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COORDINATION CHEMISTRY REVIEWS

Gold 1995

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Contents

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1. Introduction

This review covers the coordination chemistry of gold reported during 1995, and follows a similarly organised 1994 survey [1]. The literature has been searched using *Current Contents* and the Cambridge Crystallographic Data Base, implemented through the ETH, Zürich [2]; three-dimensional structural diagrams have been drawn using coordinates from the Cambridge Crystallographic Data Base, with hydrogen atoms generally omitted for clarity.

Some references from the tail-end of 1994 are included in this survey. The review is not fully comprehensive, but does give the reader a significant and representative coverage of work published; organometallic complexes (defined as those possessing

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a Au–C bond with the exceptions of cyano complexes, orthometallated species and several compounds incorporating {$Au-C_6F_5$} groups) have been excluded.

Complexes in this survey have been organised according to the oxidation of the gold centre and by the donor-type of the ligand of primary interest. In gold(I) complexes containing a $Au-P_{phosphine}$ link in combination with a different donor ligand, the latter takes priority for categorisation purposes. 'A-frame'-type complexes have been described in a separate section, as have gold-containing clusters, although polynuclear species in which the gold atoms are not within bonding contact are generally included in the appropriate gold(I) section with the emphasis put upon the ligand type rather than the polynuclear nature of the complex; organometallic clusters featuring $AuPR_3$-units have not been included in this survey.

2. Gold(III)

2.1. *Complexes with halide ligands*

A laboratory-scale preparative route to gold(III) fluoride from the constituent elements has been reported. The purity of the product was confirmed by vibrational spectroscopic, mass spectrometric and elemental analytical data [3].

The reaction of $K[AuCl_4]$ and 2,6-Ph_2py at pH 2 has given the complex [2,6-Ph_2pyH][$AuCl_4$] which has been characterised by elemental analysis, IR and ^1H NMR spectroscopies and an X-ray diffraction study. In the solid state lattice, an unusual three-centre interaction has been observed between the pyridinium N–H hydrogen atom and two of the chlorine atoms of the anion such that each H···Cl distance is 275.3 pm. Weaker C_{phenyl}–H···Cl interactions are also observed for the hydrogen atoms in the *ortho*-positions [4].

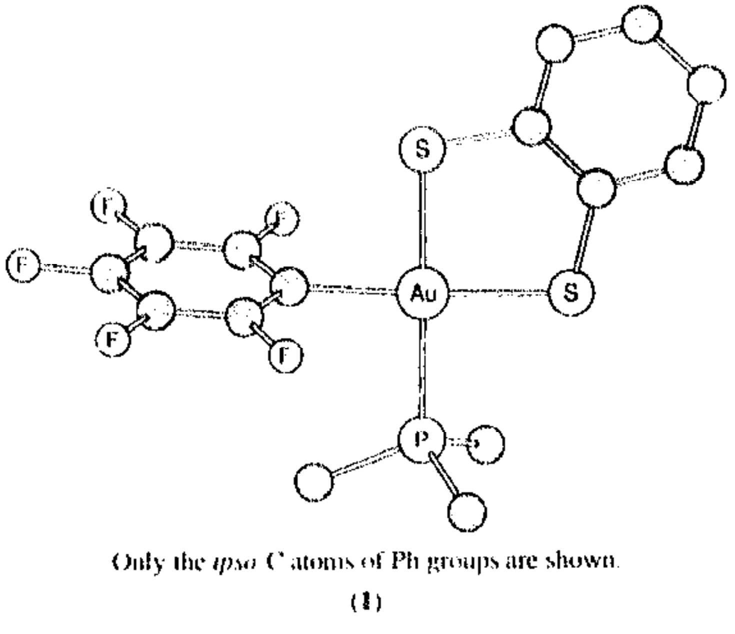
The kinetics of the reduction of $[AuCl_4]^-$, *trans*-$[AuCl_2(CN)_2]^-$ and *trans*-$[AuBr_2(CN)_2]^-$ by $SO_2 \cdot nH_2O$, $[HSO_3]^-$ or $[SO_3]^{2-}$ has been investigated using stopped-flow spectrophotometry over the pH range 0 to 2.3 and at ionic strength 1.0 M (298 K). It was shown that the reduction from gold(III) to gold(I) occurred without initial substitution at the metal centre when the gold(III):sulfur(IV) ratio was 1:1. Mechanistic details have been discussed and rate constants were determined for the reactions; the reductions occur ≈ 10^5 times faster with $[SO_3]^{2-}$ than with $[HSO_3]^-$, and the reduction of *trans*-$[AuBr_2(CN)_2]^-$ was ≈ 10 times faster than that of *trans*-$[AuCl_2(CN)_2]^-$ [5].

2.2. *Complexes with oxygen-donor ligands*

The application of benzo-15-crown-5 ether as an extracting agent for gold(III) in the presence of potassium chloride has been investigated [6].

2.3. Complexes with sulfur-donor ligands

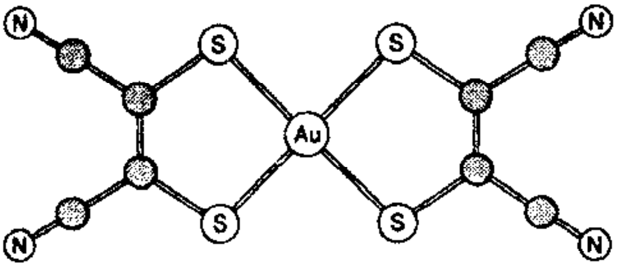
Two crystallographic studies detailing the structure of the anion $[Au(1,2\text{-}S_2C_6H_4)_2]^-$ have been carried out by the Fackler group. The first is of the $[(Ph_3P)_2N]^+$ salt [7] and the second of the $[Au(PEt_3)_2]^+$ salt [8]. The gold(III) environment is square planar as expected. Related work has looked at complex formation with gold(III) involving $[1,2\text{-}S_2C_6H_4]^{2-}$ and $[3,4\text{-}S_2C_6H_3Me]^{2-}$, (L^{2-}). The salts Na_2L were reacted in ethanol with Me_2SnCl_2 or $[(Ph_3P)_2N]_2[ZnCl_4]$ to give $[Me_2SnL]$ or $[(Ph_3P)_2N]_2[ZnL_2]$ respectively. A further tin derivative $[Me_2SnL']$ (H_2L' = 1,3-dithiole-2-thione-4,5-dithiol) has also been prepared and the tin and zinc complexes have been treated with *cis*-$[(C_6F_5)AuCl_2L'']$ (L″ = various including PPh_3) to yield gold(III) complexes of the type $[(C_6F_5)AuLL'']$. The structure of $[(C_6F_5)Au(1,2\text{-}S_2C_6H_4)PPh_3]$ (**1**) has been determined [9]. *Ab initio* calculations have been carried out on the $[Au(1,2\text{-}S_2C_6H_4)_2]^-$ anion. Results reveal that the two highest lying MOs possess π-character and originate from the symmetric and anti-symmetric combinations of the ligand HOMOs with little contribution from the gold atomic orbitals. The LUMO of $[Au(1,2\text{-}S_2C_6H_4)_2]^-$ possesses σ-character with both metal and ligand character. In addition to the theoretical study, the preparations of ten derivatives of $[Au(1,2\text{-}S_2C_6H_4)_2]^-$ have been described and their UV–VIS spectra have been recorded. From these data, it was possible to place the ligands in a spectrochemical series. The observed relationship between the electrode potentials for the reversible oxidations of the complexes and the energies of the lowest lying electronic transitions has been discussed in terms of the degree of ligand-to-metal charge transfer [10].



Only the *ipso* C atoms of Ph groups are shown.

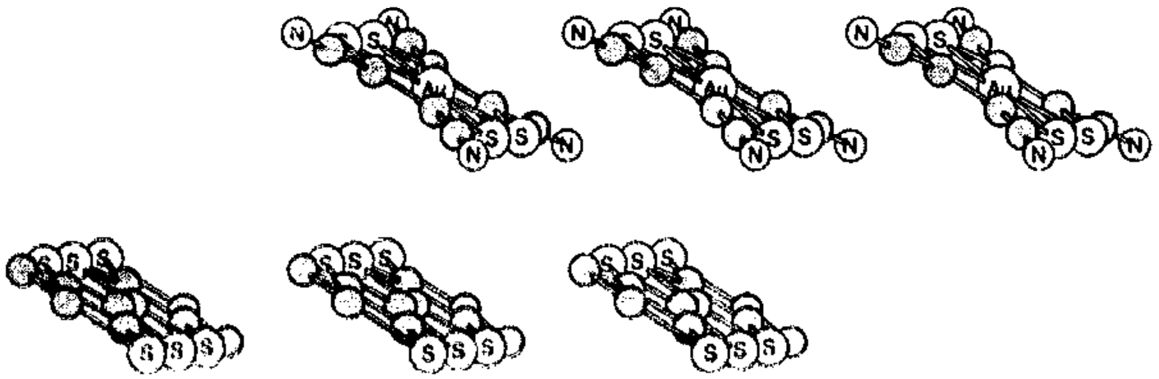
(**1**)

The results of the crystal structure determination of $[Au(PCy_3)_2][Au\{(Z)\text{-}1,2\text{-}S_2C_2(CN)_2\}_2]$ have been reported [11]. The square planar anion is shown in structure (**2**). The bis(ethylenethio)tetrathiafulvalenium salt of



(2)

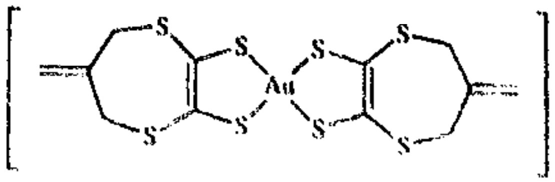
(**2**), compound (**3**), has also been the subject of a structural study. In the solid state, the anions and cations form separate stacks but planar anions do not lie directly over each other [12].



