*Coordination Chemistry Reviews, 127* (1993) 187–221

# 9. Gold

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*CONTENTS*

## *INTRODUCTION*

This review surveys the coordination chemistry of gold, published during 1991. It follows a format similar to that used in the corresponding 1990 review [1]. The results described are organized by the oxidation state of the gold centre and by donor atom type. It should be noted however that a significant number of complexes other than those detailed in Section 9.3.4 do contain gold(I) phosphine interactions. Section 9.4 deals with selected cluster species; transition metal clusters in which one or two gold(I) phosphine units bridge metal-metal, M-M, edges or cap $M_3$-faces are not, in general, included in this review. I should like to thank the Cambridge

0010-8545/93/$24.00

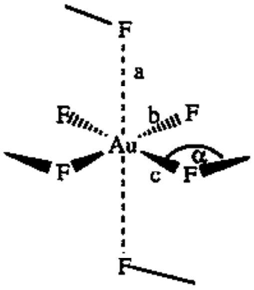
Crystallographic Data Base for providing atomic coordinates for structures **(2b)**, **(3)**, **(7)**, **(17)**, **(18)**, **(21)**, **(22)**, **(27)**, **(28)**, **(42)**-**(45)**, **(50)**, **(51)**, **(55)**, **(56)**, and **(58)**-**(66)**.

A review entitled "Inorganic chemistry and drug design" [2] has appeared and includes a section on gold anti-arthritic drugs.

## *9.1 GOLD(III)*

### *9.1.1 Complexes with halide ligands*

The results of a comparative study of silver and gold trifluorides has been reported. The crystal structure of $AuF_3$ shows that the gold(III) centre resides in an elongated octahedral environment, **(1)**; $AuF_4$-units are joined by symmetrically bridging fluorine atoms to produce helical chains. The emphasis of the paper is on silver(III) fluoride [3].



a = 2.761 (3) Å
b = 1.876 (3) Å
c = 1.998 (2) Å
α = 119.4 (2) Å

**(1)**

The UV-VIS absorption spectrum of gaseous $Au_2Cl_6$ exhibits maxima at 222, 244, and 460 nm. The results lead to a discussion of equilibria and thermodynamic constants for vaporisation reactions in the gold-chlorine system. Values of $\Delta H$ and $\Delta S$ for the equilibria given in equ. (i)-(iv) have been determined [4]. Two papers [5, 6] present X-ray photoelectron and $^{197}Au$ Mössbauer spectroscopic data on the mixed-valence states in the 3-dimensional compounds $Cs_2Au^{(I)}Au^{(III)}X_6$ (X = Cl, Br, I).

$$Au_2Cl_6\,(s) \rightleftharpoons Au_2Cl_6\,(g) \qquad (i)$$

$$2\,Au\,(s) + 3\,Cl_2\,(g) \rightleftharpoons Au_2Cl_6\,(g) \qquad (ii)$$

$$2\,AuCl\,(s) + 2\,Cl_2\,(g) \rightleftharpoons Au_2Cl_6\,(g) \qquad (iii)$$

$${}^1/_2\,Au_2Cl_6\,(s) \rightleftharpoons AuCl\,(s) + Cl_2 \qquad (iv)$$

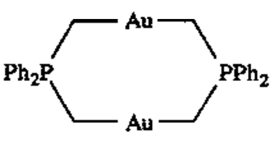
The crystal structure of the $[AuCl_4]^-$ anion has been published in several independent works. It has been found that the presence of gold(III) chloride facilitates the alcoholysis with R'OH of RCN (R and R' = Me, Et). Elemental analysis, and IR and NMR spectroscopies have been used to identify two gold-containing species in the system; these are $[RC(OR')=NH_2]^+[AuCl_4]^-$ and $RC(OR')=NH.AuCl_3$. The structure of the former has been established crystallographically. The $[AuCl_4]^-$ anions are planar (± 0.034 (4) Å) and stack in the crystal lattice; pertinent distances are Au-Cl = 2.292 (2), 2.287 (2), 2.287 (3) and 2.275 (3) Å, and between anions, the Au----Au separation is 4.264 Å [7]. Gold(III) is extracted into 1,2-$C_2H_4Cl_2$ with the macrocyclic ether benzo-15-crown-5, L, from aqueous solution containing HCl and $K^+$ ions. The effects on the efficiency of extraction of temperature, pH and the presence of other metal ions have been investigated. Crystallographic data on the extracted product show that it has the composition $[KL_2]^+[AuCl_4]^-$. IR and UV-VIS spectroscopic and thermodynamic data are also presented [8]. The compounds $Au_2Br_6$ and AuI have been prepared from $Au_2Cl_6$ by reactions with RX (R = H or alkyl; X = Br or I) [9]. The reaction of $Au_2Cl_6$ and $Ph_3CCl$ gives $[Ph_3C]^+[AuCl_4]^-$ which has been structurally characterised. The Au-Cl distances in the anion are 2.286 (5), 2.272 (6), 2.270 (6) and 2.273 (6) Å [9]. The $[AuCl_4]^-$ anion also features in the complex $[AuLCl_2][AuCl_4]$ (L = *N,N',S*-macrocycle) and is discussed in Section 9.1.3 [10].

### *9.1.2 Complexes with gold-carbon bonds*

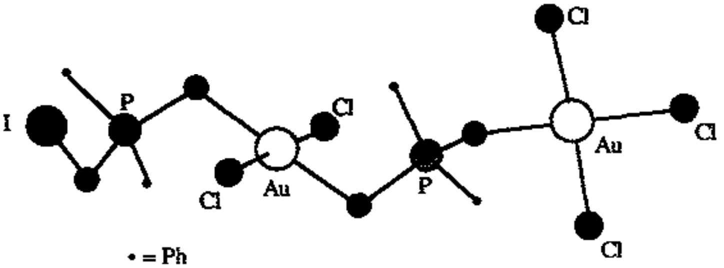
Complexes of ylides with gold(III), gold(II), (see Section 9.2.2) and gold(I) (see Section 9.3.2) have been described in several papers. The reactions of the gold(I) complex $\{Au(CH_2)_2PPh_2\}_2$, (**2a**), with an excess of ICl or $Br_2$ give the gold(III) complexes $\{Au(CH_2)_2PPh_2\}_2X_4$ where X = Cl or Br, respectively. Continued reaction causes the framework of each complex to open up and the products are the gold(III) complexes $Cl_3Au\{\mu\text{-}(CH_2)_2PPh_2\}AuCl_2(CH_2PPh_2CH_2I)$, (**2b**), and $Br_3Au\{\mu\text{-}(CH_2)_2PPh_2\}AuBr_2(CH_2PPh_2CH_2Br)$. Distances in the complexes are summarised in Table 1 [11].

Table 1: Distances in the complexes $X_3Au\{\mu\text{-}(CH_2)_2PPh_2\}AuX_2(CH_2PPh_2CH_2Y)$ / Å.

| | X = Cl; Y = I | X = Y = Br |
|---|---|---|
| Au-----Au | 6.0548 (8) | 6.126 (2) |
| Au-X ($AuX_3$-unit) | 2.263 (5)<br>2.357 (5)<br>2.282 (5) | 2.479 (6)<br>2.415 (5)<br>2.410 (5) |
| Au-X ($AuX_2$-unit) | 2.272 (5)<br>2.282 (5) | 2.406 (6)<br>2.420 (5) |



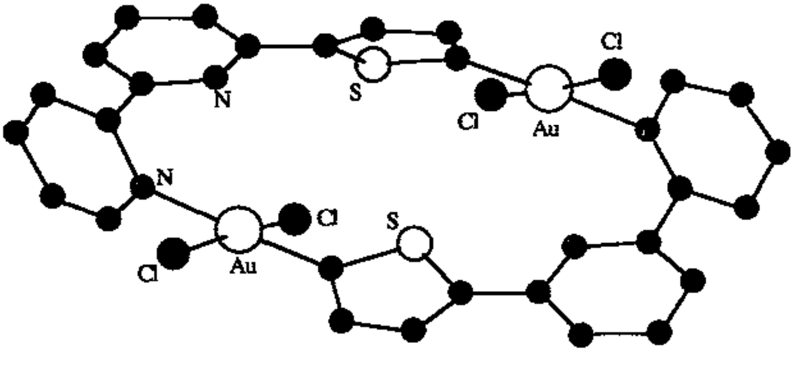
(2a)



(2b)

The reaction of AuCl(tht) with $Ph_3P{=}CHC(O)NMe_2$ leads to the gold(I) ylide complex AuCl{CH(PPh$_3$)C(O)NMe$_2$}; this undergoes oxidative addition with $Cl_2$ to yield the gold(III) product AuCl$_3${CH(PPh$_3$)C(O)NMe$_2$} [12]. These complexes are discussed further in Section 9.3.2.

The ligand 6-(2-thienyl)-2,2'-bipyridine, (HL), is a potentially tridentate *N,N',S*-ligand. When HL reacts with Na[AuCl$_4$], the gold(III) complex Au(HL)Cl$_3$ is produced in which HL is coordinated through an *N*-donor atom. On heating Au(HL)Cl$_3$, metallation occurs to give the dimeric complex, {AuLCl$_2$}$_2$, (3); distances within the coordination sphere of the gold atom are Au-C = 1.959 (29) and 2.285 (14) Å, Au-Cl = 2.255 (13), 2.285 (14), 2.275 (12) and 2.279 (12) Å, Au-N = 2.101 (25) and 2.130 (35) Å [13]. The new results correct the previously proposed cyclometallated structure, (4), for this complex [14].



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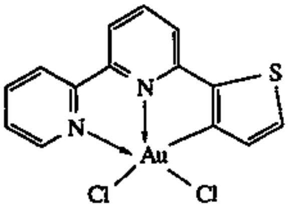
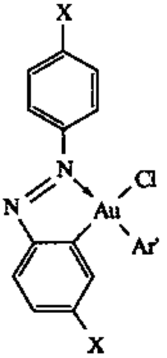


(4)

### *9.1.3 Complexes with nitrogen donor ligands*

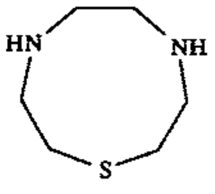
Gold(III) complexes of 2-amino-4,6-dimethylpyrimidine, L, have been prepared and have been characterised by IR, $^1$H NMR, and electronic absorption spectroscopy, conductivity and thermogravimetric analyses. The complexes AuLCl$_3$ and AuLBr$_3$ are prepared in aqueous solution from L and HAuCl$_4$.aq (1:1) or AuBr$_3$ (1:1) respectively; AuL$_2$Br$_3$ is synthesised from L and AuBr$_3$ (2:1 or 3:1) in methanol solution, and (AuL$_2$Cl$_2$).L.Cl.H$_2$O is prepared from L and HAuCl$_4$.aq (2:1 or 3:1). It is suggested that AuL$_2$Br$_3$ is dimeric, and is formulated as [AuL$_2$Br]$_2$Br$_4$; this is consistent with the observation that the complex is a 1:2 electrolyte in dmf solution. There is interest in the possible anti-arthritic activity of these complexes and the antitumour activity of [AuL$_2$Br]$_2$Br$_4$ and (AuL$_2$Cl$_2$).L.Cl.H$_2$O [15].

The application of diarylgold(III) complexes to the synthesis of biaryl compounds, Ar-Ar', (Ar = Ar' = C$_6$H$_4$N=NPh-2; Ar = C$_6$H$_4$N=NPh-2 and Ar' = C$_6$H$_4$NO$_2$-2 or C$_6$F$_5$; Ar = Ar' = C$_6$H$_3$(N=NC$_6$H$_4$Me-4')-2,Me-5; Ar = C$_6$H$_4$CH$_2$NMe$_2$-2 and Ar' = Ph, C$_6$H$_4$N=NPh-2, or C$_6$H$_3$(N=NC$_6$H$_4$Me-4')-2,Me-5) has been reported and, the authors state that the work represents the "first application of organogold(III) complexes in organic synthesis." The complex *cis*-Au(Ar)(Ar')Cl, (5), reacts with [PhCH$_2$PPh$_3$]Cl to give [PhCH$_2$PPh$_3$][AuCl$_2$] and the biaryl Ar-Ar'; similarly, *cis*-Au(Ar)(Ar')Cl reacts with PPh$_3$ and PPh$_3$/NaClO$_4$.H$_2$O to yield AuClPPh$_3$ and [(PPh$_3$)$_2$Au][ClO$_4$], respectively, in addition to Ar-Ar' [16].



