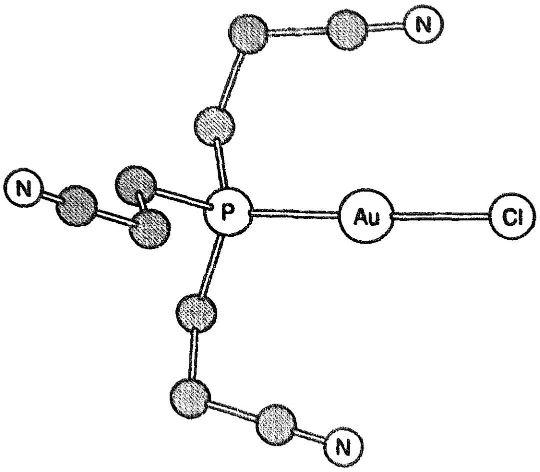
(**19**)

3.6. *Complexes with phosphorus-donor ligands*

Crystal structure determinations of simple complexes of the type [R_3PAuCl] continue to appear and this year are exemplified by those of [$(4\text{-}MeC_6H_4)_3PAuCl$] [46] and [$Me_3PAuCl$] and [$^iPr_3PAuCl$] [47]. In the solid state, molecules of [Me_3PAuCl] form helical chains by virtue of Au···Au contacts in the range 327.1 to 338.6 pm. The lack of such an extended array in [$^iPr_3PAuCl$] has been attributed to the greater steric bulk of the $^iPr_3P$ versus Me_3P substituents. Crystallographic structural determinations of [$(Me_3P)_2Au]Cl \cdot 2CHCl_3$ [47], [$(^nBu_3P)_2Au][BPh_4]$ [48] and [$(^tBu_3P)_2Au]Cl$ [49] have also been reported. In [$(Me_3P)_2Au]Cl \cdot 2CHCl_3$, the solvent molecules lie between layers composed of the gold(I) complex; the P–Au–P coordination sphere is approximately linear with the Au···Cl contact of 316.7 pm such that the Cl–Au–P angles are close to 90°. The complex [$(^tBu_3P)_2Au]Cl$ was prepared from the reactions of labile gold(I) species with the phosphine or between [$^tBu_3PAuCl$] and $Na[BH_4]$; the [$(^tBu_3P)_2Au]^+$ cations and Cl^- anions are well separated in the solid state.

The reduction of $Na[AuCl_4]$ by thiodiglycol followed by reaction with $Ph_2PCH_2NPh_2$ has been reported as one method of preparing $[(Ph_2PCH_2NPh_2)_2AuCl]$; alternatively, the complex may be obtained by treating $[Ph_3PAuCl]$ with $Ph_2PCH_2NPh_2$. The compound $[(Ph_2PCH_2NPh_2)_2AuCl]$ has been characterised by elemental analysis, ^{31}P and ^{13}C NMR spectroscopies and a crystallographic study. Each $Ph_2PCH_2NPh_2$ ligand coordinates through the phosphorus atom and the gold(I) centre is in a T-shaped environment with a P–Au–P angle of 173.2°. The Au–Cl distance is 295.1 pm, which is significantly shorter than that reported for $[(Me_3P)_2AuCl]$ (see above). Variable temperature ^{31}P NMR spectra over the range 323 to 213 K are consistent with the possible presence of the cation $[(Ph_2PCH_2NPh_2)_2Au]^+$ in addition to the 3-coordinate $[(Ph_2PCH_2NPh_2)_2AuCl]$ complex [50]. Like $Ph_2PCH_2NPh_2$, the ligand $N(CH_2PPh_2)_3$ is potentially both a nitrogen and phosphorus donor, but shows a preference for coordination through phosphorus to gold(I). It reacts with [(tht)AuX], $[Ph_3PAuX]$ or $[\{P(CH_2CH_2CN)_3\}AuX]$ ($X = NO_3$, PF_6 or BPh_4) to give the 3-coordinate complexes $[Au_2\{N(CH_2PPh_2)_3\}_2][BPh_4]_2$, $[Au\{N(CH_2PPh_2)_3\}][PF_6]$ or $[Au\{N(CH_2PPh_2)_3\}][NO_3]$. Structural characterisations have confirmed the natures of these gold-containing species; the monogold species luminesces brilliantly when subject to UV radiation [51]. The same research group has reported the crystal structure of $[\{P(CH_2CH_2CN)_3\}AuCl]$ and has revealed the presence of two polymorphs differing in the conformations of the CH_2CH_2CN chains. In one polymorph, one nitrogen atom approaches relatively closely to the gold(I) centre whilst in the second, (**20**), two nitrogen atoms do so [52]. The preparation of ligand (**21**) and its reaction with $[Me_2SAuCl]$ have been described. The gold(I) complex formed has been fully characterised and the ligand bonds to the metal centre through the phosphorus donor atom [53]. The potential uses of (**21**) as both a phosphorus and nitrogen donor ligand have been noted and the ligand has been incorporated into the tetragold complex $[L_3AuAu\{\mu\text{-}S_2C{=}C(CN)_2\}_2AuAuL_3]$ where L = (**21**); this complex luminesces strongly upon UV radiation. The bonds between the L_3Au^+ units and the dinuclear core have been described in terms of Lewis acid-base interactions [54]. Reactions between the complex $[\{P(CH_2OH)_3\}AuCl]$ and various nucleoside ligands, Nuc^-, in ethanol in the presence of $AgNO_3$ have been reported to yield water-soluble complexes of the type $[\{P(CH_2OH)_3\}Au(Nuc)]$ [55].

