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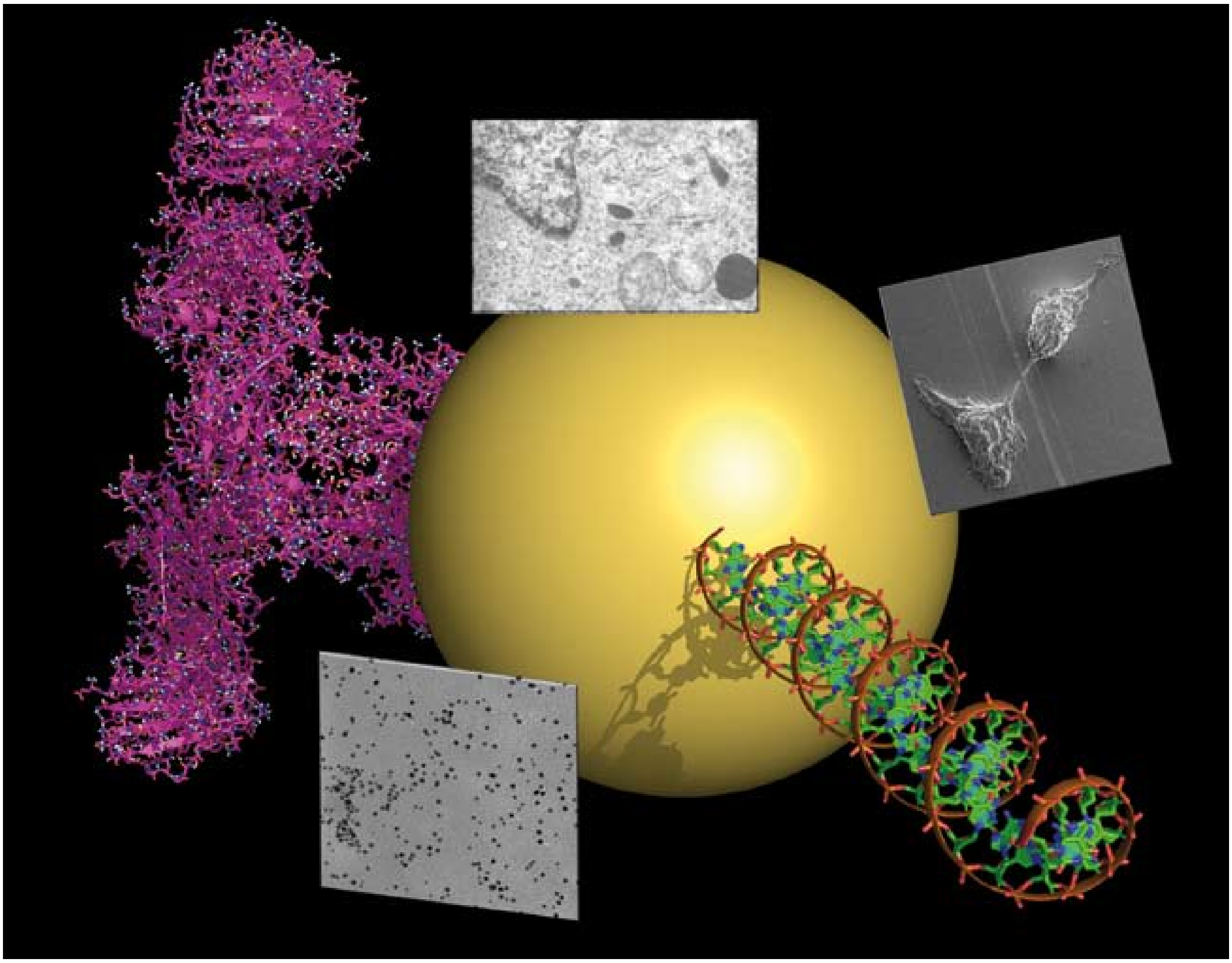

Macrocycles, catenanes, oligomers and polymers in gold chemistry†

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A *critical review* is given of the chemistry of macrocycles, catenanes, oligomers and polymers in gold chemistry. Because gold centres are typically labile towards ligand substitution, there may be an easy equilibrium between the cyclic and linear oligomeric or polymeric forms and the preferred products of self-assembly are usually determined by thermodynamic control. The ways in which the self-assembly of complex structures from simple building blocks by dynamic coordination chemistry can be manipulated by ligand design or by the use of secondary bonding forces is emphasized (39 references).

Introduction

There has been great interest in the synthesis and properties of metal-containing polymers and molecular networks, driven by their potential applications as catalysts or as functional materials.[1] Within this broad field, gold chemistry has yielded an impressive array of complexes with particular promise as optical materials, as precursors to gold coatings or as inorganic pharmaceuticals.[2] This article gives an overview of current research in organometallic and coordination oligomers and polymers of gold, with emphasis on the synthesis of materials with new and potentially useful structures.

The common oxidation states of gold are gold(I) and gold(III), which have $5d^{10}$ and $5d^{8}$ electron configurations, respectively. Gold(III) strongly favours square-planar coordination, whereas gold(I) favours linear two-coordination but can also form trigonal planar or tetrahedral complexes.[2,3] The linear gold(I) unit is particularly well suited to forming polymers. A unique feature of gold chemistry is the ability of gold(I) centres to form gold···gold secondary bonding interactions, called aurophilic interactions, which have a bond energy about the same as a hydrogen bond.[4] These aurophilic interactions, which are particularly strong for gold because they are enhanced by relativistic effects,[4] can be used in forming supramolecular polymers or in controlling the secondary structure of gold(I) polymers. As molecular materials, gold(I) complexes may be strongly emissive and the aurophilic bonding can enhance the efficiency of the emission as well as affect its energy.[4]

Dick Puddephatt

Dick Puddephatt was educated at University College London, where he studied with Alwyn Davies and Robin Clark, then did postdoctoral research with Howard Clark at the University of Western Ontario. He was a faculty member at the University of Liverpool before returning to Western, where he is Distinguished University Professor. Dick Puddephatt's research interests are in organometallic and coordination chemistry, with relevance to catalysis and materials science. The research has been recognised by several honours, including election as Officer of the Order of Canada, Fellow of the Royal Society and Fellow of the Royal Society of Canada.

Macrocycles, catenanes, oligomers and polymers with gold(I) in the backbone

(a) Compounds of formula $[\{Au(\mu\text{-}X)\}_n]$

The simplest polymeric compounds of the type $[\{Au(\mu\text{-}X)\}_n]$ are the gold(I) halides, with X = Cl, Br or I, whose zigzag chain structures are shown in Fig. 1. These chain structures have been known for many years but the significance of aurophilic interactions in controlling the packing of the chains has never been defined. In AuI, the neighbouring zigzag chains run parallel but staggered and each gold(I) centre forms two intrachain and two interchain aurophilic interactions, each with Au···Au = 3.08 Å. However, in AuCl the aurophilic interactions are between chains which cross each other and each gold(I) centre forms two intrachain aurophilic interactions with Au···Au = 3.37 Å and four interchain aurophilic interactions with Au···Au = 3.23 Å. The bromide derivative AuBr can exist in several structural forms, two of which are analogous to the AuI and AuCl structures.[2]

The polymeric chain structure **1** (Scheme 1) is also thought to be common in the thiolate derivatives $[(AuSR)_n]$ and the structure has been proved for the thiomalate derivative, which is used in treatment of rheumatoid arthritis.[5] However, the structure does not adopt the parallel chain structure **2** found for AuI (see also Fig. 1) but a double helical chain structure **3** with interchain Au···Au = 3.227(5) Å and intrachain Au···Au = 3.485(2) Å. A left-handed helix is formed when

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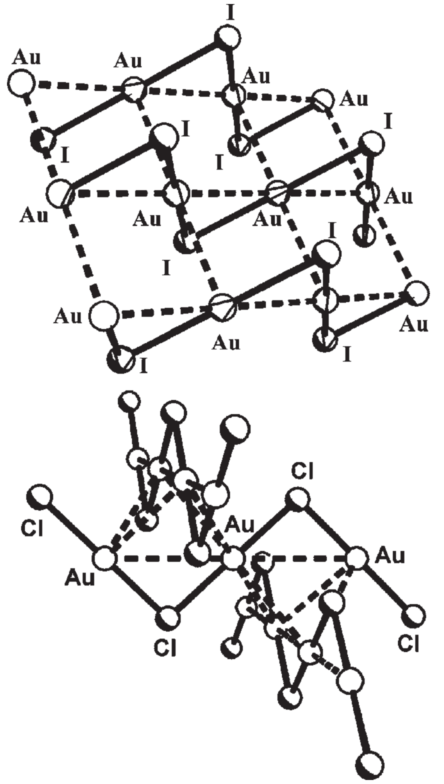
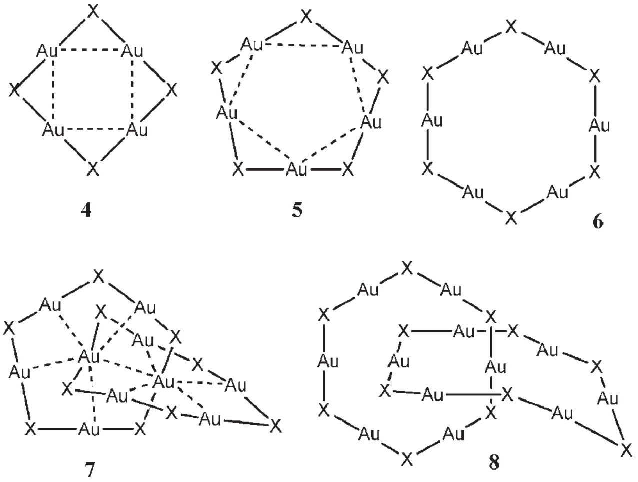
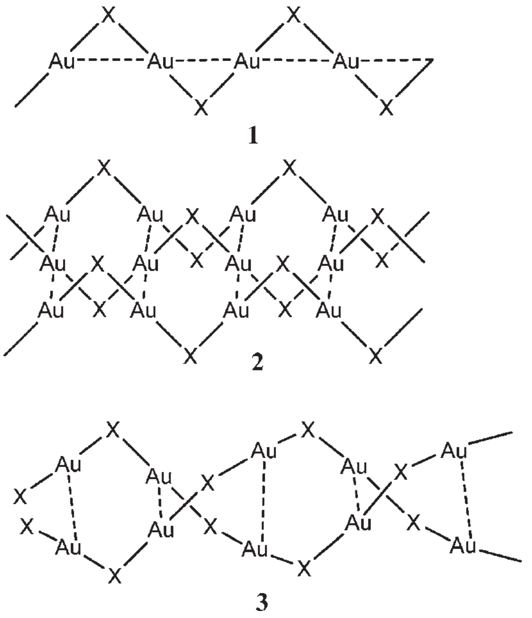


Fig. 1 Structures of the gold(I) halides: above, AuI; below, AuCl.



