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RECENT DEVELOPMENTS IN ARYLGOLD CHEMISTRY

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CONTENTS

ABBREVIATIONS

acac	acetyl acetonate
bipy	2,2′-bipyridine
Bz	benzyl
Cp	cyclopentadienyl
dppe	bis(diphenylphosphino)ethane
dppm	bis(diphenylphosphino)methane
en	ethylenediamine
Et	ethyl
H_2BiBzIm	2,2′-bibenzimidazole
L	neutral ligand
L–L	bidentate neutral ligand
Me	methyl
pap	2-(phenylazo)phenyl
pdma	*o*-phenylenebis(dimethylarsine)

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Ph	phenyl
phen	1,10-phenanthroline
pn	1,3-propylenediamine
Pr	propyl
py	pyridine
pyO	pyridine *N*-oxide
To	*p*-tolyl
tht	tetrahydrothiophene, SC_4H_8

A. INTRODUCTION

The first arylgold compounds synthesised in 1931 [1a] were well characterised as late as 1960 [1b]. During the sixties, this area developed only slowly and the review [2] by Armer and Schmidbaur (1970) collected not more than one dozen arylgold compounds. The pace then became more rapid and new material was the subject of other revisions [3,4]. In 1980, the authoritative Gmelin's monograph on gold-organic compounds [5], described over 280 arylgold derivatives.

In the present review, we consider all the literature published after the last cited comprehensive work, i.e. from the end of 1979 to July 1985. Despite the short interval of time, progress has been noteworthy in two respects: (1) the number of new compounds (495) has almost doubled those previously known; (2) a variety of new types of compounds, including heterometallic complexes with metal–metal bonds, has been reported.

Among the reasons responsible for this rapid development are: (a) the use of polyhalophenyl groups as aryl ligands, which seem to enhance the stability of the gold complexes, thereby facilitating their isolation and subsequent study; (b) the progressive availability of suitable precursors for access to previously unexplored areas, through new types of reactions.

B. ARYLGOLD(I) COMPLEXES

Neutral, anionic and cationic complexes have been reported.

(i) Neutral complexes

These are of a variety of types: mono-, bi-, poly- and heteronuclear derivatives.

Mononuclear derivatives

For a coordination number of two, only a stoichiometry R–Au–L is possible, with the neutral ligand L as the source of variety. Complexes

TABLE 1

Mononuclear derivatives of stoichiometry RAuL

R	L	Method of synthesis [a]	Ref.
4-MeC_6H_4	PPh_3	a	18, 19
$C_{10}H_7$ [b]	PPh_3	a	6
$C_{10}H_{10}N$ [c]	PMe_3	b	13
2-$Me_2NC_6H_4$	PPh_3	a,b	7
2-$Me_2NC_6H_4$	CNC_6H_{11}	b	7
2-$Me_2NCH_2C_6H_4$	PPh_3	a,b	7
(*S*) 2-$Me_2NCHMeC_6H_4$	PPh_3	a,b	7
2,6-$(MeO)_2C_6H_3$	PPh_3	a	7
2,4,6-$(MeO)_3C_6H_2$	PPh_3	a	7
2-$O_2NC_6H_4$	PPh_3	b	12
2-$O_2NC_6H_4$	$AsPh_3$	b	12
3-$O_2NC_6H_4$	PPh_3	b	12
3-$CF_3C_6H_4$	PPh_3	a	6
4-C_6FH_4	PPh_3	a	6
3,6-$C_6F_2H_3$	PPh_3	a,b	6
3,6-$C_6F_2H_3$	$AsPh_3$	a	6
2,4,6-$C_6F_3H_2$	tht	c	14
2,4,6-$C_6F_3H_2$	PPh_3	a,b	6
2,4,6-$C_6F_3H_2$	PCy_3	a,b,c	6
2,4,6-$C_6F_3H_2$	$AsPh_3$	a	6
2,3,5,6-C_6F_4H	PPh_3	a	6
4,4′-$HC_6F_4C_6F_4$	tht	a	8
4,4′-$HC_6F_4C_6F_4$	PPh_3	b	8
4,4′-$HC_6F_4C_6F_4$	phen	b	8
C_6F_5	$NH_2(CH_2)_2NH_2$	b	10
C_6F_5	$NH_2(CH_2)_3NH_2$	b	10
C_6F_5	phen	b	9
C_6F_5	tht	c	14
C_6F_5	CNMe	d	15
C_6F_5	$C(NHMe)_2$	e	15
C_6F_5	$C(NHPh)[NH(CH_2)_2NH_2]$	e	10
C_6F_5	$C(NHTo)[NH(CN_2)_2NH_2]$	e	10
C_6F_5	$C(NHPh)[NH(CH_2)_3NH_2]$	e	10
C_6F_5	$C(NHTo)[NH(CH_2)_3NH_2]$	e	10
C_6F_5	CH_2PPh_3	f	16
C_6F_5	$CH(Me)PPh_3$	f	16
C_6F_5	$CH(Et)PPh_3$	f	16
C_6F_5	$CH(Ph)PPh_3$	f	16
C_6F_5	CH_2AsPh_3	f	16
C_6F_5	PPh_2CHPPh_2Me	g	20
C_6Cl_5	tht	a,c	11, 14
C_6Cl_5	phen	b	11
C_6Cl_5	$AsPh_3$	b	11

[a] See text, Section B(i). [b] α-Naphthyl. [c] 2,4-Dimethyl-7-quinolyl.

containing S, N, P, As, isocyanide, carbene or ylide ligands have been described (Table 1).

The following synthetic methods have generally been used:

(a) Arylation with an aryllithium derivative [6,7]

$$\mathrm{ClAuL + LiR \rightarrow RAuL + LiCl} \tag{1}$$

which can be used even with bifunctional lithium compounds, albeit the presence of some binuclear compound is unavoidable [8].

$$\begin{aligned}&\mathrm{3\ ClAu(SC_4H_8) + 2\ LiC_6F_4C_6F_4Li \overset{(H_2O)}{\rightarrow} (HC_6F_4C_6F_4)Au(SC_4H_8)}\\&\quad\mathrm{+ (H_8C_4S)AuC_6F_4C_6F_4Au(SC_4H_8) + 3\ LiCl + LiOH}\end{aligned} \tag{2}$$

Both gold(I) complexes can easily be separated because of marked differences in their solubilities (e.g. from diethyl ether/n-hexane). A possible failure of this synthesis appears when rearrangement of ligands takes place, as shown in the following example [6] (eqn. (3)) an ionic end-product being the result.

$$\mathrm{2\ ClAuPCy_3 + 2\ Li(3,6\text{-}C_6F_3H_2) \rightarrow [Au(PCy_3)_2][Au(C_6F_3H_2)_2] + 2\ LiCl} \tag{3}$$

(b) Displacement of weakly coordinating ligands. Some neutral ligands, such as tetrahydrothiophene (SC_4H_8), are basic enough to stabilize gold(I), but are readily displaced by almost any other ligand [9–11] (eqn. (4))

$$\mathrm{RAu(SC_4H_8) + L \rightarrow RAuL + SC_4H_8} \tag{4}$$

Displacement of $AsPh_3$ [6] or Cl^- in chloroorgano aurate(I) [12] has also been reported (eqn. (5))

$$\mathrm{[(\mathit{o}\text{-}O_2NC_6H_4)AuCl]^- + PPh_3 \rightarrow (o\text{-}O_2NC_6H_4)AuPPh_3 + Cl^-} \tag{5}$$

and similarly the dimeric (or polymeric) $[RAu]_n$ derivatives [7,13] give monomeric neutral complexes upon reaction with neutral ligands (eqn. (6)).

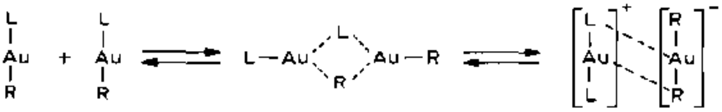
$$\mathrm{[(2\text{-}Me_2NCH_2C_6H_4)Au]_2 + 2\ PPh_3 \rightarrow 2\ (2\text{-}Me_2NCH_2C_6H_4)AuPPh_3} \tag{6}$$

Occasionally, ligand rearrangement accompanies displacement (eqn. (4)) and an ionic end-product is obtained, as observed with L = *o*-phenylenebis(dimethylarsine) (pdma) or ($SbPh_3$) [9,10].

$$\mathrm{2\ (C_6F_5)Au(SC_4H_8) + 2\ (pdma) \rightarrow [Au(pdma)_2][Au(C_6F_5)_2] + 2\ SC_4H_8} \tag{7}$$

the cationic part containing four-coordinated tetrahedral gold(I).

(c) By suitable choice of the anionic and cationic reagents the reverse



Scheme 1.

rearrangement of ligands can also be achieved [6,14] leading (eqn. (8)) to neutral complexes.

$$(Bu_4N)[Au(C_6F_3H_2)_2] + [Au(PCy_3)_2]ClO_4 \rightarrow 2\ (C_6F_3H_2)Au(PCy_3) + [NBu_4]ClO_4 \quad (8)$$

These arrangements, ionic complex ⇌ neutral complex, observed in processes (3), (7) or (8), require the migration of polyfluorophenyl groups from one gold atom to the other and are likely to occur [6,9,10] through the formation of a binuclear intermediate with bridging aryl groups, displaying 3c–2e bonds, as is shown in Scheme 1.

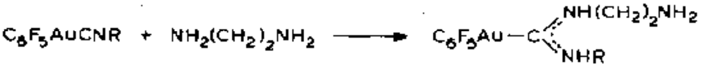
Other methods, albeit not so broad in scope as the above, have selectively been used for the synthesis of novel types of gold(I) complexes.

(d) Methylation (eqn. (9)) of $[C_6F_5AuCN]^-$ renders isocyanide complexes [15]

$$(BzPh_3P)[C_6F_5AuCN] + [Me_3O]BF_4 \rightarrow C_6F_5AuCNMe + [BzPh_3P]BF_4 + Me_2O \quad (9)$$

the ν(CN) vibration being shifted from 2140 cm^{-1} in the cyanoaurate(I) to 2265 cm^{-1} in the neutral isocyanide.

(e) Reactions between gold(I) isocyanides and nucleophile lead to arylgold carbene [9,15] as illustrated in eqn. (10).



$$C_6F_5AuCNR + NH_2(CH_2)_2NH_2 \longrightarrow C_6F_5Au{-}C(NH(CH_2)_2NH_2)(NHR) \quad (10)$$

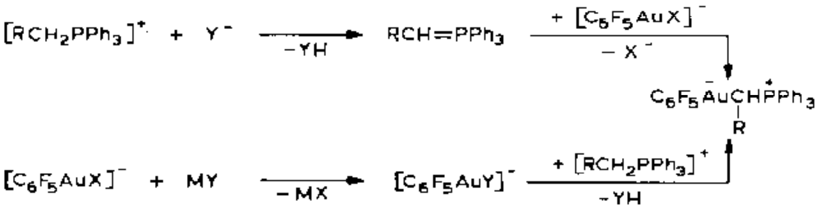
whereby the ν(CN) vibration at $\sim 2260\ cm^{-1}$ in the isocyanide is clearly shifted towards lower energies (1580–1560 cm^{-1}).

(f) Arylgold ylide complexes have been synthesised [16] by using NaH or TlC_5H_5 for simultaneous H and halogen abstraction from haloarylaurate(I) containing an appropriate cation (eqns. (11), (12))

$$[RCH_2PPh_3][C_6F_5AuX] + NaH \rightarrow C_6F_5AuCH(R)PPh_3 + NaX + H_2 \quad (11)$$

$$[RCH_2PPh_3][C_6F_5AuX] + NaC_5H_5 \rightarrow C_6F_5AuCH(R)PPh_3 + NaX + C_5H_6 \quad (12)$$

An IR band at 580–530 cm^{-1} is assigned to the ν(Au–C) vibration [17].



Scheme 2.

Two alternative reaction pathways have been discussed [16] for the above reactions (11) or (12), as represented in Scheme 2: (i) nucleophilic attack of Y^- (H^- or Cp^-, respectively) upon the cationic part of the gold precursor to form the free ylide, which subsequently displaces the halide ion in the haloaurate; or (ii) halide abstraction and substitution by Y^- in the aurate anion followed by interaction with the cationic part under hydrogen abstraction.

(g) The preceding method (eqn. (11)) can be extended to other suitable precursors [20] as shown by the following example (eqn. (13))

$$[C_6F_5AuPPh_2CH_2PPh_2Me]ClO_4 + NaH \rightarrow C_6F_5AuPPh_2\overset{-}{C}H\overset{+}{P}Ph_2Me + NaClO_4 + H_2 \qquad (13)$$

and the electron density on the methanide carbon (CH) can be donated to other metallic centres to form bi- or tri-nuclear derivatives (see eqns. (17) and (53) below).

Using these synthetic methods the neutral complexes collected in Table 1 have been obtained and some of their properties have been studied. Thus, in all the cases where conductance measurements and molecular weight determinations (isopiestic method) have been carried out, the solute behaves as non-conducting and monomeric. The ^{197}Au Mössbauer spectra of the complexes with R = 4-MeC_6H_4 [19], 2-$Me_2NCH_2C_6H_4$, (*S*)2-$Me_2NCH(Me)$-C_6H_4, 2-$Me_2NC_6H_4$ [7] confirm the presence of bicoordinated gold(I) species.

Two single crystal X-ray diffraction studies have been reported. The structures of 2,6-$(MeO)_2C_6H_3AuPPh_3$ [21] and $C_6F_5AuPPh_2CHPPh_2Me$ [20] are given in Figs. 1 and 2, respectively. The C–Au–P bonds are roughly linear (172.7 and 174.8°, respectively) and the Au–C (2.050, 2.057 Å) or Au–P (2.284 and 2.287 Å) distances are approximately coincident. The P–C distances (1.729 and 1.692 Å) in the methanide complex are significantly shorter than those (1.845 Å) found in $[(C_6F_5)_2AuPPh_2CH_2PPh_2]ClO_4$ [22] or in the binuclear $C_6F_5AuPPh_2CH(AuC_6F_5)PPh_2Me$ [20] (1,790 and 1.804 Å), pointing to electron delocalisation in the P–C–P system of the methanide complex.

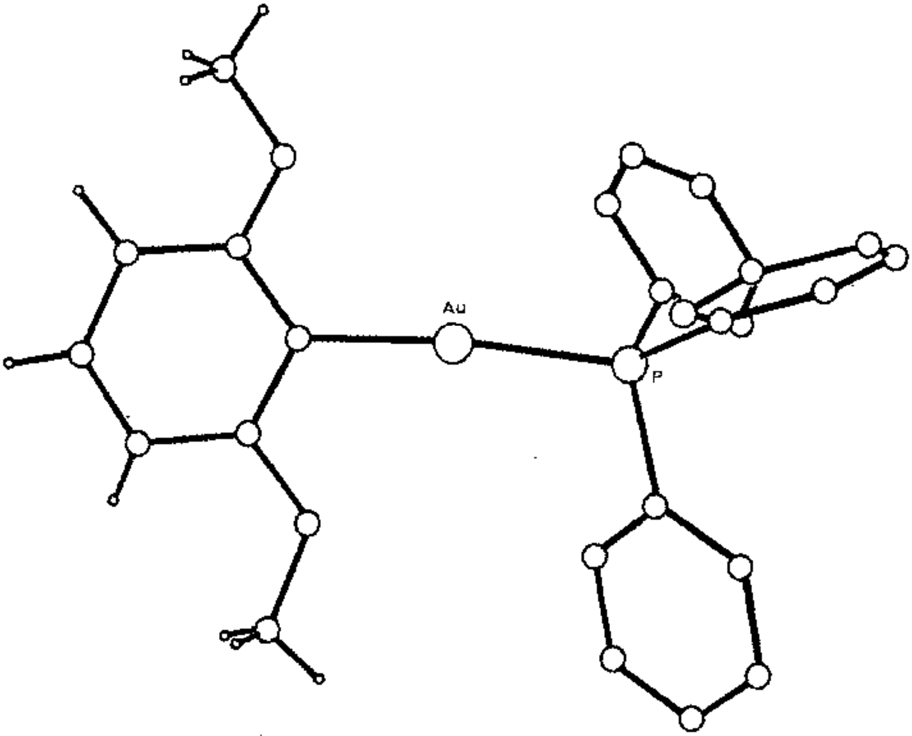


Fig. 1. Structure of 2,6-$(MeO)_2C_6H_3AuPPh_3$ [21].

Binuclear derivatives

With regard to bridging ligands, the hitherto described binuclear complexes are of three different types, containing (a) bidentate neutral ligands, (b) anionic ligands or (c) aryl groups, bridging the two gold centres (see Table 2).

(a) Two general methods have been used for the synthesis of binuclear complexes containing bidentate neutral ligands [6,8,10–12,23]. The first includes substitution processes of the type described previously in eqns. (4)–(7), as shown by eqns. (14) and (15).

$$2\ RAu(SC_4H_8) + L\text{–}L \rightarrow RAuL\text{–}LAuR + 2\ SC_4H_8 \qquad (14)$$

$$2\left[(2\text{-}O_2NC_6H_4)AuCl\right]^- + dppe$$
$$\rightarrow O_2NC_6H_4Au(dppe)AuC_6H_4NO_2 + 2\ Cl^- \qquad (15)$$

The second method uses the uncoordinated end of a potentially bidentate ligand which is acting as unidentate in a monomeric gold(I) complex either to displace (eqns. (16), (17)) a neutral ligand in another complex [10,20]

$$C_6F_5AuNH_2(CH_2)_2NH_2 + C_6F_5Au(SC_4H_8)$$
$$\rightarrow C_6F_5AuNH_2(CH_2)_2NH_2AuC_6F_5 + SC_4H_8 \qquad (16)$$

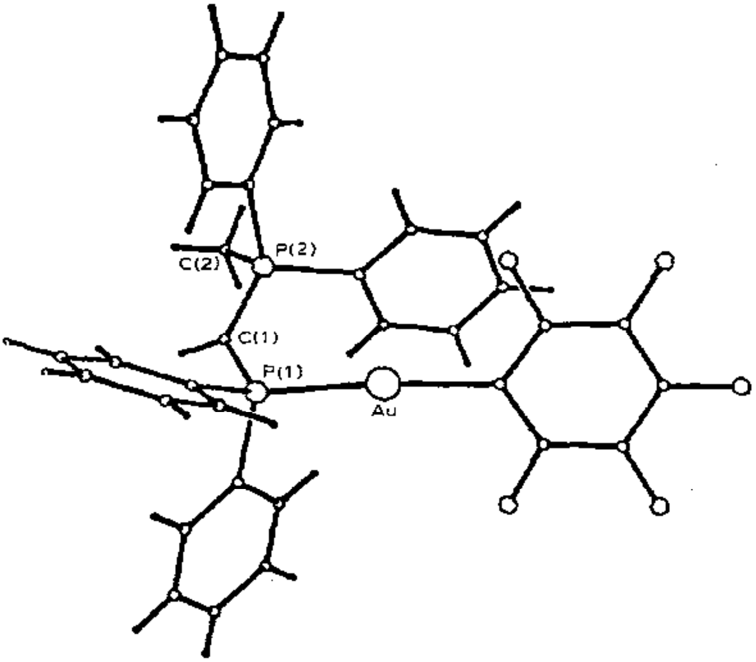
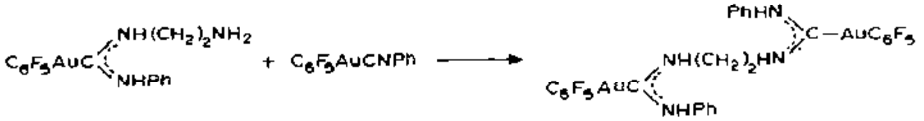


Fig. 2. Structure of $C_6F_5AuPPh_2CHPPh_2Me$ [20].

$$C_6F_5AuPPh_2\bar{C}H\overset{+}{P}Ph_2Me + C_6F_5Au(SC_4H_8)$$
$$\rightarrow C_6F_5AuPPh_2CH(AuC_6F_5)PPh_2Me + SC_4H_8 \quad (17)$$

or to add to a gold(I) isocyanide [10], giving binuclear gold(I) carbene derivatives (eqn. (18)).