The digold complex $[\{(Z)\text{-}Ph_2PCH{=}CHPPh_2\}Au_2Cl_2]$ reacts with Na_2L $[H_2L = (NC)(HS)C{=}C(SH)(CN)]$ to give a tetragold complex (**22**) in which one gold centre is in an organometallic environment but three are coordinated by phosphorus-donors of $(Z)\text{-}Ph_2PCH{=}CHPPh_2$ ligands. The product has been characterised spectroscopically, mass spectrometrically and crystallographically [56]. Gold(I) complexes of the didentate ligand dppf have been described in previous reviews in this series. When $[(dppf)Au_2Cl_2]$ reacts with an equivalent of dppf, an intermediate complex [(dppf)AuCl] forms which readily polymerises. The presence of a zig-zag chain in the solid state has been revealed by a crystal structure analysis. A further species $[Au_2(dppf\text{-}P,P')_2(\mu\text{-}dppf)][NO_3]_2 \cdot 2H_2O$ has also been reported. In both complexes, there are no significant intramolecular nor intermolecular gold–gold interactions [57]. The chemistry of the didentate ligand $1,2\text{-}(PPh_2)_2C_2B_{10}H_{10}$,



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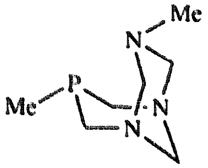

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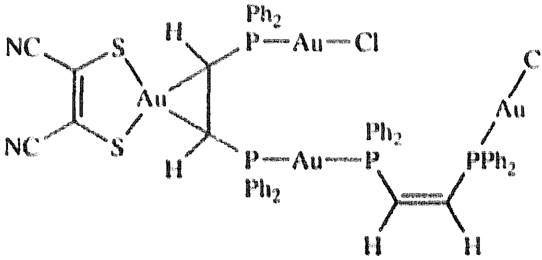
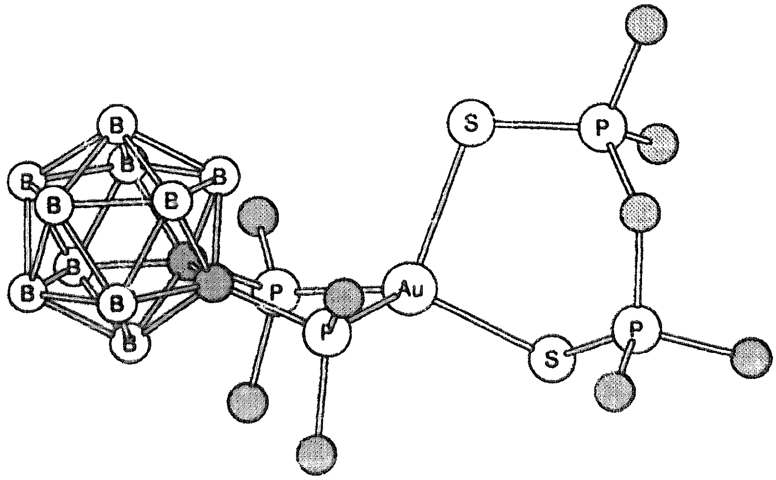