Scheme 2 Cyclic and catenated cyclic structures of gold(I) complexes AuX.

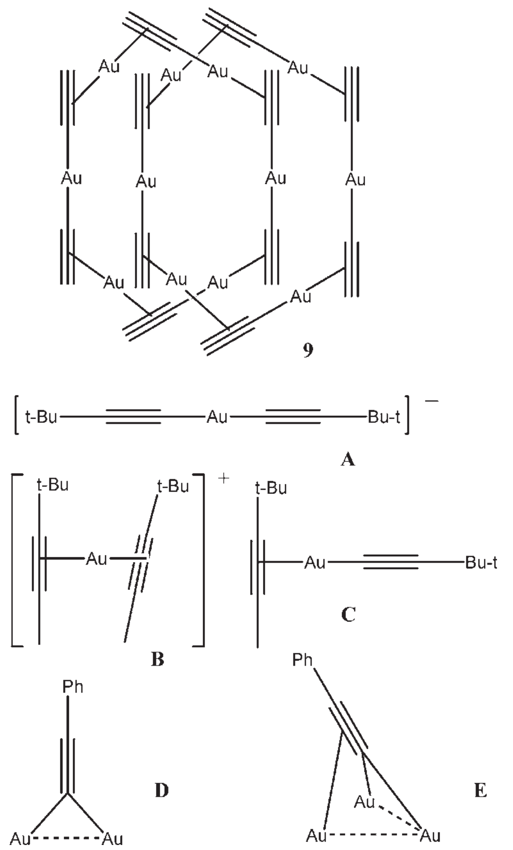
SR = (*S*)-thiomalate and a right-handed helix when SR = (*R*)-thiomalate. As well as the important medicinal use, the gold(I) thiolates have long been used for decorative applications since they can be painted onto ceramics and then fired to form thin gold films.[2,6] Gold thiolates are also present as surface species in the protected gold nanoparticles and in self-assembled monolayers on gold surfaces. When R is a relatively small alkyl or aryl group, the chain structure **1** is generally assumed, though the secondary structure is unknown in most cases.[6] However, with more sterically bulky alkyl groups cyclic structures from tetramers to hexamers, **4–6** (Scheme 2) may be formed and, in some cases, catenation of the cyclic structures has been established (**7** and **8**, Scheme 2).[7] A complex $[\mathrm{Au}_{11}(\mathrm{SR})_{11}]$, which contains catenated five- and six-membered rings, is also known and is a precursor to an antiarthritic gold drug.[7] Many of these compounds contain aurophilic bonds either within the ring or between rings, as illustrated by structure **7** in Scheme 2. An alkyltelluride derivative $[\mathrm{Au}_4(\mu\text{-TeR})_4]$ with structure **4** (Scheme 2) is also known.[7]



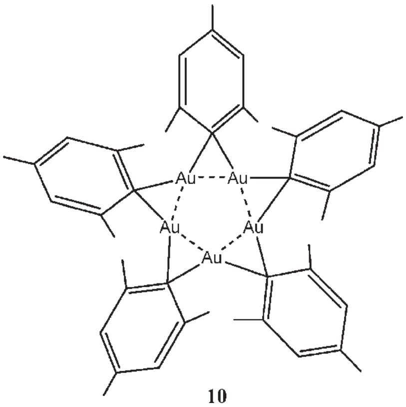
Scheme 1 Intrachain Au···Au bonds are shown only for **1**.

When $X = PR_2$, the compounds AuX may exist as polymers **1** or as cyclic complexes. The confirmed cyclic structures include **4** (X = PMesityl$_2$) and **6** (X = PCy$_2$) as well as a remarkable trimer $[\mathrm{Au}_3(\mu\text{-PR}_2)_3]$, with R = 2,4,6-*i*-Pr$_3$-C$_6H_2$.[8] A single amide derivative $[\mathrm{Au}_4(\mu\text{-NR}_2)_4]$ with structure **4** has been reported.[9] The case of the gold(I) acetylide complexes of general formula $[\{\mathrm{Au(CCR)}\}_n]$ is more complex. The *tert*-butylacetylide complex is shown to be $[\{\mathrm{Au(CCR)}\}_{12}]$, **9** (Scheme 3) in the solid state, and is comprised of two catenated $[\{\mathrm{Au(CCR)}\}_6]$ units. Individual gold(I) centres are present in the forms **A**, **B** and **C** (Scheme 3) and there are also aurophilic bonds present. Complexes with smaller alkyl or aryl substituents are usually insoluble and are assumed to be polymeric in nature. The phenyl acetylide derivative is formed as a network material with roughly planar honeycomb sheets of gold hexagons, with bridging phenylacetylide groups in either form **D** or **E** (Scheme 3). In the soluble gold acetylide derivatives, such as $[\{\mathrm{Au(CC}\text{-}t\text{-}\mathrm{Bu}\}_n]$, the structures in solutions and solid state may be different. For example, the Au$_{12}$ complex **9** (Scheme 3) was originally formulated as a tetramer based on the solution molecular weight.[10]

Complexes of the type $[(\mathrm{AuAr})_n]$, Ar = aryl, can be isolated in some cases and the structure of the mesityl complex is the star-shaped pentamer **10**.[2,11]



Scheme 3 The structure of the [2]catenane [{Au(CC-*t*-Bu)}$_{12}$], **9**, and the types of alkynylgold(I) bonds present in complexes of type [{Au(CCR)}$_n$].



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Overall, in these complexes [(AuX)$_n$] the gold(I) centres have approximately linear coordination. The primary structure can be the zigzag polymer **1**, in which roughly linear chains of gold(I) cations are bridged by anions which lie alternately on either side, or the cyclic structures **4–6**, **9** and **10**, in which all gold atoms lie toward the centre with the bridging anions to the outside. Smaller groups X give polymers, but bulkier substituents may favour formation of macrocyclic structures and very bulky substituents favor smaller ring structures. The different ring sizes in [(AuX)$_n$], n = 3–6, are made possible through variation of the angles Au–X–Au or by distortion of the (AuX)$_n$ rings from planarity. In all of these structures, there is aurophilic bonding within the primary chain or ring structure and, in many cases, the secondary structure is also influenced by aurophilic bonding. The organization of the polymeric chains in structures **2** and **3**, and the catenation of cyclic structures in **7**, **8** and **9** are illustrative examples of this effect.

(b) Compounds of formula [{Au(μ-L–X)}$_n$] (L = neutral donor and X = anionic donor)

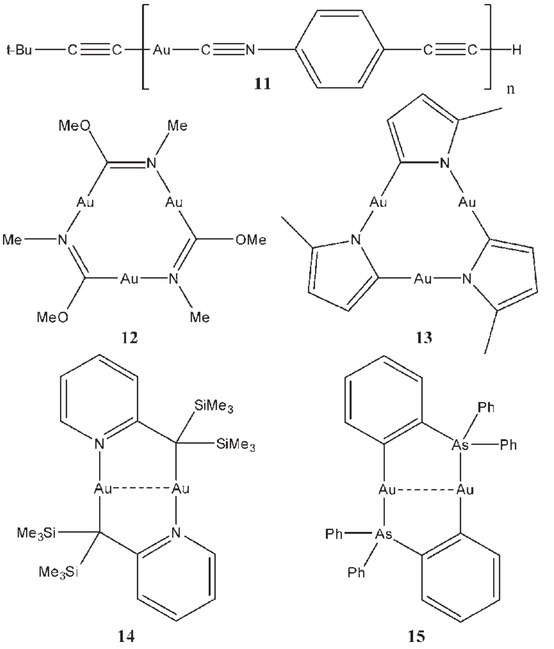
In gold(I) complexes of general formula [{Au(μ-L–X)}$_n$], with a rigid spacer group between the neutral and anionic donors, the structure can be predicted based on the ligand geometry. Thus, for example, if the natural angle between the two donor orbitals is 180, 120 or 0°, a polymer, trimer or dimer should form, as illustrated by the examples **11–15** in Scheme 4.[2,12] The mixture of oligomers **11** is formed by elimination of *t*-BuCCH from the complex *t*-BuCCAuCNC$_6$H$_4$CCH.

