

**SYNTHESIS, STRUCTURES AND  
REACTIONS OF NEW  
CYCLOMETALLATED DINUCLEAR  
GOLD COMPLEXES CONTAINING THE  
FLUORINE-SUBSTITUTED LIGANDS**

A thesis submitted in fulfilment of the requirements for the degree of  
Doctor of Philosophy

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## ***Declaration***

I certify that, except where due acknowledgement has been made, the work is that of the author alone; the work has not been submitted previously, in whole or in part, to qualify for any other academic award; the content of the thesis is the result of work which has been carried out since the official commencement date of the approved research program, and any editorial work, paid or unpaid, carried out by a third party is acknowledged.

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## *List of abbreviations*

[9]aneS <sub>3</sub>	1,4,7-trithiacyclononane
av.	average
bipy	2,2'-bipyridine
Br	broad
<sup>i</sup> Bu	<i>iso</i> -butyl, -CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>
<sup>n</sup> Bu	<i>n</i> -butyl, -CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>
Cp	cyclopentadienyl anion
Cp*	pentamethylcyclopentadienyl anion
cyclam	1,4,8,11-tetraazacyclotetradecane
d	doublet
dba	dibenzylideneacetone
dd	doublet of doublets
ddd	doublet of doublets of doublets
ddt	doublet of doublets of triplets
diars	<i>o</i> -phenylenebis(dimethylarsine), <i>o</i> -C <sub>6</sub> H <sub>4</sub> (AsMe <sub>2</sub> ) <sub>2</sub>
dien	diethylenetriamine, H <sub>2</sub> N(CH <sub>2</sub> ) <sub>2</sub> NH(CH <sub>2</sub> ) <sub>2</sub> NH <sub>2</sub>
dm	doublet of multiplets
dmmp	bis(dimethylphosphinomethyl)methylphosphine
dmpe	1,2-bis(dimethylphosphino)ethane, Me <sub>2</sub> PCH <sub>2</sub> CH <sub>2</sub> PMe <sub>2</sub>
dmpm	bis(dimethylphosphino)methane, Me <sub>2</sub> PCH <sub>2</sub> PMe <sub>2</sub>
dppe	1,2-bis(diphenylphosphino)ethane, Ph <sub>2</sub> PCH <sub>2</sub> CH <sub>2</sub> PPh <sub>2</sub>
dppm	bis(diphenylphosphino)methane, Ph <sub>2</sub> PCH <sub>2</sub> PPh <sub>2</sub>

dppm-H	bis(diphenylphosphino)methanide anion, $(\text{Ph}_2\text{PCHPPH}_2)^-$
dt	doublet of triplets
dtc	dithiocarbamate
dtp	diphenyldithiophosphate, $\text{Ph}_2\text{P(S)S}^-$
Et	ethyl, $-\text{CH}_2\text{CH}_3$
<i>i</i> -mnt	1,1-dicyanoethylene-2,2-dithiolate
IR	Infrared
<i>J</i>	Coupling constant
m	multiplet
Me	methyl, $-\text{CH}_3$
mtp	methylenediphenylthiophosphate
NMR	nuclear magnetic resonance
OBz	benzoate
OTf	triflate, trifluoromethanesulfonate anion
Ph	phenyl, $-\text{C}_6\text{H}_5$
ppm	part per million
<sup><i>i</i></sup> Pr	<i>iso</i> -propyl, $-\text{CH}(\text{CH}_3)_2$
<sup><i>n</i></sup> Pr	<i>n</i> -propyl, $-\text{CH}_2\text{CH}_2\text{CH}_3$
Py	pyridine
R.T.	room temperature
s	singlet
str.	stretch
<sup><i>t</i></sup> Bu	<i>tert</i> -butyl, $-\text{C}(\text{CH}_3)_3$
t	triplet
THF	tetrahydrofuran

tht	tetrahydrothiophene
TPP	meso-tetraphenylporphyrin
UV	ultraviolet



## ***Publications***

### ***Journal papers***

Bennett, M. A.; Bhargava, S. K.; Privér, S. H.; Mirzadeh, N.; Willis, A. C.; Wagler, J. *Perfluoro Substituted Aryl Gold Dimers and their Oxidative Addition Reactions*, *J. Chem. Soc., Dalton Trans*, in preparation.

Bennett, M. A.; Bhargava, S. K.; Privér, S. H.; Mirzadeh, N.; Willis, A. C.; Wagler, J. *Novel Trinuclear Cyclometallated Gold Complexes Containing the Fluorine-Substituted Ligands*, *J. Chem. Soc., Dalton Trans*, in preparation.

Bennett, M. A.; Bhargava, S. K.; Takahashi, M.; Privér, S. H.; Mirzadeh, N. <sup>197</sup>Au *Mössbauer Spectroscopic Studies of Cyclometalated Gold Dimers Containing 2-C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub> Ligands*, *Bull. Chem. Soc. Jpn.*, in preparation.

### ***Conference papers***

Mirzadeh, N.; Bennett, M. A.; Bhargava, S. K.; Privér, S. H.; Byrnes, M.; Willis, A. C.; Wagler, J. *Synthesis, Structure and Reactions of New Cyclometallated Dinuclear Gold Complexes Containing the 2-C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub> Ligand*, RACI Inorganic Chemistry Conference IC07, Hobart, Tasmania, February 2007.

## Summary

The dinuclear cyclometallated gold(I) complex  $[\text{Au}_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$  was prepared in high yield from the reaction of  $2\text{-LiC}_6\text{F}_4\text{PPh}_2$  with either  $[\text{AuBr}(\text{AsPh}_3)]$  or  $[\text{AuCl}(\text{tht})]$ , and from the reaction of  $2\text{-Me}_3\text{SnC}_6\text{F}_4\text{PPh}_2$  with  $[\text{AuCl}(\text{tht})]$ .

The digold(I) complex undergoes oxidative addition reactions with halogens to give the metal-metal bonded dihalodigold(II) complexes  $[\text{Au}_2^{\text{II}}\text{X}_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ), which on warming or exposure to light, isomerise to give the heterovalent gold(I)-gold(III) species  $[\text{XAu}(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)(\kappa^2\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)\text{AuX}]$  containing a four-membered cyclometallated ring on a gold(III) centre. In contrast to the behaviour of the digold(II) complexes in the tetraprotio series,  $[\text{Au}_2\text{X}_2(2\text{-C}_6\text{H}_4\text{PPh}_2)_2]$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ), which isomerise in solution to form digold(I) complexes  $[\text{Au}_2\text{X}_2(2,2'\text{-Ph}_2\text{PC}_6\text{H}_4\text{C}_6\text{H}_4\text{PPh}_2)]$ , there is no evidence for the formation of C-C coupled products in the tetrafluoro series. Unlike its protio analogue,  $[\text{Au}_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$  did not undergo oxidative addition of methyl iodide or dibenzoyl peroxide.

Whereas the tetraprotio analogue undergoes insertion of sulfur dioxide into its Au-C bonds to give the *S*-sulfinato complex  $[\text{Au}_2(\mu\text{-}2\text{-SO}_2\text{C}_6\text{H}_4\text{PPh}_2)_2]$ , the tetrafluoro dimer is inert under similar conditions, suggesting it is less reactive towards electrophiles than the protio dimer. This is also evident from the resistance of  $[\text{Au}_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$  to acid cleavage of the Au-C bonds. Indeed, the Au-C bonds were not cleaved in the presence of two equivalents of hydrochloric acid; the mononuclear complex  $[\text{AuCl}\{(2\text{-}$

$C_6F_4H)PPh_2\}$ ] derived by Au-C bond cleavage was only formed in the presence of a tenfold excess of acid.

The dihalodigold(II)  $[Au_2^{II}X_2(\mu-2-C_6F_4PPh_2)_2]$  and gold(I)-gold(III) compounds  $[XAu(\mu-2-C_6F_4PPh_2)(\kappa^2-2-C_6F_4PPh_2)AuX]$  ( $X = Cl, Br$ ) are further oxidised by halogens to give the digold(III) species  $[Au_2X_4(\mu-2-C_6F_4PPh_2)_2]$  and  $[X_3Au(\mu-2-C_6F_4PPh_2)(\kappa^2-2-C_6F_4PPh_2)AuX]$ , respectively. The complexes  $[Au_2X_4(\mu-2-C_6F_4PPh_2)_2]$  are reduced to the dihalodigold(II) complexes in the presence of one equivalent of zinc powder; further addition of zinc gave the parent digold(I) dimer.

Treatment of  $[Au_2^{II}Cl_2(\mu-2-C_6F_4PPh_2)_2]$  and  $[ClAu(\mu-2-C_6F_4PPh_2)(\kappa^2-2-C_6F_4PPh_2)AuCl]$  with an excess of silver nitrate, benzoate, acetate, trifluoroacetate or triflate gave the corresponding oxyanion complexes. Slow crystallisation of the di(benzoato)digold(II) complex from dichloromethane and methanol gave the parent digold(I) complex derived by reductive elimination. The di(triflato)digold(II) complex behaved similarly, although in this case the novel gold(I) tetramer  $[Au_4(\mu-2-C_6F_4PPh_2)_4]$  was formed together with the dimer. Two closely related gold complexes containing the chelating  $\kappa^2(C,O)$  phosphine oxide ligand,  $2-C_6F_4P(O)PPh_2$ , were isolated from the reaction of  $[ClAu(\mu-2-C_6F_4PPh_2)(\kappa^2-2-C_6F_4PPh_2)AuCl]$  with an excess of silver nitrate. The reaction of  $[Au_2^{II}Cl_2(\mu-2-C_6F_4PPh_2)_2]$  with two equivalents of potassium trifluoroethoxide failed to give the corresponding digold(II) bis(alkoxo) complex; instead, reduction took place to form the digold(I) dimer  $[Au_2(\mu-2-C_6F_4PPh_2)_2]$ .

Treatment of a solution of the di(benzoato)digold(II) complex with  $C_6F_5Li$  gave the pentafluorophenyl complex  $[Au_2(C_6F_5)_2(\mu-2-C_6F_4PPh_2)_2]$  which, when heated in

toluene, rearranged to the gold(I)-gold(III) complex  $[(C_6F_5)Au(\mu-2-C_6F_4PPh_2)(\kappa^2-2-C_6F_4PPh_2)Au(C_6F_5)]$ , analogous to the behaviour of the dihalodigold(II) complexes. The heterovalent, gold(I)-gold(III) dimethyl compound  $[Au_2^{I,III}(CH_3)_2(\mu-2-C_6F_4PPh_2)_2]$  was obtained from the reaction of the di(benzoato)digold(II) complex with dimethylzinc. This compound is structurally similar to its tetraprotio analogue.

$[Au_2(\mu-2-C_6F_4PPh_2)_2]$  reacted with the dithiocarbamate complex  $[Au_2(\mu-S_2CNEt_2)_2]$  in dichloromethane to give what is believed to be the bridging ligand scrambled product  $[Au_2(\mu-2-C_6F_4PPh_2)(\mu-S_2CNEt_2)]$  together with unreacted starting materials; the ligand scrambled product has not been completely characterised. In contrast, reaction of  $[Au_2(\mu-2-C_6F_4PPh_2)_2]$  and its protio analogue  $[Au_2(\mu-2-C_6H_4PPh_2)_2]$  in dichloromethane showed complex behaviour. On mixing equimolar amounts of the digold(II) complexes  $[Au_2Cl_2(\mu-2-C_6F_4PPh_2)_2]$  and  $[Au_2Br_2(\mu-2-C_6F_4PPh_2)_2]$  in dichloromethane, a mixture of unreacted starting materials and the halide-scrambled product  $[Au_2ClBr(\mu-2-C_6F_4PPh_2)_2]$  was formed. In contrast, the di(benzoato)digold(II) complex  $[Au_2^{II}(OCC_6H_5)_2(\mu-2-C_6F_4PPh_2)_2]$  and its protio analogue  $[Au_2^{II}(OCC_6H_5)_2(\mu-2-C_6H_4PPh_2)_2]$  did not undergo scrambling of the bridging metallated ligands.

The cycloaurated dinuclear gold complexes  $[Au_2(\mu-C_6H_3-n-F-2-PPh_2)_2]$  ( $n = 5, 6$ ) were made similarly to the 2- $C_6F_4PPh_2$  analogue from the appropriate lithium or tin reagents, though in some cases the dimers were formed in admixture with the corresponding gold(I) tetramers.

Like their tetrafluoro analogues, the 6-fluoro complexes  $[Au_2X_2(\mu-C_6H_3-6-F-2-PPh_2)_2]$  ( $X = Cl, Br, I$ ) rearrange on heating to give the heterovalent gold(I)-gold(III) species

[XAu( $\mu$ -C<sub>6</sub>H<sub>3</sub>-6-F-2-PPh<sub>2</sub>)( $\kappa^2$ -C<sub>6</sub>H<sub>3</sub>-6-F-2-PPh<sub>2</sub>)AuX]. Thus, the presence of a fluorine atom in place of hydrogen in the 6-position of the bridging aryl group is sufficient to stop the isomerisation of the digold(II) complexes [Au<sub>2</sub>X<sub>2</sub>( $\mu$ -2-C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>] at the gold(I)-gold(III) stage and to prevent subsequent C-C coupling of the aryl groups at the gold(III) centre. In contrast, the dihalodigold(II) complexes containing the 5-fluoro substituted ligand undergo reductive elimination and coupling of the metallated aryl groups to give the digold(I) biphenyldiyl complexes [Au<sub>2</sub>X<sub>2</sub>(2,2'-Ph<sub>2</sub>P-5-FC<sub>6</sub>H<sub>3</sub>C<sub>6</sub>H<sub>3</sub>-5-F-PPh<sub>2</sub>)] (X = Cl, Br, I).

The described complexes were characterised using <sup>1</sup>H NMR, <sup>31</sup>P NMR, <sup>19</sup>F NMR spectroscopy, elemental analysis, mass spectroscopy, IR spectroscopy, X-ray diffraction and <sup>197</sup>Au Mössbauer spectroscopy.

## ***Chapter 1. Introduction and literature review.***

### ***1.1 General introduction to gold chemistry.***

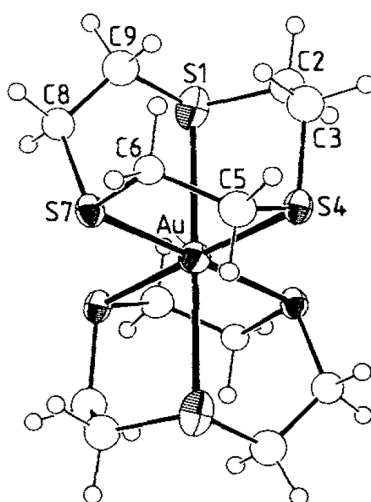
Gold has been known and highly valued since ancient times. This element shows a rich chemistry, both inorganic and organometallic, and it continues to feature strongly as a material of choice for research due to its unique chemical and physical properties.<sup>1</sup>

The chemistry of gold is dominated by the oxidation states +1 and +3, for example, the compounds  $[\text{AuCl}(\text{PPh}_3)]$  and  $\text{K}[\text{AuBr}_4]$ , corresponding to the electron configurations  $[\text{Xe}]5d^{10}$  and  $[\text{Xe}]5d^8$ , respectively. Examples of gold compounds in other less common oxidation states include -1 in alkali metal aurides such as  $\text{CsAu}$ ; +2 in  $[\text{Au}_2\text{Cl}_2(\text{CH}_2\text{PMe}_2\text{CH}_2)_2]$ , and +5 in  $[\text{XeF}_5][\text{AuF}_6]$ .<sup>1</sup> The formation of non-integer oxidation states has also been observed in gold cluster complexes. One example is the compound of formula  $[\text{Au}_9\{\text{P}(p\text{-C}_6\text{H}_4\text{CH}_3)_3\}_8][\text{PF}_6]_3$ , implying an average formal oxidation state of +0.33 for each gold atom.<sup>2</sup> The oxidation state of +2 is extremely rare

in mononuclear, planar or pseudo-octahedral  $5d^9$  gold(II) compounds. Such systems are apparently unstable, relative to those of copper(II), because the  $d_{x^2-y^2}$  orbital occupied by the unpaired electron is of high energy. However, formation of dimeric  $Au_2^{4+}$  species containing a metal-metal bond greatly stabilises such systems.<sup>3</sup>

Gold(I) compounds are generally two-coordinate, with linear geometry, for example, complexes of the type  $[AuR(L)]$  (R = anionic ligand; L = neutral ligand).<sup>4,5</sup> Higher coordination numbers have been observed; the compounds  $[AuCl(PPh_3)_2]$  and  $[Au(diars)_2]^+$  are examples in which the gold atom possesses coordination numbers of three (trigonal planar geometry) and four (tetrahedral geometry), respectively.<sup>6</sup>

The majority of the gold complexes whose empirical formulae suggest the presence of gold(II) are not paramagnetic and often contain a mixture of Au(I) and Au(III). Examples include  $AuS$ ,  $Cs[AuCl_3]$ ,  $K[AuI_3]$ ,  $[Au_2Cl_4(CO)]$  and  $K_5[Au_5(CN)_{10}I_2]$ .<sup>7-12</sup> The first and only structurally characterized mononuclear gold(II) compound is that containing the bis(1,4,7-trithiacyclononane)gold dication (Figure 1).<sup>13</sup>



**Figure 1.** Structure of the cation  $[Au([9]aneS_3)_2]^{2+}$  (reproduced from ref. 13).

Gold(III) complexes typically possess a coordination number of four with square planar geometry, such as  $\text{K}[\text{AuBr}_4]$ ,  $[\text{Au}_2\text{Cl}_6]$  and  $[(\text{C}_2\text{H}_5)_2\text{AuBr}]_2$ ; however, many Au(III) complexes may be described as highly distorted octahedral. For example, the complex  $[\text{AuCl}_2(\text{py})_2]\text{Cl}\cdot\text{H}_2\text{O}$  contains the square planar  $[\text{AuCl}_2(\text{py})_2]^+$  fragment with closely associated ionic  $\text{Cl}^-$  and  $\text{H}_2\text{O}$  in the axial sites, resulting from the efficiency of packing in the crystal.<sup>14</sup> Such contacts to the gold atom are often too short to be considered purely non-bonding.<sup>14-16</sup>

Gold(III) complexes with unusual coordination numbers of 5 and 6 have also been reported; for example  $[\text{AuCl}(\text{TPP})]$  with square pyramidal geometry and  $[\text{AuBr}_6]^{3-}$  with octahedral geometry, respectively.<sup>6</sup> Most five-coordinate gold(III) complexes are of the general formula  $[\text{AuX}_3(\text{L-L})]$ , where  $\text{X} = \text{Cl}$  or  $\text{Br}$ , and L-L is a bidentate nitrogen ligand such as 2,2'-biquinoly,<sup>17</sup> 2,9-dimethyl-1,10-phenanthroline,<sup>18</sup> or 2-(2'-pyridyl)quinoline.<sup>19</sup>

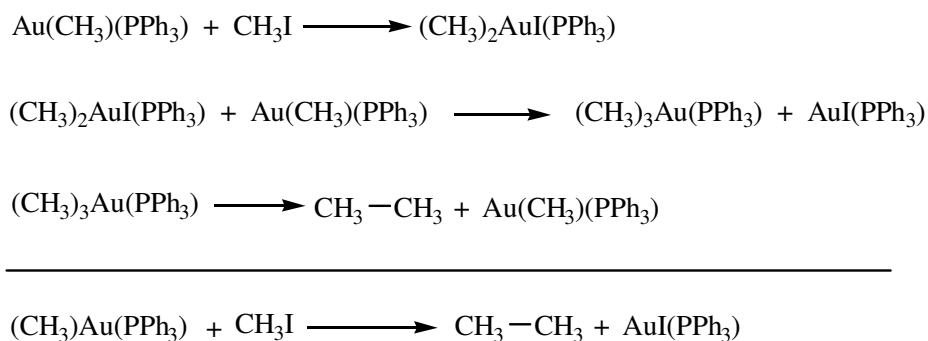
In addition to the extensive inorganic and coordination chemistry of gold, a wide variety of organogold compounds, in which gold is bonded directly to carbon, have been known for almost a century.<sup>1,20-22</sup> Increased interest in this area covers a broad range of topics, from the characterization of new compounds to the application of organogold compounds in the fields of surface coating and chemical vapour deposition.<sup>23-30</sup> The organometallic chemistry of gold has been described in a number of general reviews,<sup>1,31</sup> including ones which specifically concentrate on the synthesis and structure,<sup>32</sup> reactions<sup>33</sup> and applications of organogold compounds.<sup>34</sup>



The catalytic properties of organogold complexes have also received considerable attention in recent years.<sup>35</sup> Examples of gold-catalysed reactions include the heterogeneous oxidation of propene to propene oxide (one of the top targeted reactions in industrial chemistry)<sup>36,37</sup> and the direct synthesis of hydrogen peroxide (one of the most challenging selectivity problems in oxidation chemistry).<sup>38</sup>

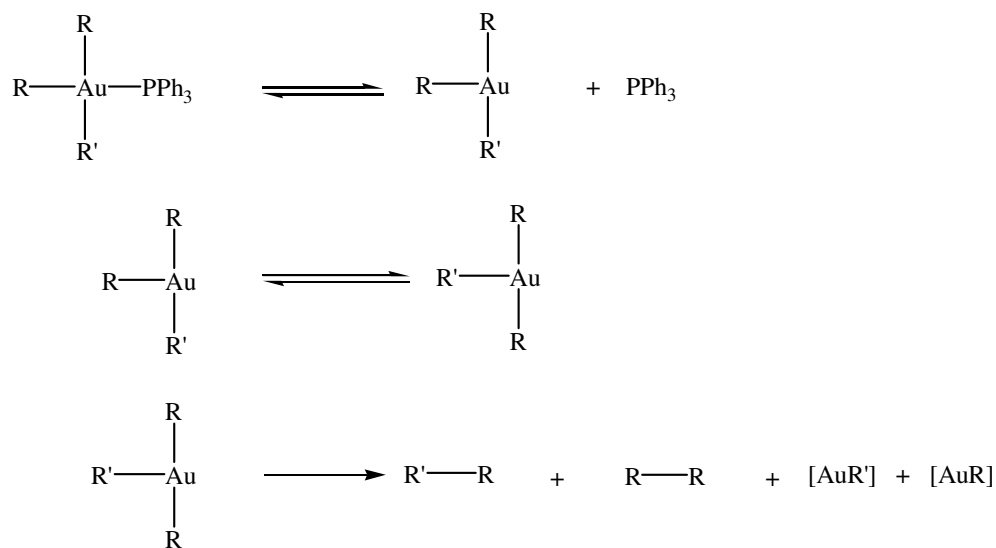
The early work on organogold chemistry dates back to 1907 when Pope and Gibson prepared dialkylgold(III) halides of the type  $[R_2AuX]$  by treatment of tetrahaloauric acid or gold trihalides with an excess of a Grignard reagent.<sup>20</sup> It was not until the 1950's that alkylgold(I) and trialkylgold(III) chemistry was developed after the discovery of organolithium reagents and the introduction of tertiary phosphines as stabilising ligands.<sup>39,40</sup> Nowadays, organogold compounds are typically synthesized by the reaction of Grignard or organolithium reagents with a gold(I) halide complex  $[AuX(L)]$  (L being a donor ligand such as  $PR_3$ ,  $SR_2$ ).<sup>31a</sup> The alternative use of tris(triphenylphosphine)gold(I)oxonium tetrafluoroborate instead of triphenylphosphinegold(I) halides as precursor has been reported in a modified synthesis of alkylgold(I) triphenylphosphine complexes, resulting in shorter reaction times and higher yields.<sup>41,42</sup>  $\sigma$ -Bonded organic complexes of mononuclear gold(I) typically undergo oxidative addition reactions with halogens, alkyl halides and dialkyl disulphides; subsequent reductive elimination at the resulting gold(III) centre and formation of univalent gold complexes may then take place.<sup>43</sup> An early example of this phenomenon is the reaction of  $[Au(CH_3)(PPh_3)]$  with  $CH_3I$ , for which a three-step mechanism was proposed (Scheme 1).<sup>44-46</sup> Initially,  $CH_3I$  oxidatively adds to the gold(I) centre generating  $[(CH_3)_2AuI(PPh_3)]$ . Ligand exchange with the starting material gives  $[AuI(PPh_3)]$  and the trimethyl compound  $[(CH_3)_3Au(PPh_3)]$ , which undergoes reductive

elimination of ethane, regenerating the Au(I) complex. The methylgold(I) complex reacts with CH<sub>3</sub>I, until it is all consumed and only [AuI(PPh<sub>3</sub>)] remains.



**Scheme 1. Overall sequence of steps for the reaction of methyl(triphenylphosphine)gold(I) with CH<sub>3</sub>I.**

Reductive elimination of trialkylgold(III) compounds has been carefully studied and there is agreement that the intramolecular reductive elimination mechanism involves the initial dissociation of a ligand, generating a three-coordinate, T-shaped intermediate. The intermediates readily undergoes *cis-trans* isomerisation, which is followed by reductive elimination to form a gold(I) species (Scheme 2).<sup>46-48</sup>

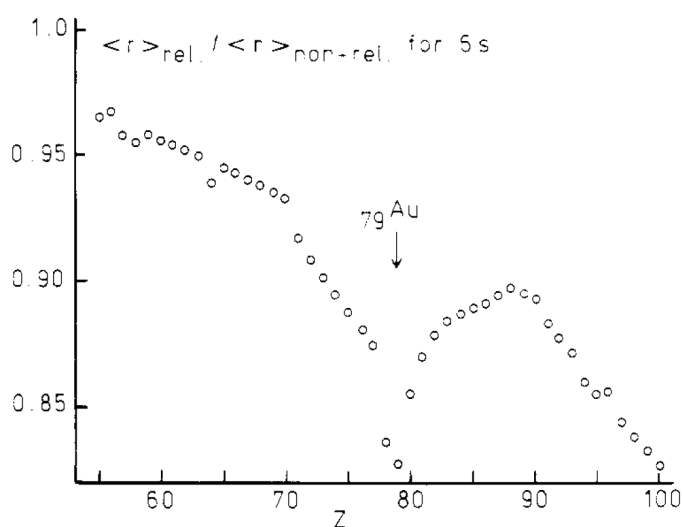


R, R' = alkyl

**Scheme 2. Reductive elimination of trialkylgold(III) complexes.**

Structural studies on both inorganic and organometallic gold complexes in the solid state have confirmed the existence of shorter-than-normal Au...Au separations, indicating an attractive interaction between formally closed-shell 5d<sup>10</sup> gold centres.<sup>14-16,49-53</sup> The term ‘aurophilicity’ was coined in 1989 to describe this unique property of gold, that is, its ability to form weak bonds with itself, which could not be rationalised by conventional concepts of chemical bonding. Aurophilicity may be described as a correlation effect enhanced by relativistic effects.<sup>54,55</sup> In heavy atoms, the average velocity of electrons that penetrate to the nucleus (the s electrons) increases under the influence of the increased nuclear charge and results in a relativistic mass increase. This increase in mass causes a decrease in orbital radius, since orbital radius is inversely proportional to electron mass. In addition to the contraction of the s orbitals, radial expansion of the 5d orbitals occurs, which allows closed-shell 5d<sup>10</sup> Au(I) compounds to interact with the gold atoms in other complexes. The relativistic contraction of the 6s shells is at a maximum for gold (Figure 2),<sup>56</sup> and as a result, the van der Waals radius of

the gold atom (1.66 Å) is less than that of silver (1.72 Å), which is in contrast to that expected for a heavier atom. Relativistic effects also account for the high resistance of gold to oxidation (compared to silver) and the attainment of higher oxidation states (compared to silver).<sup>57</sup> Auophilic interactions are undoubtedly responsible, for example, for the existence of hypervalent carbon complexes of gold, notably species containing five- and six-coordinate carbon such as  $[(\text{Ph}_3\text{PAu})_5\text{C}]^+$  and  $[(\text{Ph}_3\text{PAu})_6\text{C}]^{2+}$ , respectively.<sup>58,59</sup>

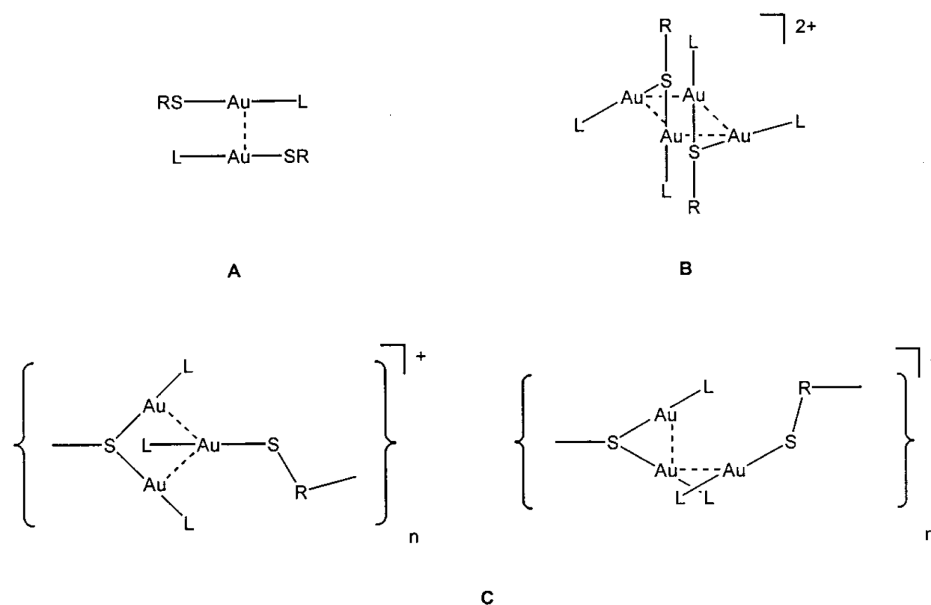


**Figure 2. The relativistic contraction of the 6s shell in the elements Cs ( $Z = 55$ ) to Fm ( $Z = 100$ ), showing the pronounced maximum of the contraction at gold ( $Z = 79$ ) (reproduced from ref. 56).**

The effects of auophilic interactions on the luminescence properties of Au(I) complexes have also been investigated and it is believed that gold-gold interactions are either responsible for or modify the luminescent behaviour observed for many gold(I) compounds.<sup>60-68</sup> The Au $\cdots$ Au interaction is expected to lower the energy of the  $\sigma^*(d_Z^2)$

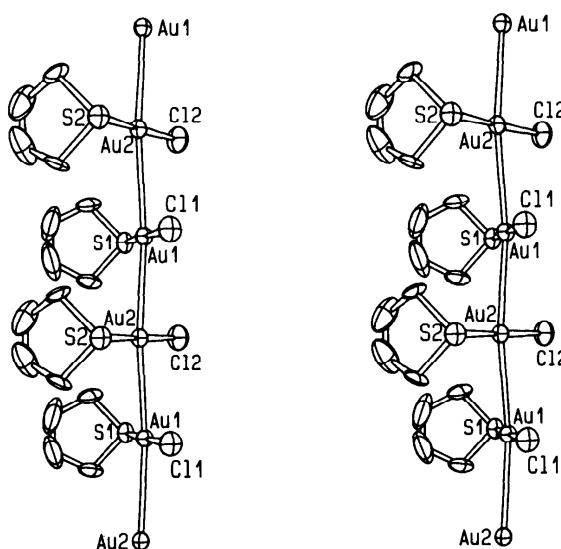
→  $\sigma(6p)$  transition leading to luminescence, where the Au...Au axis is defined as the  $z$  axis.<sup>60,69</sup>

Aurophilicity is especially significant for monovalent gold compounds in which the interactions occur perpendicularly to the molecular axis.<sup>70-72</sup> Typically observed Au-Au interatomic distances are in the range of 2.5-3.2 Å and are shorter than the van der Waals contact for metallic gold (3.32 Å).<sup>14</sup> The estimated bond energy for the gold(I)-gold(I) interaction is 7-12 kcal mol<sup>-1</sup>, which is comparable to that of hydrogen bonding.<sup>72</sup> The intermolecular association of gold complexes through Au...Au interactions can result in the formation of dimers, trimers or even tetramers (Figure 3).<sup>73</sup>



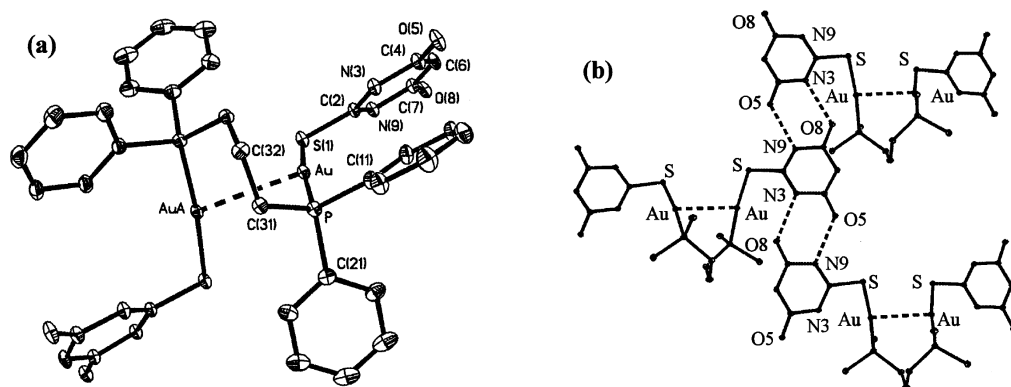
**Figure 3. Aurophilic interaction in gold thiolates A, di(gold)sulfonium salts B and mixed gold thiolate/di(gold)sulfonium units C (reproduced from ref. 73).**

Numerous examples exist of gold compounds that show short intermolecular contacts and non-bonding interactions between gold atoms in neighbouring molecules or complexes. Compounds such as [AuI(tht)] and [AuCl(tht)] (Figure 4) display short intermolecular Au···Au contacts to produce infinite chains in the solid state.<sup>74,75</sup>



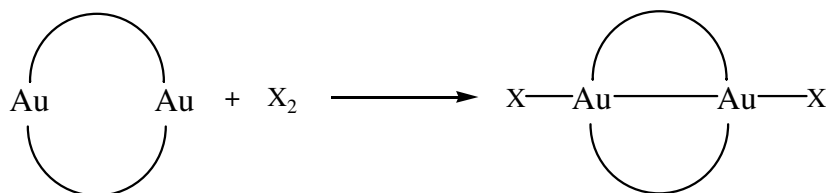
**Figure 4. Stereoscopic view [AuCl(tht)], showing the infinite chain structure through short Au···Au contacts (reproduced from ref. 75).**

Aurophilic interactions can also cooperate with hydrogen bonding to provide supramolecular associations which leads to the formation of polymer, sheet or network structures. An example of the sheet structure is shown in Figure 5, which resulted from the self-assembly of gold(I) complexes  $[\{\mu\text{-(CH}_2\text{)}_3\text{(PPh}_2\text{)}_2\}\text{(AuSC}_4\text{H}_3\text{N}_2\text{O}_2\text{)}_2]$  containing bridging 1,3-bis(diphenylphosphino)propane ligands and 2-thiobarbiturate ligands.<sup>76</sup>



**Figure 5.** Structure of  $[\{\mu\text{-(CH}_2\text{)}_3\text{(PPh}_2\text{)}_2\}\text{(AuSC}_4\text{H}_3\text{N}_2\text{O}_2\text{)}_2]$ , (a) structure of the digold(I) molecule with intramolecular Au $\cdots$ Au interaction, (b) part of the sheet structure formed by intermolecular hydrogen bonding. Only the *ipso*-carbon atoms of the phenyl groups are shown for clarity (reproduced from ref. 76).

Aurophilic interactions exist in dinuclear gold(I) complexes, which represent a special class of gold compounds. An important aspect of gold(I) dimeric systems is their ability to undergo two-electron oxidation to form dinuclear gold(II) complexes containing a gold-gold bond between the  $5d^9$ - $5d^9$  centres whose separation is, on average, *ca.* 2.6 Å (Scheme 3). These dinuclear gold(II) complexes are diamagnetic and display square planar stereochemistry about the gold atoms.

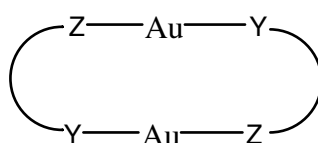


**Scheme 3.** Oxidative addition to a dinuclear gold complex.

Depending on the steric and electronic properties of the bridging ligands, a variety of small molecules can oxidatively add to dinuclear gold(I) complexes to give the corresponding Au(II) compounds. Examples include halogens, pseudohalogens and alkyl halides.<sup>77-79</sup> For a number of ligands, the resulting gold(II) complexes are not stable and cannot be characterized structurally. Isolation at low temperature can prevent commonly observed disproportionation into mixed-valence Au(I)-Au(III) compounds.

### ***1.2 Dinuclear gold complexes containing a pair of bridging ligands.***

Dinuclear gold compounds in which two gold atoms are held in close proximity by a pair of bridging ligands can be represented by the general structure shown in Figure 6.



**Figure 6. Schematic diagram of a dinuclear gold compound.**

These compounds may contain two identical or different bridging ligands. Those containing different ligands may be further subdivided into:

- a) Compounds containing a pair of bifunctional donor bridging ligands, where Y and Z are donor atoms such as P, S, As or N.
- b) Compounds containing bis(ylide) bridging ligands, where Y and Z = C or Y = C and Z = S, together with an onium centre (P or As) located within the ligand framework.

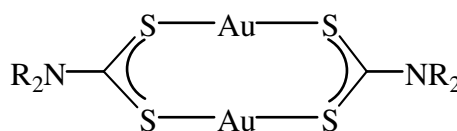


- c) Dinuclear cyclometallated compounds, where Y = N, P or As donor atom and Z = C.

### 1.2.1 Dinuclear gold compounds containing bifunctional donor ligands.

#### 1.2.1.1 Dinuclear compounds containing bifunctional sulfur ligands.

Early use of sulfur ligands in the chemistry of gold dates back to 1945, when Denko and Anderson first prepared mononuclear gold alkylxanthate complexes.<sup>80</sup> However, dinuclear gold complexes containing sulfur ligands did not appear in the literature until 1959 when Åkerström reported the dinuclear gold complex containing a pair of dialkyldithiocarbamate ligands (**A**) (Figure 7).<sup>81</sup>

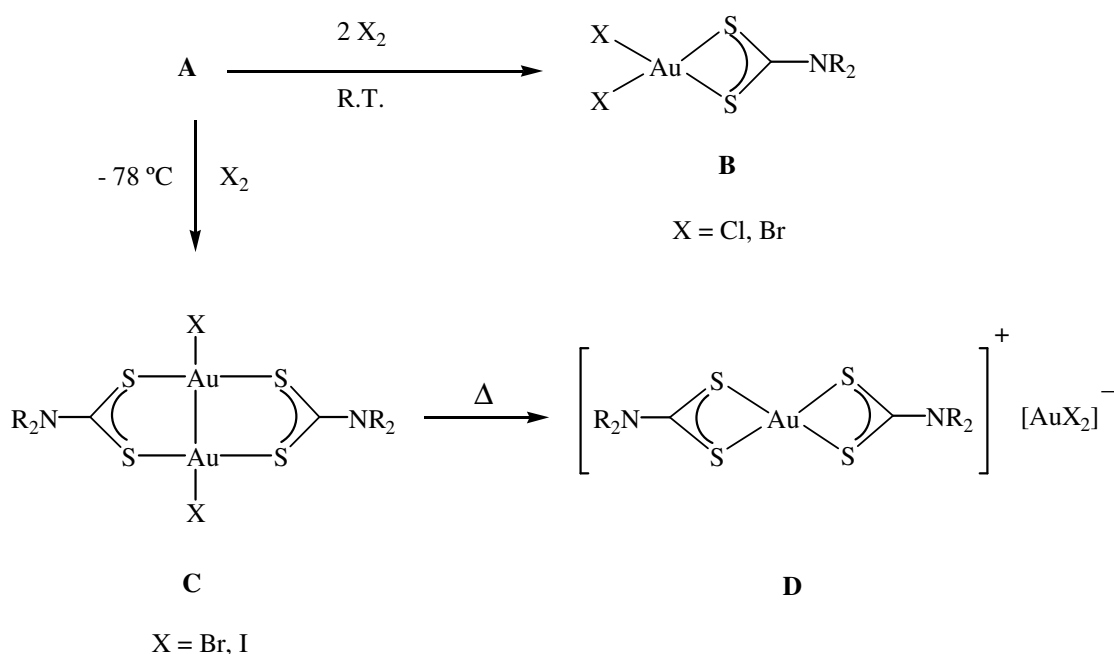


**A**

**Figure 7. Schematic diagram of a dinuclear gold compound containing dialkyldithiocarbamate ligands, where R = Me, Et, <sup>n</sup>Pr, <sup>n</sup>Bu, <sup>i</sup>Pr, <sup>i</sup>Bu, *n*-amyl, *i*-amyl.**

Other derivatives of **A**, where R = *n*-octyl, *n*-dodecyl, cyclohexyl, benzyl, allyl, morpholino and piperidino have also been prepared and characterized by elemental analysis and IR spectroscopy.<sup>81,82</sup> Molecular weight determinations suggested these compounds to be dimeric in benzene and this was later confirmed for the solid state by an X-ray crystal structure determination of the <sup>i</sup>Pr analogue.<sup>83</sup> The formation of an infinite linear gold chain with alternating intermolecular and intramolecular gold-gold distances of 2.67 Å and 3.40 Å has been confirmed in this case.<sup>83</sup> This is also observed in the Et and <sup>n</sup>Bu derivatives of **A**.<sup>84,85</sup>

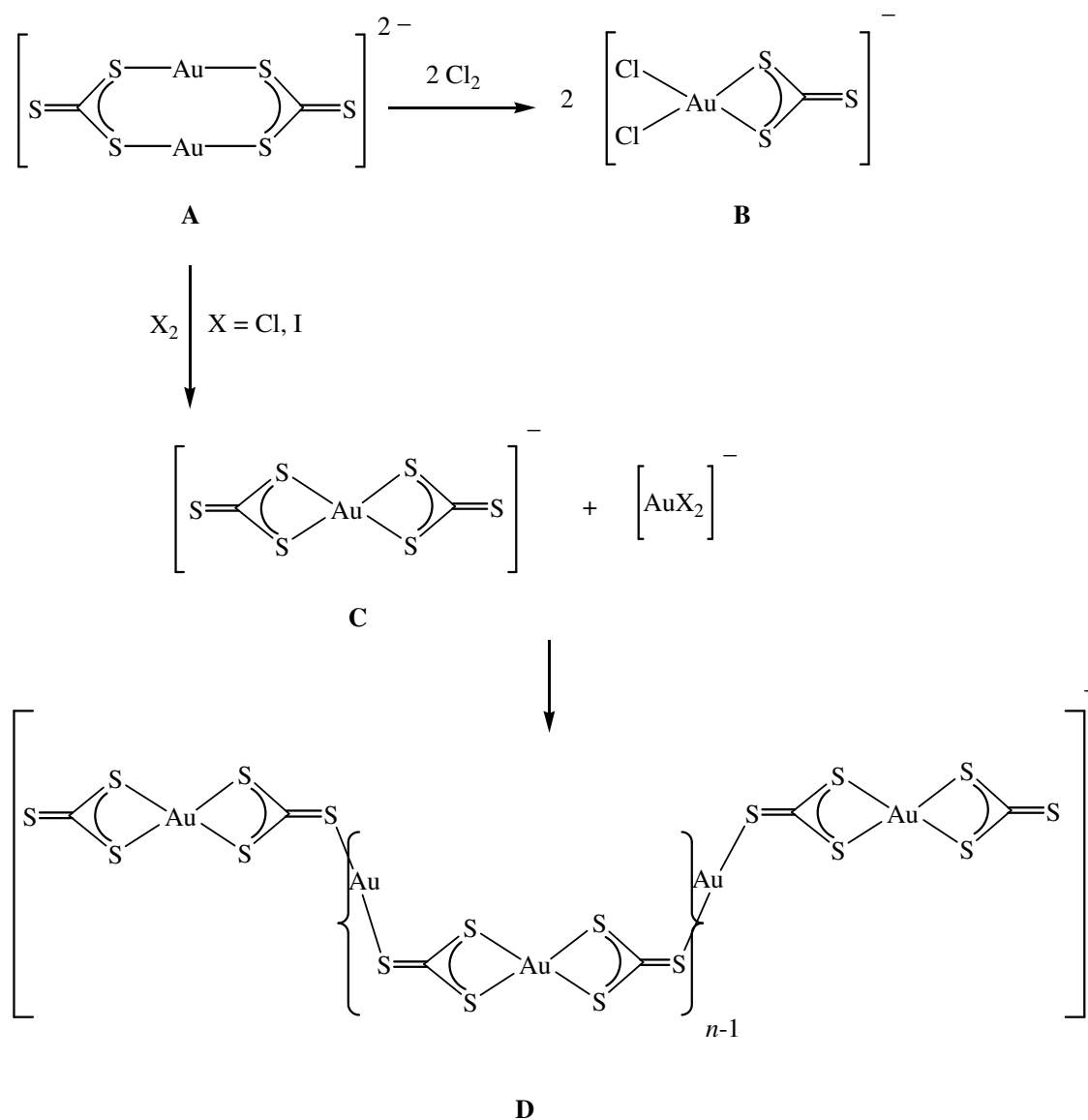
The product of oxidative addition reactions of these dialkyldithiocarbamate gold(I) complexes may vary depending on the reaction conditions, and the amount and type of oxidant (Scheme 4). Treatment of **A** with two equivalents of chlorine or bromine in chloroform at room temperature gives mononuclear gold(III) complexes (**B**, Scheme 4). Reaction with one equivalent of halogen at low temperature gives unstable, axially substituted homovalent gold(II) species (**C**, Scheme 4) which quickly isomerise on warming to give heterovalent ionic gold(I)-gold(III) compounds (**D**, Scheme 4).<sup>86-88</sup>



**Scheme 4. Oxidative addition reactions of gold(I) and isomerisation reactions of gold(II) compounds containing dithiocarbamate ligands.**

The dinuclear compounds containing bridging trithiocarbonate ligands behave similarly.<sup>89</sup> Treatment of  $[(\text{Ph}_3\text{P})_2\text{N}]_2[\text{Au}_2(\mu\text{-CS}_3)_2]$  (**A**, Scheme 5) with two equivalents of chlorine forms the mononuclear gold(III) species with a chelating sulfur ligand (**B**, Scheme 5). The reaction of **A** with one equivalent of chlorine or iodine at room temperature gives the mononuclear gold(III) complex (**C**, Scheme 5) together with

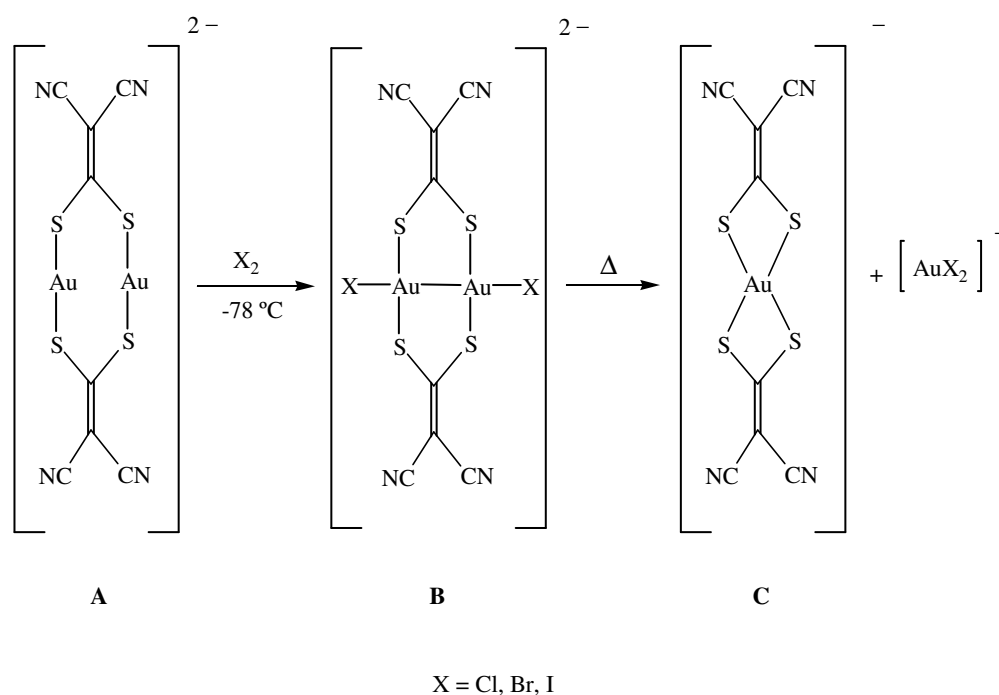
equimolar amounts of  $[\text{AuX}_2]^-$  ( $\text{X} = \text{Cl}, \text{I}$ ). Dichloromethane or acetone solutions of this mixture decompose to give an insoluble, mixed-valence polymeric complex  $[(\text{Ph}_3\text{P})_2\text{N}][\text{Au}_n^{\text{I}}\{\text{Au}^{\text{III}}(\text{CS}_3)_2\}_{n+1}]$  (**D**, Scheme 5) with an average  $n$  value of 6.<sup>89</sup>



**Scheme 5. Reactions of trithiocarbonate compounds [bis(triphenylphosphine)iminium cation omitted for clarity].**

In 1989, Fackler and co-workers reported the synthesis of the gold(I) dimer  $[\text{}^n\text{Bu}_4\text{N}]_2[\text{Au}_2(i\text{-mnt})_2]$  and undertook the first crystallographic study of dinuclear

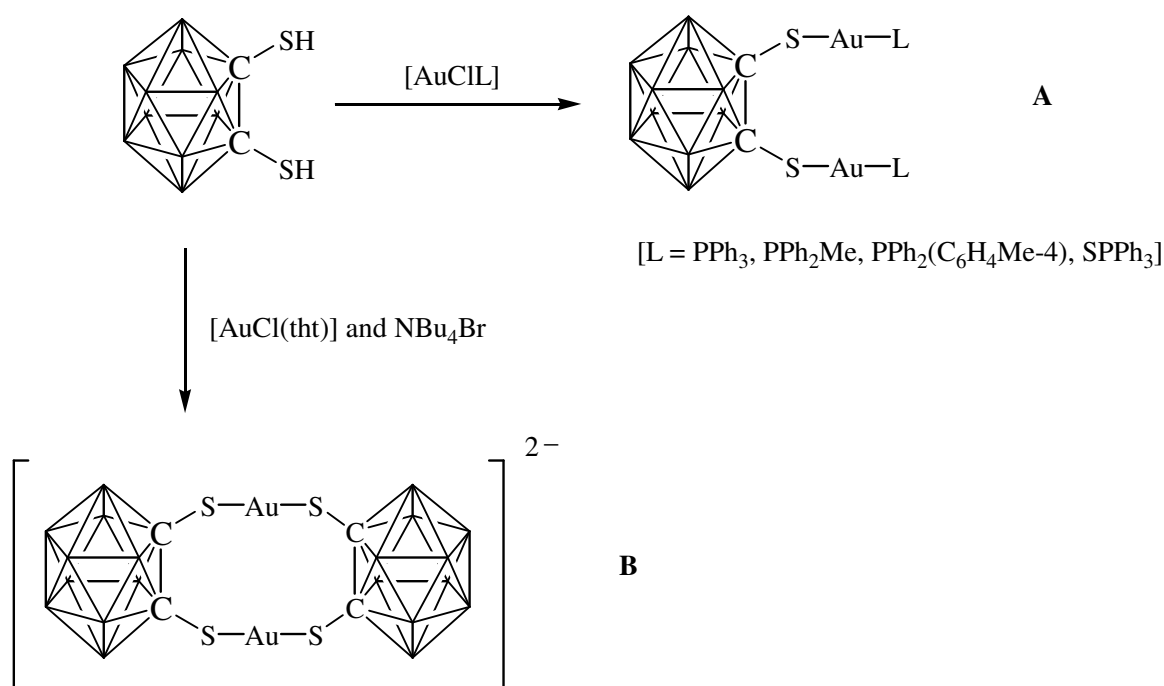
gold(II) complexes derived by oxidative addition reactions. Thus, treatment of  $[\text{}^n\text{Bu}_4\text{N}]_2[\text{Au}_2(i\text{-mnt})_2]$  (**A**, Scheme 6) with halogens at low temperature gives the digold(II) complexes  $[\text{}^n\text{Bu}_4\text{N}]_2[\text{Au}_2\text{X}_2(i\text{-mnt})_2]$  (**B**, Scheme 6) which are stable at room temperature for a limited period of time. The increased stability of these gold(II) species has been attributed to the stronger  $\sigma$ -donor properties of the *i*-mnt ligand compared to those of the dtc ligands.<sup>90</sup> Nevertheless, these gold(II) compounds undergo disproportionation (slowly when X = Cl, rapidly when X = I) to form equimolar amounts of  $[\text{Bu}_4\text{N}][\text{Au}^{\text{III}}(i\text{-mnt})_2]$  (**C**, Scheme 6) and  $[\text{Bu}_4\text{N}][\text{Au}^{\text{I}}\text{X}_2]$ . The gold-gold distances in **B** [X = Cl 2.550(1) Å, Br 2.570(5) Å] are about 0.2 Å shorter than that in the parent gold(I) compound **A**.



**Scheme 6.** Reactions of  $[\text{}^n\text{Bu}_4\text{N}]_2[\text{Au}_2(i\text{-mnt})_2]$  (tetrabutylammonium cation omitted for clarity).

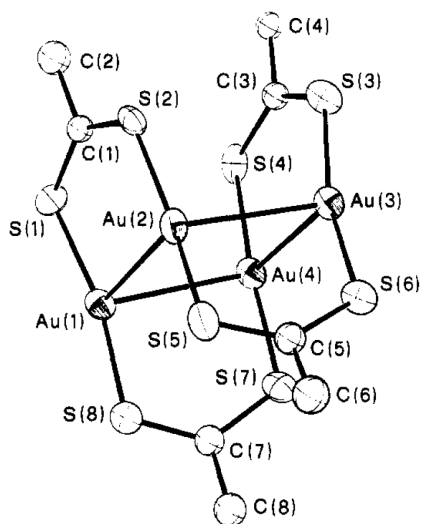
Both singly bridged neutral gold(I) complexes (**A**, Scheme 7) and doubly bridged gold(I) dianionic complexes (**B**, Scheme 7) have been prepared from the 1,2-dithiolate-*o*-

carborane ligand, of which only the former has been characterised by X-ray diffraction.<sup>91</sup> Reaction of 1,2-dithiolate-*o*-carborane with two equivalents of [AuCIL] [L = PPh<sub>3</sub>, PPh<sub>2</sub>Me, PPh<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>Me-4), SPhPh<sub>3</sub>] in the presence of Na<sub>2</sub>CO<sub>3</sub> gives the dinuclear complexes [Au<sub>2</sub>(μ-S<sub>2</sub>C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>)L<sub>2</sub>], whilst treatment of 1,2-dithiolate-*o*-carborane with [AuCl(tht)] and Bu<sub>4</sub>NBr forms the homobridged anionic derivative [Bu<sub>4</sub>N]<sub>2</sub>[Au<sub>2</sub>(μ-S<sub>2</sub>C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>)<sub>2</sub>].<sup>91</sup>



**Scheme 7. Gold(I) compounds derived from the 1,2-dithiolate-*o*-carborane ligand.**

A tetrameric structure has been observed in the gold(I) complex containing dithioacetate ligands (Figure 8).<sup>92</sup> The complex [Au<sub>4</sub>(S<sub>2</sub>CCH<sub>3</sub>)<sub>4</sub>] consists of four gold atoms located at the corners of a square, bridged by four dithioacetate ligands. The four equivalent Au-Au distances average 3.013 Å.



**Figure 8. Molecular structure of  $[\text{Au}_4(\text{S}_2\text{CCH}_3)_4]$ . Hydrogen atoms have been omitted for clarity (reproduced from ref. 92).**

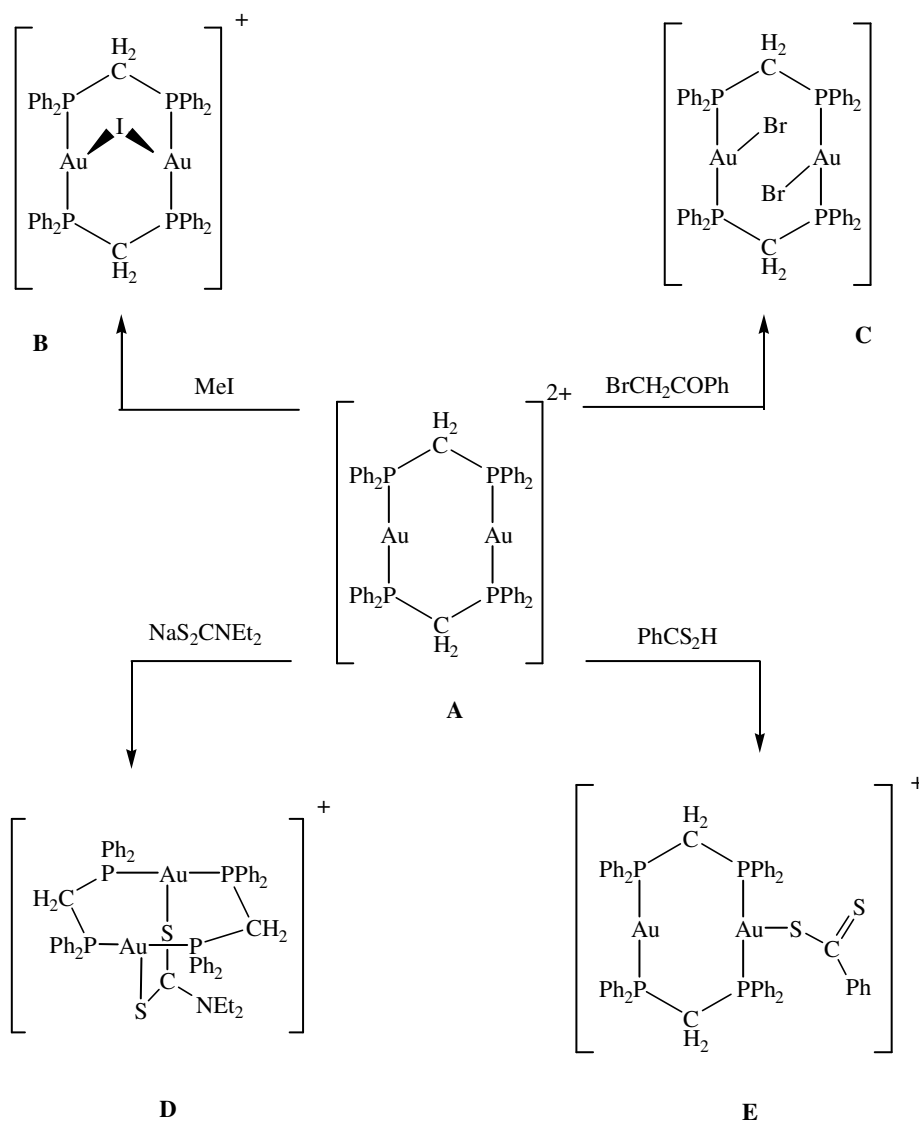
#### 1.2.1.2 Dinuclear compounds containing bifunctional phosphorus ligands.

A vast number of dinuclear transition metal complexes containing the bidentate ligand bis(diphenylphosphino)methane (dppm) have been reported.<sup>93,94</sup> The dinuclear gold complexes containing dppm,  $[\text{Au}_2(\text{dppm})_2]\text{X}_2$  ( $\text{X} = \text{Cl}, \text{Br}$ ), were obtained from interaction of dppm with gold clusters  $[\text{Au}_{13}\text{Cl}_2(\text{PMe}_2\text{Ph})_{10}](\text{PF}_6)_3$  or  $[\text{Au}_{13}\text{Br}_4(\text{PMePh}_2)_8]\text{Br}$ .<sup>95</sup> They have also been prepared by a more conventional route, from the reaction of bis[(haloaurio)diphenylphosphino]methane with dppm.<sup>51</sup> Examples of dinuclear gold(I) complexes containing dppm and other bidentate phosphorus ligands, and their Au-Au distances, are shown in Table 1.