X = H, Me
Ar' defined in text

(5)



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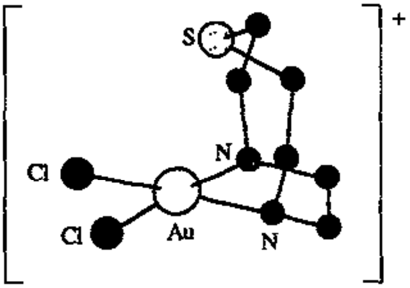
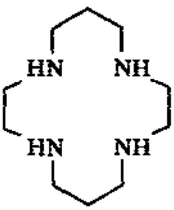


(7)

The complexes $[AuLCl_2]Cl$ and $[AuLCl_2][AuCl_4]$ have been prepared and characterised in which L is the macrocyclic ligand (**6**). Crystallographic characterisation of $[AuLCl_2][AuCl_4]$ shows that ligand L coordinates to the gold(III) centre in the cation $[AuLCl_2]^+$, (**7**), via the two *N*-donor atoms (Au-N = 2.065 (8) and 2.068 (8) Å); the sulfur atom interacts only weakly with the gold atom (Au-S = 2.973 (3) Å) [10]. Gold(III) ions complex with the macrocyclic ligands $H_4L$ = (**8**)-(**11**) in their fully protonated forms to give the complexes $[Au(\mathbf{8})]Cl(ClO_4)_2$, $[Au(\mathbf{9})]Cl_2(ClO_4)$, $[Au(\mathbf{10})](ClO_4)_3.HClO_4$ and $[Au(\mathbf{11})Cl](ClO_4)_2$. In the first three complexes, the ligands act as $N_4$-donors whereas ligand (**11**) coordinates through three nitrogen atoms only. For the ligands $H_4L$ = (**12**) and (**13**), the complexes $[Au(H_3L)](ClO_4)_2$ and $[Au(H_3L)](ClO_4)_2.HClO_4$, respectively, have been synthesised. The complex stability in solution as a function of pH is investigated; the effect of the gold(III) centre within the macrocycle is a significant finding. The results are discussed in terms of the selective uptake of gold(III) ions [17].



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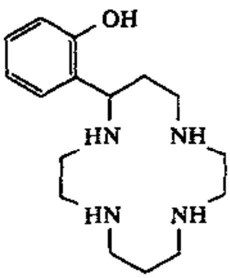

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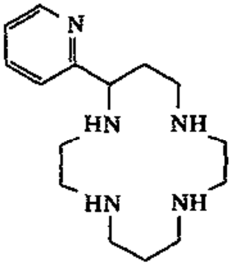
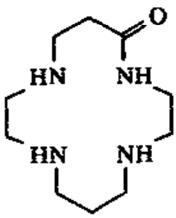
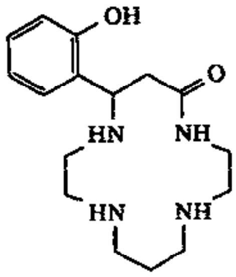


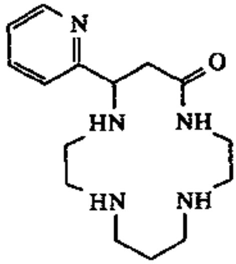
**(10)**



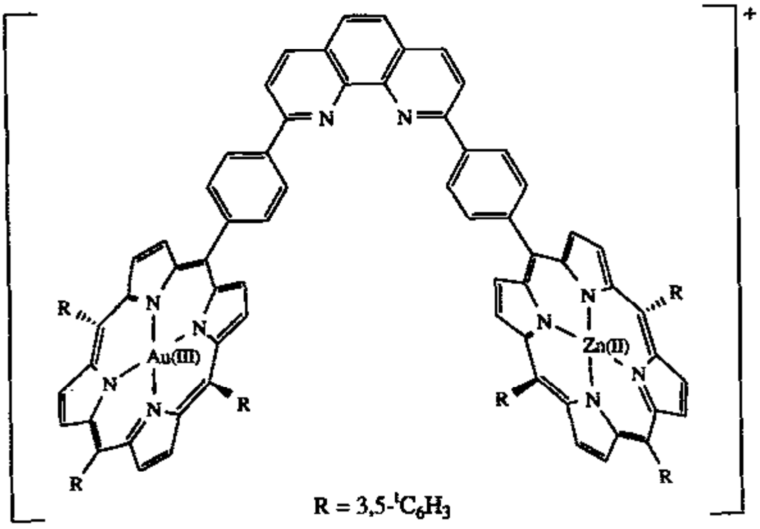
**(11)**



**(12)**



**(13)**



R = 3,5-$^tC_6H_3$

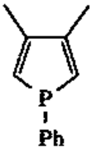
**(14)**

The synthesis of the bis-metallaporphyrin complex (**14**) has been reported; it is prepared by extending the organic framework from the gold(III) porphyrin ring and finally metallating the second porphyrin cavity by using $Zn(O_2CMe)_2$ [18].

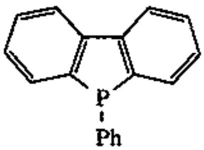
### *9.1.4 Complexes with phosphorus donor ligands*

Complexes containing phosphole ligands, (**15**) and (**16**), or $PPh_3$ of type $LAuCl_3$ have been synthesised and characterised by physical properties, electrochemical studies, IR and $^{31}P$ NMR spectroscopy. Ligand redistributions occur between the gold(III) complexes $LAuCl_3$ and $LAuBr_3$

and the gold(I) complexes LAuCl and LAuBr. The crystal structure of $Ph_3PAuBr_2Cl$ has been determined. As expected, the gold(III) centre is in a square planar environment, but the chlorine and two bromine atoms are disordered over the three sites; distances are Au-P = 2.314 (6) Å, Au-X = 2.399 (3), 2.413 (3) and 2.415 (4) Å (X = Cl/Br) [19].



**(15)**

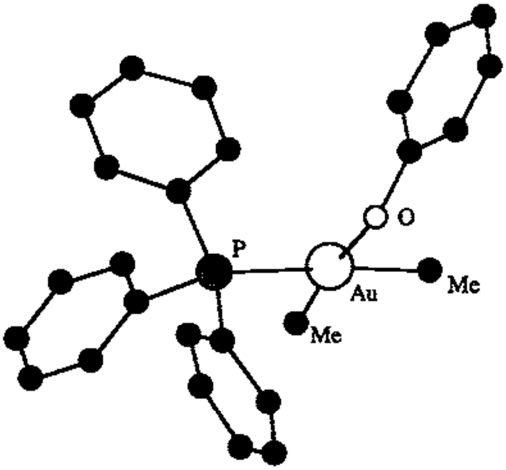


**(16)**

### *9.1.5 Complexes with oxygen donor ligands*

The fluorosulfate ion coordinates to gold(III) in the complex $\{Au(OSO_2F)_3\}_2$. The structure of $\{Au(OSO_2F)_3\}_2$ has been determined crystallographically. It is a centrosymmetric dimer; each square planar gold(III) centre is attached to two terminal, monodentate $OSO_2F^-$ ligands (Au-O = 1.959 (7) and 1.956 (9) Å) and the two metal atoms are bridged by two anions acting as *O,O'*-donors (Au-O = 2.020 (7) and 2.016 (6) Å). In the solid state, there is association between dimers with Au----O contacts of 2.757 (8) and 2.960 (7) Å which renders the overall geometry about each gold(III) centre elongated octahedral [20].

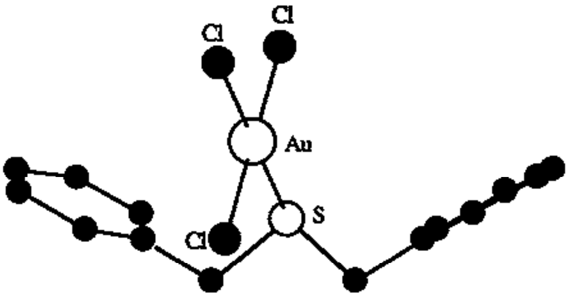
The square planar complexes *cis*-$AuMe_2(OR)(PPh_3)$ have been prepared from KOR and *cis*-$AuMe_2I(PPh_3)$ where R = Ph, $C_6H_4Me$, $CH_2CF_3$ and $CH(CF_3)_2$. Structural data are available for *cis*-$AuMe_2(OPh)(PPh_3)$, (17); important distances are Au-O = 2.09 (1) Å and Au-P = 2.402 (4) Å [21].



**(17)**

### 9.1.6 *Complexes with sulfur donor ligands*

Dibenzylsulfide, L, coordinates to gold(III) in the complex $LAuCl_3$, **(18)**, [22] and in the mixed valence compounds $AuLBr_2$ and AuLClBr [23]. The square planar complex **(18)** has been structurally characterised and distances within the coordination sphere of the metal atom are Au-S = 2.310 (3) Å and $Au\text{-}Cl_{(cis\text{-to S})}$ = 2.272 (3) (twice) and $Au\text{-}Cl_{(trans\text{-to S})}$ = 2.287 (4) Å [22]. In $AuLBr_2$, the structure is a bridged one-dimensional chain; each chain runs parallel to the crystallographic *a*-axis and is composed of alternating $Au^{(I)}LBr$ and $Au^{(III)}LBr_3$ units but a crystallographic disorder makes it difficult to distinguish between the units. The complex AuLClBr has a similar structure to $AuLBr_2$ [23].



**(18)**

### 9.1.7 *Complexes with selenium donor ligands*

The reaction of $Au_2Cl_6$ with $Ph_2Se$ yields the brown complex $Ph_2SeAuCl_3$, the structure of which has been determined. The square planar geometry is as expected; Au-Se = 2.445 (1) Å [24]. The related gold(I) complex $Ph_2SeAuCl$ has also been isolated (see Section 9.3.8) [24].

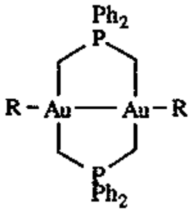
## 9.2 GOLD(II)

### 9.2.1 *Complexes with halide ligands*

In the non-stoichiometric compound $CsAu_{0.6}Br_{2.6}$, ESR spectroscopic results are consistent with a formal oxidation state of +2 for the gold centre. Powder X-ray diffraction data show that the compound exhibits a perovskite structure in the solid state; each gold ion is octahedrally sited, being associated with six bromide ions [25]. The conductivity of $CsAu_{0.6}Br_{2.6}$ is four orders of magnitude greater than that of the $Au^{(I)}\text{-}Au^{(III)}$ mixed-valence compound $Cs_2Au_2Br_6$ [5, 6, 25].

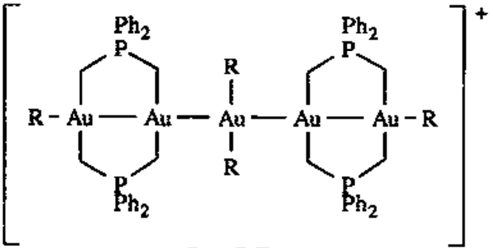
### 9.2.2 *Complexes with gold-carbon bonds*

Three papers report gold(II) ylide complexes. The reaction of $\{Au(CH_2)_2PPh_2\}_2Cl_2$ with AgX (X = $C_6F_5$, $C_6H_2F_3$-2,4,6, $NO_3$ and $MeCO_2$) eliminates silver chloride and yields the complexes $\{Au(CH_2)_2PPh_2\}_2X_2$. These complexes react with AgX'L (X' = $ClO_4$, and L = tht or $PPh_3$; X' = $NO_3$, and L = $PMe_3$) to give $[\{Au(CH_2)_2PPh_2\}_2L_2](X')_2$. Metathesis with MBr, MSCN, or $MS_2CN(CH_2Ph)_2$ generates neutral complexes which are not accessible by the initial reaction with $\{Au(CH_2)_2PPh_2\}_2Cl_2$ as the precursor. The crystal structures of $\{Au(CH_2)_2PPh_2\}_2Br_2$ and $[\{Au(CH_2)_2PPh_2\}_2(PPh_3)_2](ClO_4)_2$ have been determined [26]. A novel ylide complex, **(20)**, containing an $Au_5^{9+}$-backbone has been synthesised and structurally characterised; its formation is quite unexpected. Complex **(20)** is produced in the reaction of **(19)** with $AuR_3(OEt_2)$ (R = $C_5F_5$). The assignment of oxidation states to the gold centres in **(20)** is not straightforward and two possibilities are suggested. The authors prefer a description in which the central metal is a gold(I) centre and the remaining four are gold(II) centres. If this model is accepted, then **(20)** exhibits the first example of a square planar gold(I) environment [27].



R = $C_6F_5$

**(19)**



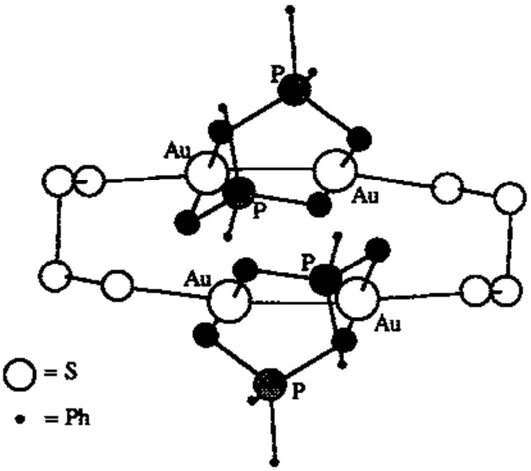
R = $C_6F_5$

**(20)**

The dimer $\{Au(CH_2)_2PPh_2\}_2\{C_6H_5CO_2\}_2$ reacts with $H_2S$ in thf solution to give a deep red product, $[\{Au(CH_2)_2PPh_2\}_2S_4]_2$, **(21)**, which has been crystallographically characterised. The structure of **(21)** may be described as two $Au_2(ylide)_2$-units inserted into an $S_8$-ring; the molecule is centrosymmetric. Each gold(II) centre exhibits a square planar geometry (Au-Au = 2.671 (2) Å) [28].

