Coordination Chemistry Reviews, 115 (1992) 117–140
Elsevier Science Publishers B.V., Amsterdam

2. Gold

Catherine E. Housecroft

CONTENTS

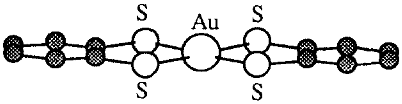
INTRODUCTION

Over the last decade, the number of published papers describing aspects of the chemistry of gold has increased greatly. The first four sections of this review deal specifically with coordination compounds of Au(IV), Au(III), Au(II) and Au(I) respectively although a few organometallic compounds, selected because of their relevance to the coordination chemist, have also been included. Section 5 reviews some of the cluster chemistry of gold. This section is not comprehensive but aims rather to highlight those areas that are novel or that exemplify new types of bonding mode for the gold atom. The present survey covers the literature of 1990 and is based upon a search of volumes 112, 113, and 114 (parts 1–10) of Chemical Abstracts. In addition, major inorganic chemistry journals have been searched independently for the period January to December 1990. I should like to thank the Cambridge Crystallographic Data Base for allowing access to coordinates for many of the structural figures in this review.

0010-8545/92/$15.00

2.1 GOLD(IV)

The radical species $Au(C_6H_4S_2)_2$, **(1)**, has been synthesised by the electrochemical oxidation of the corresponding anion. A structural study of the complex shows that the molecules are regularly stacked along the crystallographic *b*-axis; average Au–S = 2.300(1) Å. [1]



(1)

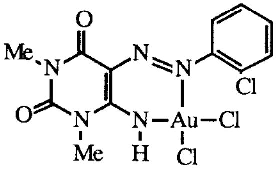
2.2 GOLD(III)

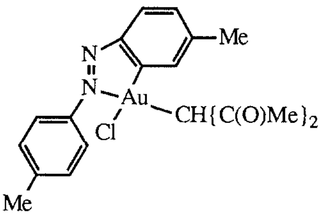
2.2.1 Complexes with halide and pseudohalide ligands

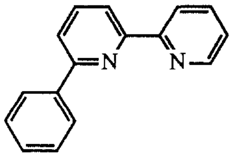
The reversible solvolysis in methanol of the chloride ion *trans* to the phenyl group in $[PhAuCl_3]^-$ has been reported. Stopped flow spectrophotometry (T < 0°C) was used to investigate the kinetics of the reaction and of the displacement of MeOH from $PhAuCl_2(MeOH)$ by various nucleophiles. The sequence of reactivity was found to be $NO_2^- < Cl^- < Br^- < N_3^- \approx I^- < NCS^- <$ thiourea. [2] The halide bridged complexes $[(F_3C)_2Au(\mu\text{-}X)]_2$ have been prepared in low yield from the reaction of gold vapour with CF_3X (X = Br, I). Mass spectral and ^{19}F n.m.r. spectroscopic data are reported and the structural characterisation of the iodide complex shows a planar framework with Au-I = 2.654 (1) and 2.658 (1) Å. [3]

2.2.2 Complexes with nitrogen donor ligands

Complexes of 1-methyl uracil and 1-methylthymine with platinum, palladium and gold have been reviewed (23 references). [4] Complex **(2)** has been prepared by the reaction of $HAuCl_4$ in ethanol with the appropriate uracil derivative; crystallographic characterisation shows square planar gold(III) with $Au\text{–}N_{(azo)}$ = 2.029(10) Å and $Au\text{–}N_{(NH)}$ = 1.992(9) Å. The thermal behaviour of **(2)** has been described. [5]







(2) **(3)** **(4)**

The first acetonylgold(III) complexes have been formed via C–H bond activation in acetone; the method involves reaction of 2-phenylazophenylgold(III) dichloride with Tl[acac] in acetone at room temperature. [6] In a later paper, the crystal structure of (3) is reported; Au-N = 2.158(3) Å. [7] The complex $LAu(2\text{-}C_6H_4NO_2)Cl$ ($HL = PhCH_2NMe_2$ and L^- is orthometallated and a bidentate ligand) has been prepared from $LAuCl_2$ and $Hg(2\text{-}C_6H_4NO_2)_2$ in the presence of Me_4NCl. Metathesis reactions of $LAu(2\text{-}C_6H_4NO_2)Cl$ with AgOOCMe, KBr and KI have been investigated. [8]

Reaction of HL, (4), with $HAuCl_4$ or its sodium salt in MeCN at 30°C or 100°C yields $(HL)AuCl_3$ for which spectroscopic data are consistent with HL behaving as a monodentate ligand via $N \rightarrow Au$ coordination. However, when LHgCl reacts with the tetrachloroaurate anion, yellow $[LAuCl][AuCl_4]$ is produced in which L is proposed to be cyclometallated. [9] This behaviour is especially surprising upon comparison with the reaction of $[AuCl_4]^-$ with 2-phenylpyridine when cyclometallates may be obtained directly. [10]

(See also Section 2.5.1 for the pseudo-cluster complex $[AuL']_3Cl_2$ (HL' = 4-chloro-3,5-diphenylpyrazole)).

2.2.3 *Complexes with oxygen donor ligands*

An interesting fluorescent complex of 2,2'-biquinoyl-*N,N'*-dioxide with Au(III) has been reported. It has been characterised by elemental analysis, conductance measurements, X-ray powder diffraction and spectroscopic methods and a 7-membered chelate ring is proposed. [11]

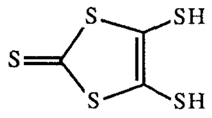
A gold(III) diethyl ether complex may be prepared by the reaction of $[Bu_4N][Au(C_6F_5)_3Br]$ and $AgClO_4$ in Et_2O. The ether ligand in $(C_6F_5)_3Au(OEt_2)$ is readily displaced by such species as THF, $OCMe_2$, $SPPh_3$, $OPPh_3$, $OAsPh_3$, NCMe, $NCCH{=}CH_2$ and $1,2\text{-}(NC)_2C_6H_4$ as well as by some cationic ligands. Many of the complexes so-formed have previously been unobtainable by other routes and thus $(C_6F_5)_3Au(OEt_2)$ appears to be a particularly useful reagent. [12]

In related papers, a gas phase electron diffraction study of $Me_2Au\{MeC(O)CHC(O)Me\}$ [13] and the photochemical decomposition of $Me_2Au\{PhC(O)CHC(O)Ph\}$ [14] have been reported. Results from the structural study confirm a square planar environment for the gold atom: $\angle OAuO = 90.9(6)^\circ$ and $\angle CAuC = 92.7(24)^\circ$ with Au-O = 2.085(7) Å and Au-C = 2.054(5) Å. [13]

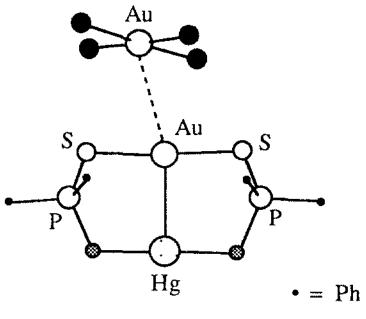
2.2.4 *Complexes with sulphur donor ligands*

The dinuclear complex $(1,2\text{-}S_2C_6H_4)_2Au_2(\mu\text{-}CH_2P(Ph)_2CH_2)_2$ has been synthesised and structurally characterised. The coordination geometry around each Au(III) centre is square planar and the two bridging ylide groups are oriented so as to generate an $Au_2C_4P_2$-ring which exhibits a chair conformation; the Au——Au separation is 4.40 Å. [15] In an accompanying paper, the cleavage of RS-SR at Au(I) to generate either Au(I) or Au(III) complexes is described. Oxidative addition occurs in the case of the reaction of PhSSPh with Au(CO)Cl to give $Au_2Cl_4(\mu\text{-}SPh)_2$, a structural determination of which shows that dimerisation to a tetragold species occurs in the solid state. [16] The oxidative addition of disulphides is also observed in the reaction of $RAuPPh_3$ (R = Me, ferrocenyl, 4-F-C_6H_4 or 4-Br-C_6H_4) with $Me_2NC(S)S\text{-}SC(S)NMe_2$ to give $RAu\{SC(S)NMe_2\}_2$ in addition to the ligand exchange product $R_2Au\{SC(S)NMe_2\}$. The success of the reaction depends upon the choice of the R group; for instance, if R = Ph, cyanomethyl or mesityl, only $R_2Au\{SC(S)NMe_2\}$ is produced. [17]

The complex anion $[AuL_2]^-$, H_2L = (5), has been structurally characterised. [18] The planar anions stack in columns along the crystallographic *b*-axis with S---S contacts of 3.52, 3.60 and 3.67 Å between the separate columns. The same complex anion has been independently characterised by spectroscopic methods and by X-ray diffraction; Au-S distances lie in the range 2.300(3)–2.312(3) Å for two independent molecules. [19] The preparative route is either the reaction of $[LAuBr_2]^-$ with $S_4N_4H_4$ or with $[Me_2SnS_2N_2]_2$. [19] The optical and magnetic properties of $K[AuL'_2]$ in which H_2L' is $(HS)_2C{=}C(CN)_2$ have been investigated. In contrast to the analogous platinum and nickel species, there is not distinct absorption in the range 5000–15000 cm^{-1} but an intense band at 21800 cm^{-1} is assigned to π–π interactions arising from the 'S-over-S' stacking of the $[AuL'_2]^-$ anions. [20] Structural parameters for this anion are given as part of a structural determination of $[AuHg\{SP(Ph)_2CH_2\}_2]^+[AuL'_2]^-$. [21] For the planar anion, distances are Au-S = 2.340(5), 2.330(5), 2.331(4) and 2.353(3) Å. The cation contains Au(I) (see Section 2.4.5) and has an interesting structure; it is characterised again in the tetrachloroaurate salt, (**6**). [22] The Au(III)-Au(I) separation (*i.e.* anion-cation separation) in (**6**) is 3.404(2) Å and the planes of the cation and anion are approximately perpendicular to one another. Molecules of (**6**) form chains within the lattice with an *intra*-molecular Hg-Au_{cation} distance of 3.079 Å and an *inter*-molecule Hg-Au_{anion} distance of 4.658 Å. [22]



(5)

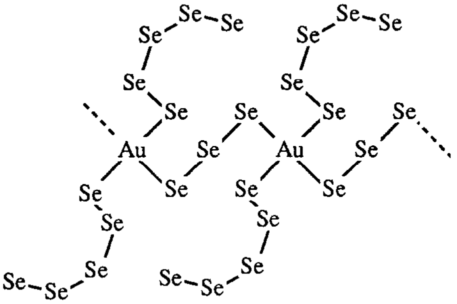


(6)

Tetramethylthiourea reacts with $AuBr_3$ to give the red complex $[Au(tmtu)_2Br_2][AuBr_2]$. However, further recrystallisation (6 days) yields the gold(I) complex, Au(tmtu)Br (see section 2.4.5). Both complexes have been structurally characterised. As expected, a square planar array of ligands surrounds the Au(III) centre in the $[Au(tmtu)_2Br_2]^+$ cation; Au-S = 2.342(3) Å. [23]