(18)

These processes (eqns. (17) and (18)) can also be extended to the synthesis of mixed gold(I)–gold(III) binuclear complexes, if the weak ligand or, respectively, the isocyanide ligand are part of a gold(III) complex, as in $(C_6F_5)_3Au(SC_4H_8)$ [20] or in $(C_6F_5)_3AuCNR$ (R = Ph, To) [10]. All these complexes are non-conducting in acetone solution and their molecular weight (isopiestic method) confirms their binuclear character. The structure of $C_6F_5AuPPh_2CH(AuC_6F_5)PPh_2Me$ has been solved [20] by X-ray diffraction (Fig. 3). Each of the two gold(I) centres displays roughly linear bonds (~ 177°, in both cases). The geometry of the (P, C-bonded) methanide ligand is noticeably changed in comparison with that observed in

TABLE 2

Binuclear derivatives of stoichiometry RAuL–LAuX

R	X	L–L	Ref.
$C_{10}H_7$ [a]	$C_{10}H_7$ [a]	$PPh_2(CH_2)_2PPh_2$	6
4-MeC_6H_4	4-MeC_6H_4	$PPh_2(CH_2)_2PPh_2$	18
4-MeC_6H_4	4-MeC_6H_4	$PPh_2(CH_2)_3PPh_2$	18
4-MeC_6H_4	4-MeC_6H_4	$PPh_2(CH_2)_4PPh_2$	18
2-$O_2NC_6H_4$	2-$O_2NC_6H_4$	$PPh_2(CH_2)_2PPh_2$	12
3,6-$C_6F_2H_3$	3,6-$C_6F_2H_3$	$PPh_2(CH_2)_2PPh_2$	6
2,4,6-$C_6F_3H_2$	2,4,6-$C_6F_3H_2$	$PPh_2CH_2PPh_2$	6
2,4,6-$C_6F_3H_2$	2,4,6-$C_6F_3H_2$	$PPh_2(CH_2)_2PPh_2$	6
4,4′-$HC_6F_4C_6F_4$	4,4′-$HC_6F_4C_6F_4$	$PPh_2CH_2PPh_2$	8
C_6F_5	C_6F_5	4,4′-bipy	10
C_6F_5	Cl	$NH_2(CH_2)_2NH_2$	10
C_6F_5	Cl	$NH_2(CH_2)_3NH_2$	10
C_6F_5	C_6F_5	$NH_2(CH_2)_2NH_2$	10
C_6F_5	C_6F_5	$NH_2(CH_2)_3NH_2$	10
C_6F_5	C_6F_5	PPh_2NHPPh_2	23
C_6F_5	C_6F_5	PPh_2CHPPh_2Me	20
C_6F_5	C_6F_5	$C(NHPh)[NH(CH_2)_2NH_2]$	10
C_6F_5	C_6F_5	$C(NHTo)[NH(CH_2)_2NH_2]$	10
C_6F_5	C_6F_5	$C(NHPh)[NH(CH_2)_3NH_2]$	10
C_6F_5	C_6F_5	$C(NHTo)[NH(CH_2)_3NH_2]$	10
C_6F_5	C_6F_5	$C(NHPh)[NH(CH_2)_2NH](PhNH)C$	10
C_6F_5	C_6F_5	$C(NHTo)[NH(CH_2)_2NH](ToNH)C$	10
C_6F_5	C_6F_5	$C(NHPh)[NH(CH_2)_2NH](ToNH)C$	10
C_6F_5	C_6F_5	$C(NHTo)[NH(CH_2)_3NH](ToNH)C$	10
C_6Cl_5	C_6Cl_5	$PPh_2CH_2PPh_2$	11
C_6Cl_5	C_6Cl_5	PPh_2NHPPh_2	23

[a] α-Naphthyl.

$C_6F_5AuPPh_2CHPPh_2Me$ (Fig. 2) and now the P–C bonds are longer (1.790 and 1.804 Å) and the P–C–P angle is closer (114.9° instead of 126.0°).

(b) Only two neutral binuclear complexes of the type $C_6F_5Au{-}X{-}AuPPh_3$ ($X = SCN, N_3$) have been reported [24]. The two processes leading to their preparation are

$$C_6F_5Au(SC_4H_8) + XAuPPh_3 \rightarrow C_6F_5Au{-}X{-}AuPPh_3 + SC_4H_8 \tag{19}$$

$$\begin{aligned}&(BzPh_3P)[C_6F_5AuX] + [O_3ClOAuPPh_3]\\&\quad \rightarrow C_6F_5Au{-}X{-}AuPPh_3 + [BzPh_3P]ClO_4\end{aligned} \tag{20}$$

but it was not possible [24] to obtain similar binuclear derivatives for X = Cl, Br, I. In these complexes the $\nu(CN)$ and $\nu(N{-}N)$ vibrations appear at 2170 and 2103 cm^{-1}, respectively, slightly displaced towards higher frequencies relative to the starting complexes.

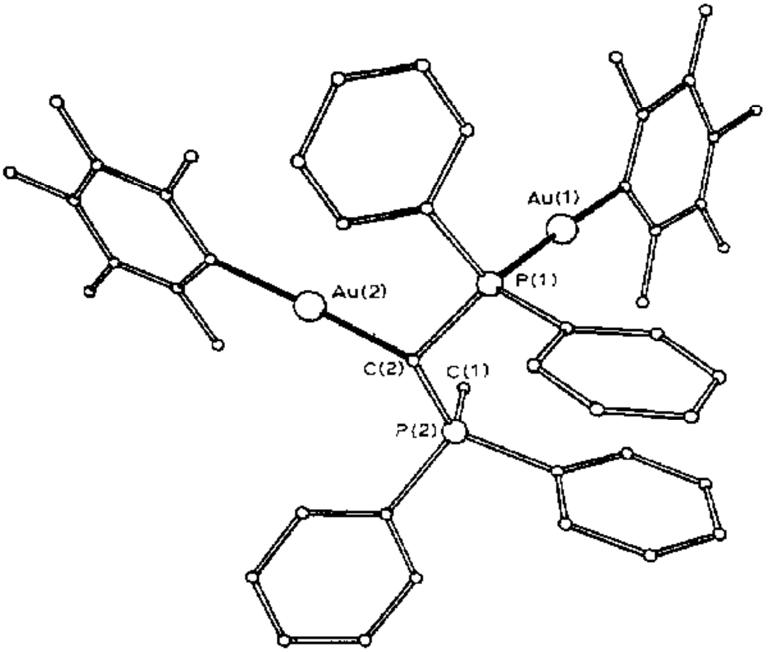


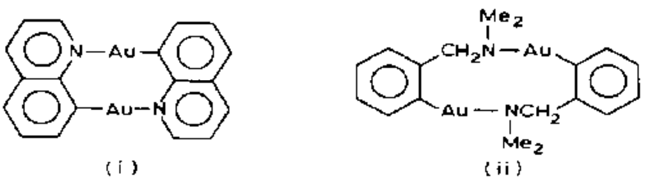
Fig. 3. Structure of $C_6F_5AuPPh_2CH(AuC_6F_5)PPh_2Me$ [20].

(c) The only genuine binuclear derivatives containing an aryl bridging ligand are $(C_4H_8S)AuC_6F_4 \cdot C_6F_4Au(SC_4H_8)$ and its substitution products $LAuC_6F_4C_6F_4AuL$ (L = PPh_3, $SbPh_3$, phen) [8]. As we have seen before, the tetrahydrothiophene derivative is always present in the reaction products (eqn. (2)) and the yield can be increased by appropriate adjustment of the stoichiometric ratio (2 : 1). Molecular weight measurements confirm the binuclear nature of these complexes [8].

A series of complexes $[RAu]_n$ for which a binuclear structure ($n = 2$) has been proposed, are obtained [13] by the reaction of functionalised aryllithium derivatives with $ClAuAsPh_3$

$$ClAuAsPh_3 + RLi \rightarrow RAu + LiCl + AsPh_3 \qquad (21)$$

where R = 8-quinolyl or 6-methoxy-8-quinolyl, or [7] by the reaction of an



(i) (ii)

Fig. 4.

organoaurate with organotin reagents

$$\mathrm{LiAuR_2 + Me_3SnBr \rightarrow RAu + Me_3SnR + LiBr} \tag{22}$$

where $\mathrm{R = 2\text{-}Me_2NCH_2C_6H_4}$ or (S) $\mathrm{2\text{-}Me_2NCHMeC_6H_4}$. The quinolyl derivatives are only slightly soluble, but a binuclear structure (Fig. 4(i)) has been proposed, although experimental data are lacking. The second type is dimeric in benzene solution and its structure (Fig. 4(ii)) has been derived from NMR data.

Polynuclear derivatives

All the hitherto reported polynuclear derivatives show the stoichiometry $[\mathrm{RAu}]_n$, with the only exception the insoluble $[\mathrm{Au_2(C_6F_4C_6F_4)(dppm)}]_n$ which precipitates [8] after addition of bis(diphenylphosphino)methane to $\mathrm{(C_4H_8S)AuC_6F_4C_6F_4Au(SC_4H_8)}$.

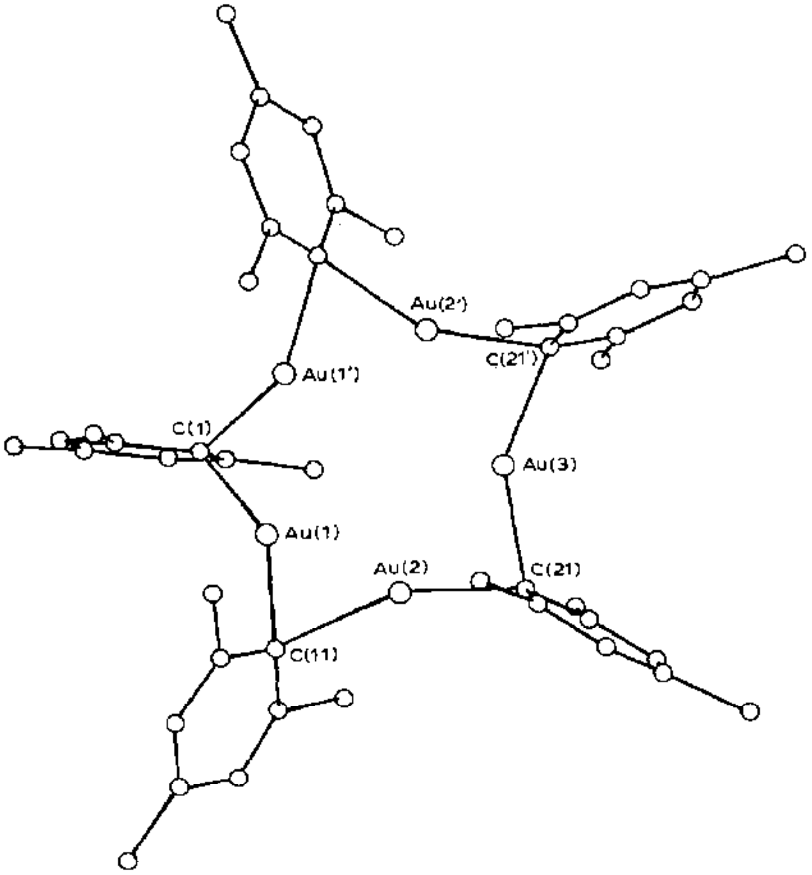


Fig. 5. Structure of $[\mathrm{2,4,6\text{-}Me_3C_6H_2)Au]_5}$ [25].

If in eqn. (21) R = 2,4-dimethyl-7-quinolyl, a slightly soluble solid $[RAu]_n$ is obtained. This polymer reacts with PPh_3 to give the monomeric $RAuPPh_3$.

Arylation of ClAu(CO) with $(2,4,6\text{-}Me_3C_6H_2)MgBr$ leads [25] to the pentanuclear $[RAu]_5$

$$5\ ClAu(CO) + 5\ (2,4,6\text{-}Me_3C_6H_2)MgBr \rightarrow [(2,4,6\text{-}Me_3C_6H_2)Au]_5 + 5\ MgClBr + 5\ CO \qquad (23)$$

whose structure (Fig. 5), established by X-ray diffraction, consists of a ten-membered ring with the aryl groups bridging pairs of gold atoms. The bonding of the aryl groups is electron deficient (3c, 2e) and the C–Au–C angles are non-linear (150.4 and 152.9°), but the Au–C distances (2.12–2.20 Å) are only slightly longer than those found in complexes with σ Au–C bonds (2.050 Å in $(2,6\text{-}(MeO)_2C_6H_3)AuPPh_3$ [21], 2.057 Å in $C_6F_5AuPPh_2CHPPh_2Me$ [20], 2.11 Å in $C_6F_5AuPPh_2CH(AuC_6F_5)PPh_2Me$ [20] and 2.050 Å in $[Au(C_6F_5)_2]^-$ [9]).

The unstable $[Au(C_6F_3H_2)]_4$ [26] can be prepared (after eqn. (24))

$$4\ (NBu_4)[Au(2,4,6\text{-}C_6F_3H_2)_2] + 4\ HPF_6 \rightarrow [Au(C_6F_3H_2)]_4 + 4\ C_6F_3H_3 + 4\ (NBu_4)PF_6 \qquad (24)$$

and is tetrameric in solution. A ring structure with (3c, 2e) bridging aryl groups has been proposed [26]. The compound decomposes above −20°C and the structure of the solid is unknown.

If, in eqn. (22), $R = 2\text{-}Me_2NC_6H_4$, again a solid of stoichiometry $[RAu]_n$ is obtained [7]. A similar Cu derivative has also been reported [27]. Due to its lack of solubility in organic solvents a polymeric nature is invoked, involving 3c, 2e bonding, in agreement with its ^{197}Au Mössbauer spectrum [7].

Heteronuclear derivatives

Neutral gold(I) complexes containing other metal centres (M′) have been prepared, the heterometallic component being lithium, copper, silver, palladium or platinum.

M′ = Li. Derivatives of stoichiometry AuR_2Li ($R = 2\text{-}Me_2NCH_2C_6H_4$, (*S*) $2\text{-}Me_2NCH(Me)C_6H_4$, $2\text{-}Me_2NC_6H_4$, $2,6\text{-}(MeO)_2C_6H_3$) have been prepared [7], according to

$$BrAuPPh_3 + 2\ RLi \rightarrow AuR_2Li + LiBr + PPh_3 \qquad (25)$$

$$RAuPPh_3 + RLi \rightarrow AuR_2Li + PPh_3 \qquad (26)$$

Because of their similarity with previously reported derivatives [28,29] a tetranuclear structure $Au_2R_4Li_2$ has been assigned, with alternate lithium and gold atoms bridged by the aryl groups; the built-in substituents are

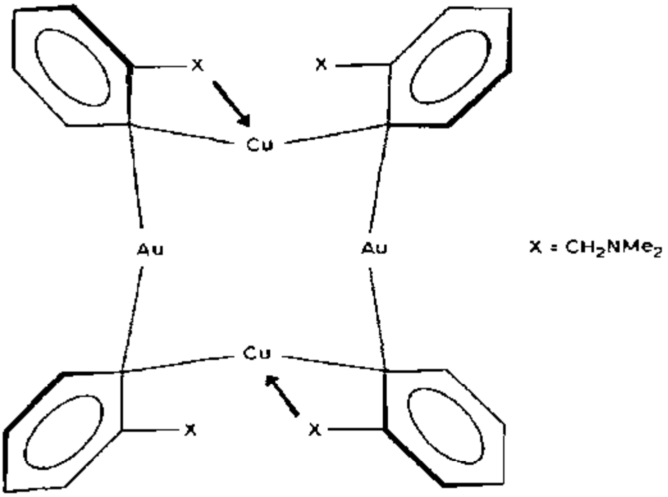


Fig. 6.

assumed to coordinate the lithium atoms exclusively, which are therefore four-coordinate, whilst the Au atoms are two coordinate [29].

M′ = Cu. $Au_2R_4Li_2$ ($R = 2\text{-}Me_2NCH_2C_6H_4$) reacts [7] with CuI, according to

$$Au_2R_4Li_2 + 2\ CuI \rightarrow Au_2R_4Cu_2 + 2\ LiI \qquad (27)$$

Molecular weight measurements confirm that this complex is tetranuclear in solution, and its ^{197}Au Mössbauer spectrum points to linear coordination for the gold atom, excluding any Au–N bonding interaction. A similar structure to that found in complexes R_4Cu_4 [30] has been prososed (Fig. 6).

M′ = Ag. These compounds are more numerous than the other types and are quite exceptional in that they present direct Au–M′ bonds, unsupported by any other bridging ligand. They belong to the type $[AuAgR_2L]_x$ but for $R = C_6F_3H_2$ or C_6Cl_5 the neutral ligand-free $[AuAgR_2]_x$ can also be prepared, by reaction of (NBu_4) $[AuR_2]$ with $AgClO_4$. When $R = C_6F_5$ a mixture of products is obtained [31–33]. Addition of the neutral ligand L to solutions containing $[AuAgR_2]$ leads to precipitation of $[AuAgR_2L)_x$, according to

$$\begin{tikzcd}
x[Bu_4N][AuR_2] + xAgClO_4 \arrow[r] & {[AuAgR_2]_x + xNBu_4ClO_4} \arrow[d, "+ xL"] \\
{[AuAgR_2]_x + xL} \arrow[r] & {[AuAgR_2L]_x}
\end{tikzcd} \qquad (28)$$

where $R = C_6F_5$ and $L = SC_4H_8$, py, bipy, phen, en, pn, pyO, $OPPh_3$, $SPPh_3$, PPh_2Me, cyclooctene, styrene, 1,3-cyclooctadiene, norbornadiene, hex-3-yne; $R = 2,4,6\text{-}C_6F_3H_2$ and $L = SC_4H_8$, py, bipy, phen, 4-MepyO, $OPPh_3$, $SPPh_3$, PPh_3; $R = C_6Cl_5$ and $L = SC_4H_8$, py, phen, $OCMe_2$.

For $R = C_6F_5$ and L = diphenylacetylene, the unstable compound $[AuAgR_2(0.5C_2Ph_2)]_x$ can be isolated. If the red crystals are dissolved in hot $OCMe_2$, C_6H_6, $C_6H_5CH_3$, $C_6H_5(OCH_3)$ or cyclohexane and the solutions are allowed to cool, crystals of $[AuAgR_2L]_x$ (L being in each case a solvent molecule) can be obtained. These complexes are not directly accessible via the original method (eqn. (28)).

Alternative, albeit less general, routes leading to complexes of the same type [32] are represented in eqns. (29) and (30).

$$x\,C_6F_5AuL + x\,C_6F_5Ag \rightarrow [AuAg(C_6F_5)_2L]_x \tag{29}$$

$$x\,O_3ClOAu(SC_4H_8) + x(NBu_4)[Ag(C_6F_5)_2] \rightarrow [AuAg(C_6F_5)_2(SC_4H_8)] + x[NBu_4]ClO_4 \tag{30}$$

Acetone solutions of these complexes are conducting, owing to equilibria such as

$$[AuAgR_2L]_x + xS \rightleftarrows x[L{-}Ag{-}S]^+[AuR_2]^- \tag{31}$$

which for $R = C_6F_5$ are more displaced towards the right.

