

**Figure 4.17** A qualitative molecular orbital scheme for a  $\sigma$ -bonded complex ion  $[\text{AuL}_2]^+$ . (Reprinted with permission from *Inorg. Chem.*, 1982, **21**, 2946. Copyright (1982) American Chemical Society.)

have, as yet, unknown structures; when painted on to pottery, then fired, they decompose to give a gold film.

#### 4.10.7 MO schemes for 2-coordinate gold(I) complexes

A typical scheme [101] for a complex  $\text{AuL}_2^+$  is shown in Figure 4.17.

A simple crystal field treatment predicts

$$5d_{z^2}(\sigma) > 5d_{xz, yz}(\pi) > 5d_{xy}, d_{x^2 - y^2}(\delta),$$

the latter expected to be essentially non-bonding, but the relative energies will be ligand dependent, with electronegative ligands increasing d orbital participation and more electropositive ligands increasing s/p participation. There will also be gold 6s and 6p mixing into the highest ligand-field orbitals. Analysis of the spectra of  $\text{Au}(\text{CN})_2^-$  gave the ordering  $d_{z^2}(\sigma) > d_{xy}, d_{x^2 - y^2}(\delta) > d_{xz}, d_{yz}(\pi)$  whereas the PE spectrum of  $(\text{Me}_3\text{P})\text{AuMe}$  was interpreted in terms of  $d_\pi \sim d_\delta > d_\sigma$ . MO calculations for  $\text{AuX}_2^-$  (X = F to I) have recently indicated  $d_\delta > d_\pi > d_\sigma$  [96].

## 4.11 Gold(II) complexes

Unstable dithiocarbamates  $\text{Au}(\text{S}_2\text{CNR}_2)_2$  have been detected in solution by ESR but the square planar  $\text{Au}(\text{S}_2\text{C}_2(\text{CN})_2)_2^{2-}$  has been isolated as a green  $\text{Bu}_4\text{N}^+$  salt; the gold(II) state appears to be stabilized by delocalization of

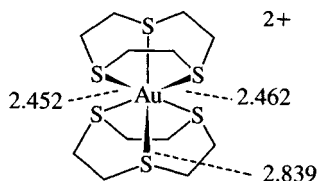
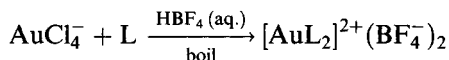


Figure 4.18 The structure of  $[(1,4,7\text{-trithiacyclononane})_2\text{Au}]^{2+}$ .

the unpaired electron as is likely in gold(II) phthalocyanine and in the green carbollide  $(\text{Et}_4\text{N})_2\text{Au}(\text{C}_2\text{B}_9\text{H}_{11})_2$  ( $\mu = 1.79 \mu_{\text{B}}$ ) [102]. A gold(II) complex of the macrocycle 1,4,7-trithiacyclononane (L) has octahedrally coordinated gold(II) (Figure 4.18); the gold(III) to gold(II) reduction in the course of the reaction should be noted.



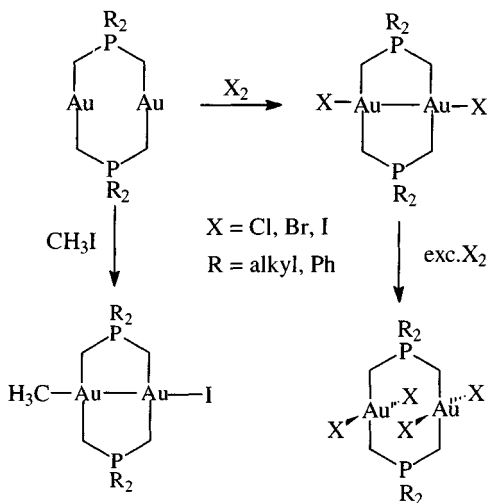
The gold(II) complex readily undergoes one electron reduction and oxidation to the corresponding gold(I) and gold(III) complexes; the tetragonally distorted geometries for the  $d^8$  and  $d^9$  systems are expected, but the tetrahedral coordination in the gold(I) complex, with one monodentate and one terdentate ligand seems to be a compromise between the tendency of the ligand to utilize all its donor atoms and the usual preference of gold(I) for digonal coordination (Table 4.11) [103].

Many gold(II) complexes are diamagnetic ylids that have square planar coordination including a gold-gold bond (Figure 4.19) synthesized by oxidative addition reactions of gold(I) compounds (use of excess halogen yields a gold(III) compound, the use of a binuclear complex in this synthesis allows oxidative addition to occur in one electron steps at each gold, whereas in a mononuclear complex a two electron gold(I) to gold(III) conversion occurs) [104].

Solvated  $\text{Au}^{2+}$ , detectable by ESR, has been generated by gold reduction of  $\text{Au}(\text{SO}_3\text{F})_3$  in  $\text{HSO}_3\text{F}$  at  $65^\circ\text{C}$ , as well as by partial pyrolysis of  $\text{Au}(\text{SO}_3\text{F})_3$  below  $140^\circ\text{C}$  [105].

Table 4.11 Characteristics of  $[\text{Au}(\{9\}\text{aneS}_3)_2]^{n+}$

	<i>n</i>		
	1	2	3
Environment	Distorted tetrahedral	Tetragonally distorted octahedron	Strongly tetragonally distorted octahedron
Au-S (Å)	2.302, 2.345, 2.767, 2.816 (average lengths)	2.452 (×2), 2.462 (×2), 2.839 (×2)	2.348 (×2), 2.354 (×2), 2.926 (×2)

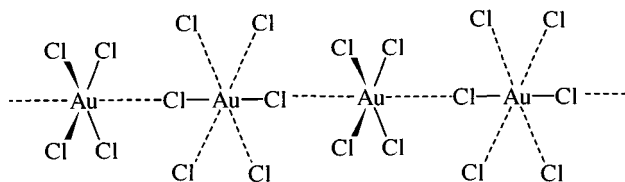


**Figure 4.19** Synthesis of gold ylid complexes, including gold(II) compounds with metal-metal bonds.

### Mixed-valence systems

A number of apparent gold(II) complexes are in fact mixed gold(I)–gold(III) compounds;  $\text{AuCl}_2$  is  $\text{Au}_2^{\text{I}}\text{Au}_2^{\text{III}}\text{Cl}_8$ ,  $\text{AuQ}$  ( $\text{Q} = \text{S, Se, Te}$ ) is  $\text{Au}^{\text{I}}\text{Au}^{\text{III}}\text{Q}_2$ ,  $\text{MAuX}_3$  ( $\text{M} = \text{alkali metal, X} = \text{halogen}$ ) is  $\text{M}_2(\text{Au}^{\text{I}}\text{X}_2\text{Au}^{\text{III}}\text{X}_4)$  and  $\text{AuX}_2(\text{Sbz}_2)$  is  $\text{Au}(\text{Sbz}_2)\cdot\text{AuX}_3(\text{Sbz}_2)$  [106]. Study of  $\text{Cs}_2\text{Au}^{\text{I}}\text{Au}^{\text{III}}\text{Cl}_6$  (Figure 4.20) in a high pressure cell mounted on a diffractometer shows that as the pressure increases, the chlorine atoms move between the gold atoms until at 5200 MPa, the gold environments are indistinguishable, formally gold(II). This is accompanied by an increase in conductivity [107].

Obviously analytical data do not distinguish between a true gold(II) complex and a mixed valence gold(I)–gold(III) species. Apart from X-ray structural determinations, techniques applicable include ESCA and  $^{197}\text{Au}$  Mössbauer spectra [108] (which will give two sets of peaks for a mixed valence compound against one for a true gold(II) compound), magnetic susceptibility and ESR (for paramagnetic compounds) [109].



**Figure 4.20** The environment of the gold atoms in  $\text{Cs}_2\text{Au}^{\text{I}}\text{Au}^{\text{III}}\text{Cl}_6$ . Weak Au–Cl interactions are shown as dotted lines.

## 4.12 Gold(III) complexes

### 4.12.1 Complexes of halogens

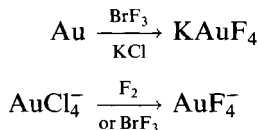
Like palladium(II) and platinum(II), gold(III) has the  $d^8$  electronic configuration and is, therefore, expected to form square planar complexes. The d-orbital sequence for complexes like  $\text{AuCl}_4^-$  is  $d_{x^2-y^2} \gg d_{xy} > d_{yz}$ ,  $d_{xz} > d_{z^2}$ ; in practice in a complex, most of these will have some ligand character.

The stability of gold(III) compared with silver(III) has been ascribed to relativistic effects causing destabilization of the 5d shell, where the electrons are less tightly held. Hartree–Fock calculations on  $\text{AuX}_4^-$  ( $X = \text{F}, \text{Cl}, \text{Br}$ ) indicate that relativistic effects make a difference of 100–200  $\text{kJ mol}^{-1}$  in favour of the stability of  $\text{AuX}_4^-$  (Table 4.12) [110].

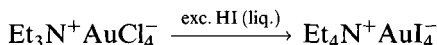
The tetrahalometallates are useful starting materials.