2.2.5 *Complexes with selenium donor ligands*

The compound $K_3[AuSe_{13}]$ has been prepared and structurally characterised. It is novel on two counts. Firstly, it is a rare example of a solid state compound containing catenated chalcogenide ligands and secondly, it exhibits the first example of a monodentate (terminal) $[Se_5]^{2-}$ ligand. The $[AuSe_{13}]^-$ anion should be formulated as $[Au(Se_3)(Se_5)_2]^-$, (7). [24]



(7)

2.2.6 *Complexes with gold–carbon bonds*

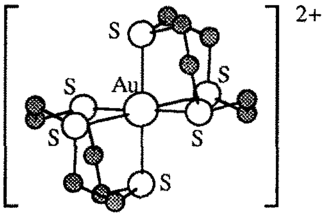
As mentioned in section 2.2.3, the ether ligand in $(C_6F_5)_3Au(OEt_2)$ is readily replaced by a variety of ligands, making this organometallic complex a useful precursor to a range of complexes inaccessible by other routes. [12] Similarly, diethyl ether is easily displaced from $R_3Au(OEt_2)$, $R_2ClAu(OEt_2)$ and $[R_2Au(OEt_2)_2]^+$ (R = 2,4,6-$C_6F_3H_2$). [25]

Gold(III) ylide complexes of type $(AuX_2)_2(\mu\text{-}L)_2$ (X = Cl, I; $L^- = [\{RO_2CCH\}_2PPh_2]^-$; R = Me, Et) have been synthesised and characterised. Au_2L_2 is first prepared from the silver(I) analogue and then reaction with excess chlorine or iodine yields the desired Au(III) product. Oxidation with Cl_2IPh or I_2 (this time not in an excess) yields a gold(II) complex (see Section 2.3). [26]

2.3 *GOLD(II)*

^{197}Au Mössbauer spectroscopy, carried out at 20K, has been used to show that the complexes $Au_2(C_6H_4Y)_2X_2$ (Y = PEt_2 or PPh_2 and X = I; Y = PPh_2 and X = Br) should be formulated as Au(II)–Au(II) rather than as Au(I)–Au(III) species. [27] Gold(II) ylide complexes $(AuX)_2L_2$ (X = Cl, I; $L^- = [\{RO_2CCH\}_2PPh_2]^-$; R = Me, Et) related to the gold(III) species mentioned above have been reported. The ylide group bridges between two gold centres, each of which also has a terminally attached halide ligand. [26]

Reaction of $K[AuCl_4]$ with 1,4,7-trithiacyclononane (L) in boiling aqueous HBF_4 and methanol leads to the air stable $[AuL_2][BF_4]_2$. The paramagnetic dicationic complex, **(8)**, has been the subject of an e.s.r. and electrochemical studies; $E^\circ(Au^{3+/2+}) = +0.15$ V and $E^\circ(Au^{2+/+}) = +0.47$ V with respect to ferrocene/ferrocenium. [28]



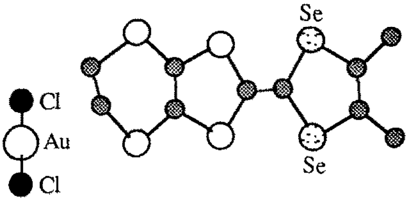
(8)

2.4 GOLD(I)

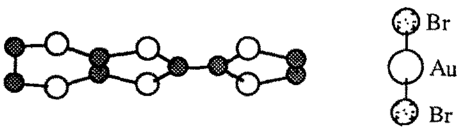
2.4.1 Complexes with halide and pseudohalide ligands

The organic superconductor, $(DMET)_2AuCl_2$, **(9)**, (DMET = 2-(4,5-dimethyldiselenol-2-ylidene)-5,6-dihydrodithiolo[4,5-*b*]dithiin) has been structurally characterised. The DMET units stack along the crystallographic *b*-axis so as to form a columnar structure which has short contacts between both the layers within a column and between the columns. Each linear $[AuCl_2]^-$ ion (Au-

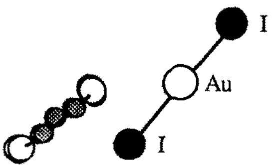
● = C
○ = S



(9)



(10)



(11)

Cl = 2.260(4) Å) resides between eight DMET units and the anions themselves form sheets within the lattice. [29] Related systems are (**10**) [30] and (**11**) [31]. Complex (**10**) is a 2:1 salt of ethylenedithiotetrathiafulvalene and $[AuBr_2]^-$ and (**11**) contains the $[AuI_2]^-$ anion with methylenedithiotetrathiafulvalene. Both are conducting salts; (see also Section 2.4.5).

A model of a weak-base anion-exchange resin loaded with gold cyanide is seen in the complex of 2-methylimidazoline with $HAu(CN)_2$. The structure consists of interpenetrating hydrogen-bonded networks lying perpendicular to one another; within the network, gold(I) centres are 3.25 Å apart. [32]

The equilibrium:

$$2\,R_3PAuCN \;=\; [(R_3P)_2Au]^+\;[Au(CN)_2]^- \qquad \text{equ. (1)}$$

has been studied for various R groups by using ^{31}P and ^{13}C n.m.r. spectroscopy. For R = Ph, there is rapid ligand scrambling with the system frozen out at ≈ 240 K. For R = Me, Et and ^iPr, slow exchange is observed, while for R = *c*-hexyl, equilibrium is only established after several days. Values of equilibrium constants are given in Table 1. [33]

Table 1 Measured equilibrium constants, *K*, for the ligand redistribution defined in equ. (1) [33]

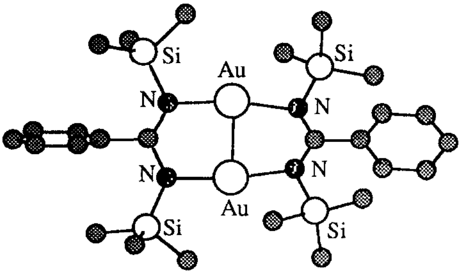
R	Ph	Me	Et	^iPr	$c\text{-}C_6H_{11}$
K	0.112 ± 0.005	0.37 ± 0.05	0.24 ± 0.02	0.29 ± 0.03	0.49 ± 0.02

Geometry optimised Hartree-Fock calculations have been carried out on the linear anions $[AuL_2]^-$ (L^- = H^-, F^-, Cl^-, Br^-, I^-, CN^-, SCN^-, Me^-, PH_3) as well as for AuMe, $AuPH_3$, $[AuPH_3]^+$, AuCN and AuSCN. Results indicate that the preference shown by Au(I) for linear coordination is increased by relativistic effects and the magnitude of these effects is dependent upon the electronegativity of the ligand. A large relativistic bond stabilisation is observed in $[AuL_2]^-$ for L^- = CN^- (39 kJ mol^{-1} per bond) or L^- = PH_3 (87 kJ mol^{-1} per bond). [34] The structure of $[Ph_4As][Au(SCN)_2]$ has also been determined since data for the anion were not previously available; Au-S = 2.295(4) Å and ∠SAuS = 180.0(1)° although the anion overall is non-linear with but ∠CSAu = 100.9(4)°. [34]

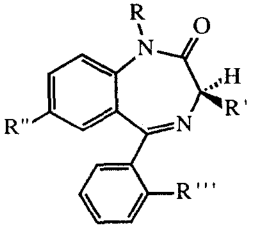
2.4.2 *Complexes with nitrogen donor ligands*

The novel dinuclear gold(I) complex (**12**) exhibiting bridging $[PhC\{NSiMe_3\}_2]^-$ ligands has been reported, as has its silver(I) analogue. Structural characterisation of (**12**) shows an Au–Au contact at 2.646(2) Å and Au-N distances averaging 2.060(7) Å. [35]

Spectroscopic [36] and structural [37] data have been described for (4-C_6H_4-NH)$AuPPh_3$. The linear N-Au-P units are strongly associated with one another in both the solid state and in solution via Au---Au interactions. The *N*-hydrogen atom in the substituted benzenesulphonanilides $PhSO_2N(H)C_6H_{4-x}R_x$ (R_x = 3,5-Cl_2, 2-MeO, 2-Br) may be replaced by a $AuPPh_3$ group in an exchange equilibrium with $PhSO_2N(AuPPh_3)C_6H_4R$ (R = H or 4-F). An electron accepting aryl group destabilises the N-H more than the N-Au bond. [38]



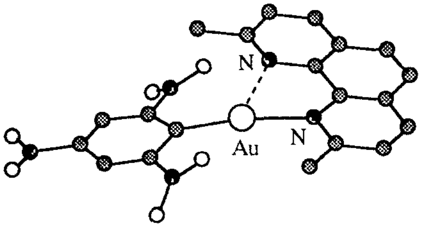
(12)



(13)

Gold(I) complexes LAuCl and $[LAuPPh_3]^+$ of the 1,4-benzodiazepin-2-ones, HL = **(13)** (R = Me, R' = R''' = H, R'' = Cl; R = CH_2-C_3H_5, R' = R''' = H, R'' = Cl; R = R' = R''' = H, R'' = NO_2; R = H, R' = OH; R'' = R''' = Cl; R = Me, R' = R''' = H, R'' = NO_2), have been prepared from reaction of Ph_3PAuCl with HL in the presence of alkali. For R = R' = R''' = H and R'' = NO_2, the complex $LAuPPh_3$ has been structurally characterised; Au-N = 2.071(3) Å, Au-P = 2.238(1) Å and $\angle$NAuP = 174.1(1)°. [39] Similar structural parameters are observed in the coordination sphere of the Au(I) atom in Et_3PAuL in which HL = 1-methylthymine. [40] Reduction of Au(III) (as tetrabromoaurate) to Au(I) by uracil or uridine in DMSO gives the corresponding 5-bromopyrimidine complex. However, if water is present, the 5-bromo-6-hydroxy-5,6-dihydropyrimidine complex is formed instead. The kinetics of this system have been investigated. [41]

Complex **(14)** exhibits an interesting coordination geometry with a non-linear C-Au-N arrangement ($\angle$CAuN = 168.4(1)°) and a secondary Au-N interaction (Au-N_{direct} = 2.136(3) Å and Au-$N_{secondary}$ = 2.573(3) Å). This complex has been synthesised as part of a study of 2,4,6-trinitrophenylgold(I) species (see Section 2.4.7). [42]



(14)

Two synthetic routes to the imidogold(I) complexes $[(Ph_3PAu)_3NR][BF_4]$ (R = Me_3C, Ph, 4-C_6H_4F, 4-C_6H_4Br, 4-$C_6H_4NO_2$) have been reported. Both methods involve the use of $[(Ph_3PAu)_3O][BF_4]$, the first with an excess of RNH_2 and the second with an excess of RNCO. A crystallographic investigation of $[(Ph_3PAu)_3NPh][BF_4]$ confirms a tetrahedral structure for the cation with Au-N = 2.035(9), 2.080(8) and 2.079(7) Å. This geometry is similar to that found for the parent oxonium ion. However, in the latter, cations dimerise in the solid state whereas in $[(Ph_3PAu)_3NPh]^+$, monocations are well separated. Gold-gold interactions exist in the cation and cause distortion from symmetry: Au-Au = 3.014(1), 2.926(1), 3.333(1) Å. [43]

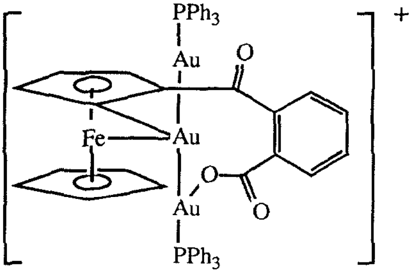
(See also Section 2.5.1 for the mixed oxidation state complex $[AuL']_3Cl_2$ (HL' = 4-chloro-3,5-diphenylpyrazole)).