The structures of these complexes have been established by X-ray crystallography, for two samples of pentafluorophenyl derivatives with $L = SC_4H_8$ and C_6H_6 [32] (Figs. 7 and 8). They are polymeric chains formed by repetition of the unit $R_2Au(\mu\text{-}AgL)_2AuR_2$ through short Au $\cdots$ Au contacts (2.889 and 3.013 Å, respectively). A striking feature is that the Au_2Ag_2

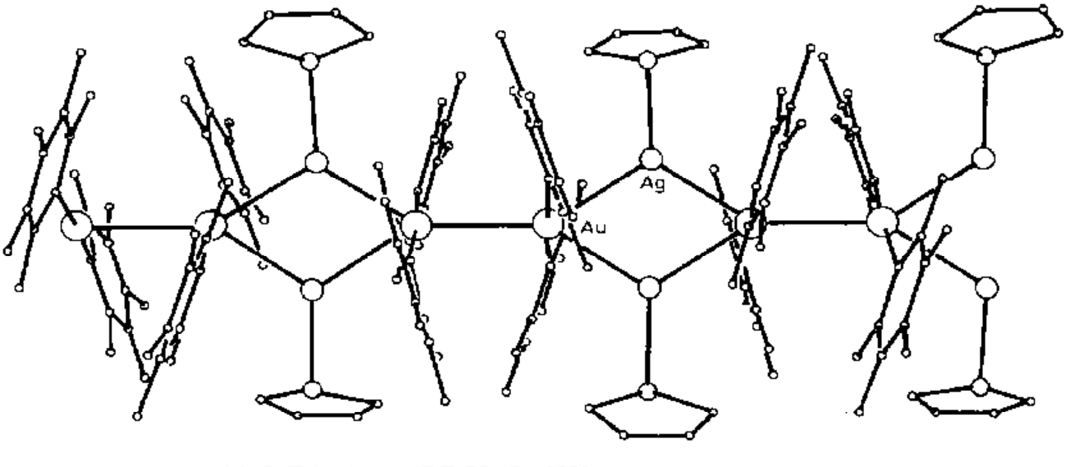


Fig. 7. Structure of $[(C_6F_5)_2AuAg(SC_4H_8)]_n$ [32].

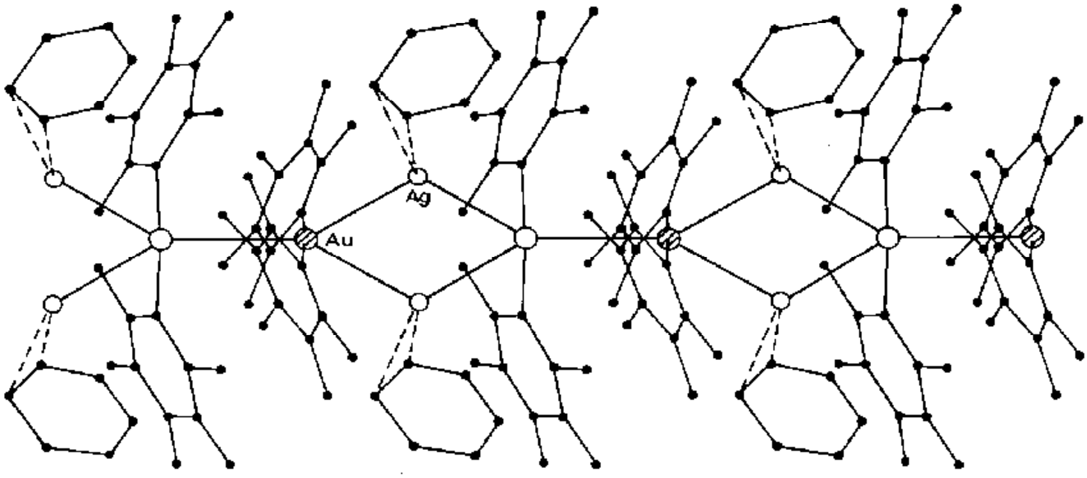
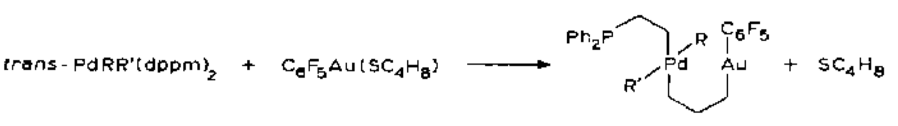


Fig. 8. Structure of $[(C_6F_5)_2AuAgC_6H_6]_n$ [32].

ring is almost regular in the SC_4H_8 derivative, but distorted in the C_6H_6 one. In the latter the *ortho* fluorine atom of the C_6F_5 group may have non-bonded interactions with the nearest silver atom (Ag · · · F distances, 2.84 Å) thus contributing both to the observed distortion and to the stability of the cluster.

The AuR_2 groups are only very slightly distorted in comparison with the free $[AuR_2]^-$ anion [9], despite the fact that the gold centre donates electron density to the silver cation, as indicated by the ^{197}Au Mössbauer spectrum [34].

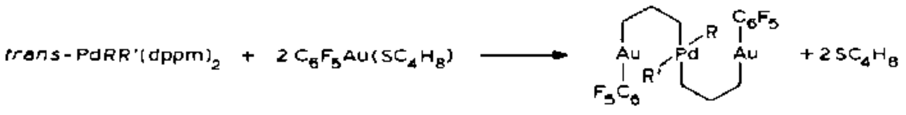
M′ = Pd. The uncoordinated end of dppm in such complexes as *trans*-PdRR′(dppm)$_2$ (in which the diphosphine is unidentate), can displace the weakly coordinating SC_4H_8 in gold complexes $C_6F_5AuSC_4H_8$, to give [35] heterobinuclear complexes (eqn. (32)).



(32)

where R = C_6F_5, R′ = C_6F_5 or Cl; or R = C_6Cl_5, R′ = C_6Cl_5.

If a 1 : 2 molar ratio is used, trinuclear derivatives are obtained (eqn. (33)).



(33)

The structure of $C_6F_5Au(dppm)Pd(C_6F_5)_2(dppm)AuC_6F_5$ (Fig. 9) has been solved by X-ray crystallography [35].

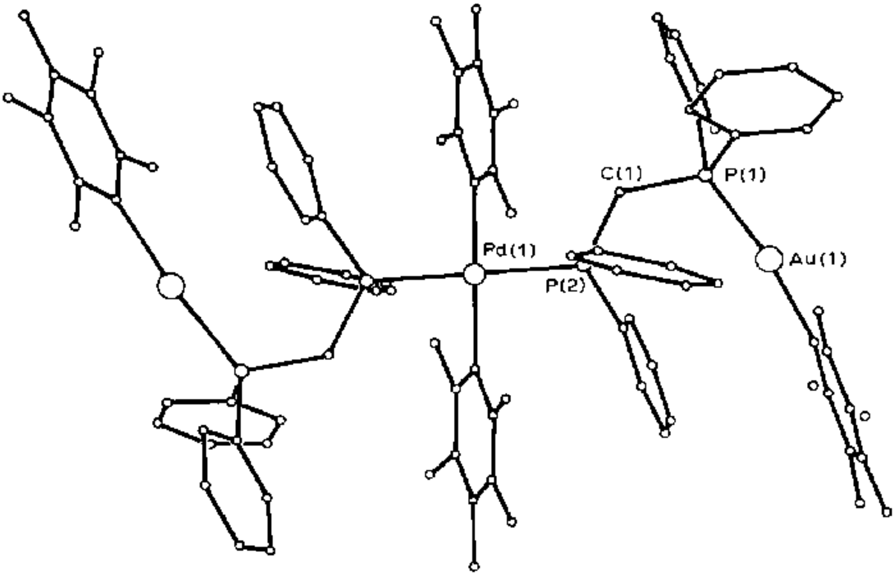


Fig. 9. Structure of $C_6F_5Au(dppm)Pd(C_6F_5)_2(dppm)AuC_6F_5$ [35].

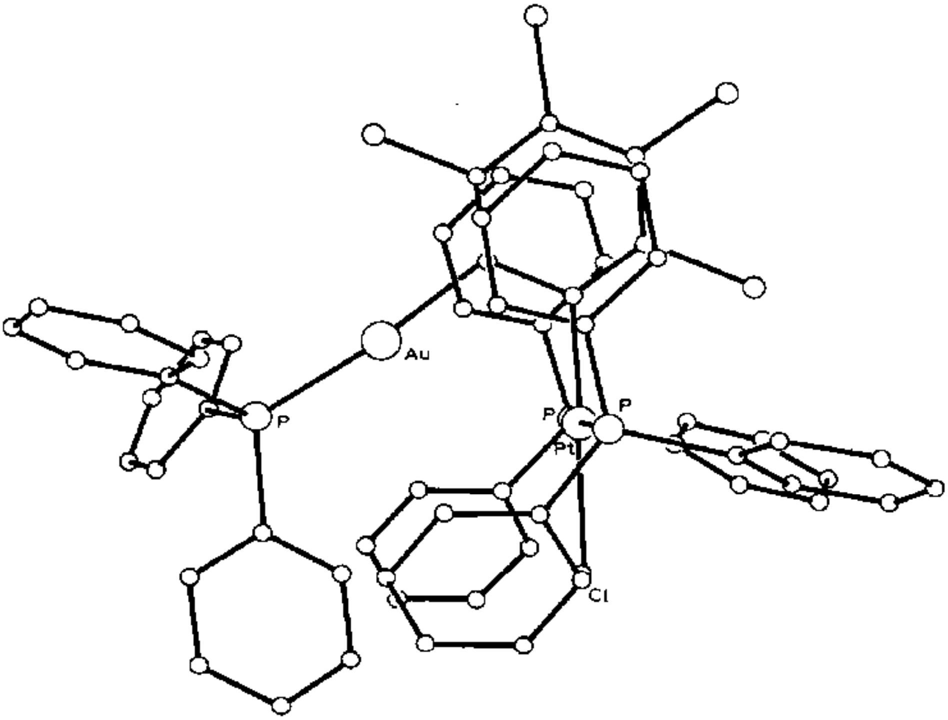


Fig. 10. Structure of $Cl(Ph_3P)Pt(\mu\text{-}C_6Cl_4)AuPPh_3$ [37].

The gold(I) centres display a roughly linear coordination (bond angles, 174.6°) and the palladium atom is square-planar and lies in a crystallographic symmetry centre.

$M' = Pt$. Since neither C_6H_5Cl, C_6H_5Br, nor C_6Cl_6 add to $Pt(PPh_3)_3$ the oxidative addition of $C_6Cl_5AuPPh_3$ seems of interest. The addition, however, does not take place via the cleavage of the Au–C bond to give a Pt–Au bonded complex, as formerly proposed [36]; instead, an *ortho*-Cl–C bond splits and the interesting complex $Cl(PPh_3)_2Pt(\mu\text{-}C_6Cl_4)AuPPh_3$ is obtained (Fig. 10) [37].

(ii) Anionic complexes

In contrast to the scarcity of anionic complexes prior to 1980, mono-, bi- and polynuclear as well as heterometallic anionic aurate(I) have now been reported.

Mononuclear derivatives

Mononuclear derivatives correspond to three different stoichiometries, $[RAuX]^-$, $[AuR_2]^-$ or $[RAuR']^-$. Complexes of the first class (where X = halide or pseudohalide) have been prepared by the following methods (see Table 3 for examples).

(a) Displacement of SC_4H_8 by X^- [8,11,15,16,38] (eqn. (34)).

$$RAu(SC_4H_8) + QX \rightarrow Q[RAuX] + SC_4H_8 \tag{34}$$

This process is used to obtain arylgold–transition metal bonds with X^- being a carbonylate anion. In such cases, however, ligand rearrangement takes place (eqn. (35)) and the gold atom linearly bridges two $Co(CO)_4$ groups after losing both the neutral and the aryl group [8,39].

$$\begin{aligned} &2\ C_6F_5Au(SC_4H_8) + 2\ [N(PPh_3)_2][Co(CO)_4] \\ &\quad \rightarrow [N(PPh_3)_2][Au(C_6F_5)_2] + [N(PPh_3)_2][Au\{Co(CO)_4\}_2] + 2\ SC_4H_8 \end{aligned} \tag{35}$$

(b) Arylation of dichloroaurate(I) with arylmercuric derivatives [12]

$$Q[AuCl_2] + HgR_2 \rightarrow Q[RAuCl] + RHgCl \tag{36}$$

Addition of $[NMe_4]Cl$ is advisable, because precipitation of the insoluble $(NMe_4)_2[Hg_2Cl_6]$ affords increased yields, due to further reaction of RHgCl (eqn. (37)) in the presence of QCl.

$$2\ Q[AuCl_2] + 2\ RHgCl + 2\ QCl \rightarrow 2\ Q[RAuCl] + Q_2[Hg_2Cl_6] \tag{37}$$

Other methods are more limited in scope.

TABLE 3

Mononuclear anionic derivatives of stoichiometry Q[RAuX]

R	X	Q [a]	Method of synthesis [b]	Ref.
$2\text{-}O_2NC_6H_4$	Cl	$BzPh_3P$	b	12
$2\text{-}O_2NC_6H_4$	Br	$BzPh_3P$	c	12
$2\text{-}O_2NC_6H_4$	I	$BzPh_3P$	c	12
$3\text{-}O_2NC_6H_4$	Cl	$BzPh_3P$	b	12
$4\text{-}O_2NC_6H_4$	Cl	$BzPh_3P$	b	12
$4,4'\text{-}HC_6F_4C_6F_4$	Cl	$N(PPh_3)_2$	a	8
C_6F_5	Cl	$N(PPh_3)_2$	a	38
C_6F_5	Cl	$BzPh_3P$	a	16
C_6F_5	Br	$MePh_3P$	a	16
C_6F_5	Br	$EtPh_3P$	a	16
C_6F_5	Br	$PrPh_3P$	a	16
C_6F_5	I	Bu_4N	a	38
C_6F_5	I	$N(PPh_3)_2$	a	38
C_6F_5	I	$MePh_3As$	a	16
C_6F_5	CN	Bu_4N	a	38
C_6F_5	CN	$BzPh_3P$	a	15
C_6F_5	CN	Et_3HN	d	15
C_6F_5	SCN	$N(PPh_3)_2$	a	38
C_6F_5	N_3	$N(PPh_3)_2$	a	38
C_6Cl_5	Cl	$N(PPh_3)_2$	a	11
C_6Cl_5	SCN	$N(PPh_3)_2$	a	11

[a] Bz = benzyl.

[b] See text, Section B(ii).

(c) Substitution of one halide ion for a different one [12]

$$Q[RAuCl] + NaX \rightarrow Q[RAuX] + NaCl \qquad (38)$$

(d) Reaction of $C_6F_5AuCNHOEt_2$ with amines [15]

$$C_6F_5AuCNHOEt_2 + NEt_3 \rightarrow (NHEt_3)[C_6F_5AuCN] + OEt_2 \qquad (39)$$

Table 3 collects the known halo- or pseudohaloaurate derivatives. All are conducting in acetone solution, the measured Λ_M values being those expected for 1 : 1 electrolytes.

Anionic complexes of the type $[AuR_2]^-$, examples of which are given in Table 4, are formed by the following methods:

(a) Arylation of $ClAu(SC_4H_8)$, using an excess of aryllithium derivative [38], is the most general method.

$$ClAu(SC_4H_8) + 2\ RLi \xrightarrow{+QX} Q[AuR_2] + LiCl + LiX + SC_4H_8 \qquad (40)$$

When $R = C_6H_5$, however, all the present gold precipitates as metallic gold,

TABLE 4

Mononuclear anionic derivatives of stoichiometry Q$[AuR_2]$

R	Q	Method of synthesis	Ref.
3-$CF_3C_6H_4$	Bu_4N	a	6
3,6-$C_6F_2H_3$	Bu_4N	a	6
3,6-$C_6F_2H_3$	$[Au(PCy_3)_2]$	b	6
2,4,6-$C_6F_3H_2$	Bu_4N	a	38
2,3,4,6-C_6F_4H	Bu_4N	a	38
4,4'-$HC_6F_4C_6F_4$	$[Au(SbPh_3)_4]$	d	8
4,4'-$HC_6F_4C_6F_4$	$[Au(pdma)_2]$	d	8
C_6F_5	$[Au(SbPh_3)_4]$	b,d	9
C_6F_5	$[Au(pdma)_2]$	d	9
C_6F_5	$[Agpy_2]$	c	32
C_6F_5	$[Ag(phen)(PPh_3)]$	c	32
C_6F_5	$[Ag(bipy)(PPh_3)]$	c	32
C_6Cl_5	$[Au(SbPh_3)_4]$	d	11
C_6Cl_5	$[Agpy_2]$	c	33

thus illustrating again the lower stability of the Au–C bond if the aryl group is not polyhaloaryl. This method is furthermore not suitable for the synthesis of aurate(III) anions, since arylation with RLi of the corresponding precursor $AuCl_3(SC_4H_8)$ causes reduction and again Q$[AuR_2]$ is obtained [38].

(b) Reaction between an anionic $[AuR_2]^-$ complex and a cationic one $[AuL_2]^+$ in some cases leads to complexes containing both anionic and cationic gold(I) [6,9]

$$(NBu_4)[Au(3,6\text{-}C_6F_2H_3)_2] + [Au(PCy_3)_2]ClO_4 \rightarrow [NBu_4]ClO_4 + [Au(PCy_3)_2][Au(3,6\text{-}C_6F_2H_3)_2] \quad (41)$$

while in other cases, ligand rearrangement occurs and neutral complexes are obtained (see eqn. (8) above).

(c) The polymeric neutral complexes $[AuAg(C_6F_5)_2L]_x$ react with neutral ligands [32,33] to give bis-aryl aurate salts

$$[AuAg(C_6F_5)_2L]_x + xL' \rightarrow x[AgLL']^+[Au(C_6F_5)_2]^- \quad (42)$$

(d) Finally, other miscellaneous methods such as those already mentioned in eqns. (3), (7) or (35) also lead to aurate(I).

Table 4 collects the hitherto reported complexes. They are conducting in acetone solutions. In some cases, e.g. $[Au(SbPh_3)_4][Au(C_6Cl_5)_2]$, the conductance values are lower than those expected for 1 : 1 electrolytes, possibly owing to equilibria such as

$$[Au(SbPh_3)_4][Au(C_6Cl_5)_2] \rightleftarrows 2\ C_6Cl_5AuSbPh_3 + 2\ SbPh_3 \quad (43)$$

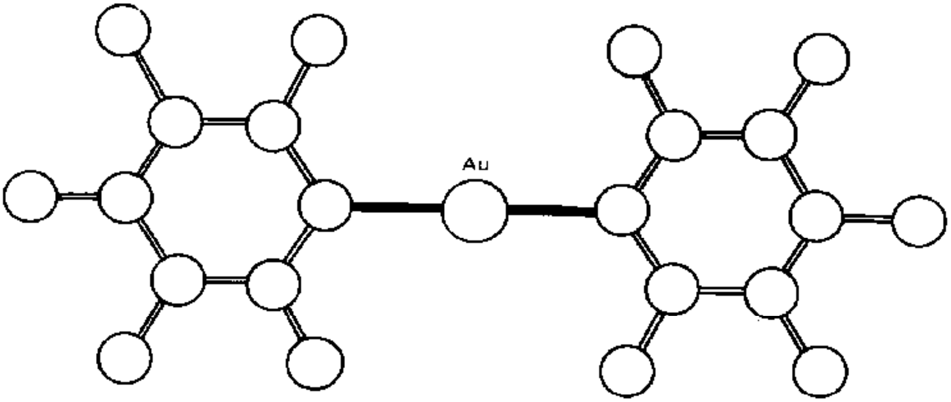


Fig. 11. Structure of $[Au(C_6F_5)_2]^-$ [9].