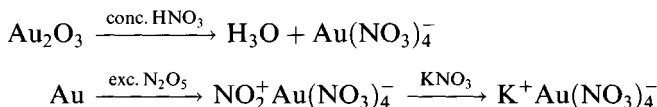
The oxidizing agent is usually concentrated  $\text{HNO}_3$  but can be the halogen itself; yellow fluoroaurates can be made directly or by substitution



The black iodide is unstable [3(d),112], tending to reduce to  $\text{AuI}_2^-$  in aqueous solution, but has been made *in situ*

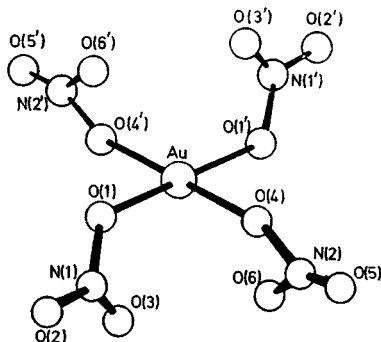


Typical bond lengths are 1.915 Å ( $X = \text{F}$ ) [113], 2.27–2.29 Å ( $\text{Cl}$ ) [114], 2.404 Å ( $\text{Br}$ ) and 2.633–2.648 Å ( $\text{I}$ ) [3(d), 115]. Other groups ( $\text{CN}$ ,  $\text{SCN}$ ) can also be introduced by substitution, while  $\text{Au}(\text{NO}_3)_4^-$  is a classic example of monodentate nitrate (Figure 4.21) ( $\text{Au}-\text{O}$  1.99–2.02 Å) and is prepared [116]:



**Table 4.12** Fundamentals from Au–X stretching in  $\text{AuX}_4^-$  ( $\text{cm}^{-1}$ ) [111]

X	$\nu_1(\text{A}_{1g})$	$\nu_5(\text{b}_{1g})$	$\nu_6(\text{E}_u)$
Cl	349	324	365
Br	213	196	252
I	148	110	186

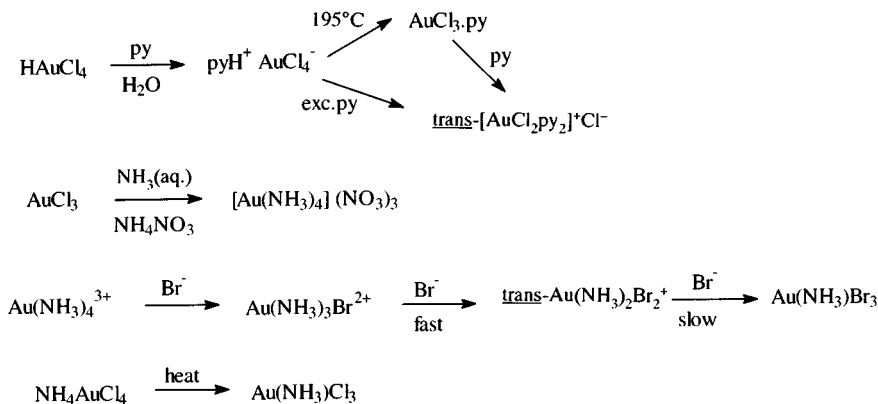


**Figure 4.21** The structure of  $\text{Au}(\text{NO}_3)_4^-$ . (Reproduced with permission from *J. Chem. Soc. (A)*, 1970, 3093.)

Apart from  $\text{Au}(\text{NO}_3)_4^-$ , relatively few complexes of gold(III), and only those with O-donors, have been examined. Two that demonstrate the preference of gold(III) for square planar coordination are  $\text{SrAu}_2(\text{MeCOO})_8$  and  $\text{SrAu}_2(\text{OH})_8$ ; in the latter  $\text{Au}(\text{OH})_4^-$  has  $\text{Au}-\text{O}$  1.98 Å [117].

#### 4.12.2 Complexes of N-donors

A variety of N-donors have been used to form complexes with gold(III). Some preparations of complexes with N-donors are shown in Figure 4.22; both  $\text{AuCl}_3\text{py}$  and  $\text{AuPy}_2\text{Cl}_2^+\text{Cl}^-$  contain square planar gold [118], as does  $\text{Au}(\text{NH}_3)_4^{3+}$  ( $\text{Au}-\text{N}$  2.02 Å), while similar bond lengths are found in  $\text{Au}(\text{NH}_3)\text{Cl}_3$  (2.01 Å) and  $\text{Au}(\text{NH}_3)_2\text{Br}_2^+\text{Br}^-$  ( $\text{Au}-\text{N}$  2.04 Å,  $\text{Au}-\text{Br}$  2.428 Å) [119]. The last can be isolated by making use of the *trans*-effect (section 4.12.6). Azide forms the square planar complex  $\text{Ph}_4\text{As}^+[\text{Au}(\text{N}_3)_4]^-$



**Figure 4.22** Syntheses of gold ammine complexes.

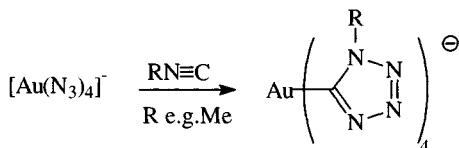


Figure 4.23 A cyclization reaction of  $\text{Au}(\text{N}_3)_4$  in which 4-coordination is retained.

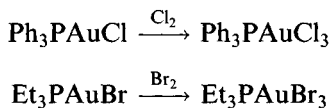
( $\text{Au}-\text{N}$  2.028 Å), which is reduced to  $\text{Au}(\text{NCO})_2^-$  by CO but in reaction with RNC undergoing an unusual cyclization (Figure 4.23) [120].

Rather less is known about complexes with bi- and tridentate ligands such as  $\text{AuCl}_3(\text{bipy})$  and  $\text{AuBr}_3(\text{phen})$ , which are probably ionic  $\text{AuX}_2\text{L}^+\text{X}^-$ ; with bulky ligands like 2,2-biquinoly, 5-coordinate complexes are obtained (section 4.12.5). Ethylene-1,2-diamine affords  $\text{Au}(\text{en})_2\text{Cl}_3$ , which in the solid state contains distorted  $\text{Au}(\text{en})_2\text{Cl}_2^+$  [121a]. In  $\text{Au}(\text{phen})(\text{CN})_2\text{Br}$ , the phenanthroline is monodentate [121b].  $[\text{Au}(\text{bipy})\text{Cl}_2]^+\text{BF}_4^-$  also has square planar coordination of gold with  $\text{Au}-\text{N}$  2.037 Å and  $\text{Au}-\text{Cl}$  2.252 Å [122].  $\text{Au}(\text{en})_3^{3+}$  reacts with  $\beta$ -diketones in template reactions [123] to afford complexes of tetradentate macrocycles (Figure 4.24).

With a tridentate ligand  $\text{Au}(\text{terpy})\text{Cl}_3 \cdot \text{H}_2\text{O}$  has, in fact,  $\text{AuCl}(\text{terpy})^{2+}$  with weakly coordinated chloride and water while  $\text{Au}(\text{terpy})\text{Br}(\text{CN})_2$  has square pyramidal gold(III): the terpyridyl ligand is bidentate, occupying the axial and one basal position [124]. Macrocyclic complexes include the porphyrin complex  $\text{Au}(\text{TPP})\text{Cl}$  (section 4.12.5); cyclam-type macrocyclic ligands have a very high affinity for gold(III) [125].

#### 4.12.3 Tertiary phosphine and arsine complexes

While tertiary phosphines and arsines tend to reduce gold(III) to gold(I), the reverse reactions can be used synthetically [126]:



The structures of both these complexes demonstrate the *trans*-influence of phosphines in lengthening the bond to the *trans*-halogen (Table 4.13).

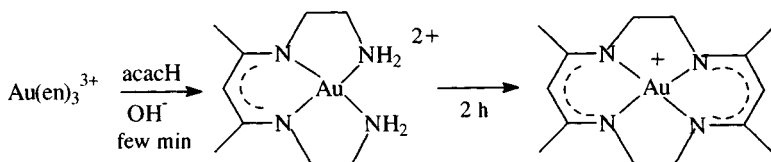


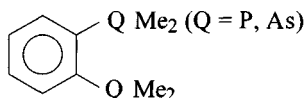
Figure 4.24 Template synthesis of a gold(III) macrocycle complex.

**Table 4.13** The *trans*-influence in complexes  $\text{AuX}_3\text{L}$ 

X	L	Au-X (Å)	
		X <i>trans</i> to L	X <i>cis</i> to L
Cl	$\text{PPh}_3$	2.347	2.273, 2.282
Cl	$\text{NH}_3$	2.277	2.282, 2.287
Cl	PhN	2.260	2.284, 2.289
Cl	Thianthrene	2.305	2.274
Me	$\text{PPh}_3$	1.923	2.100, 2.168
Ph	Cl	2.028	2.071, 2.064
Br	$\text{PEt}_3$	2.468	2.407, 2.416
Br	$\text{PPh}_3$	2.461	2.405, 2.424
Cl	$\text{Bz}_2\text{S}$	2.287	2.272
Br	$\text{Bz}_2\text{S}$	2.419	2.418, 2.425

In some cases, oxidation gives unexpected results (Figure 4.25) with concomitant formation of an Au–C bond.

Gold (I) complexes of bidentate phosphines and arsines like



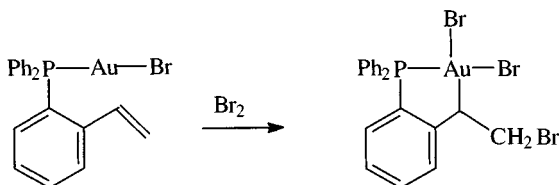
$\text{Au}(\text{diphos})_2^+$  and  $\text{Au}(\text{diars})_2^+$  can be oxidized to gold(III) species [127]. These tend to add halide ions so that  $\text{Au}(\text{diars})_2\text{I}_2^+$  has a distorted octahedral structure with very weakly bound iodides (section 4.12.5).

#### 4.12.4 Other complexes

Thiols and other sulphur ligands can be used to reduce  $\text{Au}^{3+}$  to  $\text{Au}^+$  but gold(III) complexes can be made, for example, with tetramethylthiourea (tmu),



but on recrystallization, complete reduction to  $\text{Au}(\text{tmu})\text{Br}$  occurs. Other square planar complexes characterized include  $\text{AuCl}_3(\text{SPh}_2)$  [128],



**Figure 4.25** Synthesis of an organogold(III) compound by an unusual oxidative addition reaction.

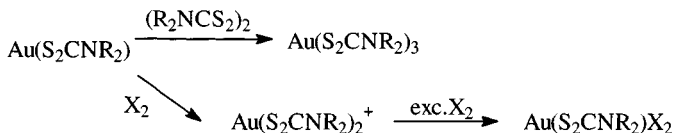


Figure 4.26 Synthesis of gold dithiocarbamate complexes.

$\text{AuCl}_3(\text{tht})$  [129],  $\text{AuX}_3[\text{S}(\text{benzyl})_2]_2$  ( $\text{X} = \text{Cl}, \text{Br}$ ) [130] and  $\text{AuCl}_3$  (thianthrene). Various dithiocarbamates and dithiolene complexes have been made, some by oxidation of gold(I) complexes (Figure 4.26).

Square planar coordination is general in these; in the tris-complexes  $\text{Au}(\text{S}_2\text{CNR}_2)_3$ , it is obtained by two dithiocarbamates being monodentate (the third is, of course, bidentate) [131]. Such planar coordination in  $[\text{Au}(\text{S}_2\text{CNEt}_2)_2]^+\text{SbF}_6^-$  involves Au–S distances of 2.316–2.330 Å [132].