2.4.3 *Complexes with phosphorus and arsenic donor ligands*

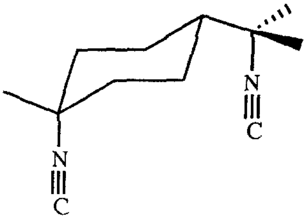
Various complexes involving Au(I)-P bonds were included above [33,34,36-40] and will not be mentioned further in this Section. Several electrochemical investigations have been described. The complexes R_3PAuCl (R = Et, Ph, OEt, OPh) and $(R_3P)_2AuCl$ (R = Ph, OEt) have been studied electrochemically and spectroelectrochemically. In MeCN, thf or CH_2Cl_2 with $[Bu_4N][ClO_4]$ as the supporting electrolyte and in the absence of water or oxygen, Au(I) is oxidised to Au(III) via an *ECE(C)* process. Reduction of Au(III) to Au(I) occurs in the presence of phosphine. [44] Electrochemical oxidation and reduction of $MeAuPPh_3$, $PhAuPPh_3$ and 4-MeO-$C_6H_4AuPPh_3$ in MeCN using Pt and Au electrodes have been described. Both processes are accompanied by the formation of Au(s) and possible mechanisms have been discussed. [45] The electrochemical behaviour of gold(I) complexes with some bidentate phosphine ligands has been reported. Values of E° (with respect to a SCE) measured for $[PF_6]^-$ salts are as follows: +0.463 V for $[(1,2\text{-}(Ph_2P)_2\text{-}C_6H_4)_2Au]^+$, +0.572 V for $[(Ph_2PCH{=}CHPPh_2)_2Au]^+$, +0.458 V for $[(dppe)_2Au]^+$, +0.752 V for $[(dppp)_2Au]^+$. [46] The redox potential E°($[Au_2(dppm)_2]^{3+/2+*}$) is −1.61(1) V (vs. SSCE). [47] The excited state of $[Au_2(dppm)_2]^{2+}$ is luminescent and, in MeCN, exhibits an absorption band at 290 nm which is assigned to a $p_\sigma \leftarrow d_{\sigma*}$ transition. The excitation of the complex dication gives rise to phosphorescence (575 nm) derived from the $^3B[(d_{\delta*})'(p_\sigma)']$ state. [47]

Simple triaryl- or trialkylphosphine gold(I) halides are commonly used as reagents in gold chemistry and the structure of $(2\text{-Me-}C_6H_4)_3PAuCl$, reported only in 1990, adds to the data available for precursors. The geometry is unexceptional: Au-P = 2.243(2) Å, Au-Cl = 2.281(3) Å and ∠PAuCl = 179.4(1)°. [48] The structure of $[(Ph_3P)_4Au][ClO_4]$ has also been detailed. [49] Interestingly, although four phenyl substituents pack around a gold(I) centre, increasing the steric requirements of the ligand may allow a three coordinate geometry around the metal atom. This phenomenon is explored in the series $[(R_2R'P)_3M][X]$ (M = Au or Ag; R ≠ R' = Ph, *c*-C_6H_{11}, *c*-C_5H_9 or *c*-C_7H_{13}; X = ClO_4 or BF_4]; (see accompanying review of silver coordination chemistry). Note that for R = R' = *c*-C_6H_{11}, a two coordinate geometry is forced upon the metal atom and the cation $[(c\text{-}C_6H_{11})_2Au]^+$ is preferred. [50]

The $[(Ph_3PAu)_3O]^+$ cation is used as a means of forming complexes which retain more than one gold atom. Synthesis of the imido-gold(I) complexes described in the preceeding Section is one example. [42] A novel transformation to form **(15)** is brought about in the reaction of $[(Ph_3PAu)_3O][BF_4]$ with $(\eta^5\text{-Cp})Fe(\eta^5\text{-}C_5H_4\text{-}C(O)\text{-}C_6H_4\text{-}2\text{-}CO_2H)$ carried out in the presence of HBF_4. [51] $[(Ph_3PAu)_3O][BF_4]$ is also used in a reaction with $1,2\text{-}(HO)_2\text{-}C_6H_4$ to give $(Ph_3PAu)_2(1,2\text{-}O_2\text{-}C_6H_4)$. The complex is stabilised by weak Au----Au interactions. [52]



(15)

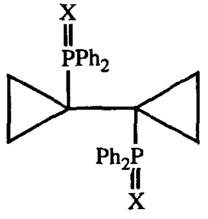


(16)

The steric requirements of the {Ph$_3$PAu}-group are sufficient to control the isomer distribution in $(Ph_3Ir)(Ph_3PAuIr)(\mu\text{-}L_4)$, where L = **(16)**. Each iridium atom carries either a terminal triphenylphosphine or gold(I) triphenylphosphine group. The asymmetry of L permits the possibility of six isomers for the complex and indeed, in the crystal structure of $(Ph_3Ir)(Ph_3PAuIr)(\mu\text{-}L_4)$, one of the four ligands is disordered in a 50:50 "head-to-tail" arrangement. Significantly though, the remaining three ligands are ordered in one preferential orientation. [53]

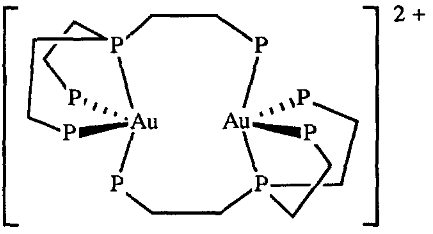
The complexes L_nAuX (for n = 1, L = 1-phenyldibenzophosphole (L'), 1-phenyl-3,4-dimethylphosphole (L") or PPh_3, X = Cl, Br, I; for n = 3, L = L' and X = Cl, Br, I or L = PPh_3 and X = Cl; for n = 4, L = L' or L", X = PF_6) have been prepared and characterised. X-ray diffraction data are available for L'AuCl, L'_3AuCl and L"AuCl. In L'AuCl, there is significant interaction between gold atoms in the two crystallographically independent molecules with Au--Au = 3.116(2) Å. [54] Pairing of molecules is also observed in $\{(2,4,6\text{-}(Me_3C)_3\text{-}C_6H_2)PH_2\}AuCl$ in which the Au---Au distance is 3.440Å. [55] Similarly, intermolecular gold(I)-gold(I) interactions are observed in the solid state structure of $\{(2\text{-Me-}C_6H_4)H_2P\}AuBr$. In this case, linear P-Au-Br units associate to give folded chains with alternating Au---Au separations of 3.097(1) and 3.380(1) Å and $\angle$AuAuAu = 103.5(1)°. [56]

Polydentate phosphines give rise to a variety of interesting species, with the structural diversity obviously being a function of ligand complexity. A review (28 references) of the coordination to gold(I) of *bis*(diphenylphosphino)methanide or -amide ligands has been presented. [57] Gold(I) complexes of L, **(17)**, have been prepared from Au(CO)Cl and an X-ray diffraction study of ClAu(L)AuCl, where L has no substituent X, illustrates a *cis*-configuration for the ligand which permits a gold-gold interaction over a distance of 3.085 Å. The energy of this d^{10}-d^{10} interaction has been estimated to be ≈6 kcal mol^{-1}. [58] Sixteen *bis*(diphosphino)gold(I) complexes have been tested for their antitumour activity. Of those investigated, $[(Ph_2PCH{=}CHPPh_2)_2Au]Cl$, $[(dppe)_2Au]Cl$ and $[(dppp)_2]Cl$ were found to be the most active against P388 leukemia, M5076 sarcoma and B16 melanoma. Changing the anion made little difference to the effective activity. [59]



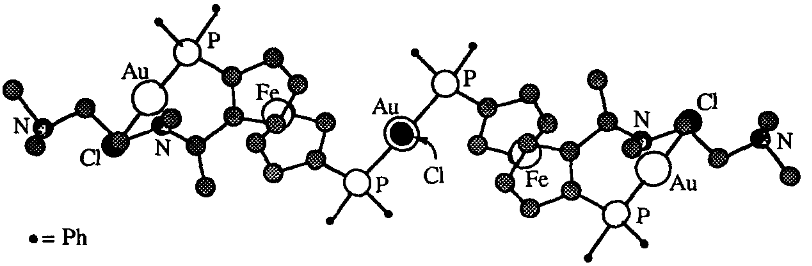
X = nothing, O or S

(17)



(18)

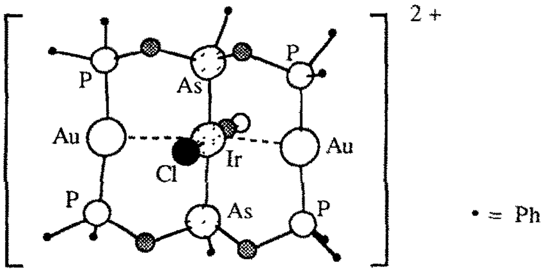
Treatment of $P(CH_2CH_2PPh_2)_3$ with Me_2SAuCl yields the colourless complex [(**18**)]Cl_2. A crystallographic study of the complex confirms the dual role of the phosphine as a chelate and as a bridging ligand in the dication (**18**); the intergold separation is 6.199 Å. The dication resists attack by both azide or thiocyanate ions but reacts with Me_2SAuCl to give $Au_4Cl_4\{P(CH_2CH_2PPh_2)_3\}$. [60] Interest in the substituted ferrocene ligand $(\eta^5\text{-}C_5H_4PPh_2)_2Fe$, dppf, has increased quite significantly over the last few years and a particularly novel derivative is (**19**), formed by an enantiomeric selective synthesis from the chiral ligand and Me_2SAuCl. Complex (**19**) consists of two homochiral LAuCl-units connected via an AuCl group through which a molecular C_2 axis runs; the central ∠PAuCl = 113(2)° and terminal ∠PAuCl = 177(2)° with Au-P(central) = 2.31(2) Å and Au-P(terminal) = 2.20(2) Å. Complex (**19**) has application as an active catalyst for enantioselective coupling of isocyanoacetate esters with aldehydes. [61]