(22)

L, has been developed with the reactions of [LAu(tht)]$^+$ with dppe, 1,2-(PPh$_2$)$_2$C$_6$H$_4$, (Z)-Ph$_2$PCH=CHPPh$_2$, Ph$_2$P(S)CH$_2$P(S)Ph$_2$ and Ph$_2$P(S)NHP(S)Ph$_2$. Displacement of the tht ligand leads to the formation of 4-coordinate gold(I) complexes in which ligand L remains as a chelating ligand. The product of the reaction with Ph$_2$P(S)CH$_2$P(S)Ph$_2$ is shown in structure (23) and an X-ray diffraction study has confirmed a tetrahedrally coordinated gold(I) centre. Each of the new complexes exhibits a high thermodynamic and kinetic stability in solution [58].



Only the *ipso*-C atoms of the Ph rings are shown.

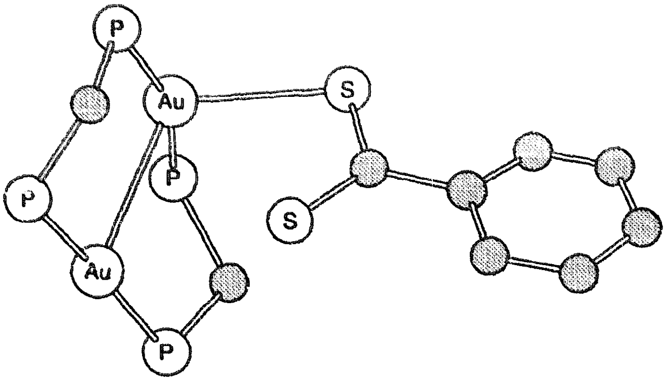
(23)

4. Dinuclear 'A-frame' and related polynuclear complexes

Although not an 'A-frame' complex, the model species $\{(PH_3)AuX\}_2$ (X = various) is representative of the types of complexes discussed in this section. A theoretical study has addressed the so-called 'aurophilic' attraction as a function of group X. The attraction was found to increase for X in the order F < Me < Cl < Br < SMe with a calculated value of 25 kJ mol^{-1} for the softest ligand [59].

The crystal structure of the monoclinic phase of the complex $[Au_2(dppm)_2]Cl_2 \cdot 2MeCN$ has been elucidated; the molecule contains a crystallographic inversion centre and the Au···Au distance is 299.4 pm [60]. A longer Au···Cl separation was observed in this structure than in the triclinic phase of the complex previously reported. The preparation and characterisation of the complex $[Au_2(dppm)_2(PhCS_2)]Cl$ have been reported. The structure of the cation (confirmed from the results of an X-ray diffraction study of the chloride salt) is shown in **(24)** and shows that the $[PhCS_2]^-$ ligand essentially bridges the Au–Au unit but with only one Au–S interaction that is bonding; the Au–S and Au′–S′ distances are 271.8 and 315.3 pm [61].

The reaction between hydrated chloroauric acid and dppm in ethanol has produced the trinuclear complex $[Au_3(dppm)_2Cl_2]Cl$ which establishes an equilibrium in solution with $[Au_2(dppm)Cl_2]$ and $[Au_2(dppm)_2Cl_2]$. A variable temperature ^{31}P NMR spectroscopic study of this system has given insight into the relative exchanges between the species present in solution. The emission properties of $[Au_3(dppm)_2Cl_2]Cl$ have been discussed and its strong emission is attributed to interactions between the gold centres [62]. The application of a luminescent coordinatively unsaturated polynuclear d^{10} polymetallic species as a DNA photocleavage agent has been demonstrated; the complex cation under study was $[Au_3(dmmp)_2]^{3+}$ where dmmp = $Me_2PCH_2P(Me)CH_2PMe_2$ [63]. The complexes $[Au_2(dppm)(CH_2PPh_2CH_2)]^+$, $[Au_2(dppe)(CH_2PPh_2CH_2)]^+$ and



Phenyl groups have been omitted from the PPh_2 groups.