**Table 1. Au-Au distances in selected dinuclear gold(I) complexes containing bidentate phosphorus ligands.**

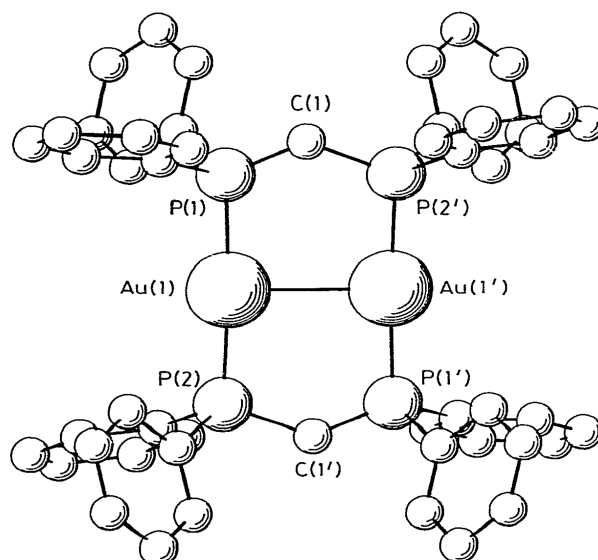
<b>Complex</b>	<b>Au-Au(Å)</b>	<b>Ref.</b>
[Au <sub>2</sub> (dppm) <sub>2</sub> ]Cl <sub>2</sub>	2.962(1)	51
[Au <sub>2</sub> (dppm) <sub>2</sub> ][BF <sub>4</sub> ] <sub>2</sub>	2.931(1)	96
[Au <sub>2</sub> (dppm) <sub>2</sub> ][BH <sub>3</sub> CN] <sub>2</sub>	2.982(2)	97
[Au <sub>2</sub> (dmpm) <sub>2</sub> ]Br <sub>2</sub>	3.023(1)	98
[Au <sub>2</sub> (dmpe) <sub>2</sub> ]Br <sub>2</sub>	2.9438(5)	98
[Au <sub>2</sub> {Ph <sub>2</sub> PC(CH <sub>2</sub> )PPh <sub>2</sub> ] <sub>2</sub> ]Cl <sub>2</sub>	2.977(1)	99
[Au <sub>2</sub> {Ph <sub>2</sub> PC{(P(O)Ph <sub>2</sub> )}PPh <sub>2</sub> ] <sub>2</sub> ][ClO <sub>4</sub> ] <sub>2</sub>	2.7639(1)	100

The reactions of [Au<sub>2</sub>(dppm)<sub>2</sub>]<sup>2+</sup> (**A**) are summarised in Scheme 8. Reaction of **A** with methyl iodide forms the iodo-bridged digold(I) A-frame cation [Au<sub>2</sub>(μ-I)(dppm)<sub>2</sub>]<sup>+</sup> in which one iodide bridges the two gold centres (**B**, Scheme 8). In contrast, treatment of **A** with BrCH<sub>2</sub>COPh gives [AuBr(dppm)<sub>2</sub>] (**C**, Scheme 8) in which one bromide ligand is associated with each gold centre. The gold-gold distances in **B** and **C** are 2.948(2) Å and 3.015(1) Å, respectively.<sup>101</sup> Reaction of **A** with one equivalent of NaS<sub>2</sub>CNEt<sub>2</sub> forms the complex [Au<sub>2</sub>(dppm)<sub>2</sub>(S<sub>2</sub>CNEt)<sup>+</sup> (**D**, Scheme 8) which contains diethyldithiocarbamate and dppm bridges. In **D** the gold-gold distance is 2.949(1) Å.<sup>97</sup> Reaction of **A** with PhCS<sub>2</sub>H affords the digold(I) cation (**E**, Scheme 8) in which the dithiobenzoate ligand coordinates to one of the gold centres through a single sulfur atom. In **E** the gold-gold distance is 3.0176(5) Å and the P-Au-P angle of the S-coordinated gold atom is reduced from *ca.* 176 to 159.66(8)°; the angle subtended at the other gold atom remains almost 180°.<sup>102</sup>



Dinuclear gold(I) complexes containing the bis(diphenylphosphino)methylamine<sup>103</sup> and bis(diphenylphosphino)methanide anion have also been reported.<sup>104,95</sup> The dinuclear gold complex  $[\text{Au}_2(\text{dppm-H})_2]$  has been characterized by single-crystal X-ray diffraction, shown in Figure 9. The structure contains an eight-membered  $\text{Au}_2\text{P}_4\text{C}_2$  ring containing two linearly coordinated gold(I) atoms separated by 2.888(3) Å.<sup>95</sup>



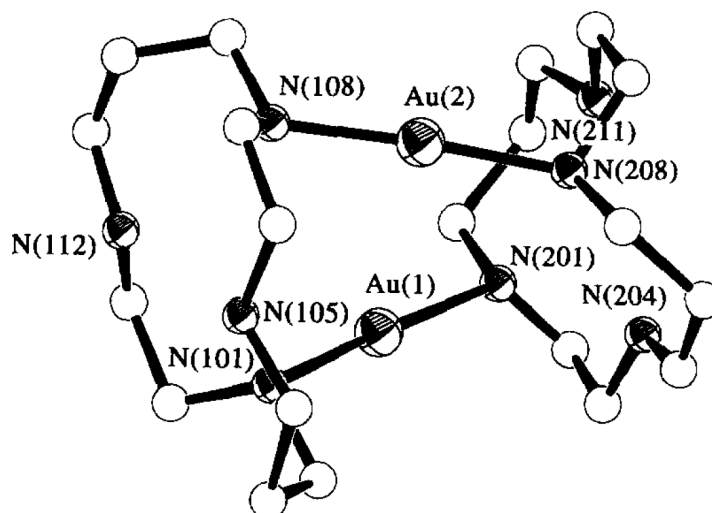


**Figure 9.** Molecular structure of  $[\text{Au}_2(\text{dppm-H})_2]$  (reproduced from ref. 95).

### 1.2.1.3 Dinuclear compounds containing bifunctional nitrogen donor ligands.

Gold(I) complexes with N-donor ligands are much less common than those with P-donor ligands owing to the soft character of the metal centre.<sup>105</sup>

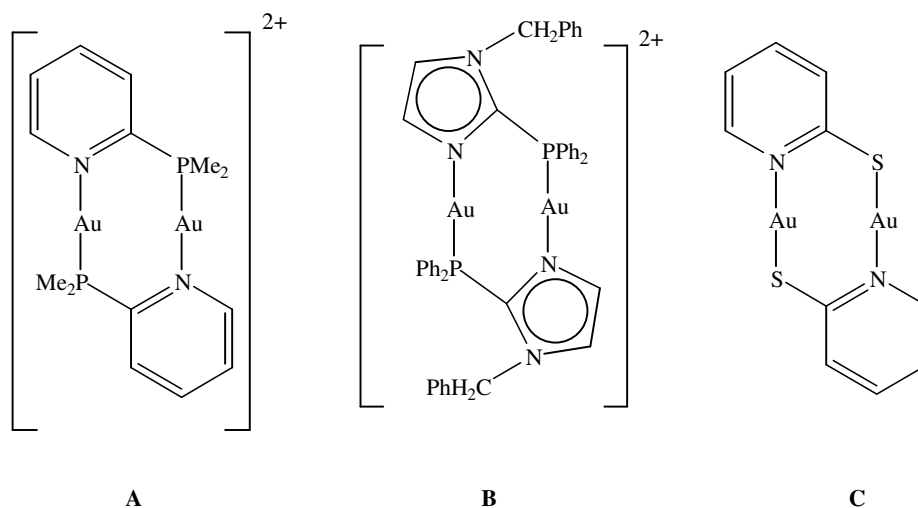
The only two examples of dinuclear gold(I) complexes containing nitrogen donor ligands are the dications  $[\text{Au}_2(\text{dien})_2]^{2+}$  and  $[\text{Au}_2(\text{cyclam})_2]^{2+}$  reported in 1995 and 1996, respectively. Both complexes have been characterized by X-ray crystallography; the structure of the cyclam complex is shown in Figure 10.<sup>106,107</sup> The intramolecular Au-Au distances of *ca.* 4.5 Å in  $[\text{Au}_2(\text{dien})_2]^{2+}$  and 3.370(1) Å in  $[\text{Au}_2(\text{cyclam})_2]^{2+}$  are indicative of no significant internal gold-gold interactions. However, intermolecular gold-gold interactions between independent  $[\text{Au}_2(\text{dien})_2]^{2+}$  units [Au-Au distance is 3.312(1) Å] lead to an infinite chain of molecules in the solid state.<sup>106,107</sup>



**Figure 10.** Molecular structure of  $[\text{Au}_2(\text{cyclam})_2]^{2+}$  (reproduced from ref. 107).

Examples of dinuclear gold complexes containing N-P donor ligands include dimers derived from 2-pyridyldimethylphosphine (**A**, Figure 11) and (1-benzyl-2-imidazolyl)diphenylphosphine (**B**, Figure 11).<sup>108,109</sup> It is noteworthy that the separation of the two gold atoms in **A** is only 2.7776(1) Å, considerably less than that in elemental gold (2.88 Å).<sup>108</sup>

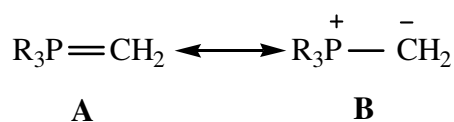
Treatment of  $[\text{AuCl}(\text{SMe}_2)]$  with one equivalent of  $2\text{-C}_5\text{H}_4\text{NS}^-$ , generated *in situ* by the deprotonation of pyridine-2-thiol,  $2\text{-C}_5\text{H}_4\text{N}(\text{SH})$  with NaOMe, gives a yellow insoluble solid, which has tentatively been assigned the formula  $[\text{Au}_2(\mu\text{-}2\text{-C}_5\text{H}_4\text{NS})_2]$  (**C**, Figure 11) based on elemental analysis. However, the low solubility of this material in organic solvents has prevented full structural characterization to date.<sup>110</sup>



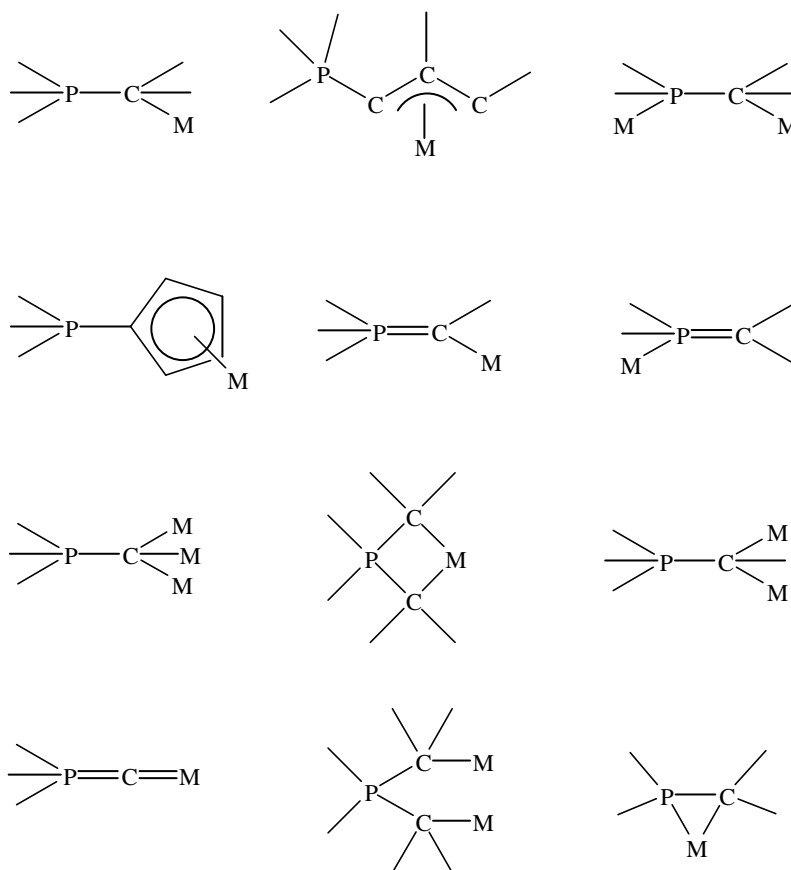
**Figure 11. Gold dimers containing N-P or N-S donor ligands.**

### ***1.3 Dinuclear gold ylide complexes.***

Ylides are characterized by strong element-carbon bonds and are distinguished by their stability towards thermal decomposition.<sup>111,112</sup> Phosphorus ylides are the most important representatives of this class of compounds and can be represented as both neutral molecules containing a formal P=C double bond (**A**) or a dipolar zwitterion (**B**); the latter structure is the dominant form (Figure 12).<sup>111</sup> They have been widely used as versatile ligands in transition metal complexes, displaying a variety of coordination modes (Figure 13).<sup>112-114</sup>



**Figure 12. Resonance stabilised phosphorus ylide ligands.**



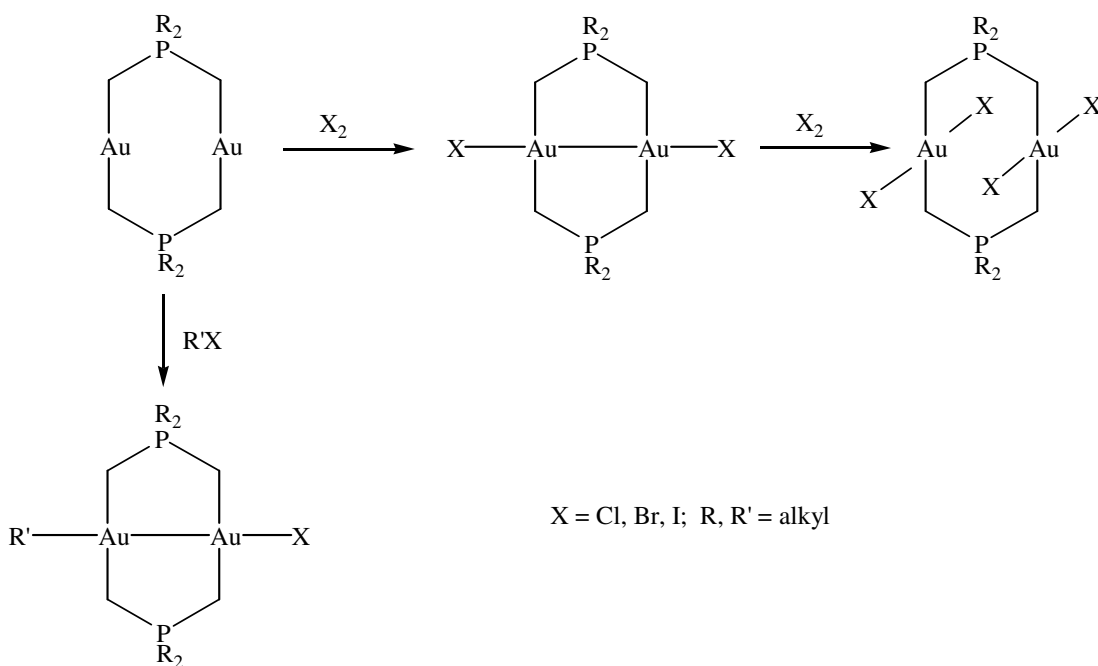
**Figure 13. Coordination modes of phosphorus ylide ligands.**

In addition to the large number of mononuclear gold(I) ylide complexes, a wide variety of dinuclear complexes, in which a bis(ylide) moiety functions as a bridging ligand, are known. The first dinuclear gold bis(ylide) complex,  $[\text{Au}_2\{(\text{CH}_2)_2\text{P}(\text{CH}_3)_2\}_2]$ , was reported by Schmidbaur and co-workers in 1973 and contains two Au-C  $\sigma$ -bonds which are stabilised by the neighbouring phosphonium centre.<sup>77,78</sup> Examples of dinuclear gold(I) complexes containing bis(ylide) ligands and their Au $\cdots$ Au separations are shown in Table 2. The Au $\cdots$ Au separations are in the range of 2.80-3.10 Å, indicative of a weak interaction between the metal atoms.

**Table 2. Au-Au distances in selected dinuclear gold(I) complexes with ylide ligands.**

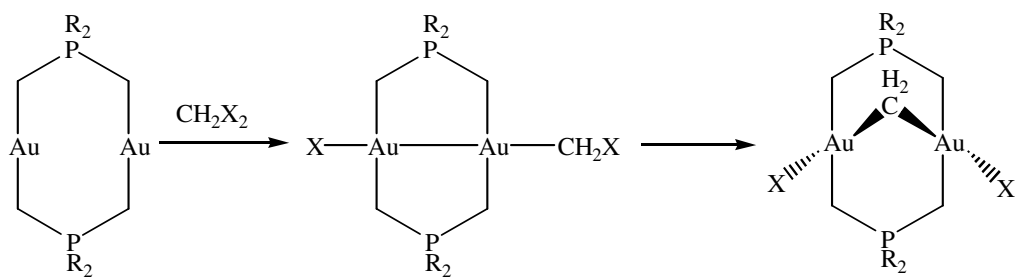
<b>Complex</b>	<b>Au-Au(Å)</b>	<b>Ref.</b>
[Au <sub>2</sub> {μ-(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub> } <sub>2</sub> ]	2.977(1)	115
[Au <sub>2</sub> {μ-(CH <sub>2</sub> ) <sub>2</sub> PMe <sub>2</sub> } <sub>2</sub> ]	3.005(3)	116
[Au <sub>2</sub> {μ-(CH <sub>2</sub> ) <sub>2</sub> PEt <sub>2</sub> } <sub>2</sub> ]	3.023(1)	117
[Au <sub>2</sub> {μ-(CH <sub>2</sub> ) <sub>2</sub> PPhMe} <sub>2</sub> ]	3.003(1)	118
[Au <sub>2</sub> {μ-(CH <sub>2</sub> ) <sub>2</sub> P(CH <sub>2</sub> ) <sub>4</sub> } <sub>2</sub> ]	3.01(1)	119

Typically, these dinuclear bis(ylide) gold(I) complexes undergo oxidative addition with one equivalent of halogen to give metal-metal bonded dihalodigold(II) complexes, which, in some cases, can be oxidised further with a second equivalent of halogen to give dinuclear gold(III)-gold(III) complexes (Scheme 9).<sup>79</sup> The dinuclear bis(ylide) gold(I) complexes react similarly with alkyl halides to give (alkyl)(halo) gold(II)-gold(II) compounds, shown in Scheme 9, which readily decompose in light to give the dihalo complexes.<sup>78,116,120-122</sup>



**Scheme 9. Oxidative addition of halogens and alkyl halides to dinuclear bis(ylide) complexes.**

Digold(II) oxidative addition products can also be obtained by addition of dihalomethanes to the bis(ylide) digold(I) complexes, shown in Scheme 10. These species, many of which have been isolated and characterised,<sup>123-126</sup> are thermodynamically unstable and slowly rearrange to bicyclic digold(III) complexes containing a methylene-bridged A-frame structure.<sup>125,127,128</sup>



**Scheme 10. Oxidative addition of dihalomethanes to dinuclear bis(ylide) gold(I) complexes.**

A large variety of other symmetric and asymmetric bis(ylide) digold complexes can be obtained by ligand substitution of the axial halide groups. Tables 3 and 4 contain examples of dinuclear gold(II) and gold(III) complexes, respectively. The Au–Au separations in the digold(II) complexes are *ca.* 0.3–0.4 Å shorter than those observed in the parent digold(I) complexes, consistent with the formation of a formal metal-metal bond, while those of the gold(III) complexes, particularly those containing the methylene bridge, are larger than in the digold(I) complexes.

**Table 3. Dinuclear Au(II) complexes containing phosphorus ylide ligands.**

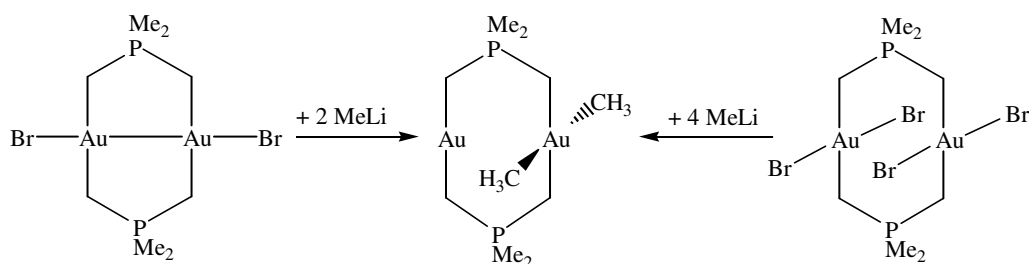
$[\text{Au}_2\text{X}_2\{(\text{CH}_2)_2\text{PR}_2\}_2]$	<b>R</b>	<b>X</b>	<b>Au-Au(Å)</b>	<b>Ref.</b>	
	Ph	Cl	2.600(1)	121	
	Ph	NO <sub>2</sub>	2.596(1)	129	
	Ph	CH <sub>3</sub> COO	2.586(1)	130	
	Ph	C <sub>6</sub> H <sub>5</sub> COO	2.587(1)	131	
	Ph	C <sub>6</sub> F <sub>5</sub>	2.675(1)	132,133	
	Ph	S <sub>2</sub> CN(CH <sub>3</sub> ) <sub>2</sub>	2.66(12)	134	
	Me	I	2.652(4)	116	
	Et	Cl	2.597(5)	135	
$[\text{Au}_2\text{XR}'\{(\text{CH}_2)_2\text{PR}_2\}_2]$	<b>R</b>	<b>X</b>	<b>R'</b>	<b>Au-Au(Å)</b>	<b>Ref.</b>
	Ph	Br	Me	2.674(1)	115
	Me	I	Me	2.695(4)	116
	Ph	I	CH <sub>2</sub> Cl	2.681(3)	123
	Ph	I	Et	2.684(4)	120
	Ph	Br	mtp	2.661(1)	136

**Table 4. Dinuclear Au(III) complexes containing phosphorus ylide ligands.**

$[\text{Au}_2\text{X}_4\{(\text{CH}_2)_2\text{PPh}_2\}_2]$	<b>X</b>	<b>Au-Au(Å)</b>	<b>Ref.</b>	
<i>cis/trans</i>	Cl	3.091(2)	137	
<i>trans/trans</i>	Cl	3.087(2)	138	
<i>trans/trans</i>	Br	3.069(2)	139	
$[\text{Au}_2\text{X}_2(\mu\text{-CH}_2)\{(\text{CH}_2)_2\text{PR}_2\}_2]$	<b>R</b>	<b>X</b>	<b>Au-Au(Å)</b>	<b>Ref.</b>
	Ph	CN	3.167(3)	140
	Ph	Me	3.118(1)	128
	Ph	C <sub>6</sub> F <sub>5</sub>	3.113(1)	141
	Ph	dtp	3.081(1)	136

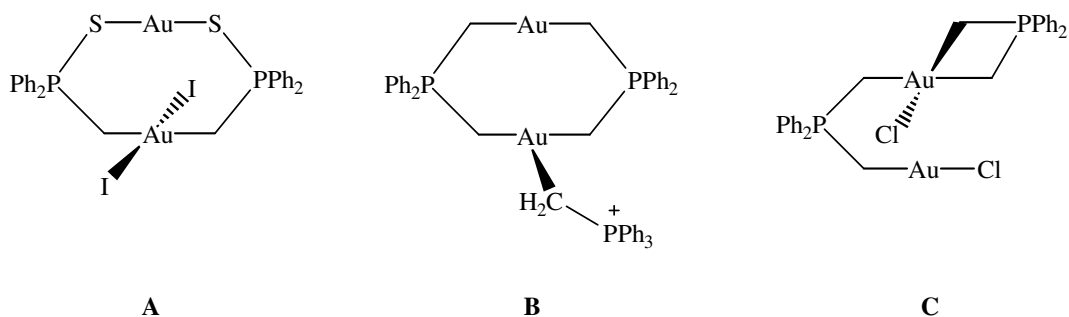


Apart from the homovalent gold complexes, a small number of heterovalent gold(I)-gold(III) compounds containing bridging bis(ylide) ligands have also been reported. Reaction of the dinuclear gold(III) complex  $[\text{Au}_2\text{Br}_4\{(\text{CH}_2)_2\text{PMe}_2\}_2]$  or the digold(II) complex  $[\text{Au}_2\text{Br}_2\{(\text{CH}_2)_2\text{PMe}_2\}_2]$  with MeLi affords heterovalent Au(I)-Au(III) dimethyl complex  $[\text{AuMe}_2\text{Au}\{(\text{CH}_2)_2\text{PMe}_2\}_2]$  in which both phosphine bis(ylide) ligands are bridging and the methyl groups are bonded to the same gold atom (Scheme 11).<sup>78</sup>



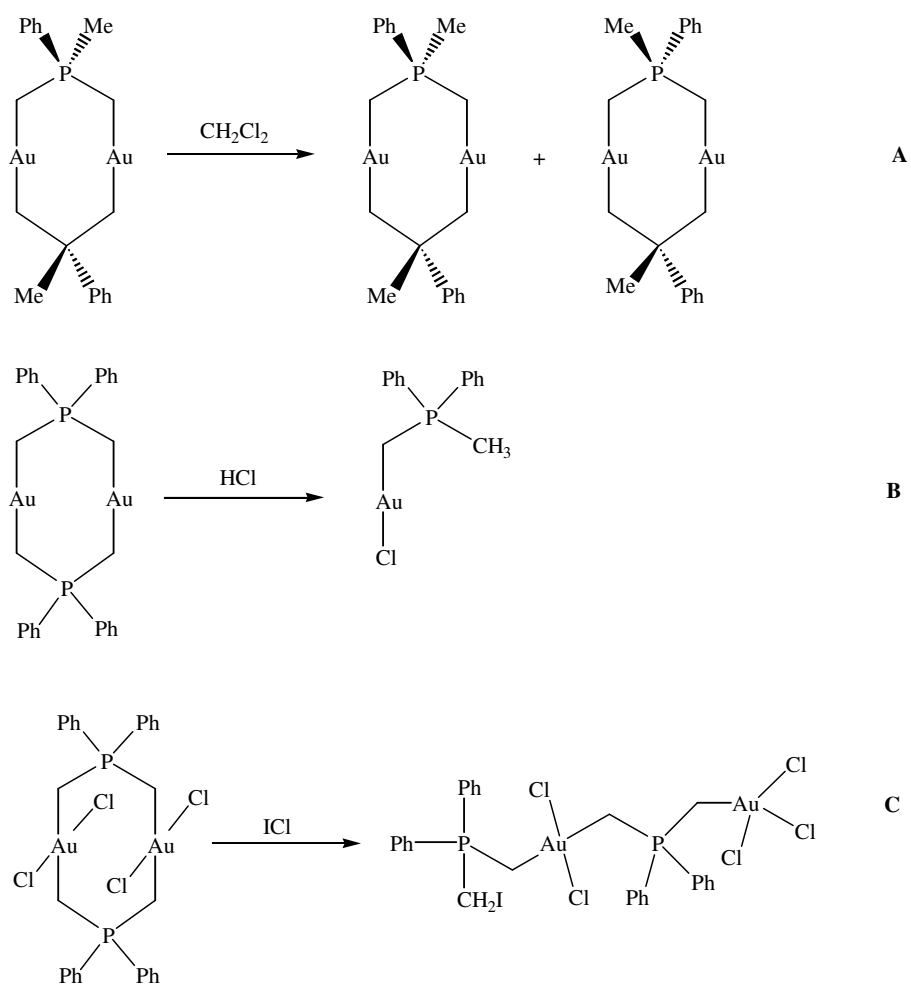
**Scheme 11. Preparation of heterovalent gold(I)-gold(III) complexes from homovalent digold(II) or digold(III) bis(ylide) compounds.**

Other examples of gold(I)-gold(III) compounds are shown in Figure 14. The diiodo complex  $[\text{Au}_2\text{Au}\{\text{S}(\text{CH}_2)_2\text{PPh}_2\}_2]$  (**A**) is formed as one of the two products [the other being the homovalent digold(II) compound] in the oxidative addition of  $\text{I}_2$  to  $[\{\text{AuCH}_2\text{P}(\text{S})\text{Ph}_2\}_2]$ ,<sup>142</sup> whilst the complex  $[\text{Au}(\text{CH}_2\text{PPh}_3)\text{Au}\{(\text{CH}_2)_2\text{PPh}_2\}_2]$  (**B**) is produced from the reaction of the digold(II) complex  $[\text{Au}_2\text{I}_2\{(\text{CH}_2)_2\text{PPh}_2\}_2]$  with  $\text{Ph}_3\text{PCH}_2$ .<sup>143</sup> The isomerisation of the homovalent metal-metal-bonded dimer  $[\text{Au}_2\text{Cl}_2\{(\text{CH}_2)_2\text{PPh}_2\}_2]$  to the heterovalent compound  $[\text{ClAu}\{\mu\text{-}(\text{CH}_2)_2\text{PPh}_2\}\text{AuCl}\{\kappa^2\text{-}(\text{CH}_2)_2\text{PPh}_2\}]$  (**C**) was the first example of this type of rearrangement to form a mixed-valence Au(I)-Au(III) complex containing a four-membered ring. The reaction is promoted by the polar solvents nitromethane and acetone, but its mechanism is unknown.<sup>144</sup>



**Figure 14. Heterovalent Au(I)-Au(III) compounds containing bridging bis(ylide) ligands.**

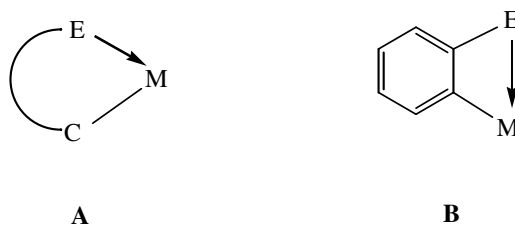
In addition to the extensive chemistry of the Au $\cdots$ Au unit in these bis(ylide) complexes, the reactivity of bridging ligands has also been investigated (Scheme 12). Examples include diastereomerisation (**A**, Scheme 12),<sup>118,137</sup> acid cleavage to form mononuclear species (**B**, Scheme 12),<sup>145</sup> and cleavage of a Au-C bond to form ring-opened dimeric complexes (**C**, Scheme 12).<sup>146</sup>



**Scheme 12. Reactivity of the bridging ligands in bis(ylide) complexes.**

### 1.4 Cyclometallated compounds.

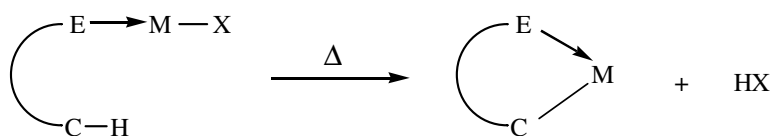
Complexes containing a covalent metal-carbon  $\sigma$ -bond and a metal-donor atom bond in a cyclic structure are described variously as cyclometallated, *ortho*-metallated or organometallic intramolecular coordination compounds. The term *ortho*-metallated specifically refers to those complexes containing an aryl-carbon  $\sigma$ -bond (Figure 15).<sup>147-149</sup>



E = donor atom, M = transition metal

**Figure 15. Cyclometallated (A) and *ortho*-metallated compounds (B).**

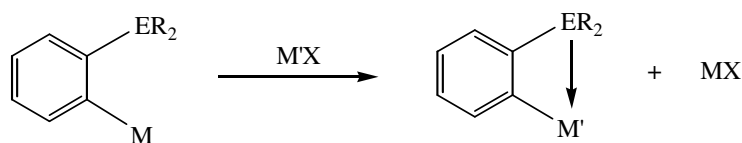
In general, formation of the metal-carbon  $\sigma$ -bond occurs by intramolecular C-H bond activation in which the ligand interacts with the metal substrate, leading to transfer of hydride to the metal centre and, frequently, subsequent elimination of the proton with a suitable leaving group (Scheme 13). An example of such complexes is the *ortho*-metallated rhodium(I) complex  $[\text{Rh}(\kappa^2\text{-P,C-C}_6\text{H}_4\text{PPh}_2)(\text{PPh}_3)_2]$ . When solutions of rhodium complex  $[\text{RhMe}(\text{PPh}_3)_3]$  are heated, elimination of methane occurs to give  $[\text{Rh}(\kappa^2\text{-P,C-C}_6\text{H}_4\text{PPh}_2)(\text{PPh}_3)_2]$ .



E = donor atom, M = transition metal

**Scheme 13. Formation of cyclometallated compounds by interaction of the ligand and metal substrate.**

Another method to produce cyclometallated complexes is the transmetallation of an aryl ligand containing a donor group in the *ortho* position from one metal to another (Scheme 14).

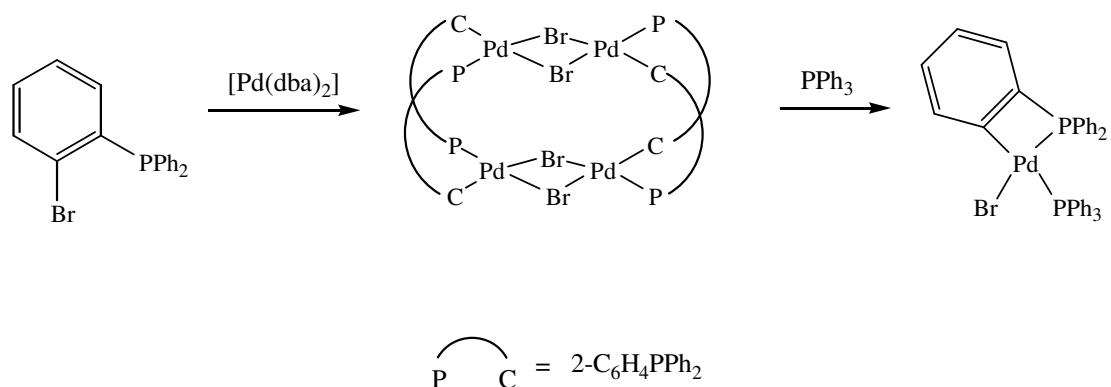


E = P, As; M = Li, MgBr; M' = transition metal; X = halide

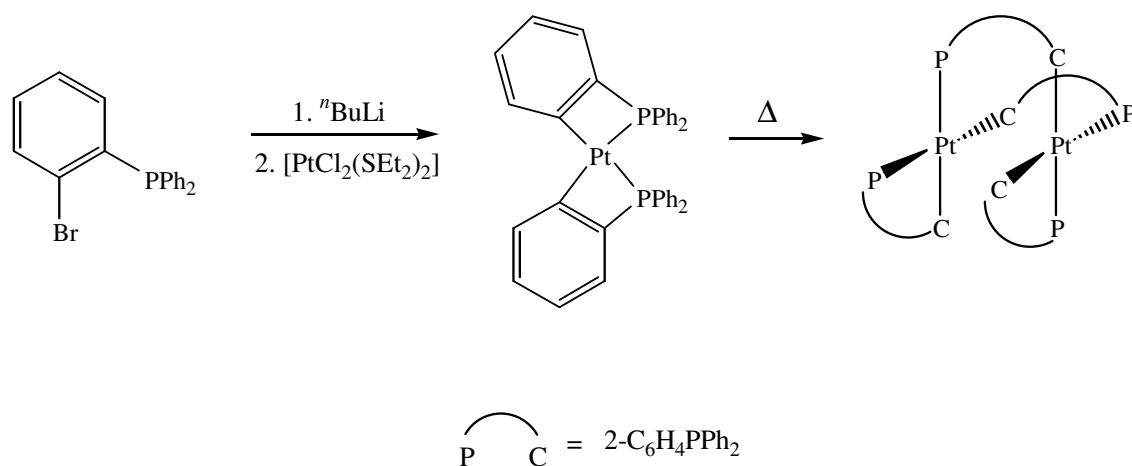
**Scheme 14. Formation of cyclometallated compounds by transmetalation.**

Cyclometallated compounds containing phosphorus,<sup>150,151</sup> nitrogen,<sup>152-154</sup> arsenic,<sup>155</sup> oxygen and sulfur<sup>156</sup> donor ligands have been reported in the literature. Cyclometallated complexes of nearly all the transition metals are known, with the majority containing a five-membered chelate ring, although examples containing ring sizes of four and six have also been reported.<sup>151</sup>

Ligands of the type [2-C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>]<sup>-</sup> can behave as chelating groups (forming a four-membered ring) or as bridging groups (forming an eight-membered ring).<sup>157</sup> There are also well-established examples of the facile interconversion between the two modes.<sup>158,159</sup> For example, a mononuclear complex containing a four-membered chelate ring is formed when the tetranuclear complex [Pd(μ-Br)(μ-2-C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>4</sub>] containing bridging ligands is treated with PPh<sub>3</sub> (Scheme 15).<sup>158</sup> Conversely, upon heating, a chelate ring in the platinum complex *cis*-[Pt(κ<sup>2</sup>-2-C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>] is opened to give the C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>-bridged complex [Pt<sub>2</sub>(μ-2-C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>(κ<sup>2</sup>-2-C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>] (Scheme 16).<sup>159</sup>

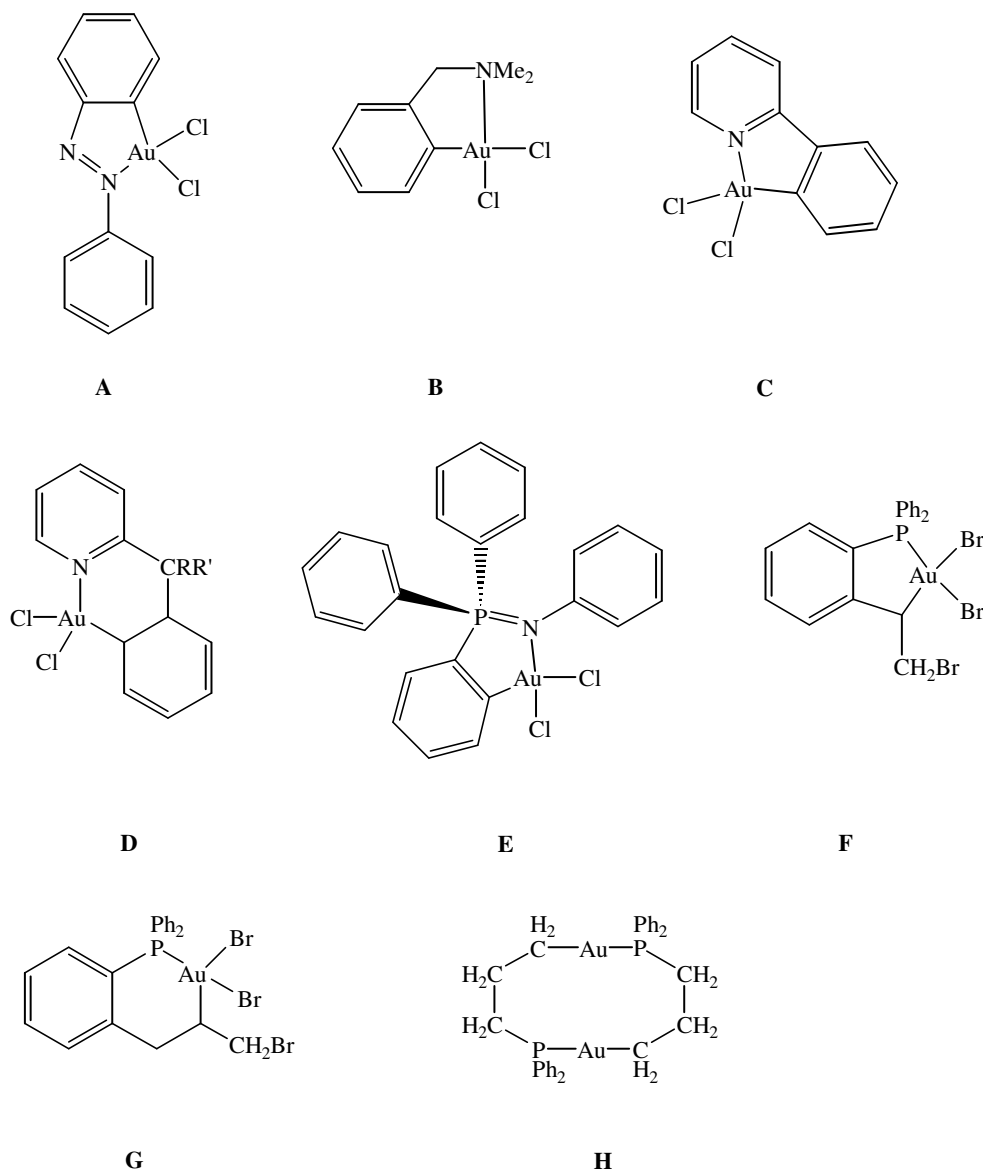


**Scheme 15. Interconversion of the bridging to chelating coordination mode of the [2-C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>]<sup>-</sup> ligand.**



**Scheme 16. Interconversion of the chelating to bridging coordination mode of the [2-C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>]<sup>-</sup> ligand.**

Cycloauration reactions have been developed based on mononuclear gold(III) complexes containing nitrogen donor ligands. In contrast, few compounds containing phosphorus donor ligands are known (Figure 16).

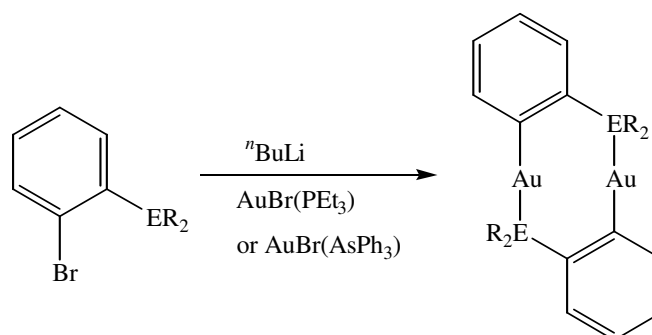


**Figure 16. Examples of cycloaurated gold complexes.**

Cycloaurated complexes have been prepared by transmetalation from the corresponding organomercury,<sup>160-164</sup> organolithium<sup>165,166</sup> and organozinc reagents,<sup>167</sup> or by direct cycloauration of coordinated ligands.<sup>168-178</sup> While many transmetalation reactions form five-membered metallacycles (*e.g.* **A-C** and **E** in Figure 16), examples of direct cycloauration to form a slightly more strained six-membered ring are known (*e.g.* **D** in Figure 16).<sup>160,162,173,176,177</sup> The cyclometallated gold(III) phosphine complexes **F** and **G** in Figure 16 are formed by the bromination of the linear gold(I) complexes of (2-

vinyl)diphenylphosphine and (2-allyl)diphenylphosphine, respectively.<sup>178,179</sup> The cyclometallated gold(I) complex  $[\text{Au}_2(\text{CH}_2\text{CH}_2\text{CH}_2\text{PPh}_2)_2]$  (**H** in Figure 16) is formed by reaction of the zinc reagent  $[\text{Zn}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PPh}_2)_2]$  with  $[\text{Au}(\text{CO})\text{Cl}]$ .<sup>167</sup>

The transmetalation reaction, using aryl lithium reagents, has been the only method of preparation reported to date for dinuclear cyclometallated gold(I) complexes. The earliest example of these types of compounds appeared in the literature in 1978. Abicht and Issleib reported the synthesis of the dimeric complex, bis{2-(diphenylphosphinomethyl)phenyl}digold(I), derived from 2-benzylidiphenylphosphine.<sup>180</sup> Crystallographic evidence was not available to confirm the cyclic structure of cyclometallated dinuclear gold(I) compounds until 1987 when Bennett and co-workers reported the first systematic study of cyclometallated dinuclear gold(I) complexes containing phosphorus and arsenic donor atoms (Scheme 17).<sup>181</sup>



E = P; R = Ph, Et and E = As; R = Me, Ph

**Scheme 17. Dinuclear complexes of gold(I) containing bridging cyclometallated ligands.**

This work was later extended to phosphine and arsine ligands containing a methyl substituent in the aryl group of the bridging ligand.<sup>166,182</sup> The Au...Au separations in these cyclometallated dinuclear gold(I) complexes are in the range 2.85-2.95 Å (Table



5). The Au...Au separations in the arsenic-containing complexes [Au<sub>2</sub>(μ-2-C<sub>6</sub>H<sub>4</sub>AsPh<sub>2</sub>)<sub>2</sub>] and [Au<sub>2</sub>(μ-C<sub>6</sub>H<sub>3</sub>-6-Me-2-AsPh<sub>2</sub>)<sub>2</sub>] [2.9358(5) Å and 2.9543(10) Å, respectively] are larger than those in their phosphorus analogues [2.8594(3) Å and 2.861(2) Å, respectively], owing to the greater atomic radius of arsenic (1.21 Å) compared to phosphorus (1.10 Å).

**Table 5. Dinuclear cyclometallated gold(I) compounds containing P and As donor ligands.**

Compound	Au-Au(Å)	Ref.
[Au <sub>2</sub> (μ-2-C <sub>6</sub> H <sub>4</sub> PEt <sub>2</sub> ) <sub>2</sub> ]	2.8617(6)	181
[Au <sub>2</sub> (μ-2-C <sub>6</sub> H <sub>4</sub> PPh <sub>2</sub> ) <sub>2</sub> ]	2.8594(3)	181
[Au <sub>2</sub> (μ-2-C <sub>6</sub> H <sub>4</sub> AsPh <sub>2</sub> ) <sub>2</sub> ]	2.9358(5)	181
[Au <sub>2</sub> (μ-C <sub>6</sub> H <sub>3</sub> -6-Me-2-PPh <sub>2</sub> ) <sub>2</sub> ]	2.861(2)	166
[Au <sub>2</sub> (μ-C <sub>6</sub> H <sub>3</sub> -6-Me-2-AsPh <sub>2</sub> ) <sub>2</sub> ]	2.9543(10)	182

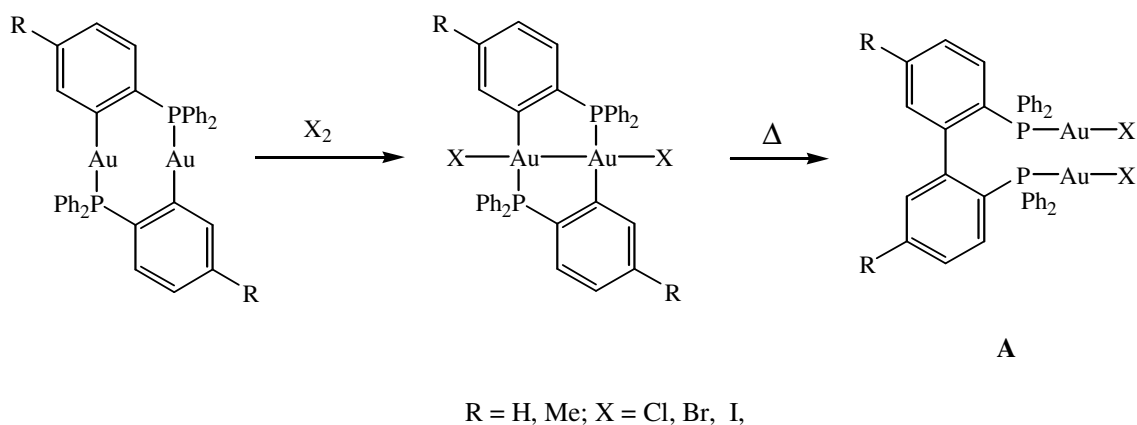
Like other dinuclear cyclometallated complexes of gold(I), [Au<sub>2</sub>(μ-2-C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>] undergoes oxidative addition at the dimetal unit with an equivalent of halogens to give homonuclear gold(II)-gold(II) complexes of the type [Au<sub>2</sub>X<sub>2</sub>(μ-2-C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>] (X = Cl, Br, I), in which the metal-metal distances [X = I; 2.5898(6) Å and 2.5960(7) Å for independent molecules] are significantly shorter than in the gold(I) precursor [2.8594(3) Å], indicative of the presence of a gold-gold bond between the 5d<sup>9</sup> metal centres.

The complexes [Au<sub>2</sub>X<sub>2</sub>(μ-2-C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>] (X = Cl, Br, I) are thermodynamically unstable, and on heating to *ca.* 50 °C for 4-6 hours rearrange by reductive coupling of the metallated aryl groups to give P-bonded digold(I) biphenyldiyl species [A (R = H), Scheme 18]. Qualitatively, the rates of rearrangement of [Au<sub>2</sub>X<sub>2</sub>(μ-2-C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>] to [Au<sub>2</sub>X<sub>2</sub>(2,2'-Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)] are in the order I > Br >> Cl.<sup>165</sup> The analogous digold(II) dihalide complexes containing methyl substituents *meta* to the Au-C bonds

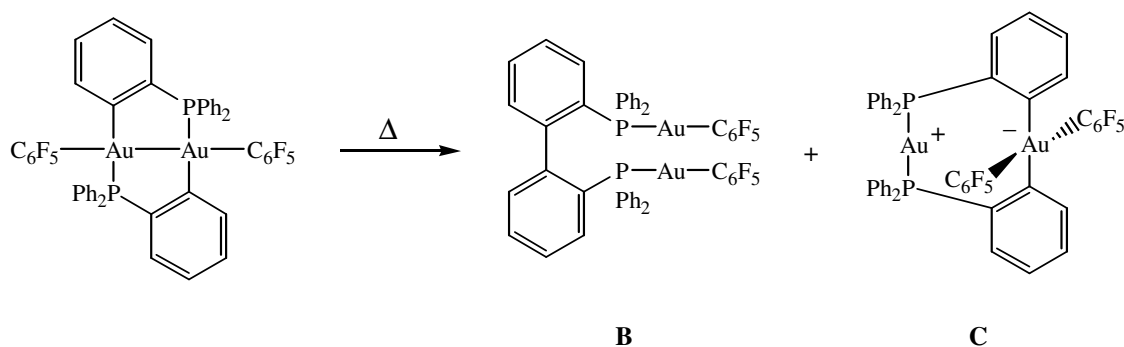
rearrange similarly, though much more rapidly, and the rate of rearrangement decreases in the order  $\text{Cl} > \text{I} > \text{Br}$  (Scheme 18).<sup>166</sup> The zwitterionic species (**C**, Scheme 19) in which the bridging aryl groups are arranged in a head-to-head mode and the phosphorus atoms of the 2- $\text{C}_6\text{H}_4\text{PPh}_2$  groups are linearly coordinated to the gold(I) atom, has been isolated and characterized as a minor product of the rearrangement reaction when  $\text{X} = \text{C}_6\text{F}_5$ ; the major product is the expected digold(I) biphenyldiyl species (**B**, Scheme 19).

It has been shown that reductive elimination that leads to C-C coupling is favoured by less electron-withdrawing anionic ligands such as halide and thiocyanate.<sup>182,183</sup> When the axial ligands are benzoate or acetate, no reductive elimination takes place.<sup>165,183,184</sup>

The similar complexes  $[\text{Au}_2\text{X}_2(\mu\text{-}2\text{-C}_6\text{H}_4\text{PR}_2)_2]$  ( $\text{R} = \text{Et}$ ,  $\text{X} = \text{C}_6\text{F}_5$ ;  $\text{R} = \textit{i}\text{Pr}$ ;  $\text{X} = \text{OBz}$ ) have also been prepared having the zwitterionic structure, illustrating the fine balance the bridging and axial ligands play in the reactivity of these dinuclear complexes.<sup>183,185</sup>

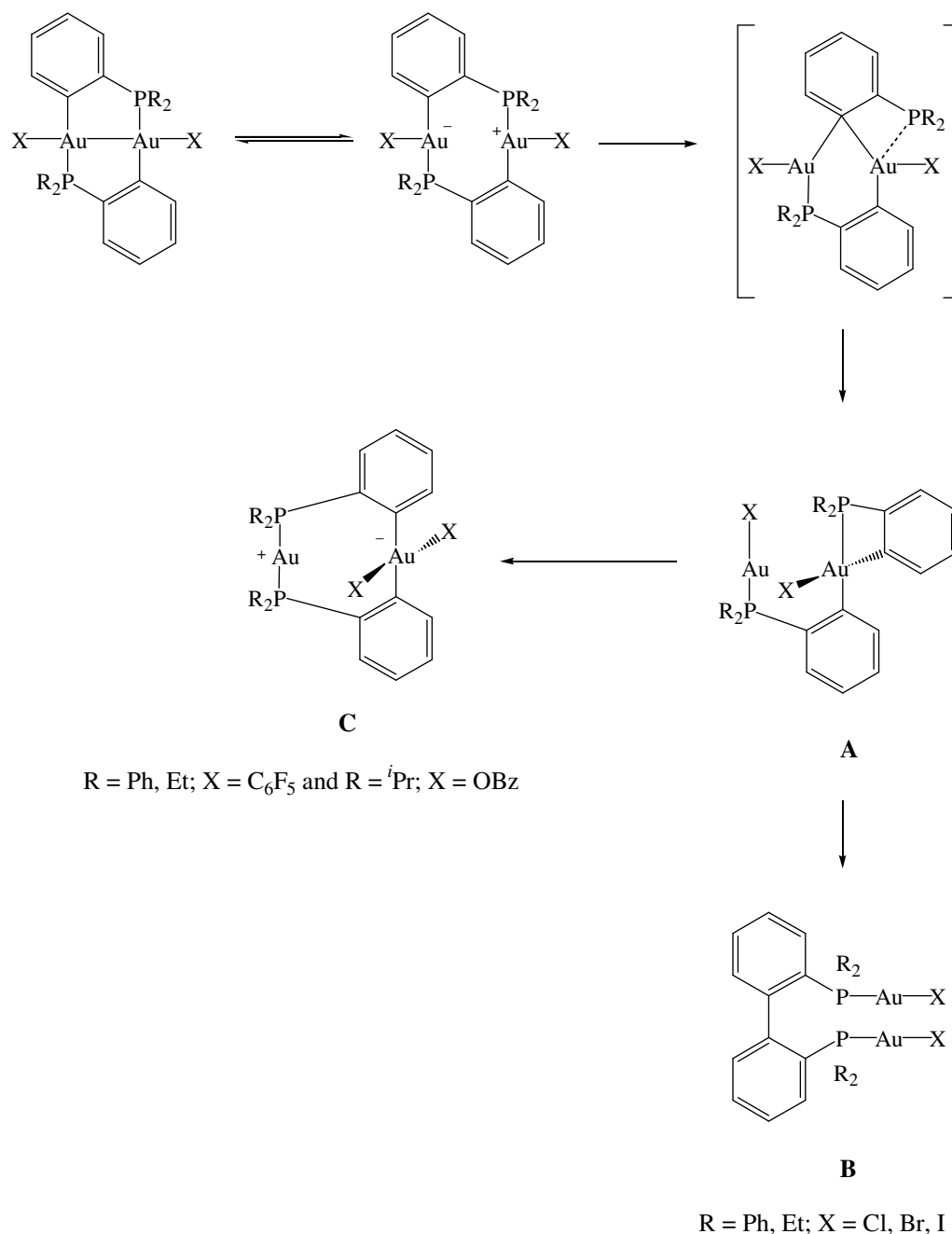


**Scheme 18. Oxidative addition reactions of gold(I) and isomerisation reactions of gold(III) compounds containing 2- $\text{C}_6\text{H}_4\text{PPh}_2$  and  $\text{C}_6\text{H}_3\text{-5-Me-2-PPh}_2$  ligands.**



**Scheme 19. Isomerisation reactions of gold(II) compounds containing 2-C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub> ligand.**

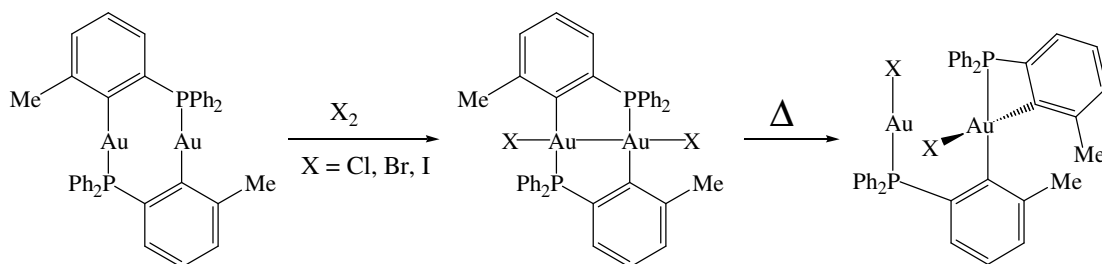
The main steps in the proposed pathway leading to the zwitterion and carbon-carbon coupled product (Scheme 20) are believed to involve a  $\sigma$ -aryl migration of the bridging ligand and isomerisation of the digold(II) compound to give a gold(I)-gold(III) species (**A**), which can either undergo reductive elimination at the gold(III) centre to give the C-C coupled product (**B**) or migration of phosphorus donor ligand and X to give the zwitterionic compound (**C**).<sup>165</sup>



**Scheme 20. The main steps in the proposed pathway leading to the C-C coupled and zwitterionic compounds.**

The chemistry of the structurally similar digold(I) complex containing a methyl substituent *ortho* to the Au-C bond has also been investigated in detail. The dinuclear complex [Au<sub>2</sub>(μ-C<sub>6</sub>H<sub>3</sub>-6-Me-2-PPh<sub>2</sub>)<sub>2</sub>] undergoes oxidative addition at the dimetal unit with an equivalent of halogens to give, initially, homodinuclear gold(II)-gold(II)

complexes that presumably possess a gold-gold single bond between the  $5d^9$  metal centres. Unlike the corresponding complexes containing the  $C_6H_3-5-Me-2-PPh_2$  or  $2-C_6H_4PPh_2$  ligands, the gold(II) complexes  $[Au_2X_2(\mu-C_6H_3-6-Me-2-PPh_2)_2]$  ( $X = Cl, Br, I$ ) do not undergo C-C coupling, but rearrange to give gold(I)-gold(III) complexes in which one of the cyclometallated ligands is chelated to the gold(III) atom (Scheme 21). The isomerisation reaction in the 6-methyl system is more rapid compared to the C-C coupling reaction in the 5-methyl and unsubstituted systems and the symmetrical digold(II) complexes  $[Au_2X_2(\mu-C_6H_3-6-Me-2-PPh_2)_2]$  can only be isolated at low temperature.<sup>166</sup>

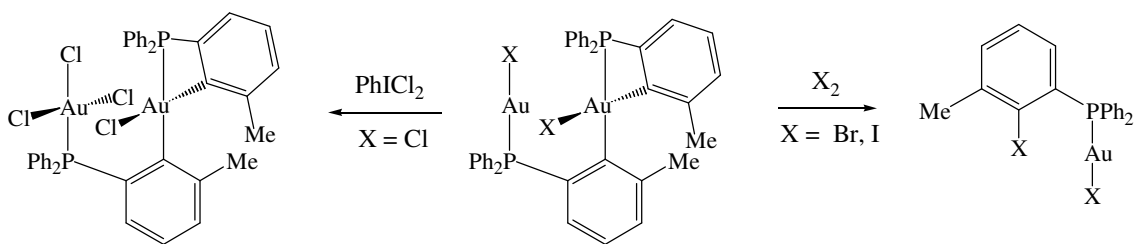


**Scheme 21. Oxidative addition reactions of gold(I) and isomerisation reactions of gold(II) compounds containing the  $C_6H_3-6-Me-2-PPh_2$  ligand.**

Based on theoretical calculations, these differences in reactivity have been attributed to steric repulsion between the 6-methyl substituents and the ligands in the axial positions, which destabilises the symmetrical dihalodigold(II) complexes in favour of their unsymmetrical gold(I)-gold(III) isomers.<sup>186</sup>

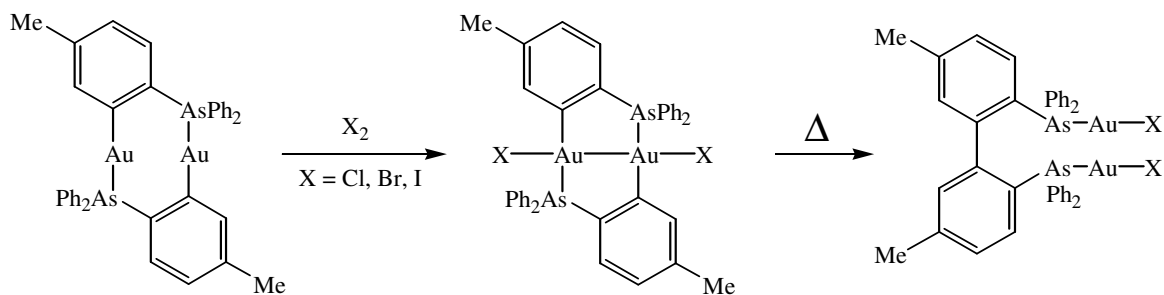
The heterovalent complexes  $[X Au(\mu-C_6H_3-6-Me-2-PPh_2)(\kappa^2-C_6H_3-6-Me-2-PPh_2) Au X]$  ( $X = Cl, Br, I$ ) can potentially be further oxidised at the Au(I) centre; however, the resulting products depend on the halogen used:  $[Cl Au(\mu-C_6H_3-6-Me-2-PPh_2)(\kappa^2-C_6H_3-$

6-Me-2-PPh<sub>2</sub>)AuCl] reacts with one equivalent of PhICl<sub>2</sub> to form the digold(III) complex [Cl<sub>3</sub>Au(μ-C<sub>6</sub>H<sub>3</sub>-6-Me-2-PPh<sub>2</sub>)(κ<sup>2</sup>-C<sub>6</sub>H<sub>3</sub>-6-Me-2-PPh<sub>2</sub>)AuCl] in which the four-membered ring remains intact. In contrast, the reaction of [XAu(μ-C<sub>6</sub>H<sub>3</sub>-6-Me-2-PPh<sub>2</sub>)(κ<sup>2</sup>-C<sub>6</sub>H<sub>3</sub>-6-Me-2-PPh<sub>2</sub>)AuX] (X = Br, I) with Br<sub>2</sub> or I<sub>2</sub> give the mononuclear Au(I) complexes [AuX(2-X-3-MeC<sub>6</sub>H<sub>3</sub>PPh<sub>2</sub>)] (X = Br, I), derived by cleavage of the two Au-C bonds (Scheme 22).<sup>166</sup>



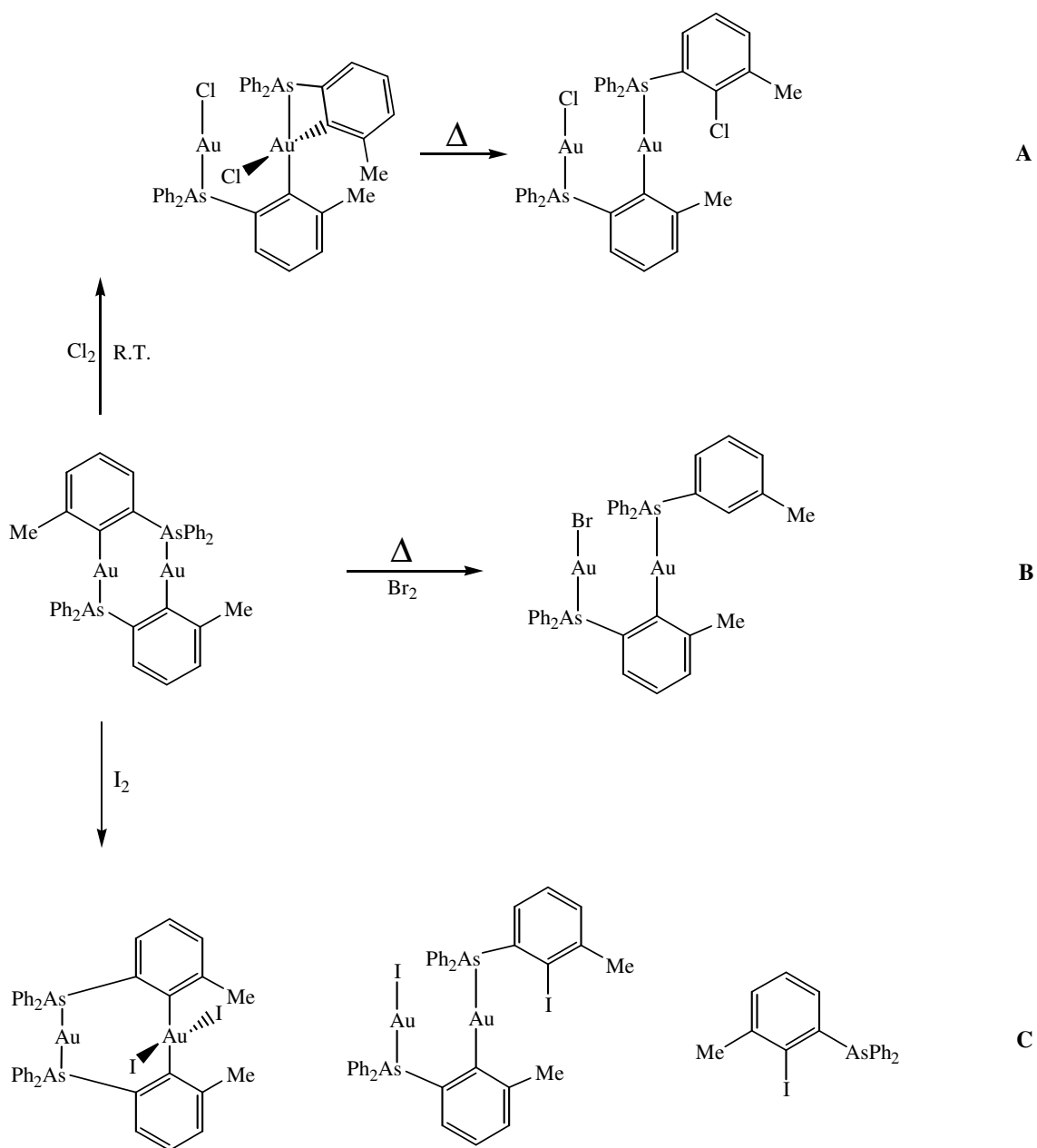
**Scheme 22. Reaction of the 6-methyl substituted, heterovalent gold(I)-gold(III) complexes [XAu(μ-C<sub>6</sub>H<sub>3</sub>-6-Me-2-PPh<sub>2</sub>)(κ<sup>2</sup>-C<sub>6</sub>H<sub>3</sub>-6-Me-2-PPh<sub>2</sub>)AuX] (X = Cl, Br, I) with halogens.**

The chemistry and reactivity of the arsenic-containing complexes of the type [Au<sub>2</sub>(μ-C<sub>6</sub>H<sub>3</sub>-*n*-Me-2-AsPh<sub>2</sub>)<sub>2</sub>] (*n* = 5, 6) have also been investigated.<sup>182</sup> The 5-methyl substituted complex behaves similarly to its phosphorus analogue. The complex undergoes addition of halogens to give the symmetric dihalodigold(II) complexes, which, on heating, isomerise to the expected carbon-carbon coupled products (Scheme 23).