(19)

The *tris*phosphine $Me_2PCH_2P(Me)CH_2PMe_2$ (dmmp) reacts with $[AuCl_4]^-$ to yield the trigold trication $[Au_3(dmmp)_2]^{3+}$ in which each of the two ligands bridges the angular Au_3-framework (∠AuAuAu = 136.26(4)° and Au-Au = 2.981(1) and 2.962(1) Å). The deviation from a linear Au_3-unit is rationalised in terms of a weak Au-----Au interaction between the terminal metal atoms. The complex is luminescent; there is a double phosphoresence with $\lambda = 467$ nm ($\tau_0 = 1.6 \pm 0.2$ μs) and 580 nm ($\tau_0 = 7.0 \pm 0.5$ μs). [62] Related (also luminescent) complex cations are

$[Cl_2Au_3L_2Ir(CO)_2]^+$ and $[Au_2L_2Ir(CN)_2]^+$ (L = $Ph_2PCH_2P(Ph)CH_2PPh_2$). The former complex is orange and exhibits a strong absorption at 454 nm with photoemissions at 568 and 660 nm. The second complex in an intense magenta colour (λ_{max} = 578 nm) and exhibits photoemissions at 612 and 782 nm. [63] A non-linear Au_3-array with ∠AuAuAu = 110.9(1)° and non-bonded Au---Au = 5.163(1) Å is also observed in LAu_3Cl_3 (L = $Ph_2PCH_2As(Ph)CH_2PPh_2$); this complex is synthesised from LAu_2Cl_2 which is itself formed from the reaction of Me_2SAuCl and L. Treatment of LAu_2Cl_2 with $[NH_4][PF_6]$ or $Tl[NO_3]$ leads to $[L_2Au_4Cl_2]^{2+}$ in which the non-linear Au_4-chain possesses Au-Au distances of 3.096(1) Å (twice) and 2.965(1) Å. [64] The same ligand spans the Au-Ir-Au unit in the complex $[Au_2Ir(CO)(Cl)L_2]^{2+}$ dication, (**20**); the complex is strongly luminescent in solution. [65] In *trans*-$PdCl_2\{As(Ph)(CH_2PPh_2AuCl)_2\}_2$, the square planar $PdAs_2Cl_2$-unit supports four "dangling" P-Au-Cl groups. [66] A structurally simpler, but related, complex is $ClAuP(Ph)_2CH_2CH_2As(Ph)_2AuCl$. This and $[\{Ph_2PCH_2CH_2AsPh_2\}_2Au]Cl$ have been the subjects of solution and X-ray diffraction studies as well as cytotoxicity investigations. In both solid state structures, the P and As sites are disordered. [67]

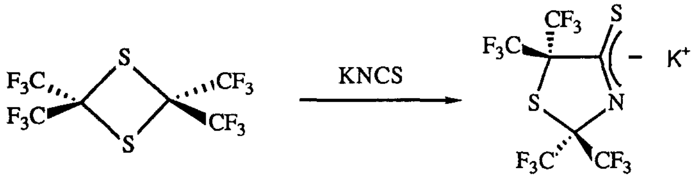


(**20**)

Coordination by arsenic atoms only is observed in a series of gold(I) and silver(I) complexes of the general formula $[M(AsR_2R')_2]X$ where M = Au or Ag; R = R' or ≠ R' = Ph, *c*-C_5H_9, *c*-C_6H_{11}; X = BF_4 or ClO_4. Phosphorus analogues have also been synthesised and characterised. (See accompanying chapter for structural data on Ag(I) complex). [68]

2.4.4 Complexes with sulphur donor ligands

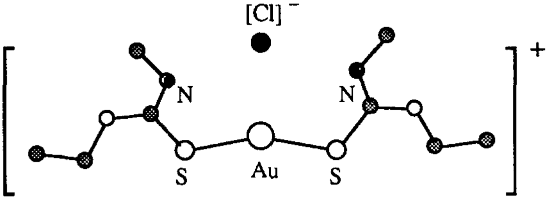
Combining $PhCH_2SSCH_2Ph$ or $Na[SCH_2Ph]$ with Ph_3PAuNO_3 in dichloromethane yields $[(Ph_3P)_2Au_2(\mu\text{-}SCH_2Ph)][NO_3]$. The cation dimerises in the solid state to form a tetra-gold species with Au–Au distances of 3.077(2) and 3.194(2) Å. [16] Complexes LAuCl and L'AuCl (HL = 8-mercaptoquinoline; HL' = 4-nitrobenzenethiol) have been prepared from Ph_3PAuCl and HL or $[(Ph_3PAu)_3O][BF_4]$ and HL' respectively. Structural data for each compound confirm a linear P-Au-S unit; in LAuCl, Au----N = 2.627(9) Å. [69] The synthesis of ligand L^- shown in equ. (2) has been reported; KL reacts with Ph_3PAuCl to give the gold(I) complex Ph_3PAuL and a structural determination of the product confirms the presence of an *S*–covalently bound terminal $AuPPh_3$ group with a linear S-Au-P arrangement. [70]



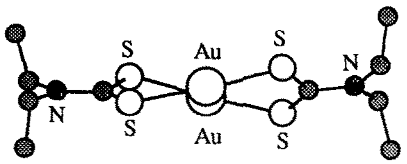
(equ. 2)

Several complexes involving heterocyclic thiones (HL = $C_3H_5NS_2$, $C_4H_4N_2S$, C_5H_5NS, $C_7H_5NS_2$ and $C_7H_6N_2S$) have been prepared and characterised. Precursors are Au(tht)Cl, $Au(tht)C_6F_5$, $[Au(tht)_2]^+$ or $[Ph_3PAu(tht)]^+$. [71] Complexes $[(Ph_3P)_nAuL]Cl$ (n = 1 or 2) in which L = imidazolidine-2-thione, 1,3-diazinine-2-one or *N*-isopropylimidazolidine-2-thione have been reported along with silver(I) analogues. Spectroscopic characterisation of the latter suggests *S*-coordination in all molecules; interest in the gold(I) complexes lies in their potential use in chemotherapy. [72] Closely related gold(I) compounds, analogues of the antiarthritic drug *auranofin*, have been studied independently. [73]

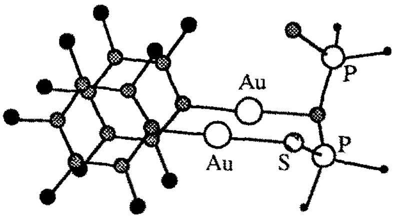
Tetramethylthiourea reacts with $AuBr_3$ to give the red complex $[Au(tmtu)_2Br_2][AuBr_2]$; (see Section 2.2.4). Further recrystallisation over a 6 day period yields the gold(I) complex, Au(tmtu)Br for which a structural study reveals an almost linear coordination environment (∠BrAuS = 175.4(1)° and Au-S = 2.265(2) Å. [23] Complex (**22**) as a structurally characterised representative member of a series of complexes exhibiting coordinated thio- and dithiocarbamate esters. [74] In (**22**), the chloride ion is hydrogen-bonded to the complex cation and thereby completes a 10-membered planar cyclic-{-HNCSAuSCNHCl-} system; the *N*-hydrogen atoms are not shown in (**22**). The maximum deviation from the plane for these ten atoms is 0.2 Å. [74] An X-ray diffraction study of *bis*(diethyldithiocarbamato)digold(I), (**23**), reveals that the lattice contains discrete dimers with an intramolecular Au-Au distance of 2.782(1) Å and Au-S lying in the range 2.28-2.30 Å. Dimers pack in linear chains supported by Au----Au interactions with the intermolecular separation being 3.004(1) Å. This is the shortest *inter*-molecular gold(I)-gold(I) separation yet observed. [75]



(22)



(23)



(24)

The gold(I) cation $[AuHg\{SP(Ph)_2CH_2\}_2]^+$ has been characterised as both the tetrachloroaurate salt, (**6**), [22] and as the $[AuL'_2]^-$ salt ($H_2L' = (HS)_2C{=}C(CN)_2$); [21] structural details are given in Section 2.2.4.

A series of gold(I) and silver(I) complexes containing the ligand HL, (HL = $Ph_2MePCH_2P(S)Ph_2$ (in both its protonated and deprotonated forms) has been reported. Complexes include $[R_3Au(HL)]^+$, R_3AuL, $(RAu)_2L$, $R_3Au(L)AuR$, $(LAuCl)_2$, $(LAuBr)_2$, $[Au_2L_2]^{2+}$ and $[Cl_2Au_2L_2]^{2+}$ in which R = C_6F_5 and $(RAu)_2L$, (**24**), has been structurally characterised. The deprotonated ligand bridges the two gold atoms and the fluorinated aryl substituents lie parallel to one another; the Au---Au separation is quite long at 3.224(2) Å. [76]

Finally in this section, a complex which uses a macrocyclic ligand as a bridge between two gold(I) centres; 1,10-dithia-4,7,13,16-tetraoxacyclooctadecane coordinates through the sulphur donors to two AuCl moieties. Full structural details for the complex have been reported. [77]

2.4.5 Complexes with selenium donor ligands

Along with the novel gold(III) selenide, (7), discussed in Section 2.2.5, a related solid state gold(I) selenide has been described by the same authors. [24] $KAuSe_5$ exhibits $[Se_5]^{2-}$ ligands which bridge between adjacent metal centres to generate chains, the latter being supported in a network by inter-chain gold-gold interactions (Au-Au = 2.950(3) Å).