With intermediate angles, the structure is less predictable and the polymers **16** and **17** fall into this category (Scheme 5). These phosphine–acetylide or pyridine–thiolate bridged polymers are formed by elimination of HCl from the precursor complexes [AuCl(R$_2$PCCH)] or [AuCl(SC$_5$H$_4$NH)], respectively.[13]

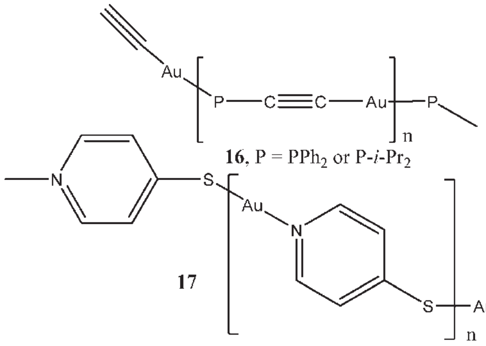
Condensation reactions of this kind can give cyclic or polymeric complexes, depending on the degree of ring strain that would be present in a macrocycle. For example, diphenylphosphinobenzoic acid with gold(I) gives a mixture of dimer **18** and trimer **19** with the *ortho*-isomer, a trimer **20** with the *meta*-isomer but a polymer **21** with *para*-diphenylphosphinobenzoic acid, according to Scheme 6. The polymer **21** can be crystallized and forms a double-stranded polymer, with the polymer strands held together by aurophilic attractions in the solid state, with Au···Au = 3.1643(9) Å, as shown in Fig. 2.[14]

(c) Compounds of formula [{Au$_2$(μ-L–L)(μ-X–X)}$_n$]

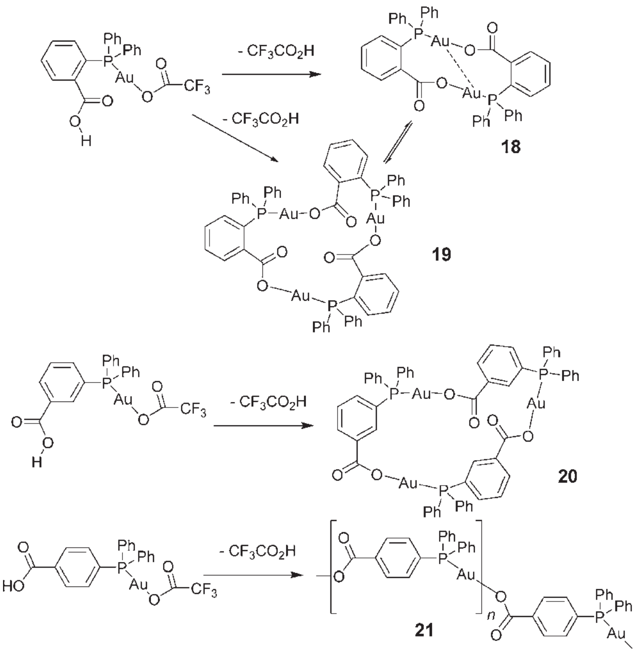
The complexes of this type have been studied in most detail with diacetylides as the anionic ligands. If both the diacetylide



Scheme 4 Polymeric, trimeric and dimeric complexes (L–X–Au)$_n$.



Scheme 5 Polymeric complexes (L–X–Au)$_n$ with a bend in the chain.



Scheme 6 Cyclic and polymeric diphenylphosphinobenzoate complexes.

and the neutral bridging ligand LL favour linear or close to linear coordination, then polymers such as **22** and **23** are formed (Scheme 7).[15] Alkynylgold(I) complexes are often strongly emissive, and the emission energies were shown to be red-shifted as the degree of aggregation of the complexes increased. Such properties are expected for conjugated, rigid-rod polymers in which a degree of delocalization of electrons along the chain direction is possible, even though the band gap is quite large in these compounds.[15,16]

If the ligand bis(diphenylphosphino)methane is used in combination with gold(I) and a linear or angular diacetylide, there is a favourable aurophilic interaction and the resulting *syn* conformation leads to formation of macrocyclic complexes such as **24–27**, shown in Scheme 8. Complex **26** undergoes photochemical *cis–trans* isomerisation about the azo group. Incorporation of silver(I) ions into **26** gives **27**, which is inert to photochemical isomerisation.[17]

If the spacer group of the diphosphine ligand is longer or the diacetylide ligand is non-linear, then there can be an easy equilibrium between macrocycles with large cavities and polymers. Some such macrocycles **28–30** are shown in Scheme 8. If the cavity is large enough, the macrocycles may self-penetrate or they may act as hosts, as illustrated in **30**.[17,18]

The dialkynes of type X(4-$C_6H_4OCH_2CCH)_2$ in combination with diphosphine ligands Z($PPh_2)_2$ have given a particularly rich chemistry, as illustrated in Scheme 9. For these compounds there may be an equilibrium between the ring structure **31**, the [2]catenane **32**, the double ring **33**, the doubly-braided catenane **34**, and higher oligomers and polymers whose structures are uncertain. The position of the equilibrium depends on the nature of both the 'hinge group' X and the spacer group Z. The [2]catenane **32** is favoured for Z = $(CH_2)_3$ and for X = CH_2, CHR or CR_2 because, in these cases, the macrocycles mesh tightly and there is favorable inter-ring aurophilic bonding. In the case with X = CHR, the macrocycles are achiral but the [2]catenane is chiral; chiral macrocycles can also be prepared by using a chiral diphosphine ligand. The doubly braided catenane **34** has been crystallized in the case with X = cyclohexylidene and Z = $(CH_2)_4$, and a space-filling diagram is shown in Fig. 3.[19]

In one case, the equilibrium between ring and [2]catenane can be switched by modification of the hinge group. Thus, the ketal substituent favours formation of the [2]catenane **37** over the ring complex **35**, but hydrolysis can give the ketone and this hinge group favours the ring complex **36** over the [2]catenane **38** (Scheme 10).[20]

The diacetylide complexes have been studied in greatest detail but the equilibrium between macrocycles and polymers has also been established for dithiolate complexes. Thus, the dithiolate complex of gold(I) with bridging *trans*-bis(diphenylphosphino)ethylene exists as a macrocycle **39** in solution but crystallizes as the ring-opened polymer **40** (Scheme 11). The individual polymer chains are associated through weak interchain attractions between AuS groups as shown in Fig. 4. Several other cyclic compounds analogous to **39** are known, but most other polymers analogous to **40** are insoluble and so are not structurally characterized.[21]

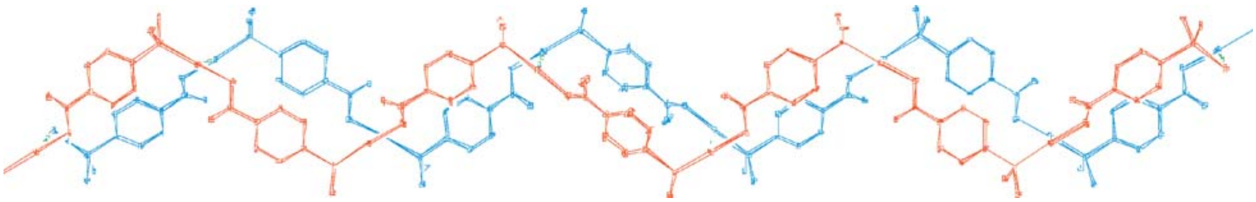
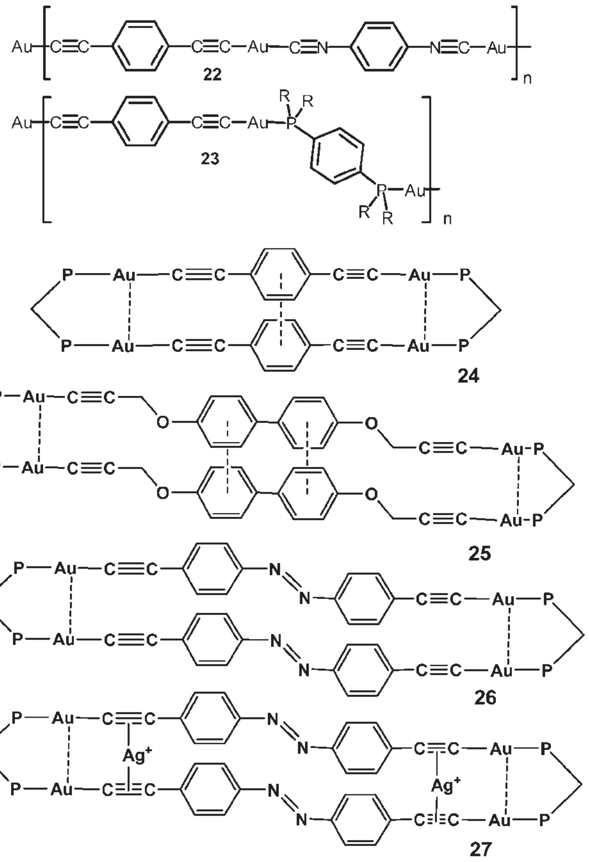
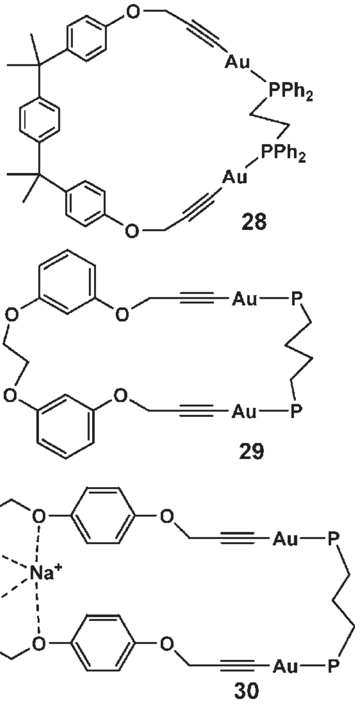


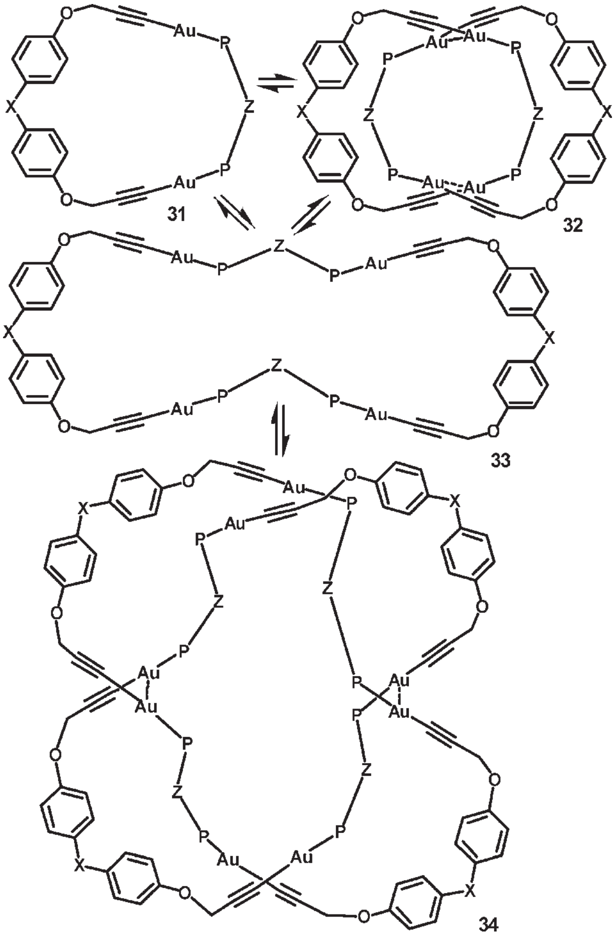
Fig. 2 Structure of the double stranded polymer **21**.