**Scheme 23. Oxidative addition reactions of gold(I) and isomerisation reactions of gold(II) compounds containing the C<sub>6</sub>H<sub>3</sub>-5-Me-2-AsPh<sub>2</sub> ligand.**

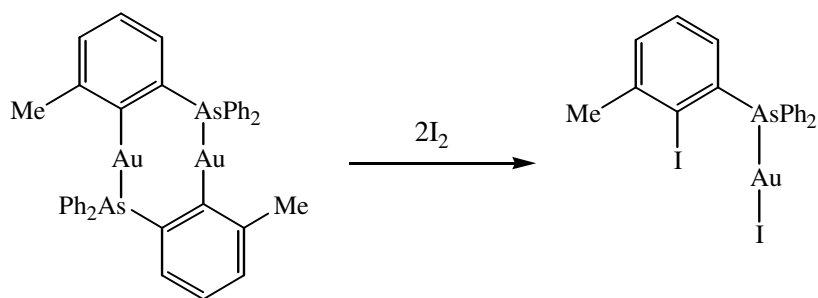
In contrast, the 6-methyl derivative exhibits complex behaviour when treated with halogens, forming different products depending on the halogen used (Scheme 24). Oxidative addition with chlorine at room temperature gives the mixed-valence Au(I)-Au(III) complex, similar to its phosphorus analogue. Unlike its phosphorus analogue, however, the heterovalent gold(I)-gold(III) complex rearranges further by reductive elimination at the Au(III) centre, forming the digold(I) product [ClAu( $\mu$ -C<sub>6</sub>H<sub>3</sub>-6-Me-2-AsPh<sub>2</sub>)Au(2-Cl-3-MeC<sub>6</sub>H<sub>3</sub>AsPh<sub>2</sub>)] (**A**, Scheme 24). Oxidative addition of bromine to [Au<sub>2</sub>( $\mu$ -C<sub>6</sub>H<sub>3</sub>-6-Me-2-AsPh<sub>2</sub>)<sub>2</sub>] does not give a pure product at room temperature; however, at 50 °C a gold(I) species can be isolated whose structure is similar to that resulting from the addition of chlorine, except that only one bromine atom is incorporated into the complex (**B**, Scheme 24). The reaction of the dimer with an equivalent of iodine forms a number of products. Together with elemental gold, three different compounds have been isolated; a zwitterionic Au(I)-Au(III) complex, the diiodo analogue of complex **A** above, and a free tertiary arsine (**C**, Scheme 24).<sup>182</sup>



**Scheme 24. Oxidative addition reactions of gold(I) and isomerisation reactions of gold(II) compound containing the  $C_6H_3-2-AsPh_2-6-Me$  ligand.**

Treatment of  $[Au_2(\mu-C_6H_3-6-Me-2-AsPh_2)_2]$  with two equivalents of iodine does not give a digold(III) addition product, but cleaves the Au-C bonds to give the mononuclear gold(I) complex  $[(2-I-3-MeC_6H_3)AsPh_2]AuI$  (Scheme 25).





**Scheme 25.** Reaction of  $[\text{Au}_2(\mu\text{-C}_6\text{H}_3\text{-6-Me-2-AsPh}_2)_2]$  with two equivalents of iodine.

### ***1.5 Dinuclear complexes containing two different bridging or anionic ligands.***

#### ***1.5.1 Scrambling reactions of the bridging ligands in digold(I) complexes.***

Heterobridged digold(I) compounds are generally formed, and can often be isolated, by mixing equimolar amounts of two different homobridged complexes containing bidentate ligands, bis(ylide) ligands or cyclometallated ligands in a suitable solvent. For example, the ligands undergo scrambling after 2 hours when dichloromethane solutions of  $[\text{Au}_2(\mu\text{-2-C}_6\text{H}_4\text{PPh}_2)_2]$  and  $[\text{Au}_2(\mu\text{-2-C}_6\text{H}_4\text{PEt}_2)_2]$  are mixed; the resulting scrambled product, which is in equilibrium with its precursors and cannot be isolated, shows an AB quartet ( $\delta_{\text{A}} = 36.7$ ,  $\delta_{\text{B}} = 35.0$ ,  $J_{\text{AB}} = 19.5$  Hz) in its  $^{31}\text{P}$  NMR spectrum.<sup>187</sup> Table 6 shows examples of isolated heterobridged digold(I) complexes together with their gold-gold distances.

**Table 6. Heterobridged dinuclear Au(I) compounds of the type [Au<sub>2</sub>(μ-L)(μ-L')] (L ≠ L').**

<b>L</b>	<b>L'</b>	<b>Au-Au(Å)</b>	<b>Ref.</b>
(CH <sub>2</sub> ) <sub>2</sub> P <sup>t</sup> Bu <sub>2</sub>	dppm-H <sup>-</sup>	2.967(1)	104
(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub>	Et <sub>2</sub> NCS <sub>2</sub> <sup>-</sup>	2.868(1)	188
(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub>	<sup>i</sup> PrOCS <sub>2</sub> <sup>-</sup>	2.8809(9)	189
(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub>	2-SC <sub>5</sub> H <sub>4</sub> N <sup>-</sup>	2.8623(7)	190
S(CH <sub>2</sub> ) <sub>3</sub> S <sup>2-</sup>	dppm	3.128(1)	191
(CN) <sub>2</sub> C <sub>2</sub> S <sub>2</sub> <sup>2-</sup>	dppe	2.867(1)	192
(CN) <sub>2</sub> C <sub>2</sub> S <sub>2</sub> <sup>2-</sup>	dmpm	2.925(3)	193
(C <sub>6</sub> H <sub>3</sub> -2-PPh <sub>2</sub> -5-Me) <sup>-</sup>	S <sub>2</sub> CN <sup>n</sup> Bu <sub>2</sub> <sup>-</sup>	2.8331(3), 2.8243(3) <sup>a</sup>	194

<sup>a</sup> Au...Au distances for two independent molecules.

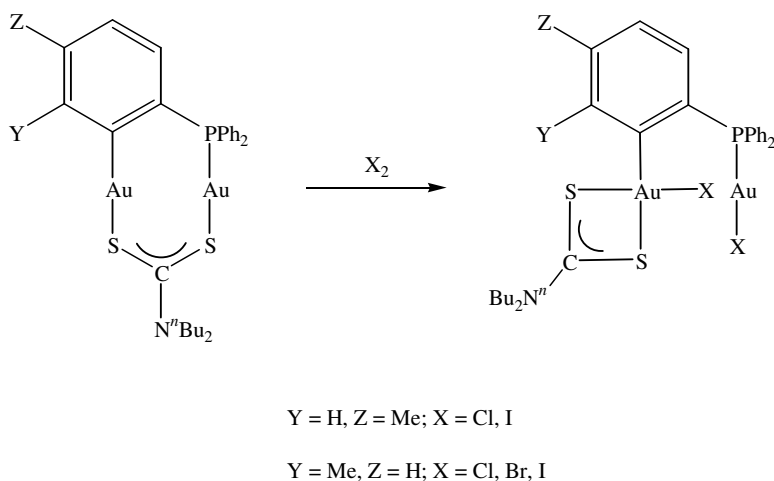
Like their homobridged counterparts, heterobridged dinuclear Au(I) compounds undergo oxidative addition with halogens to give gold-gold bonded dinuclear Au(II) compounds. Similar reactions with pseudo-halogens and alkyl halides have not been reported for these complexes. Examples of heterobridged dinuclear Au(II) compounds are shown in Table 7. The Au-Au separation decreases in these complexes by *ca.* 0.3-0.4 Å compared with the corresponding digold(I) precursors, consistent with the formation of a direct metal-metal bond.

**Table 7. Heterobridged dinuclear Au(II) compounds of the type [Au<sub>2</sub>X<sub>2</sub>(μ-L)(μ-L')] (L ≠ L').**

<b>L</b>	<b>L'</b>	<b>X</b>	<b>Au-Au(Å)</b>	<b>Ref.</b>
(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub>	dppm	Br	2.5653(10)	195
(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub>	MeOCS <sub>2</sub> <sup>-</sup>	Br	2.5660(10)	189
(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub>	2-SC <sub>5</sub> H <sub>4</sub> N <sup>-</sup>	Br	2.548(4)	190

Treatment of the heterobridged gold(I) complexes [Au<sub>2</sub>(μ-C<sub>6</sub>H<sub>3</sub>-2-PPh<sub>2</sub>-*n*-Me)(μ-S<sub>2</sub>CN<sup>n</sup>Bu<sub>2</sub>)<sub>2</sub>] (*n* = 5, 6) with one equivalent of PhICl<sub>2</sub>, Br<sub>2</sub> or I<sub>2</sub> in dichloromethane at

-70 °C gives deep orange or red solutions which are presumably the dihalodigold(II) complexes. The coloured solutions fade on warming to room temperature to form the heterovalent gold(I)-gold(III) compounds  $[\text{XAu}^{\text{I}}(\mu\text{-C}_6\text{H}_3\text{-}n\text{-Me-2-PPh}_2)\text{Au}^{\text{III}}\text{X}(\kappa^2\text{-S}_2\text{CN}^n\text{Bu}_2)]$  [ $n = 5, \text{X} = \text{Cl, I}; n = 6, \text{X} = \text{Cl, Br, I}$ ] (Scheme 26).<sup>194</sup>



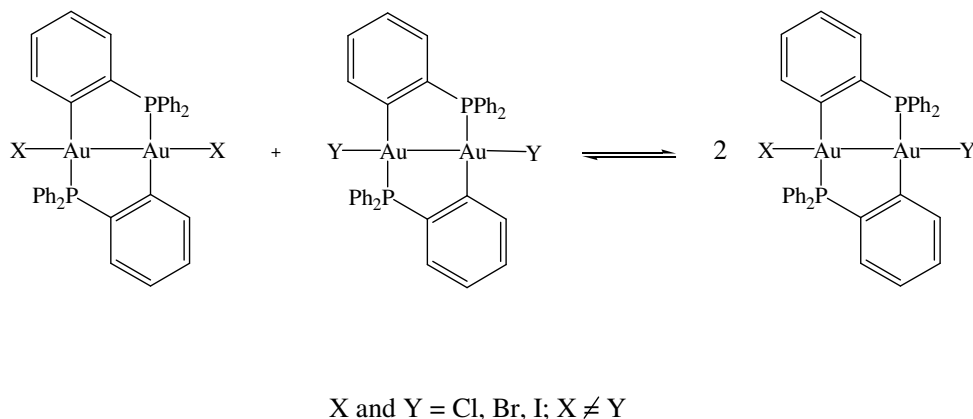
**Scheme 26.** Oxidative addition of heterobridged complexes  $[\text{Au}_2(\mu\text{-C}_6\text{H}_3\text{-}n\text{-Me-2-PPh}_2)(\mu\text{-S}_2\text{CN}^n\text{Bu}_2)]$  ( $n = 5, 6$ ).

### 1.5.2 Ligand scrambling reactions in digold(II) complexes.

As in the digold(I) chemistry above, the bridging ligands in the digold(II) complexes have also been observed to undergo scrambling reactions. The immediate formation of the mixed-ligand species  $[\text{Au}_2\text{X}_2(\mu\text{-2-C}_6\text{H}_4\text{PPh}_2)(\mu\text{-2-C}_6\text{H}_4\text{PEt}_2)]$  ( $\text{X} = \text{I}$ ), resulting from transfer of the  $2\text{-C}_6\text{H}_4\text{PR}_2$  ( $\text{R} = \text{Ph, Et}$ ) between the gold(II) centres of  $[\text{Au}_2\text{X}_2(\mu\text{-2-C}_6\text{H}_4\text{PPh}_2)_2]$  and  $[\text{Au}_2\text{X}_2(\mu\text{-2-C}_6\text{H}_4\text{PEt}_2)_2]$  is evidenced by the appearance of an AB quartet in  $^{31}\text{P}$  NMR spectrum ( $\delta_{\text{A}} = -11.9, \delta_{\text{B}} = -13.3, J_{\text{AB}} = 73$  Hz). A similar exchange occurs within 1 hour for the bromo analogues ( $\text{X} = \text{Br}$ ) ( $\delta_{\text{A}} = -3.17, \delta_{\text{B}} = -4.31, J_{\text{AB}} = 73$  Hz) and over a period of 2 hours for the chloro analogues ( $\text{X} = \text{Cl}$ ), but in these cases,

the scrambling reaction is accompanied by rearrangement of the precursors and formation of C-C coupled products  $[\text{Au}_2\text{X}_2(\mu\text{-}2,2'\text{-Ph}_2\text{PC}_6\text{H}_4\text{C}_6\text{H}_4\text{PPh}_2)]$  ( $\text{X} = \text{Cl}, \text{Br}$ ) (see Scheme 18).

In addition to the scrambling reactions of the bridging ligands, the axial anionic ligands in the gold(II) complexes also undergo exchange reactions in solution. For example, mixing equimolar amounts of  $[\text{Au}_2\text{X}_2(\mu\text{-}2\text{-C}_6\text{H}_4\text{PPh}_2)_2]$  and  $[\text{Au}_2\text{Y}_2(\mu\text{-}2\text{-C}_6\text{H}_4\text{PPh}_2)_2]$  ( $\text{X}$  and  $\text{Y} = \text{Cl}, \text{Br}, \text{I}; \text{X} \neq \text{Y}$ ) gives an approximately statistical mixture of the two symmetrical parent complexes, together with the halide-scrambled product  $[\text{Au}_2\text{XY}(\mu\text{-}2\text{-C}_6\text{H}_4\text{PPh}_2)_2]$  (Scheme 27).<sup>165</sup> In the  $^{31}\text{P}$  NMR spectrum, the scrambled product shows an AB quartet ( $J_{\text{AB}}$  ca. 75 Hz) whose chemical shift lies between those of the symmetrical precursors.<sup>165</sup>



**Scheme 27. Exchange of the anionic ligands between cyclometallated gold(II) complexes.**

## ***1.6 Fluorocarbon metal compounds.***

It is well known that replacement of hydrogen atoms by halogen atoms (especially fluorine) in alkyl or aryl ligands often has a profound stabilising effect. Fluorocarbon-transition metal complexes typically more robust than their hydrocarbon analogues, exhibiting greater thermal stability; for example,  $[(C_2F_5)_2Fe(CO)_4]$  decomposes above 100 °C, but there is no evidence for the existence of its protio analogue;<sup>196</sup>  $[(CF_3)Co(CO)_4]$  does not decompose even at its boiling point (91 °C), while  $[(CH_3)Co(CO)_4]$  is stable only at subzero temperatures;<sup>197</sup>  $[Ag(C_6H_5)]$  decomposes at 74 °C,<sup>198</sup> whereas  $[Ag(C_6Cl_5)]$  decomposes at 102 °C.<sup>199</sup>

The enhanced stability of fluorocarbon-metal  $\sigma$ -bonds may be due to the greater electronegativity of the ligands and the increase in ionic-covalent resonance energy.<sup>200-203</sup> It has also been suggested that  $\pi$  back bonding from the metal centre to the  $\alpha$ -carbon of a fluoroalkyl ligand may be responsible for the increase of stability in this case.<sup>204</sup> Additional evidence of multiple bond character between a transition metal and a fluoroalkyl ligand comes from the observation that the metal-carbon bond lengths are often shorter for fluoroalkyl derivatives than for their hydrocarbyl analogues; for example the Au-C bond length of 2.045(4) Å in  $[Au(CF_3)PPh_3]$ <sup>205</sup> is shorter than that of 2.124(28) Å in  $[Au(CH_3)PPh_3]$ .<sup>206</sup> For fluoroaryl compounds, however, the evidence is much less clear. For example, there is no significant shortening of the Au-C bond length in  $[N(PPh_3)_2][Au(C_6F_5)_4]$ <sup>133</sup> [2.0835(av.) Å] compared to those in  $[NBu_4][Au(C_6H_5)_4]$  [2.032(av.) Å].<sup>207</sup>

It is also evident that many known transition metal-carbon  $\sigma$ -bonded complexes contain stabilising ligands, notably CO,  $PR_3$ , Cp, bipy or halides; examples include the complexes  $[CpFe(CO)_2(CH_3)]$ ,  $[(CH_3)Mn(CO)_5]$  and  $[PtMe_2(PR_3)_2]$ . These ligands

block the low energy decomposition pathways, such as  $\beta$ -elimination, which readily occur in the case of transition metal-alkyl complexes. This suggests that the increase in the stability of transition metal fluoroalkyl and fluoroaryl complexes may be due not only to higher thermodynamic stability but also to lower kinetic lability.

The metal-fluorocarbon  $\sigma$ -bond is also generally less reactive than metal-alkyl or -aryl bonds; the complex  $[\text{Mn}(\text{CH}_3)(\text{CO})_5]$  undergoes facile insertion of CO to give  $[\text{Mn}(\text{COCH}_3)(\text{CO})_5]$ , whereas  $[\text{Mn}(\text{CF}_3)(\text{CO})_5]$  is inert.<sup>208</sup> It has also been noted that fluorine-substituted ligands help to stabilise metal complexes in unusual oxidation states. For example,  $[\text{Au}_2(\text{C}_6\text{F}_5)_4(\text{tht})_2]$  is the first example of an unbridged gold complex containing an  $[\text{Au}_2]^{4+}$  core in which the metal atoms are not stabilised by any chelating ligands.<sup>209</sup>

A review of the chemistry and reactivity of perfluoroarylgold complexes has recently been reported, which highlights the higher thermodynamic and kinetic stability of fluoroaryl complexes compared to the stability of their corresponding phenyl derivatives.<sup>210</sup>

### **1.7 Research objectives.**

As summarised in section 1.4, recent studies on gold(I) complexes of the type  $[\text{Au}_2(\mu\text{-C}_6\text{H}_3\text{-}n\text{-Me-2-PPh}_2)_2]$  ( $n = 5, 6$ ) have shown that the position of methyl substitution can play an important role in the chemistry and reactivity. The effect of changing the donor atoms has also been investigated by exploring the chemistry of  $[\text{Au}_2(\mu\text{-C}_6\text{H}_3\text{-}n\text{-Me-2-AsPh}_2)_2]$  ( $n = 5, 6$ ).

In view of the rich and varied chemistry that can result from subtle changes in the ligand framework, we were interested in preparing dinuclear gold complexes containing the 2- $\text{C}_6\text{F}_4\text{PPh}_2$  fragment. The stabilising effect of this ligand has already enabled the preparation of mononuclear bis(chelate) complexes of nickel(II) and palladium(II),<sup>211</sup> for which there are no analogous protio species so far known. The bis(chelate) complexes of nickel(II) and palladium(II) containing 2- $\text{C}_6\text{F}_4\text{PPh}_2$  remain unchanged in refluxing toluene; chelate ring appears to be quite stable and conversion to bridging mode is unfavourable. It also has been shown that the bis(chelate) complex of platinum(II)  $[\text{Pt}(\kappa^2\text{-2-C}_6\text{H}_4\text{PPh}_2)_2]$  forms dinuclear species  $[\text{Pt}_2(\mu\text{-C}_6\text{H}_4\text{-2-PPh}_2)(\kappa^2\text{-2-C}_6\text{H}_4\text{PPh}_2)_2]$  on heating, whilst the perfluoro analogue undergoes only *cis-trans* isomerisation and is stable with respect to the dimer formation.<sup>211</sup>

With all these results in mind, we were interested to see what effects this ligand would have on the reactivity of cyclometallated gold complexes.

## ***Chapter 2. Preparation and properties of a cycloaurated dinuclear gold(I) compound containing the 2-C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub> ligand.***

### ***2.1 Ligand preparation.***

#### ***2.1.1 (2-Bromoaryl)diphenylphosphine ligands.***

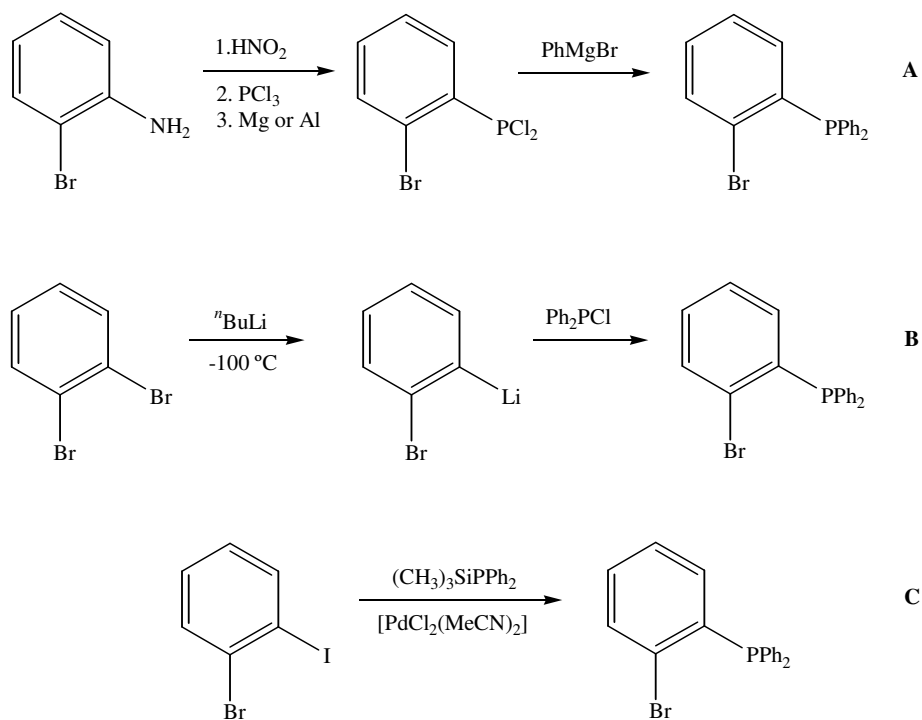
(2-Bromophenyl)diphenylphosphine is a versatile precursor for the introduction of the [2-C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>]<sup>-</sup> unit into organometallic complexes. For example, the C-Br bond can oxidatively add to [Pd(dba)<sub>2</sub>] to give the monomeric [PdBr(κ<sup>2</sup>-2-C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)(2-BrC<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)] and tetrameric [Pd(μ-Br)(μ-2-C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)]<sub>4</sub> complexes, depending on the ligand:metal ratio.<sup>158</sup> (2-Bromophenyl)diphenylphosphine also undergoes facile halogen/metal exchange with <sup>n</sup>BuLi to give the organolithium reagent 2-LiC<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>. Treatment of this reagent with a suitable metal halide complex has been used to prepare cyclometallated complexes of gold and platinum.<sup>165,212</sup> There are also examples where



(2-bromophenyl)diphenylphosphine acts as an aromatic  $\pi$ -donor ligand,<sup>213</sup> and as a chelate ligand by coordination through the phosphorus and bromine atoms.<sup>214-217</sup>

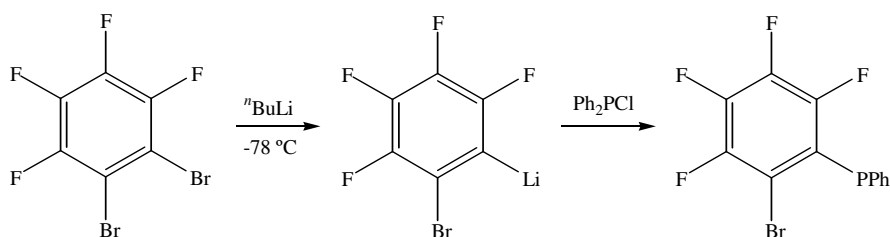
The preparation of (2-bromophenyl)diphenylphosphine has been reported by a number of literature methods:

1. The reaction of the diazonium salt formed from 2-bromoaniline with phosphorus trichloride and subsequent reduction with magnesium or aluminium to give (2-bromophenyl)dichlorophosphine, which is then treated with phenylmagnesium bromide (**A**, Scheme 28).<sup>218</sup>
2. The low temperature mono-lithiation of 1,2-dibromobenzene followed by reaction with chlorodiphenylphosphine (**B**, Scheme 28).<sup>219</sup>
3. The palladium-catalysed coupling reaction of 1-bromo-2-iodobenzene with trimethylsilyldiphenylphosphine (**C**, Scheme 28).<sup>220</sup>



**Scheme 28. Methods for the preparation of (2-bromophenyl)diphenylphosphine.**

For the preparation of the desired fluorinated phosphine ligand, (2-bromotetrafluorophenyl)diphenylphosphine, only the analogous procedure to that of method 2 has been reported in the literature, although full characterisation is lacking.<sup>221</sup> Thus, treatment of an ether solution of the commercially available 1,2-dibromotetrafluorobenzene with <sup>n</sup>BuLi at -78 °C gave the corresponding aryllithium reagent. This was subsequently treated with chlorodiphenylphosphine to give (2-bromotetrafluorophenyl)diphenylphosphine as a colourless solid in *ca.* 80% yield (Scheme 29).

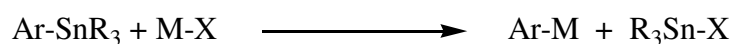


**Scheme 29. Synthesis of (2-bromotetrafluorophenyl)diphenylphosphine.**

The ESI-mass spectrum of (2-bromotetrafluorophenyl)diphenylphosphine displayed a  $[M+H]^+$  peak and the <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra contained the expected aromatic multiplets. The <sup>31</sup>P NMR spectrum showed a single resonance centred at  $\delta$  -1.58, split by coupling with three <sup>19</sup>F nuclei into a doublet of doublets of doublets with separations of 4.4, 10.4 and 20.5 Hz. The <sup>19</sup>F NMR spectrum consisted of the expected four multiplets in the region  $\delta$  -121 to -155. No attempt was made to extract the <sup>19</sup>F-<sup>19</sup>F and <sup>31</sup>P-<sup>19</sup>F coupling constants from the data.

### 2.1.2 {2-(Trimethylstannyl)tetrafluorophenyl}diphenylphosphine.

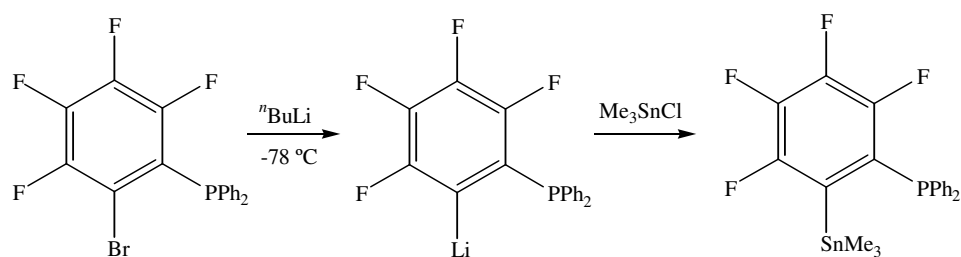
Although transmetallation reactions for the formation of transition metal-carbon  $\sigma$ -bonds generally employ Grignard or organolithium reagents, aryl transfer from (trialkyl)aryltin reagents provides an alternative method under milder reaction conditions. Thus, treating a metal halide or triflate in an inert solvent such as  $\text{CH}_2\text{Cl}_2$  with a (trialkyl)aryltin reagent usually preferentially transfers the aryl group from the tin to the metal atom, with elimination of trialkyltin halide or triflate (Scheme 30). These tin reagents have been used to prepare a number of platinum,<sup>222-239</sup> and to a lesser extent, palladium,<sup>240,241</sup> rhodium,<sup>241-243</sup> and gold complexes.<sup>244-246</sup> The step-wise addition of one and two aryl groups to platinum has also been reported.<sup>226,231</sup>



Ar = aryl  
R = alkyl  
M = transition metal  
X = halide, triflate

**Scheme 30. Aryl transfer from a (trialkyl)aryltin reagent to a transition metal.**

When an ether solution of 2-bromotetrafluorophenylphosphine, cooled to  $-78\text{ }^\circ\text{C}$ , was treated sequentially with  $^n\text{BuLi}$  and  $\text{Me}_3\text{SnCl}$ , {2-(trimethylstannyl)tetrafluorophenyl}diphenylphosphine was isolated as a colourless solid in *ca.* 87% yield (Scheme 31).



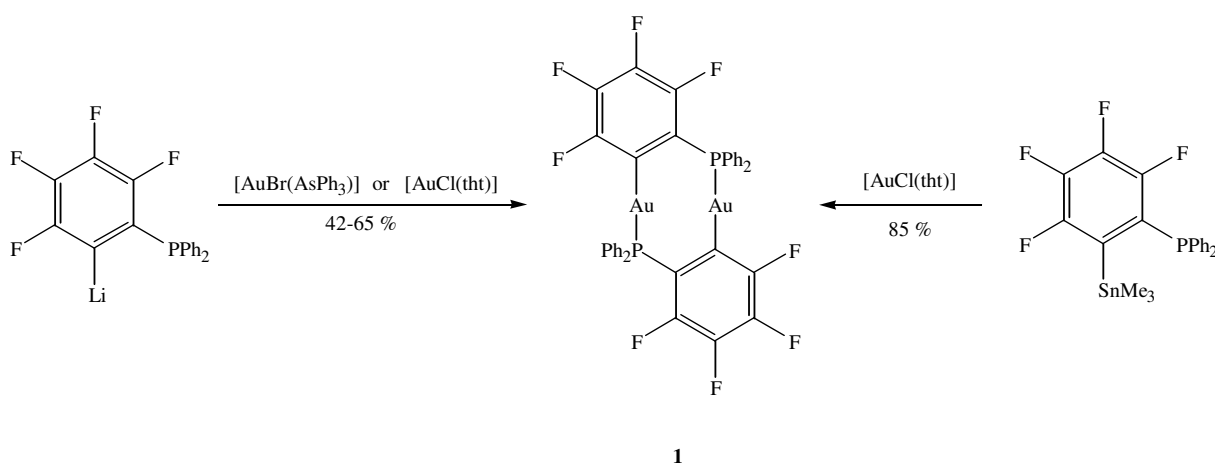
**Scheme 31. Synthesis of {2-(trimethylstannyl)tetrafluorophenyl}diphenylphosphine.**

The compound gave satisfactory elemental analysis and the ESI-mass spectrum showed a  $[M+H]^+$  peak. The  $^1\text{H}$  NMR spectrum showed in addition to the expected aromatic multiplets, a singlet resonance at  $\delta$  0.5 due to the  $\text{SnMe}_3$  group. The  $^{13}\text{C}$  NMR spectrum showed the expected aromatic multiplets together with the  $\text{SnMe}_3$  resonance at  $\delta$  -3.9, split into a doublet of doublets ( $J = 4.5, 13.3$  Hz), presumably arising from three-bond coupling to the *ortho* fluorine and phosphorus atoms on the aromatic ring. Equally spaced about the main resonance were satellites arising from the  $^{117}\text{Sn}$  and  $^{119}\text{Sn}$  isotopomers ( $J = 361$  and  $381$  Hz). The  $^{31}\text{P}$  NMR spectrum showed a doublet of multiplets centred at  $\delta$  -0.2 with poorly resolved  $^{117/119}\text{Sn}$  coupling of *ca.* 29 Hz.

## 2.2 Preparation of the cycloaurated dinuclear complex $[\text{Au}_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$ .

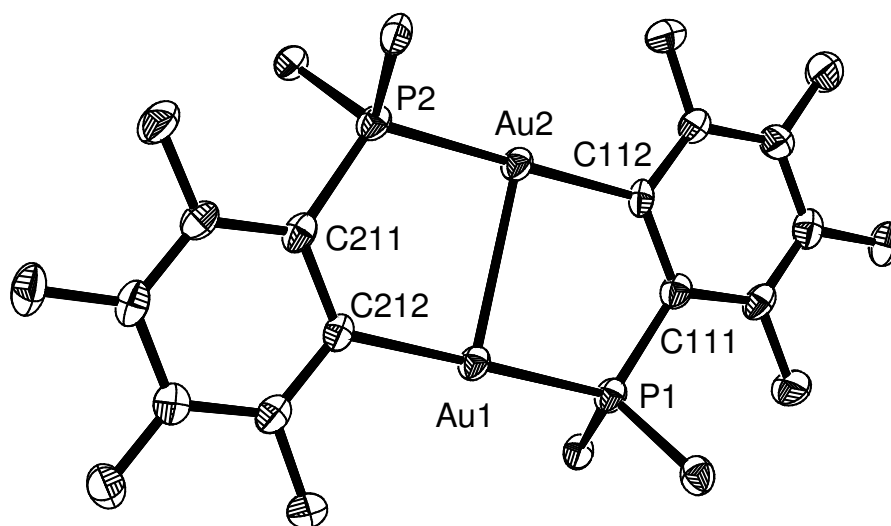
As previously mentioned (Section 1.4 in Chapter 1), transmetalation using aryl lithium reagents has provided a route to dinuclear, cyclometallated gold(I) complexes. Thus, treatment of  $2\text{-BrC}_6\text{F}_4\text{PPh}_2$  with  $n\text{-BuLi}$  gives  $2\text{-LiC}_6\text{F}_4\text{PPh}_2$ , which reacts with  $[\text{AuBr}(\text{AsPh}_3)]$  or  $[\text{AuCl}(\text{tht})]$  to give the colourless cycloaurated complex  $[\text{Au}_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$  (**1**) in *ca.* 42-65% yield (Scheme 32). Alternatively, refluxing a dichloromethane solution of {2-(trimethylstannyl)tetrafluorophenyl}diphenylphosphine

and [AuCl(tht)] for 24 hours gave **1** in 85% yield. During initial attempts to select the most suitable gold(I) precursor for the preparation of **1** a colourless solid was isolated from the reaction of [AuBr(PEt<sub>3</sub>)] with 2-LiC<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub>. This solid showed four peaks at  $\delta$  23.5, 38.0, 47.6 and 42.3 in its <sup>31</sup>P NMR spectrum, the last resonance being assigned to the cyclometallated digold(I) complex **1**; however, the identity of the other components could not be established.



**Scheme 32. Preparation of the cycloaurated gold(I) dimer [Au<sub>2</sub>( $\mu$ -2-C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>] (**1**).**

Compound **1** is poorly soluble in halogenated and aromatic solvents. The positive ion ESI-mass spectrum of **1** showed the expected parent-ion peak and the <sup>31</sup>P NMR spectrum showed a singlet at  $\delta$  42.7, *ca.* 7 ppm downfield from that of the protio analogue [Au<sub>2</sub>( $\mu$ -2-C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>]. Close examination of this resonance suggests that it is a multiplet with poorly resolved <sup>31</sup>P-<sup>19</sup>F coupling. The <sup>19</sup>F NMR spectrum showed four equally intense multiplets in the expected range. The dinuclear structure of **1**, which has been confirmed by an X-ray structural analysis, is similar to those of the gold complexes containing the C<sub>6</sub>H<sub>3</sub>-6-Me-2-PPh<sub>2</sub> and 2-C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub> moieties.<sup>166,181</sup> The molecular structure of **1**, is shown in Figure 17; selected bond distances and angles are listed in Table 8.



**Figure 17. Molecular structure of  $[\text{Au}_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$  (**1**). Ellipsoids show 30% probability levels and hydrogen atoms have been omitted for clarity. The phenyl rings of the  $\text{PPh}_2$  groups only show the *ipso* carbons.**

The structure of **1** consists of two gold(I) atoms linearly coordinated by a pair of bridging *ortho*-metallated 2- $\text{C}_6\text{F}_4\text{PPh}_2$  ligands in a head-to-tail arrangement. The  $\text{Au}\cdots\text{Au}$  separation [2.8201(4) Å] is slightly less than that in the protio analogue [2.8594(3) Å],<sup>181</sup> both distances being suggestive of an aurophilic interaction. The Au-P [2.2772(19) Å, 2.2842(19) Å] and Au-C [2.057(7) Å, 2.059(7) Å] distances are similar to those in  $[\text{Au}(\text{C}_6\text{F}_5)(\text{PPh}_3)]$  [2.27(1) Å and 2.07(2) Å, respectively],<sup>247</sup> and also agree well with those reported for the protio analogue [2.300(1) Å and 2.056(3) Å, respectively].<sup>181</sup> The Au-C bond lengths in **1** are also similar to those of 2.078(2) Å and 2.110(2) Å observed in the tetrahydrothiophene complex  $[\text{Au}_2(\text{C}_6\text{F}_5)_4(\text{tht})_2]$ .<sup>209</sup> A comparison of the Au-C bond lengths in the complexes  $[\text{Au}_2(\mu\text{-}2\text{-C}_6\text{X}_4\text{PPh}_2)_2]$  (X = H, F) does not suggest any strengthening of the metal-carbon  $\sigma$ -bonds as a result of the substitution of hydrogen by fluorine substituents.

In **1**, the Au atoms display almost perfect linear coordination with a P-Au-C angle of 177.9(2)°; the corresponding angles in the protio analogue deviate slightly more from linearity [172.8(1)°], presumably to accommodate the greater Au···Au separation.

**Table 8. Selected bond distances (Å) and angles (°) in [Au<sub>2</sub>(μ-2-C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>] (**1**).**

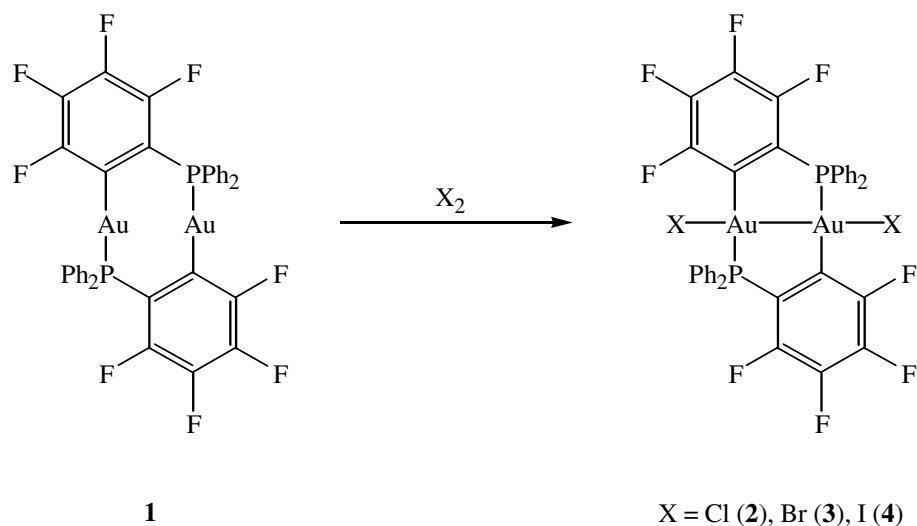
Au(1)–Au(2)	2.8201(4)		
Au(1)–P(1)	2.2772(19)	Au(2)–P(2)	2.2842(19)
Au(1)–C(212)	2.057(7)	Au(2)–C(112)	2.059(7)
P(1)–C(111)	1.817(8)	P(2)–C(211)	1.836(8)
Au(2)–Au(1)–P(1)	86.58(5)	Au(1)–Au(2)–P(2)	86.78(5)
Au(1)–C(212)–C(211)	125.0(5)	Au(2)–C(112)–C(111)	124.4(5)
Au(2)–Au(1)–C(212)	93.6(2)	Au(1)–Au(2)–C(112)	93.5(2)
P(1)–Au(1)–C(212)	176.7(2)	P(2)–Au(2)–C(112)	177.9(2)
Au(1)–P(1)–C(111)	114.4(2)	Au(2)–P(2)–C(211)	114.2(2)

### ***2.3 Oxidative addition reactions of the cycloaurated gold(I) compound***

#### ***[Au<sub>2</sub>(μ-2-C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>].***

##### ***2.3.1 Reactions with halogens and attempted reaction with dibenzoyl peroxide.***

Treatment of a dichloromethane solution of **1** with one equivalent of Cl<sub>2</sub> (derived from PhICl<sub>2</sub>), Br<sub>2</sub> and I<sub>2</sub> at -78 °C gave the metal-metal-bonded dihalodigold(II) complexes, [Au<sub>2</sub>X<sub>2</sub>(μ-2-C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>] [X = Cl (**2**), Br (**3**), I (**4**)], which were isolated in 60-80% yields (Scheme 33). The iodide is red, the bromide is orange and the chloride is yellow.



**Scheme 33. Oxidative addition reactions of  $[\text{Au}_2(\mu\text{-2-C}_6\text{F}_4\text{PPh}_2)_2]$  (**1**).**

The bromo and iodo complexes (**3** and **4** respectively) can also be made by metathetical reactions of **2** with the appropriate sodium or lithium salts. Both methods for preparing the iodide complex **4** failed to give a pure product. The expected diiododigold(II) complex was always the major product (*ca.* 80%), together with lesser amounts of unidentified products whose  $^{31}\text{P}$  NMR chemical shifts appear at  $\delta$  5 and  $\delta$  31. However, it was possible to select an X-ray quality crystal of **4** from the impure solid.

The  $^{31}\text{P}$  NMR spectra of the complexes **2-4** each show a single resonance in the region  $\delta$  -18 to -2, well removed from the chemical shift of the gold(I) dimer starting material. The  $^{31}\text{P}$  NMR chemical shifts are shifted *ca.* 4 ppm upfield from those of their protio analogues and the shielding increases in the order  $\text{I} > \text{Br} > \text{Cl}$ . The  $^{31}\text{P}$  NMR spectroscopic data for complexes **2-4**, together with that for the parent gold(I) dimer **1**, are shown in Table 9. The ESI-mass spectra of **2-4** each show a peak corresponding to the  $[\text{M-halide}]^+$  ion. The far-IR spectra of **2** and **3** show bands due to Au-Cl and Au-Br stretching vibrations at 288 and 199  $\text{cm}^{-1}$ , respectively, which are similar to those

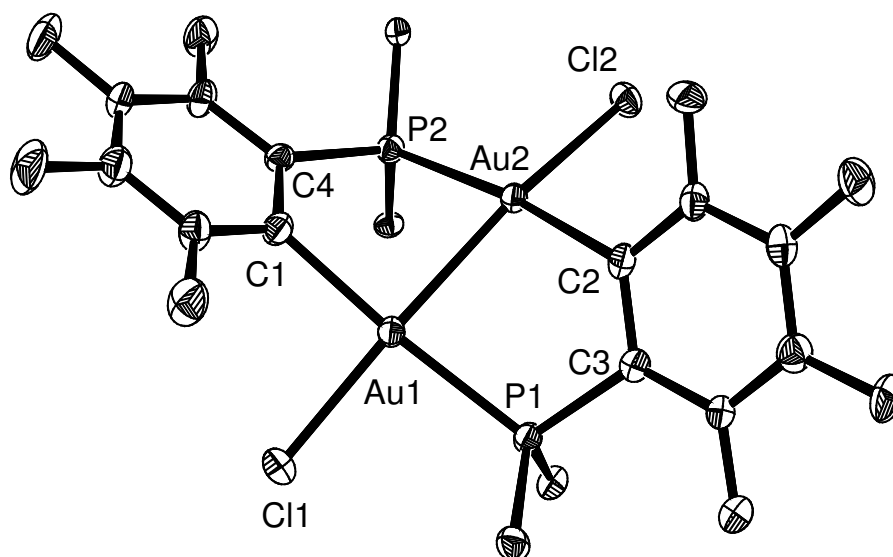


observed in their protio analogues  $[\text{Au}_2\text{X}_2(\mu\text{-2-C}_6\text{H}_4\text{PPh}_2)_2]$  ( $\text{X} = \text{Cl}$ , 278 vs/261  $\text{cm}^{-1}$ ;  $\text{Br}$ , 190  $\text{cm}^{-1}$ ),<sup>165</sup> and the Au(II) bis(ylide) complexes  $[\text{Au}_2\text{X}_2\{\mu\text{-(CH}_2)_2\text{PPh}_2\}_2]$  ( $\text{X} = \text{Cl}$ , 293  $\text{cm}^{-1}$ ;  $\text{Br}$ , 220  $\text{cm}^{-1}$ ).<sup>248</sup>

**Table 9.** <sup>31</sup>P NMR data for digold(I) and digold(II) compounds.

<b>Complex</b>	<b>Au oxidation state</b>	<b><math>\delta_{\text{P}}</math> (<math>\text{C}_6\text{D}_6</math>)</b>
$[\text{Au}_2(\mu\text{-2-C}_6\text{F}_4\text{PPh}_2)_2]$ ( <b>1</b> )	I	42.7
$[\text{Au}_2\text{Cl}_2(\mu\text{-2-C}_6\text{F}_4\text{PPh}_2)_2]$ ( <b>2</b> )	II	-2.3
$[\text{Au}_2\text{Br}_2(\mu\text{-2-C}_6\text{F}_4\text{PPh}_2)_2]$ ( <b>3</b> )	II	-8.3
$[\text{Au}_2\text{I}_2(\mu\text{-2-C}_6\text{F}_4\text{PPh}_2)_2]$ ( <b>4</b> )	II	-17.2

The molecular structures of **2-4** have been determined by single-crystal X-ray diffraction studies. The structure of **2** is shown in Figure 18 and important bond lengths of **2-4** are summarised in Table 10.



**Figure 18. Molecular structure of  $[\text{Au}_2^{\text{II}}\text{Cl}_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$  (2). Ellipsoids show 30% probability levels and hydrogen atoms have been omitted for clarity. The phenyl rings of the  $\text{PPh}_2$  groups only show the *ipso* carbons.**

**Table 10. Selected bond distances (Å) and angles (°) in [Au<sub>2</sub>X<sub>2</sub>(μ-2-C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>] [X = Cl (**2**), Br (**3**), I (**4**)].**

	<b>2</b> (X = Cl)	<b>3</b> (X = Br)	<b>4</b> (X = I)
Au(1)–Au(2)	2.5416(4)	2.5510(3)	2.5685(2)
Au(1)–P(1)	2.3290(17)	2.3329(13)	2.3398(12)
Au(1)–C(1)	2.072(17)	2.066(5)	2.062(5)
Au(2)–X(2)	2.3749(17)	2.4968(6)	2.6747(4)
Au(2)–P(2)	2.3378(17)	2.3396(12)	2.3441(12)
Au(2)–C(2)	2.067(7)	2.064(5)	2.075(4)
Au(1)–X(1)	2.3615(18)	2.4878(6)	2.6778(4)
Au(2)–Au(1)–P(1)	85.76(5)	85.36(3)	84.50(3)
Au(1)–C(1)–C(4)	120.2(5)	120.3(4)	119.9(3)
Au(2)–Au(1)–C(1)	90.3(2)	90.10(15)	88.99(13)
P(1)–Au(1)–C(1)	175.3(2)	175.13(15)	173.30(13)
Au(1)–Au(2)–X(2)	166.75(5)	164.957(17)	167.992(12)
X(1)–Au(1)–C(1)	92.2(2)	91.97(15)	92.78(13)
Au(1)–Au(2)–P(2)	83.08(4)	82.77(3)	85.09(3)
Au(2)–C(2)–C(3)	121.3(5)	119.6(4)	119.5(3)
Au(1)–Au(2)–C(2)	90.09(19)	90.44(14)	89.12(12)
P(2)–Au(2)–C(2)	172.9(2)	173.09(15)	174.18(13)
Au(2)–Au(1)–X(1)	166.28(5)	164.393(17)	169.105(11)
X(2)–Au(2)–C(2)	93.0(2)	92.86(14)	92.63(12)

The structures of **2-4** each consist of two metal-metal-bonded gold(II) atoms bridged by a pair of ligands in a head-to-tail arrangement and also coordinated to a halogen atom affording a square planar geometry about each gold atom, similar to the analogous complexes which contain 2-C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub> and C<sub>6</sub>H<sub>3</sub>-2-PPh<sub>2</sub>-6-Me as bridging ligands.<sup>165,166</sup> The Au-Au separations are shorter in these complexes [2.5416(4) Å, 2.5510(3) Å and 2.5685(2) Å for **2**, **3** and **4**, respectively] compared to that in the parent dimer **1** [2.8201(4) Å], consistent with the formation of a formal metal-metal bond, and are

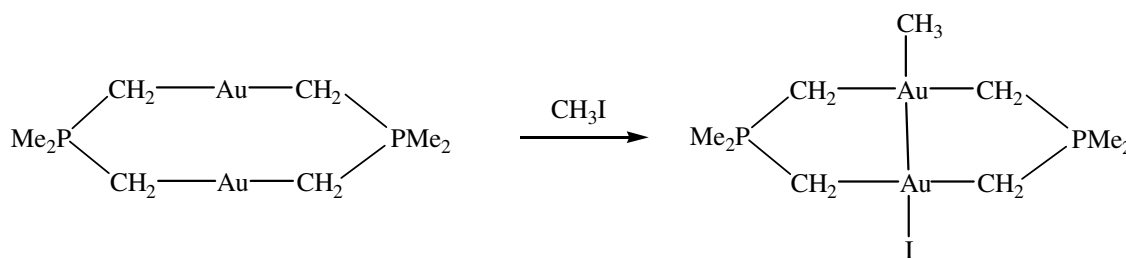
similar to that observed in  $[\text{Au}_2\text{I}_2(\mu\text{-}2\text{-C}_6\text{H}_4\text{PPh}_2)_2]$  [2.5898(6) Å and 2.5960(7) Å for two independent molecules].<sup>184</sup>

The Au-Cl distances in **2** [2.3615(18) Å and 2.3749(17) Å in the same molecule] are similar to those observed in the digold(II) bis(ylide) complex  $[\text{Au}_2\text{Cl}_2\{(\text{CH}_2)_2\text{PPh}_2\}_2]$  [2.388(8) Å].<sup>121</sup> The Au-Br distances of 2.4878(6) Å and 2.4968(6) Å in **3** are greater than those found in the mononuclear gold complex  $[\text{AuBr}_3(\text{PPh}_3)]$  [2.4170(4) Å, 2.4251(4) Å and 2.4554(4) Å],<sup>249</sup> consistent with a high *trans*-influence of the Au-Au bond. The Au-I distances of 2.6778(4) Å and 2.6747(4) Å in **4** are similar to that reported for its protio analogue [2.669(av.) Å].<sup>184</sup> In addition, the larger halogen atom causes a significant increase in the gold-halogen bond lengths in passing from X = Cl to X = I [2.3749(17) Å and 2.3615(18) Å in **2**, 2.4968(6) Å and 2.4878(6) Å in **3**, 2.6747(4) Å and 2.6778(4) Å in **4**]. The trend is similar to that observed in the mononuclear gold complexes  $[\text{AuX}(\text{PPh}_3)_2]$  [X = Cl, 2.533(4) Å; X = Br, 2.625(2) Å; X = I, 2.754(1) Å].<sup>250</sup> The C-Au-P angles [175.3(2)° and 172.9(2)° in **2**, 175.13(15)° and 173.09(15)° in **3**, 173.30(13)° and 174.18(13)° in **4**] are close to the expected 180°, whilst the X-Au-Au angles [166.28(5)° and 166.75(5)° in **2**, 164.393(17)° and 164.957(17)° in **3**, 169.105(11)° and 167.992(12)° in **4**] deviate more from linearity.

In contrast to the behaviour of  $[\text{Au}_2(\mu\text{-}2\text{-C}_6\text{H}_4\text{PPh}_2)_2]$ , complex **1** does not undergo oxidative addition of dibenzoyl peroxide to give  $[\text{Au}_2(\text{OCC}_6\text{H}_5)_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$ . Even after five days, only unchanged starting material could be recovered.

### 2.3.2 Attempted reaction with methyl iodide.

The oxidative addition of alkyl halides to electron-rich transition-metal complexes is a fundamental reaction in the chemistry and reactivity of organometallic complexes.<sup>251</sup> While the oxidative addition reaction involving a single metal centre has been studied in detail,<sup>251</sup> few well-defined examples have been reported in which oxidative addition occurs at two or more metal atom centres. The oxidative addition of methyl iodide to dinuclear gold(I) complexes was first reported by Schmidbaur *et al.*<sup>78</sup> The dinuclear gold(I) phosphorus bis(ylide) complex,  $[\text{Au}(\mu\text{-CH}_2)_2\text{PMe}_2]_2$ , reacts with  $\text{CH}_3\text{I}$  to form the Au(II)-Au(II) metal-metal single bonded complex,  $[\text{Au}_2(\text{Me})\text{I}\{\mu\text{-CH}_2)_2\text{PMe}_2]_2$  (Scheme 34).



**Scheme 34. Oxidative addition of  $\text{CH}_3\text{I}$  to a dinuclear gold(I) phosphorus ylide complex.**

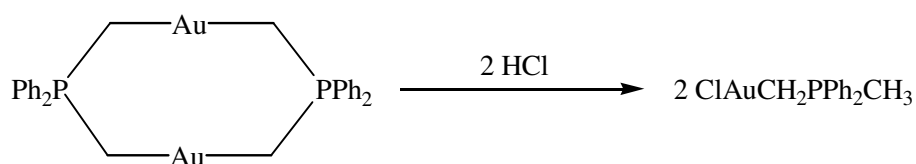
Other examples of dinuclear gold complexes which undergo oxidative addition of  $\text{CH}_3\text{I}$  include  $[\text{Au}_2\{\mu\text{-CH}_2)_2\text{PPh}_2\}_2$ ,<sup>115,116</sup>  $[\text{Au}_2(\mu\text{-2-C}_6\text{H}_4\text{PPh}_2)_2]$ ,<sup>165</sup> and  $[\mu\text{-N,N'}$ -bis(2,6-dimethylphenyl)formamidinato]digold.<sup>252</sup> In each case, the resulting product results from a one-electron oxidation of each metal centre with the formation of a gold-gold bond, capped by a methyl and iodo ligand. The methyl iodide adduct of the bis(ylide) complex  $[\text{Au}_2\{\mu\text{-CH}_2)_2\text{PMe}_2\}_2$  undergoes photochemical decomposition to form either the diiodo complex  $[\text{Au}_2\text{I}_2\{\mu\text{-CH}_2)_2\text{PMe}_2\}_2$  or a mixture of diiodo complex and  $[\text{Au}_2\{\mu\text{-CH}_2)_2\text{PMe}_2\}_2$ , depending on the amount of  $\text{CH}_3\text{I}$  present.<sup>116</sup> Addition of

methyl iodide to the bis(ylide) complexes  $[\text{Au}_2\{\mu\text{-(CH}_2)_2\text{PR}_2\}_2]$  (R = Me, Ph) has been reported to be reversible.<sup>78,115,116,253</sup>

In contrast to its protio analogue,  $[\text{Au}_2(\mu\text{-2-C}_6\text{F}_4\text{PPh}_2)_2]$  **1** did not react at all with methyl iodide; even after two days, only unchanged starting material could be recovered.

#### 2.4 Cleavage of the gold-carbon bonds.

Hydrogen chloride readily cleaves the metal-carbon bonds in gold-alkyl and gold-phenyl complexes to afford alkanes and aromatic compounds, respectively. For example,  $[\text{AuPh}(\text{PPh}_3)]$  reacts to give  $[\text{AuCl}(\text{PPh}_3)]$  when treated with one equivalent of HCl.<sup>254</sup> Protonolysis reactions of dinuclear cycloaurated complexes have also been investigated. HCl reacts with the bis(ylide) gold compound  $[\text{Au}\{\mu\text{-(CH}_2)_2\text{PPh}_2\}_2]$  to cleave two Au-CH<sub>2</sub> bonds, breaking the dimer into two monomeric Au(I) complexes (Scheme 35).<sup>255</sup>



**Scheme 35.** Acid cleavage of  $[\text{Au}_2\{\mu\text{-(CH}_2)_2\text{PPh}_2\}_2]$ .

In contrast to the ylide example above, the Au-C bonds in  $[\text{Au}_2(\mu\text{-2-C}_6\text{F}_4\text{PPh}_2)_2]$  (**1**) were not cleaved by two equivalents of concentrated HCl at room temperature, as shown by <sup>31</sup>P NMR spectroscopy. Treatment of **1** with a large excess of concentrated HCl gave the monomeric Au(I) complex  $[\text{AuCl}\{(2\text{-C}_6\text{F}_4\text{H})\text{PPh}_2\}]$  (**5**) as a colourless

solid. Elemental analysis is consistent with the proposed formation and the ESI-mass spectrum shows a peak at  $m/z$  566, corresponding to the  $[M]^+$  fragment. The  $^1\text{H}$  NMR spectrum shows the expected multiplet at  $\delta$  6.8-7.7 due to the aromatic hydrogens, and the  $^{31}\text{P}$  NMR spectrum shows a single resonance centred at  $\delta$  26.0, split into a doublet with a separation of 14.8 Hz, presumably due to coupling with the *ortho*-fluorine of the  $\text{C}_6\text{F}_4\text{HPPH}_2$  group.