Two related selenato complexes have been prepared and characterised. Triphenylphosphine gold(I) chloride reacts with 2,4,6-$^tBu_3$-C_6H_2-SeLi in toluene to give $Ph_3PAu(C_6H_2$-$^tBu_3$-2,4,6) which has been characterised by spectroscopic data (including ^{77}Se n.m.r. spectroscopy) and molecular weight determination. [78] Similarly, $PhSeSiMe_3$ reacts with the appropriate phosphine gold(I) chloride to yield pale green $Ph_3PAuSePh$ or yellow $(dppm)(AuSePh)_2$. The former complex has been the subject of an X-ray diffraction study which has confirmed an approximately linear coordination geometry at the gold atom (∠PAuSe = 175.6(1)°) and showed association between molecules in the lattice via gold-gold interactions (Au--Au = 3.118(1) Å). [79] Ph_3AuCl also reacts with PhSeSePh and $AgSbF_6$ to yield $[(Ph_3Au)_2SePh][SbF_6]$. In the cation, two Ph_3Au units are linked by a bridging-SePh ligand. In addition, pairs of cations are related by a centre of symmetry and Au--Au separations within the loose dimeric structure are 3.112(2) Å. [79]

The ligand $Ph_2PCH_2P(Se)PPh_2$, L, reacts with Au(CO)Cl to give the dimetallic cation $[Au_2L_2]^{2+}$. Structural characterisation shows that the molecule consists of a puckered 10-membered ring which is drawn into a boat-like configuration by a transannular Au--Au interaction

(3.020(1)Å). Other pertinent distances are Au-Se = 2.438(2), 2.431(2) Å and Au-P = 2.265(4), 2.271(5) Å. [80]

2.4.6 *Complexes with gold(I)–carbon or silicon bonds*

Gold(I)-carbon bonds have featured in several complexes described above but the following complexes are those in which an Au(I)-C or Au(I)-Si interaction might be considered to be the principal feature of interest. The carbonyl complex Au(CO)Cl appears quite regularly as a synthetic reagent and yet its preparation has not always been straightforward. Methods of synthesis are examined in a review which surveys halocarbonyls of palladium, platinum and gold. [81] By far the most successful route is shown in equ. (3). Au(CO)Cl is used in an interesting reaction with Cp^*_2Si in toluene at −90°C to yield the very hygroscopic complex $(\sigma\text{-}Cp^*)(\pi\text{-}Cp^*)SiAuCl$. This reacts with either py or ${}^tBuNC$ (L) to give $(\sigma\text{-}Cp^*)_2Si(L)AuCl$, which may be prepared by an alternative route, ($LAuCl + Cp^*_2Si$). [82]

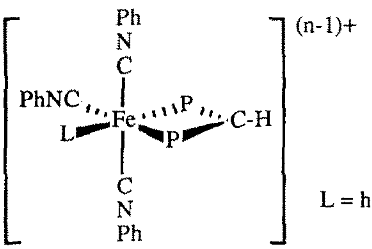
$$HAuCl_4.xH_2O \xrightarrow{SOCl_2} Au_2Cl_6 \xrightarrow{4\,CO} 2\,Au(CO)Cl + 2\,COCl_2 \qquad \text{equ. (3)}$$

Solutions of $Au(SO_3F)_3$ in HSO_3F function as superacids and dissolve ≈ 3.5 mole CO per mole of $Au(SO_3F)_3$. Reduction of Au(III) to Au(I) accompanies this dissolution of gas and solvated $[Au(CO)_2]^+$ is produced. Vibrational spectroscopic studies have characterised this cation as a linear species; ν_{CO}(Raman) = 2251 cm^{-1} and ν_{CO}(i.r.) = 2211 cm^{-1}. Solvent removal results in the formation of $Au(SO_3F)(CO)$, a white solid characterised by ν_{CO}(Raman) = 2198 cm^{-1} and ν_{CO}(i.r.) = 2195 cm^{-1}, notably at higher frequency than in free CO. [83]

Several complexes containing $Au\text{-}C_6F_{5\text{-}x}H_x$ groups have been reported in this review. Their use is seen in facilitating the displacement of the tht ligand from $(2,4,6\text{-}C_6F_3H_2)Au(tht)$ by a range of anionic ligands, X^-. Treatment of $(2,4,6\text{-}C_6F_3H_2)AuX$ with $AgClO_4$ or $(2,4,6\text{-}C_6F_3H_2)Ag$ leads to $(AuR)_4$ or $\{AuAg(2,4,6\text{-}C_6F_3H_2)_2\}_n$ or, for X^- = SCN^-, $[(2,4,6\text{-}C_6F_3H_2)AuSCNAu(2,4,6\text{-}C_6F_3H_2)]^-$. [84]

Treatment of complex (**25**) with (tht)AuCl in CH_2Cl_2 leads to the addition of an AuCl group to the sp^2 carbon. The digold derivative has also been synthesised from H[(**25**)] with 2 moles of PPh_3PAuCl in excess KOH. The Au-Au separation of 2.891(4) Å is consistent with an intergold interaction. Other related systems have also been reported. [85]

Members of a series of 2,4,6-trinitrophenylgold(I) complexes have been prepared and characterised. $Au\{C_6H_2(NO_2)_3\text{-}2,4,6\}Cl$ was first prepared from $[AuCl_2]^-$ and $Hg\{C_6H_2(NO_2)_3\text{-}2,4,6\}_2$. The chloride complex is then converted to the tht analogue and this reacts with $SbPh_3$ or excess $2,9\text{-}Me_2\text{-}1,10\text{-}phen$ to give $[Au(SbPh_3)_4][Au\{C_6H_2(NO_2)_3\text{-}2,4,6\}_2]$ or complex (**14**) (see Section 2.4.2) respectively. Structural data for the $[Au\{C_6H_2(NO_2)_3\text{-}2,4,6\}_2]^-$ anion confirm an approximately linear cooridination environment at gold (∠CAuC = 176.7(5)°) with Au-C = 2.041(13) and 2.015(12) Å. The aryl groups are rotated through 44° with respect to one another. [42]



L = halide; CNPh; PPh_3

(25)

A direct gold(I)-silicon bond is retained during the reaction of $Ph_2MePAuCl$ with $Ph_2MePAuSiPh_3$. An equilibrium is established between the product, $(Ph_2MeP)_2Au_2(Cl)(SiPh_3)$, and its precursors. An X-ray analysis of the product shows that the complex should be considered to be composed of two associated units, *viz.* $(Ph_2MeP)_2Au$ and $Au(Cl)(SiPh_3)$ with a Au-Au distance of 2.9807(4) Å. Each constituent unit is linear about the gold atom and the two units are mutually perpendicular. [86]

2.5 *CLUSTERS CONTAINING GOLD*

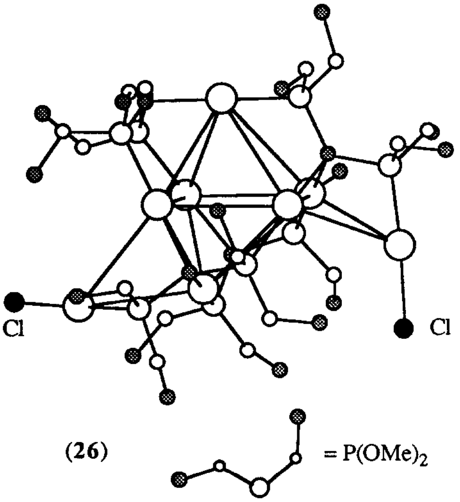
2.5.1 *Homometallic clusters*

Methods of preparation and the characterisation of supported homonuclear gold clusters (Au_x) have been reviewed (19 references); a discussion of the application of such clusters as catalysts is included. [87]

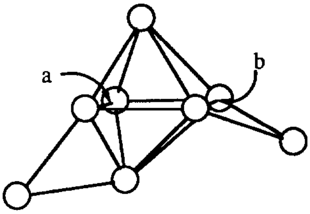
In aqua regia, the gold(I) complex $[AuL]_3$ (HL = 3,5-diphenylpyrazole) is transformed to the mixed Au(I)/Au(III) $[AuL']_3Cl_2$ (HL' = 4-chloro-3,5-diphenylpyrazole). An X-ray study of this novel product shows an Au_3-triangle supported by bridging ligands; the single Au(III) centre is coordinated to two Cl- and two N-donors. The Au---Au distances of 3.3677(6), 3.4011(7) and 3.3352(7) Å are too long to imply significant bonding interaction and the structure is probably better described as consisting of a 9-membered Au_3N_6-ring. [88]

The encapsulation of a carbon or nitrogen atom within an Au_n-cluster has been the subject of both experimental and theoretical work. Treatment of $[(Ph_3PAu)_4N][BF_4]$ with Ph_3PAuBF_4 yields $[(Ph_3PAu)_5N][BF_4]_2$ and structural details confirm the presence of a 5-coordinate nitrogen atom. ^{197}Au Mössbauer spectroscopic data are consistent with the trigonal bipyramidal cage, and show two overlapping doublets in a ratio 3:2. [89] The dicationic carbido-cluster, $[\{1,2\text{-}C_6H_4(CH_2CH_2PPh_2Au)_2\}_3C]^{2+}$ has been synthesised by the reaction of $C\{B(OMe)_2\}_4$ with 1,2-$C_6H_4(CH_2CH_2PPh_2AuCl)_2$ in the presence of CsF–HMPT. The product has been characterised by X-ray crystallography . [90] This type of cluster has been modelled by $[\{H_3PAu\}_6C]^{2+}$ and the bonding in this and in the related mono- and dicarbido clusters $[\{H_3PAu\}_mC_n]^{x+}$ (n = 1; m = 4,5 or n = 2; m = 8,10,12) has been analysed with the use of semi-empirical MO calculations. Comparisons have been made between $[\{H_3PAu\}_6C]^{2+}$ and the analogous model clusters $[\{H_3PAu\}_6B]^{+}$ and $[\{H_3PAu\}_6N]^{3+}$. [91]

The double metallation of the diphosphinomethane ligand, $(MeO)_2PCH_2P(OMe)_2$, occurs in its reaction with $AuC{\equiv}CCMe_3$ followed by recrystallisation first from CH_2Cl_2 and then from $CHCl_3$. The product cluster is (**26**); the structure of this compound consists of a distorted octahedral Au_6–core with two bridging AuCl units and the whole framework is supported by singly and doubly deprotonated ligands in either μ_3- or μ_4-modes respectively. Within the metal core, only two Au-Au distances are short enough (2.938(1) and 2.951(1) Å) to be considered as bonding. These are indicated in the core-structure of (**26**) as edges "a" and "b"; other Au---Au separations lie in the range 3.351 (1) to 4.085 (1) Å. [92]



(**26**)

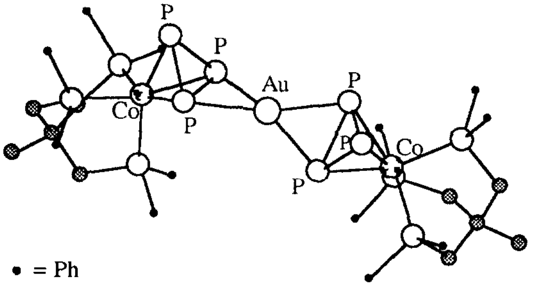


Au_8 core of (**26**)

Clusters consisting of $AuPPh_3$ units, some with additional halide ligands, have now reached particularly large proportions and the Au_{55}–core reported by Schmid [93-96] is particularly remarkable. Beginning first with some smaller clusters, the cation $[Au_9(PPh_3]_8]^{3+}$ has been the subject of spectroscopic studies and the visible spectra of the hexafluorophosphate and nitrate salts show a pressure dependence. The optical spectrum of $[Au_9(PPh_3]_8][PF_6]_3$ changes from discrete peaks to a continuous edge as the pressure is increased up to 80 kbar; the observations have been attributed to a molecular transformation from a green D_{2h} to a brown D_{4d} cage. The most significant structural alteration occurs in the range 45–60 kbar. [97] Theoretical studies include an analysis of the bonding and appropriate electron counting schemes for $[Au_{13}(PMe_2Ph)_{10}Cl_2]^+$; such molecules are categorised as "clusters of clusters". [98] A one–step synthesis to the super-cluster $Au_{55}(PPh_3)_{12}Cl_6$ has been detailed; the cluster is made by the reduction of Ph_3PAuCl by B_2H_6 in warm benzene. [93] EXAFS has been used to probe the coordination environment of the gold atoms in $Au_{55}(PPh_3)_{12}Cl_6$; a coordination number of seven (*i.e.* the number of Au-Au contacts) is consistent with a 3-shell cuboctahedral structure. The EXAFS results indicate that Au-Au separations within the Au_{55}-cage are significantly less than in bulk elemental gold. [94] The cluster has also been investigated by secondary ion and plasma desorption mass spectrometry (SIMS and PDMS respectively). [95,96] Bombardment of $Au_{55}(PPh_3)_{12}Cl_6$ with Xe^+ ions (10 keV) leads to the formation of secondary ions with masses up to 140,000 u. The results indicate the presence of $(Au_{13})_n$–superclusters and it is concluded that the core of the Au_{55}-cluster has a close packed structure of gold atoms.