Part of the packing diagram

(3)

The synthesis of the ligand H_2L and its complex formation with gold(III) to give $[AuL_2]^-$, anion (**4**), have been reported. The new complex was isolated as the tetrabutylammonium salt and was characterised by mass spectrometry, elemental analysis, near-IR spectroscopy and X-ray crystallography. In the solid state, two different conformations are adopted by the ligand in the anion. An electrochemical investigation of $[Bu_4N][AuL_2]$ has shown that the gold(III) anion exhibits three irreversible processes. The properties of this compound have been compared with those of related nickel and copper complexes [13].



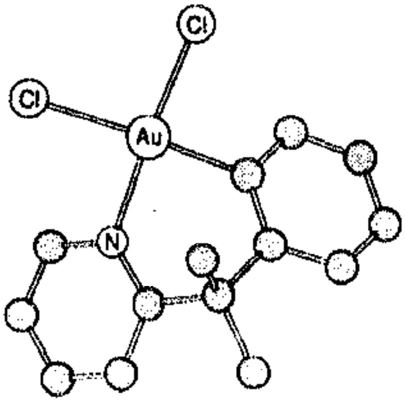
(4)

Heterometallic complexes of the type $[Cp^*M(\mu\text{-SR})_2AuCl_2]Cl$ (M = Ir or Rh; R = C_6F_5, C_6F_4H-4) involving gold(III) have been prepared and characterised. By-products of the syntheses were the gold-free complexes $[Cp^*_2Rh_2(\mu\text{-SR})Cl_2]Cl$.

The behaviour of the new complexes in solution has been studied [14]. Gold(III) and gold(I) complexes containing various sulfide ligands have been studied in solution by using dynamic NMR spectroscopic techniques in order to gain information about inversion at the sulfur centres. The results indicate that inversion occurs without Au–S bond cleavage. Kinetic parameters have been measured; the barrier to inversion at sulfur is higher for the gold(III) than the corresponding gold(I) complexes [15].

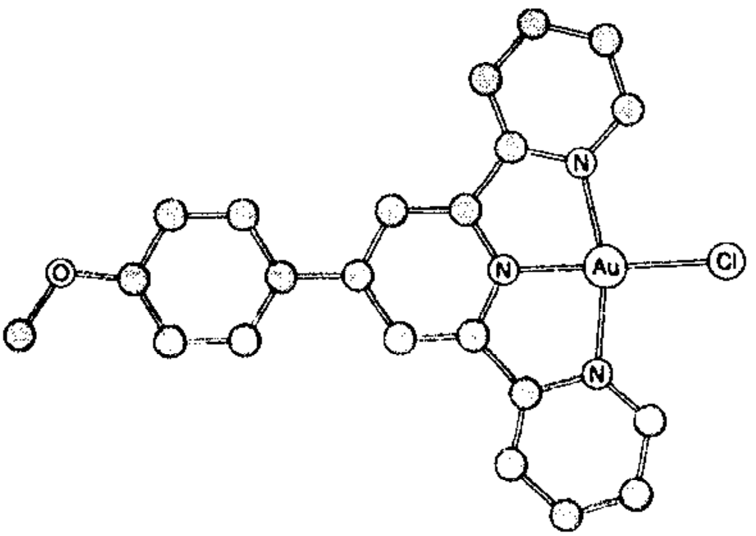
2.4. Complexes with nitrogen-containing ligands

The crystal structure of the complex [Au(bpy)Cl$_2$][BF$_4$] has been determined and confirms the expected square planar geometry at the gold(III) centre [16]. The reactions between AuCl$_3$.2H$_2$O or Na[AuCl$_4$] and HL (HL = 2-PhCR$_2$py, R$_2$ = H$_2$, MeH or Me$_2$) yield cyclometallated complexes [AuLCl$_2$] or adducts of formula [Au(HL)Cl$_3$]. When the pyridine derivatives were 2-^{t}Bupy or 2-^{t}BuCH$_2$py (HL), the products were the pyridinium salts [H$_2$L][AuCl$_4$]. The crystal structure of [AuLCl$_2$], complex (**5**), for HL = 2-PhCMe$_2$py, has been elucidated and confirms the coordination of ligand L$^-$ in an *N,C*-mode, with the 6-membered chelate ring adopting a boat-conformation. Reactions between PPh$_3$ or dppe and the cyclometallated complexes lead to the formation of [AuLCl(PPh$_3$)]$^+$ or [AuLCl(dppe)]$^+$ respectively. Insertion reactions involving carbon monoxide have also been discussed [17]. The syntheses of the luminescent compounds [AuLCl][CF$_3$SO$_3$] (L = 4′-(4-methoxyphenyl)-6′-phenyl-2,2′-bipyridine) and [AuL′Cl][ClO$_4$]$_2$ (L′ = 4′-(4-methoxyphenyl)-2,2′:6′,2″-terpyridine) have been described. Characterisations of these complexes have included an X-ray diffraction study of [AuL′Cl][ClO$_4$]$_2$ and the structure of the cation is shown in (**6**). A square planar environment for the gold(III) centre was confirmed. The interactions of the two complexes with calf-thymus DNA has been investigated using spectroscopic methods and it was found that the binding constant for [AuLCl][CF$_3$SO$_3$] is greater than that for the terpyridine-derived complex [18].



(**5**)

Gold(III) complexes [AuX$_3$L] (X = Cl or Br) containing heterocyclic ligands L (L = *N*-methylimidazole, *N*-ethylimidazole, *N*-propylimidazole, benzoxazole,



(6)

2,5-dimethylbenzoxazole, 2-aminopyrimidine, 4- or 6-hydroxypyrimidine or hypoxanthine) have been prepared and characterised by elemental analysis, and spectroscopic and conductivity methods. In each case, it was proposed that the gold(III) centre was in a square planar environment with the heterocyclic ligand *N*-bonded and monodentate [19]. Mixed ligand complexes of gold(III) involving anions of various amino acids, HL′, and the potentially *N,O*-donor ligand L where HL = 8-hydroxyquinoline have been prepared and characterised by spectroscopic techniques and conductivity methods. The complexes possess the general formula [AuLL′]Cl [20].

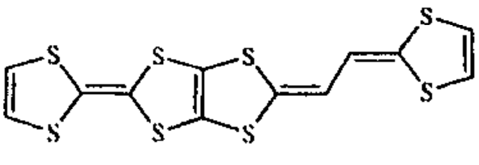
For gold(III) phosphorus coordination, see Section 3.5 and the discussion of ligand (**23**).

3. Gold(I)

3.1. Complexes with halide and pseudo-halide ligands

As part of a study of gold(I) phosphine complexes (see Section 3.5), a one-pot synthesis of the compound $[Bu_4N][AuI_2]$ from elemental gold has been described [21]. A crystallographic study of $[(Ph_3P)_2N][AuCl_2]\cdot CH_2Cl_2$ has been carried out at 173 K and has confirmed the expected linear nature of the anion [22]. A series of rod-like complexes of the type $[AuCl\{CNC_6H_4C_6H_4\text{-}4\text{-}OC_nH_{2n+1}\}]$ ($n = 4, 6, 8, 10, 12$) has been investigated. The chloro-complexes have been synthesised from [Au(tht)Cl] and the appropriate isonitriles, and may be converted to the corresponding bromo- or iodo-species. The free isonitriles are liquid crystals which exhibit nematic and (in some cases) smectic A phases, but as the gold(III) complexes, they show a significant expansion of the range in which the mesophase exists. The liquid crystal properties of the gold-containing complexes have been fully discussed [23].

The synthesis of ligand (7) has been described. Cation radical salts of (7) were prepared by electrochemical oxidation in the presence of, for example, $[Bu_4N][Au(CN)_2]$. The resistivity of $[(7)][Au(CN)_2]$ shows an abrupt drop at 4 K, thereby indicating the onset of a superconducting transition. However, the resistivity remained non-zero. The X-ray crystal structure of $[(7)][Au(CN)_2]$ revealed that in the solid state, the donor units form conducing sheets parallel to the *ac* plane [24].



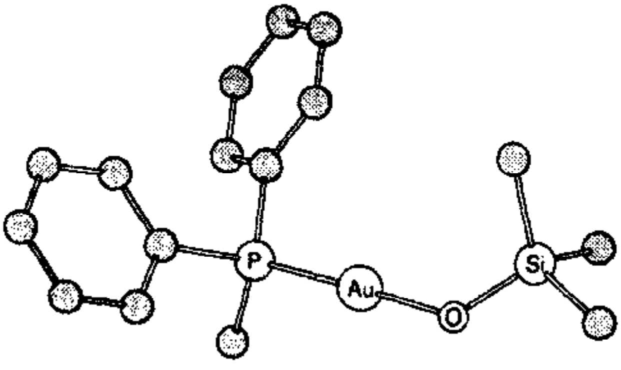
(7)

The laser excitation (at 337 nm) of the lead(II) compound $Pb[Au(CN)_2]_2$ at 78 K causes a decrease in the intensity of luminescence of this complex. By raising the temperature from 78 to 300 K, the luminescence intensity increases again. These observations have been interpreted in terms of the formation of a non-luminescent species and the process by which this occurs has been discussed [25]. The excited state properties of a series of layered compounds including $Dy[Au(CN)_2]_3$ and $Gd[Au(CN)_2]_3$ have been studied. The $[Au(CN)_2]^-$ anion exhibits a strong and structured emission at low temperatures, but emissions originating from the lanthanoid(III) ions are weak. Resonance Raman spectroscopic data have been recorded for $Dy[Au(CN)_2]_3$ and $Gd[Au(CN)_2]_3$. Detailed discussions of the photoluminescence studies have been presented [26].