### ***2.5 Attempted insertion of sulfur dioxide into the gold-carbon bonds.***

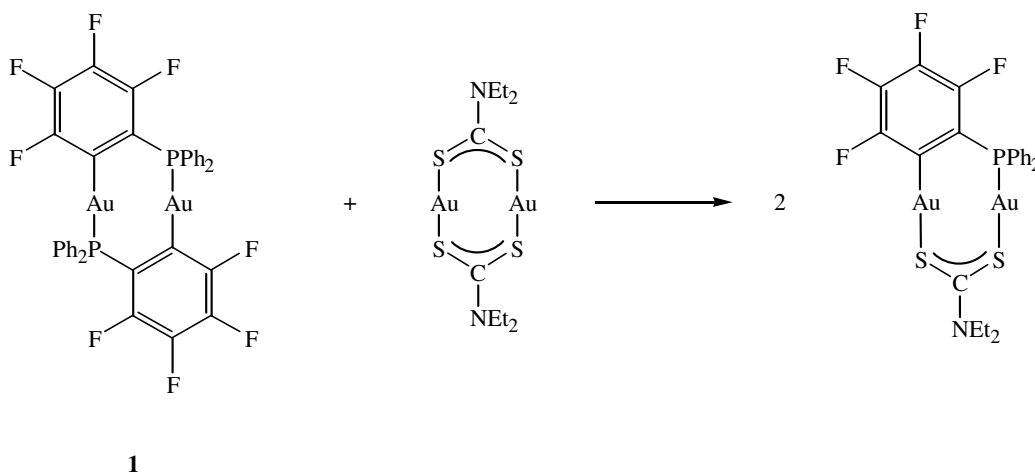
Sulfur dioxide has been found to insert into the metal-carbon bonds of many transition metal-alkyl and -aryl complexes.<sup>256-260</sup> Early work on the insertion of  $\text{SO}_2$  into the metal-carbon bonds of gold complexes dates back to 1972 when Puddephatt and co-workers treated  $[\text{MeAu}(\text{PMe}_2\text{Ph})]$  and  $[\text{Me}_3\text{Au}(\text{PMe}_2\text{Ph})]$  with sulfur dioxide to form the methylsulfinato complexes  $[\text{MeSO}_2\text{Au}(\text{PMe}_2\text{Ph})]$  and  $[\text{MeSO}_2\text{AuMe}_2(\text{PMe}_2\text{Ph})]$ , respectively.<sup>261</sup> Later, Aresta showed that  $\text{SO}_2$  inserted into the Au-C bonds of  $[(\text{Ph}_3\text{P})\text{Au}(\text{C}_6\text{H}_4\text{-2-CH=CH}_2)]$  and  $[(\text{Ph}_3\text{P})\text{AuBr}_2(\text{C}_6\text{H}_4\text{-2-CH}_2\text{CH=CH}_2)]$  to give  $[(\text{Ph}_3\text{P})\text{Au}(\text{SO}_2\text{C}_6\text{H}_4\text{-2-CH=CH}_2)]$  and  $[\text{Ph}_3\text{PAuBr}_2(\text{SO}_2\text{C}_6\text{H}_4\text{-2-CH}_2\text{CH=CH}_2)]$ , respectively.<sup>262</sup>

Unpublished work by Bennett and co-workers indicates that  $\text{SO}_2$  readily inserts into the gold-carbon bonds of  $[\text{Au}_2(\mu\text{-2-C}_6\text{H}_4\text{PR}_2)_2]$  ( $\text{R} = \text{Ph, Et}$ ), although the reaction is reversible.<sup>263</sup> The  $^{31}\text{P}$  NMR spectrum of an  $\text{SO}_2$ -saturated solution of the phenyl analogue ( $\text{R} = \text{Ph}$ ) shows an AB quartet centred at  $\delta$  42.4 with a coupling of 318.5 Hz, together with a small singlet at  $\delta$  34.9. These results are consistent with the insertion of sulfur dioxide into one and two Au-C bonds, respectively. Similar reactivity was

observed for the ethyl analogue (R = Et). Careful crystallisation of the product from the reaction of  $[\text{Au}_2(\mu\text{-}2\text{-C}_6\text{H}_4\text{PEt}_2)_2]$  with  $\text{SO}_2$  gave crystals of the *S*-bonded sulfinato compound  $[\text{Au}_2(\mu\text{-}2\text{-SO}_2\text{C}_6\text{H}_4\text{PEt}_2)_2]$ , confirming that  $\text{SO}_2$  had inserted into the two Au-C bonds. In contrast to these results, there was no evidence for the insertion of  $\text{SO}_2$  into the Au-C bonds of  $[\text{Au}_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$  (**1**), as shown by  $^{31}\text{P}$  NMR spectroscopy.

## 2.6 Attempted formation of mixed ligand gold(I) complexes.

As shown in Scheme 36, the cyclometallated digold(I) complex  $[\text{Au}_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$  (**1**) reacts with the dithiocarbamate complex  $[\text{Au}_2(\mu\text{-S}_2\text{CNEt}_2)_2]$  in dichloromethane at room temperature to give what may be the heterobridged digold complex  $[\text{Au}_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)(\mu\text{-S}_2\text{CNEt}_2)]$ .



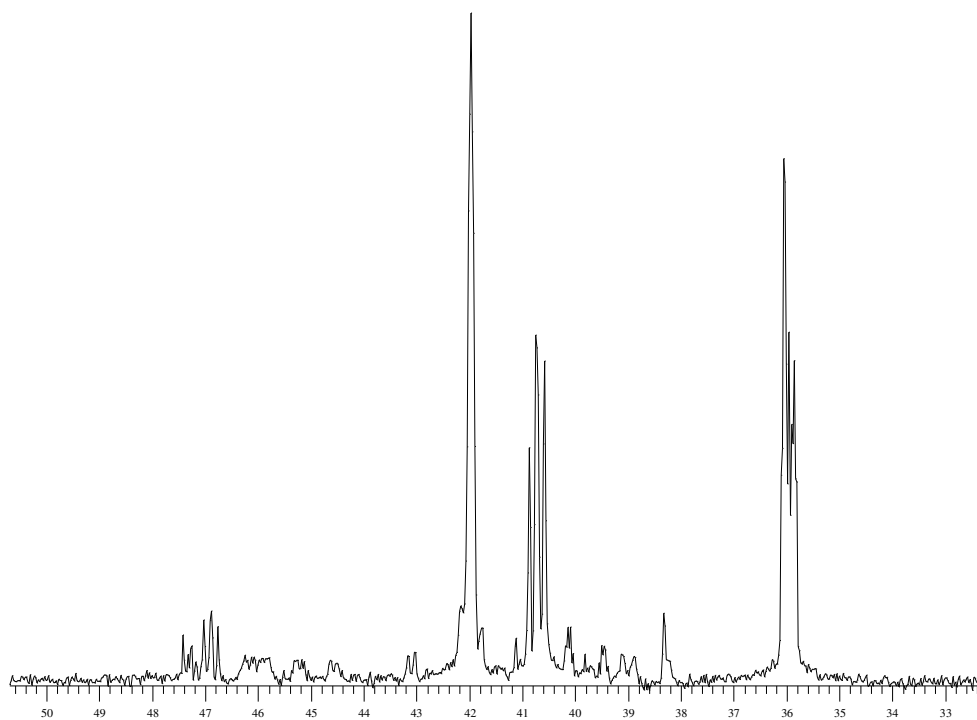
**Scheme 36. Formation of a heterobridged gold(I) dimer.**

The reaction was monitored by  $^{31}\text{P}$  NMR spectroscopy and after 4 days an equilibrium mixture of the scrambled product, which showed a singlet resonance at  $\delta$  47.0, and unreacted dimer **1** was established. Work up gave a yellow solid that is air- and moisture-stable and shows strong luminescence under UV irradiation. Several attempts



to separate the mixture have been performed, unfortunately none of which was effective. Satisfactory elemental analysis and mass spectrum could not be obtained and attempts to grow X-ray quality crystals to confirm the proposed structure were unsuccessful.

A mixture containing equimolar amounts of  $[\text{Au}_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$  (**1**) and its protio analogue in dichloromethane was set aside at room temperature and its  $^{31}\text{P}$  NMR spectrum was monitored over time. After 30 min, the solution showed a complex pattern in its  $^{31}\text{P}$  NMR spectrum (Figure 19) containing three major peaks at  $\delta$  36.1, 41.9 and 40.8; the two former are due to the starting materials, but, unexpectedly, the peak at  $\delta$  36.1 due to  $[\text{Au}_2(\mu\text{-}2\text{-C}_6\text{H}_4\text{PPh}_2)_2]$  now has fine structure. The peak at  $\delta$  40.8 consists of an approximate triplet, which may correspond in part to the AB quartet expected for the mixed dimer  $[\text{Au}_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)(\mu\text{-}2\text{-C}_6\text{H}_4\text{PPh}_2)]$ . However, there are also weaker, complex multiplets in the range  $\delta$  38-48, which suggests that other unknown species are also present. The whole spectrum is clearly more complex than that obtained by mixing solutions of  $[\text{Au}_2(\mu\text{-}2\text{-C}_6\text{H}_4\text{PPh}_2)_2]$  and  $[\text{Au}_2(\mu\text{-}2\text{-C}_6\text{H}_4\text{PEt}_2)_2]$  (Chapter 1, Section 1.5.1). At present, we cannot account for the observation, but one possibility will be discussed later in the thesis (see Chapter 6).



**Figure 19.**  $^{31}\text{P}$  NMR spectrum of the scrambling reaction between  $[\text{Au}_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$  (1) and  $[\text{Au}_2(\mu\text{-}2\text{-C}_6\text{H}_4\text{PPh}_2)_2]$ .

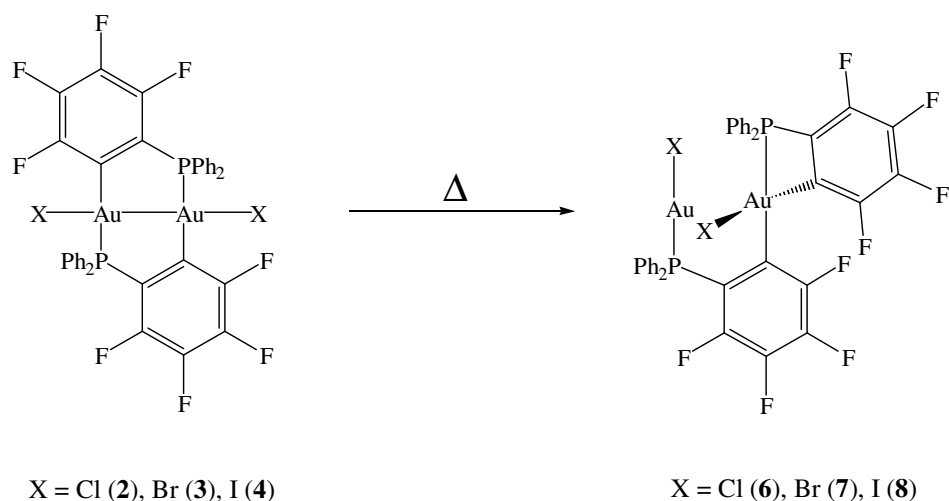
## ***Chapter 3. Reactions of homovalent digold(II) and heterovalent gold(I)-gold(III) complexes.***

### ***3.1 Reactions of dihalodigold(II) complexes.***

#### ***3.1.1 Isomerisation of the dihalodigold(II) complexes.***

When heated to 70 °C, toluene solutions of the dihalodigold(II) complexes **2-4** decolourise over 3-5 hours and the almost colourless, isomeric gold(I)-gold(III) compounds  $[\text{X Au}(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)(\kappa^2\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)\text{AuX}]$  [X = Cl (**6**), Br (**7**), I (**8**)] can then be isolated from the solutions in *ca.* 80-90% yield (Scheme 37). Isomerisation of the digold(II) diiodide occurs slowly even in the solid state, as shown by  $^{31}\text{P}$  NMR spectroscopy. The digold(I,III) dibromide (**7**) and digold(I,III) diiodide (**8**) can also be prepared by anion exchange reactions of **6** with NaBr and NaI, respectively. The  $^{31}\text{P}$  NMR spectra of **6-8** each show a pair of equally intense singlets in the regions of +40 and -80 ppm; the chemical shift of the latter resonance is typical of a phosphorus atom

in a four-membered chelate ring.<sup>264</sup> Close examination of these resonances suggests that they are multiplets with poorly resolved  $^{31}\text{P}$ - $^{19}\text{F}$  coupling.



**Scheme 37. Isomerisation of dihalodigold(II) complexes.**

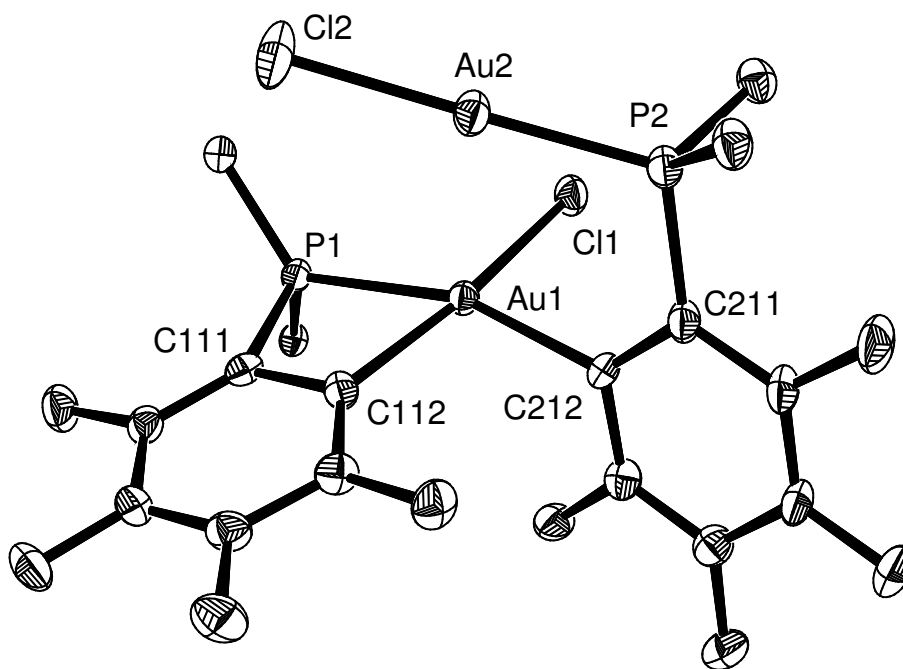
The  $^{31}\text{P}$  NMR chemical shifts, shown in Table 11, are consistent with the formulations and the ESI-mass spectra of **6-8** each show the expected parent ion peak.

**Table 11.  $^{31}\text{P}$  NMR data for the gold(I)-gold(III) complexes 6-8.**

Complex	Au oxidation state	$\delta_{\text{P}}$ ( $\text{C}_6\text{D}_6$ )
$[\text{ClAu}(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)(\kappa^2\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)\text{AuCl}]$ ( <b>6</b> )	I,III	41.0, -58.4
$[\text{BrAu}(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)(\kappa^2\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)\text{AuBr}]$ ( <b>7</b> )	I,III	44.3, -65.4
$[\text{IAu}(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)(\kappa^2\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)\text{AuI}]$ ( <b>8</b> )	I,III	46.2, -77.6

The far-IR spectrum of complex **6** shows a strong band at  $325\text{ cm}^{-1}$  due to  $\text{Au}^{\text{I}}\text{-X}$  stretching and a weaker band at  $238\text{ cm}^{-1}$  tentatively assigned to  $\text{Au}^{\text{III}}\text{-X}$  stretching. Corresponding bands for the 6-methyl analogue  $[\text{ClAu}(\mu\text{-C}_6\text{H}_3\text{-}6\text{-Me-}2\text{-PPh}_2)(\kappa^2\text{-C}_6\text{H}_3\text{-}6\text{-Me-}2\text{-PPh}_2)\text{AuCl}]$  have been observed at  $328\text{ cm}^{-1}$  and  $291\text{ cm}^{-1}$ , respectively.<sup>166</sup> The

corresponding bands for complex **7** appear at  $239\text{ cm}^{-1}$  and  $184\text{ cm}^{-1}$ . The observed IR bands are characteristic of tertiary phosphine-gold complexes.<sup>265-267</sup> The structure of **6** has been confirmed by X-ray diffraction and is shown in Figure 20; selected bond distances and angles are listed in Table 12.



**Figure 20.** Molecular structure of  $[\text{ClAu}(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)(\kappa^2\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)\text{AuCl}]$  (**6**).

Ellipsoids show 30% probability levels and hydrogen atoms have been omitted for clarity.

The phenyl rings of the  $\text{PPh}_2$  groups only show the *ipso* carbons.

In the crystal of **6**, the square planar Au(III) atom is coordinated by a chloride ligand and  $\text{C}_6\text{F}_4\text{PPh}_2$  in a four-membered chelate ring, and the Au(I) atom is linearly coordinated by chloride and the phosphorus atom of the bridging  $\text{C}_6\text{F}_4\text{PPh}_2$  group. The angle subtended at Au(III) by the four-membered ring is  $69.11(17)^\circ$ , which is typical for transition metal complexes containing *ortho*-metallated  $\text{PPh}_3$ .<sup>157</sup> The Au(III)-C bond

length in the four-membered ring [2.044(6) Å] is significantly shorter than the Au-C bond length of the bridging phosphine ligand [2.075(5) Å]. These bond lengths are also shorter than those found in the 6-methyl substituted analogue [2.092(11) Å and 2.079(11) Å, respectively] and longer than those in gold(III) complexes containing cyclometallated N-donors such as 2-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>NMe<sub>2</sub>) or 2-C<sub>6</sub>H<sub>4</sub>(N=NPh), which fall within the range of 2.01-2.03 Å.<sup>268,269</sup> The Au···Au separation of 3.0916(3) Å suggests a weak aurophilic interaction between the metal atoms.

**Table 12. Selected bond distances (Å) and angles (°) in [ClAu(μ-2-C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub>)(κ<sup>2</sup>-C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub>)AuCl] (6).**

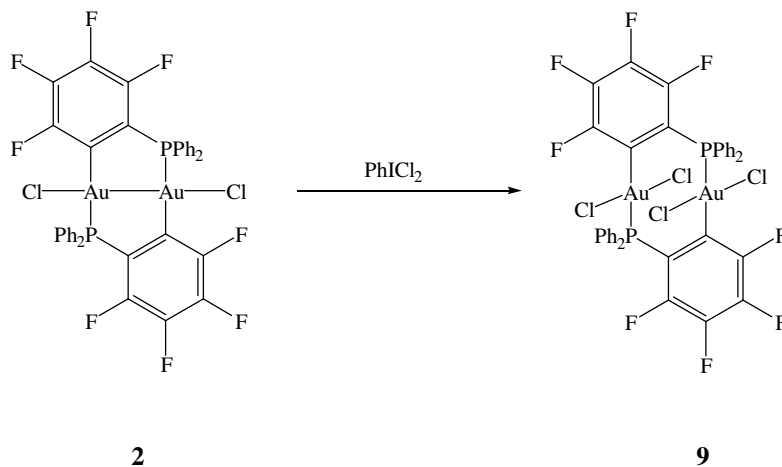
Au(1)–Au(2)	3.0916(3)		
Au(1)–P(1)	2.3474(14)	Au(2)–P(2)	2.2351(13)
Au(1)–C(212)	2.075(5)	Au(1)–C(112)	2.044(6)
Au(1)–Cl(1)	2.3418(14)	Au(2)–Cl(2)	2.2805(15)
Cl(1)–Au(1)–C(112)	91.10(16)	C(212)–Au(1)–C(112)	97.1(2)
Cl(1)–Au(1)–P(1)	100.87(5)	Au(1)–P(1)–C(111)	83.1(2)
Cl(1)–Au(1)–C(212)	92.31(16)	P(1)–C(111)–C(112)	101.6(4)
P(1)–Au(1)–C(212)	162.31(16)	Au(1)–C(112)–C(111)	106.2(4)
P(1)–Au(1)–C(112)	69.11(17)	Cl(2)–Au(2)–P(2)	176.35(7)

These types of heterovalent cyclometallated gold complexes are rare in the literature; some examples are [Au<sub>2</sub><sup>I,III</sup>Me<sub>2</sub>(μ-2-C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>],<sup>183</sup> [XAu<sup>I</sup>{μ-C<sub>6</sub>H<sub>3</sub>-6-Me-2-PPh<sub>2</sub>}{κ<sup>2</sup>-(C<sub>6</sub>H<sub>3</sub>-6-Me-2-PPh<sub>2</sub>)}Au<sup>III</sup>X] [X = Cl, Br, I],<sup>166</sup> and [Au<sub>2</sub><sup>I,III</sup>Br<sub>2</sub>{μ-(CH<sub>2</sub>)<sub>2</sub>PPh<sub>2</sub>}]<sub>2</sub>.<sup>270</sup>

The isomerisation of the symmetric digold(II) complexes **2-4** to the digold(I,III) complexes **6-8** is in contrast to the behaviour of the corresponding complexes in the protio system, which undergo C-C coupling of the metallated aryl groups.<sup>165</sup> It is similar to the behaviour of the 6-methyl substituted analogues, although the isomerisation in the 6-methyl series is much faster than in the tetrafluoro series.<sup>166</sup>

### 3.1.2 Reactions of dihalodigold(II) complexes with halogens.

The homovalent cycloaurated complex  $[\text{Au}_2\text{Cl}_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$  (**2**) contains two gold centres which can potentially be further oxidised to gold(III). Thus, treatment of a dichloromethane solution of **2** with an excess of  $\text{PhICl}_2$  at room temperature gave a pale yellow solution from which a bright yellow precipitate of empirical formula  $[\text{Au}_2\text{Cl}_4(\text{C}_6\text{F}_4\text{PPh}_2)_2]$  (**9**) (Scheme 38) was isolated after *ca.* 4 hours.



**Scheme 38.** Addition of an excess of chlorine to  $[\text{Au}_2\text{Cl}_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$  (**2**).

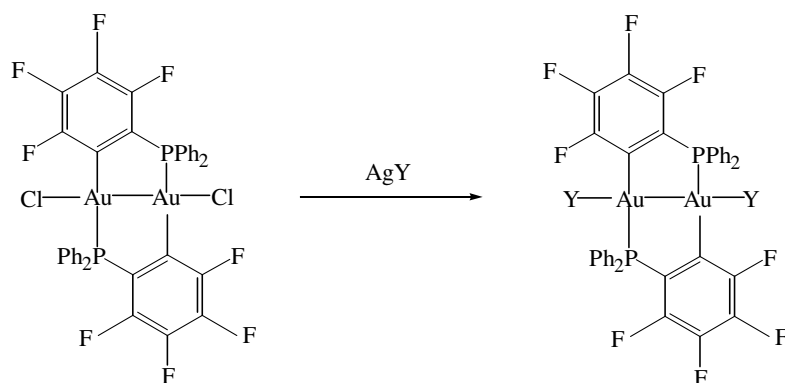
The  $^{31}\text{P}$  NMR spectrum in  $\text{CH}_2\text{Cl}_2/\text{C}_6\text{D}_6$ , acquired before complete precipitation, showed a singlet at  $\delta$  9.3, *ca.* 11.5 ppm downfield from that of the dichlorodigold(II) complex **2**. Similarly, treatment of **3** with an excess of bromine gives an orange solid of empirical formula  $[\text{Au}_2\text{Br}_4(\text{C}_6\text{F}_4\text{PPh}_2)_2]$  (**10**) whose  $^{31}\text{P}$  NMR spectrum in  $\text{CH}_2\text{Cl}_2/\text{C}_6\text{D}_6$  acquired before precipitation showed a singlet at  $\delta$  3.2. This chemical shift is *ca.* 11.5 ppm downfield from that of the dibromodigold(II) complex **3** and also similar to that of  $\delta$  4.6 reported for  $[\text{Au}_2\text{Br}_4(\mu\text{-}2\text{-C}_6\text{H}_4\text{PPh}_2)_2]$ , arising from *trans* addition of bromine to each gold atom of  $[\text{Au}_2\text{Br}_2(\mu\text{-}2\text{-C}_6\text{H}_4\text{PPh}_2)_2]$ .<sup>165</sup> Both homovalent digold(III) compounds **9** and **10** are sparingly soluble in most organic solvents. To obtain further information about the structure of these complexes, reduction reactions have been studied *in situ* by  $^{31}\text{P}$  NMR spectroscopy in  $\text{CH}_2\text{Cl}_2$ . Treating suspensions of **9** and **10** with one equivalent of zinc powder re-formed the known digold(II) complexes **2** and **3**, respectively; these were reduced to **1** upon further addition of zinc, suggesting the dimer framework has remained intact in **9** and **10**.

### 3.1.3 Ligand replacement reactions.

#### 3.1.3.1 Reactions with silver salts.

Metathesis reactions of **2** with silver acetate, nitrate, benzoate or trifluoroacetate gave the expected digold(II) complexes  $[\text{Au}_2\text{Y}_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$  [ $\text{Y} = \text{OOCCH}_3$  (**11**),  $\text{ONO}_2$  (**12**),  $\text{OOC}_6\text{H}_5$  (**13**),  $\text{OOCF}_3$  (**14**)] as pale yellow solids in yields of 80-90% (Scheme 39). All of the digold(II) oxyanion complexes show a single resonance in the region of  $\delta$  0 in their  $^{31}\text{P}$  NMR spectra. The  $^{31}\text{P}$  NMR spectroscopic data for these complexes are shown in Table 13.





2

Y = OOCCH<sub>3</sub> (**11**), ONO<sub>2</sub> (**12**), OOCCH<sub>2</sub>CH<sub>3</sub> (**13**), OOCCH<sub>2</sub>CF<sub>3</sub> (**14**)

**Scheme 39. Preparation of gold(II) oxyanion complexes.**

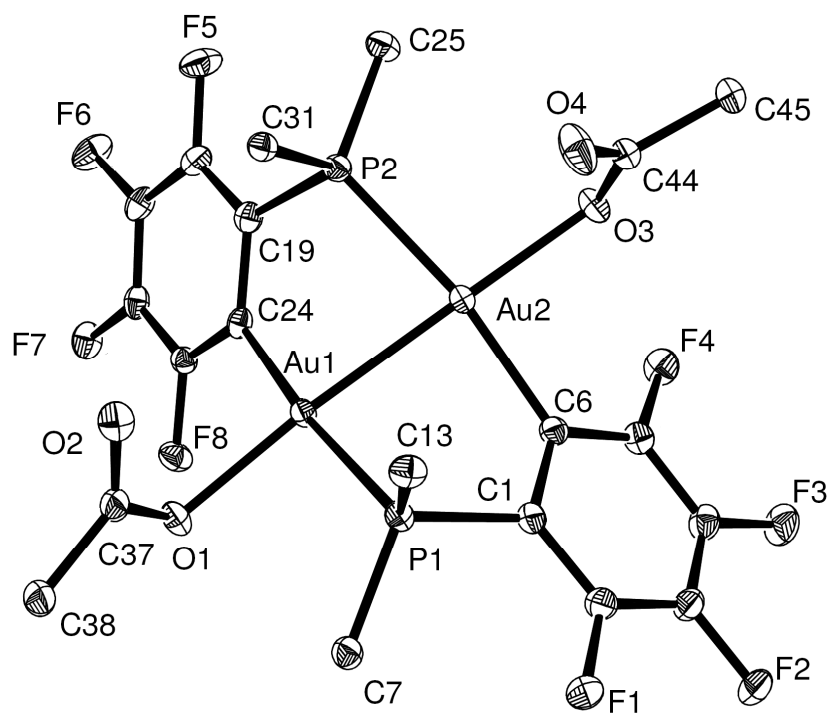
**Table 13.** <sup>31</sup>P NMR data for the gold(II) complexes [Au<sub>2</sub>Y<sub>2</sub>(μ-2-C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>] [Y = OOCCH<sub>3</sub> (**11**), ONO<sub>2</sub> (**12**), OOCCH<sub>2</sub>CH<sub>3</sub> (**13**), OOCCH<sub>2</sub>CF<sub>3</sub> (**14**)].

Compound	Au oxidation state	δ <sub>P</sub> (C <sub>6</sub> D <sub>6</sub> )
[Au <sub>2</sub> (OOCCH <sub>3</sub> ) <sub>2</sub> (μ-2-C <sub>6</sub> F <sub>4</sub> PPh <sub>2</sub> ) <sub>2</sub> ] ( <b>11</b> )	II	-1.3
[Au <sub>2</sub> (ONO <sub>2</sub> ) <sub>2</sub> (μ-2-C <sub>6</sub> F <sub>4</sub> PPh <sub>2</sub> ) <sub>2</sub> ] ( <b>12</b> )	II	-0.1
[Au <sub>2</sub> (OOCCH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub> (μ-2-C <sub>6</sub> F <sub>4</sub> PPh <sub>2</sub> ) <sub>2</sub> ] ( <b>13</b> )	II	-0.1
[Au <sub>2</sub> (OOCCH <sub>2</sub> CF <sub>3</sub> ) <sub>2</sub> (μ-2-C <sub>6</sub> F <sub>4</sub> PPh <sub>2</sub> ) <sub>2</sub> ] ( <b>14</b> )	II	-0.5

The ESI-mass spectra for complexes **11-14** did not show any parent ion peaks; typically, peaks corresponding to the loss of one or two axial ligands were observed. The IR spectrum of the acetato complex **11**, recorded as a KBr disc, shows two strong bands at 1630 and 1588 cm<sup>-1</sup> due to ν(C=O) and at 1300 cm<sup>-1</sup> due to ν(C—O). These separations are typical of unidentate acetato complexes,<sup>271</sup> and similar to those observed in [Au<sub>2</sub>(OOCCH<sub>3</sub>)<sub>2</sub>(μ-2-C<sub>6</sub>H<sub>4</sub>PR<sub>2</sub>)<sub>2</sub>] (R = Ph, Et) [*ca.* 1625 and 1590 cm<sup>-1</sup> and 1290-1300 cm<sup>-1</sup>, respectively].<sup>165</sup> The IR spectrum of complex **12** shows two strong bands at

1250 and 1510  $\text{cm}^{-1}$  due to symmetric and asymmetric  $\nu(\text{NO}_2)$  stretching vibrations, respectively. These separations are typical of unidentate nitrate complexes such as  $[\text{Re}(\text{CO})_5\text{NO}_3]$  and  $[\text{Co}(\text{NH}_3)_5\text{NO}_3]^{2+}$ .<sup>271,272</sup> They are also close to the corresponding bands in  $[\text{Au}_2(\text{ONO}_2)_2(\mu\text{-}2\text{-C}_6\text{H}_4\text{PR}_2)_2]$  (R = Ph, Et), which are observed in the ranges 1270-1255  $\text{cm}^{-1}$  and 1485-1500  $\text{cm}^{-1}$ .<sup>165</sup>

The structures of **12-14** have been solved by single-crystal X-ray diffraction analysis, confirming the unidentate binding mode of the axial ligands; the structure of **13** is shown in Figure 21; selected bond distances and angles of **12-14** are summarised in Table 14. The structures typically consist of two gold(II) atoms bridged by a pair of ligands in a head-to-tail arrangement and also coordinated to an oxygen atom of the nitrate, benzoate or trifluoroacetate groups (**12**, **13** and **14**, respectively). The gold-gold distances of *ca.* 2.51 Å for complexes **12-14** are in the range expected for a gold-gold bond and are slightly shorter than those observed in dihalodigold(II) complexes **2-4** (*ca.* 2.55 Å). The Au-Au distance of 2.52120(11) Å observed in the benzoato complex **13** is similar to that of 2.5243(7) Å found in  $[\text{Au}_2(\text{OOC}_6\text{H}_5)_2(\mu\text{-}2\text{-C}_6\text{H}_4\text{PEt}_2)_2]$ .<sup>165</sup> The Au-O distances in **13** [2.1002(15) Å and 2.1116(15) Å] are also similar to the corresponding distances in  $[\text{Au}_2(\text{OOC}_6\text{H}_5)_2(\mu\text{-}2\text{-C}_6\text{H}_4\text{PEt}_2)_2]$  [2.088(8) Å and 2.126(9) Å].



**Figure 21. Molecular structure of  $[\text{Au}_2(\text{OOC}\text{C}_6\text{H}_5)_2(\mu\text{-}2\text{-}\text{C}_6\text{F}_4\text{PPh}_2)_2]$  (13). Ellipsoids show 30% probability levels and hydrogen atoms have been omitted for clarity. The phenyl rings of the  $\text{PPh}_2$  groups only show the *ipso* carbons. Only *ipso* carbon atoms of the benzoate groups are shown.**

**Table 14. Selected bond distances (Å) and angles (°) in [Au<sub>2</sub>Y<sub>2</sub>(μ-2-C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>] [Y = ONO<sub>2</sub> (12), OOCCH<sub>3</sub> (13), OOCCH<sub>2</sub> (14)].**

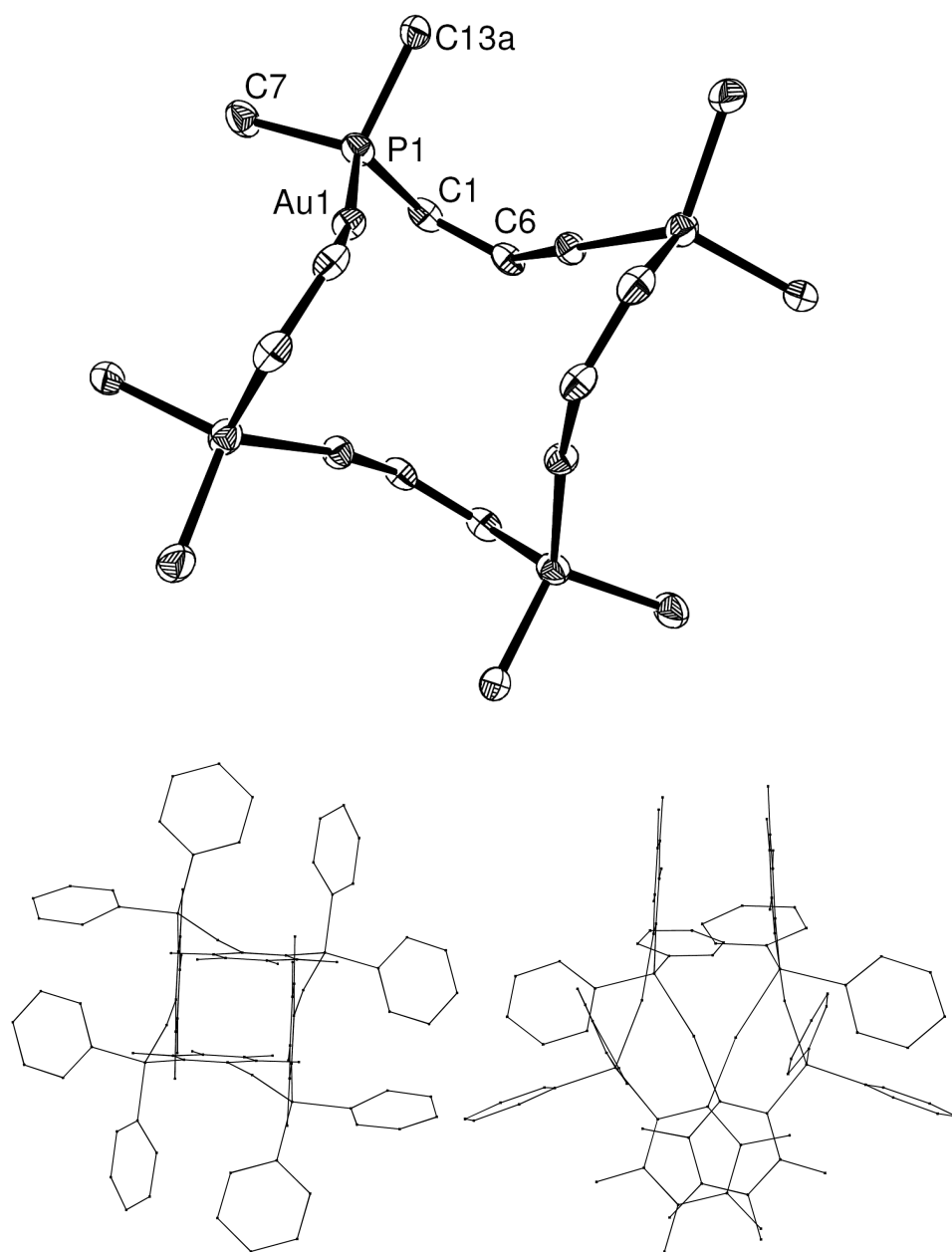
Y	ONO <sub>2</sub> (12)	OOCCH <sub>3</sub> (13)	OOCCH <sub>2</sub> (14)
Au(1)–Au(2)	2.5012(5)	2.52120(11)	2.5093(2)
Au(1)–P(1)	2.349(3)	2.3356(6)	2.3384(12)
Au(1)–C(24)	2.057(11)	2.063(2)	2.077(4)
Au(1)–O(1)	2.138(7)	2.1116(15)	2.108(4)
Au(2)–P(2)	2.349(3)	2.3380(6)	2.3394(12)
Au(2)–C(6)	2.077(10)	2.075(2)	2.071(5)
Au(2)–O(3)	2.167(7)	2.1002(15)	2.110(4)
Au(1)–Au(2)–P(2)	84.67(7)	82.433(14)	82.21(3)
Au(1)–C(24)–C(19)	119.4(8)	119.66(15)	119.0(3)
Au(1)–Au(2)–O(3)	179.3(2)	178.31(5)	179.80(15)
P(1)–Au(1)–C(24)	171.5(3)	173.81(6)	172.74(13)
Au(1)–Au(2)–C(6)	88.7(3)	88.61(6)	88.85(15)
O(1)–Au(1)–C(24)	90.5(4)	94.46(7)	91.28(16)
Au(2)–Au(1)–P(1)	82.99(7)	84.815(14)	83.91(3)
Au(2)–C(6)–C(1)	119.1(8)	120.63(16)	119.6(3)
Au(2)–Au(1)–O(1)	177.9(2)	175.93(4)	178.19(9)
P(2)–Au(2)–C(6)	173.3(3)	171.00(6)	170.93(15)
Au(2)–Au(1)–C(24)	88.8(3)	89.20(6)	88.85(13)
O(3)–Au(2)–C(6)	90.7(4)	90.93(8)	91.35(19)

Reactions of **2** or **3** with AgF caused rapid reduction to the gold(I) dimer **1**, as confirmed by X-ray diffraction analysis and <sup>31</sup>P NMR spectroscopy of the isolated solid; there was no evidence for the formation of a difluorodigold(II) complex.

Treatment of a dichloromethane solution of **2** with an excess of silver triflate resulted in the precipitation of silver chloride and a colour change from yellow to orange. After filtration and evaporation, an orange solid was obtained whose <sup>31</sup>P NMR spectrum in

$C_6D_6$  showed a singlet at  $\delta$  3.1, the chemical shift being consistent with the formation of the symmetrical digold(II) complex  $[Au_2(OTf)_2(\mu\text{-}2\text{-}C_6F_4PPh_2)_2]$  (**15**) (see Table 13). Further evidence for this formulation was obtained by the treatment of a solution of **15** with LiBr which gave the expected dibromo complex **3**, as shown by  $^{31}P$  NMR spectroscopy. However, attempts to recrystallise **15** from dichloromethane/methanol gave a colourless solid, which was shown by single-crystal X-ray crystallography to be a novel gold(I) tetranuclear complex  $[Au_4(\mu\text{-}2\text{-}C_6F_4PPh_2)_4]$  (**16**). Repeated preparations gave mixtures of digold(I) dimer **1** and tetramer in varying proportions. Compound **16** showed a singlet at  $\delta$  45.7 in the  $^{31}P$  NMR spectrum and a peak at  $m/z$  2121 due to the  $[M+H]^+$  ion in the ESI-mass spectrum. Elemental analyses are also in agreement with the empirical formula  $[AuC_6F_4PPh_2]$ .

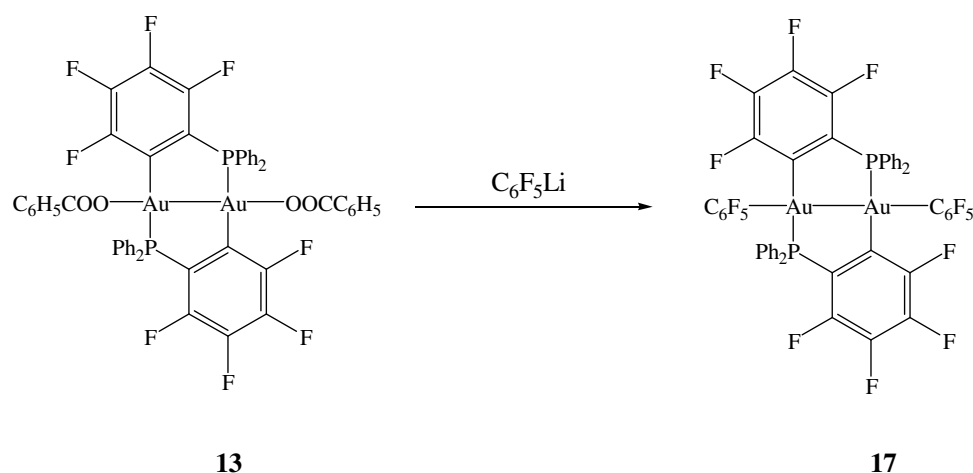
The structure of  $[Au_4(\mu\text{-}2\text{-}C_6F_4PPh_2)_4]$  **16** (Figure 22), which is a dimer of the dinuclear complex  $[Au_2(\mu\text{-}2\text{-}C_6F_4PPh_2)_2]$  (**1**), consists of four gold(I) atoms linearly bridged by four  $C_6F_4PPh_2$  fragments in a saddle-type arrangement. The Au-P [2.2882(7) Å] and Au-C [2.056(3) Å] bond lengths are similar to those in **1** and the Au $\cdots$ Au separation of 3.12972(16) Å, between neighbouring gold atoms, suggests a weak aurophilic interaction. The structure of the tetranuclear complex **16** is similar to that reported for  $[Au\{\mu\text{-}S=CNC(CH_3)=C(H)S\}]_4$ , derived by proton transfer from the amine group of  $[Au(C_6F_5)\{S=CN(H)C(CH_3)=C(H)S\}]$  to the  $C_6F_5$  ligand and subsequent elimination of pentafluorobenzene.<sup>273</sup> The Au $\cdots$ Au separations in **16** [3.12972(16) Å] are significantly longer than those in  $[Au\{\mu\text{-}S=CNC(CH_3)=C(H)S\}]_4$  [3.02(4) Å] and  $[Au_4(S_2CCH_3)_4]$  [3.013(av.) Å] (see Chapter 1).<sup>92</sup>



**Figure 22. Top: Molecular structure of  $[\text{Au}_4(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_4]$  (16). Ellipsoids show 30% probability levels and hydrogen atoms have been omitted for clarity. Only the *ipso* carbons of the phenyl groups attached to the phosphorus atoms are shown; Bottom: Stick plots showing two different views of 16. Only the two carbon atoms of the  $\text{C}_6\text{F}_4$  ring that form the macrocycle are shown.**

### 3.1.3.2 Reactions with organolithium reagents.

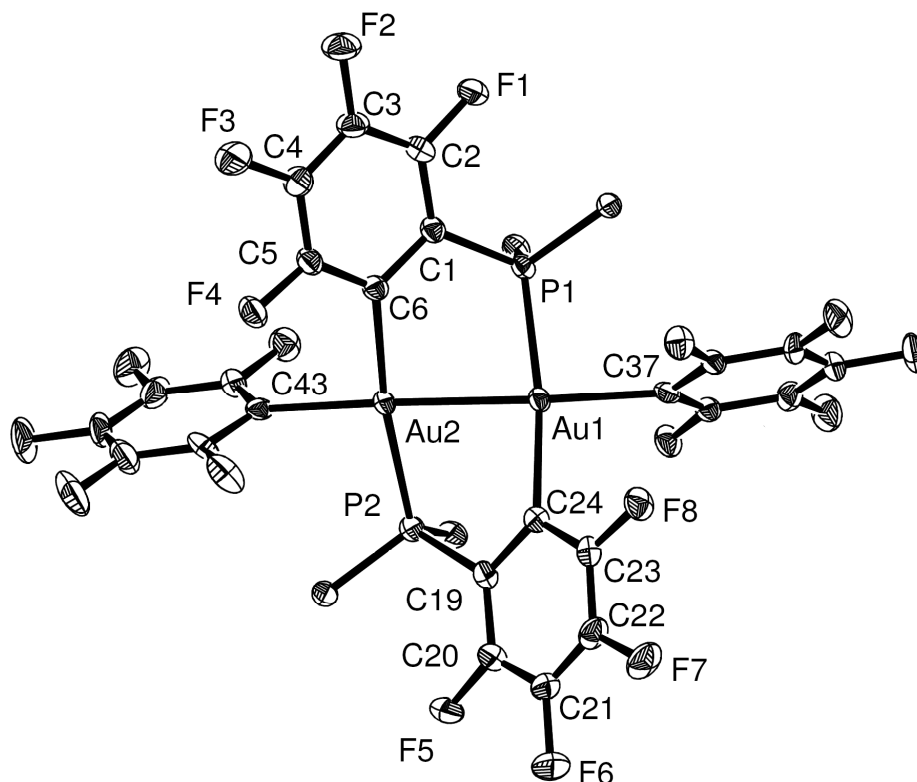
Treating a solution of **13** with two equivalents of pentafluorophenyllithium (Scheme 40) gave a yellow solution, from which the bis(pentafluorophenyl)digold(II) complex  $[\text{Au}_2(\text{C}_6\text{F}_5)_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$  (**17**) was isolated as a pale yellow solid in 80% yield. Complex **17** shows a single resonance in its  $^{31}\text{P}$  NMR spectrum at  $\delta$  -9.6, *ca.* 3 ppm upfield from that of the protio analogue.<sup>183</sup>



**Scheme 40. Preparation of a bis(pentafluorophenyl)digold(II) complex.**

The structure of **17** has been confirmed by X-ray crystallography and is shown in Figure 23; important bond lengths and angles are collected in Table 15. The structure is similar to that of  $[\text{Au}_2(\text{C}_6\text{F}_5)_2(\mu\text{-}2\text{-C}_6\text{H}_4\text{PPh}_2)_2]$ , the coordination geometry about each gold atom being close to square planar with the  $\text{C}_6\text{F}_5$  groups lying along the gold-gold axis. The gold(II)-gold(II) separation in **17** [2.5885(2) Å] is slightly shorter than that observed in the corresponding protio analogue [2.6139(4) Å],<sup>183</sup> and the bis(ylide) complex  $[\text{Au}_2(\text{C}_6\text{F}_5)_2\{\mu\text{-}(\text{CH}_2)_2\text{PPh}_2\}_2]$  [2.677(1) Å].<sup>133</sup> In **17**, the Au-C bond lengths in the bridging ligands [2.071(4) Å and 2.074(4) Å] are similar to those in the protio analogue [2.088(8) Å and 2.076(8) Å].<sup>183</sup> The Au- $\text{C}_6\text{F}_5$  bond lengths [2.129(4) Å,

2.124(4) Å] fall in the range of those observed in the protio analogue  $[\text{Au}_2(\text{C}_6\text{F}_5)_2(\mu\text{-}2\text{-C}_6\text{H}_4\text{PPh}_2)_2]$  [2.103(8) Å and 2.119(8) Å],<sup>183</sup> and those in  $[\text{Au}_2(\text{C}_6\text{F}_5)_2\{\mu\text{-(CH}_2)_2\text{PPh}_2\}_2]$  [2.145(8)-2.164(7) Å].<sup>133</sup>



**Figure 23.** Molecular structure of  $[\text{Au}_2(\text{C}_6\text{F}_5)_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$  (17). Ellipsoids show 30% probability levels and hydrogen atoms have been omitted for clarity. Only the *ipso* carbons of the phenyl groups attached to the phosphorus atoms are shown.



**Table 15. Selected bond distances (Å) and angles (°) in [Au<sub>2</sub>(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(μ-2-C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>] (17).**

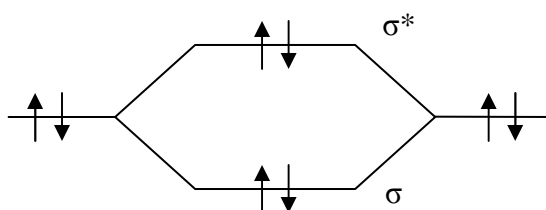
Au(1)–Au(2)	2.5885(2)		
Au(1)–P(1)	2.3243(11)	Au(2)–P(2)	2.3301(12)
Au(1)–C(24)	2.071(4)	Au(2)–C(6)	2.074(4)
P(1)–C(1)	1.801(4)	P(2)–C(19)	1.803(4)
Au(1)–Au(2)–P(2)	81.91(3)	Au(2)–Au(1)–P(1)	82.95(3)
Au(1)–C(24)–C(19)	120.0(3)	Au(2)–C(6)–C(1)	119.2(3)
Au(1)–Au(2)–C(6)	90.98(11)	Au(2)–Au(1)–C(24)	89.21(11)
P(1)–Au(1)–C(24)	172.05(12)	P(2)–Au(2)–C(6)	172.54(12)
Au(1)–Au(2)–C(43)	172.99(12)	Au(2)–Au(1)–C(37)	172.71(12)
P(1)–Au(1)–C(37)	93.15(11)	P(2)–Au(2)–C(43)	93.56(12)
C(24)–Au(1)–C(37)	94.78(16)	C(6)–Au(2)–C(43)	93.30(16)

The Au-Au separations in the digold(II) complexes [Au<sub>2</sub><sup>II</sup>X<sub>2</sub>(μ-2-C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>], summarised in Table 16, decrease in the order pentafluorophenyl > iodide > bromide > chloride > benzoate > trifluoroacetate ~ nitrate, consistent with the relative *trans*-influence of these ligands.<sup>274</sup> A similar variation has been reported for the corresponding tertiary arsine digold(II) complexes [Au<sub>2</sub>X<sub>2</sub>(μ-C<sub>6</sub>H<sub>3</sub>-5-Me-2-AsPh<sub>2</sub>)<sub>2</sub>],<sup>182</sup> and for Pt-Pt distances in the lantern or paddle-wheel diplatinum(III) (5d<sup>7</sup>-5d<sup>7</sup>) complexes containing, separately, C<sub>6</sub>H<sub>3</sub>-5-Me-2-AsPh<sub>2</sub> and P<sub>2</sub>O<sub>5</sub>H<sub>2</sub> as bridging ligands.<sup>275,276</sup> Similar variation of Au-Au bond length dependent on the *trans*-influence of axial ligands has also been observed for the phosphorus ylide gold dimers.<sup>115,133</sup>

**Table 16. Au-Au distances (Å) in the digold(II) complexes  $[\text{Au}_2^{\text{II}}\text{X}_2(\mu\text{-2-C}_6\text{F}_4\text{PPh}_2)_2]$  containing different axial anions.**

<b>X</b>	<b>Au-Au(Å)</b>
ONO <sub>2</sub> ( <b>12</b> )	2.5012(5)
CF <sub>3</sub> COO ( <b>14</b> )	2.5093(2)
C <sub>6</sub> H <sub>5</sub> COO ( <b>13</b> )	2.52120(11)
Cl ( <b>2</b> )	2.5416(4)
Br ( <b>3</b> )	2.5510(3)
I ( <b>4</b> )	2.5685(2)
C <sub>6</sub> F <sub>5</sub> ( <b>17</b> )	2.5885(2)

The cause of this effect can be understood as follows. In the digold(I) compounds, an attractive interaction between the highest occupied 5d- or 5d/6s hybrid orbital on each gold atom will generate a bonding ( $d\sigma$ ) and antibonding ( $d\sigma^*$ ) pair of molecular orbitals, as shown in Figure 24. A full, qualitative molecular orbital diagram for a typical digold(I) system,  $[\text{Au}_2(\mu\text{-dppm})_2]^{2+}$  is given in reference 277.

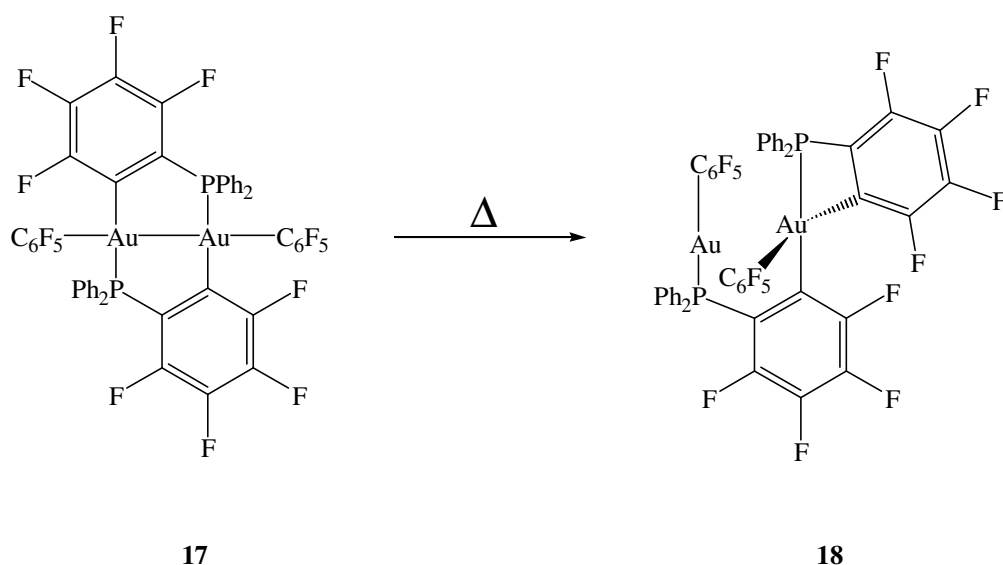


**Figure 24. Molecular orbital diagram of the highest occupied orbitals in the digold(I) compounds.**

Formation of the metal-metal bond on two-electron oxidation to digold(II) corresponds to removal of the two electrons in the antibonding  $\sigma^*$  orbital. According to current theory,<sup>274</sup> an axial ligand of high *trans*-influence makes a higher demand on metal 6s-character than one of low *trans*-influence, thus weakening the metal-metal bond. Conversely, electron-withdrawing ligands having electronegative donor atoms, such as O or Cl, which have a high s-character in their lone pair orbital, make relatively less demand on metal 6s-character, leading to a stronger metal-metal bond.

Like its 2-C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub> analogue, the bis(pentafluorophenyl)digold(II) complex **17** is not thermodynamically stable. Thus, when a toluene solution of **17** was heated to 70 °C, it decolourized within a few hours and an almost colourless complex of the same empirical formula, [Au<sub>2</sub>(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>] (**18**), was isolated in good yields. The <sup>31</sup>P NMR spectrum showed two multiplets of equal intensity at  $\delta$  50.2 and -62.4, clearly showing that two phosphorus atoms were present in different environments. The highly shielded resonance at  $\delta$  -62.4 is typical of a phosphorus atom in a four-membered ring and the observations are consistent with the proposed gold(I)-gold(III) structure [(C<sub>6</sub>F<sub>5</sub>)Au( $\mu$ -2-C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub>)( $\kappa^2$ -2-C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub>)Au(C<sub>6</sub>F<sub>5</sub>)] (Scheme 41), similar to those of **6**, **12**, **13** and **14**. The ESI-mass spectrum showed the parent ion peak at 1394 (*m/z*), consistent with the above formulation. The spectroscopic data support the proposed structure (Scheme 41), which contains a Au(III) and a Au(I) atom. The square planar Au(III) atom is coordinated by C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub> in a four-membered chelate ring and a C<sub>6</sub>F<sub>5</sub> group, and the Au(I) atom is linearly coordinated by a C<sub>6</sub>F<sub>5</sub> group and the phosphorus atom of a bridging C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub> group.

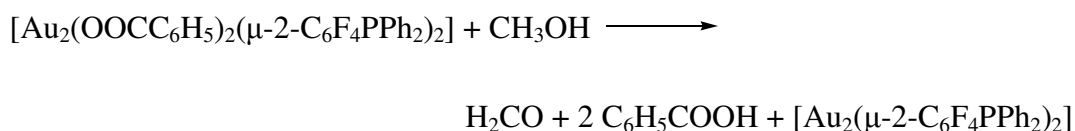
The behaviour of the bis(pentafluorophenyl)digold(II) complex **17** on heating in toluene is similar to that of **2** and **3**, but is in contrast to that of its protio analogue, which isomerises to give a mixture of P-bonded digold(I) biphenyldiyl species (major product) and a zwitterionic species (minor product) (see Chapter 1, Scheme 19).<sup>183</sup>



**Scheme 41. Rearrangement of a bis(pentafluorophenyl)digold(II) complex.**

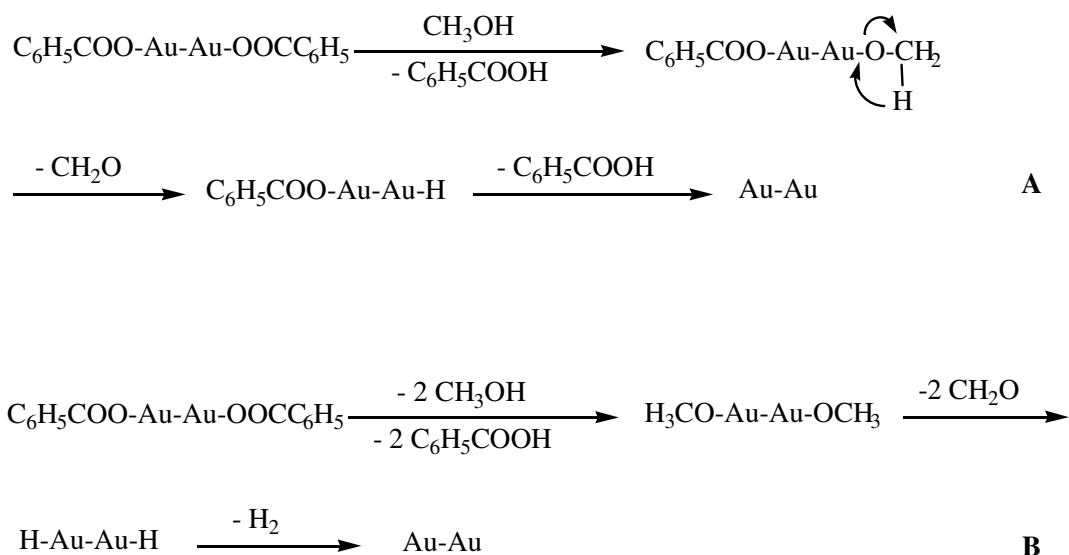
#### **3.1.4 Reduction of the di(benzoato)digold(II) complex.**

Attempts to recrystallise the di(benzoato)digold(II) complex **13** from a mixture of dichloromethane and methanol gave a colourless solid which, surprisingly, was shown by <sup>31</sup>P NMR spectroscopy and X-ray diffraction to be the parent digold(I) dimer **1**, there was no evidence for the formation of tetranuclear complex **16**. We supposed initially that the presence of methanol, which is known to act as a reducing agent, might be responsible for the formation of **1** from **13**, a plausible reaction being that shown in Scheme 42.



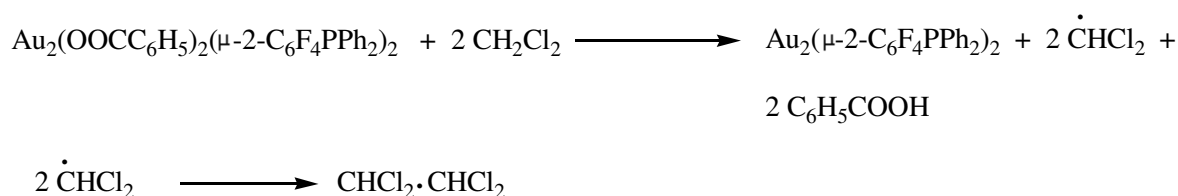
**Scheme 42. Proposed reduction of the di(benzoato)digold(II) complex.**

To test the reaction proposed in scheme 42, the reduction reaction was monitored by IR spectroscopy. As the high volatility of formaldehyde may result in losses from the liquid phase, therefore impeding its detection by IR spectroscopy, the less volatile cyclohexanol was employed instead of methanol. The formation of cyclohexanone during the reduction of **13** to **1** was confirmed *in situ* by IR spectroscopy on aliquots of the reaction solution. A strong band at  $1703 \text{ cm}^{-1}$  due to the C=O stretching vibration of cyclohexanone was observed, which was confirmed by comparison with an authentic sample of cyclohexanone. The reaction presumably proceeds by initial replacement of one (**A**, Scheme 43) or both (**B**, Scheme 43) the axial anions by alkoxide and subsequent  $\beta$ -elimination of the organic carbonyl compound to form a digold(II) mono- or dihydride. Molecular hydrido-complexes of gold are almost unknown and evidently unstable, so, not surprisingly, reductive elimination, either the appropriate acid or of dihydrogen, completes the sequence.