2.5.2 *Heterometallic clusters*

Clusters in this section have been selected so as to illustrate a variety of structural features and synthetic methods. The reaction of Ph_3PAuCl with $[HFe(CO)_3(PR_3)]^-$ (R = OMe, OEt, OPh, Me, Ph) leads quantitatively to a mixture of $H_2Fe(CO)_3(PR_3)$ and $(Ph_3PAu)_2Fe(CO)_3(PR_3)$. Crystallographic characterisation of $(Ph_3PAu)_2Fe(CO)_3(P(OEt)_3)$ confirms the presence of an $FeAu_2$-triangle with Au-Au = 2.872(2) Å and Au-Fe = 2.561(3) and 2.509(3) Å; the $P(OEt)_3$ ligand lies in the equatorial plane. [99] A related cluster anion, $[Fe_2(CO)_6(\mu\text{-}CO)_2(AuPPh_3)]^-$, contains a triangular Fe_2Au-core with Au-Fe = 2.622(1) and 2.698(1) Å and Fe-Fe = 2.605(2) Å. [100] Reaction of $Ru_2(CO)_4(PPh_3)_2(\mu\text{-}1,2\text{-}(HN)_2C_6H_4)$ with Ph_3PAuCl in the presence of $Tl[PF_6]$ places the gold(I) phosphine in a bridging position thereby generating a cationic cluster. The related $Ru_2(CO)_4((PPh_3)_2(\mu\text{-}1,2\text{-}(HN)_2C_6H_4)(\mu\text{-}AuCl)$ has been synthesised in a similar reaction and reacts further with $Ru_2(CO)_4(PPh_3)_2(\mu\text{-}1,2\text{-}(HN)_2C_6H_4)$ to give the fused cluster cation, $[\{Ru_2(CO)_4(PPh_3)_2(\mu\text{-}1,2\text{-}(HN)_2C_6H_4)\}_2Au]^+$. [101] Cluster fusion about an Au(I) centre is also observed in $[\{CH_3C(CH_2PPh_2)_3CoP_3\}Au]^+$, (27). This cation and its rhodium and iridium analogues are prepared from R_3PAuCl (R = Me or Ph) or ClAu(L')AuCl (L' = dppm or dppe) with LMP_3 (L = 1,1,1-*tris*{diphenylphosphinomethyl}ethane). [102]



(27)

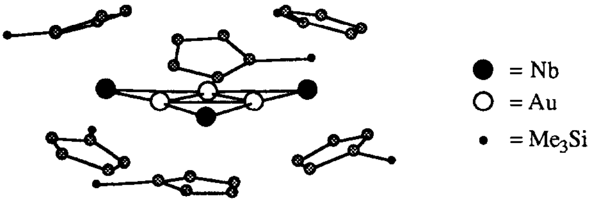
The dirhenium complex $HRe_2(CO)_8(\mu\text{-}PPh_2)$ reacts with a source of $[Ph_3PAu]^+$ [103,104] in the presence of the sterically demanding base $LiN(CHMe_2)_2$ to give $(\mu\text{-}Ph_3PAu)Re_2(CO)_8(\mu\text{-}PPh_2)$ or $(Ph_3P)_2Au_2Re_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}C(O)N(CHMe_2)_2)$. The latter compound has been structurally characterised; Re-Re = 3.122(2) Å, Re-Au = 2.977(2) Å and Au-Au = 2.709(2) Å. Electrochemical studies have also been discussed. [103]

Some interesting iridium-gold clusters have been reported. The $[(Ph_3PAu_3)O]^+$ cation has been used in the synthesis of $Fe_2(CO)_6(\mu_4\text{-}CCPh)Ir(CO)(PPh_3)Au_2(PPh_3)_2$ in which a digold-unit (proposed as a model for coordinated H_2) spans an Ir-C bond as an integral part of a cluster containing an $Fe_2C_2IrAu_2$–core. [105] An unusual terminal mode of attachment is evidenced for an

$AuPPh_3$ unit in $Ir_4(CO)_{11}PPh_2AuPPh_3$ which has been synthesised via the reaction of $Ir_4(CO)_{11}PPh_2H$ with base in the presence of $[Ph_3PAu]PF_6$. Heating $Ir_4(CO)_{11}PPh_2AuPPh_3$ in toluene leads to loss of carbon monoxide and the formation of $Ir_4(CO)_{10}(\mu\text{-}PPh_2)(\mu\text{-}AuPPh_3)$. Both clusters have been crystallographically characertised. [106] The progression from terminal to bridging gold(I) phosphine may be completed by a μ_3-capping mode and this is exemplified in the cluster anion $[Fe_2Ir_2(CO)_{12}(\mu_3\text{-}AuPPh_3)]^-$. [107] Isoelectronic with this anion (*i.e.* in terms of cluster bonding electrons) is the neutral cluster $FeCo_3(CO)_{12}AuPPh_3$, the detailed synthesis of which has been reported. [108]

Gold-boron bonds are now quite well estabilshed in cluster chemistry. The synthesis and structural characterisation of $HRu_4(CO)_{12}Au_2(PPh_3)_2B$ has been described. The boron atom is six coordinate, residing within an Ru_4Au_2-cage and, hence, $HRu_4(CO)_{12}Au_2(PPh_3)_2B$ is considered to be a metalloboride cluster. [109] Auracarboranes reported in 1990 have been included in a review. [110]

Most commonly, heterometallic gold-containing clusters appear to fall into one of three categories: (i) clusters in which one or more gold(I) phosphine fragments replace a corresponding number of hydrogen atoms in a cluster, (ii) systems in which a gold atom fuses two clusters together or (iii) clusters in which the gold atoms are the dominant constituent atoms and are therefore derived from homonuclear gold clusters. One new molecule, $(\mu\text{-}H)_6Cp''_3Nb_3Au_3$, **(28)**, ($Cp'' = \eta^5\text{-}C_5H_4SiMe_3$) has been synthesised and structurally characterised but does not conform to any of the aforementioned categories. Cluster **(28)** is prepared by the reaction of Cp''_2NbH_3 and $Au[N\{SiMe_3\}_2]PPh_3$ and is a raft molecule exhibiting a planar Nb_3Au_3–core. The bonding in the cluster has been analysed. [111] A related silver cluster has been characterised, (see following Chapter).

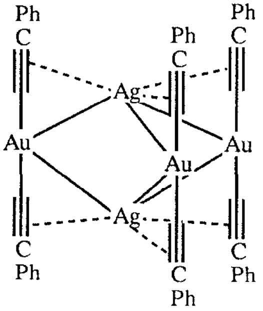


(28)

A relatively large number of clusters has been reported in which the number of gold atoms exceeds the number of other constituent cage atoms. Reaction of $[Rh(H)\{P(OR)_3\}_2]_n$ (n = 2, R = $CHMe_2$; n = 3, R = Me) with Ph_3PAuNO_3 yields either $[Au_4Rh(H)_2\{P(OCHMe_2)_3\}_2(PPh_3)_4]^+$ or $[Au_5Rh(H)\{P(OMe)_3\}_2(PPh_3)_5]^+$ depending upon R. Further treatment of the pentagold product with Ph_3PAuNO_3 gives $[Au_6Rh(H)\{P(OMe)_3\}_2(PPh_3)_6]^{2+}$. Spectroscopic data are available for all the products and the tetragold cluster has also been crystallographically characterised, revealing a trigonal bipyramidal framework with the rhodium atrom occupying an equatorial site; average distances are Au-Au = 2/904(1) Å and Au-Rh = 2.685 (1) Å. [112]

Several platinum–gold clusters have been reported. Reaction of Ph_3AuX (X = Cl or BF_4) with cationic platinum dimers, each dimer being one supported by orthometallated phenylphosphine ligands, leads to triangulo-Pt_2Au clusters. One such product, $[Pt_2\{o\text{-}C_6H_4\text{-}P(Ph)CH_2CH_2\text{–}CH_2PPh_2\}_2Au(PPh_3)][BF_4]$, has been structurally characterised and pertinent distances are Pt-Pt = 2.703 (1) Å and Au-Pt = 2.722(1) and 2.697(1) Å. [113] An Au_2Pt-framework results from the reaction of Ph_3AuCl with AgO_3SCF_3 followed by treatment with *trans*-$PtHCl(PEt_3)_2$. [114] The oxidative addition of $[Au(CN)_2]^-$ to $[Pt(AuPPh_3)_8]^{2+}$ leads to $[Pt(CN)(AuCN)(AuPPh_3)_8]^+$ which has been crystallographically characterised. In a related reaction, the cluster cation $[Pt(CO)(AuPPh_3)_8]^+$ reacts in a slow process with cyanide ion to give $Pt(CO)(AuPPh_3)_6(AuCN)_2$. [115] The cation $[Pt(AuPPh_3)_8]^{2+}$ reacts with either Hg_2X_2 or HgX_2 (X = Cl or NO_3) to give the products $[Pt(AuPPh_3)_8(HgX)_2]^{2+}$, $[Pt(AuPPh_3)_7(HgX_2)(AuX)]^+$ and $[Pt(AuPPh_3)_7(HgX)_2]^+$. Characterisation by ^{31}P and ^{195}Pt n.m.r. and i.r. spectroscopy and conductance measurements is supplemented by an X-ray diffraction study of $[Pt(AuPPh_3)_8(HgNO_3)_2][NO_3]_2$. This reveals that the platinum atom is central to the Au_8–cluster core and that the mercury groups cap two square Au_4-faces. [116] Related chemistry is reported in the addition of RNC (R = ^iPr; ^tBu) to $[Pt(AuPPh_3)_8]^{2+}$; the presence of excess RNC results in the replacement of a PPh_3 ligand. However, RNC will not displace CO from $[Pt(CO)(AuPPh_3)_8]^{2+}$. [117]