(24)

$[Au_2(Ph_2PNHPPh_2)(CH_2PPh_2CH_2)]^+$ are three of a larger group of heterobridged digold complexes that have been prepared from $[Au_2(CH_2PPh_2CH_2)_2]$ [64]. The oxidative addition of Cl_2 or Br_2 to the tetranuclear complex $[\{(C_6F_5)Au\}\{HC(PPh_2)_2\}Au_2\{(PPh_2)_2CH\}\{Au(C_6F_5)\}]$ has been described; treatment of the chloro-derivative with $[Ph_3PAgOClO_3]$ has resulted in the formation of a product in which three of the four gold centres are arranged in a linear chain within which it is not possible to assign integral oxidation states. Similar reactions with $[LAgOClO_3]$ where L = tht, $PMePh_2$ or $P(C_6H_4Me)_3$ have also been studied [65]. The reactions between $[Au_2(\mu\text{-}L)_2Cl_2]$ (L = dppe, dppb, (*Z*)-$Ph_2PCH{=}CHPPh_2$ or $Ph_2AsCH_2CH_2PPh_2$) and $K_2[S_2C{=}C(CN)_2]$ have yielded heterobridged complexes of the type $[Au_2(\mu\text{-}L)\{\mu\text{-}S_2C{=}C(CN)_2\}]$. The crystal structure of $[Au_2\{\mu\text{-}(Z)\text{-}Ph_2PCH{=}CHPPh_2\}\{\mu\text{-}S_2C{=}C(CN)_2\}]$ has been determined and an Au···Au distance of 286.7 pm is consistent with a degree of bonding interaction [66].

The rates of electron transfer from the electronically excited $[Au_2(Cy_2PCH_2CH_2PCy_2)_3]^{2+}$ to *N*-alkylpyridinium acceptors have been determined in MeCN solution at 298 K by a quenching technique. The quenching rates increase with the reaction driving force but reach a limiting value. Related studies involving $[Ir_2(1,5\text{-cod})_2(\mu\text{-pyrazolyl})_2]$ have also been carried out [67].

5. Gold clusters

5.1. *Theoretical studies*

An investigation of the gold–gold interactions in the model compounds $\{(PH_3)AuX\}_2$ was mentioned in the previous section [59]. The isolation of the tetragold cluster $[Au_4(P^tBu_3)_4]^{2+}$ has prompted a theoretical investigation of this system and calculations have been carried out using quasi-relativistic and relativistic versions of the LCAO-SCF MO method at the non-empirical CNDO/1 level. The significant effects of phosphine coordination to the bare Au_4 cluster have been discussed; it has been noted that PH_3 is a poor model for P^tBu_3 and other ligands since PH_3 is not able to model adequately the donor properties of the larger phosphines [68]. MO calculations at the extended Hückel level have been carried out on $Au_4(PR_3)_4I_2$ and strong Au–Au interactions have been evidenced. When a main group atom, E, is introduced into the gold cluster, e.g. to give a species of the type $X_nE\{AuPR_3\}_m$, electron transfer between the metal and main group fragments occurs and gold–gold interactions are reduced. In the C_{4v} $[As\{AuPR_3\}_4]^+$ cation, close Au–Au contacts and relatively strong interactions are possible [69].

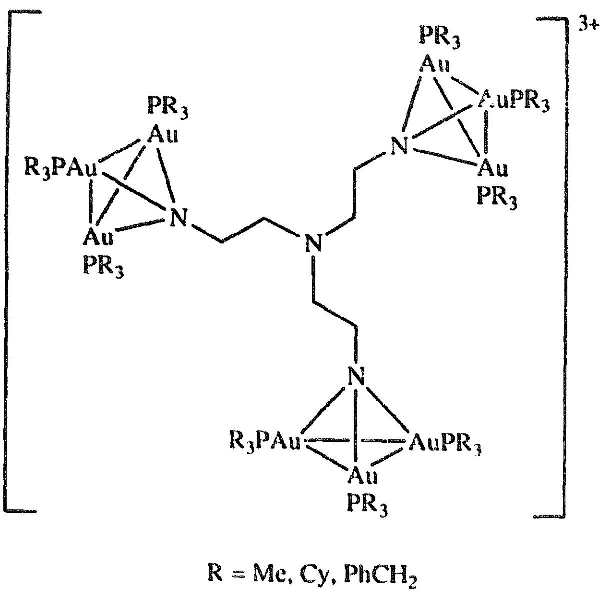
5.2. *Clusters containing a central p-block atom*