### 9.2.3 *Complexes with sulfur donor ligands*

The centrosymmetric dimer, $[\{Au(CH_2)_2PPh_2\}_2S_4]_2$, **(21)**, is described above; Au-S = 2.399 (15) and 2.413 (15) Å [28].



(21)

### 9.3 GOLD(I)

### 9.3.1 Complexes with halide and pseudo-halide ligands

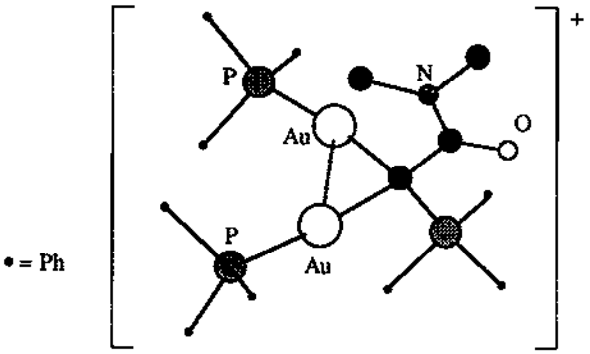
The bromide AuBr(CO) can be synthesised by the carbonylation of $Au_2Br_6$ or by treating AuBr with CO. The complex AuBr(CO) has been studied spectroscopically in solution; this includes a variable temperature investigation [29].

The photoluminescence of microcrystalline $Tl[Au(CN)_2]$ has been investigated as a function of temperature (1.7-400 K) and magnetic field (0-6 T ). The electronic structure of the complex has been probed by use of relativistically modified extended Hückel MO calculations. The results of the two studies provide evidence for the fact that a degree of covalent thallium(I)-gold(I) interaction perturbs the spectral properties exhibited by the complex. Differences are noted between the spectral features exhibited by $Tl[Au(CN)_2]$ and the salt $Cs[Au(CN)_2]$; the absorption and luminescence of $Tl[Au(CN)_2]$ occur at lower energies than those of $Cs[Au(CN)_2]$. Preliminary structural data for $Tl[Au(CN)_2]$ are presented; data were collected at 125 K and show the extent of Au-Au and Au-Tl interactions through the solid state lattice [30].

### 9.3.2 Complexes with gold-carbon bonds

The carbonyl complex complex AuBr(CO) was mentioned above [29]. Metallic gold reacts with uranium(VI) fluoride in the presence of carbon monoxide in anhydrous hydrogen fluoride to yield, quantitatively, the complex $[Au(CO)_2]^+[UF_6]^-$. This new species has been characterised by IR spectroscopy and by elemental analysis; IR spectral absorptions have been assigned [31].

The preparation of the gold(III) ylide complex $AuCl_3\{CH(PPh_3)C(O)NMe_2\}$ from gold(I) precursors was described in Section 9.1.2 [12]. The gold(I) complex $AuCl\{CH(PPh_3)C(O)NMe_2\}$ reacts with $Ph_3P{=}CHC(O)NMe_2$ in the presence of $NaClO_4$ to give the ionic complex $[Au\{CH(PPh_3)C(O)NMe_2\}_2](ClO_4)$. When the gold(I) complex $Au(acac)PPh_3$ is treated with $[Ph_3PCH_2C(O)NMe_2](ClO_4)$, the product is $[Au(PPh_3)\{CH(PPh_3)C(O)NMe_2\}](ClO_4)$ or $[Au_2(PPh_3)_2\{C(PPh_3)C(O)NMe_2\}](ClO_4)$ depending upon the conditions. The structure of the latter has been determined and the cationic complex is shown in structure (22) [12].

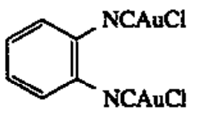


(22)

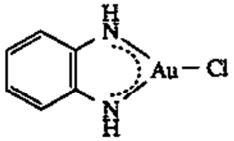
The complex $Au_2Cl_2(\mu\text{-}L)$ has been prepared from $HAuCl_4$ and L, where L = 2,5-dimethyl-2,5-diisocyanohexane. The molecular structural and spectroscopic properties of $Au_2Cl_2(\mu\text{-}L)$ provide evidence for quasi-one-dimensional linear chains which exhibit weak Au--Au interactions in the lattice. The solid state UV-VIS spectrum (KBr pellets) is characterised by an absorption at 292 nm; in solution, $\lambda_{max} = 272$ nm. It is suggested that this absorption should be assigned to a $d \rightarrow p$ transition. Other spectral data are discussed [32].

The addition of amines to the isonitrile-gold(I) complex, (23), has been studied. The product **(24)** has been isolated from reactions of **(23)** with phenylamine and 1,2-diaminobenzene; PhNCAuCl is also formed in the reaction with $PhNH_2$. Secondary amines react with **(23)** to yield either a binuclear complex, **(25)**, or carbenes of the type $AuCl\{C(NR_2)_2\}$ where $R_2 = Me_2$, $(CH_2)_4$, $(CH_2)_5$, or $(CH_2)_2O(CH_2)_2$. Other related systems have been prepared and the mechanisms of the reactions have been discussed [33].

Several reactions of the trimeric imidazole complex **(26)** have been reported. With iodine, oxidative addition to the gold(I) centres with retention of the trimeric framework is observed. With $ClCO_2Et$ and EtI, monomeric complexes LAuX where L = substituted imidazole and X = Et result; the crystal structure of $ClAu\overline{CN(CH_2Ph)CH{=}CHN}COOEt$ has been determined. When PhCOCl, $Cl_2$ or tosyl chloride react with complex **(26)**, oxidative addition with retention of the trimeric unit again occurs [34].



**(23)**



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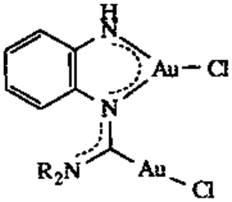
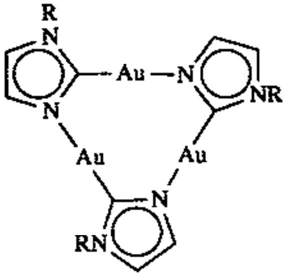


$R_2 = (CH_2)_5$

**(25)**



R = benzyl

**(26)**

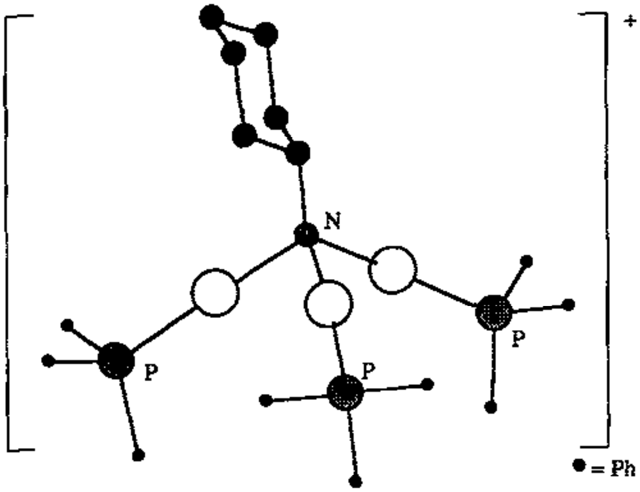
A series of gold(I) complexes of type $R_3PAuX$ with P-Au-C, P-Au-N, and P-Au-S linear coordination geometries has been the subject of a $^{197}Au$ Mössbauer spectroscopic study. The P-Au-C complexes include $Ph_3PAuC{\equiv}CPh$, $Ph_3PAuC{\equiv}C$(1-hydroxy-cyclohexyl) and derivatives of pyrimidine-2,4,6-trione [35].

### 9.3.3 *Complexes with nitrogen donor ligands*

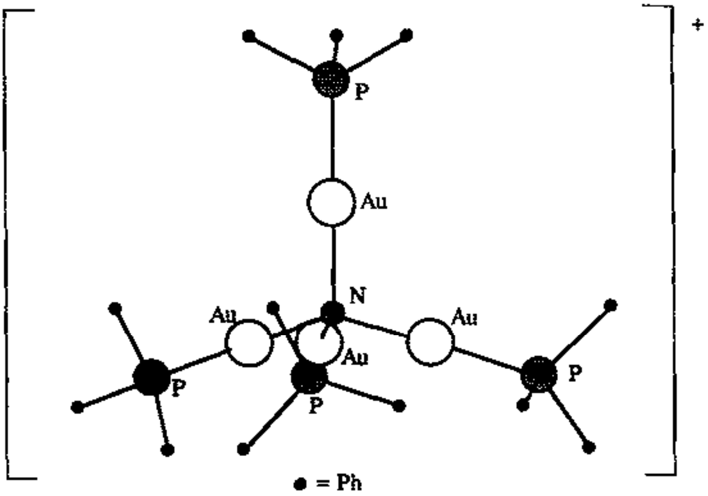
The gold(I) complexes *N*-{(*c*-$C_6H_{11})_3PAu$}-saccharine, *N*-{(*c*-$C_6H_{11})_3PAu$}-phthalimide and *N*-($Ph_3PAu$)-imidazolium picrate and two gold(I) derivatives of pyrimidine-2,4,6-trione have been investigated by $^{197}Au$ Mössbauer spectroscopy; related complexes with P-Au-C and P-Au-S coordination modes have also been studied [35].

The complex formation between gold(I) ions and acetonitrile has been studied potentiometrically (25°C, 1M $HClO_4$). Stability constants for the complexes $[Au(NCMe)]^+$ and $[Au(NCMe)_2]^+$ are $\lg\beta_1 = 1.44 \pm 0.05$ and $\lg\beta_2 = 1.77 \pm 0.09$, respectively [36].

The reactions of the amines $RNH_2$ (R = Me, Et, *n*-Pr, *i*-Pr, *t*-Bu, *c*-$C_6H_{11}$, $CH_2Ph$, or Ph) with the oxonium salt $[\{Ph_3PAu\}_3O][BF_4]$ yield $[RN\{AuPPh_3\}_3][BF_4]$. These intriguing complexes have been characterised by $^{31}P$, $^1H$ and $^{13}C$ NMR spectroscopy and for R = $^tBu$, $^{197}Au$ Mössbauer spectroscopic data have been analysed. The crystal structures of the complexes $[^tBuN\{AuPPh_3\}_3][BF_4]$ and [*c*-$C_6H_{11}N\{AuPPh_3\}_3][BF_4]$ have been determined; the structure of the cation $[c\text{-}C_6H_{11}N\{AuPPh_3\}_3]^+$ is shown in (27). Pertinent distances for the two cations are listed in Table 2 [37]. In related work, the structural features of the cations $[N\{AuPPh_3\}_4]^+$, $[P\{AuPPh_3\}_4]^+$ and $[As\{AuPPh_3\}_4]^+$ have been compared. In $[N\{AuPPh_3\}_4]^+$, (28), the nitrogen atom is tetrahedrally surrounded by four gold(I) phosphine groups; Au-N distances are 2.005 (9) Å (thrice) and 2.05 (3) Å, and Au-Au separations are 3.227 (2) Å (thrice) and 3.345 (2) Å. The tetrahedral geometry is expected but is in contrast to the unexpected square pyramidal structure of $[As\{AuPPh_3\}_4]^+$ (see Section 9.3.5) [38].



(27)

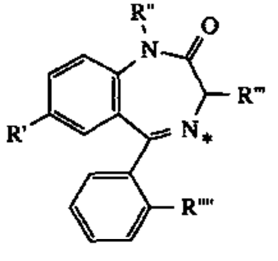


(28)

Table 2: Important structural parameters for the cations $[c\text{-}C_6H_{11}N\{AuPPh_3\}_3]^+$ and $[^tBuN\{AuPPh_3\}_3]^+$.