An unusual example involves two complexes of formula  $\text{Au}(\text{S}_2\text{CNBu}_2)(\text{S}_2\text{C}_2(\text{CN})_2)$ ; one has a molecular structure, the other is ‘ionic’  $[\text{Au}(\text{S}_2\text{CNBu}_2)_2]^+[\text{Au}[\text{S}_2\text{C}_2(\text{CN})_2]_2]^-$  [133].

The most important complex with an ‘inorganic’ C-donor is  $\text{Au}(\text{CN})_4^-$ , with Au–C 1.98 Å in the potassium salt [134].



Additionally, *trans*- $\text{Au}(\text{CN})_2\text{X}_2^-$  can be made by oxidative addition of  $\text{X}_2$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) to  $\text{Au}(\text{CN})_2^-$ .

#### 4.12.5 Coordination numbers and gold(III)

The preference of gold(III) for planar 4-coordination is such that ligands sometimes adopt unusual denticities. Therefore,  $\text{Au}(\text{NO}_3)_4^-$  has four monodentate nitrates;  $\text{Au}(\text{terpy})\text{Cl}_3 \cdot \text{H}_2\text{O}$  contains  $\text{Au}(\text{terpy})\text{Cl}^{2+}$ ;  $\text{Aupy}_2\text{Cl}_3$  is  $\text{Aupy}_2\text{Cl}_2^+\text{Cl}^-$ ;  $\text{Au}(\text{S}_2\text{CNBu}_2)_2\text{Br}$  is  $\text{Au}(\text{S}_2\text{CNBu}_2)_2^+\text{Br}^-$ ;  $\text{Au}(\text{S}_2\text{CNBu}_2)_3$  has one bidentate and two monodentate dithiocarbamates and  $\text{Au}(\text{NH}_3)_4(\text{NO}_3)_3$  has only ionic nitrates, to quote compounds already mentioned.

The tetraphenylporphyrin complex  $\text{AuCl}(\text{TPP})$  has been claimed [135] as square pyramidal; since the gold atom lies in the plane of the porphyrin ring, and the Au–Cl distance is 3.01 Å, it should be regarded as  $\text{Au}(\text{TPP})^+\text{Cl}^-$ .  $\text{Au}(\text{dien})\text{Cl}_3$  [136] has a pseudo-octahedral structure but with long Au–Cl bonds (3.12–3.18 Å) again. Five-coordination is attained in the square pyramidal 2,9-dimethylphenanthroline complexes [137]  $\text{Au}(\text{dimphen})\text{X}_3$  ( $\text{X} = \text{Cl}, \text{Br}$ ) with the gold atoms some 0.1 Å above the basal plane (Figure 4.27); in contrast  $\text{Au}(2,2'\text{-biquinoly})\text{Cl}_3$  is trigonal bipyramidal [138a].

Molecules of the deep blue–black compound  $\text{AuI}_3(\text{PMe}_3)_2$  have a trigonal bipyramidal structure in which Au–P is 2.333–2.347 Å and Au–I is 2.709–2.761 Å. It is prepared by the reaction of gold metal with  $\text{Me}_3\text{PI}_2$  [138b]





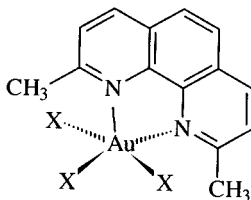
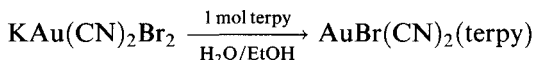


Figure 4.27 Five-coordination in the square pyramidal  $\text{Au}(\text{dimphen})\text{X}_3$  ( $\text{X} = \text{Cl}, \text{Br}$ ).

$\text{Au}(\text{diars})_2\text{I}_2^+\text{I}^-$  has 6-coordinate gold with rather long Au–I distances (3.35 Å) [139].  $\text{AuBr}(\text{CN})_2(\text{terpy})$  (Figure 4.28), made as follows,



has square pyramidal coordination, with a bidentate terpyridyl occupying the apical portion and an equatorial position *trans* to bromide [140].

#### 4.12.6 The *trans*-effect and *trans*-influence

Like the isoelectronic  $\text{Pd}^{2+}$  and  $\text{Pt}^{2+}$ ,  $\text{Au}^{3+}$  exhibits both *trans*-effects and *trans*-influence. Table 4.13 (above) lists structural data for a number of complexes  $\text{AuL}_3\text{L}$ , showing how the disparity in Au–X distances between *cis*- and *trans*-X depends on the position of L in the *trans*-effect series; for the compounds listed, the effect is least noticeable in  $\text{AuCl}_3\text{NH}_3$  as these two ligands are proximate in the series.

The *trans*-effect can be used synthetically. In the reaction of  $\text{Br}^-$  with  $\text{Au}(\text{NH}_3)_4^{3+}$ , the introduction of the first bromine weakens the Au–N bond *trans* to it so that the introduction of a second bromine is both stereospecifically *trans* and rapid. (A similar effect occurs in the corresponding chloride.) The third and fourth ammonia molecules are replaced with difficulty, permitting the isolation of  $\text{AuBr}_2(\text{NH}_3)_2^+$  (second-order rate constants at 25°C are  $k_1 = 3.40$ ,  $k_2 = 6.5$ ,  $k_3 = 9.3 \times 10^{-5}$  and  $k_4 = 2.68 \times 10^{-2} \text{ mol}^{-1} \text{ s}^{-1}$  at 25°C) [141].

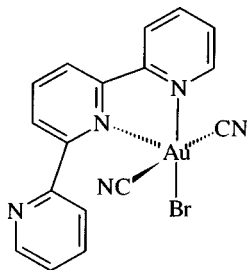


Figure 4.28 Square pyramidal 5-coordination in  $\text{AuBr}(\text{CN})_2(\text{terpy})$  made possible by terpyridyl acting as a bidentate ligand.

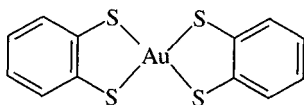


Figure 4.29 A formally gold(IV) dithiolene complex.

Factors responsible for this order include the *trans*-effect, charge neutralization, and statistical effects.

#### 4.13 Gold(IV) complexes

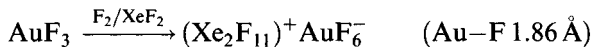
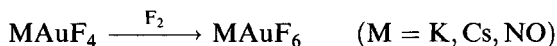
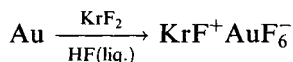
A mononuclear compound containing gold in a formal oxidation state of +4 is shown in Figure 4.29; it was produced by electrochemical oxidation of the related gold(III) species [142].

The Au–S bond length at 2.30 Å is very similar to that in the gold(III) analogue (2.299–2.312 Å) and other gold(III) complexes like Au(toluene-3,4-dithiolate)<sup>−</sup> (2.31 Å) suggesting substantial covalent character in the bond.

#### 4.14 Gold(V) complexes

A number of complexes containing the low spin d<sup>6</sup> ion, AuF<sub>6</sub><sup>−</sup> (Au–F ~ 1.86 Å) have been made [143].

Syntheses include:



AuF<sub>5</sub> is formed on heating M<sup>+</sup>AuF<sub>6</sub><sup>−</sup> (M = NO, O<sub>2</sub>); there has been interest in synthesizing AuF<sub>6</sub> by oxidation of AuF<sub>6</sub><sup>−</sup> but it is likely that the t<sub>2g</sub><sup>6</sup> configuration is too stable to be oxidized.

#### 4.15 Organometallic compounds of silver

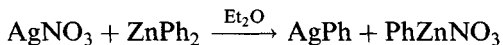
Organometallic compounds of silver [2(f), 6] are restricted to the silver(I) state and are usually light, air and moisture sensitive. Simple alkyls are unstable at room temperature though some fluoroalkyls are isolable. Therefore, perfluoroisopropylsilver is stable to 60°C as a MeCN adduct. Alkenyls

are more stable: styrenylsilver, prepared as follows, is stable for some days at room temperature.



Perfluoroisopropanylsilver sublimes *in vacuo* at 160°C.

Silver aryls are also stable, prepared using either diarylzinc or trialkylaryl-lead (or tin) compounds



AgPh is a colourless solid [144] that is rather insoluble in non-donor solvents and appears to be polymeric (AgPh)<sub>n</sub> (n > 10); in addition mixed compounds (AgPh)<sub>n</sub>.AgNO<sub>3</sub> (n = 2, 5) can also be obtained that involve silver clusters. Mesitylsilver is a thermally stable (but light-sensitive) white crystalline solid; in the solid state it is tetrameric (in contrast to the pentameric copper and gold analogues);



it tends to dissociate to a dimer in solution [145] (Figure 4.30).

With the even more sterically hindered 2,4,6-Ph<sub>3</sub>C<sub>6</sub>H<sub>2</sub> ligand, 1-coordinate (2,4,6-Ph<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)Ag has been claimed, though this is controversial [146].

Aryl compounds containing another donor atom in the *ortho*-position like Ag(C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NMe<sub>2</sub>) have also been isolated (they are probably clusters).

The acidic hydrogen in terminal alkynes can readily be replaced by silver, in a diagnostic test. [(Me<sub>3</sub>P)Ag(C≡CPh)] has a polymeric structure while [(Ph<sub>3</sub>P)Ag(C≡CPh)]<sub>4</sub> is made of [Ag(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> and [Ag(C≡CPh)<sub>2</sub>]<sup>-</sup> fragments linked so that the silver atoms form a square [147].

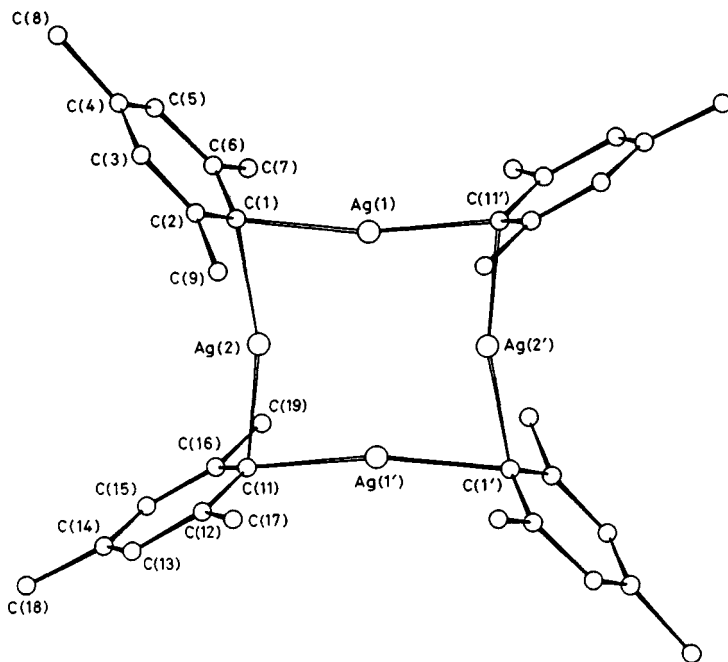
Apart from matrix-isolated binary carbonyls stable only at low temperatures, Ag(CO)B(OTeF<sub>5</sub>)<sub>4</sub> (ν(C–O) 2204 cm<sup>-1</sup>) has been isolated as a crystalline solid, as has [Ag(CO)<sub>2</sub>]<sup>+</sup>[B(OTeF<sub>5</sub>)<sub>4</sub>]<sup>-</sup> (linear C–Ag–C, Ag–C 2.14 Å).