Scheme 7 (a) Diacetylide polymers of the type [{Au_2 (μ-L–L)-(μ-X–X)}$_n$]. (b) Macrocyclic tetragold(I) acetylides containing the bridging ligand bis(diphenylphosphino)methane.



Scheme 8 Macrocyclic alkynylgold(I) complexes with large cavities.



Scheme 9 The easy equilibrium between macrocycles and catenanes.

There are interesting diaryl complexes **41** and **42** of this type in which the twist of the biaryl unit can give a symmetry analogous to the Mobius strip (Scheme 12).[21]

(d) Ionic compounds of formula [{Au(μ-L–L)}$_n$]$^{n+}$ or [{Au(μ-X–X)$_2$}$_n$]$^{n-}$

There are many examples of cyclic 1,1- or 1,2-dithiolate derivatives, such as **43–45** in Scheme 12, and they usually

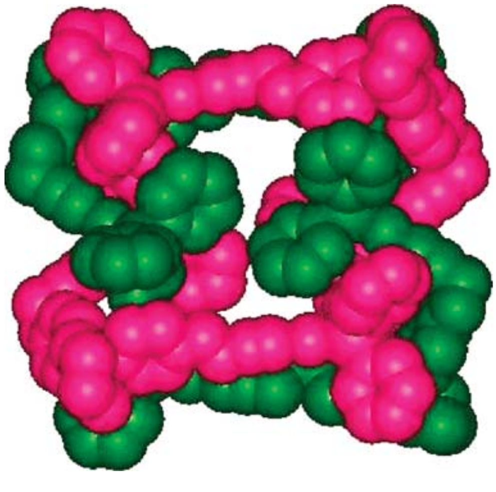
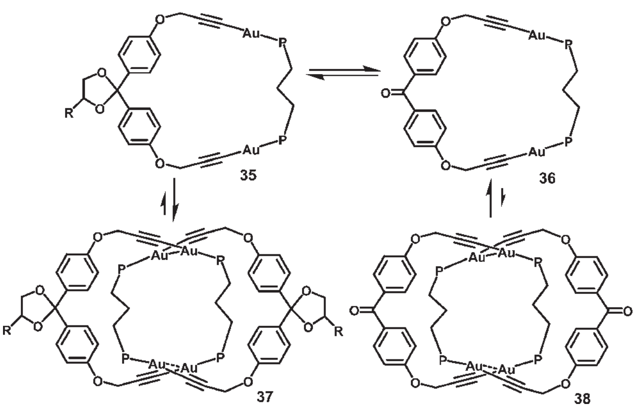
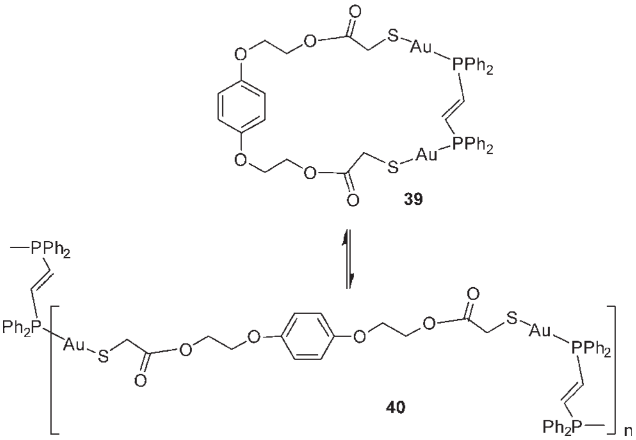


Fig. 3 Structure of the doubly braided catenane **34**.



Scheme 10 Switching the equilibrium between ring and [2]catenane by modifying the hinge group.



Scheme 11 The ring-opening polymerization of a dithiolate(diphosphine)digold(I) macrocycle.

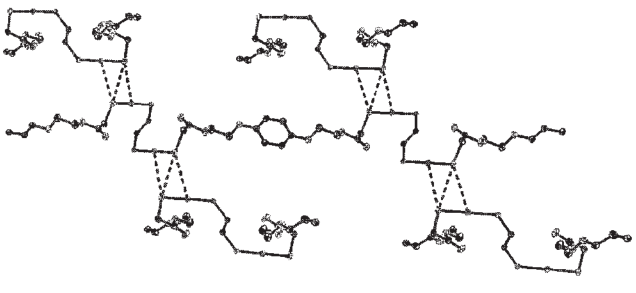
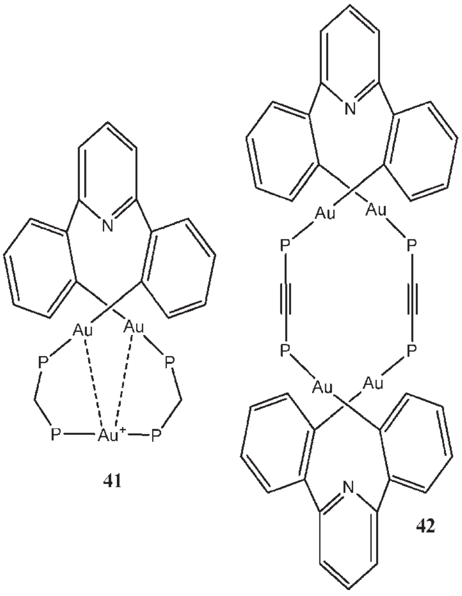
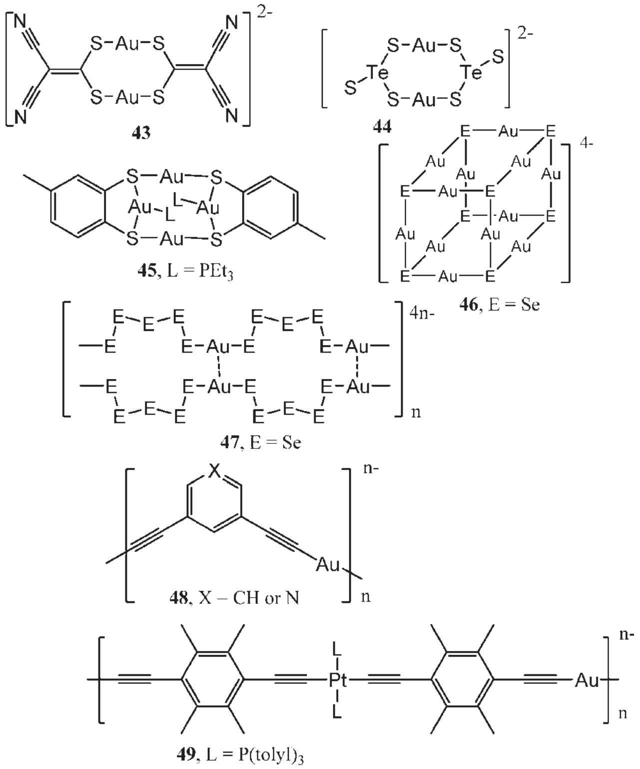


Fig. 4 The structure of the dithiolate polymer **40**. The dashed lines indicate weak interchain S···Au and Au···Au bonds. The phenyl groups of the diphosphine are omitted for clarity.

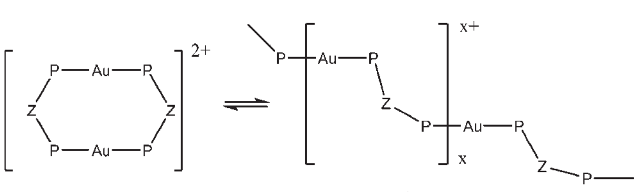
display transannular aurophilic bonding. The 1,2-dithiolates often bind additional gold centres, as illustrated in **45** (Scheme 13). Selenide and oligoselenide units form a particularly rich series of anionic complexes illustrated by the extended cubane **46**, which contains an encapsulated sodium ion, and the double chain polymer **47**, in which the chains are connected by aurophilic bonds.[2,22] The anionic diacetylide complexes such as **48** and **49** are insoluble and the detailed arrangement of the chains is not yet established.[16,23]



Scheme 12 Cyclic gold(I) complexes with twisted biaryl groups.