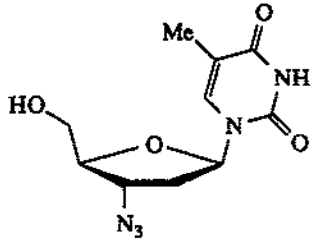
| | $[c\text{-}C_6H_{11}N\{AuPPh_3\}_3]^+$ | $[^tBuN\{AuPPh_3\}_3]^+$ |
|---|---|---|
| Au-N /Å | 2.045 (5), 2.040 (5), 2.059 (5) | 2.02 (1), 2.04 (1), 1.99(1) |
| Au-P /Å | 2.252 (2), 2.247 (2), 2.246 (2) | 2.264 (4), 2.249 (3), 2.255 (3) |
| ∠P-Au-N /deg | 176.8 (1), 171.4 (1), 172.5 (1) | 175.3 (3), 167.0 (3), 176.2 (4) |

Fast atom bombardment mass spectrometry has been used to study fragmentation patterns for gold(I) complexes with the 1,4-benzodiazepin-2-ones **(29)**-**(33)**. The complexes are $Ph_3PAuL$ where HL = **(31)** or **(32)**, ClAu(HL) where HL = **(29)**, **(30)** or **(31)**, $[Ph_3PAu(HL)](BF_4)$ where HL = **(29)**, **(30)**, **(31)** or **(33)**, and $[(Ph_3PAu)_2L](BF_4)$ where HL = **(31)**. In the complexes $Ph_3PAuL$, the gold(I) unit is coordinated at the N(R'') site. In the complexes ClAu(HL) and $[Ph_3PAu(HL)]^+$, coordination of HL to the gold(I) centre is through atom *N** (see diagram). In the cation $[(Ph_3PAu)_2L]^+$, one phosphine gold(I) unit is attached to the N(R'') site and the second to *N**. The results of the study provide an insight into the stability of the complexes [39].



| | R' | R'' | R''' | R'''' |
|---|---|---|---|---|
| **(29)** | Cl | Me | H | H |
| **(30)** | Cl | $H_2C$—◁ | H | H |
| **(31)** | $NO_2$ | H | H | H |
| **(32)** | Cl | H | OH | Cl |
| **(33)** | $NO_2$ | Me | H | H |

A series of gold(I), palladium(II), platinum(II), rhodium(III) and iridium(III) complexes incorporating the conjugate base of ligand HL, **(34)**, has been described. The gold(I) complexes are $LAuPR_3$ (R = Me, Et, Ph); the crystal structure of $LAuPMe_3$ has been determined and confirms the coordination of $L^-$ through *N*-donor atom indicated in structure **(34)**. Pertinent bond parameters in $LAuPMe_3$ are Au-N = 2.069 (9) Å, Au-P = 2.224 (3) Å, ∠N-Au-P = 177.4 (3)°. Complexes $LAuPMe_3$ and $LAuPPh_3$ exhibit anti-HIV activity similar to that of HL itself, and $LAuPMe_3$ also shows anti-inflammatory activity [40].



**(34)**

Some complexes involving *S,N*-bonded mercaptooxopurines are discussed in Section 9.3.7.

### *9.3.4 Complexes with phosphorus donor ligands*

A large range of complexes involving gold(I)-phosphorus bonds has, as in previous years, beed reported. This section describes complexes in which the Au$^{(I)}$-P bond is a primary feature and readers should scan other sections in this review for complexes in which the Au-P interaction is one of several other types. For example, a series of complexes involving P-Au-X (X = C, N, S) has been the subject of a $^{197}$Au Mössbauer spectroscopic study [35].

Molecular orbital calculations at the GAUSSIAN 90 level have addressed the bonding in the model gold(I) phosphine dimeric complex $\{H_3PAuCl\}_2$. Three geometries have been used: a $C_{2v}$ "parallel" geometry, a $C_2$ "perpendicular" geometry, and a $C_{2h}$ "antiparallel" geometry. The conculsion reached is there is Au----Au attraction which is caused by correlation effects, reinforced by relativistic effects [41].

The crystal structures of $(c\text{-}C_6H_{11})_3PAuCl$ [42] and $(3\text{-}MeC_6H_4)_3PAuCl$ [43] have been determined; structural data are given in Table 3. The geometrical parameters of $(3\text{-}MeC_6H_4)_3PAuCl$ are similar to those of the related complex $(2\text{-}MeC_6H_4)_3PAuCl$. The complex $(c\text{-}C_6H_{11})_3PAuCl$ was prepared from chloroauric acid, (reduced by 2,2'-thiodiethanol), with the phosphine ligand.

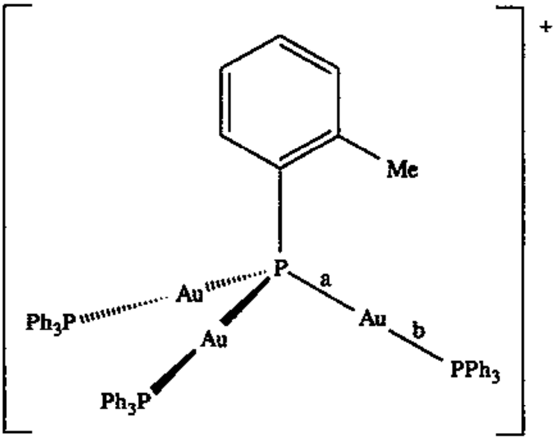
Table 3: Important structural parameters for the gold(I) complexes $(c\text{-}C_6H_{11})_3PAuCl$ and $(3\text{-}MeC_6H_4)_3PAuCl$.

| | $(c\text{-}C_6H_{11})_3PAuCl$ | $(3\text{-}MeC_6H_4)_3PAuCl$ |
|---|---|---|
| Au-Cl /Å | 2.281 (3) | 2.288 (2) |
| Au-P /Å | 2.234 (2) | 2.235 (2) |
| ∠P-Au-Cl /deg | 178.3 (1) | 175.1 (1) |

The phosphonium cations $[RP\{AuPPh_3\}_3]^+$ and $[P\{AuPPh_3\}_5]^{2+}$ have been prepared according to equations (v) and (vi). The crystal structure of $[(2\text{-}MeC_6H_4)P\{AuPPh_3\}_3]^+$, (35), has been determined and the geometry resembles that of the ammonium analogues $[c\text{-}C_6H_{11}N\{AuPPh_3\}_3]^+$ and $[{}^tBuN\{AuPPh_3\}_3]^+$, (see Table 2 and structure (27)) [44].

$$RPH_2 + [\{Ph_3PAu\}_3O][BF_4] \longrightarrow H_2O + [RP\{AuPPh_3\}_3][BF_4] \qquad \text{(v)}$$

$$[\{Ph_3PAu\}_3O][BF_4] \xrightarrow[-\,(Me_3Si)_2O]{P(SiMe_3)_3} [P\{AuPPh_3\}_5][BF_4]_2 \qquad \text{(vi)}$$

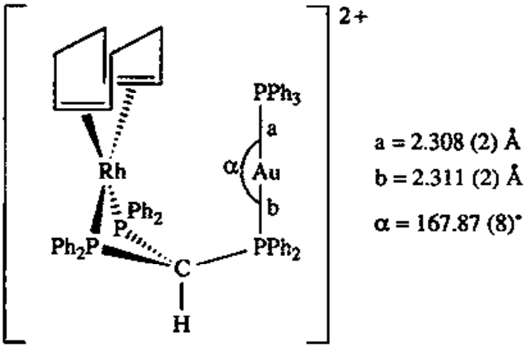


a = 2.277 (7), 2.317 (8), 2.321 (8) Å

b = 2.315 (8), 2.288 (8), 2.280 (9) Å

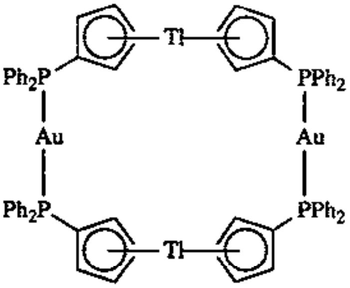
(35)

The reaction of $[Au(dppe)_2]Cl$ with 2-thiouracil, HL, and NaOH in methanol under reflux gives a unexpected result (see Section 9.3.7). The product is the ionic complex $[Au(dppe)_2][(L)(HL)]$ and the crystal structure of the complex has been determined; $^1H$ NMR spectroscopic data for $[Au(dppe)_2][(L)(HL)]$ are detailed. The geometry of the cation $[Au(dppe)_2]^+$ is unexceptional and is as previously observed in $[Au(dppe)_2]Cl.H_2O$ and $[Au(dppe)_2](SbCl_6)$ [45]. An investigation of gold(I) complexes with the ligand dppf (dppf = 1,1'-bis(diphenylphosphino)-ferrocene) has been described. Two complexes prepared analysed satisfactorily as $Au_2Cl_2(dppf)$ and $Au_2Cl_2(dppf)_2$; analyses for $[Au(dppf)_2]Cl$ were not consistent. Results of $^{197}Au$ and $^{57}Fe$ Mössbauer and $^{31}P$ NMR spectroscopies show that, in the solid state, there is no evidence for the existence of the tetrahedral cation $[Au(dppf)_2]^+$ but that in solution, this species does exist. In the solid state, results suggest that the gold(I) centres are in linear and trigonal environments [46].



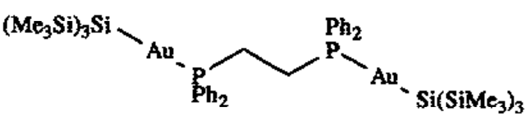
(36)

The reactions of [$Ph_3PAu(thf)$][$BF_4$] with [(cod)M{$CH(PPh_2)_3$}][$BF_4$] (M = Rh or Ir) in thf/$CH_2Cl_2$ yield the dimetallic complexes (cod)M{(μ-$(PPh_2)_2CH(PPh_2)$}$AuPPh_3$. For M = Rh, the complex, (**36**), has been structurally characterised. The reactivity of the new complexes has been investigated [47]. The tetrametallic complex (**37**) is produced when AuCl($SEt_2$) is treated with $TlC_5H_4PPh_2$. An X-ray crystallographic study of (**37**).$2C_6H_6$ has been carried out; important bond parameters around the gold(I) centres are Au-P = 2.319 (1) and 2.315 (1) Å and ∠P-Au-P = 176° [48].



(37)

Various dimetallic complexes, including "A-frame" complexes, involving gold(I) phosphine units have been reported. Reactions of (dppm)$Au_2Cl_2$ or (dppe)$Au_2Cl_2$ with LiSi(aryl)$_3$ or LiSi($SiMe_3$)$_3$ yields the complexes (dppm){AuSi(aryl)$_3$}$_2$ or (dppe){AuSi($SiMe_3$)$_3$}$_2$. Two structure types are observed; (dppe){AuSi($SiMe_3$)$_3$}$_2$, (**38**), exhibits an open structure with a crystallographic inversion centre, whilst (dppm){$AuSiPh_3$}$_2$, (**39**), has a closed structure with an Au-Au separation of 3.1680 (3) Å [49]. The reactions of [$NEt_4$]$_2$[$Fe_2(CO)_8$] with (dppm)$Au_2Cl_2$, (dppe)$Au_2Cl_2$ or (dppp)$Au_2Cl_2$ in thf gives the complexes $Fe_2(CO)_8Au_2$(μ-L) where L = dppm, dppe or dppp. The structure of $Fe_2(CO)_8Au_2(\mu\text{-dppm})$, (40), has been determined and reveals an unprecedented square $Fe_2Au_2$-framework with an Au-Au distance of 2.915 (1) Å. The complexes $Fe_2(CO)_8Au_2(\mu\text{-dppe})$ and $Fe_2(CO)_8Au_2(\mu\text{-dppp})$ react further with $[NEt_4]_2[Fe_2(CO)_8]$ but the dppm analogue does not [50].



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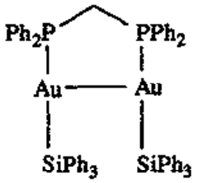
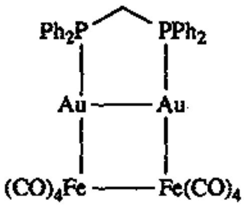


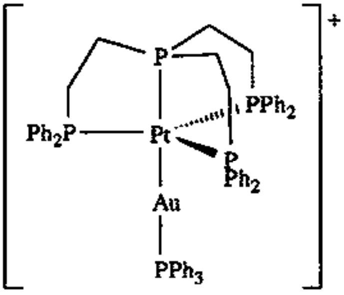
(39)



(40)

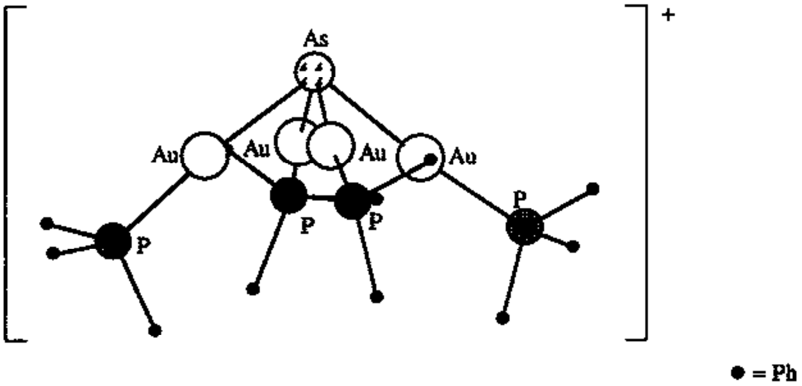
The hexafluorophosphate salt of the A-frame complex cation $[Ir(CO)(Cl)Au(\mu\text{-dppm})_2]^+$ reacts with $NH_4PF_6$ and methyl isocyanide to yield $[Ir(CNMe)_2Au(\mu\text{-dppm})_2][PF_6]_2$, the molecular structure of which has been determined (Ir-Au = 2.944 (1) Å). In its electronic spectrum, the complex $[Ir(CNMe)_2Au(\mu\text{-dppm})_2][PF_6]_2$ exhibits a strong absorption at 492 nm which is assigned to a $\sigma^*(d_z2d_z2)\rightarrow\sigma(p_zp_z)$ transition; there are also photoemissions at 540 nm (fluorescence) and at 668 nm (phosphorescence). A further isocyanide ligand can be added to $[Ir(CNMe)_2Au(\mu\text{-dppm})_2]^{2+}$ to give $[Ir(CNMe)_3Au(\mu\text{-dppm})_2]^{2+}$ for which structural data are available. The Ir-Au separation is 2.817 (1) Å which is shorter than in $[Ir(CNMe)_2Au(\mu\text{-dppm})_2]^{2+}$; this is interpreted in terms of an Ir→Au dative bond in $[Ir(CNMe)_3Au(\mu\text{-dppm})_2]^{2+}$ [51]. Related to these complexes is $[Pt(CN)_2Au(\mu\text{-dppm})_2]^+$. The structure of this cation has been determined and pertinent bond parameters are Au-P = 2.301 (10) and 2.278 (10) Å and ∠P-Au-P = 170.7 (3)°. The electronic spectrum of $[Pt(CN)_2Au(\mu\text{-dppm})_2][ClO_4]$ in acetonitrile exhibits an intense absorption at 320 nm and this is assigned to the spin allowed $^1(p_\sigma\leftarrow d_{\sigma^*})$ transition. In fluid solutions and in the solid state, the complex is photoluminescent [52].