**Scheme 43. Proposed mechanisms for the reduction of di(benzoato)digold(II) complex in the presence of alcohols.**

The di(benzoato)digold(II) complex **13** also decomposes cleanly to **1** on heating in various solvents, such as dichloromethane/methanol and dichloromethane/cyclohexanol. It is noteworthy that, although the reaction of complexes such as  $[\text{Au}_2(\text{OOC}_6\text{H}_5)_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$  occurs most readily in the presence of alcohols, it will also take place, more slowly, in  $\text{CH}_2\text{Cl}_2$  or  $\text{C}_6\text{H}_6$  alone; reduction in dichloromethane requires 2 days, but in a mixture of dichloromethane and methanol, this is reduced to 3 hours. Presumably these reactions occur by hydrogen atom abstraction from the solvent as shown in Scheme 44. The corresponding reaction with benzene would give biphenyl. The corresponding tetraprotio complex  $[\text{Au}_2^{\text{II}}(\text{OOC}_6\text{H}_5)_2(\mu\text{-}2\text{-C}_6\text{H}_4\text{PPh}_2)_2]$  behaves similarly, although the reaction is slower, and other unidentified products are formed.



**Scheme 44. Proposed mechanism for the reduction of di(benzoato)digold(II) complex in the presence of dichloromethane.**

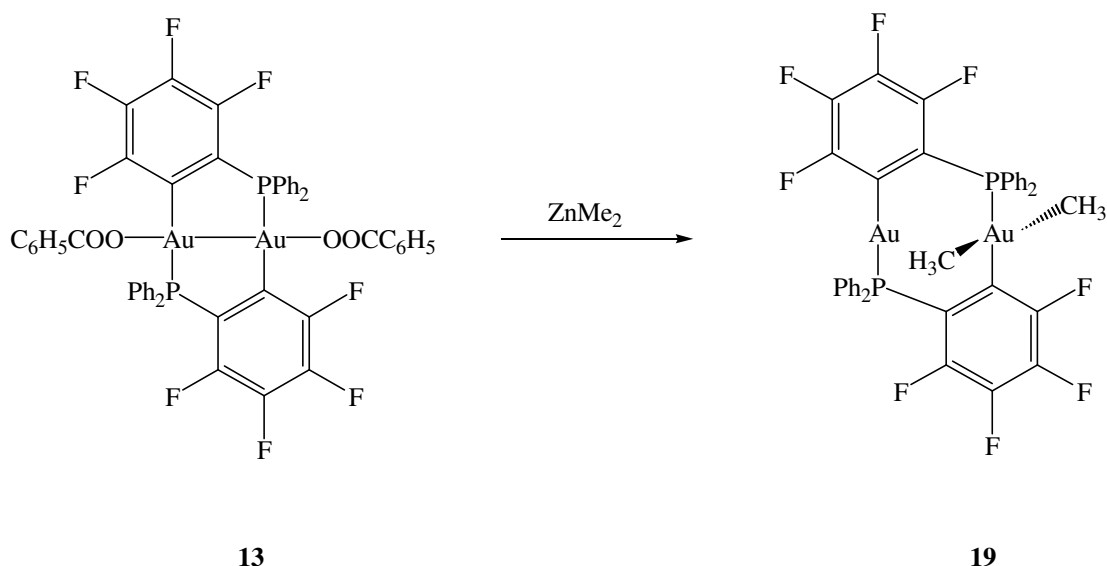
A toluene solution of the nitrate complex  $[\text{Au}_2(\text{ONO}_2)_2(\mu\text{-2-C}_6\text{F}_4\text{PPh}_2)_2]$  showed a marked difference to **13** when heated to 70 °C. The resulting  $^{31}\text{P}$  NMR spectrum consisted of two main signals of equal intensity at  $\delta$  39.3 and 65.2; the latter resonance is possibly due to a phosphine oxide which may have formed as a result of oxidation by  $\text{NO}_3^-$ . All attempts to separate the mixture were unsuccessful.

It appears that the electron-withdrawing fluorine substituents in the bridging ligand stabilise Au(I) relative to Au(II) in the tetrafluoro system and facile reduction can occur when labile ligands such as benzoate and triflate (see Section 3.1.3.1) are present in the coordination sphere.

### 3.1.5 Preparation of a digold(I,III) dimethyl derivative.

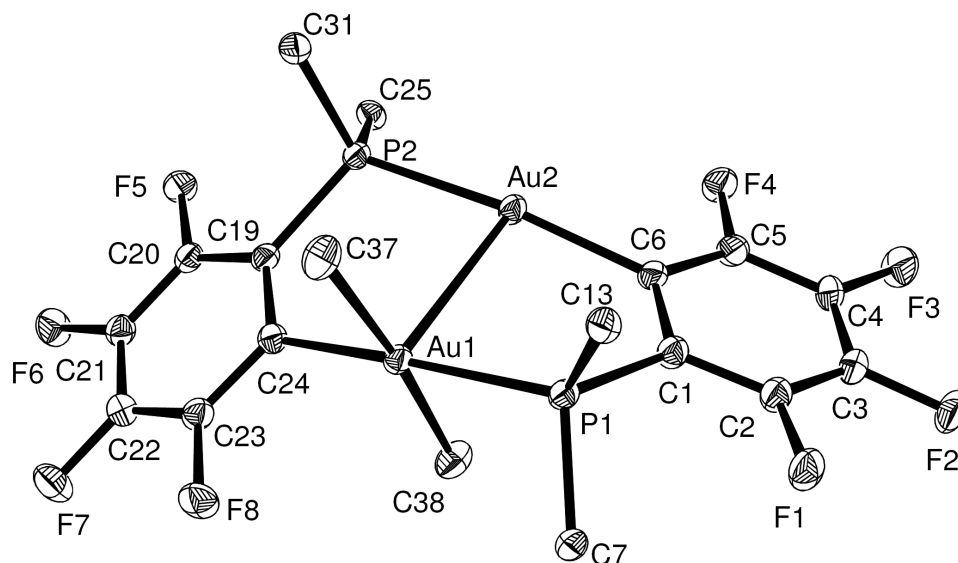
All attempts to prepare a dimethyl derivative analogous to the halide complexes **2-4** by the reaction of the dichlorodigold(II) complex **2** with methyl lithium were unsuccessful. The  $^{31}\text{P}$  NMR spectra of the product of this reaction were complex, containing a number of peaks in the range  $\delta$  18-47. In contrast, the heterovalent, gold(I)-gold(III) dimethyl compound  $[\text{Au}_2^{\text{I,III}}(\text{CH}_3)_2(\mu\text{-2-C}_6\text{F}_4\text{PPh}_2)_2]$  (**19**) was obtained cleanly by treatment of the di(benzoato)digold(II) complex **13** with an equivalent of dimethylzinc (Scheme 45). The  $^1\text{H}$  NMR spectrum shows a doublet at  $\delta$  0.56 due to the two methyl groups coordinated to the gold atom. The proton-phosphorus coupling constant of 2 Hz is similar to that observed in the corresponding protio analogue.<sup>183</sup> The  $^{31}\text{P}$  NMR spectrum shows two broad peaks at  $\delta$  20 and 36 ( $W^{1/2} = 50$  Hz) arising from inequivalent phosphorus atoms, and thus consistent with an unsymmetrical structure. The broadness may be due to the poorly resolved P-P and P-F coupling. The resonance at  $\delta$  36 is in the region expected for linearly coordinated Au(I) [*cf.*  $\delta$  42.7 for the digold(I) dimer **1**], while the down field resonance at  $\delta$  20 more closely corresponds to square planar Au(III) [*cf.*  $\delta$  9.3 for the digold(III) complex **9**].





**Scheme 45. Preparation of a gold(I)-gold(III) dimethyl compound.**

The structure of **19**, which has been confirmed by single-crystal X-ray diffraction, is shown in Figure 25; selected bond distances and angles are listed in Table 17. The structure of **19** differs from those of the dihalodigold(I,III) complexes (**6-8**) in that it does not contain a four-membered ring. In **19**, both 2-C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub> ligands are bridging in a head-to-tail fashion and the mutually *trans* methyl groups are bonded to the same gold atom. The Au(1) atom is trivalent with approximately square planar coordination while the univalent Au(2) atom shows linear coordination geometry with a P-Au-C angle of 173.80(9)°; the corresponding angle in the protio analogue deviates slightly more from linearity [171.80(9)°]. The Au-Au separation [2.85632(16) Å] is slightly greater than that observed in the parent gold(I) dimer **1**, but less than that of 2.8874(4) Å in the protio analogue [Au<sub>2</sub><sup>I,III</sup>(CH<sub>3</sub>)<sub>2</sub>(μ-2-C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>].<sup>183</sup> The Au-CH<sub>3</sub> bond lengths [2.117(3), 2.125(3) Å] are similar to those of the *trans*-methyl groups in monomeric gold(III) complexes, eg. [Au(CH<sub>3</sub>)<sub>3</sub>(PPh<sub>3</sub>)] [2.057(27)-2.168(22) Å]<sup>278</sup> and to those observed in the protio analogue [2.089(8) Å and 2.126(8) Å].



**Figure 25.** Molecular structure of  $[\text{Au}_2^{\text{III}}(\text{CH}_3)_2(\mu\text{-2-C}_6\text{F}_4\text{PPh}_2)_2]$  (19). Ellipsoids show 30% probability levels and hydrogen atoms have been omitted for clarity. Only the *ipso* carbons of the phenyl groups attached to the phosphorus atoms are shown.

**Table 17.** Selected bond distances (Å) and angles (°) in  $[\text{Au}_2^{\text{III}}(\text{CH}_3)_2(\mu\text{-2-C}_6\text{F}_4\text{PPh}_2)_2]$  (19).

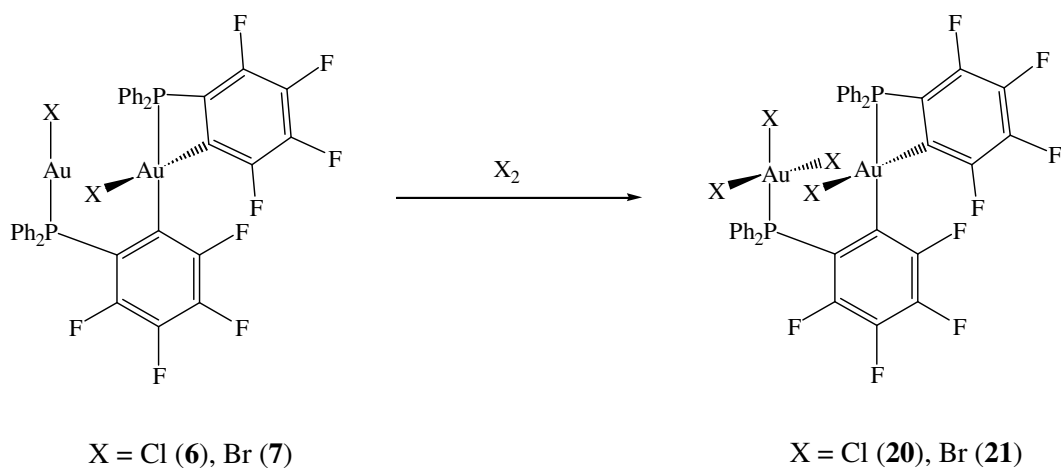
Au(1)–Au(2)	2.85632(16)		
Au(1)–C(37)	2.117(3)	Au(1)–C(38)	2.125(3)
Au(1)–P(1)	2.3276(8)	Au(2)–P(2)	2.2948(8)
Au(1)–C(24)	2.060(3)	Au(2)–C(6)	2.060(3)
P(1)–C(1)	1.831(3)	P(2)–C(19)	1.834(3)
Au(2)–Au(1)–P(1)	84.72(2)	Au(1)–Au(2)–P(2)	84.26(2)
Au(1)–C(24)–C(19)	123.7(2)	Au(2)–C(6)–C(1)	123.9(2)
Au(2)–Au(1)–C(24)	91.81(8)	Au(1)–Au(2)–C(6)	92.47(8)
P(1)–Au(1)–C(24)	171.62(8)	P(2)–Au(2)–C(6)	173.80(9)
Au(1)–P(1)–C(1)	111.12(10)	Au(2)–P(2)–C(19)	110.75(10)

Attempts to selectively cleave one of the methyl groups of **19** with hydrochloric acid or trifluoromethanesulfonic acid were not successful. No reaction was observed when  $[\text{Au}_2^{1,III}(\text{CH}_3)_2(\mu\text{-2-C}_6\text{F}_4\text{PPh}_2)_2]$  (**19**) was treated with one equivalent of concentrated HCl even after 2 days. Reaction of **19** with an equivalent amount of trifluoromethanesulfonic acid led to the formation of some digold(I) dimer **1**, together with other species whose  $^{31}\text{P}$  NMR chemical shifts appear at  $\delta$  40.5, 43.7 and 45.4; the last resonance may be due to the tetramer (**16**).

### **3.2 Reactions of the gold(I)-gold(III) complexes.**

#### **3.2.1 Reactions with halogens.**

The heterovalent, cycloaurated complexes  $[\text{XAu}(\mu\text{-2-C}_6\text{F}_4\text{PPh}_2)(\kappa^2\text{-2-C}_6\text{F}_4\text{PPh}_2)\text{AuX}]$  [ $\text{X} = \text{Cl}$  (**6**),  $\text{Br}$  (**7**)] containing a gold(I) centre can be further oxidised to gold(III). Reaction of **6** and **7** with an excess of the appropriate halogen at room temperature gave the digold(III) complexes  $[\text{X}_3\text{Au}(\mu\text{-2-C}_6\text{F}_4\text{PPh}_2)(\kappa^2\text{-2-C}_6\text{F}_4\text{PPh}_2)\text{AuX}]$  [ $\text{X} = \text{Cl}$  (**20**),  $\text{Br}$  (**21**)] in which the four-membered ring remains intact (Scheme 46). The behaviour of the heterovalent complexes **6** and **7** on treatment with halogens is in contrast to that of the 6-methyl analogues, which form different products depending on the halogen; reaction with one equivalent of  $\text{PhICl}_2$  forms a gold(III)-gold(III) complex analogous to **20**, while the reaction with bromine or iodine gives the mononuclear Au(I) complex  $[\text{AuX}(2\text{-X-3-MeC}_6\text{H}_3\text{PPh}_2)]$  ( $\text{X} = \text{Br}, \text{I}$ ),<sup>166</sup> derived by cleavage of the two Au-C bonds (Scheme 22).

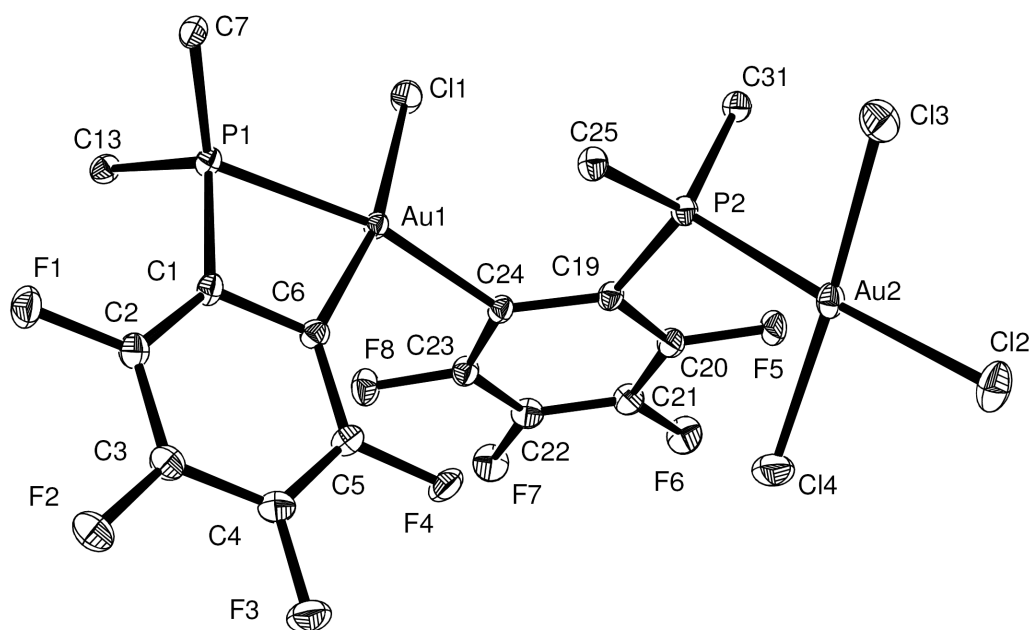


**Scheme 46. Oxidative addition reactions of 6 and 7.**

The  $^{31}\text{P}$  NMR spectra of **20** and **21** each show a pair of equally intense peaks at *ca.*  $\delta$  +30 and -60; the highly shielded resonances confirm retention of the four-membered chelate rings. The molecular structures of **20** (shown in Figure 26) and **21** have been solved by X-ray diffraction analysis; selected bond distances and angles are listed in Table 18. The complexes **20** and **21** are isomorphous and each contain two gold(III) centres bridged by a  $\text{C}_6\text{F}_4\text{PPh}_2$  unit; the large gold-gold separations (5.750 Å and 5.792 Å, respectively) suggest no aurophilic interaction. One of the gold atoms is coordinated by three halides and the phosphorus end of bridging ligand, while the other is bound to one halide and is part of a four-membered chelate ring of a second  $\text{C}_6\text{F}_4\text{PPh}_2$  ligand. The bond lengths and angles of the four-membered chelate ring in **20** and **6** are almost the same, and the gold-halide bond lengths of the  $\text{AuX}_3$  fragment are similar to those found in  $[\text{AuX}_3(\text{PPh}_3)]$  ( $\text{X} = \text{Cl}, \text{Br}$ ).<sup>279,280</sup>

In the  $\text{AuX}_3$  fragment, the Au-X bonds *trans* to phosphorus are slightly longer than those when X is *trans* to X, consistent with the higher *trans* influence of phosphorus over halide. The Au-X bond lengths when X is *trans* to phosphorus and *trans* to carbon

are almost identical in **20** [2.3329(6) Å and 2.3337(7) Å, respectively] and **21** [2.4609(6) Å and 2.4596(6) Å, respectively], suggesting that phosphorus and the fluoroaryl  $\sigma$ -carbon ligands have a similar *trans* influence. The angles subtended at Au(III) by the four-membered rings in **20** and **21** [68.87(7)° and 68.91(16)°, respectively] are typical for transition metal complexes containing *ortho*-metallated PPh<sub>3</sub>.<sup>157</sup>



**Figure 26.** Molecular structure of [Cl<sub>3</sub>Au(μ-2-C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub>)(κ<sup>2</sup>-2-C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub>)AuCl] (**20**).

Ellipsoids show 30% probability levels and hydrogen atoms have been omitted for clarity.

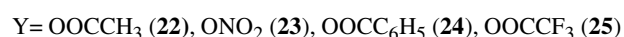
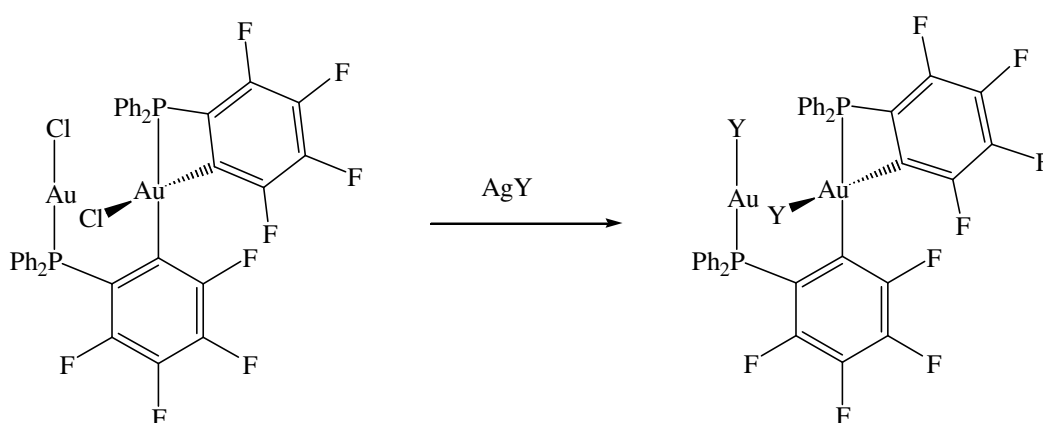
Only the *ipso* carbons of the phenyl groups attached to the phosphorus atoms are shown.

**Table 18. Selected bond distances (Å) and angles (°) in [X<sub>3</sub>Au(μ-2-C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub>)(κ<sup>2</sup>-2-C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub>)AuX] [X = Cl (20), Br (21)].**

	X = Cl (20)	X = Br (21)
Au(1)–Au(2)	5.750	5.792
Au(1)–P(1)	2.3348(6)	2.3315(14)
Au(2)–P(2)	2.3209(6)	2.3369(14)
Au(1)–C(24)	2.077(2)	2.081(5)
Au(1)–C(6)	2.029(2)	2.046(5)
Au(1)–X(1)	2.3329(6)	2.4609(6)
Au(2)–X(2)	2.3337(7)	2.4596(6)
Au(2)–X(3)	2.2866(7)	2.4290(7)
Au(2)–X(4)	2.2804(7)	2.4198(7)
X(1)–Au(1)–C(6)	168.12(7)	167.23(15)
X(1)–Au(1)–P(1)	99.70(2)	99.03(4)
X(1)–Au(1)–C(24)	88.80(7)	89.12(15)
X(2)–Au(2)–X(3)	90.92(3)	90.24(2)
X(2)–Au(2)–P(2)	176.30(3)	175.79(4)
X(2)–Au(2)–X(4)	90.26(3)	89.58(2)
P(1)–Au(1)–C(24)	167.75(7)	167.48(15)
P(1)–Au(1)–C(6)	68.87(7)	68.91(16)
P(1)–C(1)–C(6)	100.58(16)	101.2(4)
P(2)–Au(2)–X(3)	85.38(2)	85.61(4)
P(2)–Au(2)–X(4)	93.44(2)	94.61(4)
C(24)–Au(1)–C(6)	102.01(9)	102.1(2)
Au(1)–P(1)–C(1)	83.72(7)	83.79(18)
Au(1)–C(6)–C(1)	106.83(16)	106.1(4)

### 3.2.2 Reactions with silver salts.

Treatment of  $[\text{ClAu}(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)(\kappa^2\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)\text{AuCl}]$  **6** with silver acetate, nitrate, benzoate or trifluoroacetate gave the corresponding disubstituted oxyanion complexes  $[\text{YAu}(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)(\kappa^2\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)\text{AuY}]$  [ $\text{Y} = \text{CH}_3\text{COO}$  (**22**),  $\text{ONO}_2$  (**23**),  $\text{C}_6\text{H}_5\text{COO}$  (**24**),  $\text{CF}_3\text{COO}$  (**25**)] (Scheme 47). The  $^{31}\text{P}$  NMR spectra of **22-25** are similar to that of **6**, and show a pair of equally intense singlets in the regions of +35 and -50 ppm (Table 19); the chemical shifts of the latter resonances are typical of a phosphorus atom in a four-membered ring,<sup>264</sup> confirming retention of the chelate ring.

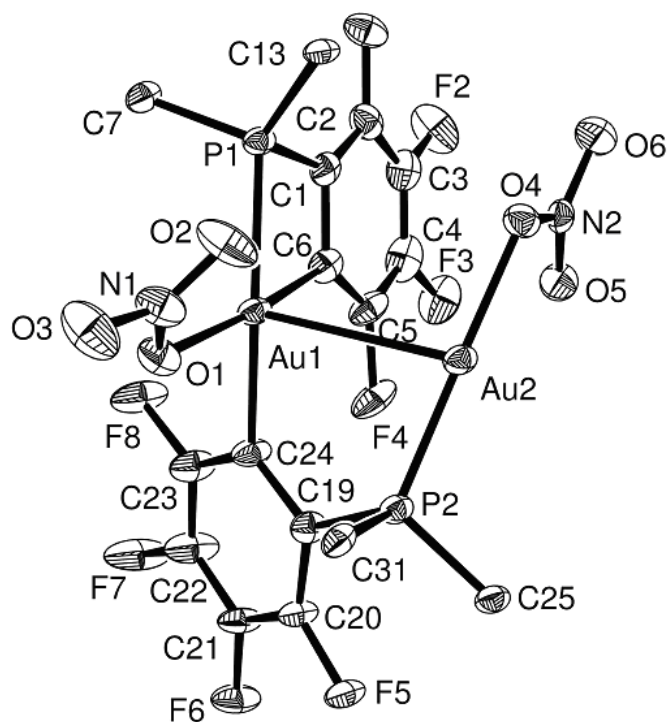


**Scheme 47. Preparation of digold(I,III) oxyanion complexes.**

**Table 19.  $^{31}\text{P}$  NMR data for complexes 22-25.**

Complex	$\delta_{\text{P}}$ ( $\text{C}_6\text{D}_6$ )
$[(\text{CH}_3\text{COO})\text{Au}(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)(\kappa^2\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)\text{Au}(\text{OOCCH}_3)]$ ( <b>22</b> )	34.7, -49.6
$[(\text{O}_2\text{NO})\text{Au}(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)(\kappa^2\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)\text{Au}(\text{ONO}_2)]$ ( <b>23</b> )	36.0, -45.0
$[(\text{C}_6\text{H}_5\text{COO})\text{Au}(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)(\kappa^2\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)\text{Au}(\text{OOC}_6\text{H}_5)]$ ( <b>24</b> )	35.5, -49.4
$[(\text{CF}_3\text{COO})\text{Au}(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)(\kappa^2\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)\text{Au}(\text{OOCF}_3)]$ ( <b>25</b> )	34.0, -47.0

The structures of **22**, **23** and **25** have been confirmed by X-ray diffraction, and the structure of **23** is shown in Figure 27; selected bond distances and angles of **22**, **23** and **25** are listed in Table 20.



**Figure 27.** Molecular structure of  $[(\text{O}_2\text{NO})\text{Au}(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)(\kappa^2\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)\text{Au}(\text{ONO}_2)]$  (**23**). Ellipsoids show 30% probability levels and hydrogen atoms have been omitted for clarity. Only the *ipso* carbons of the phenyl groups attached to the phosphorus atoms are shown.

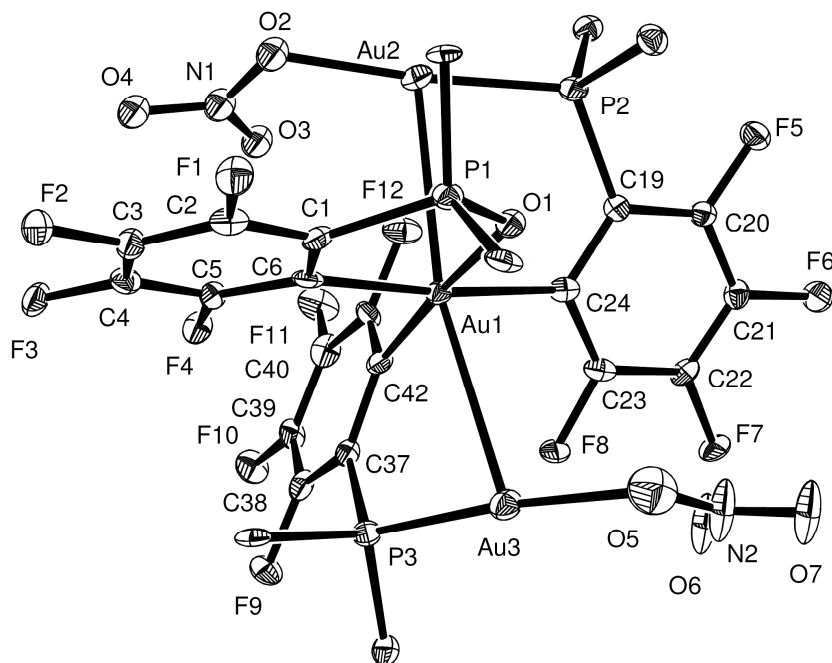


**Table 20. Selected bond distances (Å) and angles (°) in [YAu( $\mu$ -2-C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub>)( $\kappa^2$ -2-C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub>)AuY] [Y = CH<sub>3</sub>COO (**22**), ONO<sub>2</sub> (**23**), CF<sub>3</sub>COO (**25**)].**

Y	CH <sub>3</sub> COO ( <b>22</b> )	ONO <sub>2</sub> ( <b>23</b> )	CF <sub>3</sub> COO ( <b>25</b> )
Au(1)–Au(2)	3.0279(3)	3.0426(4)	3.1437(2)
Au(1)–P(1)	2.3527(13)	2.375(2)	2.3450(11)
Au(2)–P(2)	2.2200(13)	2.214(2)	2.2196(11)
Au(1)–C(6)	2.013(5)	2.005(9)	2.002(4)
Au(1)–C(24)	2.088(5)	2.084(8)	2.069(4)
Au(1)–O(1)	2.041(3)	2.086(7)	2.058(3)
Au(2)–O(4)	2.037(4)	2.090(6)	2.062(3)
O(1)–Au(1)–C(6)	174.8(6)	173.2(3)	173.26(14)
O(1)–Au(1)–P(1)	104.92(11)	108.9(2)	106.29(8)
O(1)–Au(1)–C(24)	85.95(17)	85.4(4)	82.48(14)
O(4)–Au(2)–P(2)	174.64(15)	178.97(18)	177.23(9)
P(1)–C(1)–C(6)	102.1(10)	101.6(6)	101.6(3)
P(1)–Au(1)–C(24)	166.39(14)	162.0(3)	171.13(12)
P(1)–Au(1)–C(6)	69.9(6)	68.8(3)	69.57(12)
C(6)–Au(1)–C(24)	99.1(6)	95.7(4)	101.83(17)
Au(1)–P(1)–C(1)	81.4(6)	82.0(3)	82.22(14)
Au(1)–C(6)–C(1)	105.6(10)	107.5(6)	106.6(3)

The basic structures of **22**, **23** and **25** are similar to that of **6**. The Au⋯Au separations in **22**, **23** and **25** [3.0279(3) Å, 3.0426(4) Å and 3.1437(2) Å, respectively] suggest a weak aurophilic interaction between the metal atoms. In **22**, **23** and **25**, the Au-C [2.013(5) Å, 2.005(9) Å and 2.002(4) Å, respectively] and Au-P bond lengths [2.2200(13) Å, 2.214(2) Å and 2.2196(11) Å, respectively] *trans* to the oxyanions are shorter than those found in **6**, consistent with the lower *trans* influence of oxyanions compared to chloride.

Slow crystallisation of the di(nitrato)digold(I,III) complex **23** from a mixture of dichloromethane and methanol over 2-3 days gave colourless crystals. One of these crystals was selected and surprisingly proved to be a trinuclear gold complex (**26**) of empirical formula  $C_{53}H_{30}Au_3F_{12}N_2O_7P_3$  containing two  $C_6F_4PPh_2$  and one  $C_6F_4P(O)Ph_2$  ligands (Figure 28). In light of this unexpected result, the crystals were redissolved and analysed by NMR spectroscopy. The  $^{31}P$  NMR spectrum showed the majority of the product (*ca.* 90%) to be the expected dinitrato complex **23**, together with several peaks in the range  $\delta$  20-40. Additionally, a singlet at  $\delta$  50.0 was observed, which is in the expected range for coordinated P=O, and is tentatively assigned to the phosphine oxide ligand in **26**. The pure dinitrato complex could be obtained by quickly reducing the volume of a dichloromethane/methanol solution of **23** and filtering off the precipitated solid immediately.



**Figure 28.** Molecular structure of the trinuclear gold complex **26**. Ellipsoids show 30% probability levels and hydrogen atoms have been omitted for clarity. Only the *ipso* carbons of the phenyl groups attached to the phosphorus atoms are shown.

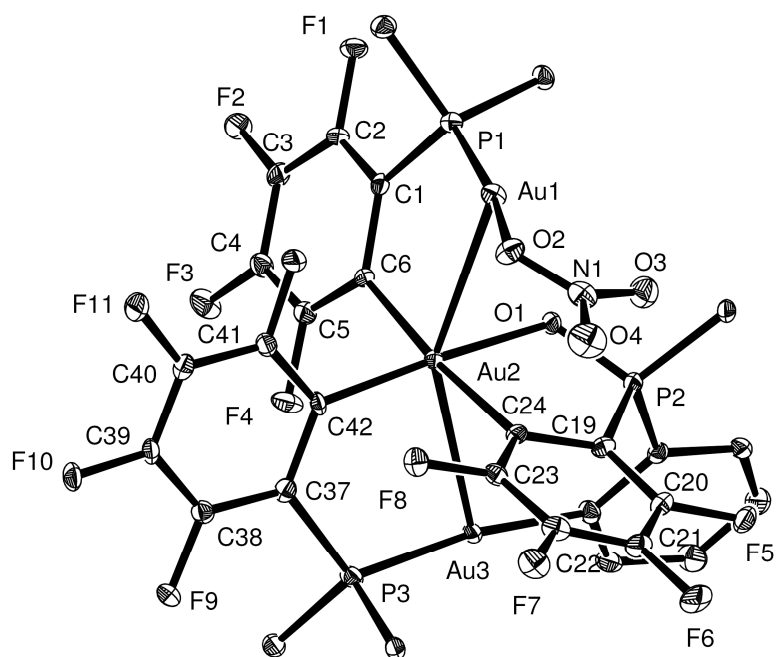
The structure of complex **26** consists of three gold atoms, bridged by two  $C_6F_4PPh_2$  ligands and capped by two monodentate *O*-bonded nitrate groups. Coordinated to the central gold atom is a bidentate  $2-C_6F_4P(O)Ph_2$  ligand, derived by oxidation of one of the  $2-C_6F_4PPh_2$  ligands. The average oxidation state of the gold atoms is 1.67. The electron density map suggests that the site of the nitrate ligand at the Au(3) position is partially occupied by a chloro ligand (*ca.* 0.7:0.3). The terminal gold atoms are univalent, with linear coordination. The central gold atom is trivalent, bonded to three fluoroaryl groups and the oxygen atom of a chelating  $2-C_6F_4P(O)Ph_2$  group, and its coordination geometry is close to square planar. The arrangement of the three gold

atoms in the trinuclear unit deviates slightly from linearity, the Au(2)-Au(1)-Au(3) angle being 163.41(2)° and the gold-gold separations [3.0506(6) Å, 3.1818(7) Å] suggest weak aurophilic interactions between the metal atoms. The gold-gold separations in **26** are slightly larger than those of 2.981(1) Å and 2.962(1) Å in trinuclear homonuclear gold(I) complex, [Au<sub>3</sub>(dmmp)<sub>2</sub>]<sup>3+</sup>; derived from the reaction of K[AuCl<sub>4</sub>] with dmmp in the presence of 2,2'-thiodiethanol in methanol.<sup>281</sup> The two Au-C bond lengths *trans* to carbon of the central gold(III) atom [(2.084(12) Å, 2.110(12) Å] are slightly greater than those observed in the parent gold(I) dimer **1** [2.057(7) Å, 2.059(7) Å], but similar to those in the [Au(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup> ion [2.075(11) Å, 2.098(13) Å].<sup>133</sup> The Au-C bond length *trans* to the oxygen atom of the C<sub>6</sub>F<sub>4</sub>P(O)PPh<sub>2</sub> ligand [2.017(11) Å] is significantly shorter than those *trans* to carbon, consistent with the weaker *trans*-influence of oxygen donor ligands.<sup>274</sup> The Au-P [2.225(3) Å, 2.219(3) Å] and Au-O [2.056(11) Å, 2.091(14) Å] bond lengths in the terminal P-Au-ONO<sub>2</sub> fragments are comparable to those observed in [(Ph<sub>3</sub>P)Au(ONO<sub>2</sub>)] [2.208(3) Å and 2.074(8) Å, respectively].<sup>282</sup>

To the best of our knowledge, this is the first structurally characterized example of a coordinated phosphine oxide complex of Au(III), although reports of a number of gold phosphine oxide complexes have appeared in the literature.<sup>283-285</sup> Phosphine oxide complexes of the heavier transition metals are relatively uncommon,<sup>286</sup> particularly if they form part of a cyclometallated ring; the complex [RhBrCl(κ<sup>2</sup>-2-C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)(κ<sup>2</sup>-2-C<sub>6</sub>H<sub>4</sub>P(O)Ph<sub>2</sub>)], as one of many products in ethanol, and isolated from the reaction of RhCl<sub>3</sub> and 2-BrC<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub><sup>287</sup> and [PtBr<sub>2</sub>(κ<sup>2</sup>-2-C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)(κ<sup>2</sup>-2-C<sub>6</sub>H<sub>4</sub>P(O)Ph<sub>2</sub>)] from the oxidative addition of bromine to [Pt(κ<sup>2</sup>-2-C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>]<sup>288</sup> are two such examples.

The presence of potentially oxidising nitrate ligands may account for the formation of the phosphine oxide in complex **26**; a similar phosphine oxidation has been observed when the platinum complex [PtCl<sub>2</sub>(dppm)] was treated with AgNO<sub>3</sub>.<sup>289</sup>

To determine if the oxidation product could be prepared reproducibly, the digold(I,III) dichloride compound **6** was treated with a tenfold excess of silver nitrate. The <sup>31</sup>P NMR spectrum of the isolated solid showed that the oxidation product may have formed in *ca.* 5% yield, as shown by a singlet at  $\delta$  51.6, consistent with a coordinated phosphine oxide. The major product was the di(nitrato)digold(I,III) complex **23** and other peaks at  $\delta$  0, 20.5, 38.8, 39.7, 68.7, 78.8 were also observed. All attempts to separate the mixture were unsuccessful, however, it was possible to select an X-ray quality crystal which proved to possess another unexpected structure. Like **26**, this new complex **27** was shown by X-ray crystallography to be a trinuclear gold compound (Figure 29). It had the empirical formula C<sub>54</sub>H<sub>29</sub>Au<sub>3</sub>F<sub>12</sub>NO<sub>4</sub>P<sub>3</sub> and, unlike **26**, had only one nitrate group.



**Figure 29.** Molecular structure of the trinuclear gold complex **27**. Ellipsoids show 30% probability levels and hydrogen atoms have been omitted for clarity. Only the *ipso* carbons of the non-metallated phenyl groups attached to the phosphorus atoms are shown.

Like **26**, the structure of **27** consists of three gold atoms in an approximately linear arrangement. These are capped by just one monodentate *O*-bonded nitrate and bridged by two  $C_6F_4PPh_2$  ligands and a tridentate  $C_6F_4P(O)Ph(C_6H_4)$  group, in which one of the phenyl rings of the phosphine oxide ligand has undergone *ortho*-metallation. The electron density map suggests that the terminal gold atom that is not bound to nitrate [Au(3)] is a mixed site containing 58% Au and 42% Ag. The nitrate ligand in **27** is also disordered, with 78% occupancy, the remaining 22% being chloride.

The terminal gold atoms are linear Au(I) and the central gold atom is square planar Au(III). In **27**, the angle between the three gold atoms [ $152.056(7)^\circ$ ] is less than that observed in **26** [ $163.41(2)^\circ$ ] and the gold-gold separations of  $3.0649 \text{ \AA}$  and  $3.0776(3) \text{ \AA}$

suggest weak aurophilic interactions between the metal atoms. The Au-C bond lengths of the central gold(III) atom [2.071(4) Å, 2.083(4) Å, 2.009(4) Å] are slightly less than the corresponding bond lengths in **26**. The Au-C bond length *trans* to the oxygen atom of the C<sub>6</sub>F<sub>4</sub>P(O)Ph(C<sub>6</sub>H<sub>4</sub>) ligand [2.009(4) Å] is significantly shorter than those *trans* to carbon, consistent with the weaker *trans*-influence of oxygen donor ligands.<sup>274</sup> The Au-P [2.2239(12)Å] and Au-O [2.085(6) Å] bond lengths in the terminal P-Au-ONO<sub>2</sub> fragment are comparable to the corresponding bond lengths in **26**. The Au-P [2.3076(12)Å] and Au-C [2.054(4)Å] bond lengths in the C<sub>6</sub>H<sub>4</sub>-Au-PPh<sub>2</sub> fragment are similar to the corresponding bond lengths in [Au<sub>2</sub>(μ-2-C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>] [2.300(1) Å and 2.056(3) Å, respectively].<sup>181</sup>

Attempts to prepare a dimethyl derivative [CH<sub>3</sub>Au(μ-2-C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub>)(κ<sup>2</sup>-2-C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub>)AuCH<sub>3</sub>] by reaction of the di(benzoato)digold(I,III) complex **24** with ZnMe<sub>2</sub> failed. Instead, the complex underwent reduction to the gold(I) dimer **1**, as shown by <sup>31</sup>P NMR spectroscopy. Presumably the corresponding dimethyl complex is formed initially and then rapidly eliminates ethane, though no attempt was made to detect it. A simultaneous change of coordination of the chelating C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub> ligand to bridging mode re-forms **1**.

### 3.3 Attempted preparation of mixed ligand digold(II) complexes.

On mixing equimolar amounts of the digold(II) complexes  $[\text{Au}_2\text{Cl}_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$  (**2**) and  $[\text{Au}_2\text{Br}_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$  (**3**) in dichloromethane at 0 °C, a statistical mixture of  $[\text{Au}_2\text{Cl}_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$ ,  $[\text{Au}_2\text{Br}_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$  and  $[\text{Au}_2\text{ClBr}(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$  was formed and the equilibrium was established within 1 hour. The presence of the mixed species is evident from the observation of an AB quartet in the resulting *in situ*  $^{31}\text{P}$  NMR spectrum whose chemical shift lies midway between those of the symmetrical precursors. The magnitude of  $J_{\text{AB}}$  (85 Hz) is close to that reported for the protio analogue.<sup>165</sup>

In contrast to the results of the axial halide scrambling experiments above, mixing equimolar amounts of  $[\text{Au}_2^{\text{II}}(\text{OCC}_6\text{H}_5)_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$  (**13**) and its protio analogue  $[\text{Au}_2^{\text{II}}(\text{OCC}_6\text{H}_5)_2(\mu\text{-}2\text{-C}_6\text{H}_4\text{PPh}_2)_2]$  did not show any evidence of bridging-ligand exchange, as shown by  $^{31}\text{P}$  NMR spectroscopy; only resonances due to unreacted starting material were observed, even after 5 days. This is in contrast to the behaviour of  $[\text{Au}_2\text{X}_2(\mu\text{-}2\text{-C}_6\text{H}_4\text{PPh}_2)_2]$  and  $[\text{Au}_2\text{X}_2(\mu\text{-}2\text{-C}_6\text{H}_4\text{PEt}_2)_2]$  [ $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ] which scramble on mixing.<sup>165</sup>



### 3.4 Attempted preparation of a digold(II) bis(alkoxo) complex.

A number of gold alkoxo complexes have been reported in the literature.<sup>290-293</sup> Generally gold alkoxides are thermally unstable due to the weak Au-O bond. While all gold(I) alkoxides [Au(OR)L] are stabilised by the presence of fairly bulky tertiary phosphines, by sterically bulky R groups, for example [Ph<sub>3</sub>PAuOR] where R = *t*Bu or 2,4,6-*t*Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>,<sup>294</sup> and by the presence of electron-withdrawing fluorine atoms in the alkoxide, most of the gold(III) alkoxides are stabilised by a variety of ancillary ligands such as C- and N-donor ligands.<sup>292</sup> On the other hand, the weak Au-O bonds are highly reactive and thus play an important role in the reactivity of such complexes. It has been shown that gold(I) and gold(III) alkoxo complexes display some ability to act as catalysts and promote the condensation of benzaldehyde with compounds containing an active methylene group.<sup>295</sup>

Surprisingly, even though trifluoroethoxide, OCH<sub>2</sub>CF<sub>3</sub>, forms stable alkoxides of gold(I) and gold(III), when a THF solution of **2** is treated with two equivalents of potassium trifluoroethoxide, generated *in situ* from KOH and CF<sub>3</sub>CH<sub>2</sub>OH, immediate reduction to the parent digold(I) dimer [Au<sub>2</sub>(μ-2-C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>] **1** takes place, as shown by <sup>31</sup>P NMR and <sup>19</sup>F NMR spectroscopy; there was no evidence for the formation of the bis(alkoxo) complex [Au<sub>2</sub>(OCH<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>(μ-2-C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>]. Presumably CF<sub>3</sub>CH<sub>2</sub>O<sup>-</sup> acts as a reducing agent by β-hydride transfer, analogous to EtO<sup>-</sup>.

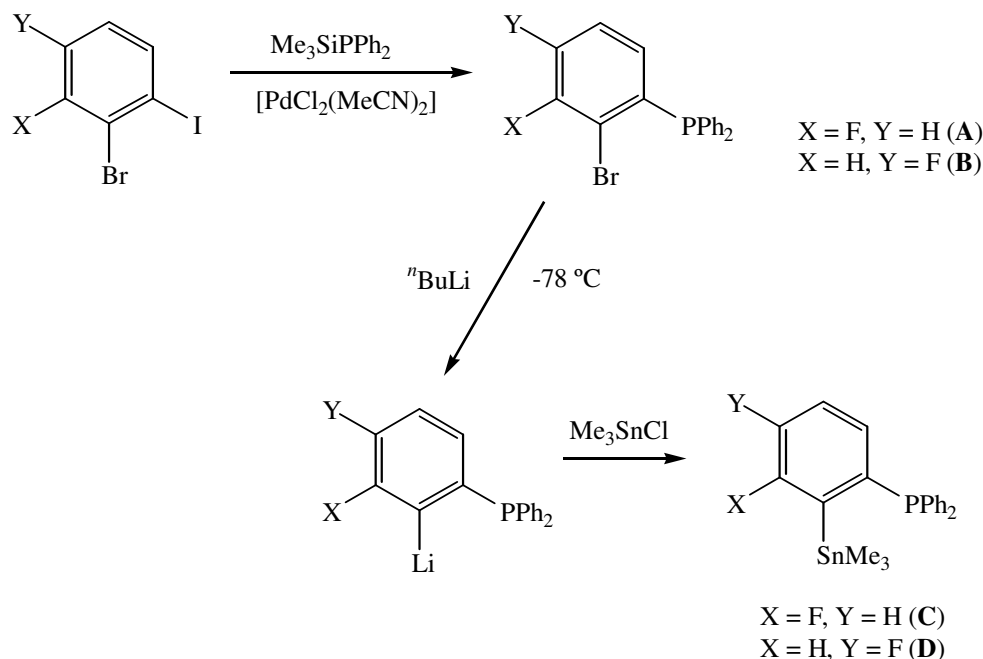
In general, the chemistry of [Au<sub>2</sub>(μ-2-C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>] **1** and its derivatives parallels that of their analogous 6-methyl substituted complexes. In particular, the symmetric digold(II) complexes [Au<sub>2</sub><sup>II</sup>X<sub>2</sub>(μ-2-C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>] (X = Cl, Br, I) rearrange to give the heterovalent

digold(I,III)  $[\text{X}\text{Au}(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)(\kappa^2\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)\text{AuX}]$ , which is in contrast to the behaviour of their protio analogues, which undergo reductive-elimination and C-C coupling to give digold(I) biphenyldiyl species. These observations suggest the presence of a substituent in the 6-position of the bridging aryl ligand, whether it be a methyl or fluoro group, is enough to alter the reactivity of the complexes. With this in mind, we were interested in preparing gold complexes containing the mono-fluoro substituted ligand fragment  $\text{C}_6\text{H}_3\text{-}6\text{-F-}2\text{-PPh}_2$  and its sterically less-demanding 5-fluoro isomer and comparing their reactivity with that of their tetrafluoro and protio analogues; the results of this investigation are presented in the following chapter.

***Chapter 4. Preparation and properties of cycloaurated dinuclear gold complexes containing the C<sub>6</sub>H<sub>3</sub>-6-F-2-PPh<sub>2</sub> or C<sub>6</sub>H<sub>3</sub>-5-F-2-PPh<sub>2</sub> ligands.***

***4.1 Preparation of the (2-bromo-*n*-fluorophenyl)diphenylphosphine and (2-trimethylstannyl-*n*-fluorophenyl)diphenylphosphine (*n* = 3, 4) ligands.***

For the preparation of the (2-bromo-*n*-fluorophenyl)diphenylphosphine (*n* = 3, 4) ligands, the palladium-catalysed coupling reaction of the appropriate aryl iodide has been employed (see Chapter 2). Thus, treatment of a toluene solution of 2-bromo-*n*-fluoroiodobenzene (*n* = 3, 4) with Me<sub>3</sub>SiPPh<sub>2</sub> in the presence of the catalyst [PdCl<sub>2</sub>(MeCN)<sub>2</sub>] at 80 °C gave the desired products as colourless solids in yields of 66-68% (**A** and **B**, Scheme 48).



**Scheme 48.** Preparation of (2-bromo-*n*-fluorophenyl)diphenylphosphine [*n* = 3 (**A**), 4 (**B**)] and (2-trimethylstannyl-*n*-fluorophenyl)diphenylphosphine [*n* = 3 (**C**), 4 (**D**)].

Both ligands gave satisfactory elemental analyses and their ESI-mass spectra displayed a peak consistent with the  $[M+H]^+$  ion. The  ${}^1\text{H}$  and  ${}^{13}\text{C}$  NMR spectra exhibited the expected aromatic resonances. The  ${}^{31}\text{P}$  NMR spectra each showed a resonance centred at *ca.*  $\delta$  -5, typical of triarylphosphines (*cf.*  $\delta$  -5.31 for  $\text{PPh}_3$ <sup>296</sup>), split into a doublet due to coupling with the  ${}^{19}\text{F}$  nucleus. The proton-coupled  ${}^{19}\text{F}$  NMR spectra showed multiplets at *ca.*  $\delta$  -110, the chemical shift being typical for aryl fluorides,<sup>297</sup> with complex fine structure due to coupling with  ${}^1\text{H}$  and  ${}^{31}\text{P}$  nuclei.

Treatment of an ether solution of **A** or **B** sequentially with  ${}^n\text{BuLi}$  and  $\text{Me}_3\text{SnCl}$  gave, after work up, (2-trimethylstannyl-*n*-fluorophenyl)diphenylphosphine [*n* = 3 (**C**), 4 (**D**)] as colourless solids in *ca.* 70% yield (Scheme 48).

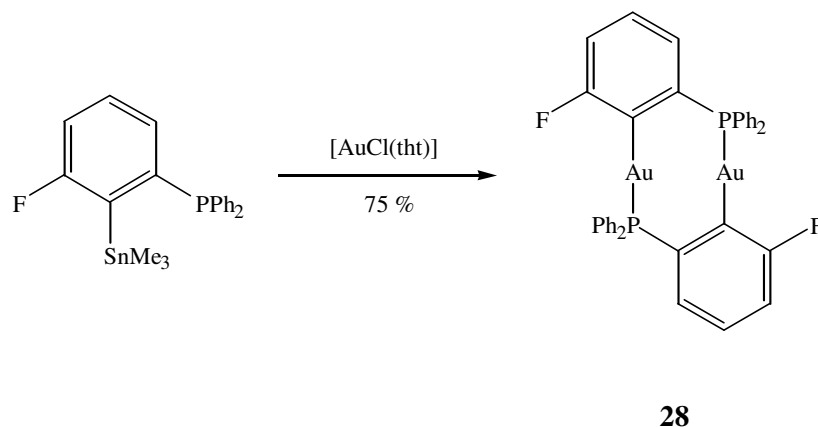
Satisfactory elemental analyses and mass spectral data are consistent with the proposed formulations. The  $^1\text{H}$  NMR spectra of **C** and **D** each show, in addition to the expected aromatic multiplets, an intense resonance at *ca.*  $\delta$  0.4 due to the  $\text{SnMe}_3$  group, split into a doublet of doublets arising from coupling to the  $^{19}\text{F}$  and  $^{31}\text{P}$  nuclei and flanked by a pair of  $^{117}\text{Sn}/^{119}\text{Sn}$  satellites ( $J = \text{ca. } 54 \text{ and } 56 \text{ Hz}$ ). Similarly, the  $^{13}\text{C}$  NMR spectra each show the expected aromatic resonances in addition to a peak at *ca.*  $\delta$  -5 due to the  $\text{SnMe}_3$  group. As expected, this resonance was split into a doublet of doublets arising from coupling to the  $^{19}\text{F}$  and  $^{31}\text{P}$  nuclei and spaced symmetrically about the main resonances were  $^{117}\text{Sn}/^{119}\text{Sn}$  satellites ( $J = \text{ca. } 350 \text{ and } 366 \text{ Hz}$ ). The  $^{19}\text{F}$  and  $^{31}\text{P}$  NMR spectra were almost identical to those of the corresponding parent ligands **A** and **B**, with additional  $^{117}\text{Sn}/^{119}\text{Sn}$  coupling.

## **4.2 Cycloaurated digold(I) complexes.**

### **4.2.1 Preparation of $[\text{Au}_2(\mu\text{-C}_6\text{H}_3\text{-6-F-2-PPh}_2)_2]$ .**

Low temperature lithiation of (2-bromo-3-fluorophenyl)diphenylphosphine followed by reaction with  $[\text{AuBr}(\text{AsPh}_3)]$  gave a colourless solid in 85% yield. The  $^{31}\text{P}$  NMR spectrum of this solid appeared as a doublet of doublets at  $\delta$  39.0 and a doublet of multiplets at  $\delta$  41.1, the former peak always being more intense (*ca.* 70%). All attempts to separate the species responsible for these peaks were unsuccessful. By analogy to the gold chemistry containing the  $\text{C}_6\text{F}_4\text{PPh}_2$  ligand (see Sections 2.2 and 3.1.3.1), the resonance at  $\delta$  39.0 is assigned to the dinuclear complex  $[\text{Au}_2(\mu\text{-C}_6\text{H}_3\text{-6-F-2-PPh}_2)_2]$  (**28**) and the resonance at  $\delta$  41.1 to the tetranuclear species  $[\text{Au}_4(\mu\text{-C}_6\text{H}_3\text{-6-F-2-PPh}_2)_4]$  (**29**). ESI-mass spectrum of this mixture showed expected  $[M+\text{H}]^+$  ion peaks due to the dimer (**28**) and tetramer (**29**), supporting the proposed peak assignments above.

Pure **28** could be prepared in 75% yield by refluxing a dichloromethane solution of (2-trimethylstannyl-3-fluorophenyl)diphenylphosphine and [AuCl(tht)] for 24 hours (Scheme 49) and the dinuclear structure was confirmed by X-ray crystallography (see later).

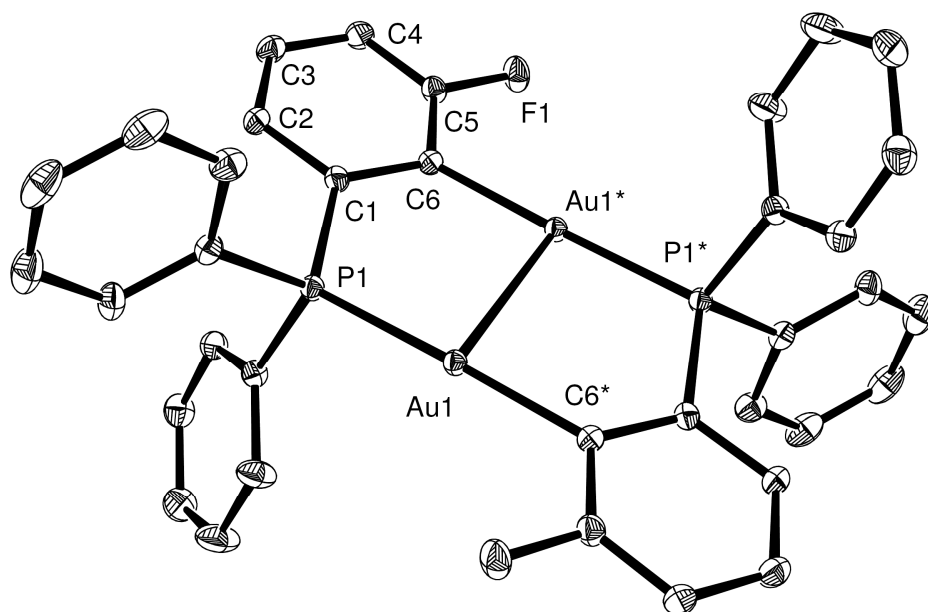


**Scheme 49. Preparation of the cycloaurated digold(I) dimer [Au<sub>2</sub>(μ-C<sub>6</sub>H<sub>3</sub>-6-F-2-PPh<sub>2</sub>)<sub>2</sub>]**

**(28).**

Complex **28** gave satisfactory elemental analysis and the <sup>1</sup>H NMR spectrum showed two sets of multiplet peaks due to the aromatic proton between δ 6.9-7.1 and 7.4-7.6. The <sup>31</sup>P NMR spectrum showed a doublet of doublets at δ 39.0 (*J* = 1.2, 2.4 Hz) arising from coupling to the two <sup>19</sup>F nuclei and is consistent with the assignment of the impure solid above. The ESI-mass spectrum showed a peak at *m/z* 952 corresponding to the [M]<sup>+</sup> ion.

An X-ray structure determination of **28** (Figure 30) confirmed the species to be a dinuclear gold complex in which two linearly coordinated gold(I) atoms are bridged by two C<sub>6</sub>H<sub>3</sub>-6-F-2-PPh<sub>2</sub> ligands. Selected bond distances and angles in **28** are listed in Table 21.



**Figure 30.** Molecular structure of  $[\text{Au}_2(\mu\text{-C}_6\text{H}_3\text{-6-F-2-PPh}_2)_2]$  (28). Ellipsoids show 30 % probability levels and hydrogen atoms have been omitted for clarity.

**Table 21.** Selected bond distances (Å) and angles (°) in  $[\text{Au}_2(\mu\text{-C}_6\text{H}_3\text{-6-F-2-PPh}_2)_2]$  (28).

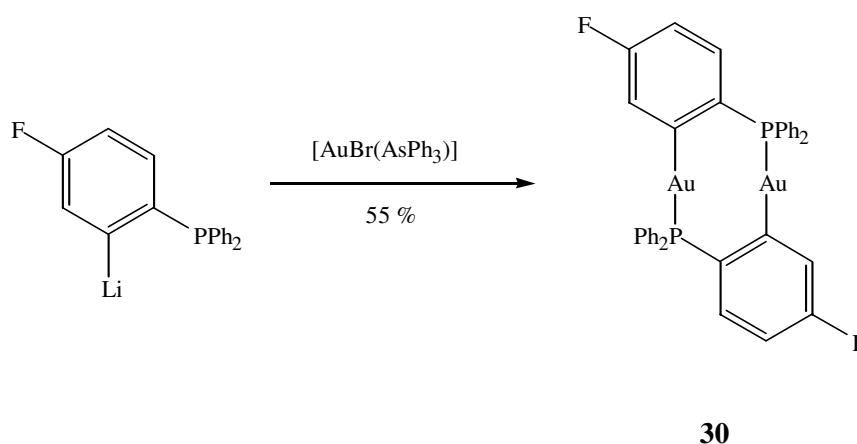
Au(1)–Au(1*)	2.87624(14)		
Au(1)–P(1)	2.2987(5)	Au(1)–C(6*)	2.061(2)
C(6*)–Au(1)–P(1)	174.62(6)	Au(1*)–Au(1)–C(6*)	94.01(6)
Au(1*)–Au(1)–P(1)	84.260(14)	Au(1)–P(1)–C(1)	115.31(7)
Au(1*)–C(6)–C(1)	123.75(15)		

\* Symmetry equivalent atoms

In **28**, the Au···Au separation [2.87624(14) Å] is larger than those observed in the tetrafluoro [2.8201(4) Å] and protio [2.8594(3) Å] analogues.<sup>181</sup> The Au-P [2.2987(5) Å] and Au-C [2.061(2) Å] distances are similar to those in [Au<sub>2</sub>(μ-2-C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>] [2.300(1) Å and 2.056(3) Å, respectively],<sup>181</sup> [Au(C<sub>6</sub>F<sub>5</sub>)(PPh<sub>3</sub>)] [2.27(1) Å and 2.07(2) Å, respectively]<sup>247</sup> and [Au<sub>2</sub>(μ-2-C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>] [2.2807(av.) Å and 2.058(av.) Å, respectively]. In **28**, the Au atoms display almost linear coordination and the P-Au-C angle [174.62(6)°] falls between that of the protio [172.8(1)°] and tetrafluoro analogues [177.9(2)°].

#### 4.2.2 Preparation of [Au<sub>2</sub>(μ-C<sub>6</sub>H<sub>3</sub>-5-F-2-PPh<sub>2</sub>)<sub>2</sub>].

The cycloaurated digold(I) compound [Au<sub>2</sub>(μ-C<sub>6</sub>H<sub>3</sub>-5-F-2-PPh<sub>2</sub>)<sub>2</sub>] (**30**) was prepared as a colourless solid by the reaction of 2-Li-4-F-C<sub>6</sub>H<sub>3</sub>PPh<sub>2</sub> with [AuBr(AsPh<sub>3</sub>)] in 55% yield (Scheme 50). The <sup>31</sup>P NMR spectrum of this solid showed a triplet resonance at δ 36.1 due to **30**, although repeated preparation gave various amounts of **30** (major product) and another species (minor product) whose chemical shift appeared at δ 40.6.