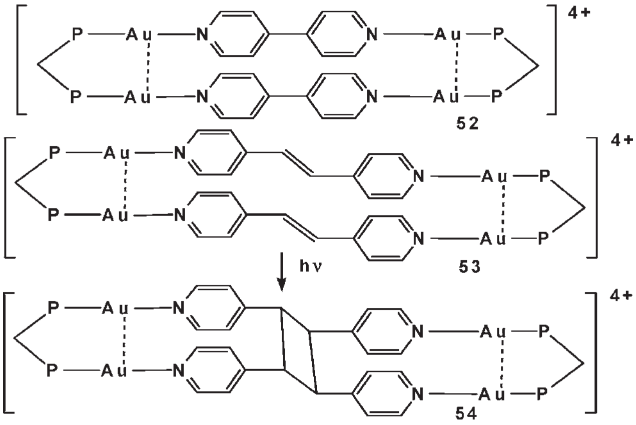


The equilibrium between rings and polymers is illustrated by the cationic compounds with diphosphine ligands Ph_2PZPPh_2



50, Z = $(CH_2)_n$, n = 1, 2, 3 or 5 **51**, Z = $(CH_2)_n$, n = 4

Scheme 13 Cationic diphosphine derivatives of gold(I); P = PPh_2.



Scheme 14 Macrocyclic complexes containing the diphosphine ligand $Ph_2PCH_2PPh_2$.

with Z = $(CH_2)_n$, shown in Scheme 14. When $n = 1$ or 2, the cyclic structure **50** is preferred because the transannular distance is short enough to allow aurophilic bonding. For higher values of n, the *syn* conformation of the diphosphine is favoured for odd values of $n = 3$ or 5 and this in turn favours formation of the macrocycle **50**, but the *anti* conformation is preferred for even value of $n = 4$ and then the polymer **51** is formed.[24]

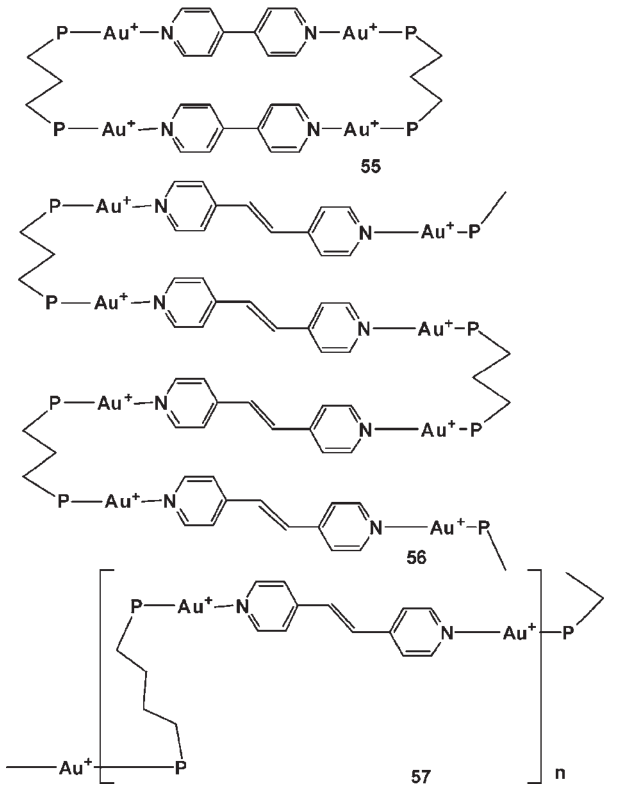
The equilibrium between macrocycles and polymers is particularly easy if a combination of a diphosphine ligand and a bipyridine ligand is used to combine with gold(I). The bipyridine ligand can be easily and reversibly displaced by weakly binding anions such as trifluoroacetate or nitrate, while the diphosphine acts as an anchor group. If the diphosphine ligand is $Ph_2PCH_2PPh_2$, there is a strong tendency to form a macrocycle with transannular Au···Au (and Ar···Ar) attractions, as illustrated by **52** and **53** in Scheme 14. In the complex **53**, the central alkene units are held close together and photolysis leads to cycloaddition to give the cyclobutane derivative **54**.[13,25]

If longer spacer groups are used in the diphosphine ligand $Ph_2P(CH_2)_nPPh_2$, the equilibrium shifts towards ring-opened forms and either rings (**55**) or polymers (**56**, **57**) may be crystallized from solution (Scheme 15). The luminescent polymers can adopt sinusoidal or stretched conformations, with *syn* or *anti* configuration at the diphosphine ligand, respectively, as illustrated in Scheme 15. The sine-wave form **56** is favoured with $n = 3$ or 5 and the stretched form **57** when $n = 4$. A similar case has been reported with the diphosphine ligand PP = 1,2-*bis*(diphenylphosphino)benzene, which gives a polymer $[\{Au_2(\mu\text{-PP})(\mu\text{-NN})\}_n]^{2n+}$ with NN = 4,4′-bipyridine but a macrocycle $[Au_4(\mu\text{-PP})_2(\mu\text{-NN})_2]^{4+}$ when NN = 1,2-bis(4-pyridyl)ethylene.[25]

If the diphosphine is the asymmetric ligand binap, the racemic binap with gold(I) and *trans*-1,2-bis(4-pyridyl)ethylene gives the syndiotactic polymer **58** (alternating *R*,*S*,*R*,*S*), while (*S*)-binap gives either the isotactic polymer **59** or a remarkable decagold oligomer **60** with unidentate bis(pyridyl) end groups (Fig. 5).[26]

The similar reactions with 4,4′-bipyridine can also give the syndiotactic polymer **61** (*R*,*S*,*R*,*S*) or the isotactic polymer **62** (*S*,*S*,*S*,*S*), but in this case the racemic ligand can also give the heterotactic polymer **63** (*S*,*S*,*R*,*R*), as illustrated in Fig. 6. This is the first time that all three stereoregular forms of any polymer have been crystallized.[26]

Non-linear bis(pyridine) ligands can form digold or tetragold macrocycles in equilibrium with ring-opened oligomers and polymers. Scheme 16 shows a gold(I) complex that exists



Scheme 15 Cyclic and polymeric complexes containing linear bipyridine ligands and diphosphines $Ph_2P(CH_2)_nPPh_2$.

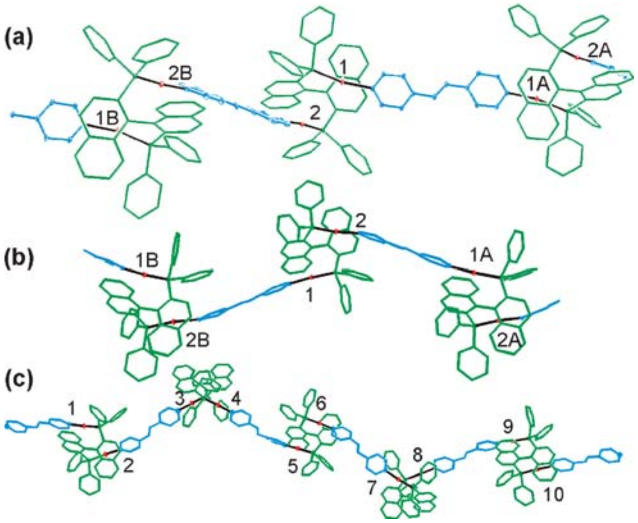


Fig. 5 Structures of binap complexes: (a) syndiotactic polymer **58**; (b) isotactic polymer **59**; (c) decagold oligomer **60**. Only the gold atoms are numbered.

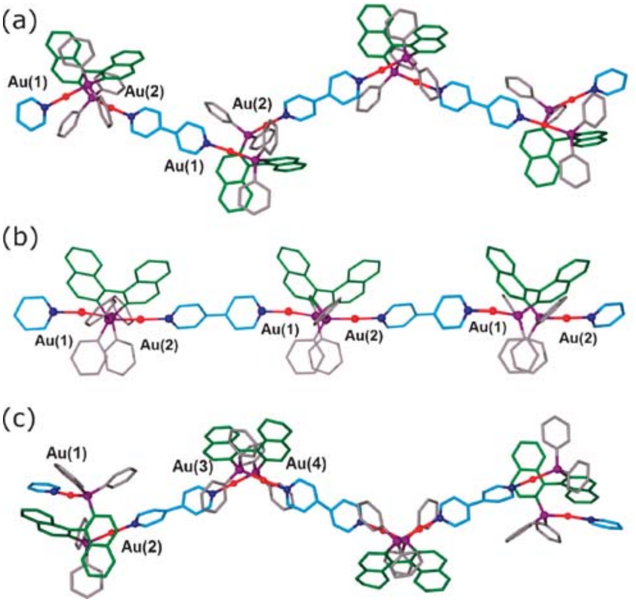
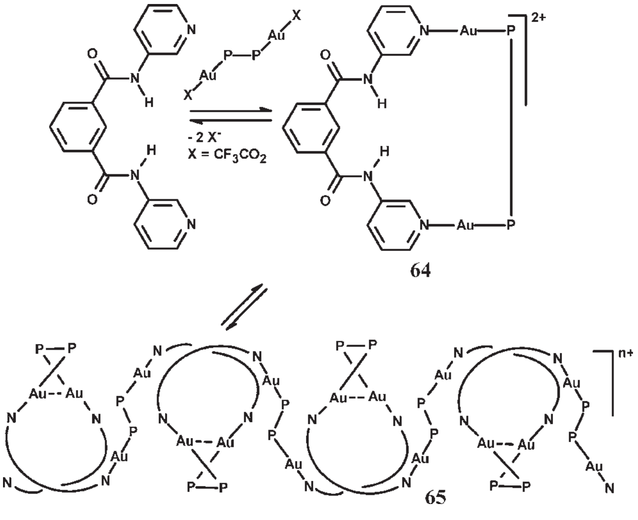


Fig. 6 Structures of 4,4′-bipyridine polymers: (a) syndiotactic polymer **61**; (b) isotactic polymer **62**; (c) heterotactic polymer **63**.