The IR C–O stretching vibration in the latter occurs between 2198 and 2207 cm<sup>-1</sup> (depending on the counter-ion) [148a]. Under high CO pressure there is evidence for [Ag(CO)<sub>3</sub>]<sup>+</sup> (ν(C–O) 2192 cm<sup>-1</sup>) [148b]. (The area has been reviewed [149].)

A pyrazolylborate Ag(CO)[HB(3,5(CF<sub>3</sub>)<sub>2</sub>pz)<sub>3</sub>] loses CO under reduced pressure: it has a linear Ag–CO grouping (Ag–C–O 175.6°, Ag–C 2.037 Å; ν(C–O) 2178 cm<sup>-1</sup>) [150].

#### 4.15.1 Complexes of unsaturated hydrocarbons

Many alkenes and arenes react directly with dissolved silver salts to afford crystals of the silver complex. Examples studied by X-ray diffraction [151] include (C<sub>6</sub>H<sub>6</sub>)AgX (X = ClO<sub>4</sub>, AlCl<sub>4</sub>) and (C<sub>8</sub>H<sub>8</sub>)AgNO<sub>3</sub>.

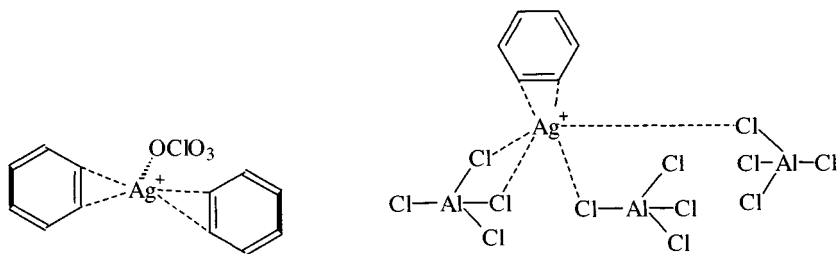


**Figure 4.30** The structure of silver mesityl. (Reproduced with permission from *J. Chem. Soc., Chem. Commun.*, 1983, 1087.)

The benzene complexes have silver bound  $\eta^2$  to two benzene rings in the perchlorate but only to one in the tetrachloro aluminate (Figure 4.31), while in the COT complex, each silver is bound to two double bonds in one molecule.

The Ag–C bonds tend to be asymmetric; study of silver cycloalkene complexes shows their stability to decrease in the order  $C_5 > C_6 > C_7 > C_8$ , corresponding to relief of strain in the cyclic molecules consequent upon the lengthening of the double bond on coordination.

Silver(I)–alkene complexation is implicated in the silver-catalysed isomerization of alkenes [152]; an example is shown in Figure 4.32.



**Figure 4.31** Silver(I) benzene complexes.

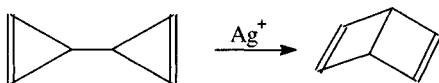


Figure 4.32 Silver-catalysed isomerization of an alkene.

Besides using chemical separations relying on different solubilities of silver–alkene complexes, mixtures of different hydrocarbons (e.g. isomeric xylenes and other polymethylated benzenes (terpenes)) can be analysed using binuclear shift reagents like  $\text{Ag}^+\text{Pr}(\text{fod})_4^-$  ( $\text{fod} = \text{Me}_3\text{CCOCHCOF}_2\text{CF}_2\text{CF}_3$ ). The ‘soft’ Lewis base (alkene or arene) binds to the silver, which in turn is bound to the paramagnetic lanthanide complex and causes shifts in the NMR spectrum of the substrate. Different xylenes, for example, afford different shifts owing to varying steric effects of the methyl groups. Using chiral shift reagents permits the observation of separate NMR signals from optically isomeric alkenes [153] (e.g.  $\alpha,\beta$ -pinene).

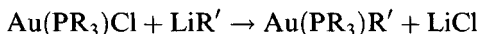
#### 4.16 Organometallic compounds of gold

There are considerable numbers of the organogold compounds [3(b), 9, 154], principally in the +1 and +3 oxidation states. Gold is unusual in transition metals in that, even in the +1 state, it has a marked preference for forming  $\sigma$ - rather than  $\pi$ -bonds, presumably related to the tendency of gold(I) to linear 2-coordination.

Current study in this area is prompted by laser-induced CVD of such volatile gold compounds, permitting direct laser writing in gold [155].

##### 4.16.1 Gold(I) complexes

Simple alkyls and aryls  $\text{AuR}$  are generally unstable but coordinative saturation ensures the stability of adducts  $\text{Au}(\text{PR}_3)\text{R}'$



(R, e.g. Me, Et, Ph; R', e.g. Me, Ph).

These are typically colourless crystalline solids, often air and moisture stable, thermally stable to over  $100^\circ\text{C}$  and soluble in covalent solvents. Therefore,  $\text{Au}(\text{PMe}_3)\text{Me}$  sublimates at  $53^\circ\text{C}$  (0.1 torr) and melts at  $70\text{--}71^\circ\text{C}$ ; gas electron diffraction on this compound [156] confirms its linear geometry ( $\text{Au}\text{--}\text{C}$  2.034 Å;  $\text{Au}\text{--}\text{P}$  2.28 Å). It is a potential CVD precursor [155a]. X-ray diffraction shows  $\text{Au}(\text{PPh}_3)\text{R}$  (R = Me,  $\text{C}_6\text{F}_5$ , Ph, 2,6-(MeO) $_2$ C $_6$ H $_3$ ) also to have digonal coordination. In  $\text{Au}(\text{PBu}_3^t)\text{Ph}$ ,  $\text{Au}\text{--}\text{C}$  is 2.055 Å and  $\text{Au}\text{--}\text{P}$  is 2.305 Å; these slightly longer bond lengths reflecting the bulk of the *t*-butyl groups [157].

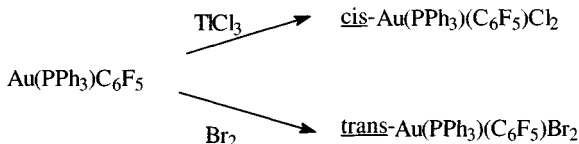


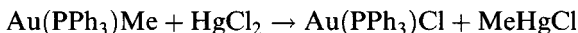
Figure 4.33 Syntheses of organogold compounds by oxidative addition to a gold(I) compound.

Another route to coordinative saturation is [158]



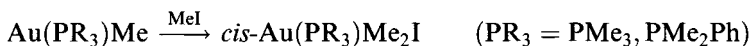
(m.p. 120–123°C) (PMPT = Me<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>N(Me)(CH<sub>2</sub>)<sub>2</sub>NMe<sub>2</sub>).

The Au–C bonds in these compounds undergo cleavage with various reactants.

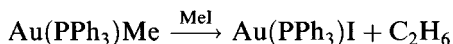


though sometimes if the Au–C bond is strong, oxidative addition to an organogold(III) compound occurs (Figure 4.33).

Addition with iodomethane can occur



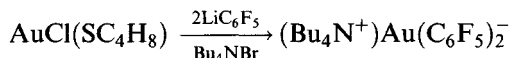
as can elimination



Fluorinated alkyls and aryls, generally more stable than the unsubstituted compounds, have been widely studied.

Several synthetic routes often exist (Figure 4.34).

Au(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub><sup>−</sup>, also with linear coordination of gold (Au–C 2.043–2.044 Å) [159], can be made:



One exceptional compound is the mesityl: photosensitive but thermally stable (Figure 4.35).

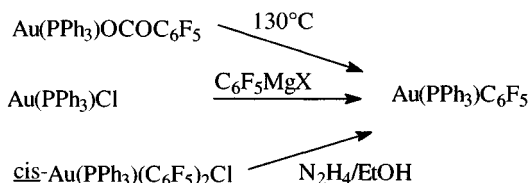
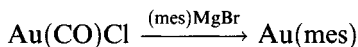
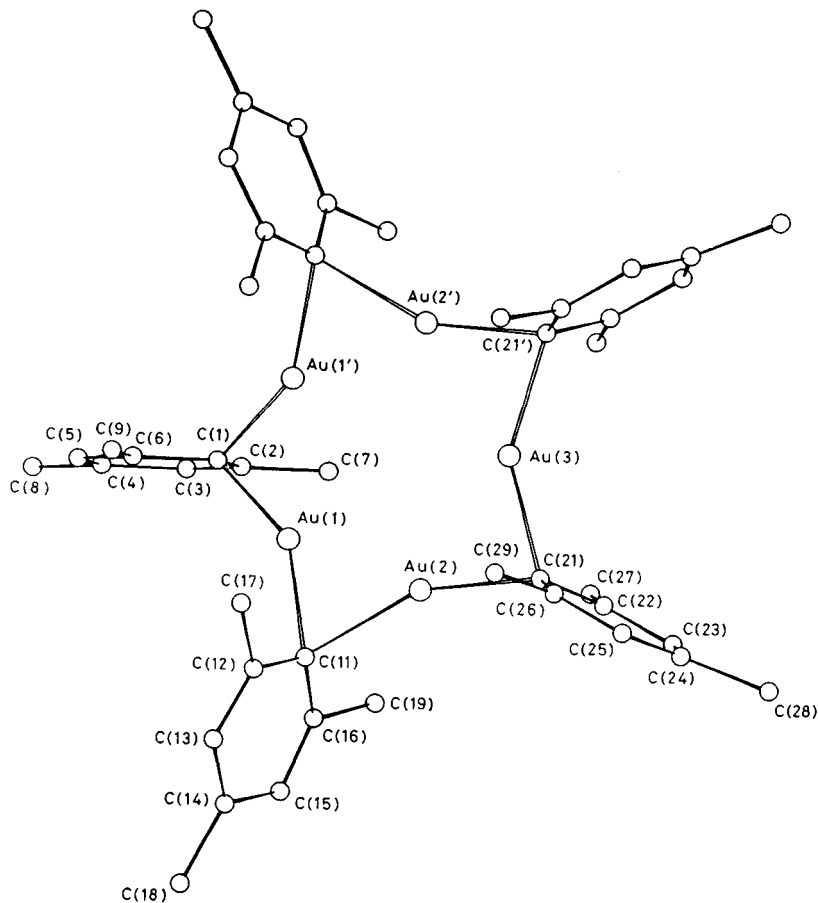


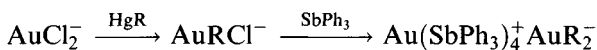
Figure 4.34 Some syntheses of a pentafluorophenylgold complex.