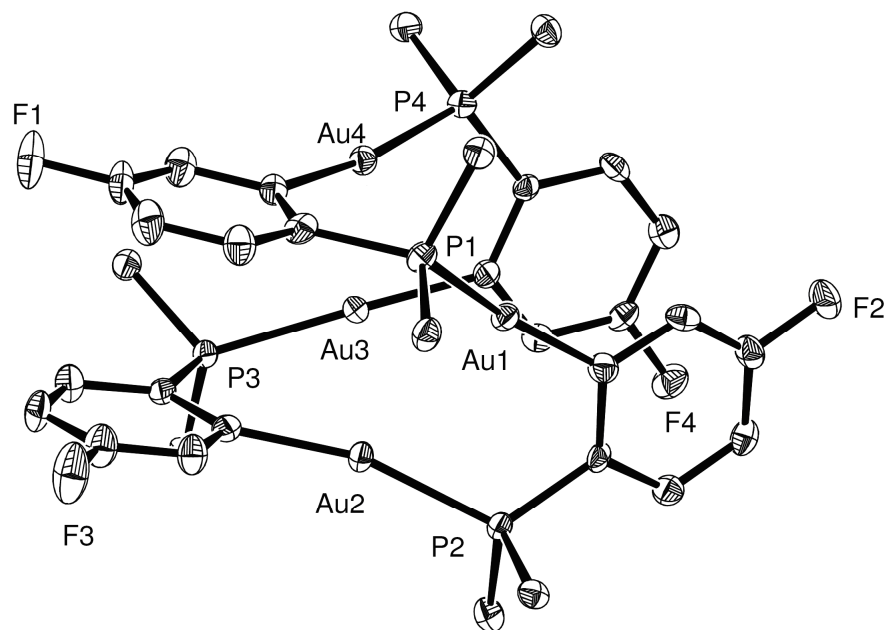
**Scheme 50.** Preparation of the cycloaurated digold(I) dimer [Au<sub>2</sub>(μ-C<sub>6</sub>H<sub>3</sub>-5-F-2-PPh<sub>2</sub>)<sub>2</sub>]

(**30**).



Curiously, attempts to prepare **30** by refluxing a dichloromethane solution of (2-trimethylstannyl-4-fluorophenyl)diphenylphosphine with [AuCl(tht)] failed to give a pure product, in contrast to the results obtained for the 6-fluoro chemistry above; the resulting  $^{31}\text{P}$  NMR spectrum of the isolated solid showed two triplet resonances at  $\delta$  36.1 (minor product) and 40.6 (major product). By analogy to the tetrafluoro analogues (Sections 2.2 and 3.1.3.1), these resonances are assigned to the dinuclear  $[\text{Au}_2(\mu\text{-C}_6\text{H}_3\text{-5-F-2-PPh}_2)_2]$  (**30**) and tetranuclear  $[\text{Au}_4(\mu\text{-C}_6\text{H}_3\text{-5-F-2-PPh}_2)_4]$  (**31**) complexes, respectively. The ESI-mass spectrum of this mixture showed expected  $[M+H]^+$  ion peaks due to the dimer (**30**) and tetramer (**31**), supporting the proposed peak assignments above.

A pure sample of complex **30**, obtained by the use of the lithium reagent, gave satisfactory elemental analysis, and the ESI-mass spectrum showed a peak at  $m/z$  953, corresponding to the  $[M-H]^+$  ion, consistent with the proposed dinuclear structure. The  $^1\text{H}$  NMR spectrum showed the expected aromatic multiplets for the  $\text{PPh}_2$  groups, together with three resonances for the 5- $\text{FC}_6\text{H}_3$  protons, split into multiplets due to complex overlapping  $^1\text{H}\text{-}^1\text{H}$ ,  $^1\text{H}\text{-}^{19}\text{F}$  and  $^1\text{H}\text{-}^{31}\text{P}$  coupling. The  $^{31}\text{P}$  NMR spectrum showed a triplet at  $\delta$  36.1, presumably arising from coupling to the two magnetically inequivalent, though chemically equivalent,  $^{19}\text{F}$  nuclei; coincidentally, both five-bond coupling constants are equal ( $J = 5.1$  Hz). The chemical shift is in the region expected for these types of dinuclear gold complexes {*cf.*  $\delta$  36.4 for  $[\text{Au}_2(\mu\text{-2-C}_6\text{H}_4\text{PPh}_2)_2]$ <sup>165</sup> and  $\delta$  42.7 for  $[\text{Au}_2(\mu\text{-2-C}_6\text{F}_4\text{PPh}_2)_2]$  **1**}. Slow crystallisation of pure **30** gave X-ray quality crystals which were, surprisingly, shown to be the tetranuclear complex (**31**) (Figure 31), analogous to  $[\text{Au}_4(\mu\text{-2-C}_6\text{F}_4\text{PPh}_2)_4]$  **16**. Presumably facile dimerisation of **30** occurs during the crystallisation process.

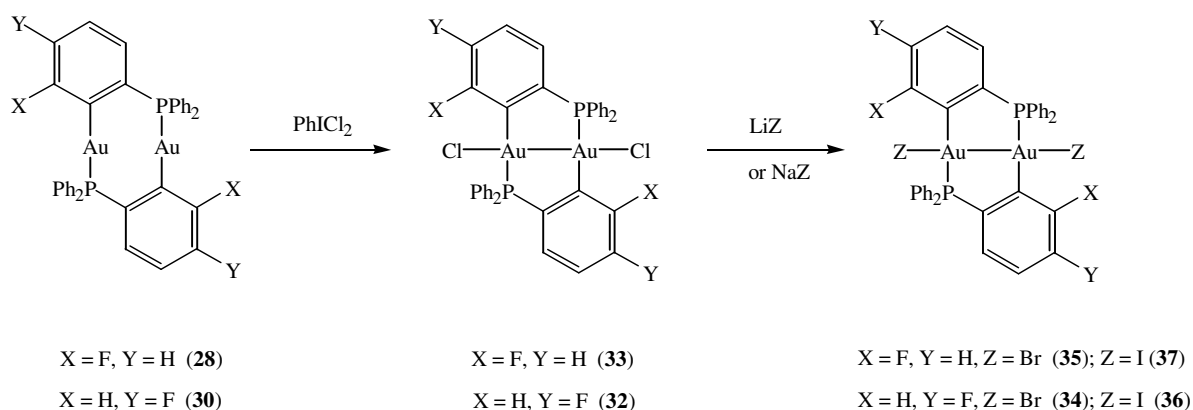


**Figure 31. Molecular structure of  $[\text{Au}_4(\mu\text{-C}_6\text{H}_3\text{-5-F-2-PPh}_2)_4]$  (**31**). Ellipsoids show 50% probability levels. Hydrogen atoms have been omitted for clarity and only the *ipso* carbons of the  $\text{PPh}_2$  groups are shown.**

In **31**, the Au-P [2.292(14)-2.3046(14) Å] and Au-C [2.053(5)-2.059(5) Å] bond lengths are similar to those in  $[\text{Au}_4(\mu\text{-2-C}_6\text{F}_4\text{PPh}_2)_4]$  **16** [2.2882(7) Å and 2.056(3) Å, respectively]. The Au⋯Au separations between neighbouring gold atoms [3.141225(av.) Å] is greater than those in **16** [3.12972(16) Å], and are indicative of a weak aurophilic interaction.<sup>70</sup>

### 4.2.3 Oxidative addition reactions of the dinuclear gold(I) complexes $[Au_2(\mu-C_6H_3-n-F-2-PPh_2)_2]$ ( $n = 5, 6$ ).

Like their tetrafluoro counterpart, dichloromethane solutions of the digold(I) complexes  $[Au_2(\mu-C_6H_3-n-F-2-PPh_2)_2]$  ( $n = 5, 6$ ) react with  $PhICl_2$  (acting as a source of  $Cl_2$ ) at low temperature to give the dichlorodigold(II) complexes  $[Au_2Cl_2(\mu-C_6H_3-n-F-2-PPh_2)_2]$  [ $n = 5$  (**32**),  $6$  (**33**)] in *ca.* 85% yield. The corresponding bromo ( $n = 5$ , **34**;  $n = 6$ , **35**) and iodo ( $n = 5$ , **36**;  $n = 6$ , **37**) complexes were prepared by treating dichloromethane solutions of **32** or **33** with an excess of the appropriate lithium or sodium salts in methanol (Scheme 51). The chloride complexes are yellow, bromide complexes are orange and the iodide complexes are red.



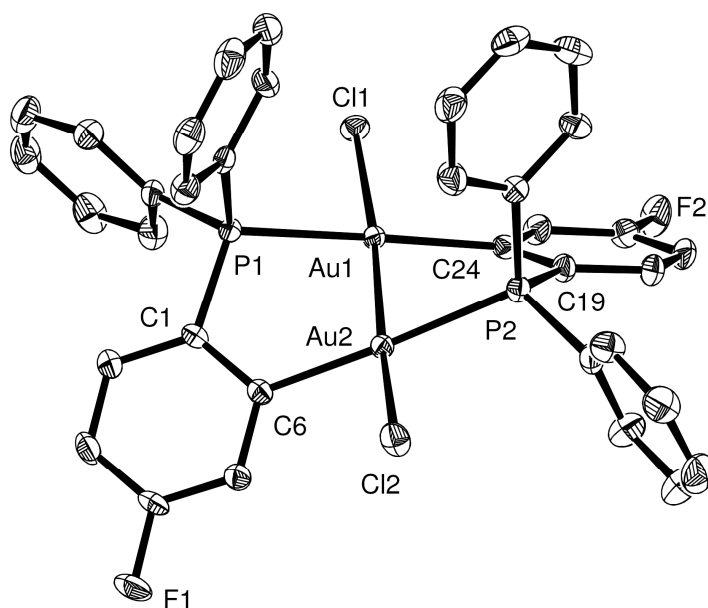
**Scheme 51. Preparation of the dihalodigold(II) complexes  $[Au_2X_2(\mu-C_6H_3-n-F-2-PPh_2)_2]$  [ $n = 5, 6$ ;  $X = Cl, Br, I$ ].**

The  $^{31}P$  NMR spectroscopic data for the dihalodigold(II) complexes, together with those for the parent gold(I) dimers **28** and **30**, are shown in Table 22. The  $^{31}P$  NMR spectra of the complexes **32-37** each show a single resonance in the region  $\delta$  -12 to +2 and are typical for digold(II) complexes of this type (Section 2.3.1). The ESI-mass spectra of **32-37** each showed the expected peak corresponding to the  $[M\text{-halide}]^+$  fragment. The molecular structures of **32** and **33** have been determined by X-ray crystallography

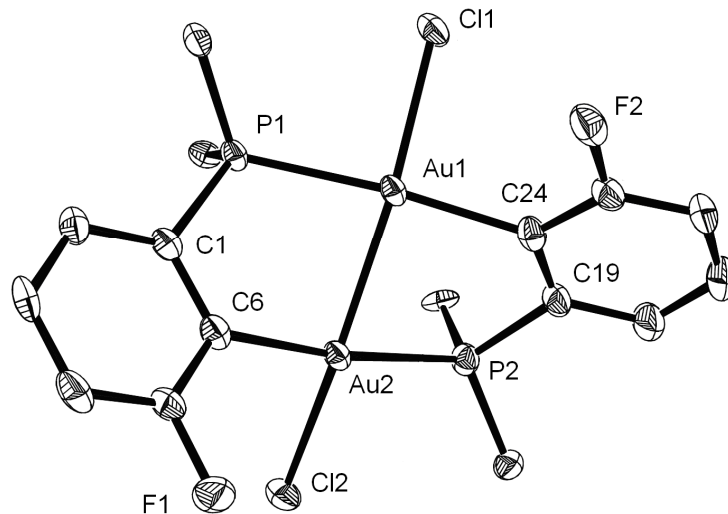
(Figures 32 and 33, respectively) and important bond lengths and angles are summarised in Table 23.

**Table 22.**  $^{31}\text{P}$  NMR data for the digold(I) and digold(II) compounds containing monofluoro ligands.

<b>Compound</b>	<b>Au oxidation state</b>	<b><math>\delta_{\text{P}}</math> (<math>\text{C}_6\text{D}_6</math>)</b>
$[\text{Au}_2(\mu\text{-C}_6\text{H}_3\text{-6-F-2-PPh}_2)_2]$ ( <b>28</b> )	I	39.0
$[\text{Au}_2(\mu\text{-C}_6\text{H}_3\text{-5-F-2-PPh}_2)_2]$ ( <b>30</b> )	I	36.0
$[\text{Au}_2\text{Cl}_2(\mu\text{-C}_6\text{H}_3\text{-5-F-2-PPh}_2)_2]$ ( <b>32</b> )	II	1.7
$[\text{Au}_2\text{Cl}_2(\mu\text{-C}_6\text{H}_3\text{-6-F-2-PPh}_2)_2]$ ( <b>33</b> )	II	0.8
$[\text{Au}_2\text{Br}_2(\mu\text{-C}_6\text{H}_3\text{-5-F-2-PPh}_2)_2]$ ( <b>34</b> )	II	-3.4
$[\text{Au}_2\text{Br}_2(\mu\text{-C}_6\text{H}_3\text{-6-F-2-PPh}_2)_2]$ ( <b>35</b> )	II	-4.2
$[\text{Au}_2\text{I}_2(\mu\text{-C}_6\text{H}_3\text{-5-F-2-PPh}_2)_2]$ ( <b>36</b> )	II	-11.6
$[\text{Au}_2\text{I}_2(\mu\text{-C}_6\text{H}_3\text{-6-F-2-PPh}_2)_2]$ ( <b>37</b> )	II	-12.0



**Figure 32.** Molecular structure of  $[\text{Au}_2\text{Cl}_2(\mu\text{-C}_6\text{H}_3\text{-5-F-2-PPh}_2)_2]$  (32). Ellipsoids show 50% probability levels and hydrogen atoms have been omitted for clarity.



**Figure 33.** Molecular structure of  $[\text{Au}_2\text{Cl}_2(\mu\text{-C}_6\text{H}_3\text{-6-F-2-PPh}_2)_2]$  (33). Ellipsoids show 50% probability levels and hydrogen atoms have been omitted for clarity. Only the *ipso* carbons of the  $\text{PPh}_2$  groups are shown.

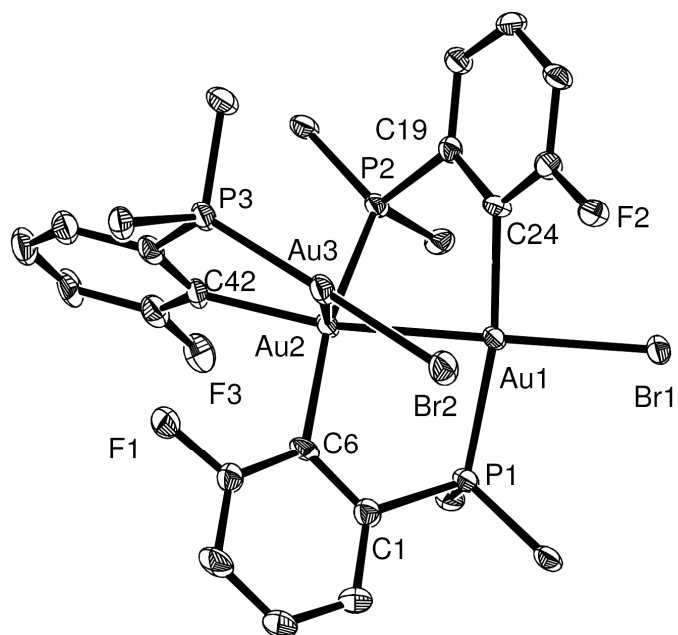
**Table 23.** Selected bond distances (Å) and angles (°) in [Au<sub>2</sub>Cl<sub>2</sub>(μ-C<sub>6</sub>H<sub>3</sub>-*n*-F-2-PPh<sub>2</sub>)<sub>2</sub>] [*n* = 5 (**32**), *n* = 6 (**33**)].

	<b>32</b>	<b>33</b>
Au(1)–Au(2)	2.56223(19)	2.5390(3)
Au(2)–P(2)	2.3327(10)	2.3383(16)
Au(2)–C(6)	2.066(4)	2.068(6)
Au(1)–Cl(1)	2.3828(9)	2.3673(15)
Au(1)–P(1)	2.3331(9)	2.3313(15)
Au(1)–C(24)	2.073(4)	2.064(6)
Au(2)–Cl(2)	2.3646(10)	2.3715(16)
Au(1)–Au(2)–P(2)	84.29(2)	82.79(4)
Au(2)–C(6)–C(1)	120.9(3)	121.6(4)
Au(1)–Au(2)–C(6)	92.29(10)	90.06(17)
P(2)–Au(2)–C(6)	176.53(11)	172.48(18)
Au(2)–Au(1)–Cl(1)	173.79(2)	170.34(4)
Cl(2)–Au(2)–C(6)	91.28(11)	93.67(17)
Au(2)–Au(1)–P(1)	82.95(2)	83.74(4)
Au(1)–C(24)–C(19)	122.4(3)	119.9(4)
Au(2)–Au(1)–C(24)	91.97(10)	91.04(17)
P(1)–Au(1)–C(24)	174.20(11)	174.47(18)
Au(1)–Au(2)–Cl(2)	175.42(3)	169.78(4)
Cl(1)–Au(1)–C(24)	93.17(11)	93.77(18)

The structures of **32** and **33** are similar to those of their protio and tetrafluoro analogues and consist of two metal-metal-bonded, square planar gold(II) atoms bridged by a pair of (C<sub>6</sub>H<sub>3</sub>-*n*-F-2-PPh<sub>2</sub>) (*n* = 5, 6) ligands in a head-to-tail arrangement and capped by two chloride groups. The Au⋯Au separations are *ca.* 0.3 Å shorter than those in the corresponding parent dimer, consistent with the formation of a formal metal-metal bond; a similar trend was observed in the protio<sup>181,184</sup> and tetrafluoro analogues. The Au-Cl distances [*n* = 6, 2.3673(15) Å and 2.3715(16) Å; *n* = 5, 2.3828(9) Å and 2.3646(10) Å]

are similar to those observed in the tetrafluoro dichlorodigold(II) complex **2** [2.3615(18) Å, 2.3749(17) Å] and bis(ylide) complex [Au<sub>2</sub>Cl<sub>2</sub>{(μ-CH<sub>2</sub>)<sub>2</sub>PPh<sub>2</sub>}<sub>2</sub>] [2.388(8) Å].<sup>121</sup> The C-Au-P angles [*n* = 6, 174.47(18)° and 172.48(18)°; *n* = 5, 174.20(11)° and 176.53(11)°] are close to the expected 180°. The Cl-Au-Au angles in **33** [170.34(5)°, 169.78(4)°] deviate more from linearity compared to those in **32** [173.79(2)°, 175.42(3)°], perhaps to accommodate the *ortho*-fluorine substituents.

Although solutions of the dibromo complex **35** appeared to be spectroscopically pure, attempts to grow a single crystal unexpectedly gave a trinuclear complex **38** of empirical formula C<sub>54</sub>H<sub>39</sub>Au<sub>3</sub>Br<sub>2</sub>F<sub>3</sub>P<sub>3</sub>, whose structure contains three gold and two bromine atoms (Figure 34). The basic structure consists of the expected digold(II) framework in which one of the axial bromide ligands has been replaced by a σ-carbon bonded [(6-FC<sub>6</sub>H<sub>3</sub>-2-PPh<sub>2</sub>)Au<sup>I</sup>Br] fragment, which is folded around to give a gold-gold separation of 3.0432(3) Å; this separation is significantly greater than that of 2.6065(3) Å where both gold atoms are bridged by two 6-FC<sub>6</sub>H<sub>3</sub>PPh<sub>2</sub> ligands. The Au-Br bond length in the linearly coordinated (6-FC<sub>6</sub>H<sub>3</sub>-2-PPh<sub>2</sub>)Au<sup>I</sup>Br fragment [2.4181(6) Å] is similar to that reported for the mononuclear gold complex [AuBr(PPh<sub>3</sub>)] [2.407(2) Å],<sup>298</sup> but significantly shorter than that in the square planar Au-Au-Br unit [2.56131(6) Å]; this bond length is longer than those observed in the corresponding tetrafluoro dibromodigold(II) complex **3** [2.4968(6) Å, 2.4878(6) Å] due to the *trans*-influence of the Au-Au bond.

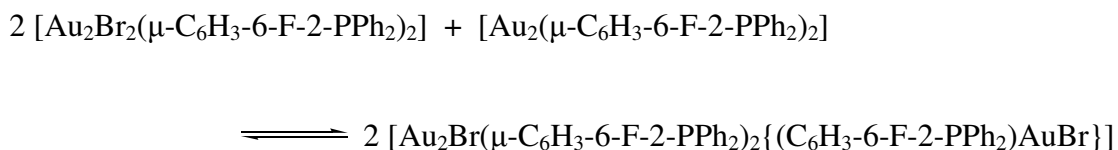


**Figure 34.** Molecular structure of **38**. Ellipsoids show 50% probability levels. Hydrogen atoms have been omitted and only the *ipso* carbons of the PPh<sub>2</sub> groups are shown for clarity.

Empirically, the structure of **38** consists of one molecule of [Au<sub>2</sub>Br<sub>2</sub>(μ-C<sub>6</sub>H<sub>3</sub>-6-F-2-PPh<sub>2</sub>)<sub>2</sub>] **35** and half a molecule of [Au<sub>2</sub>(μ-C<sub>6</sub>H<sub>3</sub>-6-F-2-PPh<sub>2</sub>)<sub>2</sub>] **28**. Presumably the sample of **35** contained a small amount, or decomposed in solution to give a small amount, of the digold(I) precursor **28**, which behaves as an arylating agent to give the trinuclear complex **38** according to Scheme 52. In light of this unexpected result, the reaction between the dibromodigold(II) complex and digold(I) precursor in 2:1 molar ratio was monitored by <sup>31</sup>P NMR spectroscopy. The <sup>31</sup>P NMR spectrum showed three small peaks at δ -4.5, -3.5 and 38.1, attributed to the expected trinuclear complex **38**. Other peaks (*ca.* 90 %) represent the starting materials, gold(I)-gold(III) complex



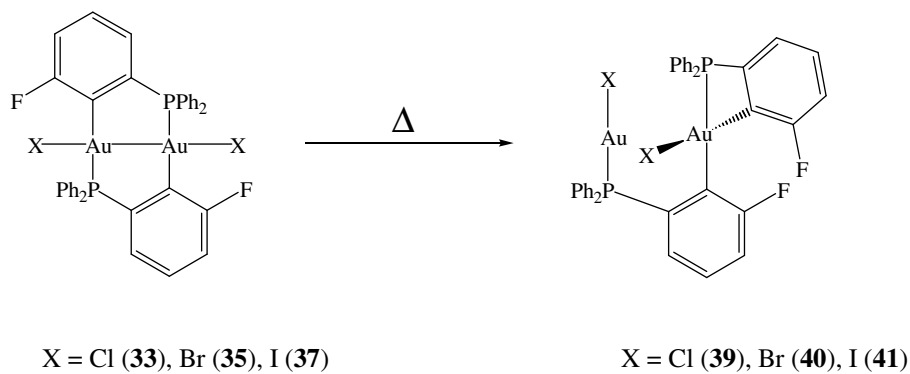
$[\text{BrAu}(\mu\text{-}2\text{-C}_6\text{H}_3\text{-}6\text{-F-}2\text{-PPh}_2)(\kappa^2\text{-C}_6\text{H}_3\text{-}6\text{-F-}2\text{-PPh}_2)\text{AuBrX}]$  (see Section 4.2.4) and some unidentified species.



**Scheme 52. Proposed formation of the trinuclear complex 38.**

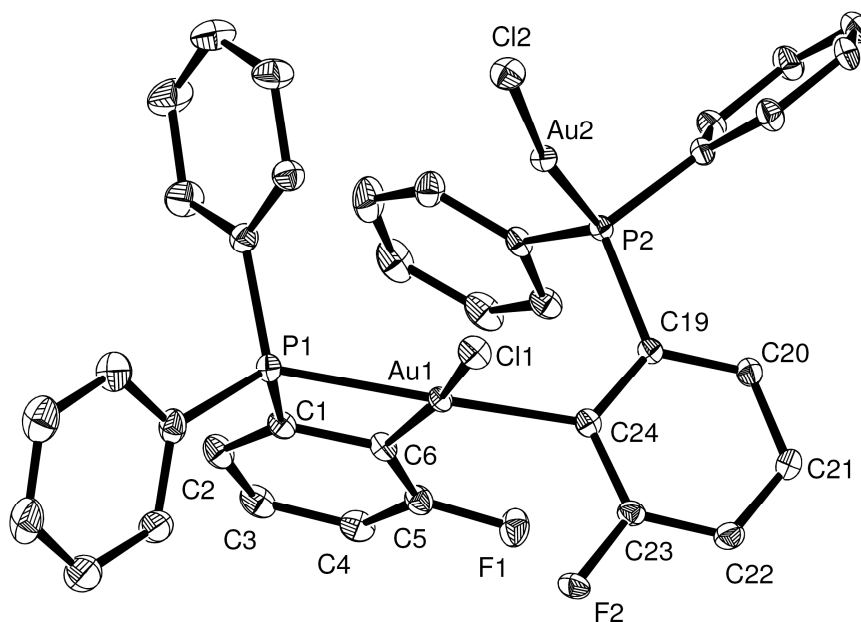
**4.2.4 Isomerisation of the dihalogold(II) complexes  $[\text{Au}_2\text{X}_2(\mu\text{-C}_6\text{H}_3\text{-}n\text{-F-}2\text{-PPh}_2)_2]$  ( $n = 5, 6$ ).**

Like their 6-methyl and tetrafluoro analogues, the 6-fluoro complexes **33**, **35** and **37** rearrange over several hours when toluene solutions are heated to 70 °C. From these solutions, almost colourless solids of structure  $[\text{XAu}(\mu\text{-}2\text{-C}_6\text{H}_3\text{-}6\text{-F-}2\text{-PPh}_2)(\kappa^2\text{-C}_6\text{H}_3\text{-}6\text{-F-}2\text{-PPh}_2)\text{AuX}]$  [ $\text{X} = \text{Cl}$ , **39**;  $\text{Br}$ , **40**;  $\text{I}$ , **41**] could be isolated in good yields (Scheme 53). The  $^{31}\text{P}$  NMR spectra for these complexes each showed a pair of resonances of equal intensity in the regions of +40 and -60 ppm, as doublets and doublet of triplets, respectively, possibly due to the  $^{31}\text{P}$ - $^{31}\text{P}$  and  $^{31}\text{P}$ - $^{19}\text{F}$  coupling. The structure of **39** has been confirmed by X-ray diffraction and is shown in Figure 35; selected bond distances and angles are listed in Table 24.



**Scheme 53. Isomerisation of the dihalodigold(II) complexes  $[\text{Au}_2\text{X}_2(\mu\text{-C}_6\text{H}_3\text{-6-F-2-PPh}_2)_2]$**

**$[\text{X} = \text{Cl (33), Br (35), I (37)}].$**



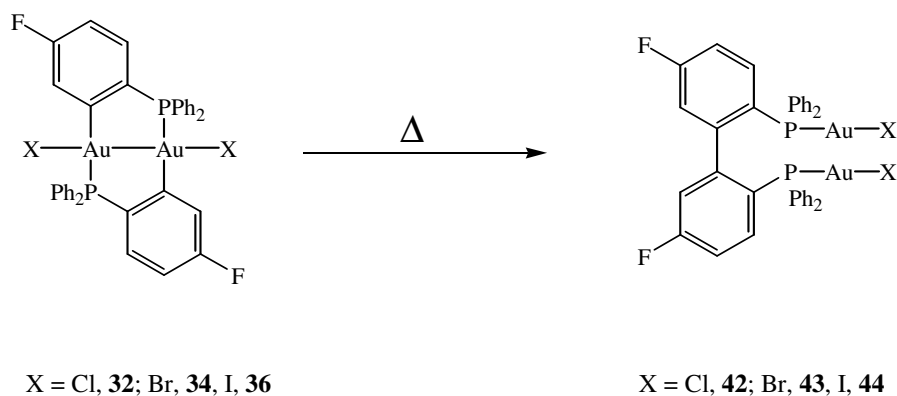
**Figure 35. Molecular structure of  $[\text{ClAu}(\mu\text{-C}_6\text{H}_3\text{-6-F-2-PPh}_2)(\kappa^2\text{-C}_6\text{H}_3\text{-6-F-2-PPh}_2)\text{AuCl}]$  (39). Ellipsoids show 30 % probability levels. Hydrogen atoms have been omitted and only the *ipso* carbon atoms of the  $\text{PPh}_2$  groups are shown for clarity.**

The structure of **39** is similar to that of its tetrafluoro analogue **6**. The angle subtended at the gold(III) centre by the four-membered ring is 68.18(9)°. The Au(III)-C bond lengths of 2.027(3) Å and 2.074(3) Å are shorter than those in the tetrafluoro analogue **6** [2.044(6) Å and 2.075(5) Å]. The Au-Cl [2.3473(7) Å, 2.3004(8) Å] and Au-P [2.3710(8) Å, 2.2256(8) Å] bond lengths in **39** are similar to the corresponding bonds observed in **6** [2.31115(av.) Å and 2.29125(av.) Å, respectively]. The Au...Au separation of 3.592 Å suggests a weak aurophilic interaction between the metal atoms.

**Table 24. Selected bond distances (Å) and angles (°) in [ClAu( $\mu$ -C<sub>6</sub>H<sub>3</sub>-6-F-2-PPh<sub>2</sub>)( $\kappa^2$ -C<sub>6</sub>H<sub>3</sub>-6-F-2-PPh<sub>2</sub>)AuCl] (**39**).**

Au(1)–Au(2)	3.5922(2)		
Au(1)–P(1)	2.3710(8)	Au(2)–P(2)	2.2256(8)
Au(1)–C(24)	2.074(3)	Au(1)–C(6)	2.027(3)
Au(1)–Cl(1)	2.3473(7)	Au(2)–Cl(2)	2.3004(8)
Cl(1)–Au(1)–C(6)	168.36(9)	C(24)–Au(1)–C(6)	97.66(12)
Cl(1)–Au(1)–P(1)	101.67(3)	Au(1)–P(1)–C(1)	83.07(11)
Cl(1)–Au(1)–C(24)	93.11(8)	P(1)–C(1)–C(6)	101.3(2)
P(1)–Au(1)–C(24)	163.96(8)	Au(1)–C(6)–C(1)	107.4(2)
P(1)–Au(1)–C(6)	68.18(9)	Cl(2)–Au(2)–P(2)	170.94(3)

In contrast to the reactivity of the 6-fluoro substituted complexes, the compounds [Au<sub>2</sub>X<sub>2</sub>( $\mu$ -C<sub>6</sub>H<sub>3</sub>-5-F-2-PPh<sub>2</sub>)<sub>2</sub>] (X = Cl, **32**; Br, **34**; I, **36**) undergo C-C coupling on heating or exposure to light to give P-bonded digold(I) biphenyldiyl species [Au<sub>2</sub>X<sub>2</sub>(2,2'-Ph<sub>2</sub>P-5-F-C<sub>6</sub>H<sub>3</sub>C<sub>6</sub>H<sub>3</sub>-5-F-PPh<sub>2</sub>)] (X = Cl, **42**; Br, **43**; I, **44**) (Scheme 54). This behaviour parallels that of the gold complexes containing the 2-C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>,<sup>165</sup> and C<sub>6</sub>H<sub>3</sub>-5-Me-2-PPh<sub>2</sub> ligands.<sup>166</sup>



**Scheme 54.** Rearrangement of the dihalodigold(II) complexes  $[\text{Au}_2\text{X}_2(\mu\text{-C}_6\text{H}_3\text{-5-F-2-PPh}_2)_2]$ .

The ESI-mass spectra of **42-44** each showed a peak corresponding to the  $[\text{M-halide}]^+$  fragment and the  $^{31}\text{P}$  NMR spectra each showed a single resonance in the region of  $\delta$  30, the chemical shift increasing in the order  $\text{Cl} < \text{Br} < \text{I}$ ; a similar trend was observed in the corresponding 5-methyl series.<sup>166</sup> The  $^{31}\text{P}$  NMR spectroscopic data for complexes **42-44** are shown in Table 25. The structures of **42** and **43** have been confirmed by X-ray diffraction; the molecular structure of **42** is shown in Figure 36. Selected bond distances and angles for complexes **42** and **43** are listed in Table 26.

**Table 25.**  $^{31}\text{P}$  NMR data for the digold(I) complexes **42-44**.

Compound	$\delta_{\text{P}}$ ( $\text{C}_6\text{D}_6$ )
$[\text{Au}_2\text{Cl}_2(2,2'\text{-Ph}_2\text{P-5-F-C}_6\text{H}_3\text{C}_6\text{H}_3\text{-5-F-PPh}_2)]$ ( <b>42</b> )	27.2
$[\text{Au}_2\text{Br}_2(2,2'\text{-Ph}_2\text{P-5-F-C}_6\text{H}_3\text{C}_6\text{H}_3\text{-5-F-PPh}_2)]$ ( <b>43</b> )	28.9
$[\text{Au}_2\text{I}_2(2,2'\text{-Ph}_2\text{P-5-F-C}_6\text{H}_3\text{C}_6\text{H}_3\text{-5-F-PPh}_2)]$ ( <b>44</b> )	31.8

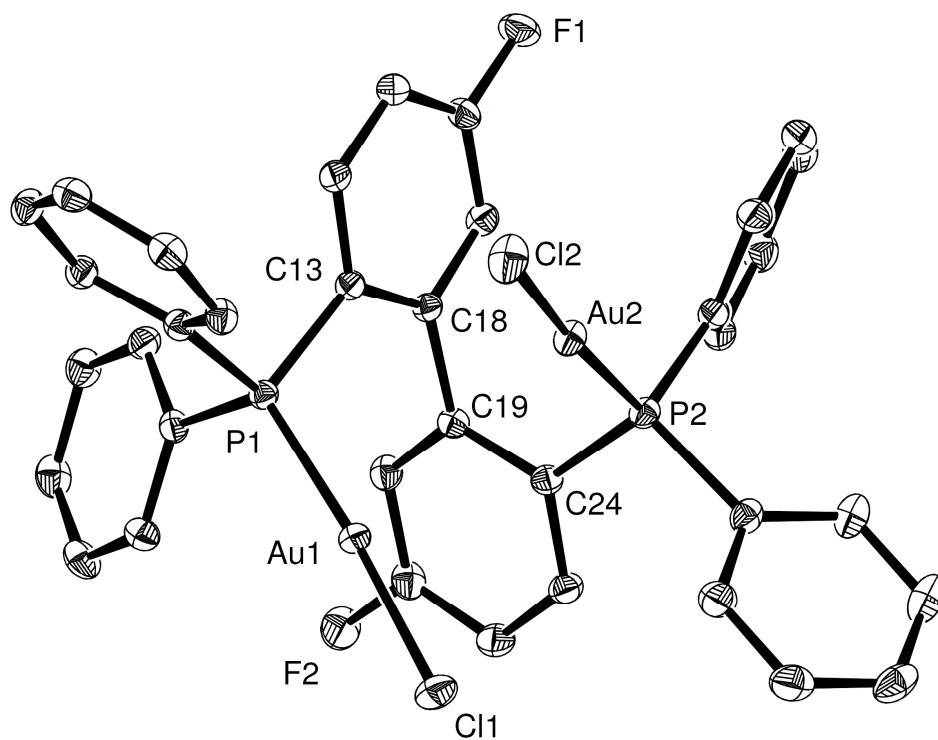


Figure 36. Molecular structure of  $[\text{Au}_2\text{Cl}_2(2,2'\text{-Ph}_2\text{P-5-F-C}_6\text{H}_3\text{C}_6\text{H}_3\text{-5-F-PPh}_2)]$  (42).

Ellipsoids show 50% probability levels and hydrogen atoms have been omitted for clarity.

Table 26. Selected bond distances (Å) and angles (°) in  $[\text{Au}_2\text{X}_2(2,2'\text{-Ph}_2\text{P-5-F-C}_6\text{H}_3\text{C}_6\text{H}_3\text{-5-F-PPh}_2)]$  [X = Cl (42), Br (43)].

	42	43
Au(1)–Au(2)	3.59669(13)	3.54623(17)
Au(1)–P(1)	2.2292(6)	2.2371(7)
Au(2)–P(2)	2.2267(6)	2.2329(8)
Au(1)–X(1)	2.2908(6)	2.4060(3)
Au(2)–X(2)	2.2900(6)	2.4037(3)
P(1)–Au(1)–X(1)	175.71(2)	175.37(2)
P(2)–Au(2)–X(2)	175.06(2)	174.64(2)
C(24)–P(2)–Au(2)	114.78(8)	114.46(10)
C(13)–P(1)–Au(1)	114.90(8)	114.29(10)

Like those observed in  $[\text{Au}_2\text{X}_2(2,2'\text{-Ph}_2\text{P-5-MeC}_6\text{H}_3\text{C}_6\text{H}_3\text{-5-MePPh}_2)]$  [ $\text{X} = \text{Cl, Br, I}$ ],<sup>166</sup> and its arsenic analogue [ $\text{X} = \text{Cl, Br, I, C}_6\text{F}_5$ ],<sup>182</sup> the molecular structures of **42** and **43** consist of a biphenyl backbone with two  $\text{Ph}_2\text{PAuX}$  ( $\text{X} = \text{Cl, Br}$ ) substituents in the 2 and 2' positions. The biphenyl backbone is twisted about the central C-C bond with the gold atoms in a *syn*-type configuration. In contrast, the unsubstituted biphenyl complex  $[\text{Au}_2(\text{C}_6\text{F}_5)_2(2,2'\text{-Et}_2\text{PC}_6\text{H}_4\text{C}_6\text{H}_4\text{PEt}_2)]$  shows alternative *anti*-arrangement.<sup>183</sup>

The gold-gold distances in **42** and **43** [3.59669(13) Å and 3.54623(17) Å, respectively] are significantly greater than that in  $[\text{Au}_2\text{I}_2(2,2'\text{-Ph}_2\text{P-5-MeC}_6\text{H}_3\text{C}_6\text{H}_3\text{-5-MePPh}_2)]$  [2.978(3) Å], but less than that in  $[\text{Au}_2(\text{C}_6\text{F}_5)_2(2,2'\text{-Ph}_2\text{As-5-MeC}_6\text{H}_3\text{C}_6\text{H}_3\text{-5-MeAsPh}_2)]$  [3.8139(4) Å]. These distances are in the range expected for weak aurophilic interactions.<sup>70</sup>

In **42** and **43**, the Au-X [ $\text{X} = \text{Cl}$ , 2.2900(6) Å and 2.2908(6) Å; Br, 2.4060(3) Å and 2.4037(3) Å] and Au-P [2.2292(6) Å and 2.2267(6) Å; 2.2371(7) Å and 2.2329(8) Å, respectively] distances are similar to those in  $[\text{AuCl}(\text{PPh}_3)]$  [2.279(3) Å and 2.235(3) Å, respectively],<sup>299</sup> and  $[\text{AuBr}(\text{PPh}_3)]$  [2.407(2) and 2.252(6) Å, respectively].<sup>298</sup> The dihedral angles of the two phenyl rings of the biphenyl units are 82.75(0.07)° and 80.58(0.09)° in **42** and **43**, respectively. They are smaller than that of 101° observed in  $[\text{Au}_2\text{I}_2(2,2'\text{-Ph}_2\text{P-5-MeC}_6\text{H}_3\text{C}_6\text{H}_3\text{-5-MePPh}_2)]$  and fall in the range of values reported for  $[\text{Au}_2\text{X}_2(2,2'\text{-Ph}_2\text{As-5-MeC}_6\text{H}_3\text{C}_6\text{H}_3\text{-5-MeAsPh}_2)]$  [ $\text{X} = \text{Cl}$  88.79(8)°, Br 85.16(11)°, I 79.74(9)° and  $\text{C}_6\text{F}_5$  75.43(18)°]. The dihedral angles in **42** and **43** decrease in the order  $\text{Cl} > \text{Br}$ , presumably to accommodate the larger halide, a similar trend was observed in 5-methyl arsenic analogues.

The behaviour of the 6-fluoro substituted dihalodigold(II) complexes  $[\text{Au}_2^{\text{II}}\text{X}_2(\mu\text{-C}_6\text{H}_3\text{-6-F-2-PPh}_2)_2]$  ( $\text{X} = \text{Cl, Br, I}$ ) parallels that of their 6-methyl and tetrafluoro analogues, despite the fact that the electronic properties of methyl and fluorine groups are different. In contrast, the less sterically demanding 5-fluoro substituted complexes behave similarly to their protio analogues. These observations suggest that the number of fluorine substituents in the metallated aryl ring is less important than their position in determining the reactivity of the digold complexes.

***Chapter 5.  $^{197}\text{Au}$  Mössbauer spectroscopic study of dinuclear cyclometallated gold complexes.***

***5.1 Gold-197 Mössbauer spectroscopy for the characterisation of gold compounds.***

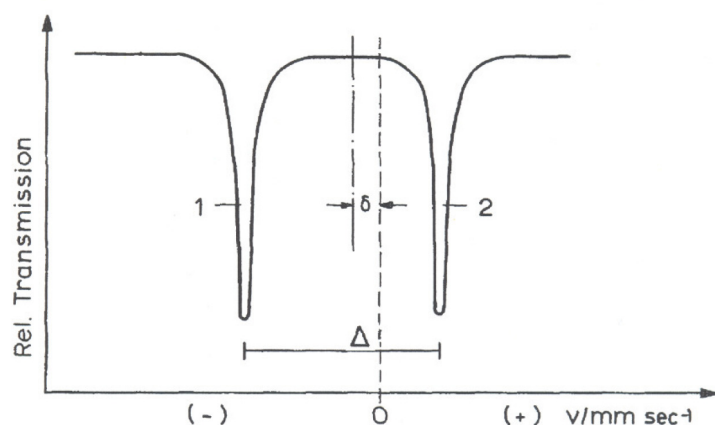
The discovery of recoilless gamma ray emission and absorption in 1957, now referred to as the Mössbauer Effect, has provided chemists with a versatile technique, called Mössbauer spectroscopy.<sup>300</sup> Mössbauer spectroscopy is a form of absorption spectroscopy in which gamma radiation excites the energy level transitions within the nucleus of some isotopes with a very low lying excited state (eg.  $^{197}\text{Au}$ ,  $^{57}\text{Fe}$ ,  $^{119}\text{Sn}$  and  $^{121}\text{Sb}$ ). These transitions reflect the symmetry and density of the electron cloud surrounding the nucleus, thus providing chemical information about the complex.



Mössbauer spectroscopy of  $^{197}\text{Au}$  was first investigated almost forty years ago by Mössbauer,<sup>301</sup> Shirley,<sup>302</sup> and Nichols.<sup>303</sup> Since then, it has proved to be one of the most powerful techniques for the characterisation of gold complexes in the solid state, particularly those compounds that are insoluble or unstable in solution.<sup>304-308</sup> Although  $^{197}\text{Au}$  Mössbauer spectroscopy is able to determine the oxidation states of the gold atom(s) and their chemical environment, two main disadvantages are apparent; the relatively large sample requirements (*ca.* 100 mg Au) and short half life of the  $\gamma$ -ray source ( $^{197}\text{Pt}$ ,  $t_{1/2} = 18$  hours) have limited its widespread use.<sup>309</sup>

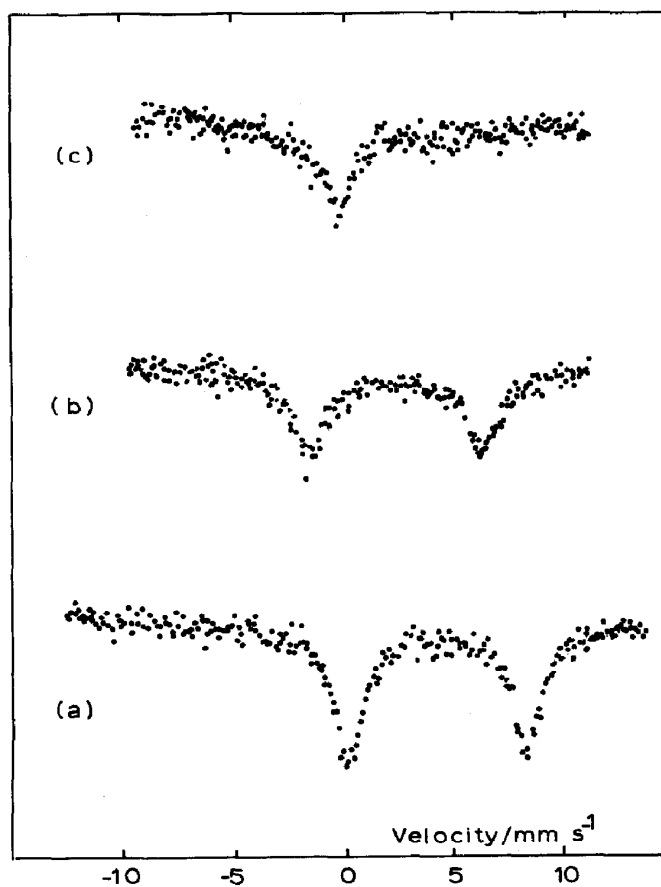
Different Mössbauer parameters have been described, among which the isomer shift (IS) and quadrupole splitting (QS) are of great significance in the chemical application of the Mössbauer Effect. The former is a measure of the total electron density at the gold nucleus, whilst the latter reflects the interaction of the nucleus with the electric field due to the surrounding electrons, thus indicating the nature and arrangement of gold-ligand bonds. Both the IS ( $\text{mm s}^{-1}$ ) and QS ( $\text{mm s}^{-1}$ ) change with the type of coordinated ligands, the coordination number and the oxidation state of the metal.

The Mössbauer transition in  $^{197}\text{Au}$  is from the 77.3 KeV level of spin 1/2 to the ground state of spin 3/2, giving a two line spectrum or doublet. The isomer shift (IS) refers to the centre of the two resonances, while the quadrupole splitting (QS) is the separation between the two peaks (Figure 37).<sup>310</sup>



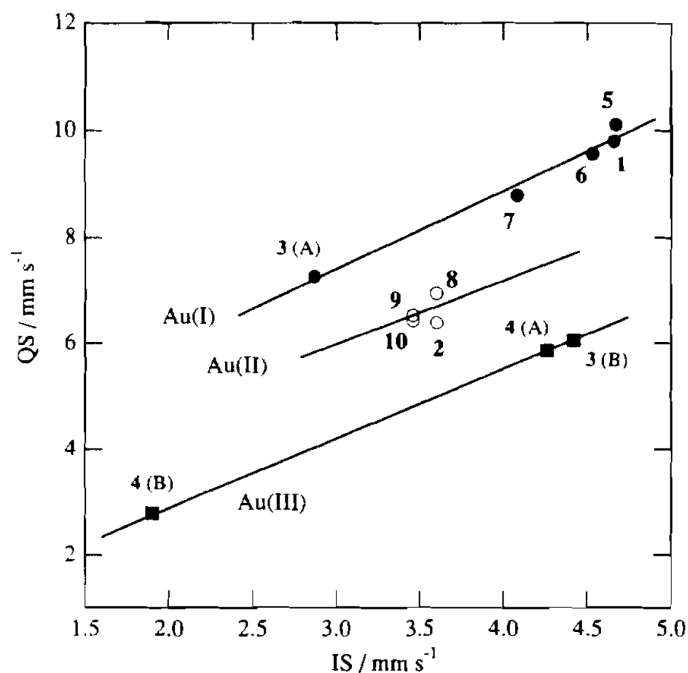
**Figure 37. Schematic Mössbauer spectrum where  $\delta$  = isomer shift and  $\Delta$  = quadrupole splitting (reproduced from ref. 310).**

If a gold atom occupies a site of high symmetry the value of QS is zero, and the Mössbauer spectrum shows a single line, like that observed for the tetrahedral ion  $[\text{Au}(\text{PPh}_3)_4]^+$ .<sup>307</sup> The Mössbauer spectra of  $[\text{Au}(\text{PPh}_3)_n]\text{ClO}_4$  ( $n = 2, 3, 4$ ) are shown in Figure 38. Splitting of the singlet into a doublet is observed when the ligand arrangements decrease the symmetry of the complex. The increase in covalency of the gold-phosphorus bond results in an increase in the value of QS.



**Figure 38.**  $^{197}\text{Au}$  Mössbauer spectra for  $[\text{Au}(\text{PPh}_3)_n]\text{ClO}_4$ ;  $n = 2$  (a),  $n = 3$  (b),  $n = 4$  (c)  
(reproduced from ref. 314).

The plots of quadrupole splitting versus isomer shift, called correlation plots, show distinct regions corresponding to different oxidation states (Figure 39). These plots can then be used to determine the oxidation states of gold atom(s) and also the chemical environments of unknown compounds.



**Figure 39.** Correlation plot for a series of dinuclear gold complexes (reproduced from ref. 311). 1  $[\text{Au}_2(\mu\text{-C}_6\text{H}_3\text{-5-Me-2-PPh}_2)_2]$ , 2  $[\text{Au}_2\text{I}_2(\mu\text{-C}_6\text{H}_3\text{-6-Me-2-PPh}_2)_2]$ , 3  $[\text{IAu}(\mu\text{-2-C}_6\text{H}_3\text{-6-Me-2-PPh}_2)(\kappa^2\text{-C}_6\text{H}_3\text{-6-Me-2-PPh}_2)\text{AuI}]$ , 4  $[\text{Cl}_3\text{Au}(\mu\text{-2-C}_6\text{H}_3\text{-6-Me-2-PPh}_2)(\kappa^2\text{-C}_6\text{H}_3\text{-6-Me-2-PPh}_2)\text{AuCl}]$ , 5  $[\text{Au}_2(\mu\text{-2-C}_6\text{H}_4\text{PEt}_2)_2]$ , 6  $[\text{Au}_2(\mu\text{-2-C}_6\text{H}_4\text{PPh}_2)_2]$ , 7  $[\text{Au}_2(\mu\text{-2-C}_6\text{H}_4\text{AsPh}_2)_2]$ , 8  $[\text{Au}_2\text{I}_2(\mu\text{-2-C}_6\text{H}_4\text{PEt}_2)_2]$ , 9  $[\text{Au}_2\text{I}_2(\mu\text{-2-C}_6\text{H}_4\text{PPh}_2)_2]$ , 10  $[\text{Au}_2\text{Br}_2(\mu\text{-2-C}_6\text{H}_4\text{PPh}_2)_2]$ .

### 5.1.1 Gold(I) compounds.

The greatest amount of Mössbauer data is available for gold(I) compounds containing linearly two-coordinated gold atoms. Of the gold(I) compounds with coordination numbers of three and four, a majority are for those containing tertiary phosphine ligands, *e.g.* the compound  $[\text{Au}(\text{PMePh}_2)_4]\text{ClO}_4$ .<sup>312</sup> Gold(I) compounds containing two-coordinated gold atoms show a positive correlation between IS and QS.<sup>301-303</sup> Softer ligands and those with higher donor ability increase the values of IS and QS. The order

is typically halide < nitrogen group < tertiary phosphine < organic group. If the gold atom is sp hybridized, ligands with a high electron donating ability will increase the population of the 6s and 6p<sub>z</sub> orbitals, leading to a rise in IS and QS, respectively.<sup>304</sup> In the series of compounds of the type [AuX(PR<sub>3</sub>)], where X may be an anionic ligand or another tertiary phosphine, a reasonably linear correlation is observed between the Mössbauer data and the Au-P bond length.<sup>307</sup>

### **5.1.2 Gold(III) compounds.**

Of the gold(III) compounds, Mössbauer data are available only for those in which the metal is four-coordinate with square-planar geometry. The data clearly show a QS-IS correlation similar to that for gold(I). Both parameters increase as the ligands become softer, and the rate of this change depends on the oxidation state of the gold atoms. The IS for gold(III) increases at only a slightly greater rate than for gold(I). Although bonds to gold(III) are more covalent and more charge is donated per ligand, donated charge goes into p and d orbitals which have a shielding effect, resulting in a reduction of electron density at the nucleus.<sup>304,309</sup>

### **5.1.3 Dinuclear gold compounds.**

Mössbauer studies of the dinuclear cyclometallated gold complexes [Au<sub>2</sub>(μ-2-C<sub>6</sub>H<sub>4</sub>PR<sub>2</sub>)<sub>2</sub>] (R = Et, Ph)<sup>313</sup> and [Au<sub>2</sub>(μ-C<sub>6</sub>H<sub>3</sub>-6-Me-2-PPh<sub>2</sub>)<sub>2</sub>]<sup>311</sup> have been reported by Bennett *et al.* It was shown that in the case of the latter, electron donation from the methyl substituents increases the 6s electron density of the gold atoms, compared to the analogous non-methylated compound. The Mössbauer data reported for the closely

related arsenic analogues,  $[\text{Au}_2(\mu\text{-C}_6\text{H}_3\text{-}n\text{-Me-2-AsPh}_2)_2]$  ( $n = 5, 6$ ), are smaller than those for the phosphorus complexes, indicating that the Au-As bond is less covalent than the Au-P bond in their phosphorus counterparts (see Table 28).<sup>314</sup>

## 5.2 <sup>197</sup>Au Mössbauer spectra.

<sup>197</sup>Au Mössbauer spectroscopic data were obtained for the cyclometallated gold(I) complex **1**, the digold(II) complexes  $[\text{Au}_2\text{X}_2(\mu\text{-2-C}_6\text{F}_4\text{PPh}_2)_2]$  [ $\text{X} = \text{Cl}$  (**2**),  $\text{ONO}_2$  (**12**)] and the gold(I)-gold(III) complexes  $[\text{XAu}(\mu\text{-2-C}_6\text{F}_4\text{PPh}_2)(\kappa^2\text{-2-C}_6\text{F}_4\text{PPh}_2)\text{AuX}]$  [ $\text{X} = \text{Cl}$  (**6**),  $\text{ONO}_2$  (**23**)]. The <sup>197</sup>Au Mössbauer spectra for **1**, **2**, **6**, **12** and **23** are shown in Figure 40 and the Mössbauer parameters are summarised in Table 27.

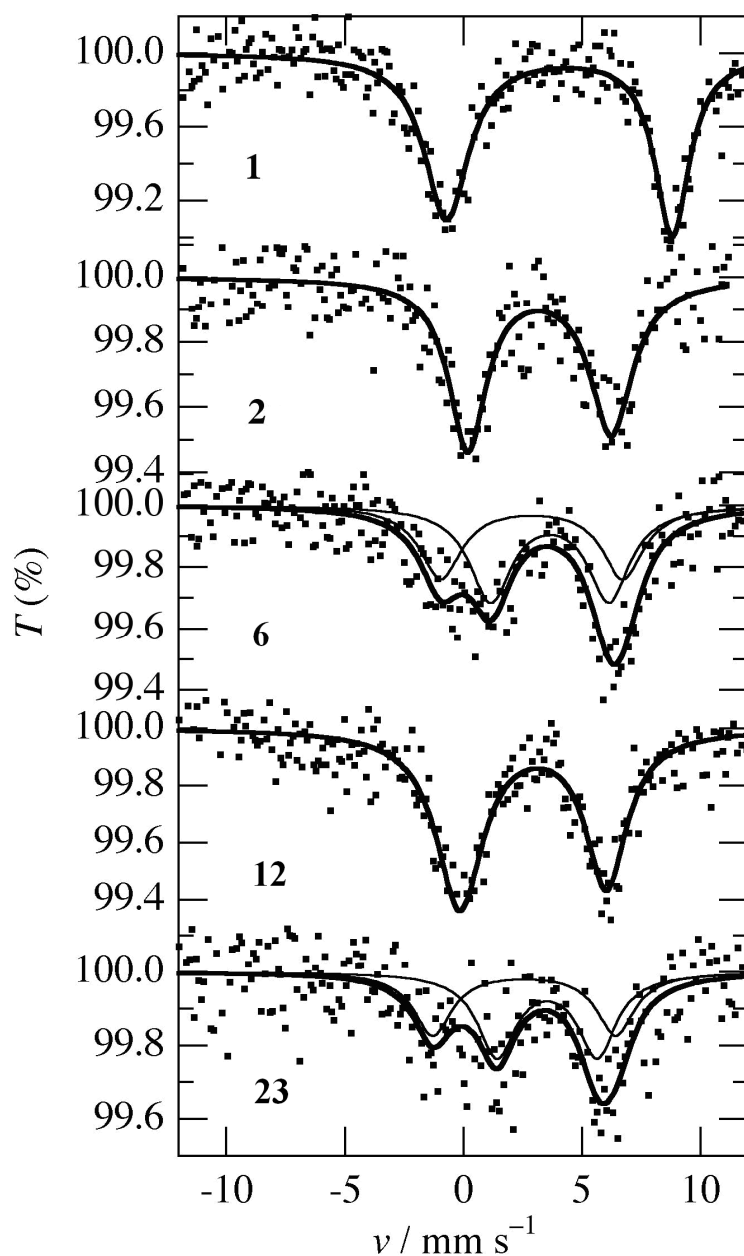


Figure 40.  $^{197}\text{Au}$  Mössbauer spectra for complexes **1**, **2**, **6**, **12** and **23** at 12 K.

The spectra of **1**, **2** and **12** show the expected well resolved quadrupole doublet, showing that the two gold atoms in these complexes are equivalent. In contrast, complexes **6** and **23** show a pair of quadrupole doublets in their spectra confirming the presence of two inequivalent gold centres.

**Table 27.**  $^{197}\text{Au}$  Mössbauer parameters for complexes **1**, **2**, **6**, **12** and **23**.

<b>Compound</b>	<b>Au Oxidation state</b>	<b>IS (mm s<sup>-1</sup>)</b>	<b>QS (mm s<sup>-1</sup>)</b>
$[\text{Au}_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$ ( <b>1</b> )	I	4.04	9.51
$[\text{Au}_2\text{Cl}_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$ ( <b>2</b> )	II	3.22	6.10
$[\text{Au}_2(\text{ONO}_2)_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$ ( <b>12</b> )	II	2.93	6.18
$[\text{ClAu}(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)(\kappa^2\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)\text{AuCl}]$ ( <b>6</b> )	I (site A)	2.88	7.69
	III (site B)	3.64	4.98
$[(\text{O}_2\text{NO})\text{Au}(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)(\kappa^2\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)\text{Au}(\text{ONO}_2)]$ ( <b>23</b> )	I (site A)	2.56	7.71
	III (site B)	3.51	4.23

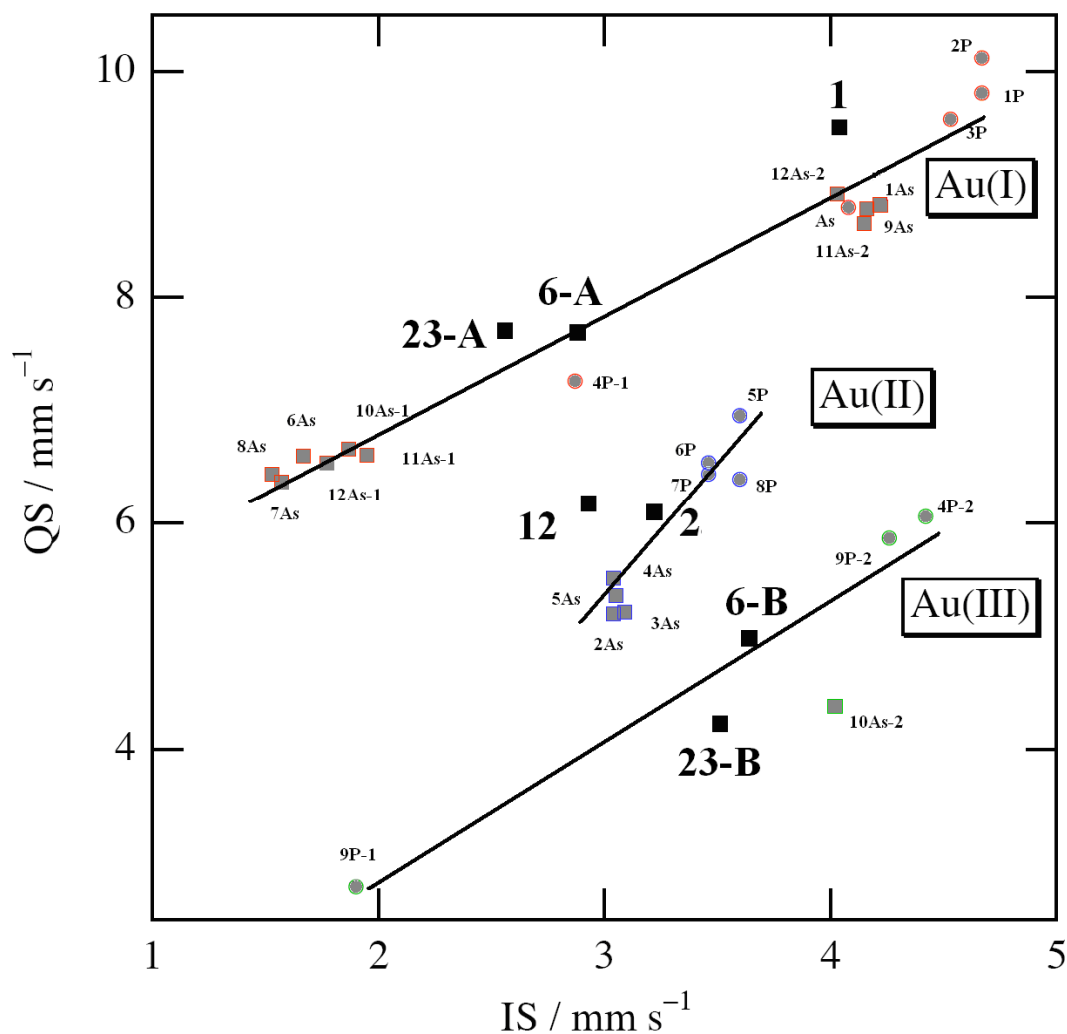
The correlation plot for **1**, **2**, **6**, **12** and **23** is shown in Figure 41. The additional data, summarised in Table 28, are taken from references 311, 313 and 314.