The reactions of $PPh_3AuCl$ with the cations $[Pt(H)\{N(CH_2CH_2PPh_2)_3\}]^+$ or $[Pt(H)\{P(CH_2CH_2PPh_2)_3\}]^+$ lead to $[Pt(AuPPh_3)\{N(CH_2CH_2PPh_2)_3\}]^+$ or $[Pt(AuPPh_3)\{P(CH_2CH_2PPh_2)_3\}]^+$, (41), isolated as the tetraphenylborate salts. The new complexes have been characterised by $^{31}P$ and $^{195}Pt$ NMR spectroscopy and by X-ray crystallography; spectroscopic data are discussed in detail [53].



**(41)**

Two isomers of the complex cation $[Rh_2(\mu\text{-}Cl)_2(CNC_8H_9)_4(\mu\text{-}AuPPh_3)_2]^{2+}$, one green (gauche-staggered) and one red (trans-eclipsed), have previously been documented; in a new study, the effect of pressure on the complex is studied. The complex $[Rh_2(\mu\text{-}Cl)_2(CNC_8H_9)_4(\mu\text{-}AuPPh_3)_2][PF_6]_2$ is prepared from $Ph_3PAuCl$ and $Rh(CNC_8H_9)_3Cl$ with $TlPF_6$ in thf; this procedure gives the green isomer in 35% yield. When the green crystals are washed with thf, the red isomer is produced. Both isomers have equivalent $^{31}P$ and $^1H$ NMR spectral properties in solution; crystallographic data are presented. The electronic spectra of the complexes in the solid state have been observed as a function as pressure and the results have been discussed in terms of the isomerisation processes [54].



**(42)**

### 9.3.5 *Complexes with arsenic donor ligands*

The structures of the cations $[N\{AuPPh_3\}_4]^+$, $[P\{AuPPh_3\}_4]^+$ and $[As\{AuPPh_3\}_4]^+$ have been compared. In $[N\{AuPPh_3\}_4]^+$, **(28)**, the nitrogen atom is tetrahedrally surrounded by four gold(I) phosphine groups (see Section 9.3.3) , but the arsonium cation, (42), exhibits a novel square-based pyramidal structure. In $[As\{AuPPh_3\}_4]^+$, the gold(I) centres are linear, the average As-Au distance is 2.50 Å and the average Au-Au separation is 2.90 Å. The changes in structure along the series $[N\{AuPPh_3\}_4]^+$, $[P\{AuPPh_3\}_4]^+$ and $[As\{AuPPh_3\}_4]^+$ are discussed in terms of the gold(I)-gold(I) interactions [38].

### *9.3.6 Complexes with oxygen donor ligands*

The synthesis and structures of the complexes $Ph_3PAuOC(O)CHMe_2$ and $Ph_3PAuOC(O)CHMe(OH)$ have been reported. In $Ph_3PAuOC(O)CHMe_2$, the Au-O distance is 2.047 (6) Å and in $Ph_3PAuOC(O)CHMe(OH)$, the corresponding distance is 2.038 (16) Å. In the solid state, pairs of molecules of $Ph_3PAuOC(O)CHMe(OH)$ are associated via hydrogen bonded interactions. The complexes can be decarboxylated ($T < 100°C$) forming $CO_2$, Au(s), $PPh_3$ and organic products, the nature of which depends on the conditions and the carboxylate group. The decarboxylation of a carboxylate copolymer of polyethene and acrylic acid yields $CO_2$, $PPh_3$, Au(s) and an unsaturated polymer [55].

The reaction of AgL, (HL is the amino acid $HO_2CCH(Me)NHC(O)Ph$), with $Ph_3PAuCl$ yields $Ph_3PAuL$. The solid state structure of $Ph_3PAuL$ shows the presence of two independent molecules. In one molecule, *A*, the amino acid chain is in an extended conformation whereas in molecule *B*, the chain is in a conformation similar to that observed for the hippurato derivative; pertinent bond parameters for molecules *A* and *B* are given in Table 4 [56].

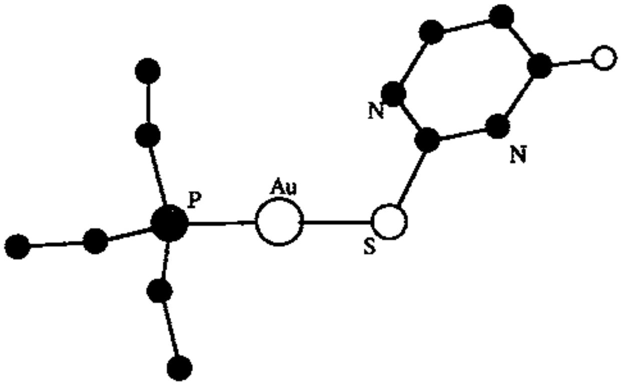
Table 4: Structural data describing the coordination sphere of the gold(I) centre in the crystallographic independent molecules of $Ph_3PAuO_2CCH(Me)NHC(O)Ph$.

| | Molecule *A* | Molecule *B* |
|---|---|---|
| Au-O /Å | 2.070 (12) | 2.069 (13) |
| Au-P /Å | 2.223 (5) | 2.210 (5) |
| ∠P-Au-O /deg | 177.9 (4) | 172.0 (4) |

### *9.3.7 Complexes with sulfur donor ligands*

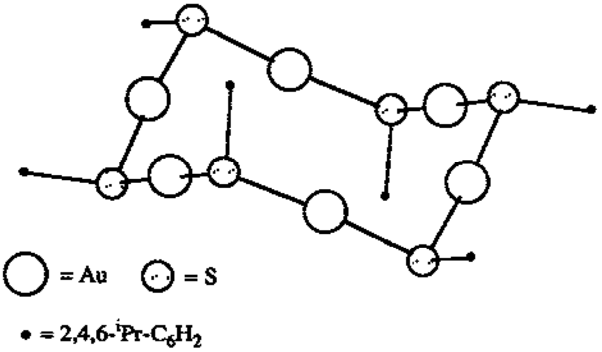
A group of gold(I) complexes with *S*-bonded $AuPPh_3$ or $Au(c\text{-}C_6H_{11})_3$-units has been the the subject of a $^{197}Au$ Mössbauer spectroscopic study; related *C*- and *N*-bonded complexes have also been analysed [35].

The reaction of $Et_3PAuCl$ and 2-thiouracil, HL, and NaOH in aqueous solution yields $Et_3PAuL$; this product contrasts with that obtained when $[Au(dppe)_2]Cl$ replaces $Et_3PAuCl$ (see Section 9.3.4). The complex $Et_3PAuL$, **(43)**, has been characterised by $^{13}C$ and $^{1}H$ NMR spectroscopy and by an X-ray crystal structure analysis; the gold(I) centre is linear with Au-S = 2.310 (2) Å, Au-P = 2.248 (2) Å, ∠S-Au-P = 176.9 (1)° [45].

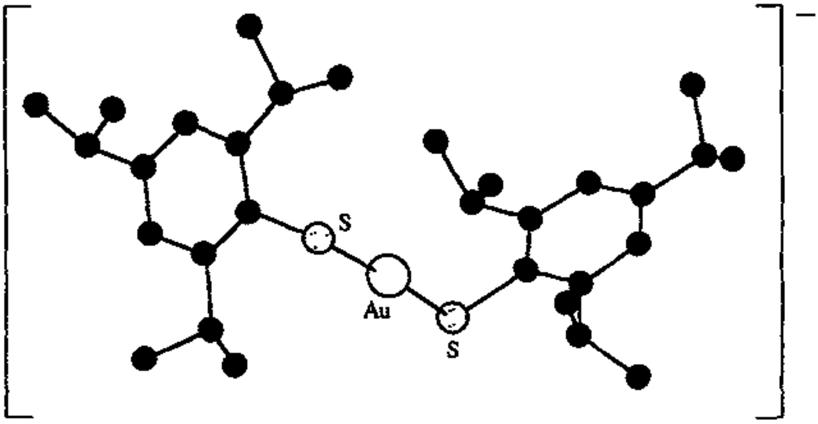


**(43)**

The thiol 2,4,6-$^{i}Pr_3C_6H_2SH$, HL, reacts with AuCl(CO) to give a hexameric thiolate of formula $\{AuL\}_6$, **(44)**. The cyclic structure of **(44)** has been confirmed crystallographically. The 12-membered ring has a chair conformation and is centrosymmetric; each gold(I) centre is linear with Au-S distances in the range 2.278 (3) Å to 2.295 (3) Å. Gold(I) iodide reacts with HL in liquid ammonia to produce $[NH_4][AuL_2]$. The complex crystallises with three moles of ammonia and an X-ray diffraction study of the complex shows that the anion, **(45)**, contains a linear gold(I) centre (∠S-Au-S = 175.6 (1)°) with Au-S bond lengths of 2.288 (4) and 2.288 (4) Å [57].



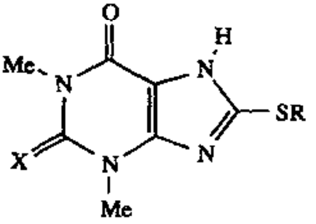
**(44)**



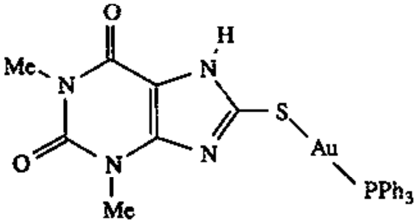
(45)

Complexes of gold(I) with a series of thioethers have been reported. $(AuCl)_2L$ and AuClL' have been prepared from $HAuCl_4$ and an excess of the ligands L and L', respectively, where L = $PhCH_2S(CH_2)_nSCH_2Ph$ ($n$ = 2, 5, 9) and L' = $Ph_2CHS(CH_2)_3Me$. Reactions of $R_3PAuCl$ (R = Et or Ph) with $PhCH_2SCH_2Ph$ or $Ph_2CHSCH_2CH_2NMe_2$ in the presence of silver(I) perchlorate lead to complexes of type $[R_3PAuL][ClO_4]$. In the cation $[Ph_3PAu(Ph_2CHSCH_2CH_2NMe_2)]^+$, the ligand is *S*- rather than *N*-bonded. An excess of the ligand $MeSCH_2CH_2PPh_2$ reacts with $HAuCl_4$ to yield $\{MeSCH_2CH_2PPh_2\}AuCl$ [58].

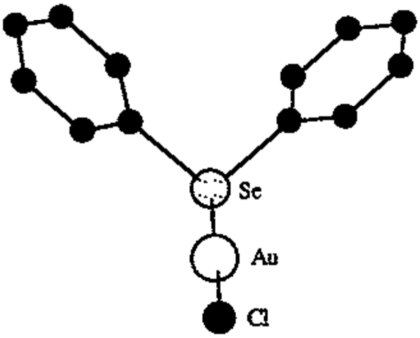
The complexes $Ph_3PAuCl$ and $Au_2Br_2(dppe)$ react with the mercaptooxopurines $H_2L$ = (46) and (47) or HL =(48) in basic solution to give the complexes $Ph_3PAuL$, $\{Ph_3PAu\}_2(\mu\text{-}L)$, $Au_2(\mu\text{-}dppe)(\mu\text{-}L)$ and $(LAu)_2(\mu\text{-}dppe)$. The new complexes exhibit either an *S*-bonded or *N,S*-bonded ligand, and have been characterised by IR, and $^1H$, $^{13}C$ and $^{31}P$ NMR spectroscopy. The structure of $Ph_3PAu(HL)$ where $H_2L$ = (46) has been determined by X-ray diffraction; molecules associate in pairs via hydrogen bonds. The gold(I) centre is linear (∠S-Au-P = 178.6 (2)°) with Au-S = 2.308 (2) Å and Au-P = 2.256 (2) Å. A substitution reaction between $Ph_3PAu(HL)$, where $H_2L$ = (46), and $Au_2Br_2(dppe)$ occurs and results in the formation of $Au_2(\mu\text{-}dppe)(\mu\text{-}L)$; the mechanism of the reaction has been discussed [59]. In related work, the intracellular accumulation and cytotoxic effects of complex (49) have been assessed [60].