**Figure 4.35** The structure of gold mesityl. (Reproduced with permission from *J. Chem. Soc., Chem. Commun.*, 1983, 1305.)

It is a pentamer with bent digonal coordination of gold ( $148\text{--}154^\circ$ ) and short Au–Au distances (2.70 Å); in solution it is a dimer. It reacts with  $\text{PPh}_3$  to form  $\text{Au}(\text{PPh}_3)(\text{mes})$ , with bidentate phosphines to afford  $(\text{mes})\text{AuPR}_2(\text{CH}_2)_n\text{PR}_2\text{Au}(\text{mes})$  ( $n = 1, 2$ ); and with  $\text{Et}_4\text{NCl}$  forming  $\text{Et}_4\text{N}^+\text{Au}(\text{mes})\text{Cl}^-$ , all with essentially linear coordination of gold [160].

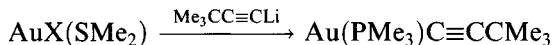
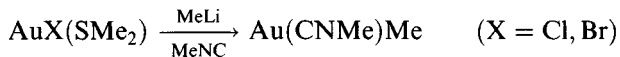
Some 2,4,6-trinitrophenyls have been made [161]



( $\text{R} = 2,4,6\text{-(NO}_2)_3\text{C}_6\text{H}_2$ ).

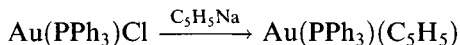
*o*-Nitrophenyls like  $\text{Au}(\textit{o}\text{-C}_6\text{H}_4\text{NO}_2)(\text{AsPh}_3)$ , also 2-coordinate, have likewise been made.

A range of alkynyls exist, for example:



X-ray diffraction confirms linear coordination in  $\text{Au}(\text{PPh}_3)(\text{C}\equiv\text{CC}_6\text{F}_5)$  and  $\text{Au}(\text{H}_2\text{NCHMe}_2)(\text{C}\equiv\text{CPh})$  with the short Au–C bonds (1.935–1.99 Å) expected for bonds to sp hybridized carbon. Decomposition of these compounds in the vapour above 150°C is a potential route to very pure gold films [162].

(Cyclopentadienyl)gold is a very unstable, even explosive, yellow solid stabilized by adduct formation with tertiary phosphines.



IR and NMR evidence indicates it to be  $\sigma$ -bonded, like  $\text{Au}(\text{PPR}_3)(\text{C}_5\text{H}_5)$  (X-ray) [163], but at room temperature the C<sub>5</sub> ring hydrogens are equivalent owing to rapid site exchange ('ring whizzing').

Though matrix-isolated gold(0) species  $\text{Au}(\text{CO})$  and  $\text{Au}(\text{CO})_2$  are very unstable, the gold(I) compound  $\text{Au}(\text{CO})\text{Cl}$  has long been known (section 4.10.5).  $\text{Au}(\text{CO})\text{Br}$  is unstable but salts of  $[\text{Au}(\text{CO})_2]^+$  of varying stability have been made;  $[\text{Au}(\text{CO})_2](\text{Sb}_2\text{F}_{11})$  is stable to 130°C [164].

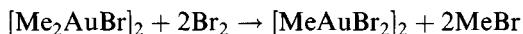
#### 4.16.2 Gold(III) complexes

Species  $\text{AuRX}_2$ ,  $\text{AuR}_2\text{X}$ ,  $\text{AuR}_3$  and  $\text{AuR}_4^-$  have all been made, with gold invariably achieving a square planar geometry, sometimes by adduct formation, dimerization or other polymerization. The first gold(III) alkyls were reported in 1907 and are, therefore, among the earliest known organo-metallics.

##### Alkyls

The alkyls have been studied in detail, particularly the methyls. Figure 4.36 depicts some of the interrelationships in them.

The monoalkyls are relatively unstable. Red crystals of  $[\text{MeAuBr}_2]_2$  are obtained by reaction of bromine with the corresponding dialkyl:



An unsymmetrical structure is indicated by reactions like those in Figure 4.37 (as well as X-ray diffraction [165a]).

The dialkyls are the best characterized in this class. All the complexes  $\text{AuR}_2\text{X}$  (X = halogen) are planar halogen-bridged dimers, stable to 70°C or more. They are best prepared from an anhydrous halide  $\text{Au}_2\text{X}_6$  or adduct  $\text{AuX}_3\text{L}$ , though if an alkyl magnesium iodide Grignard is used, the



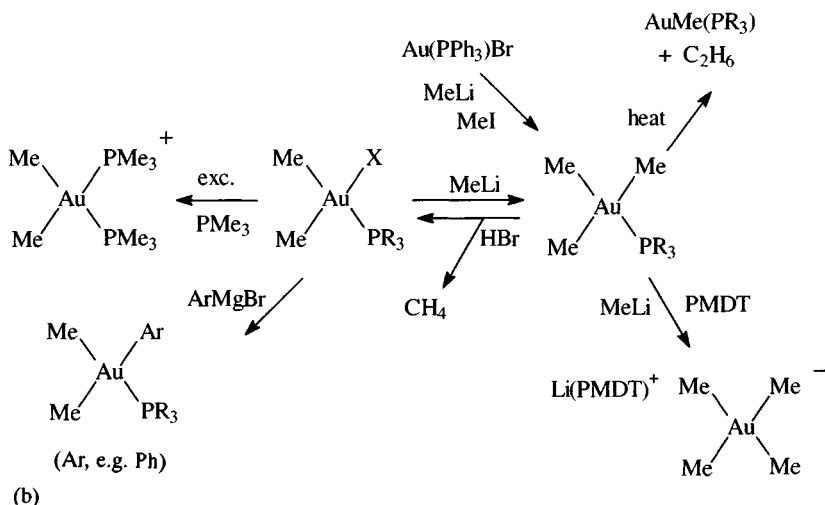
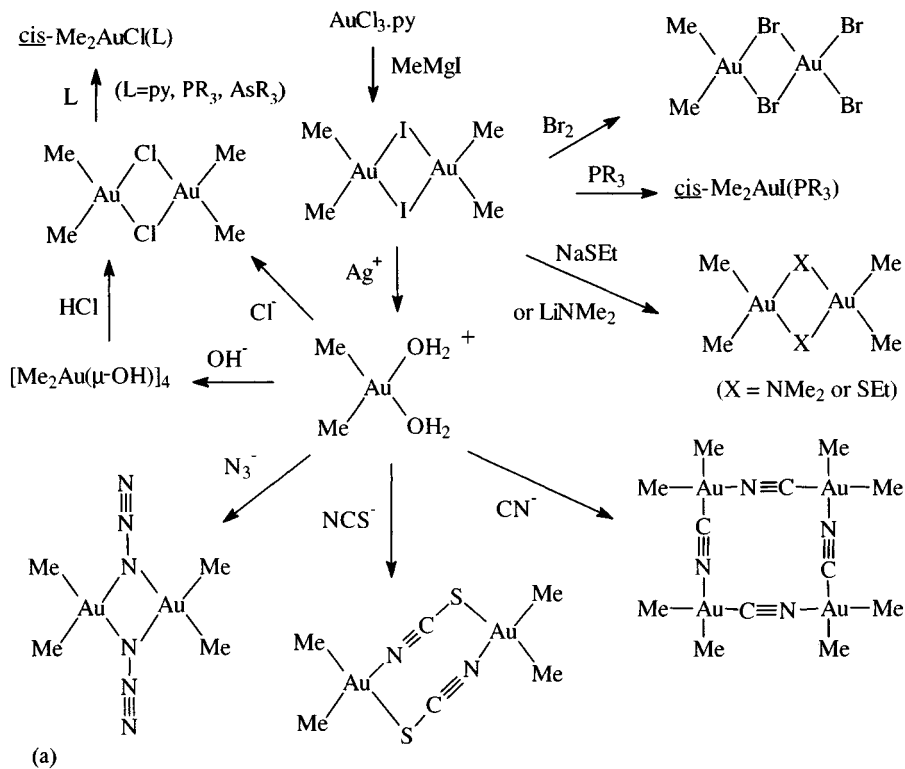


Figure 4.36 Syntheses of gold(III) methyls.

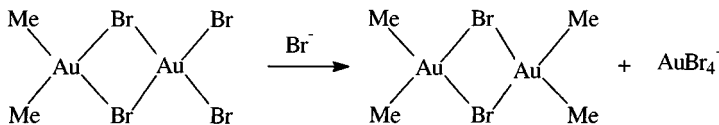
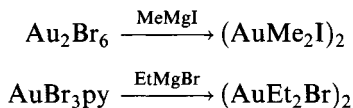


Figure 4.37 Evidence for the asymmetrical dimeric structure of methylgold dibromide.

product is the iodide  $(\text{AuR}_2\text{I})_2$ . Grignards are preferred to organolithium compounds to obviate the possibilities of further substitution.



A recent synthesis of  $(\text{AuMeCl}_2)_2$  uses  $\text{AuCl}_3$  and  $\text{SnMe}_4$  in methanol at  $-50^\circ\text{C}$  [165b].

Treatment of  $(\text{AuMe}_2\text{I})_2$  with silver nitrate gives an interesting alkyl aqua ion [166] *cis*- $\text{AuMe}_2(\text{OH}_2)_2^+$ , stable in aqueous solution, which reacts with pseudohalide ions to form  $[\text{AuMe}_2\text{X}]_2$  ( $\text{X} = \text{N}_3, \text{NCS}$  or  $\text{NCO}$ ); the corresponding cyanide is a tetramer since the cyanide group can only form linear bridges. In solution, the dimethyl gold aqua ion is in equilibrium with the hydroxy complex  $[\text{AuMe}_2(\text{OH})_2]$ , also a tetramer in the solid state (Figure 4.36). Amides and thiolates can also act as bridging ligands in dimers, as shown by X-ray diffraction [167], but the structures shown for some of the diethyl gold complexes (Figure 4.38), notably with chelating ligands, are still tentative.