The structure of the anion $[Au(C_6F_5)_2]^-$ (Fig. 11) is known as a consequence of X-ray studies of the complexes $[Au(diars)_2][Au(C_6F_5)_2]$ [9] and $[Au(SbPh_3)_4][Au(C_6F_5)_2]$ [40]. The gold atom lies in a crystallographic symmetry centre, with two exactly linear Au–C bonds of normal (2.07 Å) length.

The only aurate(I) described with two different aryl groups has been obtained [38], according to

$$C_6F_5Au(SC_4H_8) + Li(2,4,6\text{-}C_6F_3H_2) + (NBu_4)ClO_4 \\ \rightarrow (NBu_4)[C_6F_4Au(2,4,6\text{-}C_6F_3H_2)] + SC_4H_8 + LiClO_4 \qquad (44)$$

Its stability (thermal as well as against air and moisture) is comparable to that of the $Q[AuR_2]$ or $Q[AuR'_2]$ derivatives.

Binuclear derivatives

Starting from mononuclear anionic Q[AuRX] derivatives, where X is a potentially bidentate ligand, binuclear single bridged anionic complexes of stoichiometry Q[RAuXAuR] [15,24] have been prepared (eqn. (45)) by reaction with $AgClO_4$.

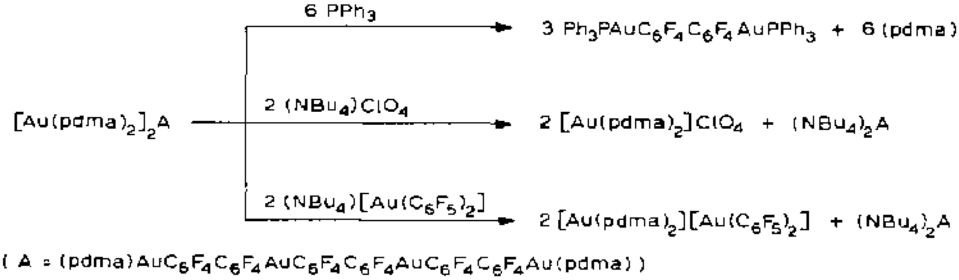
$$2\ Q[RAuX] + AgClO_4 \rightarrow Q[RAuXAuR] + AgX + QClO_4 \qquad (45)$$

where $R = C_6F_5$, $X = SCN, N_3$ and $Q = BzPh_3P$, $N(PPh_3)_2$ [24], or $R = C_6Cl_5$, $X = CN$ and $Q = BzPh_3P$ [15].

In all these complexes, the $\nu(CN)$ or $\nu(NN)$ frequencies are shifted to higher values relative to the mononuclear complexes.

Substitution of SC_4H_8 in $(H_8C_4S)AuC_6F_4C_6F_4Au(SC_4H_8)$ by an anionic ligand leads, according to eqn. (46), to a novel type of anionic binuclear complex [8]

$$(H_8C_4S)AuC_6F_4C_6F_4Au(SC_4H_8) + 2\ [N(PPh_3)_2]Cl \\ \rightarrow [N(PPh_3)_2]_2[ClAuC_6F_4C_6F_4AuCl] + 2\ SC_4H_8 \qquad (46)$$



Scheme 3.

Arylation with C_6F_5Ag [8] allows the replacement of the terminal Cl atoms by C_6F_5 groups.

$$[N(PPh_3)_2]_2[ClAuC_6F_4C_6F_4AuCl] + 2\ AgC_6F_5$$
$$\rightarrow 2\ AgCl + [N(PPh_3)_2]_2[C_6F_5AuC_6F_4C_6F_4AuC_6F_5] \qquad (47)$$

The thermally very stable compound does not decompose when heated to 300°C, whereas the precursor containing two terminal Cl atoms decomposes at 192°C.

Polynuclear derivatives

Addition of *o*-phenylenebis(dimethyl)arsine (pdma) to the neutral $(H_8C_4S)AuC_6F_4C_6F_4Au(SC_4H_8)$ gives a white solid, for which an ionic structure $[Au(pdma)_2]_2[(pdma)AuC_6F_4C_6F_4AuC_6F_4C_6F_4AuC_6F_4C_6F_4Au(pdma)]$ has been proposed [8] as the result of a ligand rearrangement (see eqns. (3), (7), (8) and Scheme 1). Despite its low solubility in acetone, conductance measurements reveal it to be a 2:1 electrolyte. Several reactions of the tetranuclear anion A are collected in Scheme 3.

Finally, the reactions of $(H_8C_4S)AuC_6F_4C_6F_4Au(SC_4H_8)$ with $[N(PPh_3)_2][Co(CO)_4]$ or $[N(PPh_3)_2][Mn(CO)_5]$ occur similarly to eqn. (35), giving $[N(PPh_3)_2][Au\{M(CO)_x\}_2]$ ($M = Co$, $x = 4$; $M = Mn$, $x = 5$) and an insoluble solid of stoichiometry $[N(PPh_3)_2][AuC_6F_4C_6F_4]$ possibly containing a polymeric anion [8].

Heteronuclear derivatives

As we have seen before (eqn. (19)), aurates of the type Q[RAuX], where X is potentially a bidentate anionic ligand (CN, CNS) acting as a unidentate ligand, can displace a weakly coordinating ligand from its site around another metal centre, a reaction which affords binuclear derivatives. If the second metal centre is different, $(NBu_4)[(C_6F_5)_3Pd(SC_4H_8)]$, or *trans*-$(C_6F_5)_2Pd(SC_4H_8)_2$ [41] heteronuclear derivatives are obtained

$$(NBu_4)[C_6F_5AuX] + (NBu_4)[(C_6F_5)_3Pd(SC_4H_8)] \rightarrow (NBu_4)_2[C_6F_5AuXPd(C_6F_5)_3] + SC_4H_8 \qquad (48)$$

$$Q[C_6F_5AuX] + \textit{trans}\text{-}(C_6F_5)_2Pd(SC_4H_8)_2 \rightarrow Q[C_6F_5AuXPd(C_6F_5)_2(SC_4H_8)] + SC_4H_8 \qquad (49)$$

where $X = SCN$, $Q = NBu_4$ or $N(PPh_3)_2$; or $X = CN$ and $Q = NBu_4$.

Substitution of SC_4H_8 by PPh_3 produces $Q[C_6F_5AuXPd(C_6F_5)_2PPh_3]$ ($Q = NBu_4$, $X = SCN$, CN) [41]. If reaction (49) is carried out in a 2 : 1 molar ratio, trinuclear derivatives $Q_2[C_6F_5AuXPd(C_6F_5)_2XAuC_6F_5]$ ($Q = NBu_4$, $X = SCN$, CN) are obtained [41].

(iii) Cationic complexes

The only known cationic complexes are of the type $[RAuPPh_2CH_2PPh_2Me]^+$ and have been prepared [20] by the processes

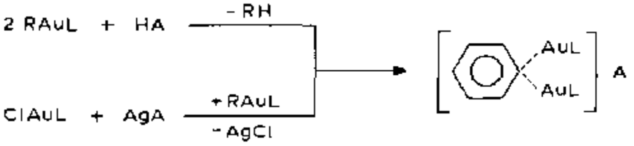
$$C_6F_5Au(SC_4H_8) + [PPh_2CH_2PPh_2Me]ClO_4 \rightarrow [C_6F_5AuPPh_2CH_2PPh_2Me]ClO_4 + SC_4H_8 \qquad (50)$$

and

$$C_6F_5AuPPh_2C(H)PPh_2Me + HA \rightarrow [C_6F_5AuPPh_2CH_2PPh_2Me]A \qquad (51)$$

where $A = ClO_4$, Cl, BF_4.

Cationic binuclear complexes of two different stoichiometries, $[RAu(L{-}L)AuL]^+$ and $[R(AuL)_2]^+$ have been reported. Only one example of the first type has been described, i.e. $[C_6F_5AuNH_2(CH_2)_2NH_2AuPPh_3]ClO_4$ [10] prepared by the reaction (similar to that in eqn. (16)) between $C_6F_5AuNH_2(CH_2)_2NH_2$ and $O_3ClOAuPPh_3$, in 1 : 1 molar ratio. The second type is better represented; the aryl group forms an electron deficient (3c, 2e) bridge between the two gold centres. They can be obtained [18,26] by the following two methods



(52)

Table 5 collects all the isolated complexes. With the more electronegative aryl groups ($R = C_6F_5$, C_6F_4H, C_6Cl_5, C_6Br_5) no reaction is observed. With

TABLE 5

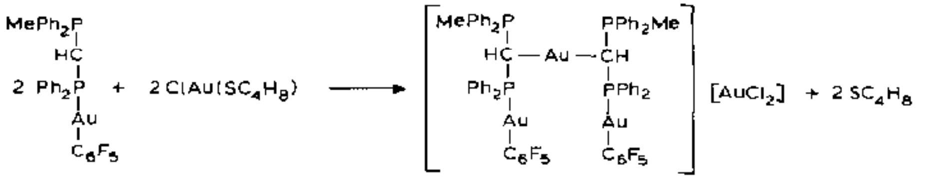
Cationic derivatives of stoichiometry $[R(AuL)_2]A$

R	L	A	Ref.
$4\text{-}MeC_6H_4$	PMe_3	BF_4	18, 19
$4\text{-}MeC_6H_4$	$1/2\ PPh_2(CH_2)_2PPh_2$	BF_4	18, 19
$4\text{-}MeC_6H_4$	$1/2\ PPh_2(CH_2)_3PPh_2$	BF_4	18, 19
$4\text{-}MeC_6H_4$	$1/2\ PPh_2(CH_2)_4PPh_2$	BF_4	18, 19
$C_{10}H_7$ [a]	PPh_3	BF_4	26
$C_{10}H_7$ [a]	PPh_3	PF_6	26
$C_{10}H_7$ [a]	$1/2\ PPh_2(CH_2)_2PPh_2$	BF_4	26
$3\text{-}CF_3C_6H_4$	PPh_3	BF_4	26
$3\text{-}CF_3C_6H_4$	PPh_3	PF_6	26
$4\text{-}C_6FH_4$	PPh_3	BF_4	26
$3,6\text{-}C_6F_2H_3$	PPh_3	BF_4	26
$3,6\text{-}C_6F_2H_3$	PPh_3	PF_6	26
$3,6\text{-}C_6F_2H_3$	PPh_3	ClO_4	26
$3,6\text{-}C_6F_2H_3$	$1/2\ PPh_2(CH_2)_2PPh_2$	BF_4	26
$2,4,6\text{-}C_6F_3H_2$	PPh_3	BF_4	26
$2,4,6\text{-}C_6F_3H_2$	PPh_3	PF_6	26
$2,4,6\text{-}C_6F_3H_2$	PPh_3	ClO_4	26
$2,4,6\text{-}C_6F_3H_2$	$AsPh_3$	BF_4	26
$2,4,6\text{-}C_6F_3H_2$	$AsPh_3$	ClO_4	26
$2,4,6\text{-}C_6F_3H_2$	$1/2\ PPh_2(CH_2)_2PPh_2$	BF_4	26

[a] α-Naphthyl.

better coordinating anions ($A = SO_4$, CF_3COO) neutral mononuclear complexes are obtained [26].

Homo or heterocationic trinuclear derivatives have also been reported [20]. They can be prepared according to the reaction



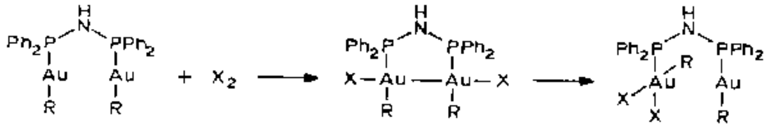
(53)

If $[Au(SC_4H_8)_2]ClO_4$ is used instead of $ClAu(SC_4H_8)$ the perchlorate of the same cation is obtained; with $AgClO_4$, the heterotrinuclear $[\{C_6F_5AuPPh_2CH(PPh_2Me)\}_2Ag]ClO_4$ is formed [20].

All the cationic complexes behave as 1 : 1 electrolytes in acetone solution.

C. ARYLGOLD(II) COMPLEXES

Arylgold(II) derivatives are still scarce; they can be obtained from suitable gold(I) precursors [23] by oxidation (with Cl_2 or Br_2) using the stoichiometric amount of halogen.



(54)

($R = C_6F_5, C_6Cl_5$; $X = Cl, Br$)

The gold(II) complexes are yellow (X = Cl) or orange (X = Br) solids and are air and moisture stable at room temperature. Their solutions in polar solvents (acetone, ethanol, diethylether) fade rapidly to turn colourless (in dichloromethane at 0°C this process is very slow) because of isomerisation to the mixed gold(III)–gold(I) derivative (eqn. (54)). The IR spectra of each isomer-pair show significant differences [23]: for the gold(II) pentafluorophenyl complexes, a single band (960 cm^{-1}) due to the C_6F_5 groups is present but is transformed into a double band (967, 957 cm^{-1}) upon isomerisation. In the gold(II) chlorocomplexes, ν(Au–Cl) appears at lower frequencies (270, 280 cm^{-1}) than in the Au(III)–Au(I) isomers (320 cm^{-1}).

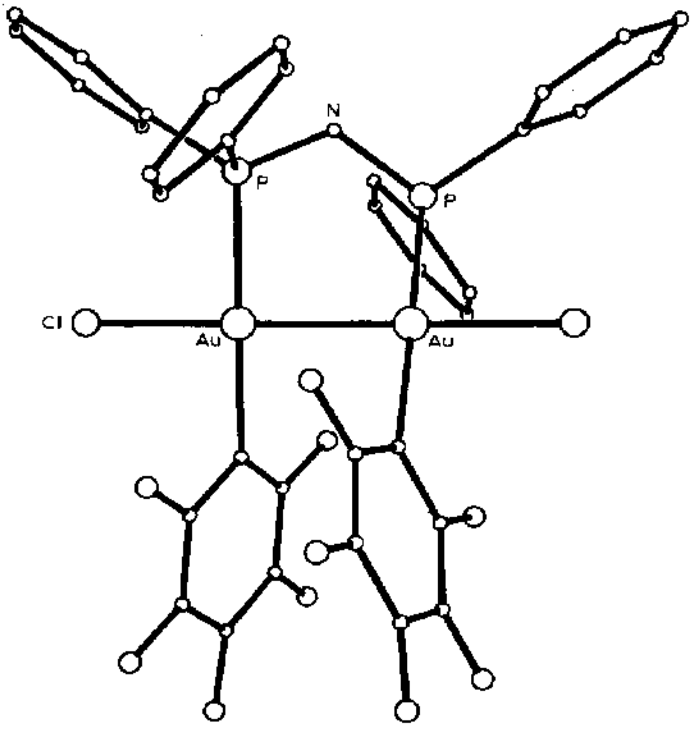
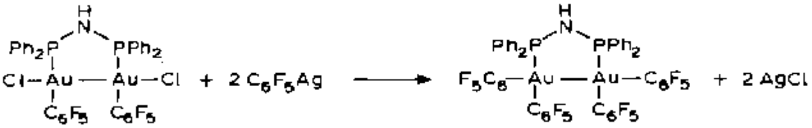


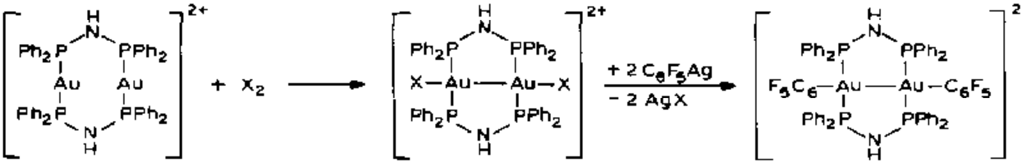
Fig. 12. Structure of $(C_6F_5)ClAuPPh_2NHPh_2PAuCl(C_6F_5)$ [23].

The structure of $[(C_6F_5)ClAu]_2(DPA)$ ($DPA = Ph_2PNHPPh_2$) has been established by X-ray diffraction (Fig. 12) confirming the novel binuclear gold(II) stereochemistry with each gold(II) centre square-planar coordinated [23], the Au–Au distance (2.577 Å) being the shortest hitherto reported [42].

Further reaction of this complex with C_6F_5Ag leads to a new [23] gold(II) derivative


(55)

Finally, other cationic arylgold(II) derivatives have been prepared via the following reaction sequence.


(56)

D. ARYLGOLD(III) COMPLEXES

These are numerous, with neutral, anionic and cationic complexes having been reported.

(i) Neutral complexes

Complexes containing one, two or three aryl groups have been described.

Complexes containing one aryl group

Mononuclear derivatives containing only one aryl group with the stoichiometry $RAuX_2L$ listed in Table 6 have been prepared by the following methods:

(a) Oxidative addition of halogen to gold(I) derivatives [11,43]

$$RAuL + X_2 \rightarrow RAuX_2L \quad (57)$$

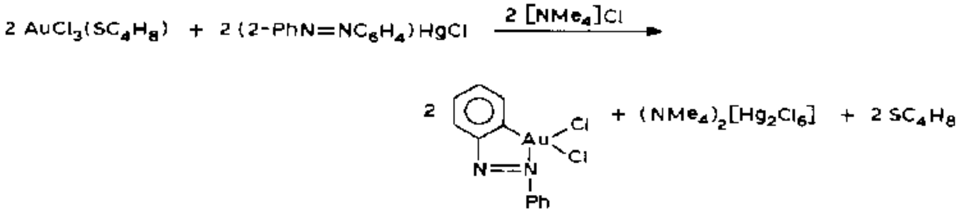
TABLE 6

Gold(III) derivatives of stoichiometry $RAuX_2L$

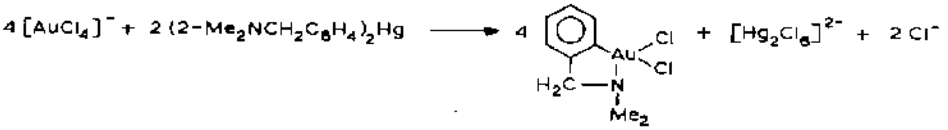
R	L	X	Method of synthesis [a]	Ref.
$2\text{-}C_6H_4N{=}NPh$	PPh_3	Cl	c	44, 45
$2\text{-}C_6H_4N{=}NPh$	$AsPh_3$	Cl	c	44, 45
$2\text{-}C_6H_4N{=}NPh$	PCy_3	Cl	c	45
$2\text{-}C_6H_4N{=}NPh$	PCy_3	I	d	45
$2\text{-}C_6H_4N{=}NPh$	PBu_3	Cl	c	45
$2\text{-}C_6H_4N{=}NPh$	$P(2\text{-}MeOC_6H_4)_3$	Cl	c	45
C_6F_5	tht	Cl	a	43
C_6F_5	tht	Br	a	43
C_6F_5	tht	I	a	43
C_6F_5	CNTo	Cl	e	43
C_6F_5	CNTo	Br	e	43
C_6F_5	CNTo	I	e	43
C_6F_5	$AsPh_3$	I	e	43
C_6F_5	pdma	Cl	e	48
C_6F_5	phen	Cl	e	48
C_6F_5	phen	Br	e	43, 48
C_6F_5	phen	I	e	43
C_6Cl_5	tht	Cl	a	11
RL				
$2\text{-}C_6H_4N{=}NPh$		Cl	b	44, 45
$2\text{-}C_6H_4N{=}NPh$		MeCOO	d	47
$2\text{-}C_6H_4N{=}NPh$		OOCCOO	d	47
$2\text{-}C_6H_4CH_2NMe_2$		Cl	b	46
$2\text{-}C_6H_4CH_2NMe_2$		Br	d	46
$2\text{-}C_6H_4CH_2NMe_2$		I	d	46
$2\text{-}C_6H_4CH_2NMe_2$		MeCOO	d	46, 49

[a] See text, Section D(i).