Gold-binding and distribution in blood and red-blood cells have been the subject of a study that has employed HPLC techniques including ion-pairing, reversed-phase and size-exclusion chromatography. Preliminary results involving patients suffering from rheumatoid arthritis have indicated that gold-uptake is patient-dependent. It has also been shown that gold in the lysate is not bound to haemoglobin but interacts instead with higher molecular weight species. The anion $[Au(CN)_2]^-$ has been detected in ultra-filtered red-blood cell lysate, and the uptake of this gold(I) anion by red-blood cells has been measured. It has also been shown that $[Au(CN)_2]^-$ enters the cell by a path other that the anion channel. It was observed that the gold-uptake was inhibited by the addition of free $[CN]^-$ anion and this suggests that loss of $[CN]^-$ from $[Au(CN)_2]^-$ is important in the process of gold-uptake by red-blood cells. The possibility of using $[Au(CN)_2]^-$ for therapy in the treatment of AIDS has been suggested [27].

3.2. *Complexes with oxygen-donor ligands*

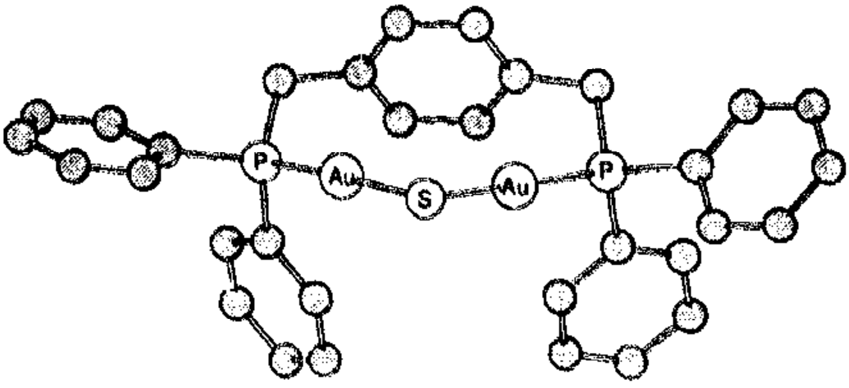
The crystal structure of the compound $[MePh_2PAu(OSiMe_3)]$ (8) has been determined; the structural features are unexceptional with an Au–O bond distance of 198.6 pm and a value for the angle O–Au–P of 177.9° [28].



(8)

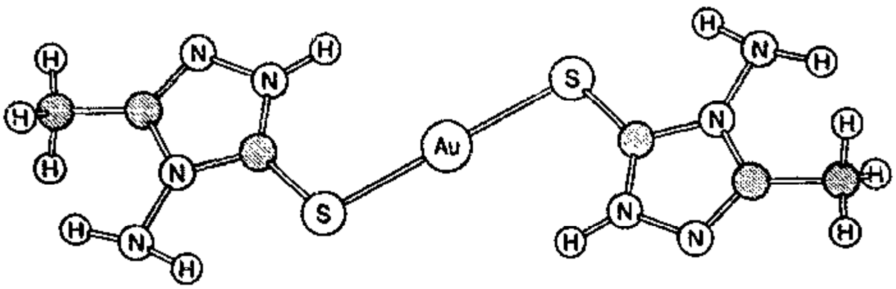
3.3. Complexes with sulfur- or selenium-donor ligands

A number of gold(I) complexes with thiolate ligands of various types have been reported. The reaction of $[(Ph_3P)_2N][Au(SH)_2]$ with CS_2 leads to the complex $[(Ph_3P)_2N][Au_2(CS_3)_2]$, described in Section 4 [29]. The reaction of $[ClAu\{1,4\text{-}(CH_2PPh_2)_2C_6H_4\}AuCl]$ (see Section 3.5) with NaSMe in $CHCl_3$ in the presence of moisture leads to the formation of the complex $[MeSAu\{1,4\text{-}(CH_2PPh_2)_2C_6H_4\}AuSMe]$. A crystal structure determination of this compound has confirmed the presence of two remote, linear gold(I) centres. When $[ClAu\{1,4\text{-}(CH_2PPh_2)_2C_6H_4\}AuCl]$ reacts with sodium sulfide under similar conditions, the product is the cyclic complex (**9**). The angle at the sulfur atom is 86.7° and the Au···Au distance is 314.7 pm [30]. Bulky thiolates have been incorporated into gold(I) complexes of the type $[Ph_3PAuSR]$ where $R = 2,4,6\text{-}Me_3C_6H_2$ or $2,4,6\text{-}{}^iPr_3C_6H_2$. Their preparations by two routes have been described for example, the reactions of $[Ph_3PAuCl]$ with RSH in thf in the presence of alcoholic KOH. The properties of these complexes have been discussed and an X-ray diffraction study of $[Ph_3PAuSC_6H_2{}^iPr_3\text{-}2,4,6]$ has been carried out [31].



(9)

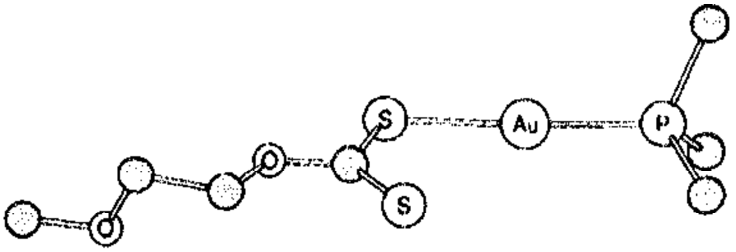
The crystal structures of the complexes $[(2\text{-}MeC_6H_4)_3PAuL]$ (HL = purine-6-thiol) and $[Cy_3PAuL']$ (HL′ = 6-methyl-2-thiouracil) have been determined. In each compound, the gold(I) centre is coordinated in a linear fashion as expected with the thionucleobases functioning as monodentate *S*-donor ligands [32]. Potentiometric



(10)

and spectrophotometric studies of the ligand 4-amino-3-methyl-1,2,4-triazoline-5-thione (HL) have established that in solution the thiol form predominates whilst in the solid state, the thione form is important. The gold(I) complex $[Au(HL)_2]Cl$ and its copper(I) analogue have been prepared and characterised by X-ray diffraction methods. In the cation $[Au(HL)_2]^+$ (**10**), the ligand is in the thione form and both ligand ring-systems lie in the same plane; the gold(I) centre is in a linear environment with Au–S = 227.6 pm [33].

Carbon-13 NMR spectroscopy has been used to study the interactions between aurothiomalate $[AuL]_n$ and $[SCN]^-$ and $[SeCN]^-$ ions in aqueous solution. The presence of $[SCN]^-$ results in further polymerisation of aurothiomalate but $[SeCN]^-$ coordinates to the gold(I) centre and the monomeric complex anion $[AuL(SeCN)]^-$ is formed. Ligand redistribution occurs to give the complexes $[Au(SeCN)_2]^-$ and $[AuL_2]^-$ but decomposition of $[Au(SeCN)_2]^-$ resulted in the formation of $[Au(CN)_2]^-$ and elemental selenium. The anion $[Au(CN)_2]^-$ also formed when $[AuL_2]^-$ was treated with $[SeCN]^-$ [34]. Related ^{13}C NMR spectroscopic studies have focused on the reactions of thiourea and selenourea with aurothiomalate. Thiourea adds to the gold centre, but in the presence of selenourea, aurothiomalate $[AuL]_n$ was reduced to gold metal and the ligand transformed to L_2 [35]. Further work from the same research group has examined the interactions of aurothiomalate with selenoethanoic acid, selenocysteine and selenocysteamine, again using ^{13}C NMR spectroscopy. In aqueous solution, complexes of the type $[AuL'_2]^-$ where $[L']^-$ is the incoming ligand were formed [36].

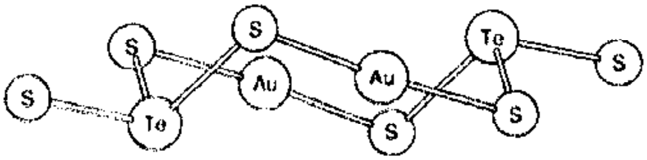


Only the *ipso*-C atoms of the aryl groups are shown.

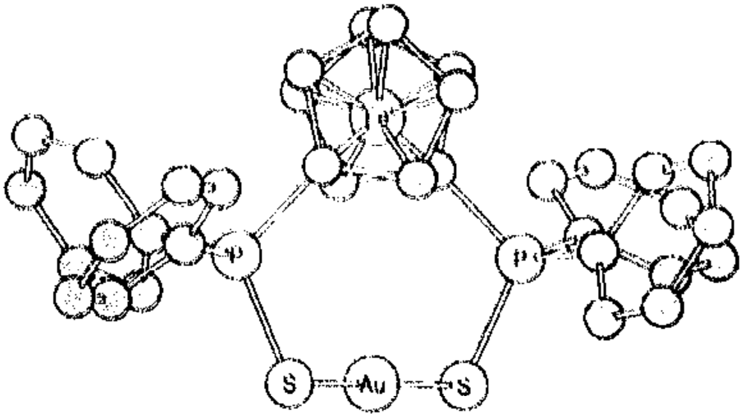
(11)

Crystal structure determinations have been carried out on the compounds $[(2\text{-}MeC_6H_4)_3PAuS_2CO^iPr]$ and $[(2\text{-}MeC_6H_4)_3PAuS_2COCH_2CH_2OMe]$ (**11**). In each compound, the sulfur-donor ligand is monodentate and the gold(I) centre is linear.