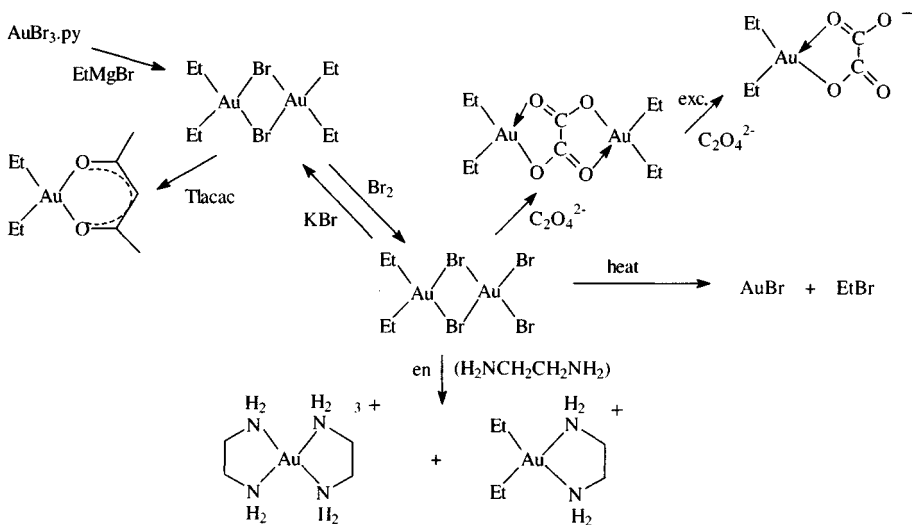
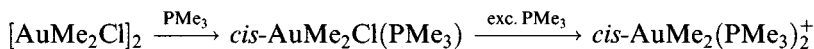


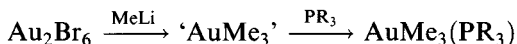
Figure 4.38 Diethyl gold(III) compounds.

Not all the gold dialkyls have dimeric structures; the halogen bridges can be cleaved with excess phosphine:

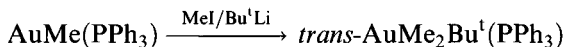


$\text{AuMe}_2(\text{acac})$  is being studied as a vehicle for laser CVD of gold films; it has the expected square planar structure in the gas phase ( $\text{Au}-\text{C}$  2.054 Å;  $\text{Au}-\text{O}$  2.085 Å) [168].

Trialkyls are only known as Lewis base adducts. Reaction of  $\text{Au}_2\text{Br}_6$  with methyl lithium at 70°C affords an unstable 'AuMe<sub>3</sub>' (which is probably  $\text{AuMe}_3\text{Br}^-$ ), but stable phosphine adducts  $\text{AuMe}_3\text{PR}_3$  ( $\text{R}$ , e.g. Me, Ph) can be made [169].

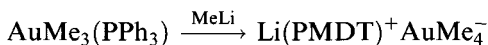


Mixed alkyls can be made



The latter isomerizes to the isobutyl analogue; it is inhibited by added  $\text{PPh}_3$  and it seems likely that the reaction proceeds via a 3-coordinate  $\text{AuR}_3$  species, also likely to be implicated in *cis-trans* isomerization reactions. *cis-AuMeEt*<sub>2</sub>( $\text{PPh}_3$ ) has  $\text{Au}-\text{P}$  2.371 Å,  $\text{Au}-\text{C}$  2.10–2.14 Å; complexes of this type react with  $\text{RLi}$ , displacing  $\text{PPh}_3$  and forming tetraalkylaurates [170].

The tetramethyl species can be isolated as a thermally stable (but air-sensitive) salt (m.p. 86–88°C)

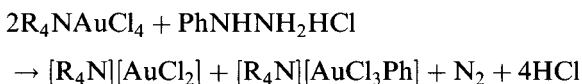


( $\text{PDMT} = \text{Me}_2\text{N}(\text{CH}_2)_2\text{NMe}(\text{CH}_2)_2\text{NMe}_2$ ) while salts with other large cations like  $\text{Bu}_4\text{NAuR}_4$  ( $\text{R} = \text{Me}, \text{Et}$ ) are benzene soluble [171].

### Aryls

Monoaryls of gold(III) are traditionally made by an unusual reaction [172].  $\text{AuCl}_3$  reacts with arenes to afford aryl halides (e.g. with benzene to give 1,2,4,5-tetrachlorobenzene) and  $\text{HCl}$ ; if, however, the reaction is quenched by adding ethanol or ether, a yellow precipitate of  $\text{AuRCl}_2$  ( $\text{R}$ , e.g. Ph) is obtained. These are believed to be dimers in solution. Stable adducts *cis-AuRCl*<sub>2</sub>( $\text{L}$ ) ( $\text{L} = \text{py}, \text{PMe}_2\text{Ph}, \text{PPh}_3, \text{SPR}_2^1$ ) have been obtained; the dipropyl sulphide adduct (Figure 4.39) has the  $\text{Au}-\text{Cl}$  distance *trans* to phenyl 0.11 Å longer than that *trans* to sulphur, showing the considerable *trans*-influence of an aryl group [173].

Another route to aryls, applicable to anionic derivatives [174] is:



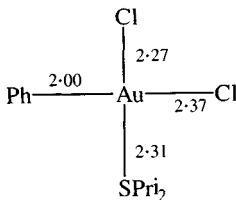
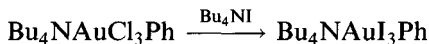


Figure 4.39 Bond lengths in *cis*-AuPhCl<sub>2</sub>(SPr<sub>2</sub>).

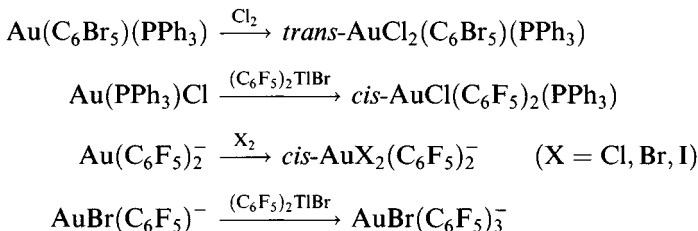
AuCl<sub>3</sub>Ph<sup>-</sup> undergoes reversible solvolysis of the chloride *trans* to phenyl [175].

The relative stability of the gold(III) iodo species should be noted:

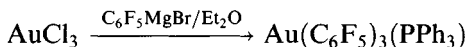


though it cannot be recrystallized [174].

Perhalogenoaryls are more stable than the unsubstituted phenyls [176] and can be synthesized conveniently by oxidation of gold(I) complexes (demonstrating the stability of the Au–C bond). The initial product of oxidation addition seems to be the *trans*-isomer, which generally rearranges to the *cis*-form:



A conventional synthesis may be used for the triaryl obtained as a Lewis base adduct



Structures of AuCl(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(PPh<sub>3</sub>), AuCl(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub><sup>-</sup> [177] and Au(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (diars) all show the preference of gold(III) for 4-coordinate planar geometry (Figure 4.40); in the last, the diarsine is monodentate [178]. (Bu<sub>4</sub>N)[AuCl<sub>2</sub>(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>] is *trans* [179].

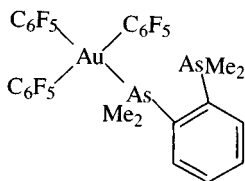


Figure 4.40 4-Coordination in AuMe<sub>3</sub>(diars) made possible by a monodentate diarsine ligand.



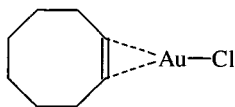


Figure 4.42 The structure of AuCl(cyclooctene).

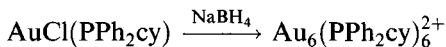
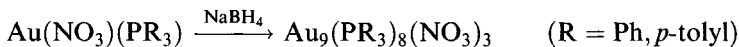
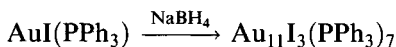
affording gold(II) species (with a metal–metal bond) or gold(III) compounds. A selection of these reactions are shown in Figure 4.41; they also show examples where a methylene group bridges between two gold atoms, the oxidative addition of  $\text{CCl}_4$  and a disproportionation reaction leading to a product with separate gold(I) and gold(III) centres [182].

#### Alkene complexes

A number of complexes  $\text{AuClL}$  have been made; those with cycloalkenes are most stable decomposing at  $50\text{--}100^\circ\text{C}$ . At present, few structural data are available, an exception being for AuCl(cyclooctene) (Figure 4.42) which has a structure with  $\eta^2$  bonding of the alkene (Figure 4.43) [183].

### 4.17 Gold cluster complexes

Gold, unlike silver, forms a wide range of cluster complexes [184] where the average oxidation state of the metal is below +1; they may be synthesized by reduction of gold(I) phosphine complexes:



Other reducing agents like  $\text{Ti}(\eta^6\text{-toluene})_2$  have also been used. Addition or removal of gold atoms from clusters can frequently be accomplished (Figure 4.44).

Crystallographic examination shows the clusters with eight or more gold atoms have structures based on an array of gold atoms surrounding a central gold atom. (Smaller polyhedra cannot accommodate a central gold because

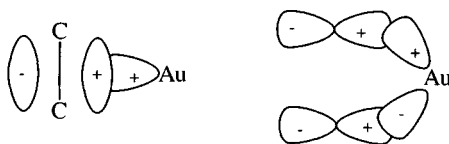


Figure 4.43 Bonding in gold alkene complexes.

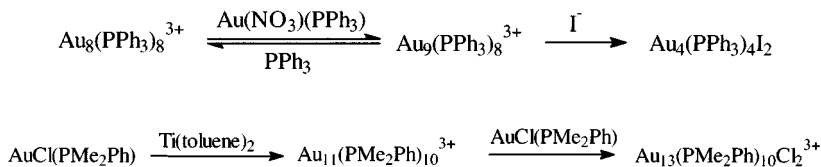


Figure 4.44 Syntheses of gold clusters.

the ‘hole’ is too small, though six golds can surround a carbon atom.) The smallest cluster, of four golds, in  $\text{Au}_4\text{I}_2(\text{PPh}_3)_4$  or  $[\text{Au}_4(\text{PBu}_3)_4]^{2+}$  has a compact tetrahedral structure [185] while  $[\text{Au}_6(\text{PPh}_3)_6]^{2+}$  has an edge-sharing bitetrahedral arrangement (Figure 4.45) and  $[\text{Au}_7(\text{PPh}_3)_7]^+$  is a pentagonal bipyramid.