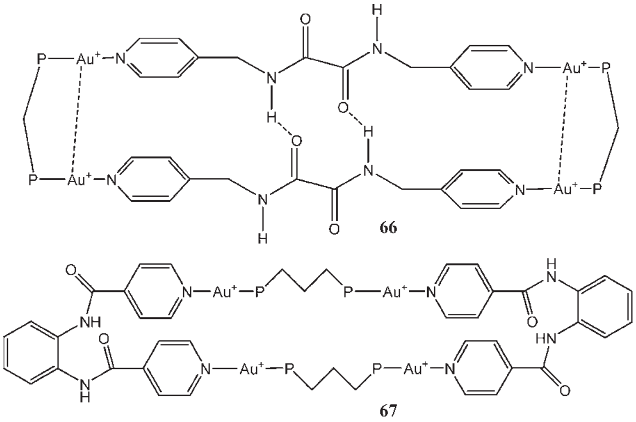
in solution as a mixture of the macrocycle **64** and the ring-opened oligomer **65** (P–P = $Ph_2PCH_2CH_2PPh_2$). The complex crystallizes selectively as the "syndiohelic" polymer which contains alternating left and right handed helical turns along the polymer chain. The helicity is induced by the amide links in the bis(pyridine) ligand.[27]

In some cases, hydrogen bonding between amide substituents can occur. Scheme 17 shows two tetragold(I) macrocycles **66**, which has intramolecular hydrogen bonds and aurophilic bonds, and **67**, which has neither. Both complexes have hydrogen bonds to anions.[27]

Complex **67** (Scheme 17) is formed with the diphosphine $Ph_2P(CH_2)_3PPh_2$ but, by increasing the chain length by one methylene group by using the diphosphine $Ph_2P(CH_2)_4PPh_2$, the polymer **68** can be isolated (Fig. 7). Individual polymer chains of **68** form $NH\cdots O{=}C$ hydrogen bonds to chains on either side to give a network structure as shown in Fig. 7.



Scheme 16 Ring-opening to give a syndiohelic polymer **65** (PP = $Ph_2PCH_2CH_2PPh_2$).



Scheme 17 Different forms of tetragold macrocycles with bis(amidopyridine) ligands.

A summary of this chemistry with gold(I), diphosphine and bis(pyridyl) ligands is shown in Scheme 18. Easy, reversible displacement of oxygen-donor anions X^- by the bis(pyridyl) ligand can give units with monodentate NN ligands. Depending on the geometry of the ligands, these compounds may form the simple ring, such as **64**, or associate to form the double ring, such as **67**, and these may undergo dynamic ring-opening reactions to give ring opened oligomers or polymers, such as **68**. The dynamic nature of these reactions allows crystalline products to be formed with very high selectivity, and so this system has given a particularly detailed picture of the mechanism of dynamic ring-opening polymerization.[25–27]

(d) Compounds of gold(I) with higher coordination numbers

The simplest 3-coordinate structures for a complex of gold(I) with a diphosphine ligand of form $[Au_2(PP)_3]^{2+}$ are **69** (all bridging diphosphines) and **70** (one bridging and two chelating diphosphines) in Scheme 19. Single ring-opening polymerization (ROP) of **69** or **70** can give the linear polymer **71** while double ROP can give the honeycomb structure **72**.[28]

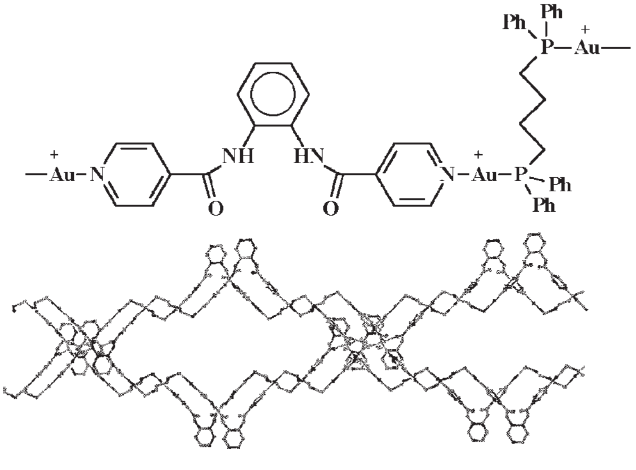
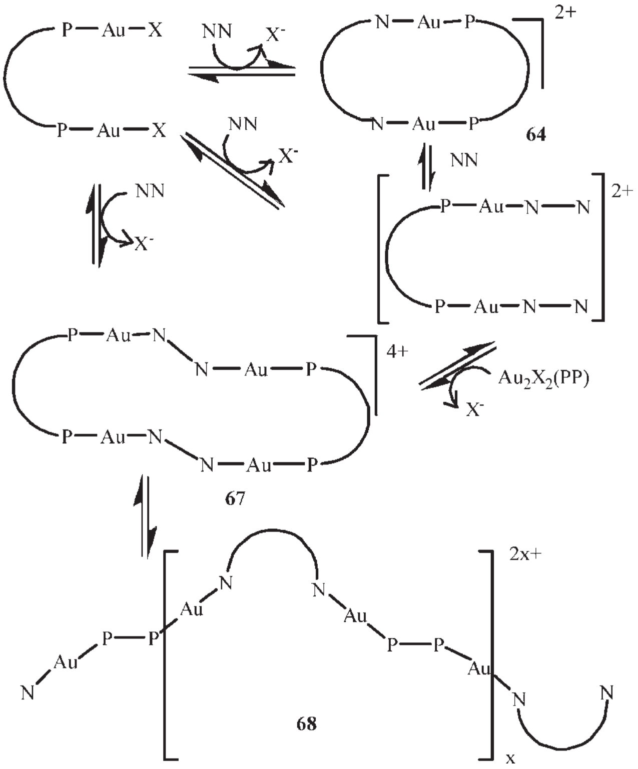


Fig. 7 The structure of polymer **68**, showing formation of a supramolecular network through inter-strand hydrogen bonding between amide groups.



Scheme 18 The equilibrium between ring **64**, double-sized ring **67**, ring-opened oligomers and polymer **68** (for structure of NN, see Scheme 17). The polymer **68** is favored if PP = $Ph_2P(CH_2)_4PPh_2$).

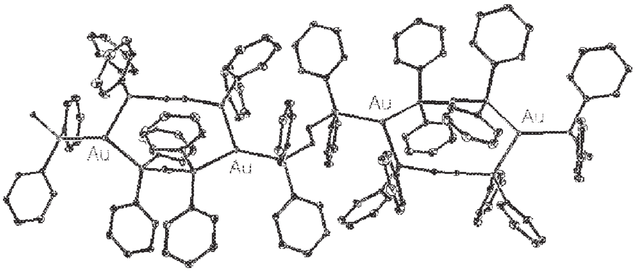
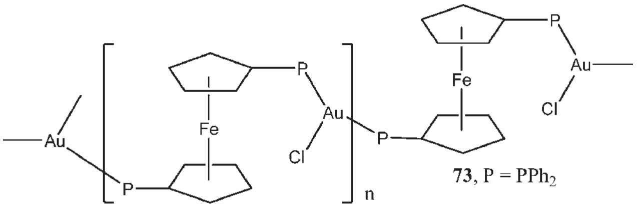


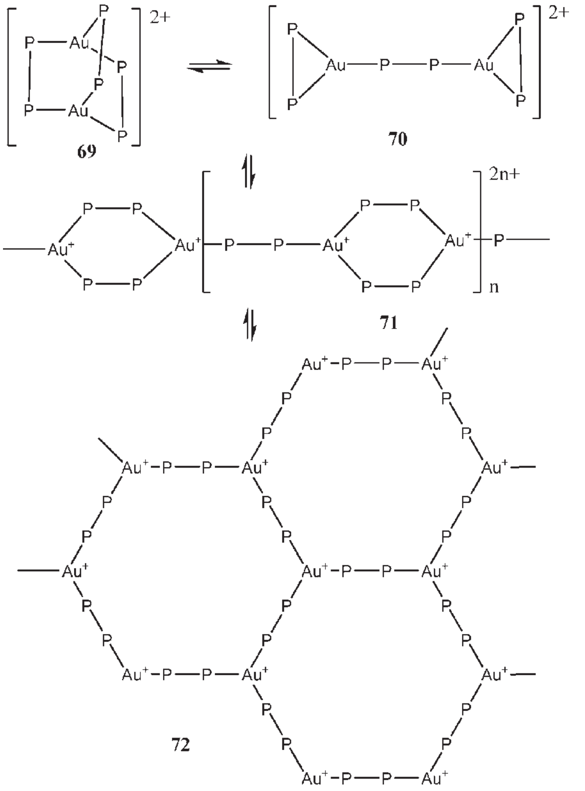
Fig. 8 The structure of polymer **71**.

The structure of a polymer of structural type **71**, with diphosphine PP = *trans*-$Ph_2PCH{=}CHPPh_2$, is shown in Fig. 8.