Clusters containing coordinated acetylide ligands include $Pt_2Au_4(C{\equiv}C^tBu)_8$, prepared from an analogous silver based molecule (see accompanying Chapter on silver coordination chemistry). [118] Three associated papers describe mixed gold–silver or gold–copper clusters with σ–π-acetylide ligands. For example, $Au_2Ag_2(C{\equiv}CPh)_4(PPh_3)_2$ may be prepared from $Au(C{\equiv}CPh)(PPh_3)$ and $Ag(C{\equiv}CPh)_n$. Novel polymers may be obtained in parallel reactions of $Au(C{\equiv}CPh)L$ (L = $AsPh_3$ or $P\{OPh\}_3$) and $Ag(C{\equiv}CPh)_n$. [119] It is also reported that $Ag(C{\equiv}CPh)$ reacts with $[Au_2(C{\equiv}CPh)_3]^-$ to yield the anion $[Au_3Ag_2(C{\equiv}CPh)_6]^-$; similar syntheses lead to $[Ag_5(C{\equiv}CPh)_6]^-$ and $[Ag_3Cu(C{\equiv}CPh)_6]^-$. Structures for the products, *e.g.*(**29**), are proposed on the basis of spectroscopic data; values of $\nu_{C\equiv C}$ imply π-bonded acetylide groups. [120] The cluster anions $[Au_3Cu_2(C{\equiv}CPh)_6]^-$, $[Au_3Ag_2(C{\equiv}CPh)_6]^-$ and $[Au_2Cu(C{\equiv}CPh)_4]^-$ are all used as precursors to $[Au_3AgCu(C{\equiv}CPh)_6]^-$. [121]



(**29**)

A series of mixed gold–silver clusters related to the high nuclearity gold clusters discussed in Section *2.5.1* has been investigated. Included in an account of the bonding and electron counting schemes for "clusters of clusters" is the cation $[Au_{13}Ag_{12}Cl_8(PPh_3)_{10}]^+$. [98] This cluster has been synthesised by the borohydride reduction of a mixture of $HAuCl_4$, PPh_3 and $[Ph_3PAgCl]_4$ and has been structurally characterised. The cluster core is comprised of four parallel pentagons, (alternating Au_5 and Ag_5) with two μ_5–capping AgCl groups and naked Au atoms joining adjacent M_5-rings. [122] The analogous bromide cluster has also been described. [123] In $Au_{18}Ag_{20}Cl_{14}\{P(C_6H_4\text{-}4\text{-}Me)_3\}$, three 13-atom gold-centred Au_7Ag_6–cluster units are fused via shared verticies and the core terminates at either end with μ_5-capping AgCl groups as did $[Au_{13}Ag_{12}Cl_8(PPh_3)_{10}]^+$. The structure of $Au_{18}Ag_{20}Cl_{14}\{P(C_6H_4\text{-}4\text{-}Me)_3\}$ (prepared by $NaBH_4$ reduction of $\{(4\text{-}Me\text{-}C_6H_4)_3P\}AuCl$ and $[\{(4\text{-}Me\text{-}C_6H_4)_3P\}AgCl]_4$) has also been described in terms of a close packed array of metal atoms. [124]

REFERENCES

1. G. Rindorf, N. Thorup, T. Bjørnholm and K. Bechgaard, *Acta Crystallogr., Sect. C,* 46 (1990) 1437.
2. E. Ahmed, R.J.H. Clark, M.L Taube and L. Cattalini, *J. Chem. Soc., Dalton Trans.,* (1990) 2701.
3. J.L. Margrave, K.H. Whitmire, R.H. Hauge and N.T. Norem, *Inorg. Chem.,* 29 (1990) 3252.
4. B. Lippert, W. Micklitz, O. Renn, G. Troetscher, I. Dieter and G. Frommer, *Pure Appl. Chem.,* 62 (1990) 1075.
5. E.C. Rodríguez, J.R. Sánchez, J. de D.L. González, J.M.S. Peregrín, M.J. Olivier, M. Quirós and A.L. Beauchamp, *Inorg. Chim. Acta,* 171 (1990) 151.
6. J. Vincente, M.-D. Bermúdez, M.-T. Chicote and M.-J. Sánchez-Santo, *J. Chem. Soc., Dalton Trans.,* (1990) 1945.
7. J. Vincente, M.-D. Bermúdez, J. Escribano, M.P. Carrillo and P.G. Jones, *J. Chem. Soc., Dalton Trans.,* (1990) 3083.
8. J. Vincente, M.-D. Bermúdez, M.-T. Chicote and M.-J. Sánchez-Santo, *J. Organometal. Chem.,* 381 (1990) 285.
9. E.C. Constable, R.P.G. Henney, T.A. Leese and D.A. Tocher, *J. Chem. Soc., Dalton Trans.,* (1990) 443.
10. E.C. Constable, personnal communication.
11. Y. Gong and M. Jiang, *Synth. React. Inorg. Met.-Org. Chem.,* 20 (1990) 115.
12. R. Usón, A. Laguna, M. LAguna, J. Jiménez and M.E. Durana, *Inorg. Chim. Acta,* 168 (1990) 89.
13. S. Shuzo, K. Iijima and T.H. Baum, *J. Chem. Soc., Dalton Trans.,* (1990) 1519.
14. T.H. Baum, *J. Electrochem. Soc.,* 137 (1990) 252.
15. D.D. Heinrich and J.P. Fackler, Jr., *Inorg. Chem.* 29 (1990) 4402.
16. S. Wang and J.P Fackler, Jr., *Inorg. Chem.* 29 (1990) 4404.
17. V.P. Dyadchenko, K.I. Grandberg, O.N. Kalinina, P.E. Krasik, O.Yu. Burtseva, M.A. Porai-Koshits, L.G. Kuz'mina and E.G. Perevalova, *Metalloorg. Khim.,* 3 (1990) 667.
18. (a) K. Honda, M. Goto, M. Kurahashi, Y. Miura, T. Nakamura, M. Matsumoto and Y. Kawabata, *Anal. Sci.,* 6 (1990) 927; (b) G. Matsubayashi and A. Yokozawa, *J. Chem. Soc., Dalton Trans.,* (1990) 3535.
19. J.C. Fitzmaurice, A.M.Z. Slawin, D.J. Williams, J.D. Woollins and A.J. Lindsay, *Polyhedron,* 9 (1990) 1561.
20. S. Kutsumizu, N. Kojima, N. Watanbe and T. Ban, *J. Chem. Soc., Dalton Trans.,* (1990) 2287.
21. S. Wang and J.P. Fackler, Jr., *Acta Crystallogr., Sect. C,* 46 (1990) 2253.
22. S. Wang and J.P. Fackler, Jr., *Organometallics,* 9 (1990) 111.
23. A.C. Fabretti, A. Giusti and W. Malavasi, *J. Chem. Soc., Dalton Trans.,* (1990) 3091.

24. Y. Park and M.G. Kanatzidis, *Angew. Chem. Int. Ed.*, 29 (1990) 914.
25. A. Laguna, M. Laguna, J. Jiménez and A.J. Fumanal, *J. Organometal. Chem.*, 396 (1990) 121.
26. J. Vicente, M.-T. Chicote and I. Saura-Llamas, *J. Chem. Soc., Dalton Trans.*, (1990) 1941.
27. M. Takeda, M. Takahashi, Y. Ito, T. Takano, M.A. Bennett and S.K. Bhargava, *Chem. Lett.*, (1990) 543.
28. A.J. Blake, J.A. Grieg, A.J. Holder, T.I. Hyde, M. Schröder and A. Taylor, *Angew. Chem. Int. Ed.*, 29 (1990) 197.
29. Y. Ishikawa, K. Saito, K. Kikuchi, I Ikemoto, K. Kobayashi and H. Anzai, *Acta Crystallogr., Sect. C*, 46 (1990) 1652.
30. A. Terzis, A. Hountas, G.C. Papavassiliou, B. Hilti and J. Pfeiffer, *Acta Crystallogr., Sect. C*, 46 (1990) 224.
31. A. Hountas, A. Terzis, G.C. Papavassiliou, B. Hilti M. Burkle, C.W. Meyer and J, Zambounis, *Acta Crystallogr., Sect. C*, 46 (1990) 228.
32. A.H. Schwellnus, L. Denner and J.C.A. Boeyens, *Polyhedron*, 9 (1990) 975.
33. A.L. Hormann-Arendt and C.F. Shaw, III, *Inorg. Chem.*, 29 (1990) 4683.
34. P. Schwerdtfeger, P.D.F. Boyd, A.K. Burrell, W.T. Robinson and M.J. Taylor, *Inorg. Chem.*, 29 (1990) 3593.
35. D. Fenske, G. Baum, A. Zinn and K. Dehnicke, *Z. Naturforsch, B*, 45 (1990) 1273.
36. K.I. Grandberg and D.N. Kravtsov, *Metalloorg. Khom.*, 2 (1989) 1009.
37. L.G. Kuz'mina, O.Yu. Burtseva, N.V. Dvortsova, M.A. Pora-Koshits and E.I. Smyslova, *Koord. Khim.*, 16 (1990) 70.
38. A.S. Peregudov, E.I. Smyslova, E.I. Fedin and D.N. Kravtsov, *Metalloorg. Khom.*, 3 (1990) 24.
39. M.A. Cinellu, S. Stoccoro, G. Minghetti, A.L. Bandini and F. DeMartin, *Inorg. Chim. Acta*, 168 (1990) 33.
40. E.R.T. Tiekink, *J. Crystallogr. Spectrosc. Res.*, 20 (1990) 371.
41. R. Ettorre and A. Sánchez-González, *Inorg. Chim. Acta*, 168 (1990) 221.
42. J. Vicente, A. Arcas, P.G. Jones and J. Lautner, *J. Chem. Soc., Dalton Trans.*, (1990) 451.
43. V. Ramamoorthy and P.R. Sharp, *Inorg. Chem.*, 29 (1990) 3336.
44. J.E. Anderson, S.M. Sawtelle and C.E. McAndrews, *Inorg. Chem.*, 29 (1990) 2627.
45. K.P. Butin, R.D. Rakhimov, V.P. Dyadchenko and O.A. Enyukova, *Metalloorg. Khim.*, 2 (1989) 1401.
46. J.V. McArdle and G.E. Bossard, *J. Chem. Soc., Dalton Trans.*, (1990) 2219.
47. C.-M. Che, H.-L. Kwong, C.-K. Poon and V.W. Yam, *J. Chem. Soc., Dalton Trans.*, (1990) 3215.
48. C.S.W. Harker and E.R.T. Tiekink, *Acta Crystallogr., Sect. C*, 46 (1990) 1546.
49. W. Yang, L. Zheng, H. Yang and Z. Li, *Xiamen Daxue Xuebao, Ziran Kexueban*, 28 (1989) 430; *CA* 112 (1990) 208299t.
50. A. Baiada, F.H. Jardine and R.D. Willett, *Inorg. Chem.*, 29 (1990) 4805.
51. T.V. Baukova and V.I. Korsunskii, *Metalloorg. Khim.*, 3 (1990) 468.
52. L.G. Kuz'mina, N.V. Dvortsova, M.A. Porai-Koshits, E.I. Smyslova and K.I. Grandberg, *Metalloorg. Khim.*, 2 (1989) 468.
53. A.G. Sykes and K.R. Mann, *J. Am. Chem. Soc.*, 112 (1990) 7247.
54. S. Attar, W.H. Bearden, N.W. Alcock, E.C. Alyea and J.H. Nelson, *Inorg. Chem.*, 29 (1990) 425.
55. H. Schmidbauer, G. Weidenhiller, O. Steigelmann and G. Mueller, *Chem. Ber.*, 123 (1990) 285.
56. H. Schmidbauer, G. Weidenhiller, O. Steigelmann and G. Mueller, *Z. Naturforsch, B*, 45 (1990) 747.
57. A. Laguna and M. Laguna, *J. Organometal. Chem.*, 394 (1990) 743.
58. K. Dziwok, J. Lachmann, G. Mueller, H. Schidbauer and D.L. Wilkinson, *Chem. Ber.*, 123 (1990) 423.
59. S.J. Berners-Price, G.R. Girard, D.T. Hill, B.M. Sutton, P.S. Jarrett, L.F. Faucette, R.K. Johnson, C.K. Mirabelli and P.J. Sadler, *J. Med. Chem.*, 33 (1990) 1386.
60. A.L. Balch and E.Y. Fung, *Inorg. Chem.*, 29 (1990) 4764.
61. A. Togni, S.D. Pastor and G. Rihs, *J. Organometal. Chem.*, 381 (1990) C21.
62. V.W.-W. Yam, T.-F. Lai and C.-M. Che, *J. Chem. Soc., Dalton Trans.*, (1990) 3747.
63. A.L. Balch, V.J. Catalano, B.C. Noll and M.M. Olmstead, *J. Am. Chem. Soc.*, 112 (1990) 7558.
64. A.L. Balch, E.Y. Fung and M.M. Olmstead, *J. Am. Chem. Soc.*, 112 (1990) 5181.
65. A.L. Balch, V.J. Catalano and M.M. Olmstead, *J. Am. Chem. Soc.*, 112 (1990) 2010.