(b) Arylation of $AuCl_3(SC_4H_8)$ with arylmercuric compounds [44–46]



(58)

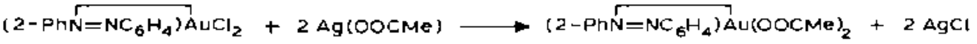


(59)

As may be noticed in these examples, the N-donor substituent is acting as a neutral ligand L.

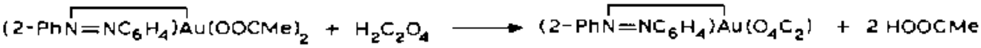
(c) Addition of other neutral ligands L to the above process (eqn. (58)) cleaves the Au–N bond and (2-PhN=NC$_6$H$_4$)AuCl$_2$L is obtained [44,45].

(d) It is possible to replace the chloride ligands by other anions, using the corresponding silver salts [45–47]



$$(2\text{-Ph}\overline{\text{N}{=}\text{NC}_6\text{H}_4\text{)Au}}\text{Cl}_2 + 2\,\text{Ag(OOCMe)} \longrightarrow (2\text{-Ph}\overline{\text{N}{=}\text{NC}_6\text{H}_4\text{)Au}}\text{(OOCMe)}_2 + 2\,\text{AgCl} \qquad (60)$$

and then the acetato ligands can be displaced with acids [47]



$$(2\text{-Ph}\overline{\text{N}{=}\text{NC}_6\text{H}_4\text{)Au}}\text{(OOCMe)}_2 + \text{H}_2\text{C}_2\text{O}_4 \longrightarrow (2\text{-Ph}\overline{\text{N}{=}\text{NC}_6\text{H}_4\text{)Au}}\text{(O}_4\text{C}_2\text{)} + 2\,\text{HOOCMe} \qquad (61)$$

(e) Substitution of a weak ligand (SC$_4$H$_8$) by other neutral ligands

$$\text{RAuCl}_2(\text{SC}_4\text{H}_8) + \text{L} \rightarrow \text{RAuCl}_2\text{L} + \text{SC}_4\text{H}_8 \qquad (62)$$

Complexes containing two different anionic ligands ((2-Ph$\overline{\text{N=NC}_6\text{H}_4\text{)Au}}$(Cl)(I)PCy$_3$ [45]; (2-Ph$\overline{\text{N=NC}_6\text{H}_4\text{)Au}}$(Cl)(OOCMe) [47] or (2-Me$_2\overline{\text{NCH}_2\text{-C}_6\text{H}_4\text{)Au}}$(Cl)(OOCMe) [49]) have been prepared by the substitution process represented in eqns. (60) or (61), carried out in the appropriate molar ratio.

The dichloroaryl gold(III) complexes obtained by the processes represented in eqns. (58) and (59) show two ν(Au–Cl) vibrations; the one (*trans* to the aryl group) appears at lower frequencies (305 and 300 cm^{-1}) than the other (*trans* to N) (370 and 350 cm^{-1}) [45,46] thus pointing to a strong *trans*-influence of the substitued aryl groups, stronger indeed than that observed for polyhalophenyl groups [43,48] ($\sim$ 330 cm^{-1}).

^{197}Au Mössbauer spectra of C$_6$F$_5$AuX$_2$(phen) (X = Cl, Br) [48] support the existence of a weak interaction with the free end of the bidentate ligand, approaching pentacoordination, although the IS values are higher [50] than those found for AuX$_3$(L–L) (X = Cl, Br; L–L = phen, 2,9-dimethylphenanthroline) in which the coordination of the bidentate ligand is asymmetric.

Neutral binuclear complexes (C$_6$F$_5$)I$_2$AuPPh$_2$(CH$_2$)$_2$PPh$_2$AuI$_2$(C$_6$F$_5$) or (2-PhN=NC$_6$H$_4$)Cl$_2$AuPPh$_2$(CH$_2$)$_2$PPh$_2$AuCl$_2$(2-C$_6$H$_4$N=NPh) can be obtained upon addition of the diphosphine to solutions of C$_6$F$_5$AuI$_2$(SC$_4$H$_8$) [43] or (2-Ph$\overline{\text{N=NC}_6\text{H}_4\text{)Au}}Cl_2$, respectively [45].

Isomerisation of binuclear gold(II) complexes leads to neutral mixed gold(III)–gold(I) complexes (eqn. (54)).

Complexes containing two aryl groups

These are more numerous than those preceding and include complexes with one, two or more gold centres.

TABLE 7

Gold(III) derivatives of stoichiometry R_2AuXL

R	X	L	Method of synthesis [a]	Ref.
$1/2\ C_{12}H_8$	Cl	PPh_3	b	53
$1/2\ C_{12}H_8$	Cl	py	b	53
$1/2\ C_{12}H_8$	Cl	tht	b	53
$1/2\ C_{12}H_8$	Br	py	h	53
$2\text{-}O_2NC_6H_4$	Cl	PPh_3	c	54, 55
$2\text{-}O_2NC_6H_4$	Cl	PCy_3	c	55
$2\text{-}O_2NC_6H_4$	Cl	py	c	54, 55
$2\text{-Me,}6\text{-}O_2NC_6H_3$	Cl	PPh_3	c	54, 55
$2\text{-Me,}6\text{-}O_2NC_6H_3$	Cl	PCy_3	c	55
$2\text{-Me,}6\text{-}O_2NC_6H_3$	Cl	py	c	55
$2,4,6\text{-}C_6F_3H_2$	Cl	PPh_3	a	51
$2,4,6\text{-}C_6F_3H_2$	Cl	tht	a	51
$2,3,5,6\text{-}C_6F_4H$	Cl	PPh_3	a	51
C_6F_5	CN	CNMe	d	15
C_6F_5	CN	$C(NHMe)_2$	e	15
C_6F_5	Cl	py	b	52
C_6F_5	Cl	$PPh_2CH_2PPh_2$	b,f	22, 56
C_6F_5	Cl	PPh_2NHPPh_2	b	23
C_6F_5	Cl	PPh_2CHPPh_2Me	g	20

[a] See text, Section D(i).

Mononuclear derivatives An important group of derivatives with the stoichiometry R_2AuXL, listed in Table 7, can be obtained by some of the following methods:

(a) Oxidation of gold(I) complexes with diaryl thallium(III) halides [51]

$$ClAuL + R_2TlCl \rightarrow cis\text{-}R_2AuClL + TlCl \tag{63}$$

when $R = C_6F_5$, $2,3,5,6\text{-}C_6F_4H$ or $2,4,6\text{-}C_6F_3H_2$, but not when $R = 4\text{-}C_6FH_4$ or $3\text{-}CF_3\text{-}C_6H_4$, because of the very low solubility of the thallium reagent.

(b) Cleavage of the bridges in the dimeric $[R_2AuCl]_2$ by addition of neutral ligands [22,23,52,53]

$$[R_2AuCl]_2 + 2\ L \rightarrow 2\ cis\text{-}R_2AuClL \tag{64}$$

(c) Addition of neutral ligands to some anionic dihalo-bisaryl derivatives causes displacement of one halide ligand [54,55]

$$(NMe_4)[R_2AuCl_2] + L \rightarrow R_2AuClL + (NMe_4)Cl \tag{65}$$

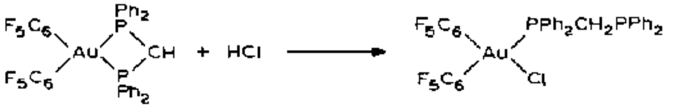
where $R = 2\text{-}O_2NC_6H_4$, $2\text{-}CH_3$ or $6\text{-}O_2NC_6H_3$. Similarly, halide abstraction takes place in the 1 : 1 reaction of $AgClO_4$ with $(NBu_4)[(C_6Cl_5)_2AuCl_2]$, though both reaction products $[(C_6Cl_5)_2AuCl]_2$ and AgCl are insoluble and the mixture cannot be resolved. Addition of neutral ligands (see method (b)) allows the separation of the monomeric $(C_6Cl_5)_2AuClL$ [11].

Other methods are more limited in scope and have only been used in certain cases.

(d) Methylation of $(NBu_4)[(C_6F_5)_2Au(CN)_2]$ with $(Me_3O)BF_4$ leads [31] to $(C_6F_5)_2Au(CN)(CNMe)$, as mentioned above for gold(I) (eqn. (9)).

(e) Starting from the just cited gold(III) complex, reaction with NH_2Me affords [31] the carbene $(C_6F_5)_2Au(CN)[C(NHMe)_2]$ (see eqn. (10)).

(f) Reaction of HCl with $(C_6F_5)_2\overline{AuPPh_2CHP}Ph_2$ [56] causes protonation of the methanide group (CH) and opening of the ring



(66)

(g) The reaction of the cationic complex $[(C_6F_5)_2AuCl(PPh_2CH_2PPh_2Me)]ClO_4$ with NaH simultaneously causes deprotonation of the methylene group and anion elimination (see eqn. (13) for a similar reaction in gold(I) complexes) to give [20] $(C_6F_5)_2AuCl(PPh_2CHPPh_2Me)$.

(h) Substitution of the chloride ion in R_2AuClL by other anionic ligands [53]

$$C_{12}H_8AuCl(py) + NaBr \rightarrow C_{12}H_8AuBr(py) + NaCl \qquad (67)$$

where $C_{12}H_8 = 2,2'$-biphenyl. Table 7 collects the hitherto reported complexes of this type. Although no X-ray structure has been solved, a *cis*-configuration has been assigned to all of them; two IR bands in the ~ 800 cm^{-1} region support this proposal for the C_6F_5 derivatives.

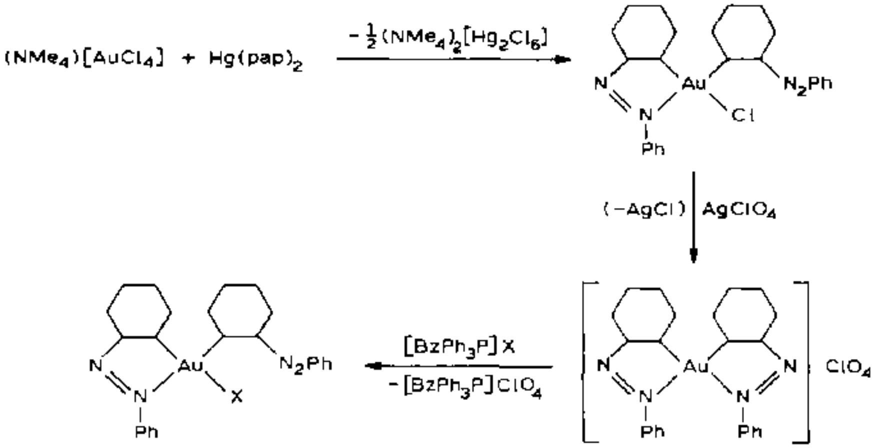
Other neutral mononuclear bisaryl gold(III) complexes (not included in Table 7) contain two aryl groups with some substituents which allows the aryl group to act as a chelating ligand, as in (2-phenylazo)phenyl [57]. The reaction sequence shown in Scheme 4 leads to such gold(III) complexes.

In other cases, the chelating ligand is an anionic one, as in the following examples:

$(NBu_4)[(C_6F_5)_2AuCl_2]$ or $[C_{12}H_8AuCl]_2$ react with Tl(acac) [52,53] to give $R_2Au(acac)$ ($R = C_6F_5$; $R_2 = C_{12}H_8$) where acac (acetyl acetonate) is the anionic chelating ligand.

The reaction of $[(C_6F_5)_2\overline{AuPPh_2CH_2P}Ph_2]ClO_4$ with NaH proceeds similarly to eqn. (13) to give [58]

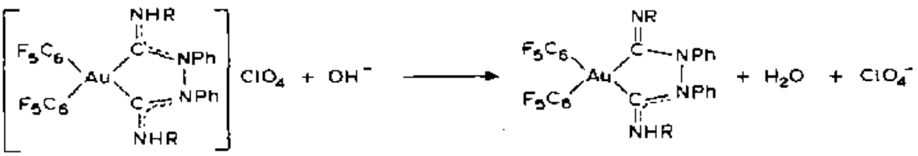
(68)



(X = Cl, Br, I, CN, OOCMe; pap = (2-phenylazo)phenyl)

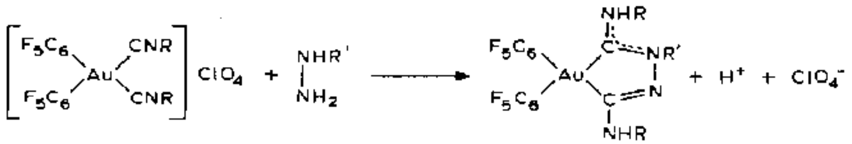
Scheme 4.

Finally eqns. (69) and (70) summarise other processes using cationic complexes as starting products [59].



(69)

where R = Ph, To.



(70)

where R = Ph, To; R′ = H, Ph.

The structure of the derivative where R is *p*-tolyl and R′ is Ph has been determined (Fig. 13). The gold atom lies in a square-planar environment; the rigidity of the five-membered ring causes some distortion, but the Au–C_6F_5 distances are similar to those found for other gold–pentafluorophenyl complexes.

Binuclear derivatives Complexes of stoichiometry $[R_2AuX]_2$ where a double halide bridge connects the two gold(III) centres are prepared [52] by the

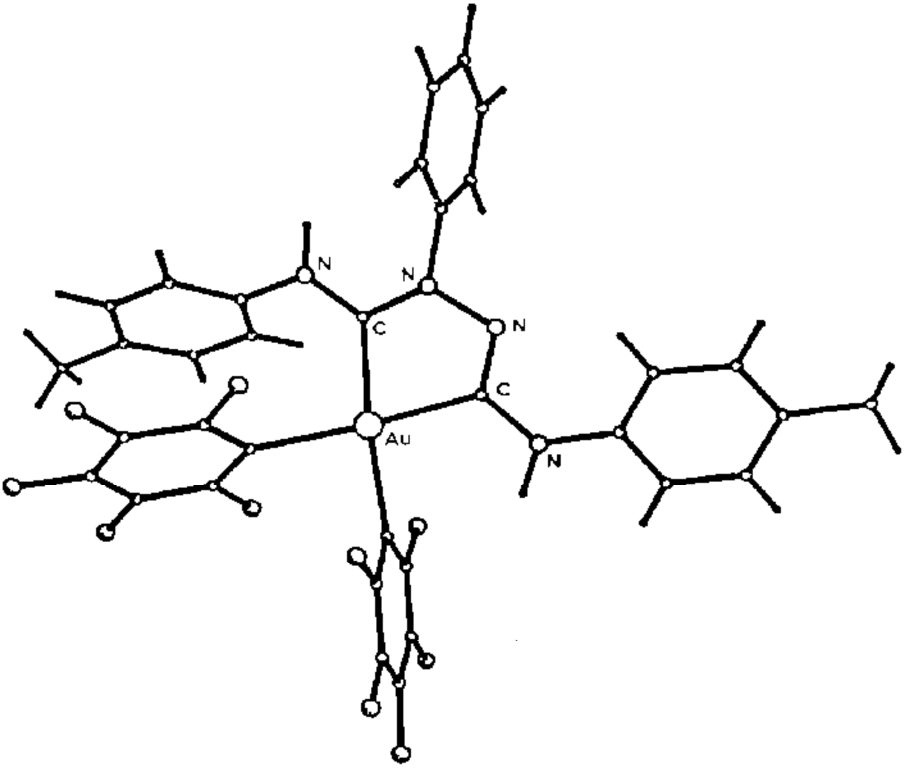
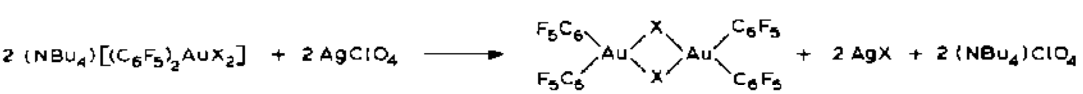


Fig. 13. Structure of $(C_6F_5)_2\overline{AuC(NHTo)NPhN{=}C}(NHTo)$ [59].

(2 : 2) reaction of dihalo-bis(pentafluorophenyl)aurate(III) with silver perchlorate



(71)

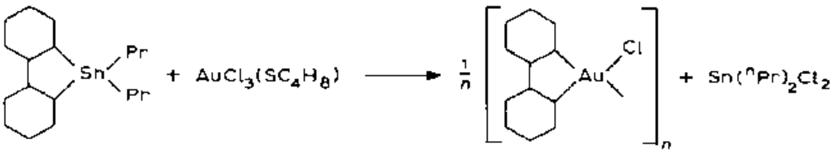
where X = Cl, Br.

Further reaction of the Cl-bridged derivatives with alkaline or silver salts of other anions (X = SCN, N_3, CF_3COO) or with $NCSAuPPh_3$ (eqn. (72)) gives the corresponding substitution products [52].

$$\left[(C_6F_5)_2AuCl\right]_2 + 2\ NCSAuPPh_3 \rightarrow \left[(C_6F_5)_2Au(SCN)\right]_2 + 2\ ClAuPPh_3 \tag{72}$$

The molecular weights (isopiestic method, in chloroform solutions) confirm their binuclear nature.

A possibly binuclear compound has been prepared [53] by the reaction of a stannacycle with $Cl_3Au(SC_4H_8)$



(73)

Its lack of solubility precludes the determination of its molecular weight, but binuclearity ($n = 2$) has been assigned on the grounds of analogy with other derivatives of similar stoichiometry [53].

Addition of 2,2′-bibenzimidazole (H_2BiBzIm) to $(C_6F_5)_2Au(acac)$ displaces the bidentate anionic ligand (in the form of acetylacetone) and forms a binuclear complex $[(C_6F_5)_2Au]_2BiBzIm$, with the azole acting as a tetradentate ligand [60].