High nuclearity clusters  $[\text{Au}(\text{AuPR}_3)_n]^{x+}$  with central gold atoms adopt two types of structure; those with  $12n + 18$  electrons have essentially spherical structures, whereas those with  $12n + 16$  electrons have the peripheral atoms on the surface of a toroid.

$\text{Au}_{13}(\text{PMe}_2\text{Ph})_{10}\text{Cl}_2^{3+}(\text{PF}_6)_3$  has an icosahedron of golds surrounding the central gold.

The bonding in the centred clusters is believed to involve principally gold 6s orbitals, the 5d being filled and essentially core-like, and the 6p too high in energy to be utilized. ‘Surface’ gold atoms use  $s/p_z$  hybrid orbitals, the ‘outwardly’ directed part of the hybrid is involved in forming the Au– $\text{PR}_3$  bond and the ‘inwardly’ directed part bonds to the central atom, overlapping with its 6s and 6p orbitals. There is also peripheral metal–metal bonding on the ‘surface’ of the cluster, but this is less important, as the Au–Au distances between surface gold atoms are 0.2–0.3 Å longer than the radial Au–Au distances.

There is evidently a flat potential energy surface for these clusters as different skeletal isomers can actually be isolated in the solid state for  $\text{Au}_9[\text{P}(\text{C}_6\text{H}_4\text{OMe})_3]_8(\text{NO}_3)_3$ : a brown form has a  $\text{D}_{4d}$  crown structure and a green form has a  $\text{D}_{2h}$  structure. In solution, however, they share a common structure with identical  $^{31}\text{P}$  NMR spectra; either the solution cluster has a regular arrangement of phosphines, or it is fluxional [186].

$[\text{Au}_{39}(\text{PPh}_3)_{14}\text{Cl}_6]\text{Cl}_2$  has a 1:9:9:1:9:9:1 layered structure in which the central gold is surrounded by other golds [187].

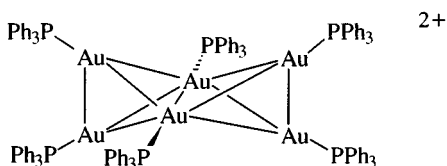
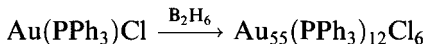


Figure 4.45 The edge-sharing bitetrahedral structure of  $[\text{Au}_6(\text{PPh}_3)_6]^{2+}$ . (Reproduced with permission from *J. Chem. Soc., Dalton Trans.*, 1991, 3211.)

A very large cluster  $\text{Au}_{55}(\text{PPh}_3)_{12}\text{Cl}_6$  of as yet unknown structure has been reported. Physical measurements indicate the bonding to be substantially metallic in character [188].



Apart from gold-centred clusters, several hetero-atom clusters have been made [189]. The oxo-centred cluster has been used as a starting material in synthesis [190].

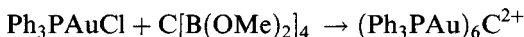
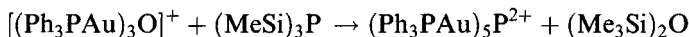
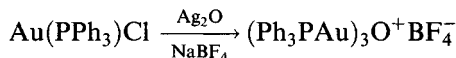
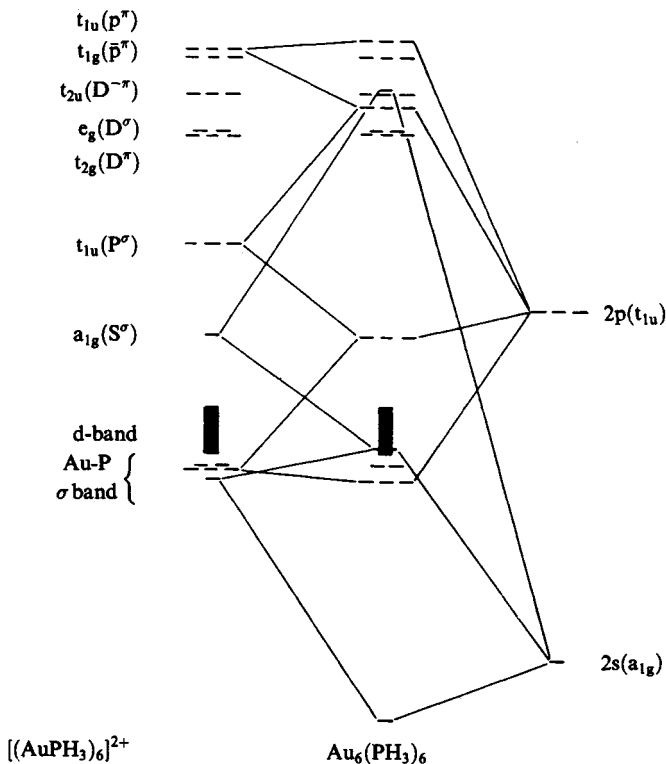


Figure 4.46 shows a MO scheme for the  $\text{Au}_6\text{C}$  framework; the six golds use 5p hybrids to overlap with the carbon s and p orbitals (as they do in



**Figure 4.46** Orbital interaction diagram for the  $\text{Au}_6\text{C}$  framework in  $(\text{H}_3\text{PAu})_6\text{C}^{2+}$  showing the important bonding interactions of the carbon 2s and 2p orbitals with the MOs of the gold cluster. (Reprinted from *J. Organomet. Chem.*, **384**, 405, 1990, with kind permission from Elsevier Science S.A., P.O. Box 564, 1001 Lausanne, Switzerland.)



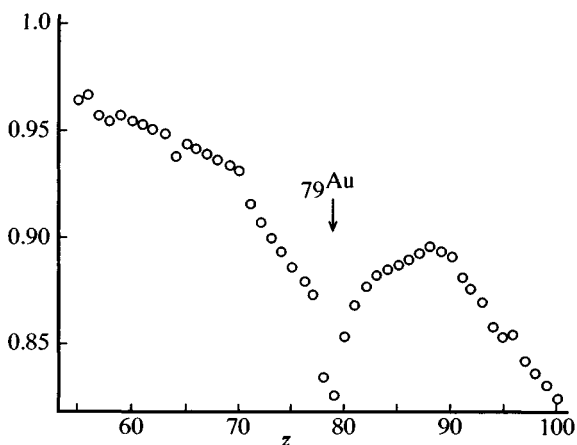
gold-centred clusters), resulting in four bonding orbitals (in addition to the 30 gold d orbitals).

An electron count shows ( $6 \times 11$ ) electrons contributed by gold, four from carbon; deducting two for the positive charge, leaves 68 electrons, which just occupy the four bonding MOs plus the gold 5d orbitals [191].

#### 4.18 Relativistic effects in gold chemistry

For atoms of high atomic number, the properties of the valence electrons are modified [192]. The s electrons that approach the nucleus most closely are attracted strongly by the high nuclear charge and acquire velocities near enough to the speed of light to have a substantial, relativistic increase in velocity and mass. This causes contraction of the s shells. It is seen from Figure 4.47 that the effect is most pronounced at gold. (The effect occurs in addition to the 'lanthanide contraction', which itself roughly cancels out the expected increase in size of the atom owing to the outermost orbital being 6s rather than 5s in silver: without relativistic effects, the radii of silver and gold would be the same.) Outer electrons, therefore, also contract owing to orthogonality. The effect is not confined to the s orbitals; in the case of gold, as far as bonding orbitals are concerned, the effect of relativity is to stabilize 6s considerably, stabilize 6p rather less, and destabilize 5d slightly. This leads to the small 5d–6s (and large 6s–6p) separations noted for gold.

Chemical and physical effects are manifold [193]. The contraction leads to gold forming shorter and stronger covalent bonds and is likely to be



**Figure 4.47** Relativistic contraction of the 6s shell in the elements Cs ( $Z = 55$ ) to Fm ( $Z = 100$ ) showing how relativistic effects on electrons become most pronounced at gold. (Reprinted with permission from *Acc. Chem. Res.*, 1979, **12**, 226. Copyright (1979) American Chemical Society.)

responsible for the 'aurophilic' interactions between neighbouring molecules as well as for gold clusters and gas-phase  $\text{Au}_2$  molecules. It is responsible for the high ionization energies of gold (and hence its 'noble' character) and high electron affinity (leading to the isolability of  $\text{Cs}^+\text{Au}^-$ ).

On a 'metallic' level, physical properties like the heats of atomization and boiling point are higher than extrapolation would predict. The density of gold is some 18% higher than 'non-relativistic' calculation predicts so that the Au–Au distance in gold is shorter than the Ag–Ag distance in silver. The colour of gold results from the 5d to Fermi level transitions occurring *c.* 2.3 eV, causing gold to absorb in the blue–violet region, reflecting red and yellow; the corresponding transition in silver is in the UV >3.5 eV.

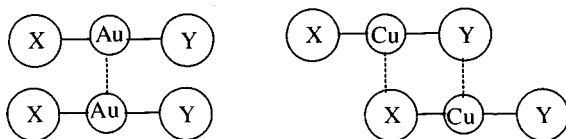
The non-relativistic band structures of silver and gold are very similar so that, were it not for relativistic effects, 'gold would look silver'.

#### 4.19 Aurophilicity

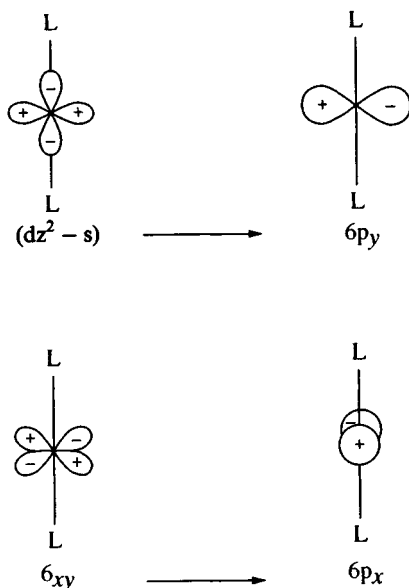
Many gold complexes have unusually short Au–Au contacts in the solid state. Therefore, linear X–Au–Y gold complexes often have packing to give Au–Au distances in the range 2.7–3.3 Å (Figure 4.48) whereas in corresponding copper or silver compounds metal–halogen contacts determine solid state packing (X, Y = halogen or neutral donor).