The reaction of six equivalents of $[Me_3PAuCl]$ with two equivalents each of silver(I) oxide and sodium tetrafluoroborate leads to the formation of the tetrafluoroborate salt of $[(Me_3PAu)_6O_2]^{2+}$ in high yield. Crystallographic studies have revealed that the cation consists of two Au_3O-cores with two of the gold centres in each core combining to give an Au_4-tetrahedron that is central to the $[(Me_3PAu)_6O_2]^{2+}$ system [70]. The reaction between $(Me_3Si)_2S$ and $[(Me_3PAu)_3O]^+$ has provided a route to the sulfur-centred cluster $[(Me_3PAu)_3S]^+$ which has been isolated as the tetrafluoroborate salt. Analogous reactions with $[(^iPr_3PAu)_3O]^+$ and $[(MePh_2PAu)_3O]^+$ have also been carried out. The structures of all three products have been confirmed by X-ray diffraction investigations and show pairwise cation-interactions via Au···S interactions. In $[(Me_3PAu)_3S]^+$, aggregation is extended further to give chains in the solid state [71]. The compound $[(Ph_3PAu)_4S][CF_3SO_3]$ has been prepared by the reaction of $[(Ph_3PAu)_2S]$ with two equivalents of $[Ph_3PAu(O_3SCF_3)]$ in dichloromethane. In the ^{31}P NMR spectrum, one resonance was observed. A crystal structure determination showed that the sulfur atom caps the four gold centres with angles Au–S–Au in the range 73.5 to 75.6°. The gold atoms define a butterfly shape with Au···Au separations between 288.3 and 293.8 pm and an internal dihedral angle of 150°. In the solid state, the cations are paired by virtue of Au···S interactions [72].

Dendritic systems have been prepared by the reactions between $[(Ph_3PAu)_3O]^+$ and the amines $RN(CH_2CH_2CH_2NH_2)_2$ (R = Me, Cy, $PhCH_2$) or $N(CH_2CH_2NH_2)_3$ in thf. The isolated products include salts of the cations (**25**) and have been characterised by elemental analyses, mass spectrometry and NMR spectroscopy. The crystal structure of $[(\mathbf{26})][BF_4]\cdot$thf, (crystallised from a product of degradation), has been determined, confirming the presence of a Au_3N-cluster unit [73].

5.3. *Polynuclear clusters*

The synthesis of an octagold cluster with an unusual core-structure has been described: $[Au_8L_6]^{2+}$ (**27**) [L = P(Mes)$_3$] forms when $[(LAu)_3O]^+$ or $[(LAu)_2OH]^+$ reacts with carbon monoxide. Other products include $[(LAu)_4]^{2+}$. The tetrafluoroborate salts of $[Au_8L_6]^{2+}$ and $[(LAu)_4]^{2+}$ have been characterised in solution by ^{31}P and ^1H NMR spectroscopies and in the solid state by X-ray diffraction methods.



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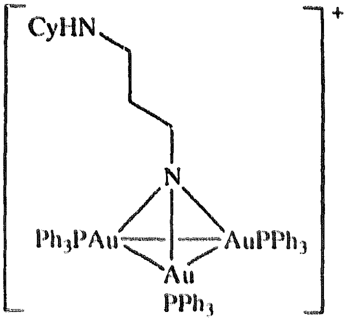
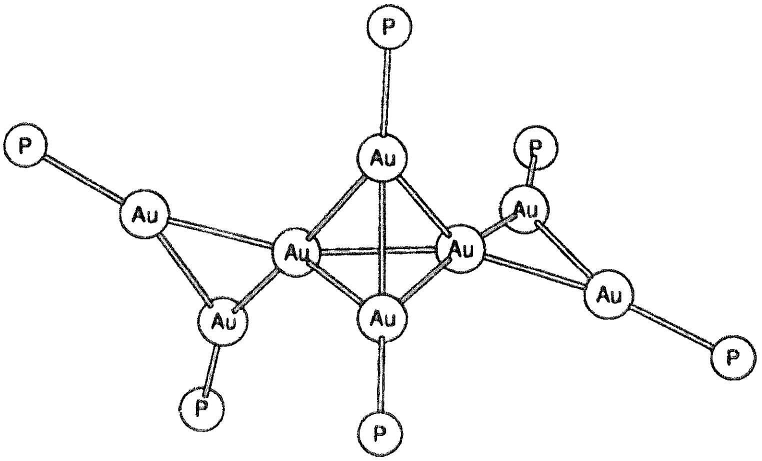