Another route leading to the preparation of binuclear complexes starts from mononuclear derivatives containing one potentially bidentate ligand, whose free end can displace some weakly coordinating ligand from other mononuclear complexes. The potentially bidentate ligand can be a pseudohalide [15,24]

$$(NBu_4)[(C_6F_5)_2Au(CN)_2] + O_3ClOAuPPh_3 \rightarrow (C_6F_5)_2(CN)Au(CN)AuPPh_3 + (NBu_4)ClO_4 \tag{74}$$

$$(BzPh_3P)[C_6F_5AuX] + O_3ClOAu(C_6F_5)_2PPh_3 \rightarrow (Ph_3P)(C_6F_5)_2AuXAuC_6F_5 + (BzPh_3P)ClO_4 \tag{75}$$

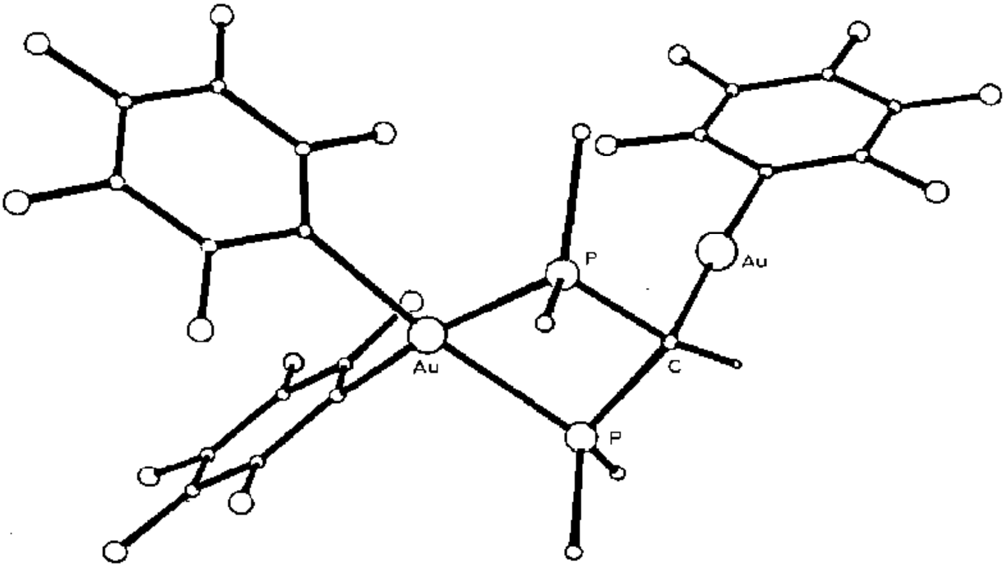


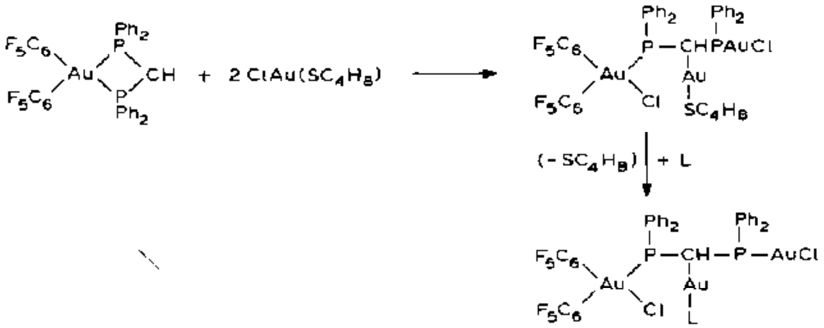
Fig. 14. Structure of $(C_6F_5)_2\overline{AuPPh_2CHP}Ph_2AuC_6F_5$ [58].

where X = SCN, N_3, or a neutral ligand [22]

$$(C_6F_5)_2ClAuPPh_2CH_2PPh_2 + C_6F_5Au(SC_4H_8)$$
$$\rightarrow (C_6F_5)_2ClAuPPh_2CH_2PPh_2AuC_6F_5 + SC_4H_8 \qquad (76)$$

Methanide complexes, such as $(C_6F_5)_2ClAuPPh_2CHPPh_2Me$ or $(C_6F_5)_2\overline{AuPPh_2CHPPh_2}$ can also be used for the same purpose, owing to the excess of electron density on the CH carbon atom. Thus, they react [20,56,58] with $XAu(SC_4H_8)$ to give mixed binuclear gold(III)–gold(I) derivatives $(C_6F_5)_2ClAuPPh_2CH(AuX)PPh_2Me$ (X = Cl, C_6F_5) or $(C_6F_5)_2\overline{AuPPh_2\text{-}CHPPh_2}AuX$ (X = C_6F_5; 2,4,6-$C_6F_3H_2$). Figure 14 shows the structure of the C_6F_5 derivative [58].

Polynuclear derivatives As we have just mentioned, the methanide $(C_6F_5)_2\overline{AuPPh_2CHPPh_2}$ reacts with $C_6F_5Au(SC_4H_8)$ to give the binuclear complex $(C_6F_5)_2\overline{AuPPh_2CH(AuC_6F_5)PPh_2}$. Surprisingly, if an excess of $ClAuSC_4H_8$ is used, addition of the second $ClAuSC_4H_8$ molecule causes the cleavage of one Au–P bond [56] leading to the only reported trinuclear gold complexes



(77)

The SC_4H_8 group can easily by displaced by other neutral ligands (L = $AsPh_3$, PPh_3, py, 4-Mepy). The structure of the py derivative has been determined and is shown in Fig. 15, with the gold(III) atom in a square-planar arrangement and the two gold(I) atoms linear.

$[C_{12}H_8AuCN]_n$ resulting from the replacement of Cl by CN in $[C_{12}H_8AuCl]_2$ [53] could be tetrameric, in analogy with $[Me_2AuCN]_4$.

Polymeric complexes containing CN bridges have been obtained from dicyanogold(III) derivatives. Remarkable differences arise depending on whether the *trans* or the *cis* complex is used. Thus, *trans*-$(NBu_4)[(C_6F_5)_2\text{-}Au(CN)_2]$ reacts with either $O_3ClOAu(SC_4H_8)$ or $AgClO_4$ to give [15] insoluble products $[NCAu(C_6F_5)_2CNM]_n$ (M = Au, Ag, respectively) whose

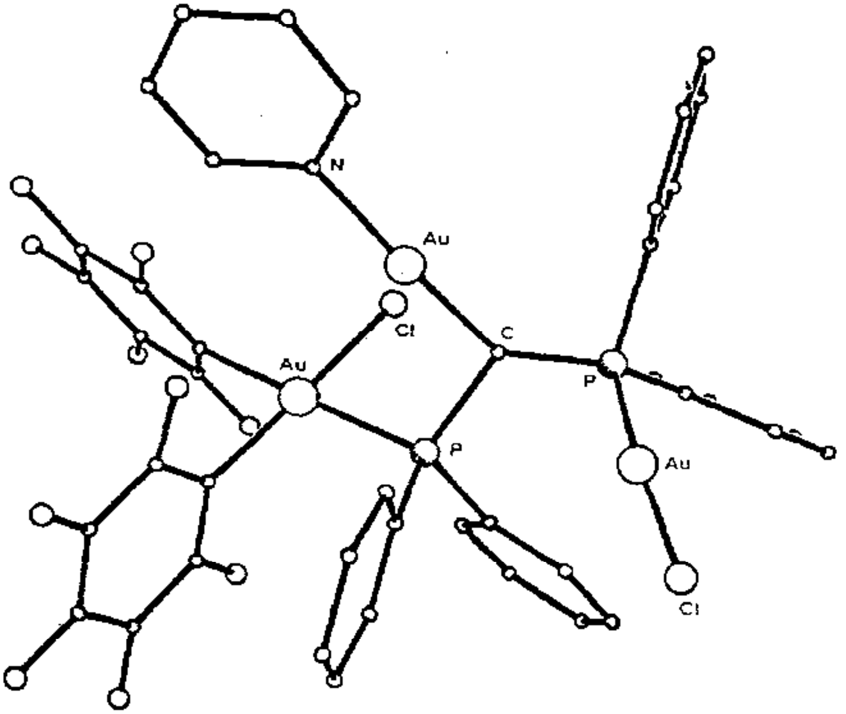
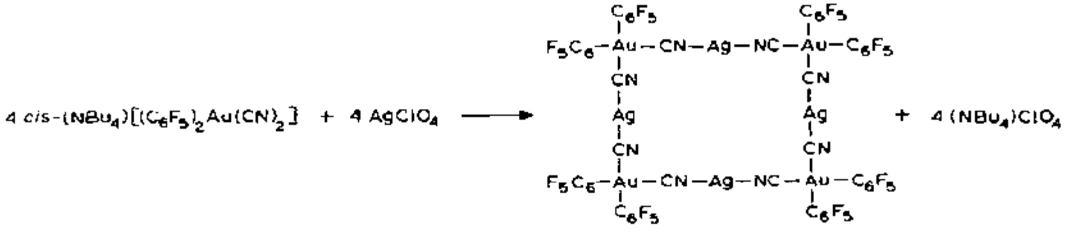


Fig. 15. Structure of $(C_6F_5)_2ClAuPPh_2CH(Aupy)PPh_2AuCl$ [56].

IR spectra show that both C_6F_5 groups are mutually *trans* and therefore the structure should be a chain of CN-bridged metal atoms.

The reaction of *cis*-$(NBu_4)[(C_6F_5)_2Au(CN)_2]$ with $AgClO_4$ [60] also succeeds with stereoretention and since the two CN groups must be mutually *cis*, a cyclic tetramer is formed (eqn. (78)) as shown by measurements of its molecular weight



(78)

Complexes containing three aryl groups
These can be mono-, bi- and heteronuclear.

Mononuclear derivatives These are most numerous and are of two different types R_3AuL and RR'_2AuL.

The first type includes only pentafluorophenyl derivatives, prepared by the following methods:

(a) Oxidatioin of $C_6F_5AuSC_4H_8$ with $(C_6F_5)_2TlCl$ [61,62]

$$C_6F_5AuSC_4H_8 + (C_6F_5)_2TlCl \rightarrow (C_6F_5)_3AuSC_4H_8 + TlCl \qquad (79)$$

(b) Because of the ready displacement of the SC_4H_8 ligand in the above complex by other neutral ligands, this compound has been used as a precursor for the synthesis of $(C_6F_5)_3AuL$ complexes, where L = NH_3, py, PPh_2Me, $PPh_2CH_2PPh_2$, $P(OPh)_3$, $AsPh_3$, pdma, $SbPh_3$, CNTo [61,62], PPh_2NHPPh_2 [23].

(c) Methylation of $[(C_6F_5)_3AuCN]^-$ with $[Me_3O]BF_4$ gives the isocyanide $(C_6F_5)_3AuCNMe$ [15], a reaction similar to that represented in eqn. (9).

(d) Reactions of $(C_6F_5)_3Au$(isocyanide) with amines afford the corresponding $(C_6F_5)_3Au$(carbene), (for a similar reaction with gold(I) complexes, see eqn. (10)) where carbene = $C(NHMe_2)$ [15], $C(NHTo)_2$, $C(NHTo)(NEt_2)$, $C(NHTo)(NHCH_2NH_2)$ [62], $C(NHTo)[NH(CH_2)_3NH_2]$ [10].

(e) The 1:1 reaction between $(NBu_4)[(C_6F_5)_3AuBr]$ and $AgClO_4$ [62] in diethyl ether

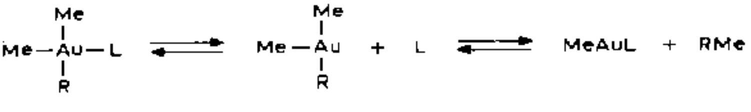
$$(NBu_4)\left[(C_6F_5)_3AuBr\right] + AgClO_4$$
$$\rightarrow (C_6F_5)_3Au(OEt_2) + AgBr + (NBu_4)ClO_4 \qquad (80)$$

(f) In a similar way as for Au(I) (eqn. (11)) phosphonium or arsonium salts of halo-tris(pentafluorophenyl)aurate(III) react with NaH [16] to give the ylides $(C_6F_5)_3Au(CH_2EPh_3)$ (E = P, As).

(g) The methanide complex $(C_6F_5)_3AuPPh_2CHPPh_2Me$ can be prepared by reacting $[(C_6F_5)_3AuPPh_2CH_2PPh_2Me]ClO_4$ with NaH [20] (see eqn. (13) for a similar process involving gold(I) compounds).

Complexes of the second type RR'_2AuL have been prepared by method (a) (eqn. (79)), i.e. by oxidation of $C_6F_5AuSC_4H_8$ with R'_2TlCl (R′ = 2,3,5,6-C_6F_4H; 2,4,6-$C_6F_3H_2$ [51]) or by method (b), i.e. substitution of SC_4H_8 in $RR'_2AuSC_4H_8$ by PPh_3 [62].

Mixed complexes of similar stoichiometry, containing one aryl and two alkyl groups, such as RMe_2AuL, have been prepared by arylating the precursors Me_2AuXL with Grignard reagents (L = PPh_3; R = 4-$MeOC_6H_4$, 4-C_6FH_4, 2-$MeOC_6H_4$, 2-MeC_6H_4 [63], 4-MeC_6H_4 [63,64]; R = C_6H_5, L = P(4-$MeOC_6H_4)_3$, P(4-$MeC_6H_4)_3$, P(4-$C_6FH_4)_3$, P(2-$MeC_6H_4)_3$, PPh(2-$MeC_6H_4)_2$, PPh_2(2-MeC_6H_4) [63], PPh_3 [63–65], PMe_3 [65]. According to their NMR data [63] they are the *cis* isomers. The electronic and steric properties of the ligands [63] influence the thermolysis in methanol solution for which the following reaction path (eqn. (81)) has been proposed.



$$\text{Me}-\overset{\text{Me}}{\underset{\text{R}}{\text{Au}}}-\text{L} \rightleftarrows \text{Me}-\overset{\text{Me}}{\underset{\text{R}}{\text{Au}}} + \text{L} \rightleftarrows \text{MeAuL} + \text{RMe} \qquad (81)$$

Their reactions with electrophiles, such as HCl, $HgCl_2$ or PtI_2 $(PMe_2Ph_2)_2$, lead to selective cleavage of the gold–aryl bond and formation of $Me_2AuX\text{-}PPh_3$ [64].

The reaction of SO_2 with *cis*-$(C_6H_5)Me_2AuPMe_3$ leads to its insertion in one of the Au–Me bonds and formation of an *S*-sulphinate complex $(C_6H_5)MeAu(SO_2Me)PMe_3$ with stereoretention [65]. With $(C_6H_5)\text{-}Me_2AuPPh_3$ a different elimination reaction takes place, which produces C_6H_5Me and the gold(I) complex $(MeO_2S)AuPPh_3$ [65].

Binuclear derivatives Some of the mononuclear complexes mentioned above contain potentially bidentate ligands with one uncoordinated P-donor, ($(C_6F_5)_3AuPPh_2CH_2PPh_2$ [22]; $(C_6F_5)_3AuPPh_2NHPPh_2$ [23]) or C-donor ($(C_6F_5)_3AuPPh_2CHPPh_2Me$ [20]) end which is able to displace other ligands in monomeric gold(I) complexes

$$(C_6F_5)_3Au(L\text{–}L) + XAuSC_4H_8 \rightarrow (C_6F_5)_3Au(L\text{–}L)AuX + SC_4H_8 \qquad (82)$$

where X = Cl, C_6F_5, or in $(C_6F_5)_3AuC(NHTo)[NH(CH_2)_nNH_2]$ ($n = 2$ or 3). The free amine end reacts with gold(III) and gold(I) isocyanides to give gold(III)–gold(III) or gold(III)–gold(I) double carbene [10], similar to those obtained according to eqn. (18).

In some cases, the binuclear derivative is directly formed, irrespective of the molar ratio. For instance, reaction of $(C_6F_5)_3Au(SC_4H_8)$ with $PPh_2(CH)_2PPh_2$ always gives $(C_6F_5)_3AuPPh_2(CH_2)_2PPh_2Au(C_6F_5)_3$ and the mononuclear derivative has not so far been prepared [61,62].

Other binuclear complexes with a pseudohalide as a bridging ligand have also been obtained by processes similar to that of eqn. (20), by reacting $(BzPh_3P)[(C_6F_5)_3AuX]$ with $O_3ClOAuPPh_3$ or $O_3ClOAu(C_6F_5)_2PPh_3$ to give $(C_6F_5)_3AuXAuPPh_3$ (X = SCN, CN) [15] or, respectively, $(C_6F_5)_3Au\text{-}SCNAu(C_6F_5)_2PPh_3$ [24].

Heteronuclear derivatives Gold(III)–palladium(II) complexes have been obtained [35] by reaction *trans*-$(C_6F_5)_2Pd(dppm)_2$ with $(C_6F_5)_3Au(SC_4H_8)$ (1 : 1 molar ratio: $(C_6F_5)_3Au(dppm)Pd(C_6F_5)_2(dppm)$; 1 : 2 molar ratio: $(C_6F_5)_3Au(dppm)Pd(C_6F_5)_2(dppm)Au(C_6F_5)_3$) [35] (see also eqns. (32) and (33)).

(ii) Anionic complexes

Anionic complexes containing one, two, three or four aryl groups have been reported.

Complexes containing one aryl group

Displacement of the N-donor end of the 2-(phenylazo)phenyl ligand in complexes of the type $(2\text{-Ph}\overline{\text{N=NC}_6\text{H}_4\text{)A}}\text{uCl}_2$ by addition of Cl^- [45] (eqn. (83)) or displacement of SC_4H_8 in $\text{C}_6\text{F}_5\text{AuX}_2(\text{SC}_4\text{H}_8)$ by halide [43] (eqn. (84)) (where $\text{X} = \text{X}' = \text{Cl, Br}$; $\text{X} = \text{Br}$, $\text{X}' = \text{Cl}$) are the two methods leading to the synthesis of all the reported anionic monoaryl gold(III) complexes.

$$\left(2\text{-Ph}\overline{\text{N=NC}_6\text{H}_4\text{)A}}\text{uCl}_2 + [\text{BzPh}_3\text{P}]\text{Cl} \rightarrow (\text{BzPh}_3\text{P})[(2\text{-PhN=NC}_6\text{H}_4)\text{AuCl}_3] \qquad (83)$$

$$\text{C}_6\text{F}_5\text{AuX}_2(\text{SC}_4\text{H}_8) + (\text{BzPh}_3\text{P})\text{X}' \rightarrow (\text{BzPh}_3\text{P})[\text{C}_6\text{F}_5\text{AuX}_2\text{X}'] + \text{SC}_4\text{H}_8 \qquad (84)$$

With $\text{X}' = \text{SCN}$ in eqn. (84) ligand exchange takes place and a mixture of $[(\text{C}_6\text{F}_5)\text{Au(SCN)}_2\text{Br}]^-$ and $[\text{C}_6\text{F}_5\text{AuBr}_3]^-$ is formed. The two components can be separated because of the lower solubility of the tribromo derivative in diethyl ether [43].

All these complexes are 1 : 1 electrolytes.

Complexes containing two aryl groups

Complexes of three types *trans*-$[\text{R}_2\text{AuX}_2]^-$, *trans*-$[\text{RR}'\text{AuX}_2]^-$ and *cis*-$[\text{R}_2\text{AuX}_2]^-$ have been reported.

Trans-dihalo derivatives can be prepared by the following methods:

(a) Oxidative addition of halogen to aryl aurate(I) [11,38]

$$(\text{NBu}_4)[\text{R}_2\text{Au}] + \text{X}_2 \rightarrow (\text{NBu}_4)[\text{R}_2\text{AuX}_2] \qquad (85)$$

where $\text{R} = 2,4,6\text{-C}_6\text{F}_3\text{H}_2$ and $\text{X} = \text{Cl, Br, I}$; $\text{R} = \text{C}_6\text{F}_5$ and $\text{X} = \text{Cl, Br, I}$; $\text{R} = \text{C}_6\text{Cl}_5$ and $\text{X} = \text{Cl, Br}$.

If the starting aryl aurate(I) contains two different aryl groups, *trans*-complexes of the second type are produced. For instance, addition of X_2 to $(\text{NBu}_4)[\text{C}_6\text{F}_5\text{AuC}_6\text{F}_3\text{H}_2]$ gives [38] *trans*-$[(\text{C}_6\text{F}_5)(\text{C}_6\text{F}_3\text{H}_2)\text{AuX}_2]^-$ ($\text{X} = \text{Br, I}$).