However, in $[(2\text{-}MeC_6H_4)_3PAuS_2CO^iPr]$, the conformation of the $[S_2CO^iPr]^-$ ligand is such that the oxygen atom faces the gold centre with an Au···O separation of 289 pm. In complex (**11**), no such close gold–oxygen approach is observed but the ligand conformation allows a secondary Au···S interaction (334.7 pm) in addition to the primary coordination (Au–S = 227.8 pm). Variable temperature ^1H and ^{31}P NMR spectroscopic data did not indicate that conformational changes such that both *S,S′* and *S,O*- coordination could occur in a given complex [37]. The reaction between gold(I) cyanide and $[Me_4N]_2[TeS_3]$ in dmf has yielded the novel compound $[Me_4N]_2[Au_2(TeS_3)_2]$ which has been characterised by spectroscopic methods (far-IR) and X-ray crystallography. The complex dianion (**12**) possesses a cyclic structure in which the gold(I) centres are in linear S–Au–S environments, but out of bonding range (Au···Au = 358.2 pm) [38].



(**12**)

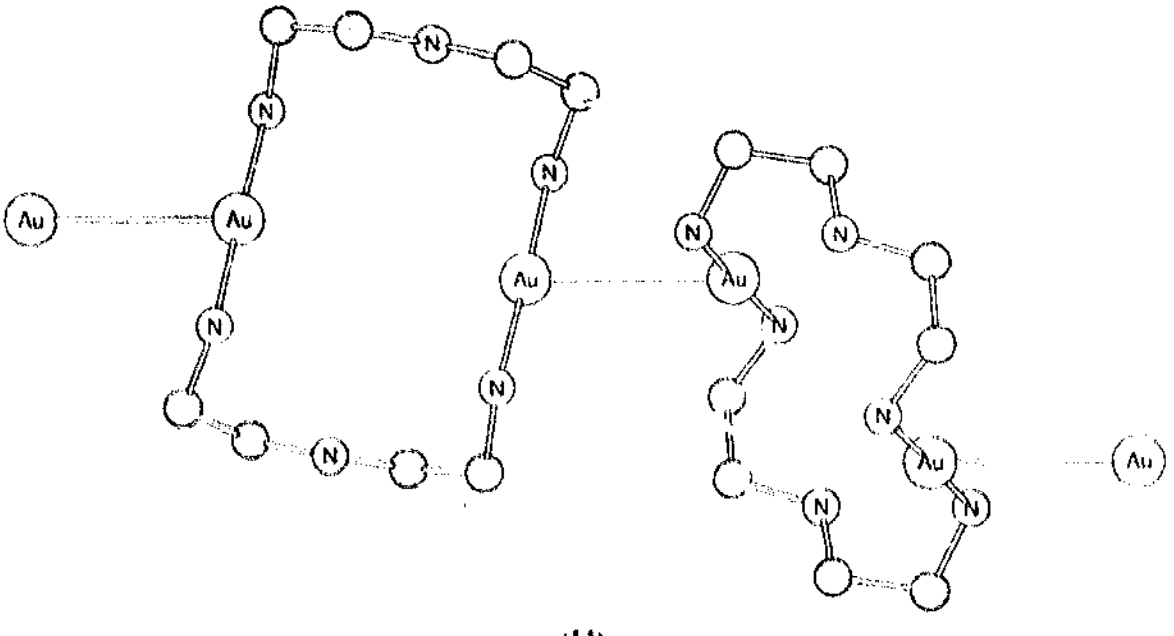


(**13**)

When tetrachloroaurate reacts with $Cy_2P(O)C(S)NHMe$, L, in the presence of thiodiglycol, the product is [LAuCl]. The nature of the pale green, air-stable complex has been confirmed spectroscopically and by X-ray diffraction studies. The geometry of the gold(I) centre is linear, defined by the chloro ligand and the sulfur atom of ligand L [39]. The reaction of equal numbers of moles of $[Au(tht)_2][CF_3SO_3]$ and $[(\eta^5\text{-}C_5H_4P(S)Ph_2)_2Fe]$ leads to the formation of complex (**13**). Structural characterisation of the product shows that the ligand binds through the two sulfur-donor atoms to give a linear S–Au–S coordination sphere. This forces the observed conformation upon the $(\eta^5\text{-}C_5H_4PPh_2)_2Fe$-part of the ligand [40].

3.4. Complexes with nitrogen-donor ligands

Investigations have been carried out of the reactions between the gold(I) complex [$Ph_3PAu(acac)$] and ammonium salts [HL][X] (L = 2-nitroaniline, 4-methoxyaniline, Ph_2NH, Et_2NH; X = CF_3SO_3; L = Me_3N, X = ClO_4). The products are of the type [Ph_3PAuL]X in which the *N*-donor mode of the amine has been established by X-ray diffraction methods for the salt [$Ph_3PAu(NMe_3)$][ClO_4]. In the linear coordination sphere of the gold(I) centre, the bond distances are Au–P = 223.1 pm and Au–N = 210.8 pm. No intermolecular Au···Au interactions were observed in the solid state lattice [41]. The preparation of the complex [$Au_2(dien)_2$][BF_4]$_2$ has provided an interesting example of a polymeric gold(I) complex. Infrared and NMR spectroscopic characterisations have been supported by a crystallographic study which shows that the solid state structure of the complex consists of cyclic [$Au_2(dien)_2$]$^{2+}$ units connected into chains by Au···Au interactions (331.2 pm) as shown in structure (**14**). Within each ring the two gold atoms are out of bonding range (>450 pm) [42].



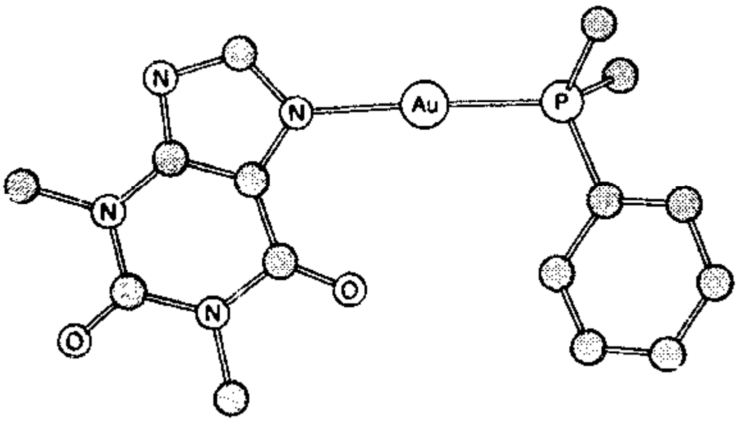
(**14**)

The coordination of a nitrogen-containing heterocyclic ligand is exemplified by the complex [$Me_2PhPAuL$] (**15**) where HL is a derivative of purine. The ligand is monodentate, resulting in the expected linear coordination geometry for the gold(I) centre [43].

See also Section 5.1 for gold(I)-amine complex formation, e.g. structure (**28**) [44].

3.5. Complexes with phosphorus-donor ligands

In this section, gold(I) complexes in which phosphine ligands are those of primary interest are discussed although some dppm complexes are described in Section 4.

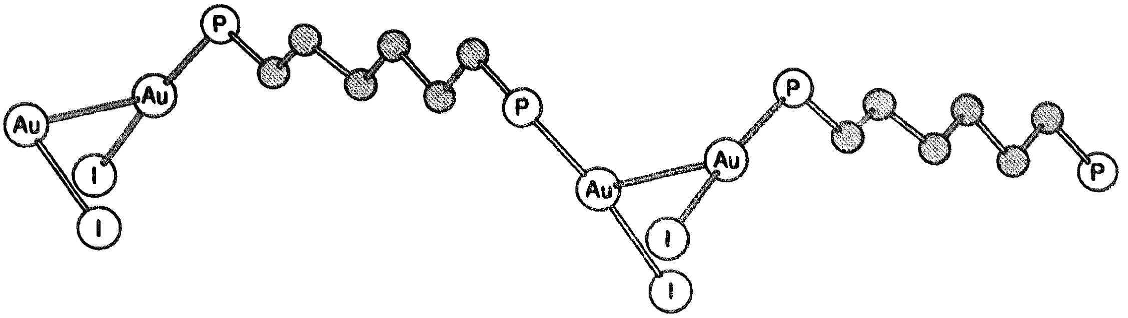


(15)

Many other phosphine-containing complexes have already been detailed in previous sections and will not be discussed further here. A paper of general as well as specialist interest deals with electrospray mass spectrometry; spectrometric data for various cationic gold(I) phosphine species have been recorded. Parent ions for cations of the type $[Au(PR_3)_2]^+$ and $[Au(PR_3)_3]^+$ were observed but this was not the case for ions of formula $[Au(PR_3)_4]^+$. Fragmentation of $[Au(PR_3)_3]^+$ to $[Au(PR_3)_2]^+$ occurred readily [45]. The crystal structure of $[(^tBu_3P)_2Au][BF_4]\cdot 2CH_2Cl_2$ has been determined, confirming the expected linear environment of the gold(I) centre; see Section 5.1 [46].

It has been shown that crystals of the gold(I) complexes $[Ph_3PAuCl]$ and $[Ph_3PAuBr]$ and their triphenylarsine analogues exhibit dual phosphorescences from two excited states. For each complex, the higher energy system at 360 nm has been assigned to an intra-ligand phosphorescence originating from a phenyl-localised $^3\pi$-π^* state, while the lower energy system is at 460 nm. Detailed discussions of the systems have been presented [47]. The complexes $[\{2,4,6\text{-}(MeO)_3C_6H_2\}_3PAuX]$ (X = Cl, Br, I) may be prepared from the reactions of $\{2,4,6\text{-}(MeO)_3C_6H_2\}_3P$ with $[(Me_2S)AuX]$. The three compounds have been structurally and spectroscopically characterised. In the far-IR spectra, absorptions at 313, 218 and 183 cm^{-1} have been assigned to the mode ν(Au–X) where X = Cl, Br and I respectively. When each compound is treated with an equivalent of $\{2,4,6\text{-}(MeO)_3C_6H_2\}_3P$, L, the product is $[AuL_2]^+X^-$ as shown by ^{31}P NMR spectroscopy. Comparisons have been made between the solid state ^{31}P NMR spectroscopic properties of the complexes $[\{2,4,6\text{-}(MeO)_3C_6H_2\}_3PAuX]$ with those of their triphenylphosphine analogues [21]. The preparation of the complex $[Au(PPh_3)_3][SiF_5]$ has been described. The results of an X-ray diffraction analysis have shown that the silicon(IV) centre is trigonal bipyramidal whilst the gold(I) centre is trigonal planar; anions and cations are well separated in the lattice [48].