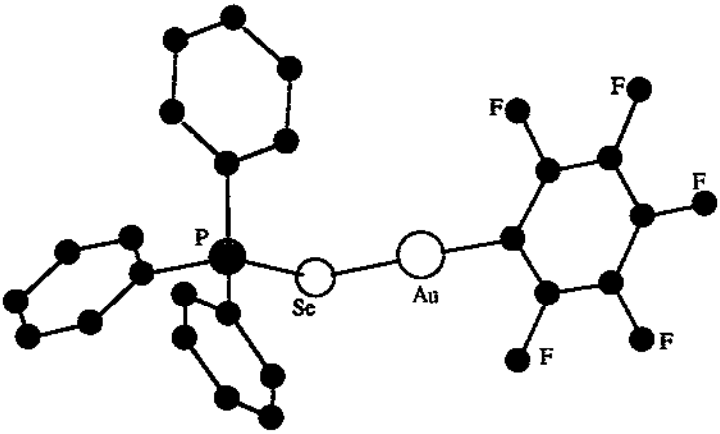
(46) X = O R = H
(47) X = S R = H
(48) X = O R = Me



**(49)**



**(50)**

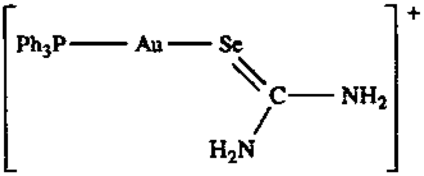


**(51)**

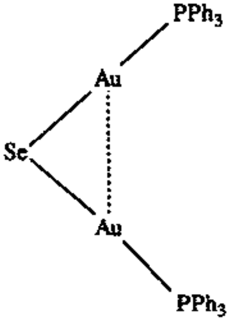
### *9.3.8 Complexes with selenium donor ligands*

The synthesis of the green gold(I) complex $Ph_2SeAuCl$ has been reported, in addition to that of the gold(III) complex $Ph_2SeAuCl_3$ (see Section 9.1.7). The crystal structure of $Ph_2SeAuCl$, **(50)**, has been determined; the gold(I) coordination shell is linear with Au-Se = 2.378 (1) Å [24]. The structure of the complex $Ph_3PSeAuC_6F_5$, **(51)**, has also been determined [61].

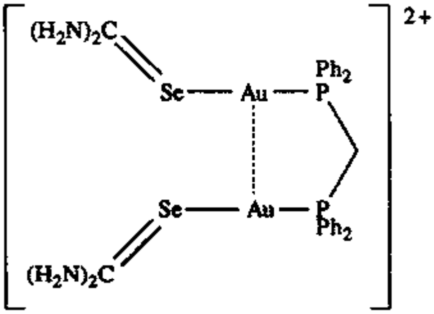
Selenourea and $Ph_3PAuCl$ react to give the complex $[Ph_3PAuSe{=}C(NH_2)_2]Cl$. This complex reacts in aqueous sodium carbonate to yield $(Ph_3PAu)_2Se$, and further reaction with $Ph_3PAuCl$ and $AgSbF_6$ produces the salt $[(Ph_3PAu)_3Se][SbF_6]$. The crystal structures of $[Ph_3PAuSe{=}C(NH_2)_2]Cl$, [**(52)**]Cl, and $(Ph_3PAu)_2Se$, **(53)**, have been elucidated. In cation **(52)**, bond parameters around the gold(I) centre are (in one of two independent molecules) Au-Se = 2.412 (2) Å, Au-P = 2.259 (5) Å, and ∠Se-Au-P = 176.5 (1)° and in **(53)**, Au-Se distances are 2.394 (1) and 2.398 (1) Å and the Au---Au separation is 3.051 (1) Å. The reaction of selenourea with $Au_2Cl_2(dppm)$ leads to $[\{AuSe{=}C(NH_2)_2\}_2(\mu\text{-}dppm)]Cl_2$, [**(54)**]$Cl_2$, and the structure of this complex has been determined by X-ray diffraction. Cation **(54)** has a "closed" conformation with a Au----Au separation of 3.236 (1) Å; Au-Se distances are 2.430 (1) and 2.426 (1) Å [62].



**(52)**



**(53)**



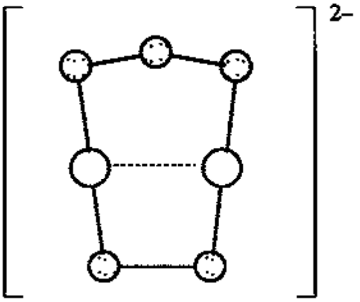
**(54)**

The cations $[(Ph_3PSe)_2Au]^+$ and $[(Ph_3PSe)AuPPh_3]^+$ have been prepared and isolated as the hexafluoroantimonate salts. The complex cation $[(PhMe_2PSe)AuPPh_3]^+$ has also been synthesised, but only in low yield. The crystallographically determined structures of $[(Ph_3PSe)_2Au]^+$ and $[(PhMe_2PSe)AuPPh_3]^+$ show the gold(I) environment in each to be linear as expected (Table 5). The rather long Au-Se bond in $[(PhMe_2PSe)AuPPh_3]^+$ is attributed to the *trans*-influence of the phosphine ligand. In $[(Ph_3PSe)_2Au]^+$, the conformation of the ligands is defined by the torsion angle ∠P-Se---Se-P = 59° [63].

Table 5: Selected structural data for $[(Ph_3PSe)_2Au]^+$ and $[(PhMe_2PSe)AuPPh_3]^+$.

| | $[(Ph_3PSe)_2Au]^+$ | $[(PhMe_2PSe)AuPPh_3]^+$ |
|---|---|---|
| Au-Se /Å | 2.390 (1), 2.395 (1) | 2.422 (1) |
| Au-P /Å | | 2.270 (3) |
| ∠X-Au-Se (X = Se or P) /deg | 172.6 (1) | 175.8 (1) |

Two new gold(I) polyselenide complex anions $[Au_2(Se_2)(Se_3)]^{2-}$, **(55)**, and $[Au_2(Se_2)(Se_4)]^{2-}$, **(56)**, have been prepared and structurally characterised; they are the first such complexes to be isolated from solution. The salts produced are $[Ph_4P]_2[Au_2(Se_2)(Se_3)]$, $[PPN]_2[Au_2(Se_2)(Se_3)]$ and $[Ph_4P]_2[Au_2(Se_2)(Se_4)]$. Infrared spectral absorptions for the modes $\nu_{SeSe}$ and $\nu_{AuSe}$ have been assigned. In anion **(55)**, pertinent bond distances are Au-Se = 2.388 (1), 2.401 (3), 2.399 (4) and 2.401 (4) Å, and Au-----Au = 3.004 (2) Å whilst in **(56)**, which contains a $C_2$ axis, Au-Se = 2.433 (5) and 2.355 (5) Å, and Au---Au = 3.132 (3) Å [64].



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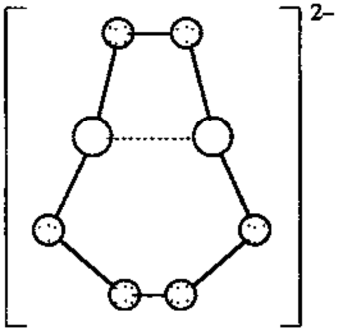


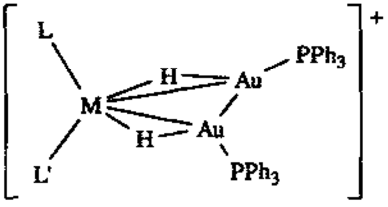
**(56)**

## 9.4 CLUSTERS

An overview of recent developments in the chemistry of homometallic and heterometallic clusters containing gold atoms has been presented (37 references) [65].

Molecular orbital calculations (self-consistent discrete-variational Xα-method) have been carried out on the model clusters $[\{Au(PH_3)\}_6X_n]^{n+}$ where X is an interstitial atom (X = B, *n* = 1; X = C, *n* = 2; X = N, *n* = 3). The electronic structures of $[Au_6]^{2+}$ and $[\{Au(PH_3)\}_6]^{2+}$ have also been investigated. A primary result of the work is that there is a major contribution from each Au 5*d* AO and this contribution is as important as that of the Au 6*s* orbital; this conclusion is in contrast to the results of previous calculations on similar models. The new results, and in particular the role of the gold 5*d*-6*s* hybridisation, can be applied to other clusters of gold atoms, for example $[\{Au(PH_3)\}_5X_n]^{n+}$ (X = C, *n* = 1; X = N, *n* = 2) [66].

The cationic triplatinum cluster $[Pt_3(\mu_3\text{-}H)(\mu\text{-}dppm)_3]^+$ reacts with a source of $[AuPPh_3]^+$ to yield $[Pt_3(\mu_3\text{-}H)(\mu_3\text{-}AuPPh_3)(\mu\text{-}dppm)_3]^{2+}$; with an excess of $[AuPPh_3]^+$, the complex formed is $[Pt_3(\mu_3\text{-}AuPPh_3)_2(\mu\text{-}dppm)_3]^{2+}$. The cation $[Pt_3(\mu_3\text{-}H)(\mu_3\text{-}AuPPh_3)(\mu\text{-}dppm)_3]^{2+}$ undergoes reversible deprotonation and the gold(I) fragment can be removed from the deprotonated complex by adding $PPh_3$. Related systems are also presented and the results are discussed in terms of electrophilic substitution at a triplatinum-cluster core. The crystal structure of $[Pt_3(\mu_3\text{-}AuPMe_3)_2(\mu\text{-}dppm)_3][PF_6]_2$ has been determined [67].



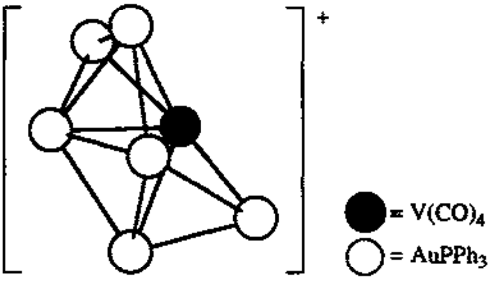
M = Ru
L = Cp*
L' = $P(c\text{-}C_6H_{11})_3$

M = Nb
L = L' = $\eta^5\text{-}C_5H_4(SiMe_3)_2$

M = Nb
L = L' = $\eta^5\text{-}C_5H_3(SiMe_3)_2\text{-}1,3$

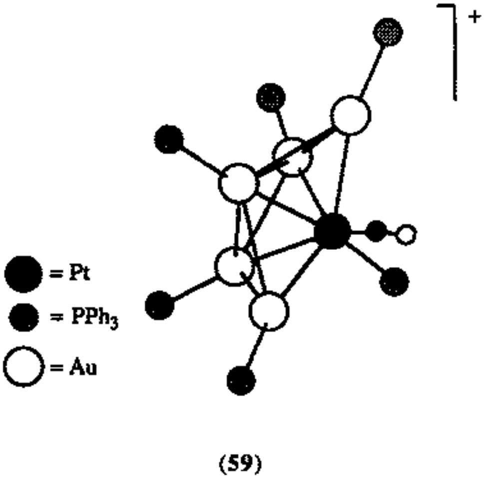
**(57)**

Complexes of type **(57)** have been prepared by reacting $MH_3LL'$ with $[AuPPh_3][PF_6]$. The products have been characterised spectroscopically. Related clusters have also been reported and amongst these is the raft species $Au_3Nb_3(\mu\text{-}H)_6(\eta\text{-}C_5H_4SiMe_3)_6$ which has been crystallographically characterised [68]. The reaction in thf of $Ph_3PAuV(CO)_6$ with $Ph_3PAu(NCO)$ and $Ph_3PAuN_3$ under conditions of photolysis leads to $\{Ph_3PAu\}_3V(CO)_5$, $[\{Ph_3PAu\}_6V(CO)_4]^+$, and homometalic gold clusters. The cationic cluster $[\{Ph_3PAu\}_6V(CO)_4]^+$, **(58)**, crystallises as $[\{Ph_3PAu\}_6V(CO)_4]_2[PF_6][(OH)_x,F_y].2EtOH$ where $x+y = 1$; the $Au_6V$-core is a bicapped trigonal bipyramid [69].