(b) Reaction of *trans*-$(\text{NBu}_4)[(\text{C}_6\text{F}_5)_2\text{AuCl}_2]$ with sodium or potassium salts of CN^- [16] or SCN^- [52] leads to substitution of the two halides by pseudohalide.

(c) Starting from $(\text{C}_6\text{F}_5)_2\text{Au(CN)}_2\text{HOEt}_2$, hydrogen abstraction with NEt_3 gives [15] $(\text{NHEt}_3)[(\text{C}_6\text{F}_5)_2\text{Au(CN)}_2]$ (see also eqn. (39)).

(d) The polymeric $[trans\text{-}(\text{C}_6\text{F}_5)_2\text{Au(CN)}_2\text{M}]_n$ ($\text{M} = \text{Ag, Au}$) react with neutral ligands under cleavage of the CN-bridges and formation [15] of *trans*-$[\text{ML}_2][(\text{C}_6\text{F}_5)_2\text{Au(CN)}_2]$ ($\text{M} = \text{Ag}$; $\text{L} = \text{py, phen, PPh}_3$; $\text{M} = \text{Au}$, $\text{L} = \text{PPh}_3$).

Only the dibromo and diiodo derivatives are coloured (yellow or reddish brown, respectively). All these complexes behave as 1 : 1 electrolytes. The assignment of the *trans*-configuration is based on the single band due to C_6F_5 or $C_6F_3H_2$ (at 800 or 1100 and 800 cm^{-1}) along with another single band due to ν(Au–X) (at 360 cm^{-1} (X = Cl) or 260 cm^{-1} (X = Br) [38]) observed in their IR spectra [11,15,38].

The third type, *cis*-diaryl complexes, can be prepared by the following methods:

(a) Upon standing, solutions of *trans*-$[R_2AuX_2]^-$ change to the *cis* isomers [38,52] (R = C_6F_5, X = Cl, Br, SCN; R = 2,4,6-$C_6F_3H_2$, X = Cl, Br, I). This isomerisation takes place slowly when X = Cl, SCN and requires several hours in refluxing dichloromethane, but in the other cases it goes to completion at room temperature.

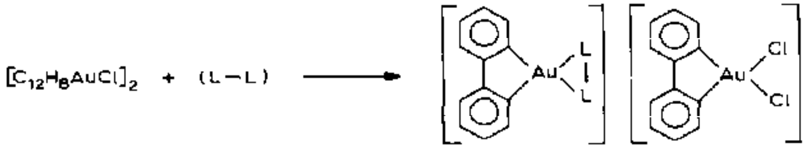
(b) By oxidation of aurate(I) with $TlCl_3$ [11,38].

$$(NBu_4)[AuR_2] + TlCl_3 \rightarrow cis\text{-}(NBu_4)[R_2AuCl_2] + TlCl \qquad (86)$$

where R = C_6F_5, 2,4,6-$C_6F_3H_2$, C_6Cl_5.

(c) Substitution reactions, starting from *cis*-$[R_2AuX_2]^-$ and introducing a different X′ ligand, by reaction with MX′. Thus, *cis*-$(NBu_4)[R_2AuX'_2]$ (R = C_6F_5, X′ = CN [15]; $R_2 = C_{12}H_8$, X′ = I, CN, SCN [53]) and *cis*-$(NMe_4)[R_2AuX'_2]$ (X′ = CN, R = 2-$O_2NC_6H_4$, 2-Me,6-$O_2NC_6H_3$ [54,55]) have been prepared.

(d) Addition of bidentate ligands to binuclear complexes [53]



(87)

where (L–L) = bipy, phen, or similarly [52].

$$[(C_6F_5)_2AuCl]_2 + (L\text{–}L) \rightarrow [(C_6F_5)_2Au(L\text{–}L)][(C_6F_5)_2AuCl_2] \qquad (88)$$

where (L–L) = bipy, phen, pdma.

(e) Reaction [53] between tetrahaloaurate(III) and stannacycles

$$Q[AuX_4] + C_{12}H_8SnPr_2 \rightarrow Q[C_{12}H_8AuX_2] + Pr_2SnX_2 \qquad (89)$$

where Q = NMe_4, X = Cl; Q = NBu_4, X = Br.

(f) Arylation of tetrahaloaurate with organomercuric reagents [54,55]

$$(NMe_3)[AuCl_4] + 2\ HgR_2 \rightarrow cis\text{-}(NMe_4)[R_2AuCl_2] + 2\ RHgCl \qquad (90)$$

where R = 2-$O_2NC_6H_4$, 2-Me,6-$O_2NC_6H_3$.

The IR spectra of the complexes with C_6F_5 or $C_6F_3H_2$ show two bands in the 800 cm^{-1} or, respectively, in the 800 and 1100 cm^{-1} regions [38] and the dichloro complexes also have two bands due to ν(Au–Cl) [38,53,55]. $(NBu_4)[C_{12}H_8Au(NSC)_2]$ contains [53] N-bonded NCS ligands, while in all other gold(III) complexes containing SCN, the ligand is S-bonded.

Complexes containing three aryl groups

These are of the types $[R_3AuX]^-$ or $[RR'_2AuX]^-$ and have been prepared by the following methods:

(a) The method most frequently used starts from neutral $R_3AuSC_4H_8$ and displaces the tetrahydrothiophene by a halide or pseudohalide ligand [15,16,61,62].

$$(C_6F_5)_3Au(SC_4H_8) + QX \rightarrow Q[(C_6F_5)_3AuX] + SC_4H_8 \tag{91}$$

where X = Cl, Br, I, CN, SCN, N_3 and Q = $BzPh_3P$, $MePh_3P$, $EtPh_3P$, $PrPh_3P$, $MePh_3As$. If the starting compound contains different aryl groups, as in $(C_6F_5)_2(C_6F_3H_2)Au(SC_4H_8)$, the corresponding mixed aurate(III) can be obtained [62]. If X is a carbonylate anion, aurate(III) with Au–M_T bonds of the type $Q[(C_6F_5)_3Au{-}M^*]$ [39] can be obtained (Q = $N(PPh_3)_2$, M^* = $Co(CO)_4$, $Mn(CO)_5$; Q = NBu_4, M^* = $Mo(C_5H_5)(CO)_3$, $W(C_5H_5)(CO)_3$). Interestingly, addition of PPh_3 or $P(OPh)_3$ to $[N(PPh_3)_2][(C_6F_5)_3AuCo(CO)_4]$ does not cleave the metal–metal bond, and only one CO group is displaced [39].

(b) Addition of acids HA (A = Cl, BF_4) to diethyl ether solutions of $(BzPh_3P)[(C_6F_5)_3AuCN]$ gives $(C_6F_5)_3Au(CN)HOEt_2$, which further reacts [15] with NEt_3 to give $(NHEt_3)[(C_6F_5)_3Au(CN)]$ (see eqn. (39)).

(c) The reaction between $[(C_6F_5)_2AuCl]_2$ and $(NBu_4)[AuR_2]$ where the aurate(I) acts as an arylating agent [52] under partial decomposition

$$\begin{aligned}[(C_6F_5)_2AuCl]_2 + 2\,(NBu_4)[AuR_2] \rightarrow\ & (NBu_4)[(C_6F_5)_2RAuCl] \\ & + 2\,Au + R{-}R \end{aligned} \tag{92}$$

where R = C_6F_5; 2,4,6-$C_6F_3H_2$.

(d) Direct arylation of $Cl_3Au(SC_4H_8)$ with (2,4,6-$C_6F_3H_2$)Li in the presence of NBu_4Br affords [38] a mixture of $(NBu_4)[Au(C_6F_3H_2)_2]$ (62%) and $(NBu_4)[(C_6F_3H_2)_3AuBr]$ (15%). On the other hand, oxidative arylation of $(NBu_4)[Au(C_6F_3H_2)_2]$ with $(C_6F_3H_2)_2TlCl$ (1 : 1 ratio) gives a similar mixture of unreacted $(NBu_4)[Au(C_6F_3H_2)_2]$ (31%) and $(NBu_4)[(C_6F_3H_2)_3AuCl]$ (33%).

(e) If equimolar amounts of $C_6F_5Au(dppm)AuC_6F_5$ and $TlCl_3$ or of ClAu(dppm)AuCl and $(C_6F_5)_2TlCl$ are reacted, only one of the four gold(I) atoms undergoes oxidation to gold(III) [22] and the ionic complex $[ClAu(dppm)Au(dppm)AuCl][(C_6F_5)_3AuCl]$ can be isolated.

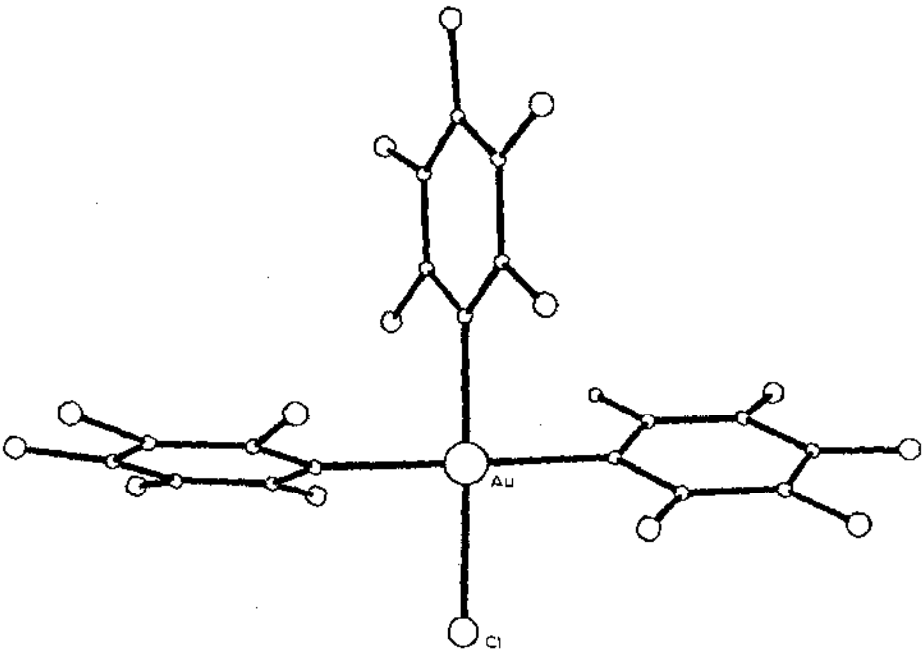
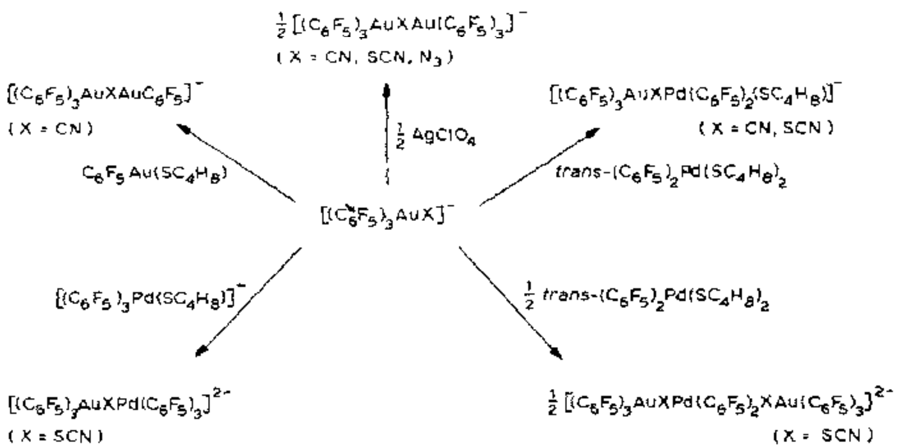


Fig. 16. Structure of $[(C_6F_5)_3AuCl]^-$ [22].

In solution, all these complexes behave as 1 : 1 electrolytes. The structure of the $[(C_6F_5)_3AuCl]^-$ anion has been determined [22] and presents (Fig. 16) the expected square-planar geometry.

Anionic binuclear and heteropolynuclear complexes can be obtained using $[(C_6F_5)_3AuX]^-$ (X = pseudohalide) as a precursor, when X is a potentially bidentate ligand [15,24,41], as summarised in Scheme 5.



Scheme 5.

Complexes containing four aryl groups

Neither the direct arylation with aryl lithium reagents of gold(III) substrate nor the oxidative addition with R_2TlX to arylaurate(I) give satisfactory results, $[AuR_4]^-$ always being formed in low yields. Thus, the reactions of $Cl_3Au(SC_4H_8)$ or $[AuCl_4]^-$ with RLi give $[AuR_4]^-$ ($R = C_6F_5$, 45% [66], $R = 2,3,4,6\text{-}C_6F_4H$, 14% [38]), along with $[AuR_2]^-$ (the latter due to partial reduction). With $R = 2,4,6\text{-}C_6F_3H_2$ a mixture of $[AuR_2]^-$ and $[AuR_3Br]^-$ is obtained. On the other hand, oxidation of $[AuR_2]^-$ with R_2TlCl gives mixtures of $[AuR_2]^-$ (13%) and $[AuR_4]^-$ (53%) for $R = C_6F_5$ or of $[AuR_2]^-$ (31%) and $[AuR_3Cl]^-$ (33%) for $R = 2,4,6\text{-}C_6F_3H_2$ [38].

Arylation of $(C_6F_5)_3Au(SC_4H_8)$ with C_6F_5Li affords only $[Au(C_6F_5)_4]^-$ in 22% yield, because of partial reduction to $[Au(C_6F_5)_2]^-$ [62].

The best reported synthesis of $[AuR_4]^-$ anions [62] (95% yield) is the further arylation of triarylchloroaurate(III) with C_6F_5Ag [67]

$$[N(PPh_3)_2][(C_6F_5)_3AuCl] + C_6F_5Ag \rightarrow [N(PPh_3)_2][Au(C_6F_5)_4] + AgCl \tag{93}$$

while the same reaction starting from $(NBu_4)[C_6F_5(C_6F_3H_2)_2AuBr]$ affords [62] $(NBu_4)[(C_6F_5)_2Au(C_6F_3H_2)_2]$ (65% yield).

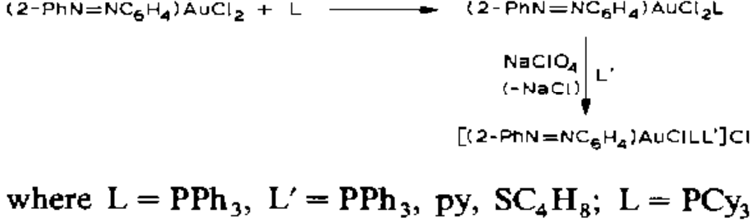
(iii) Cationic complexes

Cationic gold(III) complexes with one, two or three aryl groups have been described.

Complexes containing one aryl group

Three different stoichiometries are known: $[RAuLX_2]^+$, $[RAuL_3]^{2+}$ and $[RXAu(L\text{–}L)_2AuXR]^{2+}$. Complexes of the first type have been prepared by the following methods:

(a) Addtion of a neutral ligand L to $(2\text{-Ph}\overline{\mathrm{N{=}NC_6H_4)A}}\mathrm{uCl_2}$ displaces the N-donor end of the 2-(phenylazo)phenyl ligand. Addition of $NaClO_4$ to the resulting neutral complexes, in the presence of another neutral ligand L′ gives [45] cationic derivatives



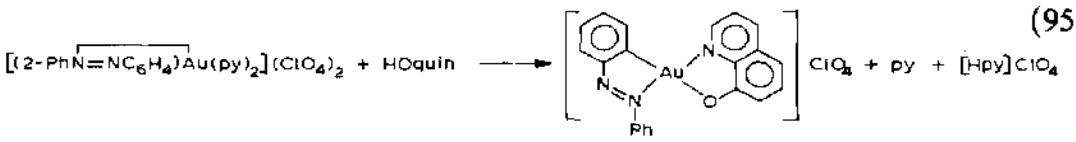
(94)

where $L = PPh_3$, $L' = PPh_3$, py, SC_4H_8; $L = PCy_3$, $L' = PCy_3$, py, L–L′ = phen.

(b) Addition of PPh_3 to $(2\text{-Me}_2\overline{NCH_2C_6H_4)Au}Cl_2$ does not displace the N-donor end, but instead one of the chloride ligands, to give $[(2\text{-Me}_2\overline{NCH_2C_6H_4)Au}Cl(PPh_3)]Cl$ [46]. Other neutral ligands ($AsPh_3$, py, SC_4H_8) can also be introduced to give $[(2\text{-Me}_2\overline{NCH_2C_6H_4)Au}ClL]ClO_4$.

(c) Reaction of $(LR)Au(OOCMe)_2$ ($LR = 2\text{-Me}_2NCH_2C_6H_4$, $2\text{-PhN{=}NC}_6H_4$ with $[Hpy]ClO_4$ affords [47,49] cationic complexes $[(LR)Au(OOCMe)py]ClO_4$.

(d) $[(2\text{-Ph}\overline{N{=}NC_6H_4)Au}(py)_2](ClO_4)_2$ reacts with 8-hydroxyquinoline [47] according to



(95)

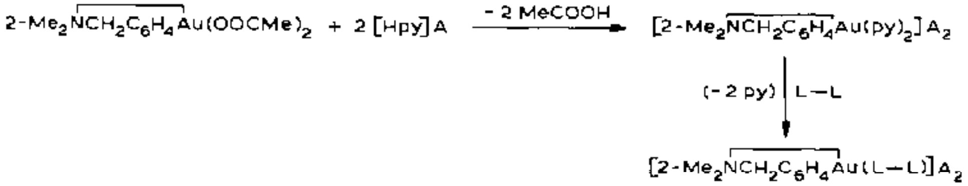
(e) $C_6F_5AuX_2(L\text{–}L)$ ($L\text{–}L$ = phen, X = Cl, Br; $L\text{–}L$ = pdma, X = Cl) react with $AgClO_4$ (1 : 1 molar ratio) to give [48] cationic complexes of the type $[C_6F_5AuX(L\text{–}L)]ClO_4$.

In solution all these complexes behave as 1 : 1 electrolytes.

The following three methods lead to complexes of the type $[RAuL_3]^{2+}$.

(a) Halogen abstraction with $AgClO_4$ acting on the neutral $C_6F_5AuX_2$-(phen) (X = Cl, Br) in the presence of PPh_3 gives [48] $[C_6F_5Au(phen)\text{-}PPh_3](ClO_4)_2$.

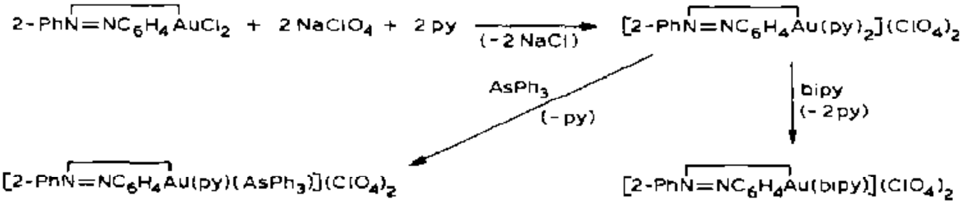
(b) From $2\text{-Me}_2\overline{NCH_2C_6H_4Au}(OOCMe)_2$ through the following sequence [49].



$$\begin{tikzcd} 2\text{-Me}_2\overline{NCH_2C_6H_4Au}(OOCMe)_2 + 2\,[Hpy]A \arrow[r, "-2\,MeCOOH"] & {[2\text{-Me}_2\overline{NCH_2C_6H_4Au}(py)_2]A_2} \arrow[d, "L-L", "(-2\,py)"'] \\ & {[2\text{-Me}_2\overline{NCH_2C_6H_4Au}(L-L)]A_2} \end{tikzcd} \qquad (96)$$

where A = ClO_4, $L\text{–}L$ = phen, bipy, Me_4en, phenen; A = BF_4, $L\text{–}L$ = phen.