Another form of three-coordinate gold(I) polymer is complex **73**, which contains the $[\{AuCl(PP)\}_n]$ chains with a chloride ligand coordinated to each gold(I) centre.[3,28]



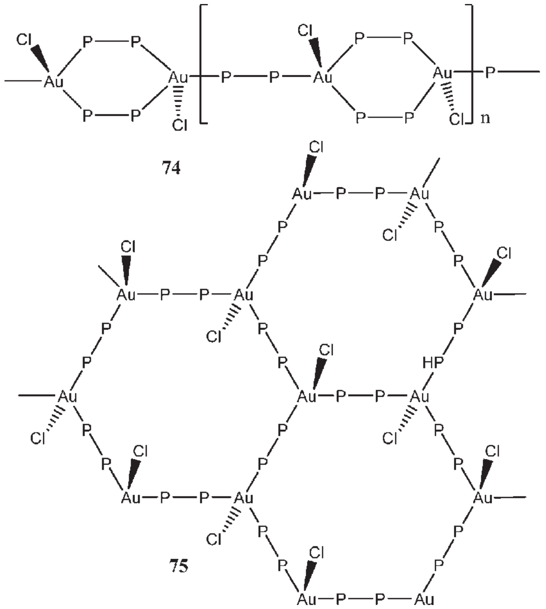
73, P = PPh_2



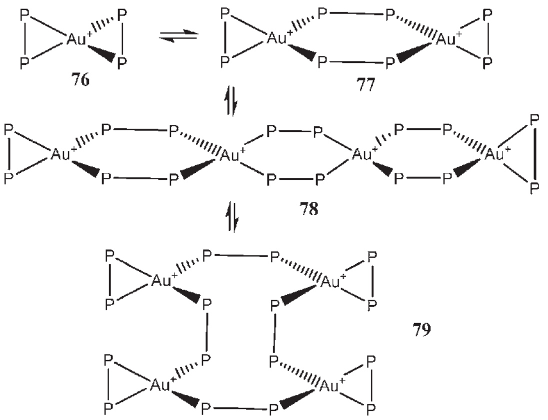
Scheme 19 Ring-opening polymerization to give a polymer and double ring-opening polymerization to give a honeycomb sheet structure.

Complex **73** is related to the two-coordinate gold(I) polymer **51**, $[\{Au(PP)\}_n]^{n+}$ by coordination of an anion to each gold(I) centre.[24,28] In a similar way, addition of chloride to each gold(I) centre in the polymer or honeycomb structure $[\{Au_2(PP)_3\}_n]^{2n+}$, **71** or **72**, can give the polymer or puckered sheet structure $[\{Au_2Cl_2(PP)_3\}_n]$, **74** or **75** (Scheme 20), in which the gold(I) centres are four-coordinate.[28]

Another route to four-coordinate macrocycles and oligomers is by ring-opening reactions of the *bis*(chelate) complex



Scheme 20 The polymer and puckered sheet structures **74** and **75** with four-coordinate gold(I) centres.

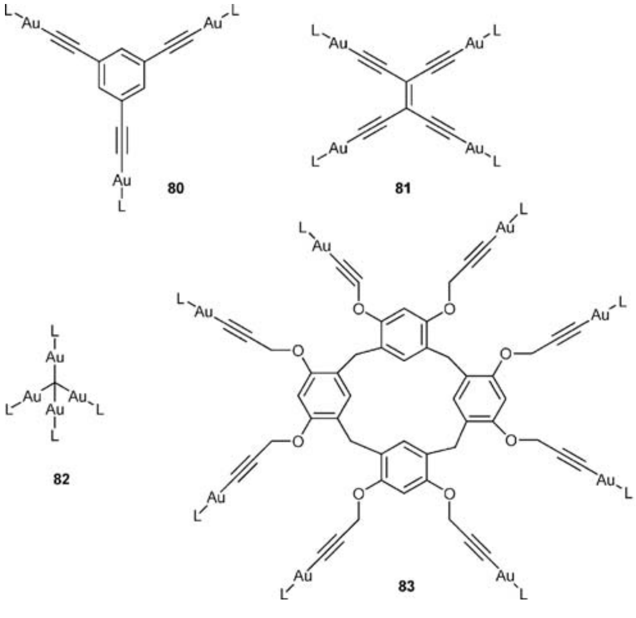


Scheme 21 Ring-opening oligomerization of four-coordinate gold(I) diphosphine complexes.

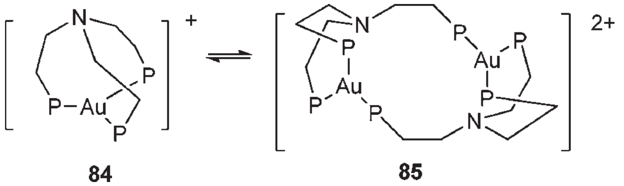
$[Au(PP)_2]^+$. Studies by NMR spectroscopy, with PP = $py_2P(CH_2)_2Ppy_2$ and py = 2-, 3- or 4-pyridyl, indicate that the reactions may occur according to Scheme 21, in which the bis(chelate) complex **76** may ring-expand to give **77** and then **78** or **79**.[28]

(e) Compounds with polydentate ligands

There are many polynuclear gold(I) complexes, such as the acetylide complexes **80–83** shown in Scheme 22 which can be described as starburst complexes. If the terminal ligand L is replaced by a bridging diphosphine, then insoluble complexes, which are likely to have sheet or network structures, are formed. The structures of these materials are likely to be interesting, but it is a considerable challenge to obtain them in crystalline form. The situation is similar with polythiolate or polyphosphine complexes.[16,29]



Scheme 22 Precursors to polymer, sheet or network materials containing alkynylgold(I) units.



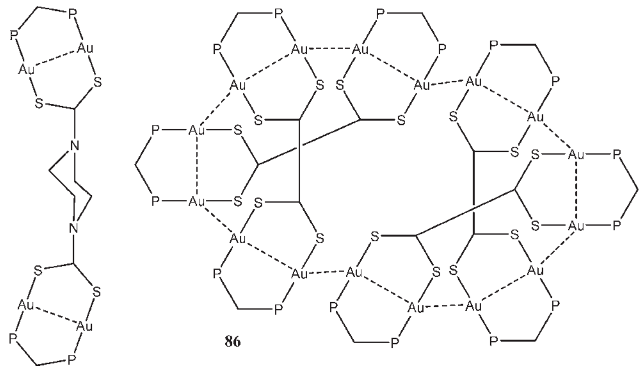
Scheme 23 Equilibrium between monomer and dimer.

One system in which the first step in potential ring-opening polymerization of such complexes is shown in Scheme 23. The trigonal gold(I) complex **84** can ring open to give the binuclear complex **85** (P = PPh_2).[30] Clearly, there is potential for further advances in this area.

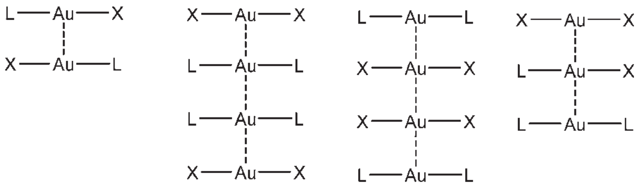
(f) Supramolecular macrocycles, oligomers, polymers and networks

Aurophilic bonding is a dominant feature of gold(I) chemistry and it can be used in the self-assembly of complex structures of many kinds. The self-assembly into cyclic arrays is not common, but a beautiful example of formation of a chiral cyclic supramolecular tetramer of tetranuclear gold(I) bis(dithiocarbamate) derivative **86** is shown in Scheme 24.[31]

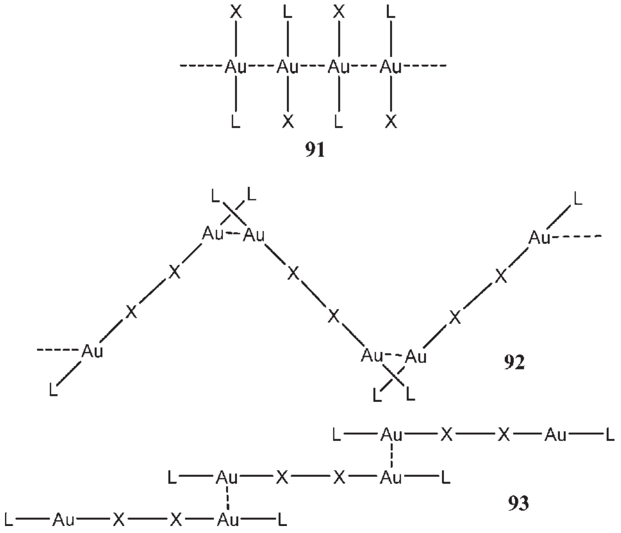
Dimers **87** or oligomers **88–90** (Scheme 25) are formed more commonly. If the components are ionic complexes $[AuL_2]^+$ and $[AuX_2]^-$, it is most common for the ions to alternate so that ionic attractions reinforce the aurophilic bonds. However, there are exceptions including the tetramers **88** (L = pyridine, X = Br) and **89** (L = PMe_2Ph, X = $GeCl_3$), in which the two central ions have like charge. There can be easy redistribution



Scheme 24 A chiral cyclic tetramer of a tetranuclear gold(I) bis(dithiocarbamate) complex.



Scheme 25 Supramolecular gold(I) oligomers.


91

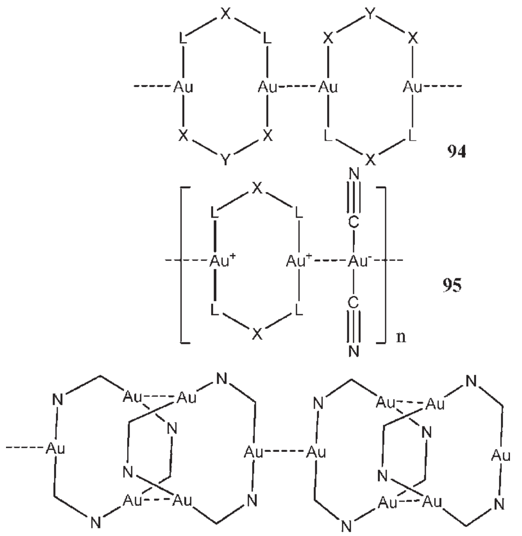
92

93

Scheme 26 Supramolecular gold(I) polymers.

of neutral and anionic ligands, and **90** (L = 2-aminopyridine, X = Cl) contains neutral [AuXL] with an aurophilic bond to both $[AuL_2]^+$ and $[AuX_2]^-$.[2,31] There are several cases in which it is established that complexes which form supramolecular polymers through aurophilic bonding in the solid state may break down to give oligomers analogous to **87–90** in solution, and that the aggregation has a particularly marked effect on the emission properties of the complexes.[31]

The most common form of supramolecular polymerization of gold(I) complexes is shown in structure **91** (Scheme 26). If the groups L and X are not sterically demanding (*e.g.* L = RNC, X = CN), then further association between these chains can occur to give ribbon or sheet structures.[2,13,15,32] If the molecule contains a linear or angular digold(I) unit, then polymers such as **92** or **93** can be formed, where X–X can represent a diacetylide ligand for example.[15,29]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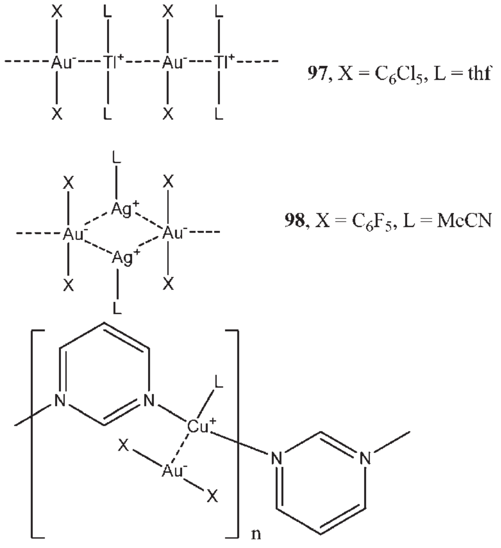
96

Scheme 27 Supramolecular polymers of macrocycles.