**(58)**

A series of papers reports clusters with PtAu$_x$-cores. The cluster cations $[\mathrm{Pt(H)\{AuPPh_3\}_8}]^+$ and $[\mathrm{Pt(H)\{AuPPh_3\}_6(PPh_3)}]^+$ have been synthesised and characterised by using multinuclear NMR spectroscopy. The dication $[\mathrm{Pt(H)\{AuPPh_3\}_7(PPh_3)}]^{2+}$ reacts with $[\mathrm{SnCl_3}]^-$ to yield $[\mathrm{Pt(H)\{AuPPh_3\}_7(SnCl_3)}]^+$. Catalytic tests on the new clusters show that the compounds are not active with respect to the hydrogenation and isomerisation of hexanes at room temperature and pressure [70]. Nucleophilic addition of bromide, iodide and cyanide ions, ($X^-$), to the cluster dication $[\mathrm{Pt\{AuPPh_3\}_6(PPh_3)}]^{2+}$ and nucleophilic additions/substitutions of the ligands $\mathrm{P(OMe)_3}$ and $\mathrm{P(OCH_2)_3CMe}$, (L), have been studied. The products are $[\mathrm{Pt\{AuPPh_3\}_6(PPh_3)(X)}]^+$ and $[\mathrm{Pt\{AuPPh_3\}_6(PPh_3)(L)}]^{2+}$ respectively. The cluster $[\mathrm{Pt\{AuPPh_3\}_6(PPh_3)}]^{2+}$ also reacts with $\mathrm{Hg_2(NO_3)_2}$ to yield $[\mathrm{Pt\{AuPPh_3\}_5(PPh_3)(HgNO_3)_2}]^+$. Other related reactions are reported. Two new clusters have been structurally characterised; both $[\mathrm{Pt\{AuPPh_3\}_5(PPh_3)(CO)}]^+$, **(59)**, and $[\mathrm{Pt\{AuPPh_3\}_5(PPh_3)(HgNO_3)_2}]^+$, **(60)**, possess cores which are described as "spheroidal fragments of centred icosahedra" [71].



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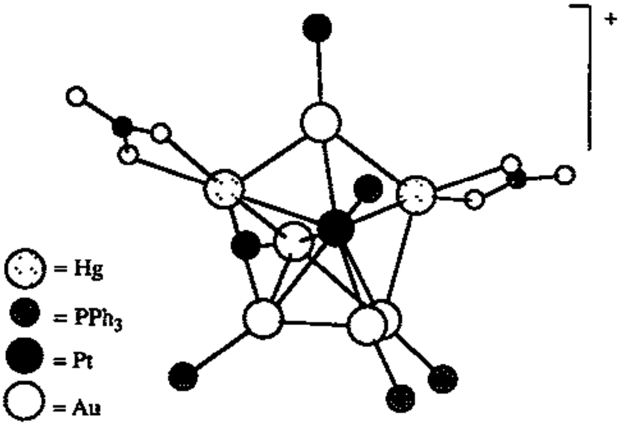

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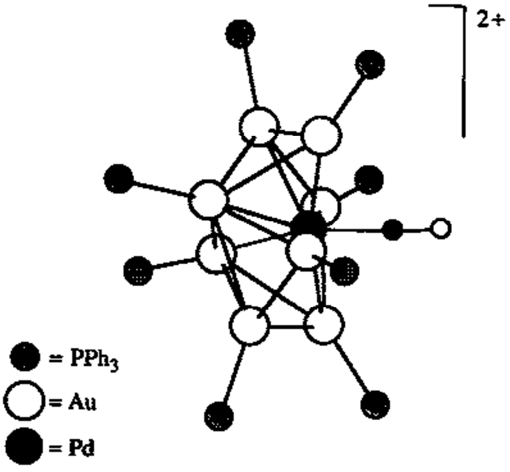

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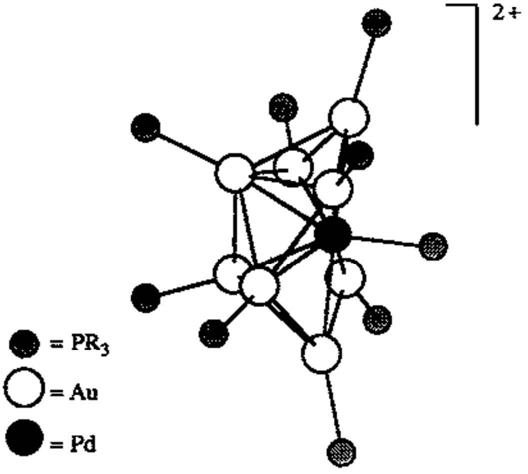

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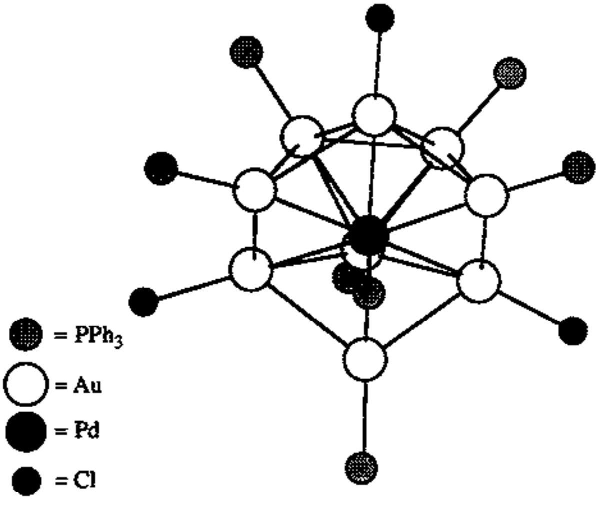


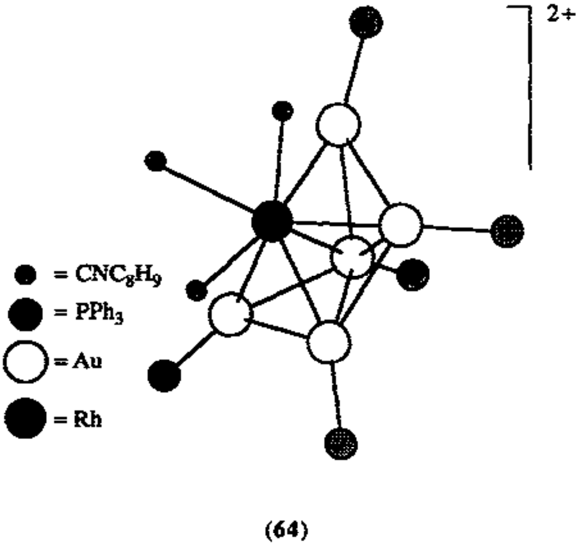
**(63)**

In a related study, nucleophilic addition/substitution reactions of $P(OMe)_3$ and $P(OCH_2)_3CMe$, (L), with $[Pd\{AuPPh_3\}_8]^{2+}$ and $[Pd\{AuPPh_3\}_6(PPh_3)]^{2+}$ have been investigated. The new cluster dications $[Pd\{AuPPh_3\}_6\{P(OMe)_3\}\{AuP(OMe)_3\}_2]^{2+}$ and $[Pd\{AuPPh_3\}_6\{P(OCH_2)_3CMe\}_2]^{2+}$ have been characterised by FAB-mass spectrometry, $^{31}P$ and $^{1}H$ NMR and IR spectroscopies. The results of an electrochemical study of $[Pd\{AuPPh_3\}_8]^{2+}$ have been discussed. Structural data for $[Pd(CO)\{AuPPh_3\}_8]^{2+}$, **(61)**, and

$[Pd\{AuPPh_3\}_6\{P(OMe)_3\}\{AuP(OMe)_3\}_2]^{2+}$, **(62)**, illustrate that the two cluster cores are "spheroidal fragments of centred icosahedra" [72]. The results of a variable temperature $^{31}P$ NMR spectroscopic study of $[Pt(H)\{AuPPh_3\}_7(PPh_3)]^{2+}$ and related clusters show that fluxional processes are operative in solution at room temperature; spectra of all clusters studied exhibit sharp resonances. Lowering the temperature slows down the rate of exchange and the low temperature spectra can be interpreted in terms of the known solid state structures of the clusters [73]. Nucleophilic attack by iodide, chloride and thiocyanate ions, $(X^-)$, on $[Pt\{AuPPh_3\}_8]^{2+}$ produces the neutral clusters $Pt\{AuPPh_3\}_6(AuX)_3(PPh_3)$ and for X = Cl, the structure of the cluster, **(63)**, has been confirmed crystallographically. The platinum centre interacts with six $AuPPh_3$ and three AuCl units as well as a triphenylphosphine ligand [74]. Halide-for-phosphine exchange occurs when the dications $[Pt\{AuPPh_3\}_8(CO)]^{2+}$ and $[Pt(H)\{AuPPh_3\}_7(PPh_3)]^{2+}$ react with $Cl^-$, $Br^-$ or $I^-$ ions, the products being $[Pt\{AuPPh_3\}_7(AuX)(CO)]^+$ and $[Pt(H)\{AuPPh_3\}_6(AuX)(PPh_3)]^{2+}$, respectively. These have been characterised by $^{31}P$, $^{13}C$ and $^{195}Pt$ NMR spectroscopy [74]. Related work illustrates that the reactions of $[Pt\{AuPPh_3\}_8]^{2+}$ and $[Pt\{AuPPh_3\}_8(CO)]^{2+}$ with CuCl give $[Pt(CuCl)\{AuPPh_3\}_8]^{2+}$ and $[Pt(CuCl)\{AuPPh_3\}_8(CO)]^{2+}$, respectively. The structure of the former has been determined and further chemistry of the products is described [75].

Electronic absorption and MCD spectroscopic studies of the cluster dication $[\{AuPPh_3\}_8]^{2+}$ (as the nitrate salt) in acetonitrile solution have been reported. The results are discussed in terms of appropriate bonding models; there is evidence for an Au $5d \rightarrow 6s$ transition. The results are compared with those for $[\{AuPPh_3\}_9]^{2+}$ [76].

The reaction of $Ph_3PAuCl$ with $Rh(CNC_8H_9)_3Cl$ gives a red solution from which the cluster cations $[Rh(CNC_8H_9)_3(AuPPh_3)_5]^{2+}$, **(64)**, and $[Rh(CNC_8H_9)_2(AuPPh_3)_6(AuCl)_2]^{2+}$, **(65)**, can be isolated. The synthesis of $[Rh(CO)_2(AuPPh_3)_7]^{2+}$, **(66)**, has also been reported. The new clusters have been characterised by $^{31}P$ NMR and IR spectroscopy, FAB-mass spectrometry and X-ray crystallography [77].



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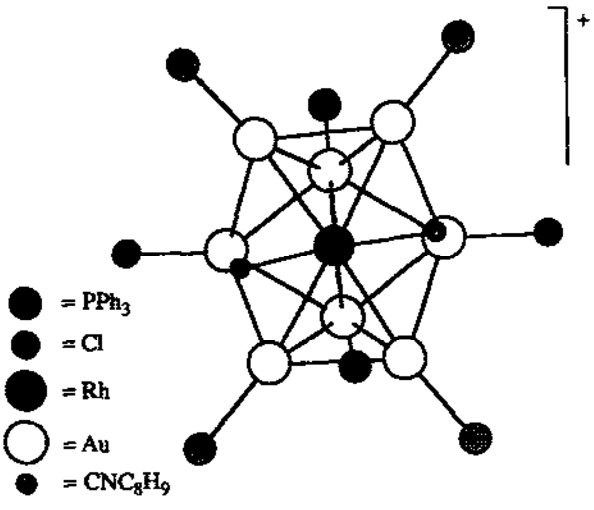

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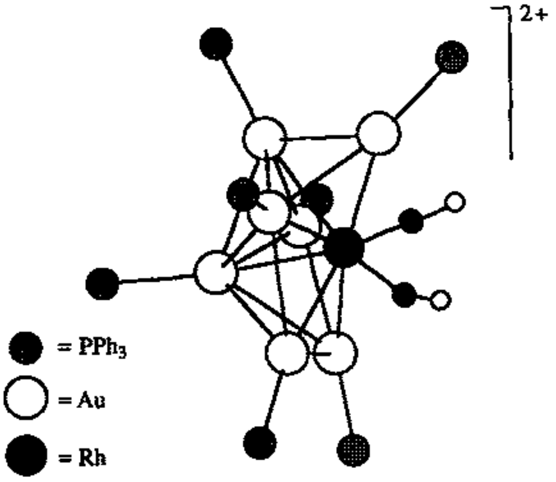
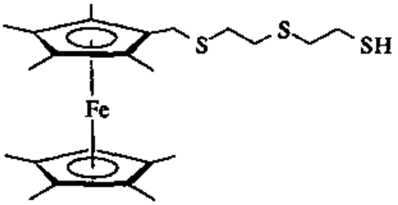


**(66)**

The results of XPS and UPS studies on $Au_{55}$-clusters and of $Ph_3PAuCl$ embedded in a matrix have been discussed. The spectra are compared with those of bulk gold; the valence and core level spectra of the cluster species show shifts of bands and the Fermi level to higher energies [78]. The preparation (from phosphine, $HAuCl_4$, $AgSbF_6$, and $NaBH_4$) and structure of the giant cluster $[\{(4\text{-}MeC_6H_4)_3P\}_{10}Au_{13}Ag_{12}Cl_7][SbF_6]_2$ have been reported. The core is close to possessing a staggered-eclipsed-staggered configuration [79]. In a related study, the structure of the cationic cluster $[(Ph_3P)_{10}Au_{13}Ag_{12}Br_8]^+$ has been elucidated; the core here exhibits an exact staggered-eclipsed-staggered configuration [80].