(c) Similar complexes containing 2-(phenylazo)phenyl have also been prepared [47] (Scheme 6).



$$\begin{tikzcd} 2\text{-Ph}\overline{N{=}NC_6H_4Au}Cl_2 + 2\,NaClO_4 + 2\,py \arrow[r, "(-2\,NaCl)"'] & {[2\text{-Ph}\overline{N{=}NC_6H_4Au}(py)_2](ClO_4)_2} \arrow[dl, "AsPh_3"', "(-py)"] \arrow[d, "bipy", "(-2\,py)"'] \\ {[2\text{-Ph}\overline{N{=}NC_6H_4Au}(py)(AsPh_3)](ClO_4)_2} & {[2\text{-Ph}\overline{N{=}NC_6H_4Au}(bipy)](ClO_4)_2} \end{tikzcd}$$

Scheme 6.

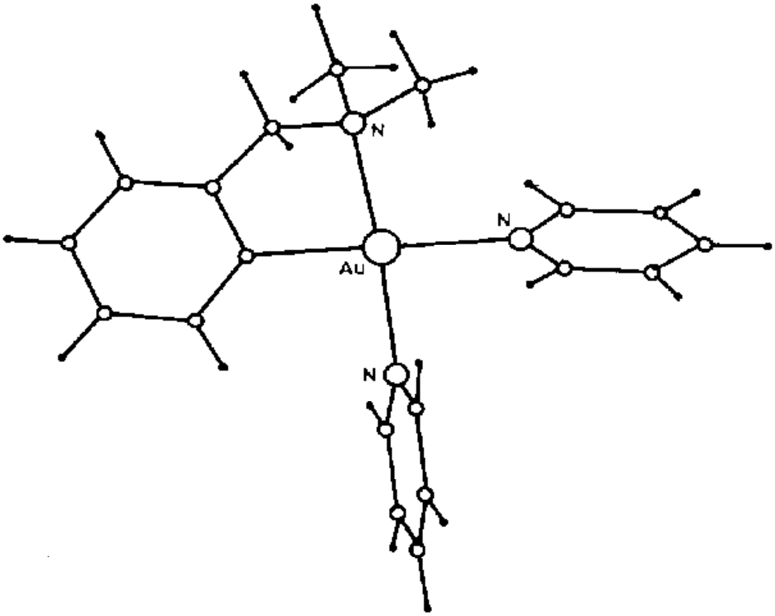


Fig. 17. Structure of $[2\text{-}\mathrm{Me_2}\overline{\mathrm{NCH_2C_6H_4Au}}\mathrm{(py)_2}]^{2+}$ [49].

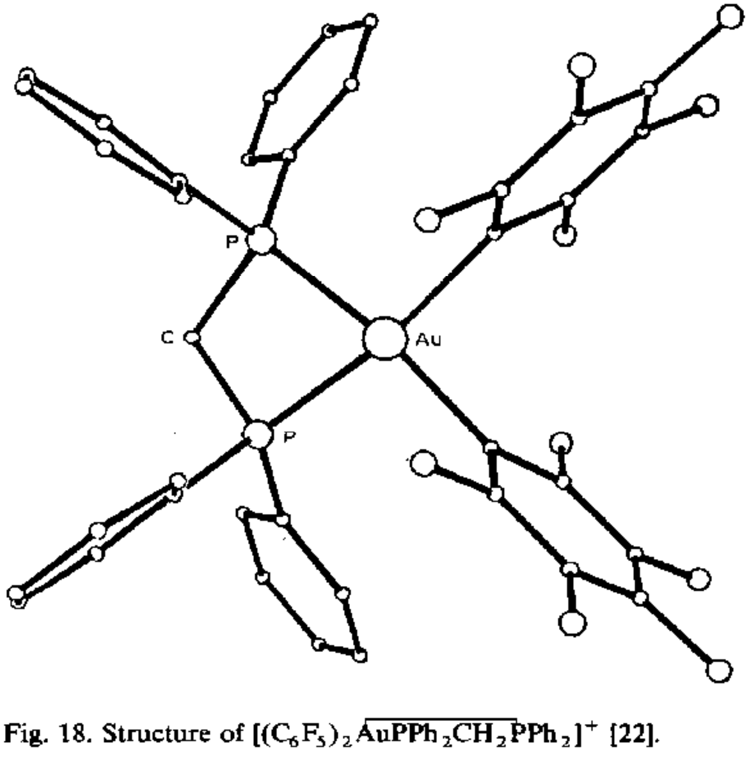


Fig. 18. Structure of $[(\mathrm{C_6F_5})_2\overline{\mathrm{AuPPh_2CH_2P}}\mathrm{Ph_2}]^+$ [22].

The structure of the $[2\text{-}Me_2\overline{NCH_2C_6H_4Au}(py)_2]^{2+}$ cation [49] is represented in Fig. 17. The stronger *trans* influence of the phenyl group is reflected in the longer Au–N (*trans* to phenyl) distance (2.155 Å) relative to the Au–N (*trans* to N) distance 2.016 Å).

The only known cationic binuclear complex $[(2\text{-}PhN{=}NC_6H_4)\text{-}ClAu(dppe)_2AuCl(C_6H_4N{=}NPh\text{-}2)](ClO_4)_2$ can be prepared [45] from $(2\text{-}Ph\overline{N{=}NC_6H_4)Au}Cl_2$ and dppe in the presence of $NaClO_4$.

Complexes containing two aryl groups

Mono-, bi- and trinuclear cationic complexes have been described; the mononuclear complexes are the most numerous and belong to very diverse stoichiometries.

(a) The 1 : 2 reaction between *cis*-$(NBu_4)[(C_6F_5)_2AuCl_2]$ and $AgClO_4$, in acetone or diethylether [60] leads to precipitation of AgCl and solutions which possibly contain *cis*-$[(C_6F_5)_2AuS_2]^+$ ($S = OEt_2$, $OCMe_2$); if dry-evaporated, however, metallic gold is deposited. These solutions can be used for the synthesis of cationic complexes [10,59,60] by addition of a neutral ligand which enhances their stability

$$\begin{tikzcd}
cis\text{-}(NBu_4)[(C_6F_5)_2AuCl_2] \arrow[r, "+\,2\,AgClO_4", "-\,2\,AgCl"'] & cis\text{-}[(C_6F_5)_2AuS_2]ClO_4 \arrow[d, "2\,L"] \\
& cis\text{-}[(C_6F_5)_2AuL_2]ClO_4
\end{tikzcd}$$

(97)

where $L = SC_4H_8$, PPh_2Me, CNPh, CNTo and $L_2 = NH_2(CH_2)_2NH_2$, $NH_2(CH_2)_3NH_2$, bipy, pdma. Addition of dppe to solutions of $(NMe_4)[R_2AuCl_2]$ ($R = 2\text{-}O_2NC_6H_4$, $2\text{-Me},6\text{-}O_2NC_6H_3$ [55]) in the presence of $NaClO_4$ gives (in a similar reaction) $[R_2Au(dppe)]ClO_4$. Molar conductance determinations at different dilution have confirmed the mononuclear nature of the solute.

(b) $(C_6F_5)_2AuCl(dppm)$ [22] or $(2\text{-}PhN{=}NC_6H_4)(2\text{-}Ph\overline{N{=}NC_6H_4)Au}Cl$ [57] react with $AgClO_4$ under precipitation of AgCl and the free coordination site is occupied by the P- or N-donor end of the potentially bidentate ligand, leading to the formation of $[(C_6F_5)_2\overline{AuPPh_2CH_2P}Ph_2]ClO_4$ or, respectively, $[(2\text{-}Ph\overline{N{=}NC_6H_4)_2Au}]ClO_4$. The crystal structures of both cations have been established by X-ray crystallography (Figs. 18 and 19). The Au–C distance is slightly shorter in the azo derivative (1.99 and 2.00 Å) than in the bis(pentafluorophenyl) complex (2.071 Å).

(c) Protonation with acids HA (A = weakly coordinating anion, such as ClO_4 or BF_4) of the methanide $(C_6F_5)_2\overline{AuPPh_2CHP}Ph_2$ (see eqn. (68)), leads [56] to $[(C_6F_5)_2\overline{AuPPh_2CH_2P}Ph_2]A$.

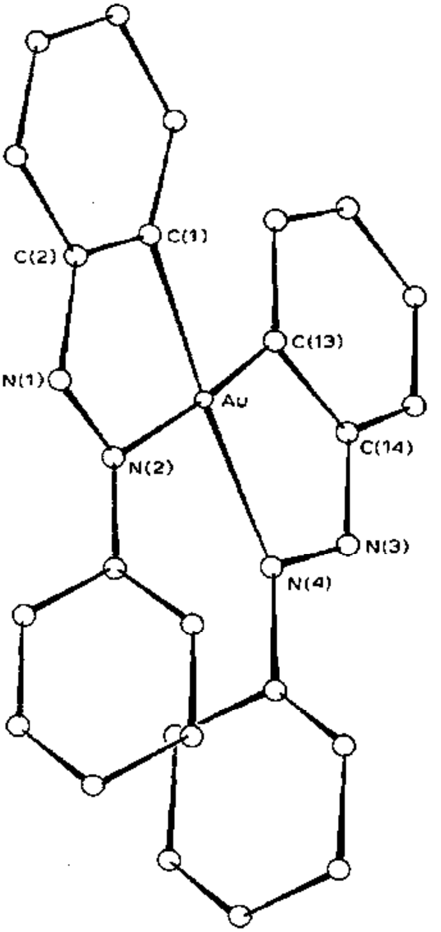
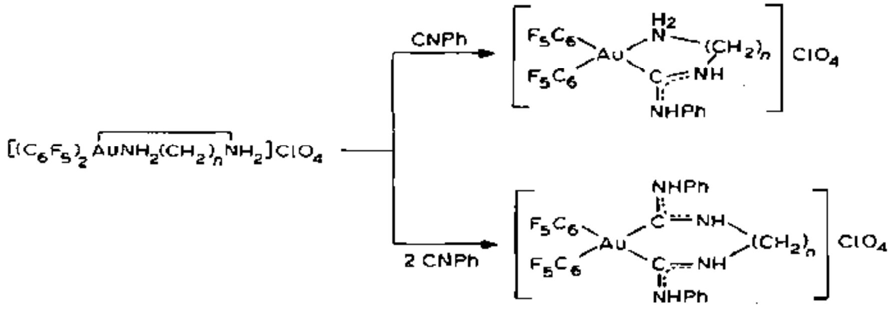


Fig. 19. Structure of $[(2\text{-Ph}\overline{\text{N=NC}_6\text{H}_4)_2\text{Au}}]^+$ [57].

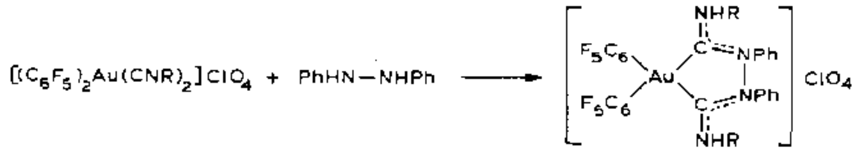
(d) The reaction between $(2\text{-PhN=NC}_6\text{H}_4)(2\text{-Ph}\overline{\text{N=NC}_6\text{H}_4)\text{Au}}(\text{OOCMe})$ and $(\text{Hpy})\text{ClO}_4$ [57] affords the cationic complex $[(2\text{-PhN=NC}_6\text{H}_4)(2\text{-Ph}\overline{\text{N=NC}_6\text{H}_4)\text{Au}}(\text{py})]\text{ClO}_4$.

(e) Insertion of one or two isocyanide molecules in complexes of the type $[(\text{C}_6\text{F}_5)_2\overline{\text{AuNH}_2(\text{CN}_2)_n\text{N}}\text{H}_2]\text{ClO}_4$ gives [10] cationic complexes



(98)

(f) Hydrazobenzene adds [59] to the two cationic gold(III), isocyanides $[(C_6F_5)_2Au(CNR)_2]ClO_4$ (R = Ph, To) to give

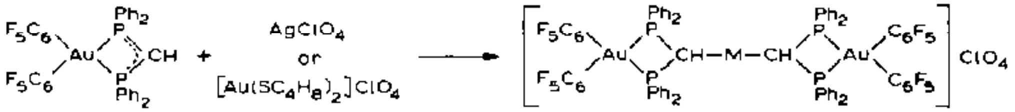


(99)

(g) The novel mononuclear cationic $[(C_6F_5)_2ClAuPPh_2CH_2PPh_2Me]ClO_4$ can be synthesised [20] by reacting the dimer $[(C_6F_5)_2AuCl]_2$ with $[PPh_2CH_2PPh_2Me]ClO_4$.

Cationic bi- or trinuclear complexes have been prepared from mononuclear derivatives containing one electron-rich ligand which can donate electron density to other metal centres, as can be seen from the following examples [22,58].

$$(C_6F_5)_2ClAu(dppm) + O_3ClOAuPPh_3 \rightarrow \left[(C_6F_5)_2ClAu(dppm)AuPPh_3\right]ClO_4 \qquad (100)$$



(101)

where M = Au, Ag. The structure of the trinuclear gold complex has been

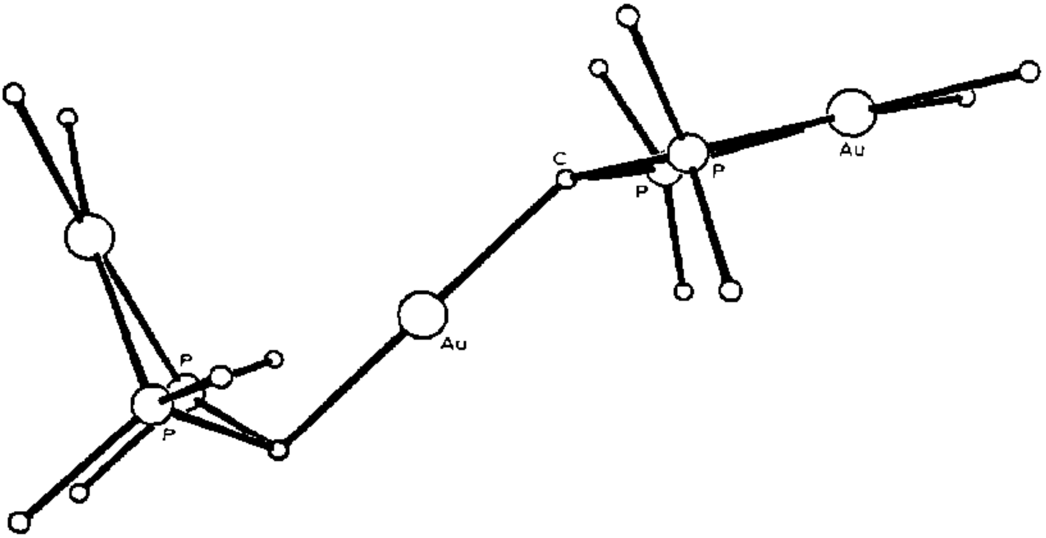


Fig. 20. Structure of $[(C_6F_5)_2AuPPh_2CHPPh_2AuPPh_2CHPPh_2Au(C_6F_5)_2]^+$ [58].

determined [58] by X-ray crystallography (Fig. 20). The three gold atoms and both CH methanides lie on the molecular symmetry plane. The Au–P–C–P rings display different geometries, only one being roughly planar. Reaction of the gold–silver complex with SC_4H_8 gives the binuclear $[(C_6F_5)_2\overline{AuPPh_2\underline{CHP}}\underline{Ph_2}Ag(SC_4H_8)]ClO_4$.

Complexes containing three aryl groups

The mononuclear $[(C_6F_5)_3AuPPh_2CH_2PPh_2Me]A$ ($A = BF_4$, ClO_4) can be obtained by methylating the free P- end in $(C_6F_5)_3Au(dppm)$ with $(Me_3O)BF_4$ [62] or displacing the neutral ligand in $(C_6F_5)_3Au(SC_4H_8)$ with $(PPh_2CH_2PPh_2Me)ClO_4$ [20].

Reaction between $(C_6F_5)_3Au(dppm)$ and $O_3ClOAuPPh_3$ affords [61] the binuclear $[(C_6F_5)_3Au(dppm)AuPPh_3]ClO_4$ whereas a similar reaction between $(C_6F_5)_3Au(dppm)Pd(C_6F_5)_2(dppm)$ and $O_3ClOAuPPh_3$ gives [35] the heterotrinuclear $[(C_6F_5)_3Au(dppm)Pd(C_6F_5)_2(dppm)AuPPh_3]ClO_4$.

E. CONCLUDING REMARKS AND FURTHER OUTLOOK

As may be seen from the foregoing discussion, the field of arylgold compounds has undergone a substantial modification. In 1980 it was justifiable to write [68] "...in the period after 1970, arylgold chemistry developed more rapidly, and the number of compounds reported in the literature is now comparable to that of the alkylgold species". At the present time not only with respect to the number but also to the diversity of new types of aryl-derivatives the situation can be considered to be reversed.

There are, moreover, a series of circumstances which allow one to expect a promising expansion in the future.

(1) The most recent developments have been achieved despite the fact that few laboratories are permanently dedicating at least part of their work to the reviewed field. Since the actual broad basis offers a better starting point for research in a variety of directions than the very limited one existing only a few years ago any increase of attention paid to this field should surely be rewarding.

(2) At the present time, mononuclear gold(I) complexes of all the plausible stoichiometries are known, but some types are only very poorly represented and anionic derivatives with mixed aryl groups are still very scarce.

(3) The field of gold(I) compounds containing O-donor ligands remains practically unexplored, perhaps because qualitative models predict a low stability for them. But as has been the case with other predictions in the past this is not the last word of wisdom and neutral compounds of the type [LAu(O-donor)] where O-donor stands for an anionic group, may easily be prepared starting from now existent precursors.

(4) The number of gold(II) compounds is fairly limited, all of them being binuclear derivatives. Here remains much scope for future research.

(5) Since many of the new arylgold derivatives contain polyhalophenyl groups, it seems tempting to conclude that these aryl ligands have an intrinsically high stabilizing effect. It is advisable to prove whether the assumed lack of stability, which leads to decomposition during the attempted syntheses of other aryl-gold derivatives, is based on sound grounds or is due to the arylating agents chosen (lithium or Grignard reagents, in most cases) which may be responsible for the observed reduction (to Au(I) or Au(0)). We need more diversified arylating methods.

(6) The use of some tin derivatives [53] allows the syntheses of stable biphenylgold(III) complexes and the use of arylmercuric compounds leads to functionalised arylgold(III) complexes [12], which owing to interaction with substituents would not be accessible by arylation with RLi. This route has opened a promising future in a neglected area.

(7) The syntheses of organometallic compounds in high oxidation states, and not only in gold chemistry, could be imaginable and perhaps feasible if new non-reducing arylating agents could be found. For instance, R_2TlX reagents transfer their two aryl groups to the metal centre of the starting complex; because of poor solubility these reactions are restricted however to a few R_2TlX compounds. No systematic exploration of the behaviour of similar reagents based on other *p*-block metals has hitherto been undertaken.

(8) Last, but not least, the use of special bi- or tridentate ligands, e.g. bifunctional ylides, manipulated diphosphines or diarsines, to introduce a methanide or imidophosphinate group, aryl groups with donor substituents, etc. has only very recently begun to be studied.

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