The coordination to gold(I) of didentate bisphosphine ligands have included an investigation of $Ph_2P(CH_2)_6PPh_2$ (dpph). The crystal structures of $[(dpph)Au_2Cl_2]$ and $[(dpph)Au_2I_2]$ **(16)** have been elucidated, and in each the dpph carbon backbone is in an extended conformation. Compound **(16)** is polymeric in the solid state by virtue of intermolecular Au···Au interactions over distances of 312 pm. The chains so-formed are described as being 'interwoven' to give layers that dictate the cleavage planes of crystals of (**16**) [49]. The didentate ligands $^{i}Pr_2PCH_2CH_2P^{i}Pr_2$ and 1,2-$(^{i}Pr_2P)_2C_6H_4$ contain bulky substituent groups and have been incorporated into the gold(I) complexes $[ClAu(\mu\text{-}^{i}Pr_2PCH_2CH_2P^{i}Pr_2)]_n$ and $[Au(PEt_3)(1,2\text{-}(^{i}Pr_2P)_2C_6H_4)]Cl$. These compounds have been shown to be selective catalysts for hydroboration of imines and thiazolines using catecholborane [50].



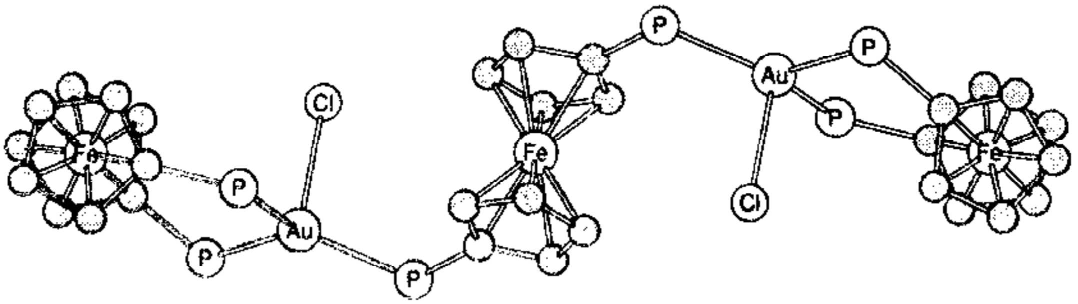
Phenyl groups have been omitted.

(**16**)

The syntheses of the complexes $[\{(Z)\text{-}Ph_2PCH{=}CHPPh_2\}Au_2X_2]$ and $[\{(E)\text{-}Ph_2PCH{=}CHPPh_2\}Au_2X_2]$ ($X = Cl$, Br, I or 4-SC_6H_4Me) have been described. The complexes have been characterised by elemental analysis and UV–VIS, ^{1}H and ^{31}P NMR spectroscopies. Photochemical studies have revealed a remarkable (*Z*)- to (*E*)-isomerisation of the coordinated ligand in contrast to the lack of such a conversion for the free ligand. Isomerisation from the (*E*)- to (*Z*)-complex was not observed [51]. The didentate ligand 1,4-$(Ph_2PCH_2)_2C_6H_4$ forms the gold(I) complex $[\{1,4\text{-}(Ph_2PCH_2)_2C_6H_4\}Au_2Cl_2]$. In the solid state, the rigid backbone of the ligand holds the two gold(I) centres in remote positions, but there is a degree of close approach of gold centres between molecules with Au···Au separations of 399 pm. The reactions of $[ClAu\{1,4\text{-}(CH_2PPh_2)_2C_6H_4\}AuCl]$ with NaSMe and Na_2S were described in Section 3.3 [30].

The reaction of dppf with two equivalents of $[(Me_2S)AuCl]$ in CH_2Cl_2 has yielded the dinuclear gold(I) complex $[(dppf)_3Au_2Cl_2]$ (**17**). Structural data for this complex have revealed chelating modes of two dppf ligands and a bridging mode for the third; in each ligand, the cyclopentadienyl ligands are mutually staggered. Each gold(I) centre is 4-coordinate in a distorted tetrahedral environment [52]. The preparation of $[(\eta^5\text{-}C_5Me_4PPh_2)_2Fe]$ (dppf*) has been detailed. This didentate ligand reacts with 2 equivalents of [(tht)AuCl] to give the complex $[(dppf^*)Au_2Cl_2]$, but in a reaction with 1 equivalent of [(tht)AuCl], the product was the 3-coordinate gold(I) complex [(dppf*)AuCl]. An X-ray diffraction study of the latter has been carried out and the Au–P and Au–Cl bond distances were found to be greater than in related 2-coordinate species. Carbon-13 NMR spectroscopic data have been recorded and it has been noted that [(dppf*)AuCl] is stable in solution for at least several hours. The gold(I) complexes have also been investigated by electrochemical methods and ^{197}Au Mössbauer spectroscopy. The chloro ligands in

$[(dppf^*)Au_2Cl_2]$ and $[(dppf^*)AuCl]$ may be substituted by C_6F_5 groups. The cytotoxicity of the complexes has been assessed but they were not found to be better than presently documented drugs [53].

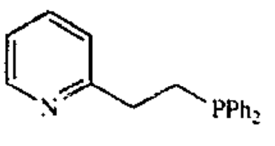


Phenyl groups have been omitted.

(17)

Complex formation between gold(I) and several ligands that are potential *N,P*-donors has been investigated. Ligand (**18**) forms the gold(I) complex $[Au(\mathbf{18})_2]^+$ which has been isolated as the hexafluorophosphate salt and characterised by IR and multinuclear NMR spectroscopies. Coordination is through the phosphorus donors only and gives the gold(I) centre the expected linear geometry as confirmed by an X-ray diffraction study. Variable temperature NMR spectroscopic data have been used to explore ligand exchange processes in solution. In the corresponding silver(I) and copper(I) complexes, ligand (**18**) coordinates in an *N,P*-mode [54]. Ligand (**19**) forms both mononuclear and dinuclear complexes with gold(I) depending upon the potential anion present. In $[(\mathbf{19})AuCl]$, the ligand coordinates through the phosphorus donor atom and this has been confirmed by the results of an X-ray diffraction study. In the compounds $[Au_2(\mathbf{19})_2]X_2$ (X = PF_6, BF_4 or NO_3), ligand (**19**) adopts a bridging mode. The new complexes have been characterised by IR, NMR and ^{197}Au Mössbauer spectroscopic techniques [55]. The reaction between $K[AuCl_4]$, and ligand (**20**) in methanol has resulted in the formation of the complex $[KAu_2(\mathbf{20})_3]^{3+}$ which has been isolated and characterised as the perchlorate salt. Crystallographic data have established that the two gold(I) centres are bridged by three ligands and that this complex provides a cavity in which the potassium ion is encapsulated. The phosphorus donor atoms of (**20**) coordinate to the gold(I) centres, whilst the nitrogen donors bind the potassium ion. The complex $[KAu_2(\mathbf{20})_3]^{3+}$ exhibits a room temperature emission upon photoexcitation between 300 and 400 nm [56]. The compound $MeSCH_2CH_2PPh_2$ may potentially function as a didentate ligand but in the complex $[(MeSCH_2CH_2PPh_2)AuCl]$, it binds only through the phosphorus donor atom. This has been confirmed by the results of a crystallographic study and the P–Au–Cl angle is 177.9(1)° [57].

The reaction between $[(\mathbf{21})]Br$ and two equivalents of gold(I) chloride leads to the formation of the complex $[AuCl(\mathbf{21})][AuBrCl]$. A similar reaction can be carried out using $[(\mathbf{21})][CF_3SO_3]$ and from this, the product is $[AuCl(\mathbf{21})][CF_3SO_3]$, the nature of which in the solid state has been established by X-ray crystallography.



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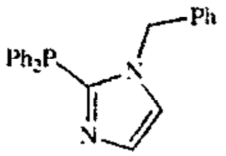

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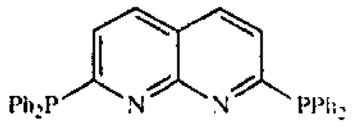

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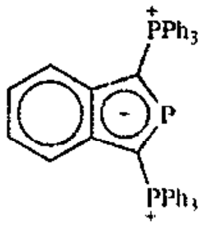
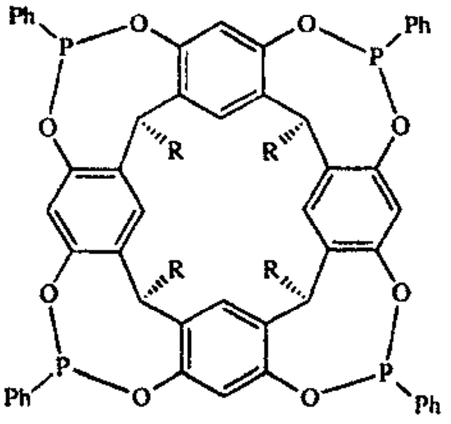


(21)

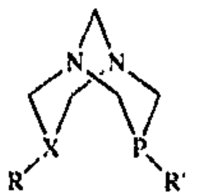
The reactions of [AuCl(**21**)][CF$_3$SO$_3$] with LiF, (Me$_2$N)$_3$P=O or (Et$_2$N)$_2$C=NH have been investigated [58].