**Table 28.**  $^{197}\text{Au}$  Mössbauer parameters for dinuclear gold complexes.

<b>Compound</b>	<b>Au Oxidation state</b>	<b>IS (mm/s)</b>	<b>QS (mm/s)</b>
$[\text{Au}_2(\mu\text{-C}_6\text{H}_3\text{-6-Me-2-PPh}_2)_2]$ ( <b>1P</b> ) <sup>b</sup>	I	4.67	9.81
$[\text{Au}_2(\mu\text{-2-C}_6\text{H}_4\text{PEt}_2)_2]$ ( <b>2P</b> ) <sup>a</sup>	I	4.67	10.12
$[\text{Au}_2(\mu\text{-2-C}_6\text{H}_4\text{PPh}_2)_2]$ ( <b>3P</b> ) <sup>a</sup>	I	4.53	9.58
$[\text{IAu}(\mu\text{-2-C}_6\text{H}_3\text{-6-Me-2-PPh}_2)$ $(\kappa^2\text{-C}_6\text{H}_3\text{-6-Me-2-PPh}_2)\text{Au}]$ ( <b>4P</b> ) <sup>b</sup>	I	2.87	7.26
$[\text{Au}_2\text{I}_2(\mu\text{-2-C}_6\text{H}_4\text{PEt}_2)_2]$ ( <b>5P</b> ) <sup>a</sup>	III	4.42	6.06
$[\text{Au}_2\text{I}_2(\mu\text{-2-C}_6\text{H}_4\text{PPh}_2)_2]$ ( <b>6P</b> ) <sup>a</sup>	II	3.60	6.96
$[\text{Au}_2\text{I}_2(\mu\text{-2-C}_6\text{H}_4\text{PPh}_2)_2]$ ( <b>6P</b> ) <sup>a</sup>	II	3.46	6.54
$[\text{Au}_2\text{Br}_2(\mu\text{-2-C}_6\text{H}_4\text{PPh}_2)_2]$ ( <b>7P</b> ) <sup>a</sup>	II	3.46	6.44
$[\text{Au}_2\text{I}_2(\mu\text{-C}_6\text{H}_3\text{-6-Me-2-PPh}_2)_2]$ ( <b>8P</b> ) <sup>b</sup>	II	3.46	6.44
$[\text{Cl}_3\text{Au}(\mu\text{-2-C}_6\text{H}_3\text{-6-Me-2-PPh}_2)$ $(\kappa^2\text{-C}_6\text{H}_3\text{-6-Me-2-PPh}_2)\text{AuCl}]$ ( <b>9P</b> ) <sup>b</sup>	II	3.60	6.39
$[\text{Cl}_3\text{Au}(\mu\text{-2-C}_6\text{H}_3\text{-6-Me-2-PPh}_2)$ $(\kappa^2\text{-C}_6\text{H}_3\text{-6-Me-2-PPh}_2)\text{AuCl}]$ ( <b>9P</b> ) <sup>b</sup>	III	4.26	5.87
$[\text{Cl}_3\text{Au}(\mu\text{-2-C}_6\text{H}_3\text{-6-Me-2-PPh}_2)$ $(\kappa^2\text{-C}_6\text{H}_3\text{-6-Me-2-PPh}_2)\text{AuCl}]$ ( <b>9P</b> ) <sup>b</sup>	III	1.90	2.79
$[\text{Au}_2(\mu\text{-2-C}_6\text{H}_4\text{AsPh}_2)_2]$ ( <b>As</b> ) <sup>a</sup>	I	4.08	8.80
$[\text{Au}_2(\mu\text{-C}_6\text{H}_3\text{-5-Me-2-AsPh}_2)_2]$ ( <b>1As</b> ) <sup>c</sup>	I	4.22	8.82
$[\text{Au}_2\text{Cl}_2(\mu\text{-C}_6\text{H}_3\text{-5-Me-2-AsPh}_2)_2]$ ( <b>2As</b> ) <sup>c</sup>	II	3.04	5.20
$[\text{Au}_2\text{Br}_2(\mu\text{-C}_6\text{H}_3\text{-5-Me-2-AsPh}_2)_2]$ ( <b>3As</b> ) <sup>c</sup>	II	3.09	5.21
$[\text{Au}_2\text{I}_2(\mu\text{-C}_6\text{H}_3\text{-5-Me-2-AsPh}_2)_2]$ ( <b>4As</b> ) <sup>c</sup>	II	3.05	5.50
$[\text{Au}_2(\text{OOCCH}_2)_2(\mu\text{-C}_6\text{H}_3\text{-5-Me-2-AsPh}_2)_2]$ ( <b>5As</b> ) <sup>c</sup>	II	3.05	5.36
$[\text{Au}_2\text{Cl}_2(2,2'\text{-Ph}_2\text{As-5-MeC}_6\text{H}_3\text{C}_6\text{H}_3\text{-5-Me-AsPh}_2)]$ ( <b>6As</b> ) <sup>c</sup>	I	1.67	6.60
$[\text{Au}_2\text{Br}_2(2,2'\text{-Ph}_2\text{As-5-MeC}_6\text{H}_3\text{C}_6\text{H}_3\text{-5-Me-AsPh}_2)]$ ( <b>7As</b> ) <sup>c</sup>	I	1.57	6.37
$[\text{Au}_2\text{I}_2(2,2'\text{-Ph}_2\text{As-5-MeC}_6\text{H}_3\text{C}_6\text{H}_3\text{-5-Me-AsPh}_2)]$ ( <b>8As</b> ) <sup>c</sup>	I	1.53	6.44
$[\text{Au}_2(\mu\text{-C}_6\text{H}_3\text{-6-Me-2-AsPh}_2)_2]$ ( <b>9As</b> ) <sup>c</sup>	I	4.16	8.79
$[\text{ClAu}(\mu\text{-2-C}_6\text{H}_3\text{-6-Me-2-AsPh}_2)$ $(\kappa^2\text{-C}_6\text{H}_3\text{-6-Me-2-AsPh}_2)\text{AuCl}]$ ( <b>10As</b> ) <sup>c</sup>	I	1.87	6.66
$[\text{ClAu}(\mu\text{-2-C}_6\text{H}_3\text{-6-Me-2-AsPh}_2)$ $(\kappa^2\text{-C}_6\text{H}_3\text{-6-Me-2-AsPh}_2)\text{AuCl}]$ ( <b>10As</b> ) <sup>c</sup>	III	4.02	4.38
$[\text{ClAu}\{\mu\text{-C}_6\text{H}_3\text{-6-Me-2-AsPh}_2\}\text{Au}$ $(\text{AsPh}_2\text{-2-Cl-3-Me-C}_6\text{H}_3)]$ ( <b>11As</b> ) <sup>c</sup>	I	1.95	6.61
$[\text{ClAu}\{\mu\text{-C}_6\text{H}_3\text{-6-Me-2-AsPh}_2\}\text{Au}$ $(\text{AsPh}_2\text{-2-Cl-3-Me-C}_6\text{H}_3)]$ ( <b>11As</b> ) <sup>c</sup>	I	4.15	8.66
$[\text{BrAu}(\mu\text{-C}_6\text{H}_3\text{-6-Me-2-AsPh}_2)$ $\text{Au}\{\text{AsPh}_2(3\text{-MeC}_6\text{H}_4)\}]$ ( <b>12As</b> ) <sup>c</sup>	I	1.77	6.54
$[\text{BrAu}(\mu\text{-C}_6\text{H}_3\text{-6-Me-2-AsPh}_2)$ $\text{Au}\{\text{AsPh}_2(3\text{-MeC}_6\text{H}_4)\}]$ ( <b>12As</b> ) <sup>c</sup>	I	4.03	8.92

a) Ref. 313, b) Ref. 311, c) Ref. 314.



**Figure 41.** Plot of QS against IS for dinuclear gold complexes.

The plot shows three distinct regions, corresponding to Au(I), Au(II) and Au(III) oxidation states. The oxidation states of the gold atoms in complexes **1**, **2**, **6**, **12** and **23** lie close to similar oxidation states within the expected regions: +1 in **1**, +2 in **2** and **12**, and mixed-valence state Au(I)-Au(III) in **6** and **23**. The IS and QS values of **1**, **2**, **6**, **12** and **23** are smaller than those of cyclometallated digold complexes **1P-9P**, indicating that both the s and p electron density of the gold atoms are decreased in these complexes due to the electron withdrawing effect of the fluorine atoms.

The Mössbauer parameters for **1**, **2**, **6**, **12** and **23** indicate that the Au-P bond covalency of dinuclear complexes containing 2-C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub> is more similar to that of Au-As bond of the arsenic complexes, while there is a significant decrease in the Au-P bond covalency of tetrafluoro complexes compared to that of protio and 6-methyl phosphorous complexes. The Au(I) atoms in the mixed-valence Au(I)-Au(III) compounds **6** and **23** are located in the low IS and QS region in the expected Au(I) area of the plot, indicating the different chemical environment compared to the symmetrical gold(I) dimers.

The digold(II) complexes are located in the region expected for Au(II) complexes of the plot. The two gold atoms containing the four-membered ring unit (complexes **6** and **23**) lie in the Au(III) region of the plot, close to the gold(III) atoms containing similar chemical environments and away from the gold(III) atom containing the P-Au-X<sub>3</sub> unit. Among the gold(II)-gold(II) (**2** and **12**) and gold(I)-gold(III) (**6** and **23**) complexes, the value of IS increases in the order X = ONO<sub>2</sub> < Cl, which is in agreement with the expectation based on the softness of the ligand. This result is in contrast to the observations for the mononuclear organogold complexes [AuX(PPh<sub>3</sub>)] (X = I, Br, Cl, OCOCH<sub>3</sub>, N<sub>3</sub>, CN, CH<sub>3</sub>) and also for the dinuclear biphenyldiyl complexes **6As-8As**, in which the values of IS increase as the ligands become harder.<sup>303,314</sup>

## ***Chapter 6. Conclusions and future directions.***

### ***6.1 Conclusions.***

The fluorine-substituted carbanions 2-C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub> and C<sub>6</sub>H<sub>3</sub>-*n*-F-2-PPh<sub>2</sub> (*n* = 5, 6) behave similarly to 2-C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub> and its methyl-substituted derivatives in forming dinuclear gold(I) complexes of the type Au<sub>2</sub>(carbanion)<sub>2</sub> in which each gold atom displays its usual linear coordination. The new digold(I) complexes also undergo the typical two-centre, two-electron oxidative addition reactions with halogens to form digold(II) complexes Au<sub>2</sub>X<sub>2</sub>(carbanion)<sub>2</sub>. Both the digold(I) and digold(II) fluorine-substituted compounds are structurally similar to their tetraprotio- and methyl-substituted analogues. Complete replacement of hydrogen by fluorine in the carbanion generally seems to cause a small contraction in the Au...Au separation in both series of compounds. Thus, the Au...Au distance in [Au<sub>2</sub>(μ-2-C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>] (**1**) [2.8201(4) Å] is significantly less than the corresponding distance in [Au<sub>2</sub>(μ-2-C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>] [2.8594(3) Å]<sup>181</sup> and in [Au<sub>2</sub>(μ-C<sub>6</sub>H<sub>3</sub>-6-Me-2-PPh<sub>2</sub>)<sub>2</sub>][2.861(2) Å].<sup>166</sup> Similarly, the Au-Au distance in [Au<sub>2</sub>I<sub>2</sub>(μ-2-C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>]

[2.5685(2) Å] is significantly less than that in [Au<sub>2</sub>I<sub>2</sub>(μ-2-C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>] [2.5898(6) Å and 2.5960(7) Å for two independent molecules].<sup>184</sup> In the bis(benzoato) complexes [Au<sub>2</sub>(OCC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>(μ-2-C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>] and [Au<sub>2</sub>(OCC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>(μ-2-C<sub>6</sub>H<sub>4</sub>PEt<sub>2</sub>)<sub>2</sub>], however, the Au-Au distances are equal, within experimental error [2.52120(11) Å and 2.5243(7) Å,<sup>165</sup> respectively]. It is not possible to generalise about the effect on the Au-Au separation of partial fluorine substitution. Unexpectedly, the Au-Au distance in the digold(I) complex [Au<sub>2</sub>(μ-C<sub>6</sub>H<sub>3</sub>-6-F-2-PPh<sub>2</sub>)<sub>2</sub>] [2.8762(4) Å] is the greatest in the series, it is even greater than that in the 6-methyl derivatives (see above), indicating that this is not a steric effect. In the dichlorodigold(II) complexes of 2-C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub>, C<sub>6</sub>H<sub>3</sub>-5-F-2-PPh<sub>2</sub> and C<sub>6</sub>H<sub>3</sub>-6-F-2-PPh<sub>2</sub>, the Au-Au distances [2.5416(4) Å, 2.56223(19) Å and 2.5390(3) Å, respectively] show a fairly small and non-systematic variation. Complete or partial replacement of hydrogen by fluorine in the carbanion does not show any significant changes in the Au-P [2.2807(av.) Å, 2.2987(5) Å and 2.300(1) Å in tetrafluoro, 6-fluoro and protio system, respectively] and Au-C [2.058(av.) Å, 2.061(2) Å and 2.056(3) Å in the tetrafluoro, 6-fluoro and protio system, respectively] bond lengths.

As mentioned in Chapter 3, there is a systematic lengthening of Au-Au distance in the digold(II) (5d<sup>9</sup>-5d<sup>9</sup>) complexes [Au<sub>2</sub>X<sub>2</sub>(μ-2-C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>] as the axial ligand X is varied from X = ONO<sub>2</sub> [2.5012(5) Å] to X = C<sub>6</sub>F<sub>5</sub> [2.5885(2) Å], corresponding with the increasing *trans*-influence of the ligand. Electron-withdrawing ligands with a weaker *trans*-influence result in a stronger metal-metal bond. When the axial ligand is methyl, which is high in the *trans*-influence series, the digold(II) complex cannot be isolated, in both the 2-C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub> and 2-C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub> series. Presumably the Au-Au bond is weakened so much that the rearranged gold(I)-gold(III) structure [Au<sub>2</sub><sup>I,III</sup>(CH<sub>3</sub>)<sub>2</sub>(μ-2-C<sub>6</sub>Z<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>] (Z = H, F) becomes more stable.

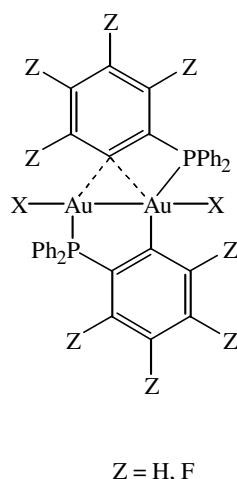
The Au-C bonds of  $[\text{Au}_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$  are cleaved only by a large excess of concentrated HCl and are more robust than those of  $[\text{Au}_2(\mu\text{-}2\text{-C}_6\text{H}_4\text{PPh}_2)_2]$ . The greater robustness of the tetrafluoro system is also evident from the fact that it is readily accessible from  $[\text{AuCl}(\text{tht})]$  as starting material, whereas attempts to make  $[\text{Au}_2(\mu\text{-}2\text{-C}_6\text{H}_4\text{PPh}_2)_2]$  from  $[\text{AuCl}(\text{tht})]$  resulted in reduction to gold metal.<sup>165</sup> The failure of  $\text{SO}_2$  to insert into the Au-C bonds of  $[\text{Au}_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$  is an example of the decreasing tendency of M-C  $\sigma$ -bonds with more electron-withdrawing ligands to insert small molecules such as CO and  $\text{SO}_2$ .<sup>256,315</sup> Despite these observations, the greater stability of the Au-C bonds in the tetrafluoro system over those in the tetraprotio system is not reflected in the Au-C bond lengths, which are not significantly different (see above).

The digold(I) complex of  $2\text{-C}_6\text{F}_4\text{PPh}_2$  is clearly less reactive towards oxidative addition than its  $2\text{-C}_6\text{H}_4\text{PPh}_2$  counterpart, being inert towards methyl iodide and dibenzoyl peroxide. The reaction of  $[\text{Au}_2(\mu\text{-}2\text{-C}_6\text{H}_4\text{PPh}_2)_2]$  with methyl iodide gives the diiododigold(II) complex as the final product, though there is evidence for an intermediate iodo(methyl)digold(II) species.<sup>165</sup> Similar behaviour is observed in the bis(ylide) series based on  $[\text{Au}_2\{(\mu\text{-CH}_2)_2\text{PPh}_2\}_2]$ , where the very light-sensitive iodo(methyl) complex can be isolated.<sup>116</sup> Presumably the electron-withdrawing effect of the fluorine atoms disfavors the oxidative addition of methyl iodide to  $[\text{Au}_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$ . The addition of dibenzoyl peroxide to  $[\text{Au}_2(\mu\text{-}2\text{-C}_6\text{H}_4\text{PPh}_2)_2]$  is probably a free-radical process and the electron-withdrawing fluorine atoms in the  $2\text{-C}_6\text{F}_4\text{PPh}_2$  presumably disfavor electron transfer to the benzoyl radicals.

The most obvious difference in the chemistry of the  $[\text{Au}_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$  and  $[\text{Au}_2(\mu\text{-}2\text{-C}_6\text{H}_4\text{PPh}_2)_2]$  systems lies in the isomerisation behaviour of the digold(II) complexes.

The complexes  $[\text{Au}_2\text{X}_2(\mu\text{-}2\text{-C}_6\text{H}_4\text{PPh}_2)_2]$  ( $\text{X} = \text{Cl, Br, I, C}_6\text{F}_5$ ) rearrange to digold(I) complexes of a 2,2'-biphenyldiyl ligand (see Section 1.4 in Chapter 1),  $[\text{Au}_2\text{X}_2(\mu\text{-}2,2'\text{-Ph}_2\text{PC}_6\text{H}_4\text{C}_6\text{H}_4\text{PPh}_2)]$ , whereas the corresponding  $[\text{Au}_2\text{X}_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$  complexes rearrange to gold(I)-gold(III) complexes  $[\text{XAu}(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)(\kappa^2\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)\text{AuX}]$  (Scheme 37 and 41, Chapter 3); there is no evidence for the formation of C-C coupled products in the latter case. Compounds of the latter type were originally proposed as the precursors to the C-C coupled product in the 2-C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub> system but they could not be isolated or detected. An important difference is that, in the 2-C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub> system, reductive elimination of the aryl groups at the gold(III) atom does not occur. The effect of the four fluorine substituents is thus similar to that of a 6-methyl substituent in the protio system. In the 6-methyl series, reductive elimination does not occur (probably because of steric hindrance)<sup>186</sup> and the gold(I)-gold(III) complexes are the final product.

The rearrangement from digold(II) to gold(I)-gold(III) clearly requires ligand migration. In the isomerisation of  $[\text{Au}_2^{\text{II}}\text{X}_4(\mu\text{-Ph}_2\text{PNHPPH}_2)]$  to  $[\text{XAu}^{\text{I}}(\mu\text{-Ph}_2\text{PNHPPH}_2)\text{Au}^{\text{III}}\text{X}_3]$ , the migrating group is halide,<sup>316</sup> but in the case of the dithiocarbamate (Scheme 4, Chapter 1), trithiocarbamate (Scheme 5, Chapter 1), *i*-mnt (Scheme 6, Chapter 1) and bis(ylide) (Chapter 1, page 33) systems, one-ended dissociation of the bridging group followed by re-association at the neighbouring gold atom must also take place. For  $[\text{Au}_2\text{X}_2(\mu\text{-}2\text{-C}_6\text{Z}_4\text{PPh}_2)_2]$  ( $\text{Z} = \text{H, F}$ ), one can postulate dissociation of the phosphorus atom of one of the bridging groups, thus allowing the carbanion to pass from one gold atom to the next via a two-electron, three-centre transition state shown in Figure 42. There are many examples of stable digold(I) complexes containing bridging aryl groups,<sup>317,318</sup> but none for digold(II) or digold(III).



**Figure 42. Transition state in isomerisation of digold(II) complexes  $[\text{Au}_2\text{X}_2(\mu\text{-}2\text{-C}_6\text{ZPPh}_2)_2]$  ( $\text{Z} = \text{H}, \text{F}$ ) to gold(I)-gold(III) complexes.**

In the  $2\text{-C}_6\text{H}_4\text{PPh}_2$  series, the digold(II) complexes having nitrate, acetate, trifluoroacetate and benzoate as the axial ligands do not undergo C-C coupling on heating; in the  $2\text{-C}_6\text{F}_4\text{PPh}_2$  series the digold(II) complexes containing those ligands do not rearrange to the corresponding gold(I)-gold(III) isomers, even though these complexes can be made by metathetical anion replacement from the gold(I)-gold(III) halides and are quite stable (Chapter 3). Isomerisation is facilitated by polarisable anions and disfavoured by hard anions in the axial position, even though the hard anions are better leaving groups. This seems at first sight counter-intuitive: one might have expected hard anions to leave a greater formal positive charge on the gold atoms, which should in turn favour carbanion migration. The most important factor that determines whether isomerisation takes place or not appears to be the strength of the Au(II)-Au(II) bond, as judged by its length; as noted above, the shortest (and presumably strongest) bonds occur for the most electronegative ligands.<sup>165</sup> Another factor, which has been suggested by theoretical calculations, may be the existence of aurophilic interactions in



the transition state for isomerisation. These may be stronger when polarised ligands such as iodide are present in the coordination sphere.<sup>186,319</sup>

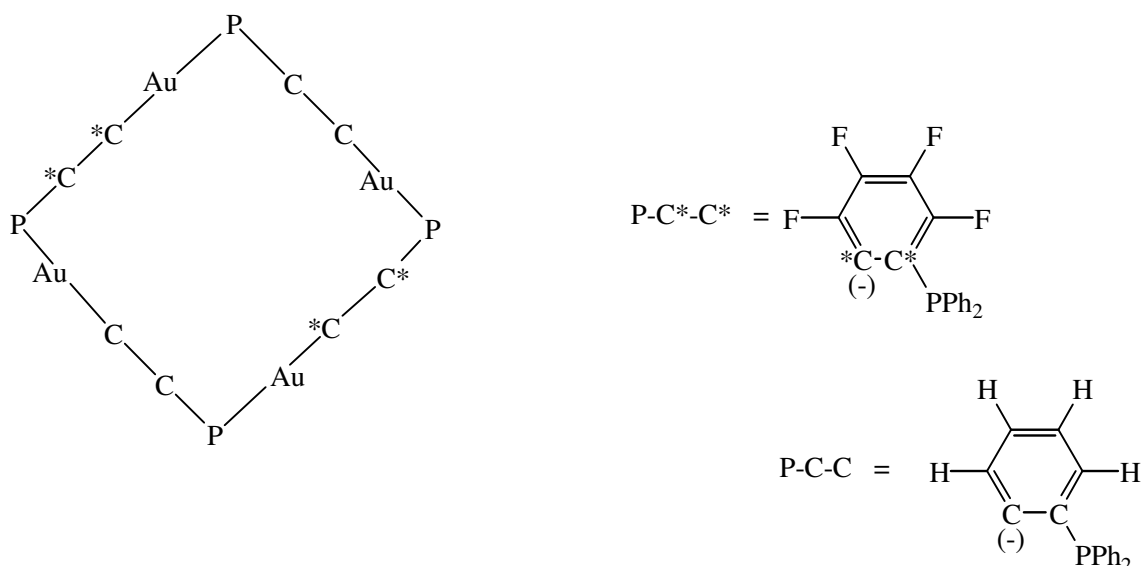
Qualitatively, isomerisation from Au(II)-Au(II) to Au(I)-Au(III) is much slower in the 2-C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub> than in the 6-MeC<sub>6</sub>H<sub>3</sub>-2-PPh<sub>2</sub> system; the latter occurs below room temperature within minutes whereas the former requires hours in hot toluene. Calculations show that the 6-methyl substituent causes a bending of the eight-membered ring in the digold(II) complexes that favours the transition state leading to the Au(I)-Au(III) isomer.<sup>186</sup> Although the Van der Waals radius of F (1.35 Å) is greater than that of H (1.20 Å), it is considerably less than that of CH<sub>3</sub> (2.00 Å), so there is a less pronounced steric driving force for isomerisation.

The isomerisation in the 2-C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub> system also appears to be slower than the formation of the 2-2'-diphenyldiyl complexes in the 2-C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub> system, even though in the latter case there is the additional step of reductive elimination at the gold(III) atom. However, since the presumed Au(I)-Au(III) intermediates in the coupling are not usually detectable, the reductive elimination must be fast compared to the migration. It seems, therefore, that 2-C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub> does not migrate between the metal centres as readily as its 2-C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub> or C<sub>6</sub>H<sub>3</sub>-6-Me-2-PPh<sub>2</sub> counterparts.

Independent evidence for this conclusion comes from a comparison of the palladium(II) chemistry of 2-C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub> and 2-C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>. The former forms an isolable bromo-bridged dimer, [Pd<sub>2</sub>(μ-Br)<sub>2</sub>(κ<sup>2</sup>-2-C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>], which rearranges to a stable bromo-bridged tetramer [Pd<sub>4</sub>(μ-Br)<sub>4</sub>(μ-2-C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub>)<sub>4</sub>] in solution over a period of hours; the carbanion 2-C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub> gives only the corresponding tetramer, the dimer being detectable only as a

transient intermediate.<sup>320</sup> These effects may result from a strengthening of the Au-C bonds by the electron-withdrawing fluorine substituents.

As noted in Chapter 2 (Section 2.6), the <sup>31</sup>P NMR pattern of a mixture of [Au<sub>2</sub>(μ-2-C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>] **1** and its protio analogue [Au<sub>2</sub>(μ-2-C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>] is considerably more complex than the simple AB pattern expected from the presence of the dinuclear scrambled species [Au<sub>2</sub>(μ-2-C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub>)(μ-2-C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)]. The fact that <sup>31</sup>P resonances appear as far downfield as δ 47 suggests the possibility that a mixture of tetranuclear species [Au<sub>4</sub>(μ-2-C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub>)<sub>n</sub>(μ-2-C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>4-n</sub>] (*n* = 0-4) (see Figure 43) is present {*cf.* δ 45.7 for the tetranuclear complex [Au<sub>4</sub>(μ-2-C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub>)<sub>4</sub>] **16**}, in addition to the expected mixed dimer. So far, there is evidence in only one case, [Au<sub>2</sub>(μ-C<sub>6</sub>H<sub>3</sub>-5-F-2-PPh<sub>2</sub>)<sub>2</sub>] (**30**) that a dimer can be converted into a tetramer at room temperature, and the process is qualitatively much slower than that of the scrambling process discussed here. Nevertheless, the formation of the tetramers might be induced by initial dissociation of phosphorus atom from either of the dimers {[Au<sub>2</sub>(μ-2-C<sub>6</sub>Z<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>] (*Z* = H, F)}, leading to association of the dimers and migration of phosphorus from one gold atom to the gold atom of a neighbouring dimer.



**Figure 43. Gold complexes of high nuclearity resulting from the reaction of  $[\text{Au}_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$  (1) and  $[\text{Au}_2(\mu\text{-}2\text{-C}_6\text{H}_4\text{PPh}_2)_2]$ .**

The presence of just one fluorine atom, at the 6-position of the aromatic ring of the bridging ligand, is sufficient to block the reductive elimination step, resulting in the formation of the gold(I)-gold(III) complexes  $[\text{XAu}(\mu\text{-C}_6\text{H}_3\text{-6-F-2-PPh}_2)(\kappa^2\text{-C}_6\text{H}_3\text{-6-F-2-PPh}_2)\text{AuX}]$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ). Although, as described above, this may be a steric effect caused by the larger Van der Waals radius of F relative to that of H, an electronic effect may also play a role in strengthening the Au(III)-C interaction in the  $\text{C}_6\text{H}_3\text{-6-F-2-PPh}_2$  and, by implication, in the  $2\text{-C}_6\text{F}_4\text{PPh}_2$  complexes as well.

There are few direct, thermochemical determinations of metal-carbon bond dissociation energies (BDE), especially in transition metal compounds, and trends in their values are not well understood. It has been shown that relative BDE values for  $\text{L}_n\text{M-X}$  [ $\Delta D(\text{M-X})$ ] correlate linearly with absolute thermochemical BDE values for  $\text{H-X}$  [ $D(\text{H-X})$ ], X being a range of C-, N-, and O-based ligands.<sup>321</sup> In the field of C-H activation of fluoroarenes

by reactive transition metal-based fragments such as  $[\text{RhCp}(\text{PMe}_3)]$  and  $[\text{ReCp}^*(\text{CO})_2]$ , aryl derivatives containing *ortho*-fluorine atoms, such as 2,6- $\text{C}_6\text{H}_3\text{F}_2$ , are the thermodynamically favoured products.<sup>322,323</sup> For the series  $[\text{ReH}(\text{Cp})(\text{CO})_2(\text{C}_6\text{H}_{5-n}\text{F}_n)]$  ( $n = 0-5$ ), a plot of DFT-calculated  $D(\text{C-H})$  values for the arene against DFT-calculated  $\Delta D(\text{Re-C})$  values gives a linear plot with a slope of 2.25. The plot shows clearly that substitution of fluorine at the *ortho*-position markedly increases the Re-C bond energy, possibly owing to an increase in ionic character and in M-C back-bonding.<sup>324</sup> If a similar effect were operative in the gold complexes, it would tend to raise the activation energy for the reductive elimination step leading to the biphenyldiylbis(diphenylphosphine) complexes.

It follows from the lower reactivity of  $[\text{Au}_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$  than  $[\text{Au}_2(\mu\text{-}2\text{-C}_6\text{H}_4\text{PPh}_2)_2]$  to oxidative addition that the digold(II) complexes of 2- $\text{C}_6\text{F}_4\text{PPh}_2$  are more readily reduced back to their digold(I) precursor, thus demonstrating the relative stabilisation of the lower oxidation state by the electron-withdrawing fluorine substituents. The effect is shown by facile reduction of the digold(II) complexes containing axial O-donor anions, such as benzoate and triflate, to the gold(I) complexes by alcohols, such as methanol and cyclohexanol. The products are either the usual digold(I) dimer or a novel tetramer,  $[\text{Au}_4(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_4]$ , or a mixture of the two.

The tetrameric gold(I) complexes  $[\text{Au}_4(\mu\text{-carbanion})_4]$  are dimers of the digold(I) complexes in which the carbanions bridge a ring of four gold atoms. No rational synthesis of these accidentally discovered complexes has been found. In the case of 2- $\text{C}_6\text{F}_4\text{PPh}_2$ , the tetramer is formed as the main product of reduction of  $[\text{Au}_2(\text{OTf})_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$ , together with dimer, but other similar reductions, e.g., of the benzoate and

trifluoroethoxide, give exclusively dimer. The tetramer  $[\text{Au}_4(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_4]$  has not been detected by  $^{31}\text{P}$  NMR spectroscopy as a by-product in the preparation of the dimer from gold(I) precursors and  $2\text{-LiC}_6\text{F}_4\text{PPh}_2$  or  $2\text{-Me}_3\text{SnC}_6\text{F}_4\text{PPh}_2$ , whereas the corresponding tetramers are formed during similar reactions in the monofluoro systems containing  $\text{C}_6\text{H}_3\text{-}n\text{-F-}2\text{-PPh}_2$  ( $n = 5, 6$ ) fragments. The dimers and tetramers evidently co-exist in solution at room temperature and do not interconvert rapidly the  $^{31}\text{P}$  NMR time-scale. We do not know whether they interconvert at higher temperature and, if so, which form is the more stable, although, as mentioned above, the dimer  $[\text{Au}_2(\mu\text{-C}_6\text{H}_3\text{-}5\text{-F-}2\text{-PPh}_2)_2]$  appears to form the corresponding tetramer slowly at room temperature in solution. Since the possible existence of tetramers was not suspected in the earlier work on  $2\text{-C}_6\text{H}_4\text{PPh}_2$ , we also do not know whether the tetramer  $[\text{Au}_4(\mu\text{-}2\text{-C}_6\text{H}_4\text{PPh}_2)_4]$  can be made or detected.

The reaction of the digold(I,III) dichloride complex in the tetrafluoro system with an excess of silver nitrate yields the novel trinuclear phosphine oxide gold complex in which the phosphine oxide ligand has undergone *ortho*-metallation. The mixed site of silver and gold in this structure indicates that the  $\text{AgNO}_3$  not only acts by removing the chloride ligands as insoluble  $\text{AgCl}$ , but also as a source of  $\text{Ag}^+$  ions, which can be incorporated into the complex. This result suggests that it should be possible to prepare silver complexes of  $2\text{-C}_6\text{F}_4\text{PPh}_2$ . A tetranuclear complex in which a mesityl group bridges silver and gold,  $[\{(\text{Ph}_3\text{P})\text{Au}(\mu\text{-C}_6\text{H}_2\text{Me}_3)\text{Ag}(\text{tht})\}_2]^{2+}$  is known.<sup>325</sup>

The Mössbauer parameters (IS and QS values) for the complexes containing  $2\text{-C}_6\text{F}_4\text{PPh}_2$  show an decrease compared to those of the protio analogues, consistent with electron withdrawal property of  $2\text{-C}_6\text{F}_4\text{PPh}_2$  ligand. This decrease shows that the

gold-carbon bond and gold-phosphorus bond in tetrafluoro complexes are less covalent compared to those in the corresponding protio complexes.

## **6.2. Future directions.**

The realisation that the 2-C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub> group strengthens Au-C bonds suggests that its behaviour with other transition metals such as copper and silver should be studied. The conversion from bridging to chelating modes in tetrafluoro system is quite slow, which would assist in isolating species that would otherwise rapidly isomerise in the C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub> chemistry. It would be interesting to explore the chemistry of tetrafluoro, 5- and 6-fluoro substituted arsenic analogues to see what the effect of changing the donor atom has on the reactivity of these complexes. The novel tetranuclear gold complex clearly deserves further study; in particular, a rational synthesis needs to be developed. Stepwise oxidation addition of halogens to each of the four gold nuclei would also be worth exploring. Similarly, it would also be of interest to determine if the tetranuclear species in the original protio system could be synthesised. It is also interesting to see if dimer and tetramer interconvert at higher temperature and which form is the more stable. Theoretical calculations may give an indication on the relative stabilities of the dinuclear and tetranuclear species in tetrafluoro and mono-fluoro systems. There are also some aspects of the tetrafluoro system that remain to be explored: Can the axial anions in the digold(II) complexes be replaced by neutral ligands? Will these complexes isomerise on heating?

## ***Chapter 7. Experimental.***

### ***7.1 General procedures.***

Most syntheses were performed under an atmosphere of dry argon with the use of standard Schlenk techniques, although the solid gold complexes, once isolated, were air-stable.

Solvents were dried by refluxing over sodium/benzophenone (ether, hexane, THF, benzene and toluene), calcium hydride (dichloromethane) or magnesium (methanol) and distilled under dry nitrogen or argon prior to use. The compounds [AuBr(AsPh<sub>3</sub>)],<sup>326</sup> [AuCl(tht)],<sup>327</sup> 2-BrC<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub>,<sup>221</sup> PhICl<sub>2</sub>,<sup>328</sup> and Me<sub>3</sub>SiPPh<sub>2</sub><sup>220</sup> were prepared by the appropriate literature procedure. The required organic ligand precursors, the cyclometallated gold complexes and their derivatives were generally prepared following literature procedures; the full details are given below. All other compounds were commercially available and used as received.

## ***7.2 Physical measurements.***

Melting points were determined on a Gallenkamp melting point apparatus in open glass capillaries.  $^1\text{H}$  (300 MHz),  $^{19}\text{F}$  (282 MHz) and  $^{31}\text{P}$  (121 MHz) NMR spectra were recorded on a Bruker Avance 300 spectrometer in  $\text{C}_6\text{D}_6$ , unless otherwise stated. Coupling constants ( $J$ ) are given in Hertz and chemical shifts ( $\delta$ ) are given in ppm, internally referenced to residual solvent signals ( $^1\text{H}$ ), internal  $\text{CFCl}_3$  ( $^{19}\text{F}$ ) or external 85%  $\text{H}_3\text{PO}_4$  ( $^{31}\text{P}$ ). Elemental analyses were performed by the Microanalytical Unit of the Research School of Chemistry at the Australian National University (ANU), Canberra. Mass spectra were recorded at ANU on a Bruker Apex 3 FTICR mass spectrometer and infrared spectra were obtained at RMIT University on a Perkin Elmer Spectrum 2000 FT-IR spectrometer as KBr (4000-400  $\text{cm}^{-1}$ ) or polyethylene disks (400-150  $\text{cm}^{-1}$ ).

### ***7.2.1 X-ray crystallography.***

Crystals suitable for single-crystal X-ray diffraction were obtained by layering a  $\text{CH}_2\text{Cl}_2$  solution with hexane or methanol. Selected crystal data and details of data collection and structure refinement are listed in Appendix 1.

The crystals were mounted on a glass capillary using a drop of inert oil (PARATONE) and transferred to a stream of cold nitrogen. The reflection data were collected and the structures were solved by Dr. Anthony Willis and Dr. Jörg Wagler (Research School of Chemistry, Australian National University) on a Nonius Kappa CCD diffractometer equipped with a 95 mm camera and graphite-monochromated  $\text{Mo K}\alpha$  radiation ( $\lambda =$



071073 Å), in  $\phi$ - and  $\omega$ -scan modes. Data integration was carried out with the DENZO software<sup>329</sup> and multi-scan absorption correction was performed with the SORTAV program.<sup>330</sup> The crystal structures were solved by direct methods using SIR92,<sup>331</sup> SHELXS-97,<sup>332</sup> or the Patterson method of SHELXS-97. Structure refinement was carried out as a full-matrix least-squares refinement on  $F^2$  using SHELX-L97,<sup>333</sup> or the CRYSTALS program package.<sup>334</sup> Calculations were performed with use of the crystallographic software CRYSTALS.<sup>335</sup>

### ***7.2.2 Mössbauer measurements.***

<sup>197</sup>Au Mössbauer spectra were acquired by Professor Masashi Takahashi at Toho University, Japan, on a Wissel Mössbauer spectrometer system consisting of a MDU-1200 function generator, DFG-1200 driving unit, MVT-100 velocity transducer and MVC-1200 laser calibrator. Both the Mössbauer source and the absorber were cooled to a temperature of 12 K in a cryostat incorporating a closed cycle refrigerator, and a pure Ge solid state detector was used for counting the  $\gamma$ -rays.<sup>336</sup> The  $\gamma$ -ray source (210 MBq) was prepared by neutron irradiation of a 40 mg disc of enriched metallic <sup>196</sup>Pt in the JRR-4 reactor at the Japan Atomic Energy Agency (JAEA). The absorber thickness was 50-130 mg Au cm<sup>-2</sup>. The data were analysed by least squares methods and the isomer shifts are given relative to the <sup>197</sup>Pt/Pt source at 12 K.

### 7.3 Ligand precursor syntheses.

#### 7.3.1 Preparation of 2-bromo-4-fluoroaniline.

2-Bromo-4-fluoroaniline was prepared following the literature method reported by Roche (A, Appendix 2).<sup>337</sup>

To a suspension of KBr (0.24 mol, 28.5 g), ammonium molybdate (0.002 mol, 2.5 g) and 4-fluoroaniline (0.2 mol, 22.0 g) in acetic acid (200 mL) was added sodium perborate (0.21 mol, 32.3 g). The mixture was stirred at room temperature for 2 hours, after which the reaction was quenched by the addition of a saturated aqueous Na<sub>2</sub>CO<sub>3</sub> solution (600 mL). The mixture was extracted with ethyl acetate (3 × 200 mL) and the combined organic phases were dried (MgSO<sub>4</sub>). The filtered solution was evaporated under reduced pressure to give a golden-brown oil which was distilled *in vacuo* (80-82 °C / 4 mm Hg) to give the title compound as a yellow oil (28.5 g, 73%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 3.95 (br s, 2H, NH<sub>2</sub>), 6.68 (dd,  $J_{\text{HH}} = 8.9$  Hz,  $J_{\text{FH}} = 5.2$  Hz, 1H, aromatic), 6.86 (dt,  $J_{\text{HH}} = 2.8, 8.4$  Hz,  $J_{\text{FH}} = 8.4$  Hz, 1H, aromatic), 7.18 (dd,  $J_{\text{HH}} = 2.9$  Hz,  $J_{\text{FH}} = 8.1$  Hz, 1H, aromatic). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 108.5 (d,  $J_{\text{FC}} = 10.1$  Hz), 115.1 (d,  $J_{\text{FC}} = 22.2$  Hz), 115.8 (d,  $J_{\text{FC}} = 8.1$  Hz), 119.0 (d,  $J_{\text{FC}} = 25.3$  Hz), 140.5 (d,  $J_{\text{FC}} = 2.9$  Hz), 155.2 (d,  $J_{\text{FC}} = 240.8$  Hz). <sup>19</sup>F NMR (CDCl<sub>3</sub>): δ -125.9 (dt,  $J_{\text{FH}} = 5.1, 8.0, 8.0$  Hz). ESI-MS ( $m/z$ ): 190 [ $M$ ]<sup>+</sup>.

### 7.3.2 Preparation of 2-bromo-4-fluoroiodobenzene.

A general procedure for the preparation of aryl iodides from aryl amines has been employed to prepare the title compound (B, Appendix 2).<sup>220</sup>

Concentrated sulfuric acid (60 mL) was slowly added to a cooled suspension of 2-bromo-4-fluoroaniline (0.15 mol, 28.0 g) in water (200 mL). Sodium nitrite (0.16 mol, 11.0 g) in water (50 mL) was added dropwise, keeping the temperature below 5 °C, and the mixture was stirred for 30 min. The resulting diazonium solution was filtered into a solution of potassium iodide (0.18 mol, 29.9 g) in water (120 mL) and the dark mixture was stirred at room temperature for 30 min, then at 50 °C for 30 min. Solid sodium metabisulfite (5 g) was added and the black oil was extracted with dichloromethane (3 × 50 mL). The combined organic extracts were dried (MgSO<sub>4</sub>), filtered, and the solvents were evaporated. The resulting oil was distilled *in vacuo* (90-93 °C / 5 mm Hg) to give the title compound as a pink oil in 87% yield (38.5 g), which was stored over copper turnings to remove traces of iodine.

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 6.78 (dt,  $J_{\text{HH}} = 2.8, 8.5$  Hz,  $J_{\text{FH}} = 8.2$  Hz, 1H, aromatic), 7.38 (dd,  $J_{\text{HH}} = 2.9$  Hz,  $J_{\text{FH}} = 8.4$  Hz, 1H, aromatic), 7.79 (dd,  $J_{\text{HH}} = 8.8$  Hz,  $J_{\text{FH}} = 5.8$  Hz, 1H, aromatic). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 94.7 (d,  $J_{\text{FC}} = 3.9$  Hz), 116.1 (d,  $J_{\text{FC}} = 21.1$  Hz), 120.5 (d,  $J_{\text{FC}} = 24.7$  Hz), 130.1 (d,  $J_{\text{FC}} = 10.3$  Hz), 140.8 (d,  $J_{\text{FC}} = 8.3$  Hz), 162.4 (d,  $J_{\text{FC}} = 251.9$  Hz). <sup>19</sup>F NMR (CDCl<sub>3</sub>): δ -112.5 (dt,  $J_{\text{FH}} = 5.8, 8.1, 8.1$  Hz). ESI-MS (*m/z*): 300 [*M*]<sup>+</sup>.

### 7.3.3 Preparation of 2-bromo-3-fluoroiodobenzene.

2-Bromo-3-fluoroiodobenzene was prepared following by the procedure described by Heiss, except that  $\text{BrCH}_2\text{CH}_2\text{Br}$  was used as the brominating agent instead of  $\text{BrCF}_2\text{CF}_2\text{Br}$  (C, Appendix 2).<sup>338</sup>

To a solution of  $n\text{BuLi}$  (1.6 M in hexanes, 0.06 mol, 37.5 mL) in THF (50 mL) cooled to 0 °C was added  $i\text{Pr}_2\text{NH}$  (0.06 mol, 8.4 mL). The mixture was stirred at 0 °C for 30 min, cooled to -78 °C and stirred for a further 15 min. 3-Fluoroiodobenzene (0.06 mol, 7.0 mL) was slowly added to the cooled mixture, which was then stirred for 2 hours at -78 °C, during which time a thick white precipitate formed.  $\text{BrCH}_2\text{CH}_2\text{Br}$  (0.12 mol, 10.3 mL) was added to the suspension, which was stirred for 15 min at -78 °C and then allowed to warm to room temperature. The slightly turbid, yellow solution was evaporated under reduced pressure to leave a brown suspension to which  $\text{CH}_2\text{Cl}_2$  was added. The mixture was dried ( $\text{MgSO}_4$ ), filtered, and the solvent was removed under reduced pressure to give an orange-brown oil. Distillation *in vacuo* (80-84 °C / 1.5 mm Hg) gave the title complex as a colourless oil which solidified on standing (5.5 g, 30%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.03 (ddd,  $J = 5.2, 8.1, 13.3$  Hz, 1H, aromatic),  $\delta$  7.09 (dt,  $J = 8.2, 8.1, 1.7$  Hz, 1H, aromatic),  $\delta$  7.65 (dm,  $J_{\text{HH}} = 8.3$  Hz, 1H, aromatic).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  102.5 (s), 115.9 (d,  $J_{\text{FC}} = 23.2$  Hz), 117.5 (d,  $J_{\text{FC}} = 21.4$  Hz), 129.8 (d,  $J_{\text{FC}} = 7.9$  Hz), 135.4 (d,  $J_{\text{FC}} = 2.7$  Hz), 158.7 (d,  $J_{\text{FC}} = 250.6$  Hz).  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -96.3 (dd,  $J = 5.4, 8.8$  Hz). ESI-MS ( $m/z$ ): 300  $[M]^+$ .

## 7.4 Ligand synthesis.

### 7.4.1 Preparation of (2-bromotetrafluorophenyl)diphenylphosphine.<sup>221</sup>

To a solution of 1,2-dibromotetrafluorobenzene (32 mmol, 9.85 g) in ether (100 ml) cooled to -78 °C was added <sup>n</sup>BuLi (1.6 M in hexanes, 32 mmol, 20.0 mL) dropwise. After stirring for 30 min, chlorodiphenylphosphine (32 mmol, 5.8 mL) was slowly added. The solution was stirred at -78 °C for 2 hours and then allowed to warm to room temperature overnight. The resulting suspension was hydrolysed, the ether layer was separated and the aqueous phase was extracted with ether (3 × 50 mL). The combined organic phases were dried (MgSO<sub>4</sub>), filtered and the solvent was removed *in vacuo*. The yellow gummy solid was recrystallised from hot methanol to give the title product as a colourless solid (10.3 g, 78%).

m.p: 66-67 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.2-7.6 (m, 10H, aromatics). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 128.7 (d, *J* = 7.2), 129.2 (s), 132.9 (dd, *J* = 1.5, 21.2), 133.7 (dd, *J* = 3.5, 11.4) due to the PPh<sub>2</sub> carbons and low intensity peaks at δ 112.7 (m), 122.8 (m), 140.1 (m), 141.7 (m), 145.3 (m), 146.4 (m) due to the C<sub>6</sub>F<sub>4</sub>Br carbons. <sup>31</sup>P NMR (CDCl<sub>3</sub>): δ -1.6 (ddd, *J* = 4.4, 10.4, 20.5 Hz). <sup>19</sup>F NMR (CDCl<sub>3</sub>): δ -121.8 (m), -126.6 (m), -150.2 (m), -154.1 (m). ESI-MS (*m/z*): 413 [*M*+H]<sup>+</sup>

### 7.4.2 Preparation of {(2-trimethylstannyl)tetrafluorophenyl}diphenylphosphine.

A solution of 2-BrC<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub> (16 mmol, 6.6 g) in ether (100 mL) was cooled to -78 °C and treated slowly with a solution of <sup>n</sup>BuLi (1.6 M in hexanes, 16 mmol, 10.0 mL). After stirring for 30 min, Me<sub>3</sub>SnCl (1.0 M in hexanes, 16 mmol, 16.0 mL) was added dropwise to the solution, which was stirred at -78 °C for 2 hours. After being allowed to

warm to room temperature, the suspension was hydrolysed and the ether layer separated. The aqueous phase was extracted with ether (3 × 50 mL) and the combined organic phases were dried (MgSO<sub>4</sub>). After filtration, the solvent was removed and the gummy solid was recrystallised from hot methanol to give white crystals of the title compound (6.9 g, 87%).

m.p: 77-79 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.50 (s, with <sup>117</sup>Sn/<sup>119</sup>Sn satellites *J* = 56.5 Hz, 9H, SnMe<sub>3</sub>), 7.2-7.4 (m, 10H, aromatics). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ -3.9 (dd, *J* = 4.5, 13.3 Hz with <sup>117</sup>Sn/<sup>119</sup>Sn satellites *J* = 369.5 Hz) together with 128.5 (d, *J* = 6.4 Hz), 128.8 (s), 132.4 (dd, *J* = 1.8, 18.9 Hz), 134.6 (dd, *J* = 2.2, 9.2 Hz) due to the PPh<sub>2</sub> carbons and low intensity peaks at δ 125.5 (m), 140.7 (m), 141.5 (m), 148.7 (m), 150.1 (m), 150.7 (m) due to the C<sub>6</sub>F<sub>4</sub> carbons. <sup>31</sup>P NMR (CDCl<sub>3</sub>): δ -0.2 (ddd, *J*<sub>PF</sub> = 1.6, 2.9, 22.8 Hz with <sup>117</sup>Sn/<sup>119</sup>Sn satellites *J* = 29.4 Hz). <sup>19</sup>F NMR (CDCl<sub>3</sub>): δ -119.1 (m), -120.4 (m), -151.3 (m), -153.2 (m). ESI-MS (*m/z*): 499 [*M*+H]<sup>+</sup>. Anal. Calcd. for C<sub>21</sub>H<sub>19</sub>F<sub>4</sub>PSn: C 50.75, H 3.85, F 15.29. Found: C 51.04, H 3.96, F 15.32.

#### **7.4.3 Preparation of (2-bromo-3-fluorophenyl)diphenylphosphine.**

To a solution of 2-bromo-3-fluoriodobenzene (16.1 mmol, 4.9 g) and [PdCl<sub>2</sub>(MeCN)<sub>2</sub>] (0.4 mmol, 0.1 g) in dry toluene (20 mL) was added (trimethylsilyl)diphenylphosphine (17.5 mmol, 4.5 g). The resulting dark solution was stirred at 85 °C for 3 days and then allowed to cool to room temperature. Dichloromethane was added and the solution was washed with saturated aqueous NaHCO<sub>3</sub>. The organic layer was separated and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 50 mL). The combined organic extracts were dried over MgSO<sub>4</sub>, filtered, and the solvents were evaporated to give an orange

semi-solid. The crude product was passed down a silica-gel column, eluting with toluene/hexane (1:1) to give a colourless oil, which was crystallised from hot methanol to afford the title product as a white solid (3.8 g, 66%).

m.p: 139-141 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  6.50 (m, 1H, aromatic), 7.12 (m, 2H, aromatics), 7.2-7.6 (m, 10H, aromatics).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  116.0 (dd,  $J_{\text{FC}} = 20.3$  Hz,  $J_{\text{PC}} = 31.1$  Hz), 116.3 (d,  $J_{\text{FC}} = 22.9$ ), 128.4 (d,  $J_{\text{PC}} = 7.5$  Hz), 128.7 (d,  $J_{\text{PC}} = 7.4$  Hz), 129.2 (s), 129.6 (dd,  $J_{\text{FC}} = 1.5$  Hz,  $J_{\text{PC}} = 3.3$  Hz), 134.0 (d,  $J_{\text{PC}} = 20.5$  Hz), 135.3 (d,  $J_{\text{PC}} = 10.5$  Hz), 141.0 (dd,  $J_{\text{FC}} = 1.1$  Hz,  $J_{\text{PC}} = 14.3$  Hz), 159.1 (dd,  $J_{\text{FC}} = 249$  Hz,  $J_{\text{PC}} = 5.4$  Hz).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -4.5 (d,  $J_{\text{PF}} = 9.4$  Hz).  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -105.4 (m). ESI-MS ( $m/z$ ): 359  $[\text{M}+\text{H}]^+$ . Anal. Calcd. for  $\text{C}_{18}\text{H}_{13}\text{BrFP}$ : C 60.19, H 3.65, Br 22.25, P 8.62. Found: C 60.18, H 3.82, Br 22.04, P 8.47.

#### ***7.4.4 Preparation of (2-trimethylstannyl-3-fluorophenyl)diphenylphosphine.***

To a solution of (2-bromo-3-fluorophenyl)diphenylphosphine (2.6 mmol, 0.9 g) in ether (50 mL) cooled to -78 °C was added  $n\text{BuLi}$  (1.6 M in hexanes, 2.6 mmol, 1.6 mL). The suspension was stirred for 30 min and then  $\text{Me}_3\text{SnCl}$  (1.0 M in hexanes, 2.6 mmol, 2.6 mL) was slowly added. The mixture was stirred at -78 °C for 2 hours and then allowed to warm to room temperature. The resulting suspension was hydrolysed, the organic layer was separated and the aqueous phase was extracted with ether ( $3 \times 50$  mL). The combined organic extracts were dried over  $\text{MgSO}_4$ , filtered, and solvent was evaporated to give a gummy solid which crystallised from hot methanol to give the title product as a white solid (0.77 g, 68%).

m.p: 58-60 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.48 (t,  $J_{\text{PH}} = J_{\text{FH}} = 1.4$  Hz with  $^{117}\text{Sn}/^{119}\text{Sn}$  satellites  $J = 54.2, 56.5$  Hz, 9H,  $\text{SnMe}_3$ ), 6.6-7.4 (m, 13H, aromatics).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -4.7 (dd,  $J = 4.1, 11.2$  Hz with  $^{117}\text{Sn}/^{119}\text{Sn}$  satellites  $J = 349.9, 366.1$  Hz), 115.1 (d,  $J_{\text{FC}} = 25.3$  Hz, with  $^{117}\text{Sn}/^{119}\text{Sn}$  satellites  $J = 16.2$  Hz), 128.8 (d,  $J_{\text{PC}} = 5.0$  Hz), 128.9 (s), 129.0 (d,  $J_{\text{PC}} = 2.9$  Hz with  $^{117}\text{Sn}/^{119}\text{Sn}$  satellites  $J = 34.4$  Hz), 131.0 (d,  $J_{\text{PC}} = 9.2$  Hz), 133.5 (d,  $J_{\text{PC}} = 18.6$  Hz), 136.9 (dd,  $J_{\text{PC}/\text{FC}} = 40.7, 62.1$  Hz), 138.0 (d,  $J_{\text{PC}} = 25.3$  Hz with  $^{117}\text{Sn}/^{119}\text{Sn}$  satellites  $J = 16.2$  Hz), 148.0 (dd,  $J_{\text{PC}/\text{FC}} = 6.1, 11.1$  Hz with  $^{117}\text{Sn}/^{119}\text{Sn}$  satellites  $J = 22.9$  Hz), 167.9 (dd,  $J_{\text{FC}} = 237.7$  Hz,  $J_{\text{PC}} = 22.8$  Hz).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -2.5 (d,  $J_{\text{PF}} = 1.6$  Hz with  $^{117}\text{Sn}/^{119}\text{Sn}$  satellites  $J = 37.9, 40.6$  Hz).  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -91.4 (br s, with  $^{117}\text{Sn}/^{119}\text{Sn}$  satellites  $J = 60.4$  Hz). ESI-MS ( $m/z$ ): 445  $[M+H]^+$ . Anal. Calcd. for  $\text{C}_{21}\text{H}_{22}\text{FPSn}$ : C 56.93, H 5.00, F 4.29, P 6.99. Found: C 57.01, H 5.03, F 4.15, P 6.87.

#### 7.4.5 Preparation of (2-bromo-4-fluorophenyl)diphenylphosphine.

(2-Bromo-4-fluorophenyl)diphenylphosphine was prepared similarly to (2-bromo-3-fluorophenyl)diphenylphosphine (Section 7.4.3) and obtained as a colourless solid in 81% yield from 2-bromo-4-fluoriodobenzene (50.8 mmol, 15.3 g),  $[\text{PdCl}_2(\text{MeCN})_2]$  (0.98 mmol, 0.25 g) and (trimethylsilyl)diphenylphosphine (53.8 mmol, 13.9 g).

m.p: 86-88 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  6.75 (ddd,  $J_{\text{HH}} = 8.6$  Hz,  $J_{\text{FH}} = 6.4$  Hz,  $J_{\text{PH}} = 2.2$  Hz, 1H, aromatic), 6.96 (dt,  $J_{\text{HH}} = 2.4, 8.4$  Hz,  $J_{\text{FH}} = 8.4$  Hz, 1H, aromatic), 7.2-7.5 (m, 11H, aromatics).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  114.9 (d,  $J = 20.2$  Hz), 120.4 (d,  $J = 24.2$  Hz), 128.7 (d,  $J_{\text{PC}} = 7.3$  Hz), 129.1 (s), 129.9 (dd,  $J = 9.1, 33.2$  Hz), 133.8 (d,  $J_{\text{PC}} = 29.5$  Hz), 134.4 (dd,  $J = 4.1, 12.2$  Hz), 135.6 (d,  $J_{\text{PC}} = 2.6$  Hz), 135.7 (s), 162.7 (d,  $J = 253$  Hz).



$^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -5.8 (d,  $J_{\text{PF}} = 3.7$  Hz).  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -111.5 (ddt,  $J_{\text{PF}} = 3.1$  Hz,  $J_{\text{FH}} = 6.3, 8.2$  Hz). ESI-MS ( $m/z$ ): 359 [ $M+H$ ] $^+$ . Anal. Calcd. for  $\text{C}_{18}\text{H}_{13}\text{BrFP}$ : C 60.19, H 3.65, Br 22.25, P 8.62. Found: C 60.52, H 3.79, Br 21.96, P 8.65.

#### 7.4.6 Preparation of (2-trimethylstannyl-4-fluorophenyl)diphenylphosphine.

The title compound was made analogously to (2-trimethylstannyl-3-fluorophenyl)diphenylphosphine (Section 7.4.4) on the same scale in 85% yield.

m.p: 77-79 °C.  $^1\text{H}$  NMR:  $\delta$  0.32 (d,  $J = 1.2$  Hz, with  $^{117}\text{Sn}/^{119}\text{Sn}$  satellites  $J = 53.1, 55.4$  Hz, 9H,  $\text{SnMe}_3$ ), 6.6-7.5 (m, 13H, aromatics).  $^{13}\text{C}$  NMR:  $\delta$  -6.1 (d,  $J = 10.3$  Hz with  $^{117}\text{Sn}/^{119}\text{Sn}$  satellites  $J = 331.7, 352.2$  Hz), 116.4 (d,  $J = 22.5$  Hz), 122.8 (dd,  $J = 17.5, 21.5$  Hz with  $^{117}\text{Sn}/^{119}\text{Sn}$  satellites  $J = 45.5, 79.7$  Hz), 128.7 (d,  $J = 3.2$  Hz), 128.9 (s), 133.5 (d,  $J = 18.4$  Hz), 136.7 (d,  $J = 6.2$  Hz with  $^{117}\text{Sn}/^{119}\text{Sn}$  satellites  $J = 38.9, 51.3$  Hz), 138.3 (d,  $J = 10.2$  Hz), 140.4 (t,  $J = 2.0$  Hz, with  $^{117}\text{Sn}/^{119}\text{Sn}$  satellites  $J = 34.73, 41.1$  Hz), 156.6 (dd,  $J = 2.9, 70.7$  Hz), 163.7 (d,  $J = 253.9$  Hz).  $^{31}\text{P}$  NMR:  $\delta$  -4.2 (d,  $J_{\text{PF}} = 5.8$  Hz with  $^{117}\text{Sn}/^{119}\text{Sn}$  satellites  $J = 30.1, 41.6$  Hz).  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -112.6 (t,  $J = 6.59$  Hz), ESI-MS ( $m/z$ ): 445 [ $M+H$ ] $^+$ . Anal. Calcd. for  $\text{C}_{21}\text{H}_{22}\text{FPSn}$ : C 56.93, H 5.00, F 4.29, P 6.99. Found: C 56.16, H 5.24, F 3.97, P 6.31.

## 7.5 Preparation of the gold complexes containing the C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub> fragment.

### 7.5.1 Preparation of the digold(I) complex [Au<sub>2</sub>(μ-2-C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>] (1).