## *9.4 SURFACES*

Two papers describe the interaction of sulfur donor ligands with gold surfaces. The alkanethiols $HS(CH_2)_{11}(OCH_2CH_2)_xOH$ ($x$ = 3-7) have been prepared. On gold surfaces, the thiols form "self-assembled monolayers" (SAMs). These have been investigated by using X-ray photoelectron spectroscopy and the properties of the monolayers have been described [81]. Three ferrocenyl thiols and disulfides, including **(67)**, have been used to modify the selectivity of gold micor-electrodes on an $Si_3N_4$ substrate. The systems have been characterised by the use of Auger electron spectroscopy and electrochemical methods [82].



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## *REFERENCES*

1. C.E. Housecroft, *Coord. Chem. Rev.*, 115 (1992) 117.
2. P.J. Sadler, *Adv. Inorg. Chem.*, 36 (1991) 1.
3. B. Zemva, K. Lutar, A. Jesih, W.J. Casteel, A.P. Wilkinson, D.E. Cox, R.B. Vondreele, H. Borrmann and N. Bartlett, *J. Am. Chem. Soc.*, 113 (1991) 4192.
4. D.S. Rustad and N.W. Gregory, *Polyhedron*, 10 (1991) 633.
5. H. Kitagawa, N. Kojima and T. Nakajima, *J. Chem. Soc., Dalton Trans.*, (1991) 3121.
6. H. Kitagawa, N. Kojima and H. Sakai, *J. Chem. Soc., Dalton Trans.*, (1991) 3211.
7. R.A. Potts, D.L. Gaj, W.F. Scheider, N.S. Dean, J.W. Kampf and J.P. Oliver, *Polyhedron*, 10 (1991) 1631.
8. H.W. Yang, Z.X. Zhou, M.R. Zhang, X.X. Zhang and B.Y. Ruan, *Polyhedron*, 10 (1991) 1025.
9. D.B. Dell'Amico, F. Calderazzo, A. Morvillo, G. Pelizzi and P. Robino, *J. Chem. Soc., Dalton Trans.*, (1991) 3009.
10. U. Heinzel and R. Mattes, *Polyhedron*, 10 (1991) 19.
11. R.G Raptis, J.P. Fackler, J.D. Basil and D.S. Dudis, *Inorg. Chem.*, 30 (1991) 3072.
12. J. Vicente, M.T. Chicote, M.C. Lagunas and P.G. Jones, *J. Chem. Soc., Dalton Trans.*, (1991) 2579.
13. E.C. Constable, R.P.G. Henney, P.R. Raithby and L.R. Sousa, *Angew. Chem., Int. Ed., Engl.*, 30 (1991) 1363.
14. E.C. Constable, R.P.G. Henney and T.A. Leese, *J. Organomet. Chem.*, 361 (1989) 277.
15. D. Kovala-Demertzi, *Bull. Chem. Soc. Jpn.*, 64 (1991) 744.
16. J. Vicente, M.D. Bermudez and J. Escribano, *Organometallics*, 10 (1991) 3380.

17. E. Kimura, Y. Kurogi and T. Takahashi, *Inorg. Chem.*, 30 (1991) 4117.
18. V. Heitz, S. Chardon-Noblat and J.-P. Sauvage, *Tetrahedron Lett.*, 32 (1991) 197.
19. S. Attar, J.H. Nelson, W.H. Bearden, N.W. Alcock, L. Solujić and E.B. Milosavjević, *Polyhedron*, 10, (1991) 1939.
20. H. Willner, S.J. Rettig, J. Trotter and F. Aubke, *Can. J. Chem.*, 69 (1991) 391.
21. T. Sone, M. Iwata, N. Kasuga and S. Komiya, *Chem. Lett.*, (1991) 1949.
22. K. Takahashi, *Bull. Chem. Soc. Jpn.*, 64 (1991) 2572.
23. K. Takahashi, and H. Tanino, *Chem. Lett.*, (1991) 1977.
24. P.G. Jones and C. Thone, *Z. Naturforsch, B*, 46 (1991) 50.
25. H. Kitagawa, N. Kojima, N. Matsushita, F. Ban and I. Tsujikawa, *J. Chem. Soc., Dalton Trans.*, (1991) 3115.
26. R. Uson, A. Laguna, M. Laguna, J. Jimenez and P.G. Jones, *J. Chem. Soc., Dalton Trans.*, (1991) 1361.
27. R. Uson, A. Laguna, M. Laguna, J. Jimenez and P.G. Jones, *Angew. Chem., Int. Ed., Engl.*, 30 (1991) 198.
28. L.C. Porter and J.P. Fackler, *Acta Crystallogr., Sect. C*, 47 (1991) 2351.
29. D.B. Dell'Amico, F. Calderazzo, P. Robino and A. Segre, *J. Chem. Soc., Dalton Trans.*, (1991) 3017.
30. Z. Assefa, F. Destefano, M.A. Garepapaghi, J.H. Lacasce, S. Ouellete, M.R. Corson, J.K. Nagle and H.H Patterson, *Inorg. Chem.*, 30 (1991) 2868.
31. M. Adelhelm, W. Bacher, E.G. Hohn and E. Jacob, *Chem. Ber.*, 124 (1991) 1559.
32. D. Perreault, M. Drouin, A. Michel and P.D Harvey, *Inorg. Chem.*, 30 (1991) 2.
33. W.P. Fehlhammer and W. Finck, *J. Organomet. Chem.*, 414 (1991) 261.
34. F. Bonati, A. Burini, B.R. Pietroni and B. Bovio, *J. Organomet. Chem.*, 408 (1991) 271.
35. F. Bonati, A. Burini, B.R. Pietroni, E. Torregiani, S. Calogero and F.E. Wagner, *J. Organomet. Chem.*, 408 (1991) 125.
36. L.D. Tsvelodub and V.I. Malkova, *Sib. Khim. Zh.*, (1991) 72; *Chem. Abstr.*, 115 (1991) 264476x.
37. A. Grohmann, J. Riede and H. Schmidbaur, *J. Chem. Soc., Dalton Trans.*, (1991) 783.
38. E. Zeller, H. Beruda, A. Kolb, P. Bissinger, J. Riede and H. Schmidbaur, *Nature*, 352 (1991) 141.
39. G. Banditelli, A.L. Bandini, M.A. Cinellu, G. Minghetti, M. Scandola and P. Traldi, *Inorg. Chim. Acta*, 183 (1991) 51.
40. T. Pill, K. Polborn, A. Kleinschmidt, V Erfle, W. Breu, H. Wagner and W. Beck, *Chem. Ber.*, 124 (1991) 1541.
41. P. Pyykko and Y.F. Zhao, *Angew. Chem. Int. Ed., Engl.*, 30 (1991) 604.
42. J.A. Muir, S.I. Cuadrado and M.M. Muir, *Acta Crystallogr., Sect. C*, 47 (1991) 1072.
43. C.S.W. Harker and E.R.T. Tiekink, *Acta Crystallogr., Sect. C*, 47 (1991) 878.
44. H. Schmidbaur, G. Weidenhiller and O. Steigelmann, *Angew. Chem., Int. Ed., Engl.*, 30 (1991) 433.
45. C.S.W. Harker, E.R.T. Tiekink and M.W. Whitehouse, *Inorg. Chim. Acta*, 181 (1991) 23.
46. A. Houlton, R.M.G. Roberts, J. Silver and R.V. Parish, *J. Organomet. Chem.*, 418 (1991) 269.
47. H. Elamouri, A.A. Bahsoun, J. Fischer, J.A. Osborn and M.T. Youinou, *Organometallics*, 10 (1991) 3582.
48. G.K. Anderson and N.P. Rath, *J. Organomet. Chem.*, 414 (1991) 129.
49. H. Piana, H. Wagner and U. Schubert, *Chem. Ber.*, 124 (1991) 63.
50. S. Alvarez, O. Rossell, M. Seco, J. Vallis, M.A. Pellinghelli and A. Tiripicchio, *Organometallics*, 10 (1991) 2309.
51. A.L. Balch and V.J. Catalano, *Inorg. Chem.*, 30 (1991) 1302.
52. H.K. Yip, C.-M. Che and S.-M. Peng, *J. Chem. Soc., Chem. Commun.*, (1991) 1626.
53. M. Peter, P. Peringer and E.P. Müller, *J. Chem. Soc., Dalton Trans.*, (1991) 2459.
54. K.L. Bray, H.G. Dickamer, D.M.P. Mingos, M.J. Watson and J.R. Shapley, *Inorg. Chem.*, 30 (1991) 864.
55. J.P. Fackler, M.N.I. Khan, C. King, R.J. Staples and R.E.P. Winpenny, *Organometallics*, 10 (1991) 2178.
56. P.G. Jones and R. Schelbach, *Inorg. Chim. Acta*, 182 (1991) 239.
57. I. Schroter and J. Strähle, *Chem. Ber.*, 124 (1991) 2161.
58. A. Von Petersenn, *Arch. Pharm.*, 324 (1991) 411; *Chem. Abstr.*, 115 (1991) 125635k.
59. E. Colacio, A. Romerosa, J. Ruiz, P. Román, J.M. Gutiérrez-Zorrilla, A. Vegas, M. Martín-Ripoll, *Inorg. Chem.*, 30 (1991) 3743.
60. M.P. Arizti, A. Garciaorad, F. Sommer, L. Silvestro, P. Massiot, P. Chevallier, J.M. Gutiérrez-Zorrilla, E. Colacio, M.M. Depancorbo and H. Tapiero, *Anticancer Res.*, 11 (1991) 625.

61. P.G. Jones and C. Thone, *Chem. Zeit.*, 115 (1991) 366.
62. P.G. Jones and C. Thone, *Chem. Ber.*, 124 (1991) 2725.
63. P.G. Jones and C. Thone, *Inorg. Chim. Acta*, 181 (1991) 291.
64. S.P. Huang and M.G. Kanatzidis, *Inorg. Chem.*, 30 (1991) 3572.
65. D.M.P. Mingos and M.J. Watson, *Transition Metal Chem. (London)*, 16 (1991) 285.
66. A. Gorling, N. Rosch, D.E. Ellis and H. Schmidbaur, *Inorg. Chem.*, 30 (1991) 3986.
67. N.C. Payne, R. Ramachandran, G. Schoettel, J.J. Vittal and R.J. Puddephatt, *Inorg. Chem.*, 30 (1991) 4048.
68. A. Antiñolo, F.A. Jalón, A. Otero, M. Fajardo, B. Chaudret, F. Lahoz and J.A. López, *J. Chem. Soc., Dalton Trans.*, (1991) 1861.
69. K. Wurst, J. Strähle, G. Beuter, D.b. Dell'Amico and F. Calderazzo, *Acta Chem. Scand.*, 45 (1991) 844.
70. J.J. Bour, P.P.J. Schlebos, R.P.F. Kanters, M.F.J. Schoondergang, H. Addens, A. Overweg and J.J. Steggerda, *Inorg. Chim. Acta*, 181 (1991) 195.
71. L.N. Ito, A.M.P. Felicissimo and L.H. Pignolet, *Inorg. Chem.*, 30 (1991) 387.
72. L.N. Ito, A.M.P. Felicissimo and L.H. Pignolet, *Inorg. Chem.*, 30 (1991) 988.
73. R.P.F. Kanters, P.P.J. Schlebos, J.J. Bour, J.J. Steggerda, W.E.J.R. Maas and R. Janssen, *Inorg. Chem.*, 30 (1991) 1709.
74. M.F.J. Schoondergang, J.J. Bour, G.P.F. Van Strijdonck, P.P.J. Schlebos, W.P. Bosman, J.M.M. Smits, P.T. Beurskens and J.J. Steggerda, *Inorg. Chem.*, 30 (1991) 2048.
75. M.F.J. Schoondergang, J.J. Bour, P.P.J. Schlebos, A.W.P. Vermeer, W.P. Bosman, J.M.M. Smits, P.T. Beurskens and J.J. Steggerda, *Inorg. Chem.*, 30 (1991) 4704.
76. H.R.C. Jaw and W.R. Mason, *Inorg. Chem.*, 30 (1991) 3552.
77. S.G. Bott, H. Fleischer, M. Leach, D.M.P. Mingos, H. Powell, D.J. Watkin and M.J. Watson, *J. Chem. Soc., Dalton Trans.*, (1991) 2569.
78. M. Quinten, I. Sander, P. Steiner, U. Steiner, U. Kreibig, K. Fauth and G. Schmid, *Z. Phys D: At., Mol. Clusters*, 20 (1991) 377; *Chem. Abstr.*, 115 (1991) 145543g.
79. B.K. Teo and H. Zhang, *Inorg. Chem.*, 30 (1991) 3115.
80. B.K. Teo, X.B. Shi and H. Zhang, *J. Am. Chem. Soc.*, 113 (1991) 4329.
81. C. Pale-Grosdemange, E.S. Simon, K.L. Prime and G.M. Whitesides, *J. Am. Chem. Soc.*, 113 (1991) 12.
82. J.J. Hickman, D. Ofer, C.F. Zou, M.S. Wrighton, P.E. Laibinis and G.M. Whitesides, *J. Am. Chem. Soc.*, 113 (1991) 1128.