(26)

A tetrahedral Au_4-core features in both cations, with two vertex-fused Au_3-units increasing the nuclearity to eight in the larger cluster [74].

The contributions of Pignolet and coworkers to this area have included the reaction of metallic mercury with $[Ph_3PPt(AuPPh_3)_6][NO_3]_2$ to yield $[Ph_3PPt(AuPPh_3)_6(HgNO_3)][NO_3]$; halide-for-nitrate exchange results in the formation of the cations $[Ph_3PPt(AuPPh_3)_6(HgX)]^+$ (X = Cl, Br, I) and treatment of $[Ph_3PPt(AuPPh_3)_6(HgNO_3)]^+$ with CO leads to the formation of $[Ph_3PPt(AuPPh_3)_6(CO)]^{2+}$. When the cation $[Ph_3PPt(AuPPh_3)_6(HgNO_3)]^+$ reacts with $Na[Co(CO)_4]$, the product is the cluster $[Ph_3PPt(AuPPh_3)_6HgCo(CO)_4]^+$. The characterisations of the products have included the X-ray crystal structure of $[Ph_3PPt(AuPPh_3)_6(HgNO_3)][NO_3]$ and these results show that the octametal-core possesses an unusual shape which lies between the limits of a cube and a geometry derived from a fragment of an icosahedron [75]. Studies on a series of platinum–gold and palladium–gold clusters have concluded that these systems are excellent catalysts for H_2/D_2 equilibration (to form HD) [76]. Related, but independent, studies have



Mesityl groups have been omitted.

(27)

focused on the reaction of $[HPt(AuPPh_3)_7][NO_3]_2$ with $[Ph_3PAg][NO_3]$. After treatment with sodium chloride, the isolated cluster species was $[Pt_2(AuPPh_3)_{10}Ag_{13}Cl_7]$ which has been characterised by FAB-MS, IR and ^{31}P NMR spectroscopies, cyclic voltammetry and an X-ray diffraction analysis. The cluster core consists of two, platinum-centred icosahedral units which share a common silver atom [77]. It has been reported that triphenylphosphine gold(I) azide and chloride react together with $[(dppe)Pd(N_3)_2]$ to yield the cluster $[(Ph_3PAu)_6(dppeAu_2)(AuCl)_4Pd]$ with the elimination of N_2 and PPh_3. Fast atom bombardment mass spectrometry was used to establish the nuclearity of the product and this has been confirmed by the results of a crystallographic study. The core-structure consists of a palladium-centred icosahedron. It is significant that during the reaction, the dppe ligand is transferred from the palladium to the gold centres although the presence of a didentate ligand is not a requirement for the assembly of this cluster core. An analogous product has been obtained using $[(Ph_3P)_2Pd(N_3)_2]$ in place of $[(dppe)Pd(N_3)_2]$ [78].

The syntheses and structures of the compounds $[(Ph_3PAu)_6Co(CO)_2][PF_6]$ and $[(Ph_3PAu)_7Co(CO)_2][PF_6]_2$ have been described. The cluster precursor in each case was $[(Ph_3PAu)_4Co(CO)_3]^+$. Structural investigations have confirmed the cluster compositions. The core of $[(Ph_3PAu)_6Co(CO)_2]^+$ consists of a bicapped trigonal bipyramid while that of $[(Ph_3PAu)_7Co(CO)_2]^+$ is considered as a cobalt-centred fragment of an icosahedron [79].

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