A solution of 2-BrC<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub> (1.2 mmol, 0.5 g) in ether (15 mL), cooled to -78 °C, was treated with <sup>n</sup>BuLi (1.6 M in hexanes, 0.9 mmol, 0.57 mL) over 30 min to give a pale yellow solution. To this, a cooled suspension of [AuBr(AsPh<sub>3</sub>)] (1.0 mmol, 0.58 g) in ether (10 mL) was added via cannula, the temperature being kept at -78 °C for one hour. Stirring was continued for 3 hours at -40 °C and then the suspension was slowly warmed to room temperature overnight. The white solid was isolated by filtration and washed successively with ether (10 mL), methanol (10 mL) and hexane (20 mL). The crude product was extracted with hot dichloromethane and filtered through Celite. Evaporation of the filtrate gave [Au<sub>2</sub>(μ-2-C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>] as a colourless solid (0.4 g, 65%). The use of [AuCl(tht)] as the gold precursor gave a yield of about 47%.

<sup>1</sup>H NMR: δ 6.9-7.7 (m, 20H, aromatics). <sup>31</sup>P NMR: δ 42.7 (br s). <sup>19</sup>F NMR: δ -107.1 (dd, *J* = 16.3, 34.8 Hz), -121.3 (m), -148.3 (ddt, *J* = 6.3, 20.5, 34.8 Hz), -156.4 (t, *J* = 21.2 Hz). ESI-MS (*m/z*): 1060 [*M*]<sup>+</sup>. Anal. Calcd. for C<sub>36</sub>H<sub>20</sub>Au<sub>2</sub>F<sub>8</sub>P<sub>2</sub>: C 40.78, H 1.90, P 5.84. Found: C 40.58, H 2.05, P 5.69.

Alternatively, **1** can be prepared by the reaction of [AuCl(tht)] with 2-Me<sub>3</sub>SnC<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub>: To a stirred solution of [AuCl(tht)] (1.3 mmol, 0.4 g) in dichloromethane (20 mL) was added 2-Me<sub>3</sub>SnC<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub> (1.3 mmol, 0.6 g) and the mixture was refluxed for 4 hours, during which time **1** precipitated out. The solvent was removed *in vacuo* and the white

solid was recrystallised from dichloromethane/hexane to give  $[\text{Au}_2(\mu\text{-2-C}_6\text{F}_4\text{PPh}_2)_2]$  as a colourless solid (0.56 g, 84%).

In an analogous reaction to that described above, treatment of an ether solution of 2- $\text{BrC}_6\text{F}_4\text{PPh}_2$  (1.2 mmol, 0.5 g) with  $n\text{BuLi}$  (1.6 M in hexanes, 0.9 mmol, 0.57 mL) at  $-78\text{ }^\circ\text{C}$ , followed by the addition of an ether solution of  $[\text{AuBr}(\text{PEt}_3)]$  (1.0 mmol, 0.4 g) gave a colourless solid (80%).  $^{31}\text{P}$  NMR:  $\delta$  23.5 (m), 38.0 (m), 42.3 (br s), 47.6 (br s).

### **7.5.2 Preparation of the dihalodigold(II) complexes $[\text{Au}_2\text{X}_2(\mu\text{-2-C}_6\text{F}_4\text{PPh}_2)_2]$ [ $\text{X} = \text{Cl}$ (2), Br (3), I (4)].**

A stirred solution of  $[\text{Au}_2(\mu\text{-2-C}_6\text{F}_4\text{PPh}_2)_2]$  (**1**) (0.1 mmol, 0.1 g) in dichloromethane (20 mL) cooled to  $-78\text{ }^\circ\text{C}$  was treated dropwise with a solution of  $\text{PhICl}_2$ ,  $\text{Br}_2$  or  $\text{I}_2$  (0.1 mmol) in  $\text{CH}_2\text{Cl}_2$  (20 mL), the temperature being kept at  $-78\text{ }^\circ\text{C}$ . After the addition was complete, the flask was shielded from light and the solution was stirred at  $-78\text{ }^\circ\text{C}$  for 1 hour, then at  $-40\text{ }^\circ\text{C}$  for 1 hour. During the work-up, the temperature was maintained below  $-30\text{ }^\circ\text{C}$ . The volume of the solution was reduced to half under reduced pressure and hexane was added, precipitating out the product. The solvent was cannulated from the solid, which was washed with hexane and dried *in vacuo*. Yields were typically 60-80%.

**2** (yellow solid):  $^1\text{H}$  NMR:  $\delta$  6.9-7.9 (m, 20H, aromatics).  $^{31}\text{P}$  NMR:  $\delta$  -2.3 (br s).  $^{19}\text{F}$  NMR:  $\delta$  -112.5 (m), -127.7 (m), -144.6 (m), -154.3 (m). ESI-MS ( $m/z$ ): 1095  $[\text{M-Cl}]^+$ . Far-IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 288 (Au-Cl str.). Anal. Calcd. for  $\text{C}_{36}\text{H}_{20}\text{Au}_2\text{Cl}_2\text{F}_8\text{P}_2$ : C 38.22, H 1.78, P 5.48. Found: C 38.23, H 2.06, P 5.67.

**3** (orange solid):  $^1\text{H}$  NMR:  $\delta$  6.8-7.8 (m, 20H, aromatics) together with peaks at  $\delta$  0.89 and 1.24 due to hexanes.  $^{31}\text{P}$  NMR:  $\delta$  -8.3 (br s). ESI-MS ( $m/z$ ): 1141  $[\text{M}-\text{Br}]^+$ . Far-IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 199 (Au-Br str.). Anal. Calcd. for  $\text{C}_{36}\text{H}_{20}\text{Au}_2\text{Br}_2\text{F}_8\text{P}_2$ : C 35.44, H 1.65, P 5.08. Found: C 35.30, H 1.68, P 5.01.

**4** (red solid):  $^1\text{H}$  NMR:  $\delta$  6.9-7.8 (m, 20H, aromatics).  $^{31}\text{P}$  NMR:  $\delta$  -17.2 (br s). ESI-MS ( $m/z$ ): 1186  $[\text{M}-\text{I}]^+$ .

Alternatively, complexes **3** and **4** may be obtained by anion exchange reactions of **2** in dichloromethane with the appropriate sodium or lithium salts in methanol. Yields were 90-95%. Both methods for preparing the iodide complex **4** failed to give a pure product.

### 7.5.3 Preparation of $[\text{AuCl}\{\text{2-C}_6\text{F}_4\text{H}\}\text{PPh}_2]$ (**5**).

To a solution of  $[\text{Au}_2(\mu\text{-2-C}_6\text{F}_4\text{PPh}_2)_2]$  (**1**) in dichloromethane was added a 10-fold excess of concentrated hydrochloric acid and the mixture was stirred for 30 min. The solution was concentrated under reduced pressure and hexane was added to precipitate a colourless solid which was isolated by filtration. The monomeric complex  $[\text{AuCl}\{\text{2-C}_6\text{F}_4\text{H}\}\text{PPh}_2]$  was washed with hexane and air dried. Yields were *ca.* 80%.

$^1\text{H}$  NMR:  $\delta$  6.8-7.7 (m, 11H, aromatics).  $^{31}\text{P}$  NMR:  $\delta$  26.1 (d,  $J = 14.8$  Hz). ESI-MS ( $m/z$ ): 1095  $[\text{M}-\text{Cl}]^+$ . Anal. Calcd. for  $\text{C}_{18}\text{H}_{11}\text{AuClF}_4\text{P}$ : C 38.15, H 1.96, Cl 6.26, F 13.41. Found: C 38.22, H 1.99, Cl 6.26, F 13.18.

No reaction was observed when  $[\text{Au}_2(\mu\text{-2-C}_6\text{F}_4\text{PPh}_2)_2]$  (**1**) was treated with two equivalents of concentrated hydrochloric acid.

**7.5.4 Preparation of the dihalodigold(I,III) complexes [XAu( $\mu$ -2-C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub>)( $\kappa^2$ -2-C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub>)AuX] [X = Cl (**6**), Br (**7**), I (**8**)].**

The appropriate digold(II) complex [Au<sub>2</sub>X<sub>2</sub>( $\mu$ -2-C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>] [X = Cl (**2**), Br (**3**), I (**4**)] (1.8 mmol) was heated in toluene (20 mL) to 70 °C for 1-4 hours, during which time the solution became almost colourless. Addition of hexane precipitated the colourless dihalodigold(I,III) compound which was filtered off, washed with hexane and dried *in vacuo*. Yields were 80-90%.

**6:** <sup>1</sup>H NMR:  $\delta$  7.1-8.7 (m, 20H, aromatics). <sup>31</sup>P NMR:  $\delta$  -58.4 (br s), 41.0 (br s). ESI-MS (*m/z*): 1095 [*M*-Cl]<sup>+</sup>. Anal. Calcd. for C<sub>36</sub>H<sub>20</sub>Au<sub>2</sub>Cl<sub>2</sub>F<sub>8</sub>P<sub>2</sub>: C 38.22, H 1.78, P 5.48. Found: C 38.23, H 1.92, P 5.71.

**7:** <sup>1</sup>H NMR:  $\delta$  7.0-8.7 (m, 20H, aromatics). <sup>31</sup>P NMR:  $\delta$  -65.4 (br s), 44.3 (br s). ESI-MS (*m/z*): 1139 [*M*-Br]<sup>+</sup>. Anal. Calcd. for C<sub>36</sub>H<sub>20</sub>Au<sub>2</sub>Br<sub>2</sub>F<sub>8</sub>P<sub>2</sub>: C 35.44, H 1.65. Found: C 35.99, H 2.16.

**8:** <sup>1</sup>H NMR:  $\delta$  6.9-8.3 (m, 20H, aromatics). <sup>31</sup>P NMR:  $\delta$  -77.6 (br s), 46.2 (br s). ESI-MS (*m/z*): 1187 [*M*-I]<sup>+</sup>. Anal. Calcd. for C<sub>36</sub>H<sub>20</sub>Au<sub>2</sub>F<sub>8</sub>I<sub>2</sub>P<sub>2</sub>: C 32.90, H 1.53. Found: C 33.13, H 1.83.

Alternatively, complexes **7** and **8** may be obtained by anion exchange of **6** in dichloromethane with the appropriate sodium or lithium salts in methanol. Yields were typically 90-95%.

**7.5.5 Preparation of the digold(III) complexes  $[Au_2X_4(\mu\text{-}2\text{-}C_6F_4PPh_2)_2]$  [ $X = Cl$  (**9**),  $Br$  (**10**)].**

To a solution of  $[Au_2X_2(\mu\text{-}2\text{-}C_6F_4PPh_2)_2]$  [ $X = Cl$  (**2**),  $Br$  (**3**)] (0.05 mmol) in dichloromethane (10 mL) cooled to  $-30\text{ }^\circ\text{C}$  was added a solution of  $PhICl_2$  or  $Br_2$  (0.25 mmol) in dichloromethane (10 mL). The mixture was stirred at this temperature for 30 min, warmed to room temperature and stirred for 2 hours, during which time the product precipitated out. The solid was isolated by filtration, washed with hexane and dried *in vacuo*. Yields were 90-95%.

**9** (yellow solid):  $^{31}\text{P}$  NMR( $\text{CH}_2\text{Cl}_2/\text{C}_6\text{D}_6$ ):  $\delta$  9.3 (br s). Anal. Calcd. for  $\text{C}_{36}\text{H}_{20}\text{Au}_2\text{Cl}_4\text{F}_8\text{P}_2$ : C 35.97, H 1.68, F 12.64. Found: C 35.47, H 1.91, F 12.28.

**10** (orange solid):  $^{31}\text{P}$  NMR( $\text{CH}_2\text{Cl}_2/\text{C}_6\text{D}_6$ ):  $\delta$  3.2 (br s). Anal. Calcd. for  $\text{C}_{36}\text{H}_{20}\text{Au}_2\text{Br}_4\text{F}_8\text{P}_2$ : C 31.33, H 1.46, F 11.01. Found: C 29.22, H 1.53, F 10.24.

**7.5.6 Preparation of  $[Au_2Y_2(\mu\text{-}2\text{-}C_6F_4PPh_2)_2]$  [ $Y = CH_3COO$  (**11**),  $ONO_2$  (**12**),  $C_6H_5COO$  (**13**),  $CF_3COO$  (**14**)].**

The dichlorodigold(II) complex **2** was dissolved in  $\text{CH}_2\text{Cl}_2$  and treated with a 50-100% molar excess of the appropriate silver salt. The suspension was shielded from light and stirred for 3 hours at room temperature. The insoluble silver salts were removed by filtration through Celite and the volume of the solution reduced by half under reduced pressure. Addition of hexane precipitated out the pale yellow products, which were isolated by filtration, washed with hexane and dried. Yields were quantitative.

**11:**  $^1\text{H}$  NMR:  $\delta$  1.64 (s, 6H,  $\text{CH}_3\text{COO}$ ), 7.0-7.6 (m, 20H, aromatics).  $^{31}\text{P}$  NMR:  $\delta$  -1.3 (br s). ESI-MS ( $m/z$ ) = 1119 [ $M\text{-CH}_3\text{COO}+\text{H}$ ] $^+$ . Anal. Calcd. for  $\text{C}_{40}\text{H}_{26}\text{Au}_2\text{F}_8\text{O}_4\text{P}_2$ : C 40.77, H 2.22, P 5.26. Found: C 42.51, H 2.90, P 5.31.

**12:**  $^1\text{H}$  NMR:  $\delta$  7.0-7.5 (m, 20H, aromatics).  $^{31}\text{P}$  NMR:  $\delta$  -0.1 (br s). ESI-MS ( $m/z$ ) = 1059 [ $M\text{-2}(\text{NO}_3)$ ] $^+$ . Anal. Calcd. for  $\text{C}_{36}\text{H}_{20}\text{Au}_2\text{F}_8\text{N}_2\text{O}_6\text{P}_2$ : C 35.61, H 1.70, N 2.37, P 5.23. Found: C 36.71, H 1.86, N 2.34, P 4.94.

**13:**  $^1\text{H}$  NMR:  $\delta$  6.9-7.5 (m, 20H, aromatics),  $\delta$  8.0 (m, 10H, aromatics).  $^{31}\text{P}$  NMR:  $\delta$  -0.1 (br s). ESI-MS ( $m/z$ ): 1181 [ $M\text{-C}_6\text{H}_5\text{COO}$ ] $^+$ . Anal. Calcd. for  $\text{C}_{50}\text{H}_{30}\text{Au}_2\text{F}_8\text{O}_4\text{P}_2$ : C 46.1, H 2.32, P 4.76. Found: C 46.42, H 3.00, P 4.71.

**14:**  $^1\text{H}$  NMR:  $\delta$  6.8-7.5 (m, 20H, aromatics).  $^{31}\text{P}$  NMR:  $\delta$  -0.5 (br s). ESI-MS ( $m/z$ ) = 1173 [ $M\text{-CF}_3\text{COO}$ ] $^-$ . Anal. Calcd. for  $\text{C}_{40}\text{H}_{20}\text{Au}_2\text{F}_{14}\text{O}_4\text{P}_2$ : C 37.35, H 1.57, P 4.82. Found: C 37.64, H 1.73, P 4.77.

### **7.5.7 Reduction of the di(benzoato)digold(II) complex.**

A solution of **13** (0.08 mmol, 0.1 g) in dichloromethane (3 mL) and cyclohexanol (10 mL) was stirred for 7 hours at room temperature. The  $^{31}\text{P}$  NMR spectrum, acquired *in situ*, showed a peak at  $\delta$  42.7 due to the digold(I) complex [ $\text{Au}_2(\mu\text{-2-C}_6\text{F}_4\text{PPh}_2)_2$ ] (**1**). The IR spectrum of aliquots of the reaction solution showed a strong band at  $1703\text{ cm}^{-1}$  due to  $\text{C}=\text{O}$  stretching, confirming the formation of cyclohexanone during the reduction of **13** to **1**. The di(benzoato)digold(II) complex (0.08 mmol, 0.1 g) also decomposes cleanly to **1** on heating in dichloromethane (20 mL) for 2 days.

### 7.5.8 Preparation of $[Au_4(\mu\text{-}2\text{-}C_6F_4PPh_2)_4]$ (**16**).

A solution of **2** (0.1 mmol, 0.1 g) in dichloromethane (20 mL) was cooled to  $-30\text{ }^\circ\text{C}$  and treated with silver triflate (0.5 mmol, 0.1 g). The mixture was stirred for 15 min in the dark at  $-30\text{ }^\circ\text{C}$  and then at room temperature for 10 min. The orange solution was filtered through Celite, methanol (20 mL) was added to the filtrate and the solution left in the refrigerator for 4 days, during which time a white solid precipitated out. The solvent was evaporated and the white residue was recrystallised from dichloromethane/hexane to give **16** in 80% yields. Different preparation gave different mixtures of digold(I) dimer **1** and tetramer.

$^{31}\text{P}$  NMR:  $\delta$  45.7 (br s). ESI-MS ( $m/z$ ) = 2121  $[M+H]^+$ . Anal. Calcd. for  $C_{72}H_{40}Au_4F_{16}P_4$ : C 40.78, H 1.90, F 14.33, P 5.84. Found: C 39.88, H 1.96, F 14.65, P 5.67.

### 7.5.9 Preparation of $[Au_2(C_6F_5)_2(\mu\text{-}2\text{-}C_6F_4PPh_2)_2]$ (**17**).

A solution of  $C_6F_5Br$  (0.55 mmol, 69  $\mu\text{L}$ ) in ether (30 mL) was cooled to  $-78\text{ }^\circ\text{C}$  and treated dropwise with a solution of  $n\text{BuLi}$  (1.6 M in hexanes, 0.55 mmol, 350  $\mu\text{L}$ ). The mixture was stirred for 1 hour and then treated with a solution of  $[Au_2(OOCC_6H_5)_2(\mu\text{-}2\text{-}C_6F_4PPh_2)_2]$  (**13**) (0.25 mmol, 0.35 g) in toluene (20 mL). After being stirred at  $-78\text{ }^\circ\text{C}$  for 30 min and then at room temperature for 3 hours, the yellow solution was filtered through Celite. The filtrate was evaporated and the residue was recrystallised from dichloromethane/hexane to give **17** as a yellow solid (0.3 g, 85%).



$^1\text{H}$  NMR:  $\delta$  6.7-7.4 (m, 20H, aromatics).  $^{31}\text{P}$  NMR:  $\delta$  -9.6 (br s). ESI-MS ( $m/z$ ): 1433  $[\text{M}+\text{K}]^+$ , 1417  $[\text{M}+\text{Na}]^+$ . Anal. Calcd. for  $\text{C}_{48}\text{H}_{20}\text{Au}_2\text{F}_{18}\text{P}_2$ : C 41.34, H 1.45, F 24.52. Found: C 41.58, H 1.49, F 24.89.

#### 7.5.10 Preparation of $[(\text{C}_6\text{F}_5)\text{Au}(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)(\kappa^2\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)\text{Au}(\text{C}_6\text{F}_5)]$ (**18**).

A solution of  $[\text{Au}_2(\text{C}_6\text{F}_5)_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$  (**17**) (1.43 mmol, 2.0 g) in toluene (20 mL) was heated to 70 °C for 4 hours. The solvent was removed *in vacuo* and the residue recrystallised from dichloromethane/hexane to give the title product as a pale yellow solid (1.8 g, 90%).

$^1\text{H}$  NMR:  $\delta$  6.7-7.6 (m, 20H, aromatics).  $^{31}\text{P}$  NMR:  $\delta$  -62.4 (m), 50.2 (m). ESI-MS ( $m/z$ ): 1394  $[\text{M}]^+$ . Anal. Calcd. for  $\text{C}_{48}\text{H}_{20}\text{Au}_2\text{F}_{18}\text{P}_2$ : C 41.34, H 1.45, F 24.52. Found: C 41.33, H 1.54, F 24.25.

#### 7.5.11 Preparation of $[\text{Au}_2^{\text{III}}(\text{CH}_3)_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$ (**19**).

A solution of complex **13** (0.15 mmol, 0.2 g) in toluene (20 mL) was cooled to -78 °C and treated dropwise with dimethylzinc (1.0 M in heptanes, 0.2 mmol, 0.2 mL). The solution was shielded from light, stirred at -78 °C for 1 hour and then slowly allowed to warm to room temperature overnight. The solvent was evaporated and the residue was dissolved in dichloromethane. Hexane was added to precipitate the product in 70-80% yield.

$^1\text{H}$  NMR:  $\delta$  0.56 (d,  $J_{\text{PH}} = 2.0$  Hz, 6H,  $\text{CH}_3$ ), 6.9-7.6 (m, 20H, aromatics).  $^{31}\text{P}$  NMR:  $\delta$  19.8 (m), 36.1 (br s). Anal. Calcd. for  $\text{C}_{38}\text{H}_{26}\text{Au}_2\text{F}_8\text{P}_2$ : C 41.85, H 2.40. Found: C 41.93, H 2.40.

#### 7.5.12 Reaction of $[\text{Au}_2^{\text{I,III}}(\text{CH}_3)_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$ (**19**) with acids.

A solution of **19** (0.18 mmol, 0.2 g) in dichloromethane (20 mL) was treated with one equivalent of trifluoromethanesulfonic acid (0.18 mmol, 16  $\mu\text{L}$ ) at room temperature. The  $^{31}\text{P}$  NMR spectrum, acquired *in situ*, showed four peaks at  $\delta$  40.5, 42.7, 43.7 and 45.4. The two peaks at  $\delta$  42.7 and 45.4 are probably due to dimeric (**1**) and tetrameric (**16**) gold(I) complexes, respectively.

No reaction was observed when  $[\text{Au}_2^{\text{I,III}}(\text{CH}_3)_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$  (**19**) was treated with one equivalent of concentrated hydrochloric acid.

#### 7.5.13 Preparation of the digold(III) complexes $[\text{X}_3\text{Au}(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)(\kappa^2\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)\text{AuX}]$ [ $\text{X} = \text{Cl}$ (**20**), $\text{Br}$ (**21**)].

To a solution of  $[\text{XAu}(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)(\kappa^2\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)\text{AuX}]$  [ $\text{X} = \text{Cl}$  (**6**),  $\text{Br}$  (**7**)] (0.05 mmol) in dichloromethane (10 mL) cooled to  $-30$   $^\circ\text{C}$  was added a solution of  $\text{PhICl}_2$  or  $\text{Br}_2$  (0.25 mmol) in dichloromethane (10 mL). The mixture was warmed to room temperature and stirred for 2 hours. Hexane was added and the volume reduced under reduced pressure until the product began to precipitate. The solid was isolated by filtration, washed with hexane and dried *in vacuo*. Yields were 90-95%.

**20** (yellow solid):  $^{31}\text{P}$  NMR:  $\delta$  -60.7 (m), 37.7 (m). Anal. Calcd. for  $\text{C}_{36}\text{H}_{20}\text{Au}_2\text{Cl}_4\text{F}_8\text{P}_2$ : C 35.97, H 1.68, Cl 11.80. Found: C 35.60, H 1.73, Cl 11.91.

**21** (orange solid):  $^{31}\text{P}$  NMR:  $\delta$  -67.6 (m), 27.6 (m). Anal. Calcd. for  $\text{C}_{36}\text{H}_{20}\text{Au}_2\text{Br}_4\text{F}_8\text{P}_2$ : C 31.33, H 1.46. Found: C 31.83, H 1.45.

**7.5.14 Preparation of the digold(I,III) complexes  $[\text{XAu}(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)(\kappa^2\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)\text{AuX}]$  [ $\text{X} = \text{CH}_3\text{COO}$  (**22**),  $\text{ONO}_2$  (**23**),  $\text{C}_6\text{H}_5\text{COO}$  (**24**),  $\text{CF}_3\text{COO}$  (**25**)].**

Complex **6** was dissolved in  $\text{CH}_2\text{Cl}_2$  and treated with a 10% molar excess of the appropriate silver salt. The suspension was stirred for several hours at room temperature, while being protected from light. The insoluble silver salts were removed by filtration and the volume of the solution was reduced to half under reduced pressure. Hexane was added to precipitate the products, which were isolated by filtration, washed with hexane and dried *in vacuo* to give the title compounds as white or pale yellow solids in yields of 90-95%.

**22** (white solid):  $^{31}\text{P}$  NMR:  $\delta$  -49.6 (br s), 34.7 (br s).

**23** (yellow solid):  $^1\text{H}$  NMR:  $\delta$  7.0-8.1 (m, 20H, aromatics).  $^{31}\text{P}$  NMR:  $\delta$  -45.0 (br s), 36.0 (br s). ESI-MS ( $m/z$ ): 1059 [ $M\text{-H-}2(\text{NO}_3)$ ] $^+$ .

**24** (yellow solid):  $^1\text{H}$  NMR:  $\delta$  6.7-8.1 (m, 30H, aromatics).  $^{31}\text{P}$  NMR:  $\delta$  -49.4 (br s), 35.5 (br s). ESI-MS ( $m/z$ ): 1181 [ $M\text{-C}_6\text{H}_5\text{COO}$ ] $^+$ . Anal. Calcd. for  $\text{C}_{50}\text{H}_{30}\text{Au}_2\text{F}_8\text{O}_4\text{P}_2$ : C 46.10, H 2.32, F 11.67. Found: C 46.49, H 2.71, F 11.25.

**25** (white solid):  $^1\text{H}$  NMR:  $\delta$  6.8-8.1 (m, 20H, aromatics).  $^{31}\text{P}$  NMR:  $\delta$  -47.0 (br s), 34.0 (br s). ESI-MS ( $m/z$ ): 1059 [ $M\text{-H-}2(\text{CF}_3\text{COO})$ ] $^+$ .

### **7.5.15 Reaction of the di(benzoato)digold(I,III) complex **24** with ZnMe<sub>2</sub>.**

A solution of complex **24** (0.15 mmol, 0.2 g) in toluene (20 mL) was cooled to -78 °C and treated dropwise with dimethylzinc (1.0 M in heptanes, 0.2 mmol, 0.2 mL). The solution was shielded from light, stirred at -78 °C for 1 hour and then slowly allowed to warm to room temperature overnight. The volume was reduced *in vacuo* and hexane was added to precipitate the product as a white solid in 70-80% yield, which appeared to be digold(I) dimer **1** as shown by <sup>31</sup>P NMR spectroscopy (δ 42.7).

### **7.5.16 Attempted preparation of a bis(alkoxo)digold(II) complex.**

[Au<sub>2</sub>Cl<sub>2</sub>(μ-2-C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>] **2** (0.18 mmol, 0.2 g) was dissolved in THF (20 mL) and the solution was treated with two equivalents of potassium trifluoroethoxide, generated *in situ* from KOH and CF<sub>3</sub>CH<sub>2</sub>OH. Immediately the colour of solution changed from yellow to colourless. The solvent was evaporated and the residue was dissolved in dichloromethane. Hexane was added to precipitate the product in 95% yield. <sup>31</sup>P NMR and <sup>19</sup>F NMR spectroscopy confirmed the product to be a dinuclear [Au<sub>2</sub>(μ-2-C<sub>6</sub>F<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>] **1**.

## **7.6 Preparation of the gold complexes containing mono-fluoro phosphine ligands.**

### **7.6.1 Preparation of the 6-fluoro-substituted digold(I) complex [Au<sub>2</sub>(μ-C<sub>6</sub>H<sub>3</sub>-6-F-2-PPh<sub>2</sub>)<sub>2</sub>] (**28**).**

To a solution of 2-Me<sub>3</sub>Sn-3-FC<sub>6</sub>H<sub>3</sub>PPh<sub>2</sub> (2.26 mmol, 1.0 g) in dichloromethane (40 mL) was added [AuCl(tht)] (2.26 mmol, 0.72 g) and the mixture was refluxed for 24 hours.

The volume was reduced and hexane added to precipitate the title complex as a white solid which was isolated by filtration, washed with hexane and dried *in vacuo* (1.6 g, 75%).

$^1\text{H}$  NMR:  $\delta$  6.9-7.6 (m, 26H, aromatics).  $^{31}\text{P}$  NMR:  $\delta$  39.0 (dd,  $J = 1.2, 2.4$  Hz). ESI-MS ( $m/z$ ): 953 [ $M+H$ ] $^+$ . Anal. Calcd. for  $\text{C}_{36}\text{H}_{26}\text{Au}_2\text{F}_2\text{P}_2$ : C 45.40, H 2.75, F 3.99, P 6.50. Found: C 44.93, H 2.81, F 3.74, P 6.45.

Alternatively, an analogous reaction to that for the preparation of the digold(I) complex  $[\text{Au}_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$  (**1**) (Section 7.5.1), using 2-Br-3-FC<sub>6</sub>H<sub>3</sub>PPh<sub>2</sub> (2.8 mmol, 1.0 g),  $^n\text{BuLi}$  (1.6 M in hexanes, 2.8 mmol, 1.7 mL) and  $[\text{AuBr}(\text{AsPh}_3)]$  (2.8 mmol, 1.6 g), gave a mixture of the dinuclear complex  $[\text{Au}_2(\mu\text{-C}_6\text{H}_3\text{-}6\text{-F-}2\text{-PPh}_2)_2]$  and tetranuclear species  $[\text{Au}_4(\mu\text{-C}_6\text{H}_3\text{-}6\text{-F-}2\text{-PPh}_2)_4]$  in 78% yield. The  $^{31}\text{P}$  NMR spectrum of this solid showed a doublet of doublets at  $\delta$  39.0 ( $J = 1.2, 2.4$  Hz) due to the dimer and a doublet of multiplets at  $\delta$  41.1 ( $J = ca. 5$  Hz) due to the tetramer; the former peak was always more intense (*ca.* 70%). The ESI-mass spectrum of this mixture showed the expected [ $M+H$ ] $^+$  ion peaks due to the dimer and tetramer at  $m/z$  953 and 1905, respectively.

#### **7.6.2 Preparation of the 5-fluoro-substituted digold(I) complex $[\text{Au}_2(\mu\text{-C}_6\text{H}_3\text{-}5\text{-F-}2\text{-PPh}_2)_2]$ (**30**).**

A solution of 2-Br-4-FC<sub>6</sub>H<sub>3</sub>PPh<sub>2</sub> (1.6 mmol, 0.6 g) in ether (20 mL) was cooled to -78 °C and  $^n\text{BuLi}$  (1.6 M in hexanes, 1.6 mmol, 1.0 mL) was added slowly. The mixture was stirred for 30 min and a suspension of  $[\text{AuBr}(\text{AsPh}_3)]$  (1.6 mmol, 0.97 g) in ether (20 mL) was added via cannula. The resulting mixture was stirred at -78 °C for two hours

and then allowed to warm to room temperature overnight. The white solid was isolated by filtration and washed successively with ether (10 mL), methanol (10 mL) and hexane (20 mL). The crude product was extracted with hot dichloromethane and the extract was filtered through Celite. Evaporation of the solution gave  $[\text{Au}_2(\mu\text{-C}_6\text{H}_3\text{-5-F-2-PPh}_2)_2]$  as a colourless solid (0.88 g, 55%).

$^1\text{H}$  NMR:  $\delta$  6.7-8.1 (m, 26H, aromatics).  $^{31}\text{P}$  NMR:  $\delta$  36.1 (t,  $J = 5.1$  Hz). ESI-MS ( $m/z$ ): 953  $[\text{M}+\text{H}]^+$ . Anal. Calcd. for  $\text{C}_{36}\text{H}_{26}\text{Au}_2\text{F}_2\text{P}_2$ : C 45.40, H 2.75, F 3.99. Found: C 45.28, H 2.78, F 3.57.

Alternatively, an analogous reaction to that for the preparation of the digold(I) complex  $[\text{Au}_2(\mu\text{-C}_6\text{H}_3\text{-6-F-2-PPh}_2)_2]$  (Section 7.6.1), using 2-Me<sub>3</sub>Sn-4-FC<sub>6</sub>H<sub>3</sub>PPh<sub>2</sub> (2.3 mmol, 1.0 g) and  $[\text{AuCl}(\text{tht})]$  (2.3 mmol, 0.7 g), gave a mixture of the dinuclear complex  $[\text{Au}_2(\mu\text{-C}_6\text{H}_3\text{-5-F-2-PPh}_2)_2]$  and tetranuclear complex  $[\text{Au}_4(\mu\text{-C}_6\text{H}_3\text{-5-F-2-PPh}_2)_4]$ . The  $^{31}\text{P}$  NMR spectrum of this solid showed two triplet resonances at  $\delta$  40.6 (t,  $J = 6.0$  Hz) and 36.1 (t,  $J = 5.2$  Hz). The former was always the major peak (*ca.* 70%) and is assigned to the tetramer. ESI-mass spectrum of this mixture showed expected  $[\text{M}+\text{H}]^+$  ion peaks due to the dimer and tetramer at  $m/z$  953 and 1905, respectively.

### **7.6.3 Preparation of the 6-fluoro- and 5-fluoro- substituted dihalodigold(II) complexes $[\text{Au}_2\text{X}_2(\mu\text{-C}_6\text{H}_3\text{-}n\text{-F-2-PPh}_2)_2]$ ( $\text{X} = \text{Cl, Br, I}$ ; $n = 5, 6$ ).**

In an analogous reaction to that for the preparation of  $[\text{Au}_2\text{Cl}_2(\mu\text{-2-C}_6\text{F}_4\text{PPh}_2)_2]$  (**2**) (Section 7.5.2), treating a dichloromethane solution of  $[\text{Au}_2(\mu\text{-C}_6\text{H}_3\text{-}n\text{-F-2-PPh}_2)_2]$  ( $n = 5, 6$ ) with an equimolar amount of  $\text{PhICl}_2$  in dichloromethane gave the desired

dichlorodigold(II) complex  $[\text{Au}_2\text{Cl}_2(\mu\text{-C}_6\text{H}_3\text{-}n\text{-F-2-PPh}_2)_2]$  ( $n = 5, 6$ ) as a yellow solid in 80-90% yield.

$[\text{Au}_2\text{Cl}_2(\mu\text{-C}_6\text{H}_3\text{-5-F-2-PPh}_2)_2]$  **32**:  $^1\text{H NMR}$ :  $\delta$  5.6-8.1 (m, 26H, aromatics).  $^{31}\text{P NMR}$ :  $\delta$  1.7 (t,  $J = 6.0$  Hz). ESI-MS ( $m/z$ ): 987  $[\text{M-Cl}]^+$ . Anal. Calcd. for  $\text{C}_{36}\text{H}_{26}\text{Au}_2\text{Cl}_2\text{F}_2\text{P}_2$ : C 42.25, H 2.56, Cl 6.93, F 3.71. Found: C 43.07, H 3.07, Cl 6.67, F 3.22.

$[\text{Au}_2\text{Cl}_2(\mu\text{-C}_6\text{H}_3\text{-6-F-2-PPh}_2)_2]$  **33**:  $^1\text{H NMR}$ :  $\delta$  6.2-7.5 (m, 26H, aromatics).  $^{31}\text{P NMR}$ :  $\delta$  0.8 (t,  $J = 5.0$  Hz). ESI-MS ( $m/z$ ): 987  $[\text{M-Cl}]^+$ . Anal. Calcd. for  $\text{C}_{36}\text{H}_{26}\text{Au}_2\text{Cl}_2\text{F}_2\text{P}_2$ : C 42.25, H 2.56, Cl 6.93, F 3.71. Found: C 43.79, H 2.92, Cl 7.11, F 3.18.

A dichloromethane solution of  $[\text{Au}_2\text{Cl}_2(\mu\text{-C}_6\text{H}_3\text{-}n\text{-F-2-PPh}_2)_2]$  ( $n = 5, 6$ ) (1 mmol) cooled to  $-30$  °C was treated with a methanol solution of sodium bromide or sodium iodide (3 mmol). After the mixture had been stirred for 15 min at  $-30$  °C, the solvents were evaporated under reduced pressure and the residue was extracted with cold dichloromethane ( $-30$  °C). Filtration through Celite and evaporation of the solvent gave the dihalodigold(II) complexes  $[\text{Au}_2\text{X}_2(\mu\text{-C}_6\text{H}_3\text{-}n\text{-F-2-PPh}_2)_2]$  ( $n = 5, 6$ ) as orange ( $\text{X} = \text{Br}$ ) or red ( $\text{X} = \text{I}$ ) solids in 75-90% yields.

$[\text{Au}_2\text{Br}_2(\mu\text{-C}_6\text{H}_3\text{-5-F-2-PPh}_2)_2]$  **34**:  $^1\text{H NMR}$ :  $\delta$  6.2-7.5 (m, 26H, aromatics).  $^{31}\text{P NMR}$ :  $\delta$  -3.4 (t,  $J = 6.0$  Hz). ESI-MS ( $m/z$ ): 1111  $[\text{M+H}]^+$ . Anal. Calcd. for  $\text{C}_{36}\text{H}_{26}\text{Au}_2\text{Br}_2\text{F}_2\text{P}_2$ : C 38.87, H 2.36, Br 14.37, F 3.42. Found: C 39.48, H 2.57, Br 13.46, F 3.52.

[Au<sub>2</sub>Br<sub>2</sub>(μ-C<sub>6</sub>H<sub>3</sub>-6-F-2-PPh<sub>2</sub>)<sub>2</sub>] **35**: <sup>1</sup>H NMR: δ 6.2-7.5 (m, 26H, aromatics). <sup>31</sup>P NMR: δ -4.2 (t, *J* = 4.6 Hz). ESI-MS (*m/z*): 1033 [*M*-Br]<sup>+</sup>. Anal. Calcd. for C<sub>36</sub>H<sub>26</sub>Au<sub>2</sub>Br<sub>2</sub>F<sub>2</sub>P<sub>2</sub>: C 38.87, H 2.36, Br 14.37, F 3.42. Found: C 39.59, H 2.66, Br 14.10, F 3.41.

[Au<sub>2</sub>I<sub>2</sub>(μ-C<sub>6</sub>H<sub>3</sub>-5-F-2-PPh<sub>2</sub>)<sub>2</sub>] **36**: <sup>1</sup>H NMR: δ 6.8-8.1 (m, 26H, aromatics). <sup>31</sup>P NMR: δ -11.6 (t, *J* = 5.0 Hz). ESI-MS (*m/z*): 1079 [*M*-I]<sup>+</sup>. Anal. Calcd. for C<sub>36</sub>H<sub>26</sub>Au<sub>2</sub>F<sub>2</sub>I<sub>2</sub>P<sub>2</sub>: C 35.85, H 2.17, F 3.15, I 21.04. Found: C 36.14, H 2.27, F 2.91, I 21.11.

[Au<sub>2</sub>I<sub>2</sub>(μ-C<sub>6</sub>H<sub>3</sub>-6-F-2-PPh<sub>2</sub>)<sub>2</sub>] **37**: <sup>1</sup>H NMR: δ 6.7-8.2 (m, 26H, aromatics). <sup>31</sup>P NMR: δ -12.1 (t, *J* = 4.0 Hz). ESI-MS (*m/z*): 1207 [*M*+H]<sup>+</sup>. Anal. Calcd. for C<sub>36</sub>H<sub>26</sub>Au<sub>2</sub>F<sub>2</sub>I<sub>2</sub>P<sub>2</sub>: C 35.85, H 2.17, F 3.15, I 21.04. Found: C 36.25, H 2.56, F 2.90, I 21.25.

#### **7.6.4 Preparation of the 6-fluoro-substituted phosphine digold(I,III) complexes [XAu(μ-C<sub>6</sub>H<sub>3</sub>-6-F-2-PPh<sub>2</sub>)(κ<sup>2</sup>-C<sub>6</sub>H<sub>3</sub>-6-F-2-PPh<sub>2</sub>)AuX] [X = Cl (39), Br (40), I (41)].**

The appropriate digold(II) complex [Au<sub>2</sub>X<sub>2</sub>(μ-C<sub>6</sub>H<sub>3</sub>-6-F-2-PPh<sub>2</sub>)<sub>2</sub>] (X = Cl, Br, I) was heated in toluene to 70 °C for 1-3 hours, during which time the solution became almost colourless. Hexane was added to precipitate the colourless dihalodigold(I,III) compounds which were filtered off, washed with hexane and dried *in vacuo*. Yields were 80-90%.

**39**: <sup>1</sup>H NMR: δ 6.6-8.1 (m, 20H, aromatics). <sup>31</sup>P NMR: δ -56.3 (ddd, *J* = 5.2, 13.4, 18.6 Hz), 37.7 (d, *J* = 13.4 Hz). ESI-MS (*m/z*): 987 [*M*-Cl]<sup>+</sup>. Anal. Calcd. for C<sub>36</sub>H<sub>20</sub>Au<sub>2</sub>Cl<sub>2</sub>F<sub>2</sub>P<sub>2</sub>: C 42.25, H 2.56, Cl 6.93, F 3.71, P 6.05. Found: C 42.13, H 2.77, Cl 6.58, F 3.37, P 5.81.



**40:**  $^{31}\text{P}$  NMR (toluene/ $\text{C}_6\text{D}_6$ ):  $\delta$  -63.8 (ddd,  $J = 5.2, 12.6, 17.8$  Hz), 39.2 (d,  $J = 13.3$  Hz).

**41:**  $^{31}\text{P}$  NMR (toluene/ $\text{C}_6\text{D}_6$ ):  $\delta$  -76.1 (ddd,  $J = 5.2, 12.2, 17.5$  Hz), 41.4 (d,  $J = 13.4$  Hz).

**7.6.5 Preparation of the 5-fluoro-substituted phosphine gold(I) complexes  $[\text{Au}_2\text{X}_2(2,2'\text{-Ph}_2\text{P-5-F-C}_6\text{H}_3\text{C}_6\text{H}_3\text{-5-F-PPh}_2)]$  [ $\text{X} = \text{Cl}$  (42),  $\text{Br}$  (43),  $\text{I}$  (44)].**

Coloured toluene solutions of the appropriate dihalodigold(II) complexes  $[\text{Au}_2\text{X}_2(\mu\text{-C}_6\text{H}_3\text{-5-F-2-PPh}_2)_2]$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) were heated to 60 °C for 3 hours. The resulting colourless solutions were evaporated to small volume under reduced pressure and the carbon-carbon coupled products were precipitated almost quantitatively by the addition of hexane.

**42:**  $^1\text{H}$  NMR:  $\delta$  5.9-8.0 (m, 26H, aromatics).  $^{31}\text{P}$  NMR:  $\delta$  27.3 (s). ESI-MS ( $m/z$ ): 987  $[\text{M-Cl}]^+$ . Anal. Calcd. for  $\text{C}_{36}\text{H}_{26}\text{Au}_2\text{Cl}_2\text{F}_2\text{P}_2$ : C 42.25, H 2.56, Cl 6.93, F 3.71. Found: C 41.92, H 2.67, Cl 6.57, F 4.04.

**43:**  $^1\text{H}$  NMR:  $\delta$  5.9-8.1 (m, 26H, aromatics).  $^{31}\text{P}$  NMR:  $\delta$  29.0 (s). ESI-MS ( $m/z$ ): 1033  $[\text{M-Br}]^+$ . Anal. Calcd. for  $\text{C}_{36}\text{H}_{26}\text{Au}_2\text{Br}_2\text{F}_2\text{P}_2$ : C 38.87, H 2.36, F 3.42. Found: C 38.35, H 2.52, F 3.88.

**44:**  $^1\text{H}$  NMR:  $\delta$  5.8-8.1 (m, 26H, aromatics).  $^{31}\text{P}$  NMR:  $\delta$  31.7 (s). ESI-MS ( $m/z$ ): 1079  $[\text{M-I}]^+$ . Anal. Calcd. for  $\text{C}_{36}\text{H}_{26}\text{Au}_2\text{F}_2\text{I}_2\text{P}_2$ : C 38.85, H 2.17, F 3.15. Found: C 35.67, H 2.27, F 2.85.

## 7.7 Mixed ligand digold(I) and digold(II) complexes.

### 7.7.1 Reaction of $[\text{Au}_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$ with $[\text{Au}_2(\mu\text{-S}_2\text{CNEt}_2)_2]$ .

A suspension of  $[\text{Au}_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$  (**1**) (0.1 mmol, 0.1 g) and  $[\text{Au}_2(\mu\text{-S}_2\text{CNEt}_2)_2]$  (0.1 mmol, 0.08 g) in dichloromethane (20 mL) was stirred for 4 days at room temperature. The  $^{31}\text{P}$  NMR spectrum, recorded *in situ*, showed a singlet resonance at  $\delta$  47.0. The volume of the solution was reduced to half under reduced pressure. Hexane was added to precipitate the product, which were isolated by filtration, washed with hexane and dried *in vacuo*. Satisfactory elemental analysis and mass spectrum of the isolated solid could not be obtained.

### 7.7.2 Reaction of $[\text{Au}_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$ with $[\text{Au}_2(\mu\text{-}2\text{-C}_6\text{H}_4\text{PPh}_2)_2]$ .

A suspension of  $[\text{Au}_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$  (**1**) (0.1 mmol, 0.1 g) and  $[\text{Au}_2(\mu\text{-}2\text{-C}_6\text{H}_4\text{PPh}_2)_2]$  (0.1 mmol, 0.09 g) in dichloromethane (20 mL) was stirred for 2 days at room temperature. The  $^{31}\text{P}$  NMR spectrum of the resulting solution showed three major peaks at  $\delta$  36.1, 41.9 and 40.8 together with multiplets in the range  $\delta$  38-48.

### 7.7.3 Reaction of $[\text{Au}_2\text{Cl}_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$ with $[\text{Au}_2\text{Br}_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$ .

A solution of  $[\text{Au}_2\text{Cl}_2(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$  (**2**) (0.1 mmol, 0.11 g) and  $[\text{Au}_2\text{Br}_2(\mu\text{-}2\text{-C}_6\text{H}_4\text{PPh}_2)_2]$  (**3**) (0.1 mmol, 0.12 g) in dichloromethane (20 mL) was stirred for 1 hour at 0 °C. The resulting *in situ*  $^{31}\text{P}$  NMR spectrum showed an AB quartet pattern ( $\delta_{\text{A}} = -2.3$ ,  $\delta_{\text{B}} = -8.3$ ,  $J_{\text{AB}} = 85$  Hz) assigned to  $[\text{Au}_2\text{ClBr}(\mu\text{-}2\text{-C}_6\text{F}_4\text{PPh}_2)_2]$ , together with peaks due to the starting materials.

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Compound	1	2	6
Formula	C <sub>36</sub> H <sub>20</sub> Au <sub>2</sub> F <sub>8</sub> P <sub>2</sub> .2(Au <sub>0.02</sub> )	2(C <sub>36</sub> H <sub>20</sub> Au <sub>2</sub> Cl <sub>2</sub> F <sub>8</sub> P <sub>2</sub> ).2.5(CH <sub>2</sub> Cl <sub>2</sub> )	C <sub>36</sub> H <sub>20</sub> Au <sub>2</sub> Cl <sub>2</sub> F <sub>8</sub> P <sub>2</sub> .CH <sub>2</sub> Cl <sub>2</sub>
fw	1067.91	2474.98	1216.26
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
<i>a</i> , Å	12.7411 (5)	17.2172 (1)	10.1958 (1)
<i>b</i> , Å	12.9877 (6)	21.7718 (2)	16.5651 (2)
<i>c</i> , Å	19.6902 (8)	22.8310 (2)	22.7112 (3)
β, deg	99.839 (2)	111.2521 (5)	-
<i>V</i> , Å <sup>3</sup>	3210.4 (2)	7976.18 (11)	3835.80 (8)
<i>Z</i>	4	4	4
Cryst dimens (mm)	0.34 × 0.31 × 0.22	0.30 × 0.09 × 0.08	0.40 × 0.10 × 0.08
D <sub>calc</sub> (Mg m <sup>-3</sup> )	2.209	2.061	2.106
μ (mm <sup>-1</sup> )	9.475	7.796	8.070
T(K)	200	200	200
No. indep reflns ( <i>R</i> <sub>int</sub> )	7378 (0.077)	8879 (0.086)	7309 (0.042)
No. obsd reflns [ <i>I</i> > 3σ( <i>I</i> )]	4549	8879	7309
No. params refined	441	992	507
<i>R</i> <sub>F</sub>	0.0429	0.0246	0.0261
<i>R</i> <sub>w</sub>	0.0458	0.0287	0.0302
<i>P</i> <sub>max</sub> / <i>P</i> <sub>min</sub> (e Å <sup>-3</sup> )	1.5/-2.92	1.10/-1.15	5.22/-2.05

Compound	13	16	17
Formula	C <sub>53</sub> H <sub>37</sub> Au <sub>2</sub> F <sub>8</sub> O <sub>4</sub> P <sub>2</sub>	C <sub>75.44</sub> H <sub>46.88</sub> Au <sub>4</sub> C <sub>16.88</sub> F <sub>16</sub> P <sub>4</sub>	C <sub>48.25</sub> H <sub>20.50</sub> Au <sub>2</sub> C <sub>10.50</sub> F <sub>18</sub> P <sub>2</sub>
fw	1345.7	2412.93	1415.74
Crystal system	Monoclinic	Tetragonal	Triclinic
Space group	P21/n	P42/n	P-1
a, Å	12.14090 (10)	15.9440 (3)	11.2743 (3)
b, Å	15.8124 (2)	15.9440 (3)	13.8378 (3)
c, Å	24.6158 (3)	14.7921 (2)	15.6632 (3)
α, deg	90	90	72.6380 (10)
β, deg	99.8870 (10)	90	72.0350 (10)
γ, deg	90	90	86.0370 (10)
V, Å <sup>3</sup>	4655.48 (9)	3760.32 (11)	2217.89 (9)
Z	4	2	2
D <sub>calc</sub> (Mg m <sup>-3</sup> )	1.920	2.131	2.120
μ (mm <sup>-1</sup> )	6.444	8.192	6.822
T, K	110 (2)	110 (2)	100 (2)
Cryst dims (mm)	0.27 × 0.10 × 0.10	0.17 × 0.15 × 0.09	0.26 × 0.12 × 0.07
Theta range, deg	2.71-36.00	2.90-35.00	2.70-29.00
Reflections collected / unique (R <sub>int</sub> )	15499 / 22018 (0.0754)	41538 / 8284 (0.0415)	55739 / 11780 (0.0559)
Data / Restraints / Parameters	22018 / 0 / 623	8284 / 25 / 283	11780 / 136 / 733
Final R indices [I > 2σ(I)]	R1 = 0.0312, wR2 = 0.0557	R1 = 0.0318, wR2 = 0.0722	R1 = 0.0332, wR2 = 0.0770
R indices (all data)	R1 = 0.0529, wR2 = 0.0594	R1 = 0.0527, wR2 = 0.0774	R1 = 0.0473, wR2 = 0.0810
Largest diff. peak and hole (e.Å <sup>-3</sup> )	2.125, -2.019	1.689, -1.669	3.005, -1.953

Compound	19	20	23
Formula	C <sub>38</sub> H <sub>26</sub> Au <sub>2</sub> F <sub>8</sub> P <sub>2</sub>	C <sub>37</sub> H <sub>22</sub> Au <sub>2</sub> Cl <sub>6</sub> F <sub>8</sub> P <sub>2</sub>	C <sub>36</sub> H <sub>20</sub> Au <sub>2</sub> F <sub>8</sub> N <sub>2</sub> O <sub>6</sub> P <sub>2</sub>
fw	1090.46	1287.12	1184.41
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	P-1	P-1	P21/c
<i>a</i> , Å	11.9272 (2)	10.7369 (2)	10.1875 (3)
<i>b</i> , Å	12.2979 (2)	14.4038 (2)	34.2523 (12)
<i>c</i> , Å	14.2430 (2)	14.5209 (2)	10.5338 (3)
$\alpha$ , deg	71.7130 (10)	60.9030 (10)	90
$\beta$ , deg	66.9410 (10)	82.7430 (10)	90.854 (2)
$\gamma$ , deg	64.2670 (10)	88.0100 (10)	90
<i>V</i> , Å <sup>3</sup>	1705.37	1945.64 (6)	3675.3 (2)
<i>Z</i>	2	2	4
<i>D</i> <sub>calc</sub> (Mg m <sup>-3</sup> )	2.124	2.197	2.141
$\mu$ (mm <sup>-1</sup> )	8.759	8.094	8.151
T, K	110 (2)	100 (2)	110 (2)
Cryst dims (mm)	0.29 × 0.14 × 0.09	0.29 × 0.20 × 0.12	0.21 × 0.19 × 0.10
Theta range, deg	2.65-35.00	2.63-38.00	2.68-27.36
Reflections collected / unique ( <i>R</i> <sub>int</sub> )	66388 / 14975 (0.0732)	80292 / 21176 (0.0631)	29664 / 8226 (0.0790)
Data / Restraints / Parameters	14975 / 0 / 451	21176 / 0 / 496	8226 / 0 / 505
Final R indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	R1 = 0.0363, wR2 = 0.0897	R1 = 0.0338, wR2 = 0.0838	R1 = 0.0530, wR2 = 0.1288
R indices (all data)	R1 = 0.0468, wR2 = 0.0936	R1 = 0.0419, wR2 = 0.0868	R1 = 0.0716, wr2 = 0.1368
Largest diff. peak and hole (e.Å <sup>-3</sup> )	5.705, -3.880	5.374, -5.879	3.913, -2.628

Compound	26	27
Formula	C <sub>55</sub> H <sub>32</sub> Au <sub>3</sub> Cl <sub>2.45</sub> F <sub>12</sub> N <sub>1.55</sub> O <sub>5.65</sub> P <sub>3</sub>	C <sub>54.63</sub> H <sub>30.26</sub> Ag <sub>0.42</sub> Au <sub>2.58</sub> Cl <sub>1.48</sub> F <sub>12</sub> N <sub>0.78</sub> O <sub>3.34</sub> P <sub>3</sub>
fw	1803.58	1677.83
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
<i>a</i> , Å	13.7448(5)	11.6042(3)
<i>b</i> , Å	14.2558(6)	13.1692(3)
<i>c</i> , Å	32.8620(13)	17.8417(3)
$\alpha$ , deg	94.0390(10)	80.6680(10)
$\beta$ , deg	95.747(2)	79.8200(10)
$\gamma$ , deg	118.718(2)	80.6780(10)
<i>V</i> , Å <sup>3</sup>	5566.6(4)	2623.03(10)
<i>Z</i>	4	2
<i>D</i> <sub>calc</sub> (Mg m <sup>-3</sup> )	2.152	2.124
$\mu$ (mm <sup>-1</sup> )	8.183	7.609
<i>T</i> , K	100(2)	100(2)
Cryst dimens (mm)	0.18 × 0.18 × 0.06	0.13 × 0.09 × 0.03
Theta range, deg	2.56-26.00	2.55-30.00
Reflections collected / unique ( <i>R</i> <sub>int</sub> )	81884 / 21753 (0.0993)	56598 / 15080 (0.0610)
Data / Restraints / Parameters	21753 / 59 / 1480	15080 / 0 / 724
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> 1 = 0.0628, <i>wR</i> 2 = 0.1326	<i>R</i> 1 = 0.0374, <i>wR</i> 2 = 0.0888
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0963, <i>wR</i> 2 = 0.1422	<i>R</i> 1 = 0.0555, <i>wR</i> 2 = 0.0943
Largest diff. peak and hole (e.Å <sup>-3</sup> )	3.187, -2.989	2.414, -2.377

Compound	28	31	32
Formula	C <sub>36</sub> H <sub>26</sub> Au <sub>2</sub> F <sub>2</sub> P <sub>2</sub>	C <sub>73</sub> H <sub>54</sub> Au <sub>4</sub> Cl <sub>2</sub> F <sub>4</sub> P <sub>4</sub>	C <sub>41.40</sub> H <sub>38.50</sub> Au <sub>2</sub> Cl <sub>2.60</sub> F <sub>2</sub> P <sub>2</sub>
fw	952.44	1989.81	1122.07
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	P-1	P21/c	P21/c
a, Å	9.0115 (2)	14.2878 (2)	16.6877(2)
b, Å	9.5208 (2)	16.7228 (3)	20.0851 (3)
c, Å	10.0842 (2)	27.8198 (4)	11.64580 (10)
α, deg	89.7260 (10)	90	90
β, deg	78.8100 (10)	101.9280 (10)	95.7130 (10)
γ, deg	63.1070 (10)	90	90
V, Å <sup>3</sup>	753.54	6503.52 (18)	3883.98 (8)
Z	1	4	4
D <sub>calc</sub> (Mg m <sup>-3</sup> )	2.099	2.032	1.919
μ (mm <sup>-1</sup> )	9.867	9.230	7.846
T, K	100 (2)	100 (2)	100 (2)
Cryst dims (mm)	0.22 × 0.20 × 0.10	0.13 × 0.11 × 0.05	0.34 × 0.30 × 0.17
Theta range, deg	2.60-40.00	2.55-28.00	2.65-33.00
Reflections collected / unique (R <sub>int</sub> )	33955 / 9335 (0.0637)	80637 / 15654 (0.0746)	80609 / 14619 (0.0834)
Data / Restraints / Parameters	9335 / 0 / 191	15654 / 33 / 805	14619 / 42 / 466
Final R indices [I > 2σ(I)]	R1 = 0.0271, wR2 = 0.0650	R1 = 0.0355, wR2 = 0.0674	R1 = 0.0402, wR2 = 0.1046
R indices (all data)	R1 = 0.0315, wR2 = 0.0663	R1 = 0.0606, wR2 = 0.0731	R1 = 0.0542, wR2 = 0.1100
Largest diff. peak and hole (e.Å <sup>-3</sup> )	3.972, -3.023	1.505, -1.756	4.666, -4.155

Compound	33	38	39
Formula	C <sub>36.91</sub> H <sub>28.48</sub> Au <sub>2</sub> Cl <sub>3.16</sub> F <sub>2</sub> O <sub>0.33</sub> P <sub>2</sub>	C <sub>61.50</sub> H <sub>48</sub> Au <sub>3</sub> Br <sub>2</sub> Cl <sub>3</sub> F <sub>3</sub> P <sub>3</sub>	C <sub>37</sub> H <sub>28</sub> Au <sub>2</sub> Cl <sub>4</sub> F <sub>2</sub> P <sub>2</sub>
fw	1083.17	1793.98	1108.27
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	P-1	P21/n	P-1
a, Å	9.57140 (10)	19.0219(3)	8.84910 (10)
b, Å	19.3795 (3)	11.9992(2)	11.4657 (2)
c, Å	20.7246 (4)	26.0829(4)	18.1948 (3)
α, deg	72.6120 (10)	90	87.2030 (10)
β, deg	80.9120(10)	103.3430(10)	77.6010 (10)
γ, deg	82.9700	90	86.2500 (10)
V, Å <sup>3</sup>	3610.92 (10)	5792.65(16)	1798.00
Z	4	4	2
D <sub>calc</sub> (Mg m <sup>-3</sup> )	1.992	2.057	2.047
μ (mm <sup>-1</sup> )	8.476	9.229	8.574
T, K	100 (2)	100(2)	100 (2)
Cryst dims (mm)	0.20 × 0.05 × 0.04	0.25 × 0.17 × 0.07	0.41 × 0.12 × 0.05
Theta range, deg	2.62-27.00	2.75-29.00	2.83-35.00
Reflections collected / unique (R <sub>int</sub> )	74858 / 15753 (0.0674)	67386 / 15370 (0.0697)	67525 / 15839 (0.0700)
Data / Restraints / Parameters	15753 / 35 / 864	15370 / 61 / 715	15839 / 27 / 434
Final R indices [I > 2σ(I)]	R1 = 0.0376, wR2 = 0.0841	R1 = 0.0413, wR2 = 0.1017	R1 = 0.0340, wR2 = 0.0827
R indices (all data)	R1 = 0.0563, wR2 = 0.0896	R1 = 0.0562, wR2 = 0.1079	R1 = 0.0447, wr2 = 0.0864
Largest diff. peak and hole (e.Å <sup>-3</sup> )	2.450, -1.945	3.753, -3.555	4.081, -3.527

Compound	42
Formula	C <sub>36</sub> H <sub>26</sub> Au <sub>2</sub> Cl <sub>2</sub> F <sub>2</sub> P <sub>2</sub>
fw	1023.34
Crystal system	Monoclinic
Space group	P21/c
<i>a</i> , Å	11.01700 (10)
<i>b</i> , Å	15.97300 (10)
<i>c</i> , Å	18.1351 (2)
$\alpha$ , deg	90
$\beta$ , deg	90.4610 (10)
$\gamma$ , deg	90
<i>V</i> , Å <sup>3</sup>	3191.21 (5)
<i>Z</i>	4
<i>D</i> <sub>calc</sub> (Mg m <sup>-3</sup> )	2.130
$\mu$ (mm <sup>-1</sup> )	9.490
T, K	100 (2)
Cryst dimens (mm)	0.30 × 0.25 × 0.22
Theta range, deg	2.79-35.00
Reflections collected / unique ( <i>R</i> <sub>int</sub> )	76037 / 14036 (0.0554)
Data / Restraints / Parameters	14036 / 0 / 397
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> 1 = 0.0266, <i>wR</i> 2 = 0.0576
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0367, <i>wR</i> 2 = 0.0599
Largest diff. peak and hole (e.Å <sup>-3</sup> )	2.100, -1.949