The calixresorcinarene (**22**) and a related compound (**22a**) with eight OPPh$_2$ groups (emanating from the eight oxygen atoms shown in compound (**22**)) have been prepared. Compound (**22**) reacts with [(Me$_2$S)AuCl] to give the complex [(**22**)(AuCl)$_4$]. When the octadentate ligand, (**22a**), is used in a similar reaction, the product is proposed from spectroscopic data to be [(**22a**)(AuCl)$_8$]. Molecular mechanics calculations have been performed on this latter compound, but [(**22**)(AuCl)$_4$] has been fully characterised by an X-ray diffraction analysis. Three of the four gold(I) chloride groups form a 'picket fence' arrangement but the fourth is folded into the cavity. In solution, the ^{31}P NMR spectrum shows equivalent phosphorus centres down to −80°C suggesting that exchange of the two types of PAuCl-units is facile [59]. Systems with large numbers of phosphine donor groups on the periphery are potential building blocks for dendrimers and this has been demonstrated by two groups. For example, the compound N(CH$_2$CH$_2$NHC(O)C$_6$H$_4$PPh$_2$)$_3$ reacts with [(Me$_2$S)AuCl] with the formation of P–Au–Cl units. Similar reactions have lead to related species. This work represents preliminary studies into dendrimer systems [60]. A high nuclearity gold-containing dendrimer has been prepared by the reaction of an excess of [(tht)AuCl] with a system represented as [core]–CH=N–N(Me)CH$_2$PPh$_2$ which contains 3072 PPh$_2$ groups. In principle, 3072 gold atoms can be incorporated into the dendrimer: in solution, only one ^{31}P NMR spectroscopic signal was observed. Gold complexes in this series were observed by high-resolution electron microscopy [61].

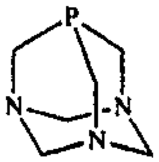
The synthesis of compounds (**23**) and reactions with [(Me$_2$S)AuCl] or AuCl have been described. Several novel species have been structurally characterised. The crystal structure of [Au(**23**)$_2$]Cl·CHCl$_3$ for X=P, R=R′=Me reveals a 4-coordinate gold(I) centre attached to the two phosphorus donor atoms of the two ligands. In [(**23**)AuCl] for X=N, R=Me, R′=Ph, the gold(I) centre is in a linear environment.



R = CH$_2$CH$_2$Ph
(**22**)



R, R′ = various, e.g. Me, Et, Ph
X = N or P
(**23**)



(**24**)

with the ligand functioning as a monodentate *P*-donor. Amongst the compounds characterised by X-ray diffraction was the gold(III) complex [Me$_2$Au(**23**)][Me$_2$AuCl$_2$] for X = N, R = R′ = Me. Each gold(III) centre is square planar as expected and the ligand (**23**) functions as an *N*,*P*-donor via the NMe and PMe groups. Ligands (**23**) with X = N are related to 1,3,5-triaza-7-phosphaadamantane, compound (**24**). The coordination chemistry of this ligand with respect to gold(I) has been of active interest in 1995 within the Fackler group. The syntheses of the complexes [L$_n$AuCl] (n = 1, 2, 3 or 4) where L = (**24**) or [AuL′]$^{2-}$, [AuL′$_2$]$^{5-}$ and [AuL′$_3$]$^{8-}$ where Na$_3$L′ = P(C$_6$H$_4$SO$_3$Na-3)$_3$ have been described. The products are water soluble, and the species [AuL$_3$]$^+$ and [AuL′$_3$]$^{8-}$ exhibit strong luminescences in the solid state and in solution. The intensity of the luminescence of [AuL′$_3$]$^{8-}$ is not pH dependent but is solvent dependent [62]. The reaction between [(Me$_2$S)AuCl] and ligand (**24**) in aprotic solvents has given the complex [(**24**)AuCl], whilst the protonated complex [{(**24**)HCl}AuCl] has been prepared by treating [(tht)AuCl] with protonated ligand. The structural characteristics of [(**24**)AuCl] and [{(**24**)HCl}AuCl] have been determined and it has been noted that protonation influences the intermolecular Au⋯Au contacts, lengthening the distance from 309.2 to 332.2 pm. The photoluminescent properties of the complexes have been investigated and differences have been explained in terms of changes in the gold–gold interactions; detailed discussions of these properties have been presented. The complex [(**24**)AuCl] may be converted to the corresponding bromo or iodo species, to [(**24**)AuMe] by reaction with MeLi in Et_2O, and to [{(**24**)Me}AuCl][CF_3SO_3] by treatment with CF_3SO_3Me [63,64]. A further report concerns the properties of the complexes [(**24**)AuBr], [(**24**)AuI] and [{(**24**)H}AuI][AuI_2] and the photoluminescent spectra of these species have been compared with those of [(**24**)AuCl]. Protonating ligand (**24**) has a significant influence on the spectrum, as was noted above. A correlation has been established between the low-energy emission and the Au···Au distance in each complex and this can now provide distance data from spectroscopic observations for other complexes in this family. Extended Hückel MO calculations have been carried out and the results support the fact that decreasing the intermolecular Au···Au distance causes a decrease in the HOMO-LUMO energy separation [65]. The reaction between the compound [(**24**)AuCl], PhSH and KOH in methanol leads to the formation of [(**24**)AuSPh]; the related derivatives [(**24**)AuSR] in which R = 2-$MeOC_6H_4$, 2-ClC_6H_4, 3-ClC_6H_4 and 4-ClC_6H_4 have also been prepared, as have the compounds [$Ph_3PAuSPh$], [$Ph_3PAuSPC_6H_4OMe$-2] and [$Ph_3PAuSC_6H_4Cl$-2]. The new compounds have been characterised by elemental analysis, ^1H and ^{31}P NMR spectroscopies and, for representative members of the series, X-ray diffraction studies. Each compound luminesces at 77 K in the solid state and the excitation has been assigned to an LMCT (S→Au) transition [66]. The preparation of [$(\mathbf{24})_3AuI$]$I_3 \cdot 2H_2O$ and its structural characterisation have been described. Its emission spectrum is temperature dependent: at 77 K, a yellow emission (598 nm) is observed while at 140 K, the emission is orange (686 nm). A novel reaction between [$(\mathbf{24})_3AuI$]I_3 and Na[BPh_4] takes place to yield the derivative [(**24**)AuPh] in which the gold(I) centre is in the anticipated linear C–Au–P environment [67].

3.6. Complexes with arsenic-donor ligands

The crystal structures of two forms of the complex [$Ph_3AsAuCl$] have been determined; the forms are distinguished by their different crystal habits of needles or prisms, and in their molecular structures by the orientations of the phenyl substituents. Differences in the Raman spectra of these forms of [$Ph_3AsAuCl$] have been observed [68]. Crystals of the gold(I) complexes [Ph_3PAuCl], [Ph_3PAuBr], [$Ph_3AsAuCl$] and [$Ph_3AsAuBr$] exhibit dual phosphorescences from two excited states; see Section 3.5 [47].

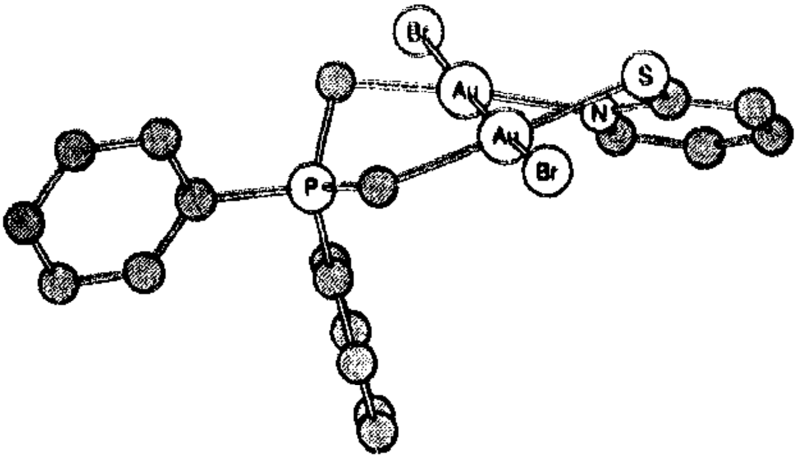
3.7. Complexes with germanium-donor ligands

The novel compounds [$(Ph_3P)_nAuGeCl_3$] ($n = 1$, 2,3) containing Au–Ge bonds have been prepared and characterised. The synthetic strategy involved the insertion of $GeCl_2$ into the Au–Cl bond of [$(Ph_3P)_nAuCl$]. An X-ray diffraction study has confirmed the direct Au–Ge interactions [69].