These short Au–Au contacts may be compared with distances of 2.88 Å in metallic gold and 2.60 Å in gaseous  $\text{Au}_2$ . The term 'aurophilicity' has been coined by H. Schmidbaur to describe the phenomenon [189, 194]. The interactions can occur as pairs, squares, linear chains or two-dimensional arrays of gold centres. Examples include the association between dimer units in the dithiocarbamates  $\text{Au}(\text{dtc})_2$  (Figure 4.16) and the ionic tetrahydrothiophen complexes  $\text{Au}(\text{tht})_2^+\text{AuX}_2^-$  (X = halogen), where cations and anions stack with Au–Au 2.97–2.98 Å (X = I). The interaction is such that  $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$  pair up, despite their charge, with Au–Au 3.24 Å in the sodium salt. Likewise in  $\text{Aupy}_2^+\text{AuCl}_2^-$ , cations pair up at 3.42 Å apart [10, 195].

It certainly does not seem that these interactions continue in solution, so that their magnitude is weaker than solvation forces. Theoretical explanation has suggested that the unused, filled, 6s–5d<sub>z</sub> hybrid (section 4.1) interacts with vacant 6p<sub>x</sub>,p<sub>y</sub> orbitals at right angles to the digonal bonds (Figure 4.49).



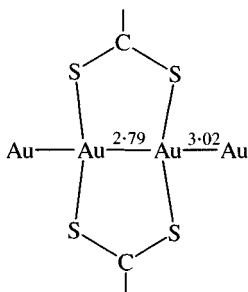
**Figure 4.48** The contrast in intermolecular forces between X–Au–Y and X–Cu–Y systems (X, Y: halogen or neutral donor).



**Figure 4.49** Interaction of a filled hybrid orbital with vacant  $6p_x, 6p_y$  orbitals leading to aurophilic forces. (From K.P. Hall and D.M.P. Mingos, *Progr. Inorg. Chem.*, 1984, **32**, 264. Copyright © 1990 John Wiley. Reprinted by permission of John Wiley & Sons, Inc.)

A recent *ab initio* calculation on  $(\text{ClAuPH}_3)_2$  suggests, however, that, at a distance of around  $3.4 \text{ \AA}$ , the effect is largely caused by ligand dipole–dipole attractions reinforced by relativistic effects [196]. Estimates of the Au–Au forces are in the range  $25\text{--}35 \text{ kJ mol}^{-1}$ , slightly weaker than hydrogen bonds, i.e. by no means negligible [196, 197].

Intramolecular Au–Au interactions are found in some binuclear complexes  $(\text{AuX})_2$ , where X is a chelating ligand like dithiocarbamate, phosphine ylid ( $\text{R}_2\text{P}(\text{CH}_2)_2^-$ ) or bidentate phosphines. Therefore, in  $[\text{Au}(\text{S}_2\text{CNBu}_2)_2]$  the Au–Au distance is  $2.78 \text{ \AA}$  (Figure 4.50).



**Figure 4.50** Short intramolecular Au–Au contacts in  $[\text{Au}(\text{S}_2\text{CNBu}_2)_2]$ .

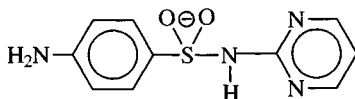


Figure 4.51 The ligand in silver(I) sulfadiazine.

#### 4.20 Silver and gold compounds in medicine

Silver compounds have been known for a long time to possess anti-bacterial properties. Silver(I) sulfadiazine (Figure 4.51 shows the ligand) is a slow release agent for  $\text{Ag}^+$ . It is used as a cream to prevent infections in severe burns. It has a chain structure with each silver bound to three nitrogens from different pyrimidine rings and an oxygen from a sulphonyl group. (There is also a weak  $\text{Ag}-\text{Ag}$  interaction (2.92 Å)). Anti-bacterial interaction is believed to involve  $\text{Ag}-\text{DNA}$  interactions [198].

Gold compounds were first used in 1929 by French doctors to treat rheumatoid arthritis. Two of the most commonly used are aurothiomalate (myocrisin) and aurothioglucose (solganol) (Figure 4.52), given by injection of their solutions in doses of up to 25 mg a week for some years.

These drugs are gold(I) thiolates of the type  $(\text{AuSR})_n$  of ill-defined structure (they are usually obtained as powder), probably oligomers with 2-coordinate gold. Use of the S-donor ligands affords lability of the complexes in the body and also stabilizes the gold(I) state against disproportionation in aqueous solution. A disadvantage of this approach is that the compounds are restricted to vascular fluids (e.g. blood, lymph) until biological ligands break up the oligomers and they are vulnerable to ingestion by white cells [199].

The recently introduced gold(I) phosphinethioglucose derivative (auranofin, Ridura) (Figure 4.53) can be taken orally and is absorbed more slowly than myocrisin.

The monomeric non-polar molecular structure enables it to pass through cell walls relatively easily (myocrisin passes easily into the red blood cells of smokers, possibly owing to ingested cyanide in the smoke reacting to form monomeric  $\text{Au}(\text{SR})\text{CN}^-$ ).

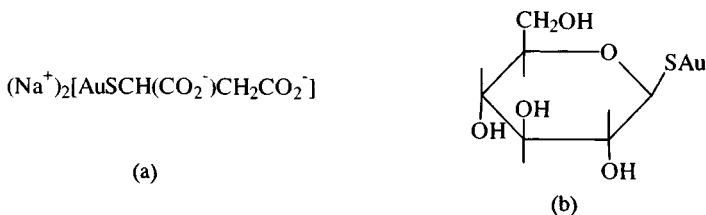


Figure 4.52 (a) Myocrisin; (b) solganol.

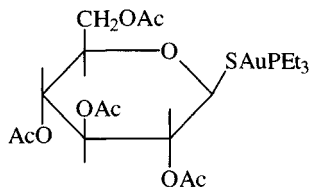


Figure 4.53 Auranofin.

Gold compounds are also being studied as possible anti-cancer agents, after the success of platinum compounds. *cis*-Complexes analogous to  $\text{Pt}(\text{NH}_3)\text{Cl}_2$  have not been made; the oxidizing nature of gold(III) would make them toxic; and gold(III) complexes are kinetically more labile. The gold(I) complex  $\text{Au}(\text{dppe})_2^+\text{Cl}^-$  (section 4.10.3) has shown some activity but has been found to be a cardiovascular toxin; corresponding copper and silver complexes also appear to have some activity so that the role of the metal may be to deliver toxic diphosphine to the cells.

The compound  $\text{Au}(\text{dmamp})(\text{O}_2\text{CMe})_2$  ( $\text{dmamp} = 2\text{-Me}_2\text{NC}_6\text{H}_4$ ) displays some anti-tumour activity and is undergoing tests on its anti-bacterial activity [200].

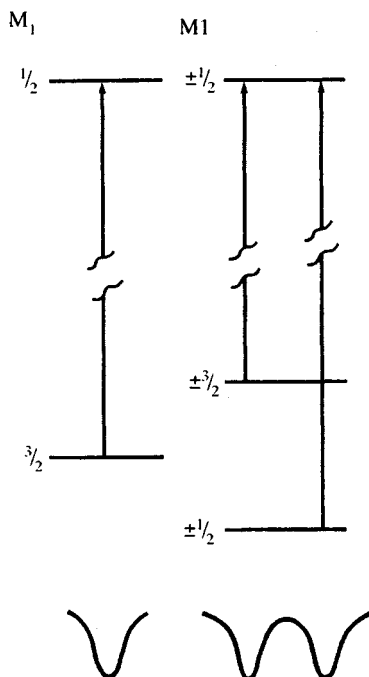
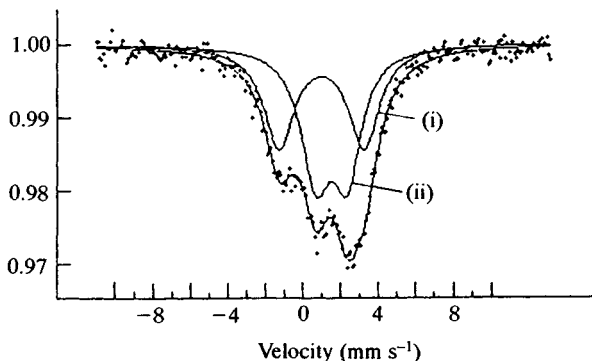


Figure 4.54 The effect of an electric field gradient (EFG) creating asymmetry in the electron distribution round a gold nucleus, leading to a quadrupole splitting in the Mössbauer spectrum. (Reproduced with permission from *Gold Bull.*, 1982, 15, 53, published by World Gold Council.)



**Figure 4.55** The Mössbauer spectrum of  $\text{Cs}_2(\text{AuI}_2)(\text{AuI}_4)$  showing separate resonance from (i) the gold(I) and (ii) the gold(III) sites. (Reproduced with permission from *J. Chem. Soc., Dalton Trans.*, 1991, 3211.)

#### 4.21 Mössbauer spectroscopy of gold complexes

In Mössbauer spectroscopy of gold complexes [201],  $\gamma$ -rays from an excited  $^{197}\text{Au}$  nucleus (derived from  $^{197}\text{Pt}$  (18h) by  $\beta$ -decay) are used to irradiate a sample of the gold compound. The gold atoms in the sample generally will have a different environment to the source, so that it is necessary to 'vibrate' the sample through a velocity range, measuring the  $\gamma$ -radiation, being excited from the  $M_1 = 3/2$  ground state to the  $M_1 = 1/2$  excited state. A typical spectrum shows twin peaks, a doublet. The centre of the doublet defines the **isomer shift**, a measure of the electron density at the gold nucleus, changes in which reflect changes in the 6s population principally. The splitting between the lines, the **quadrupole splitting**, reflects asymmetry in the electron distribution around the gold nucleus, which causes an electric field gradient that interacts with the quadrupole moment of the  $I = 3/2$  ground state, causing it to split and give two transitions (Figure 4.54).

Mössbauer spectra with  $^{197}\text{Au}$  can:

1. Distinguish between different oxidation states
2. Distinguish between different coordination numbers for a given donor atom
3. Show whether a compound contains gold(II) or a mixture of gold(I) and gold(III) (Figure 4.55).