66. A.L. Balch, E.Y. Fung and M.M. Olmstead, *Inorg. Chem.*, 29 (1990) 3203.
67. O.M.N. Dhubhghaill, P.J. Sadler and R. Kuroda, *J. Chem. Soc., Dalton Trans.*, (1990) 2913.
68. A. Baiada, F.H. Jardine and R.D. Willett, *Inorg. Chem.*, 29 (1990) 3042.
69. L.G. Kuz'mina, N.V. Dvortsova, O.Yu. Burtseva, M.A. Porai-Koshits, E.I. Smyslova and K.I. Grandberg, *Metalloorg. Khim.*, 3 (1990) 364.
70. J. Sundermeyer, H.W. Roesky, J. Lautner and P.G. Jones, *Chem. Ber.*, 123 (1990) 433.
71. R. Usón, A. Laguna, M. Laguna, J. Jiménez, M.P. Gómez, A. Sainz and P.G. Jones, *J. Chem. Soc., Dalton Trans.*, (1990) 3457.
72. M.S. Hussain, M.L. Hossain and A. Al-Arfaj, *Transition Metal Chem. (London)*, 15 (1990) 120.
73. A.A. Isab and C.F. Shaw, III, *J. Inorg. Biochem.*, 38 (1990) 91.
74. U. Casellato, G. Fracasso, R. Graziani, L. Sindellari, A. Gonzales-Sanchez and M. Nicolini, *Inorg. Chim. Acta*, 167 (1990) 21.
75. D.D. Heinrich, J.C. Wang and J.P. Fackler, Jr., *Acta Crystallogr., Sect.C*, 46 (1990) 1444.
76. R. Usón, A. Laguna, M. Laguna, M.N. Fraile, I. Lázaro, M.C. Gimeno, P.G. Jones, C. Reihs and G.M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, (1990) 333.
77. A.A. Dvorkin, E.V. Fesenko, L.I. Budarin, Yu.A. Simonov and T.I. Malinovskii, *Dokl. Akad. Nauk, SSSR*, 311 (1990) 1126.
78. I. Wagner and W.-W. du Mont, *J. Organometal. Chem.*, 395 (1990) C23.
79. P.G. Jones and C. Thöne, *Chem. Ber.*, 123 (1990) 1975.
80. H. Schmidbauer, J. E. von Eschenbach, O. Kumberger and G. Müller, *Chem. Ber.*, 123 (1990) 2261.
81. F. Calderazzo, *J. Organometal. Chem.*, 400 (1990) 303.
82. P. Jutzi and A. Moehrke, *Angew. Chem. Int. Ed.*, 29 (1990) 893.
83. H. Willner and F. Aubke, *Inorg. Chem.*, 29 (1990) 2195.
84. A. Laguna, M. Laguna, J Jiménez and A.J. Fumunal, *J. Organometal. Chem.*, 396 (1990) 121.
85. V. Riera, J. Ruiz, X. Solans and E. Tauler, *J. Chem. Soc., Dalton Trans.*, (1990) 1607.
86. J. Meyer, H. Piana, H. Wagner and U. Schubert, *Chem. Ber.*, 123 (1990) 791.
87. T. Castro, Y.Z. Li, R. Rifenberger, E. Choi, S.B. Park and R.P. Andres, *A.C.S. Symp. Ser.* 437 (1990) 329.
88. R.G. Raptis and J.P. Fackler, Jr., *Inorg. Chem.*, 29 (1990) 5003.
89. A. Grohmann, J. Riede and H. Schmidbauer, *Nature (London)*, 345 (1990) 140.
90. O. Steigelmann, P. Bissinger and H. Schmidbauer, *Angew. Chem. Int. Ed.*, 29 (1990) 1399.
91. D.M.P. Mingos and R.P.F. Kanters, *J. Organometal. Chem.*, 384 (1990) 405.
92. N.C. Payne, R. Ramachandran, I. Treurnicht and R.J. Puddephatt, *Organometallics*, 9 (1990) 880.
93. G. Schmid, *Inorg. Synth.*, 27 (1990) 214.
94. M.C. Fairbanks, R.E. Benfield, R.J. Newport and G. Schmid, *Solid State Commun.*, 73 (1990) 431.
95. H. Feld, A. Leute, D. Rading, A. Benninghoven and G. Schmid, *J. Am. Chem. Soc.*, 112 (1990) 8166.
96. H. Feld, A. Leute, D. Rading, A. Benninghoven and G. Schmid, *Z. Phys. D: At., Mol. Clusters*, 17 (1990) 73.
97. J.L. Coffer, J.R. Shapley and H.G. Drickamer, *Inorg. Chem.*, 29 (1990) 3900.
98. B.K. Teo and H. Zhang, *Polyhedron*, 9 (1990) 1985.
99. L.W. Arndt, C.E. Ash, M.Y. Darensbourg, Y.M. Hsiao, C.M. Kim, J. Reibenspies and K.A. Youngdahl, *J. Organometal. Chem.*, 394 (1990) 733.
100. O. Rossell, M. Seco and P.G. James, *Inorg. Chem.*, 29 (1990) 348.
101. A. Anillo, J.A. Cabeza, R. Obeso-Rosete and V. Riera, *J. Organometal. Chem.*, 393 (1990) 423.
102. M. Vaira, P. Stoppioni and M. Peruzzini, *J. Chem. Soc., Dalton Trans.*, (1990) 109.
103. H.J. Haupt, C. Heinekamp and U. Floerke, *Z. Anorg. Allg. Chem.*, 585 (1990) 168.
104. H.J. Haupt, C. Heinekamp and U. Floerke, *Inorg. Chem.*, 29 (1990) 2955.
105. M.I. Bruce, P.E. Corbin, P.A. Humphrey, G.A. Koutsantonis, M.J. Liddell and E.R.T. Tiekink, *J. Chem. Soc., Chem. Commun.*, (1990) 674.
106. D. Braga, F. Grepioni, F. Livotto and M.D. Vargas, *J. Organometal. Chem.*, 391 (1990) C28.
107. R. Della-Pergola, L. Garlaschelli, F. Demartin, M. Manassero, N. Masciocchi and M. Sansoni, *J. Chem. Soc., Dalton Trans.*, (1990) 127.

108. A.A. Low and J.W. Lauher, *Inorg. Synth.*, 27 (1990) 188.
109. A.K. Chipperfield, C.E. Housecroft and A.L. Rheingold, *Organometallics*, 9 (1990) 681.
110. C.E. Housecroft, *Specialist Periodical Reports, R.S.C.*, 19 (1991) in press.
111. A. Antinolo, J.K. Burdett, B. Chaudret, O. Eisenstein, M. Fajardo, F. Jalon, F. Lahoz, J.A. Lopez and A. Otero, *J. Chem. Soc., Chem. Commun.*, (1990) 17.
112. B.D. Alexander, A.M. Mueting and L.H. Pignolet, *Inorg. Chem.*, 29 (1990) 1313.
113. M.A. Bennett, D.E. Berry and K.A. Beveridge, *Inorg. Chem.*, 29 (1990) 4148.
114. P. Braunstein, H. Lehner and D. Matt, *Inorg. Synth.*, 27 (1990) 218.
115. J.J Bour, P.P.J. Schlebos, R.P.F. Kanters, W.P Bosman, J.M.M. Smitts, P.T. Beurskens and J.J. Steggerda, *Inorg. Chim. Acta*, 171 (1990) 177.
116. J.J Bour, W. Van der Berg, P.P.J. Schlebos, R.P.F. Kanters, M.F.J. Schoondergang, W.P Bosman, J.M.M. Smitts, P.T. Beurskens, J.J. Steggerda and P. van der , *Inorg. Chem.*, 29 (1990) 2971.
117. R.P.F. Kanters, P.P.J. Schlebos, J.J Bour, J. Wijnhoven, E. van der Berg and J.J. Steggerda, *J. Organometal. Chem.*, 388 (1990) 233.
118. P. Espinet, J. Forniés, F. Martinez, M. Tómas, E. Lalinde, M.T. Moreno, A. Riuz and A.J. Welch, *J. Chem. Soc., Dalton Trans.* (1990) 791.
119. O.M. Abu–Salah, *J. Organometal. Chem.*, 387 (1990) 123.
120. O.M. Abu–Salah, A.R.A. Al-Ohaly and Z.F. Mutter, *J. Organometal. Chem.*, 389 (1990) 427.
121. O.M. Abu–Salah, A.R.A. Al-Ohaly and Z.F. Mutter, *J. Organometal. Chem.*, 391 (1990) 267.
122. M. Hong, Z. Huang, B. Kang, X. Lei and H. Lui, *Inorg. Chim. Acta*, 168 (1990) 163.
123. B.K. Teo, H. Zhang and X. Shi, *Inorg. Chem.*, 29 (1990) 2083.
124. B.K. Teo, H. Zhang and X. Shi, *J. Am. Chem. Soc.*, 112 (1990) 8552.