4. Dinuclear species

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

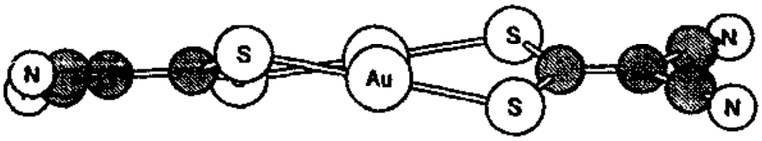
This section includes complexes with $Au_2(\mu\text{-dppm})_2$-cores and related species in which the digold-core is supported by bridging disulfur-containing ligands. A paper concerned with ligand-transfer reactions has appeared and described reactions of $[AuX_2]^-$ (X = Cl or Br) with $[Au_2(\mu\text{-dppm})_2][ClO_4]_2$ to yield complexes with both dinuclear and trinuclear cores. Ligand substitution occurs when 2 equivalents of the cation $[Au(PPh_3)_2]^+$ react with $[Au_2(\mu\text{-}S_2CNR_2)_2]$ (R = Me, CH_2Ph), $[Au_2(\mu\text{-}S_2COR)_2]$ (R = Me, Et) or $[Au_2(2\text{-Spy})_2]$ (2-HSpy = 2-HSC_5H_4); the products have the general formula $[(Ph_3PAu)_2(\mu\text{-L})]^+$ where L is the bridging ligand from the starting complex. Further studies in this work have been concerned with the syntheses of mixed-bridge compounds of the type $[Au_2(\mu\text{-}S_2CNR_2)(\mu\text{-L}')]^+$ where R = Me, CH_2Ph, and L′ = dppm or dppe [70]. The heterobridged complex cations $[Au_2(\mu\text{-2-Spy})(\mu\text{-L}')]^+$ (L′ = dppm or dppe have been prepared by displacement of one equivalent of L′ from $[Au_2(\mu\text{-L}')_2]^{2+}$; the perchlorate salts have been characterised by IR and NMR spectroscopies and electrochemical methods. The related organometallic complex $[Au_2(\mu\text{-2-Spy})(\mu\text{-}CH_2PPh_2CH_2)]$ has also been prepared and its structure confirmed by X-ray crystallography. This complex undergoes addition of Br_2 and the product (**25**) of this reaction has been fully characterised. A significant twisting of the P_2Au_2NS-core of the complex occurs upon dibromine addition as well as a decrease in the Au–Au bond distance from 286.2 to 254.7 pm [71].



(**25**)

The crystal structure of *catena*-$[Au_2(S_2PPh_2)_2]$ has been determined [72] as has that of the salt $[(Ph_3P)_2N][Au_2\{\mu\text{-}S_2C_2(CN)_2\}_2]\cdot Me_2CO$. The core of the $[Au_2\{S_2C_2(CN)_2\}_2]^-$ anion is slightly twisted as structure (**26**) illustrates [73]. A related compound is $[(Ph_3P)_2N]_2[Au_2(\mu\text{-}S_2C{=}NCN)_2]$ and an X-ray diffraction study of this compound has been carried out, confirming the doubly-bridged digold core [74]. The first example of a trithiocarbonatogold(I) complex has been reported: $[(Ph_3P)_2N][Au_2(CS_3)_2]$ was prepared by the reaction of $[(Ph_3P)_2N][Au(SH)_2]$ with

CS_2. The solid state structure of $[(Ph_3P)_2N][Au_2(CS_3)_2]$ shows the presence of a near planar $[Au_2(CS_3)_2]^-$ anion (27) in which the Au–Au distance is short (279.99 pm). This contact pulls the gold atoms slightly away from being in linear S–Au–S environments (∠S–Au–S = 172.8°) [29].



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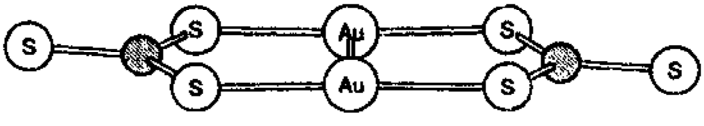


(27)

4.2. Heterometallic dinuclear and gold-bridged complexes

The heterometallic cationic complexes $[LRhH(AuPPh_3)]^+$ have been prepared starting from the rhodium(I) complexes [LRhH] where $L = P(CH_2CH_2PPh_2)_3$ or $N(CH_2CH_2PPh_2)_3$. Both products have been characterised by X-ray diffraction and detailed ^1H, ^{31}P and ^{103}Rh NMR spectroscopic studies. In $[\{P(CH_2CH_2PPh_2)_3\}RhH(AuPPh_3)]^+$, the hydride ligand adopts an Au–H–Rh bridging position [75].

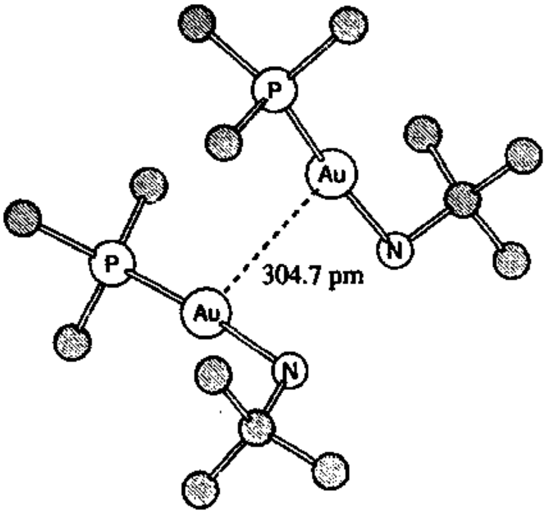
The reaction of $[Pt_2(\mu\text{-dppm})_2(CN)_2]$ with an equivalent of $[(Me_2S)AuCl]$ has given the heterometallic complex $[(NC)_2Pt_2(\mu\text{-dppm})_2(\mu\text{-AuCl})]$, crystallised as the dichloromethane solvate. The location of the gold(I) chloride unit as a bridge across the Pt_2-unit has been confirmed by the results of an X-ray diffraction study (Pt–Au = 263.3 and 264.8(2) pm). Bonding within the Pt–Au–Pt unit has been described in terms of a 3-centre 2-electron interaction. Related work with mercury(II) halides has also been detailed [76]. Absorption and excitation spectroscopic data for dppm-bridged complexes containing gold–platinum, gold–rhodium and gold–iridium cores have been recorded and analysed [77].

5. Gold clusters

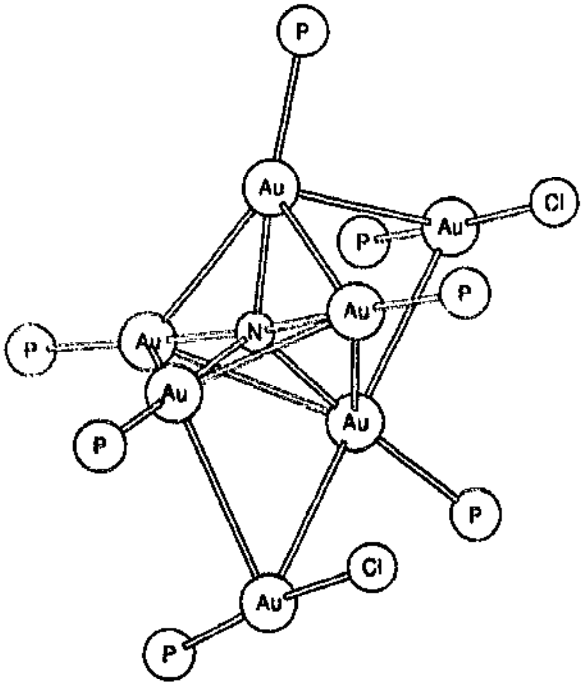
5.1. Clusters containing a central p-block atom

Gold clusters in which a *p*-block atom plays a central, structural role have become increasingly significant over recent years with Schmidbauer's work dominating the area. The reactions between $[R'_3PAu][BF_4]$ and *tert*-butylamine or benzylamine have yielded the products $[R_3PAuNH_2R][BF_4]$ (R = ^tBu or CH_2Ph, R′ = Me; R = ^tBu, $R'_3P = MePh_2P$), but when the starting gold(I) complex was $[(Me_3PAu)_3O][BF_4]$, the products were $[(Me_3PAu)_3NR][BF_4]$ ($R = {}^tBu$ or CH_2Ph). Slow hydrolysis of $[(Me_3PAu)_3NCH_2Ph][BF_4]$ gave the compound $[(Me_3PAu)_2NHCH_2Ph][BF_4]$. Changing the amine in the reaction with $[(Me_3PAu)_3O][BF_4]$ to $(Me_3Si)_2NH$ resulted in the formation of $[(Me_3PAu)_3NSiMe_3][BF_4]$ and $[(Me_3PAu)_4N][BF_4]$, the product being controlled by the reaction conditions. Each new compound has been characterised by spectroscopic methods and the results of X-ray diffraction studies have been reported for $[Me_3PAuNH_2^tBu][BF_4]$, $[MePh_2PAuNH_2^tBu][BF_4]$ and $[(Me_3PAu)_2NHCH_2Ph][BF_4]$. In both $[Me_3PAuNH_2^tBu][BF_4]$ and $[(Me_3PAu)_2NHCH_2Ph][BF_4]$, dimer-formation between cations occurs by virtue of Au···Au interactions as structure (**28**) shows for $[Me_3PAuNH_2^tBu]^+$ [44]. By reacting hexamethyldisilazane or Ph_3SiNH_2 with $[(R_3PAu)_3O][BF_4]$ ($R = Me$, Et, ${}^iPr$, Ph, $2\text{-}MeC_6H_4$, or $R_3 = MePh_2$), it has been possible to isolate the series of compounds $[(R_3PAu)_3NSiMe_3][BF_4]$ and $[(R_3PAu)_3NSiPh_3][BF_4]$. These have been characterised in solution by ^{31}P and ^{14}N NMR spectroscopies, and representative complexes have been studied by X-ray crystallography. Decomposition of the salts has given a means of forming $[(R_3PAu)_5N]^{2+}$ for $R = Me$ or Ph; the crystal structure of $[(Ph_3PAu)_5N][BF_4]_2$ has been determined at −41°C [78]. Hexamethyldisilazane reacts with $[(Me_3PAu)_3O][BF_4]$ and $[Me_3PAuCl]$ to give the high nuclearity cluster dication $[(Me_3PAu)_7Cl_2(\mu_5\text{-}N)]^{2+}$ (**29**). Isolated as the tetrafluoroborate salt, this novel species has been fully characterised. The solid state structure consists of a nitrogen-centred trigonal bipyramidal arrangement of gold centres, with two edge-bridging Me_3PAuCl-groups [79]. A further reaction that has been investigated is that of $[(Et_3PAu)_3O][BF_4]$ with $(Me_3Si)_2NH$, the product of which has been fully characterised. When $[({}^tBu_3PAu)_3O][BF_4]$ reacts with ammonia (≈1:1) at −78°C in dichloromethane, the product has been confirmed crystallographically to be the salt $[({}^tBu_3PAu)_4N][BF_4]$. In the Au_4N-core of the cation, two of the six Au–Au distances are significantly longer than the other four. If the synthesis is carried out with an excess of ammonia, the ratio of Au:N in the products is less than 4:1. These complexes have been characterised by NMR spectroscopic and mass spectrometric methods. Solutions containing these nitrogen-centred products slowly decompose to give $[({}^tBu_3P)_2Au][BF_4]$ as the isolated product. The crystal structure of $[({}^tBu_3P)_2Au][BF_4]\cdot 2CH_2Cl_2$ has been determined, and the crystal lattice contains two independent cations [46].

The sulfur-centred complex cation $[{}^tBuS(AuPPh_3)_2]^+$ has been isolated as the tetrafluoroborate salt from the reaction between ${}^tBuSH$ and $[(Ph_3PAu)_3O][BF_4]$ in the presence of $NaBF_4$. In the solid state, pairing of the cations occurs to give centrosymmetric tetragold units as structure (**30**) illustrates (Au···Au distances are 329.3 and 320.6(1) pm). When ${}^tBuSH$ is replaced by $HSCH_2CH_2SH$ in the synthesis, $[(Ph_3PAu)_3(SCH_2CH_2S)][BF_4]$ is formed in high yield. In solution, only one ^{31}P NMR spectroscopic signal was observed for this compound at −60°C but in the solid state, two types of phosphorus environments are confirmed; one 3-coordinate and two linear gold centres are present in the cation $[(Ph_3PAu)_3(SCH_2CH_2S)]^+$ (**31**). Within each Au_3-unit, the Au···Au distances are 328.4 and 312.9(1) pm, but the cations are well separated within the lattice [80].



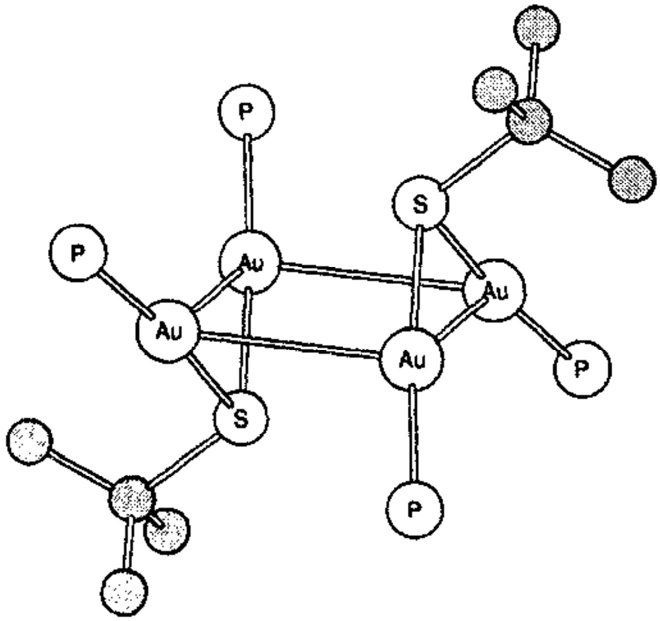
(28)



Methyl groups have been omitted.

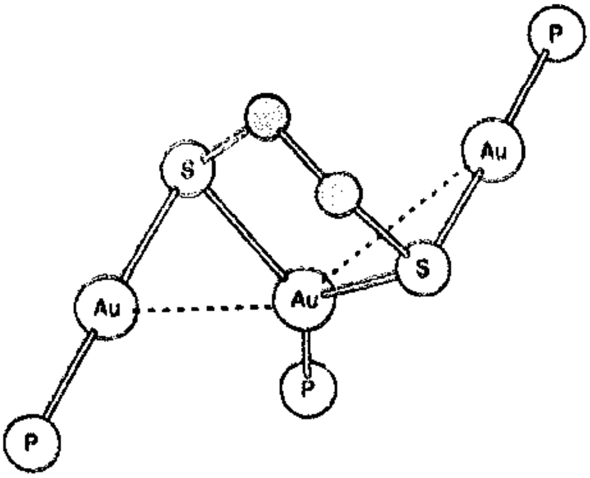
(29)

The aggregation of gold(I) centres around oxygen atoms has been further exemplified. The crystal structure of the compound $[(^iPr_3PAu)_3O][BF_4]$ has been established. In the solid state, although there are Au–Au bonding interactions within each cation, the cations are well separated from each other and the lack of intermolecular contacts is attributed to the bulky nature of the isopropyl substituents [81]. The reaction of $[\{(2\text{-}MeC_6H_4)_3PAu\}_3O][BF_4]$ with $[\{(2\text{-}MeC_6H_4)_3PAu][BF_4]$



Phenyl groups have been omitted.

(30)



Phenyl groups have been omitted.

(31)

in thf and dichloromethane at −78°C has produced the compound $[\{(2\text{-MeC}_6H_4)_3PAu\}_4O][BF_4]_2$; an analogous reaction involving triphenylphosphine derivatives has also been carried out, and both products have been characterised by elemental analysis, mass spectrometry and solution NMR spectroscopy. The $[(R_3PAu)_4O]^{2+}$ cations are seen as analogues of '$[H_4O]^{2+}$' and the crystallographic analysis of $[\{(2\text{-MeC}_6H_4)_3PAu\}_4O][BF_4]_2$ has confirmed that the core of the cation is composed of an oxygen-centred tetrahedron of gold atoms (Au–Au = 335.9 pm).

Both $[\{(2\text{-}MeC_6H_4)_3PAu\}_4O][BF_4]_2$ and $[(Ph_3PAu)_4O][BF_4]_2$ are thermally stable up to, for R = 2-MeC_6H_4, 202°C and for R = Ph, 117°C [82].

5.2. *Polynuclear clusters*

A redetermination of the crystal structure of $[Ph_3PAu)_7][OH]$ has been carried out. The core of the cation consists of a flattened pentagonal bipyramid with an apical–apical Au–Au distance of 258.3 pm [83].

Pignolet *et al.* have given a comprehensive review of the chemistry and spectroscopic properties of phosphine-stabilised, palladium or platinum-centred gold clusters [84]. New work in this field has included the reactions of $[M(AuPPh_3)_8]^{n+}$ (M = Pd or Pt; *n* = 2 or M = Au, *n* = 3) with mercury to yield the cations $[Hg_2M(AuPPh_3)_8]^{2+}$ for M = Pd or Pt, or $[Hg_2Au(AuPPh_3)_8]^{3+}$. Comparative reactions have been carried out using mercury(II) in place of elemental mercury. Structural details of the clusters have been discussed, and the behaviour of oxidising agents, carbon monoxide and chloride ion towards the clusters has been studied [85].

When $[Pt(AuPPh_3)_8][NO_3]_2$ reacts with $AgNO_3$ under H_2, the products have been shown to be $[Pt(H)(AgNO_3)(AuPPh_3)_8[NO_3]$ and $[Pt(H)(AgNO_3)_2(AuPPh_3)_8[NO_3]$. Both compounds have been studied by X-ray crystallography, and the means by which cluster growth may take place has been discussed [86]. The same authors have given an account of the reactions of $[Pt(AuPPh_3)_8][NO_3]_2$ under a dihydrogen atmosphere with sources of copper(I) to give hydrido-containing clusters such as $[Pt(H)(CuCl)(AuPPh_3)_8][NO_3]$ and $[Pt(H)(CuCl)_2(AuPPh_3)_8][NO_3]$. It was found that the Bronsted basicity of the solvent was an important factor in controlling the reaction pathway. Treatment of $[Pt(H)(PPh_3)(AuPPh_3)_7][NO_3]_2$ with $[Ph_3PCuCl]$ produces the cluster cation $[Pt(H)(PPh_3)(CuCl)(AuPPh_3)_6]^{+}$ which has been characterised by multinuclear NMR spectroscopy and mass spectrometry. A series of related reactions has been carried out and the results discussed [87]. A series of new clusters containing copper, platinum and gold has been prepared from the reactions between $[\{Ph_3PCuX\}_4]$ (X = Cl, Br or I) and $[Pt(AuPPh_3)_8][NO_3]_2$. Compound characterisation has been by elemental analysis, solution NMR spectroscopic techniques and, for $[(PtPPh_3)(AuPPh_3)_6Cu_4Cl_3(PPh_3)][NO_3]$ and $[(PtPPh_3)(AuPPh_3)_6Cu_4I_3][NO_3]$, X-ray diffraction studies. The intimate incorporation of the copper centres into each central core has been discussed [88]. The reaction between $[Ph_3PAuN_3]$, $[Ph_3PAuCl]$ and $[(Ph_3P)_2Pd(N_3)_2]$ under conditions of photolysis leads to the formation of the palladium-centred cluster $[Pd(AuPPh_3)_8(AuCl)]$, the structure of which has been confirmed by X-ray structural analysis. The gold atoms form an icosahedral cage surrounding the palladium atom [89].

Indium(I) chloride reacts with $[Ph_3PAuCl]$ in thf in the presence of dppe to yield the novel cluster $[(dppe)_2Au_3In_3Cl_6(thf)_6]$. This has been characterised by ^1H NMR and ^{197}Au Mössbauer spectroscopies, and an X-ray diffraction study has revealed that the cluster-core is composed of an Au_3 triangle capped by two indium atoms with an additional indium atom bridging one Au–Au edge. The compound is described as being the first mixed-valent, mixed-metal gold-indium cluster [90].

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