97, X = C_6Cl_5, L = thf

98, X = C_6F_5, L = MeCN

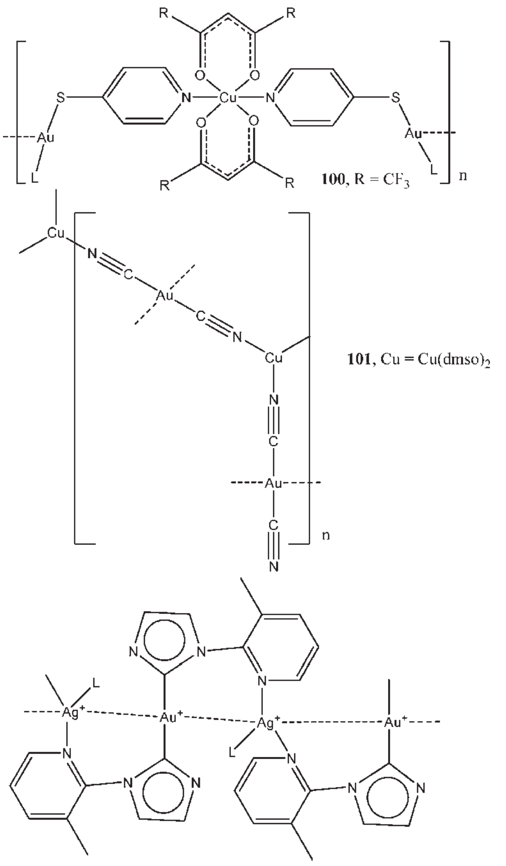
99, X = C_6F_5, L = MeCN

Scheme 28 Supramolecular polymers with Au···M metallophilic bonds.

Macrocyclic gold(I) complexes can also associate through aurophilic bonding to form polymers. For example, the diacetylide diphosphine bridged macrocycles such as **31** (Scheme 9) can self-assemble to give supramolecular polymers of general form **94** (Scheme 27).[19] Cationic diphosphine-bridged macrocycles of type **50** (Scheme 13) can self-assemble to form the polymer **95** (Scheme 27) in the presence of the anionic connecting ions $[Au(CN)_2]^-$.[24] Finally, the trigold(I) macrocycles such as [{Au(2-pyridyl)}$_3$] can self-assemble to give offset columnar polymeric structures such as **96** (Scheme 27, N–C = 2-pyridyl).[12]

Gold(I) can form secondary bonds to several other metal ions, especially with d^{10} or $d^{10}s^2$ electron configurations, and interesting supramolecular polymeric structures can result from these interactions. Complexes **97–99** (Scheme 28) contain Au···Tl, Au···Ag and Au···Cu metallophilic bonds. Complex **97** exhibits interesting vapochromic properties resulting from reversible displacement of solvent molecules at the thallium(I) centres.[33] In complex **99**, the gold(I) units are not part of the polymer backbone but are appended to the copper(I) centres.

Another important class of materials is formed by using gold(I) complexes as ligands and then using metallophilic bonds to increase dimensionality or to reinforce a polymeric structure. Some examples are shown in Scheme 29. In complex **100**, a 4-pyridinethiolate complex of gold(I) is used as a ligand for copper(II) hexafluoroacetylacetonate, and then aurophilic bonding causes self-assembly of a supramolecular polymer. A particularly impressive range of polymeric and network materials with interesting optical and magnetic properties has been developed by using $[Au(CN)_2]^-$ as a terminal or bridging ligand. One example, is the copper(II) complex **101** which forms a zigzag polymer through bridging dicyanoaurate ions, with a terminal dicyanoaurate ion also bound to each copper (II) centre. These primary polymer chains interdigitate to allow



100, R = CF_3

101, Cu = $Cu(dmso)_2$

102, L = EtCN

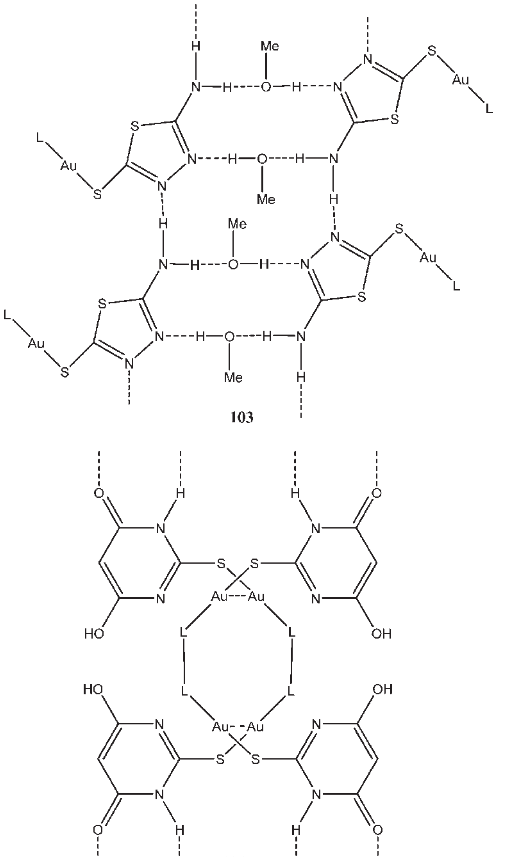
Scheme 29 Polymers formed by using gold(I) complexes as ligands.

Au···Au bonding, involving all $[Au(CN)_2]^-$ ligands, so as to form a network material. Other examples are known with primary sheet or network structures, which interconnect through aurophilic bonding. Complex **102** shows an example in which a pyridyl derivative of a carbene ligand bridges between gold(I) and silver(I) centres to form a helical polymer which is reinforced by intrachain Au···Ag interactions.[34]

Hydrogen bonding between gold(I) complexes can give another form of supramolecular polymer, as illustrated by **103** (Scheme 30), in which solvent methanol molecules are also involved in the self-assembly of a ribbon polymer. Of course, it is possible to combine hydrogen bonding with aurophilic bonding and an example is given in the thiobarbiturate complex **104**, which self-assembles to give a sheet structure. Many other examples of gold(I) oligomers, polymers and networks are currently under investigation because the hydrogen-bonding patterns are known from organic and biochemical precedent, so the structures can be engineered.[35]

3. Oligomers and polymers with gold(I) at the periphery

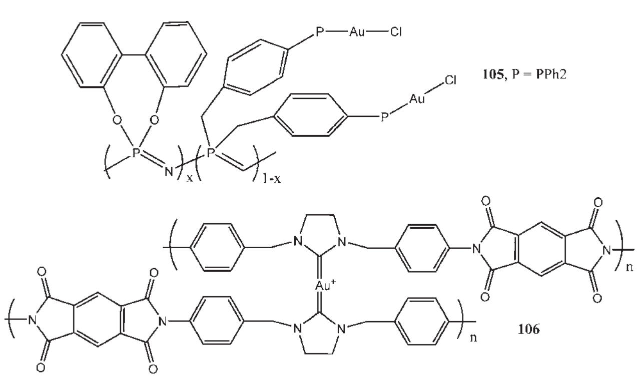
Insoluble polymers with functional side groups to coordinate to gold have long been used for recovery of gold from dilute solutions or to concentrate gold for analytical purposes, but there has been recent interest in the synthesis and properties of more soluble polymers for applications in materials or catalysis. Compound **105** in Scheme 31 is a polyphosphazene with diphenylphosphine donors appended to some of the side groups, which are used to bind gold(I) centres. Compound **106** contains gold(I) carbene units sandwiched between polymer chains.[36]



103

104

Scheme 30 Hydrogen bonded supramolecular polymers.

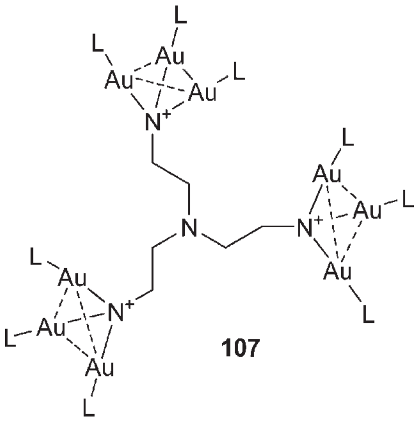


105, P = PPh2

106

Scheme 31 Polymers with appended gold(I) centres (P = PPh_2).

The synthesis of oligomers and polymers with highly branched architectures has been a topic of great interest. The first generation in a dendrimer contains a branched group such as complex **107**. This complex also illustrates how gold(I) units may cluster about a central atom, forming aurophilic bonds to neighbouring gold(I) centres.[37]



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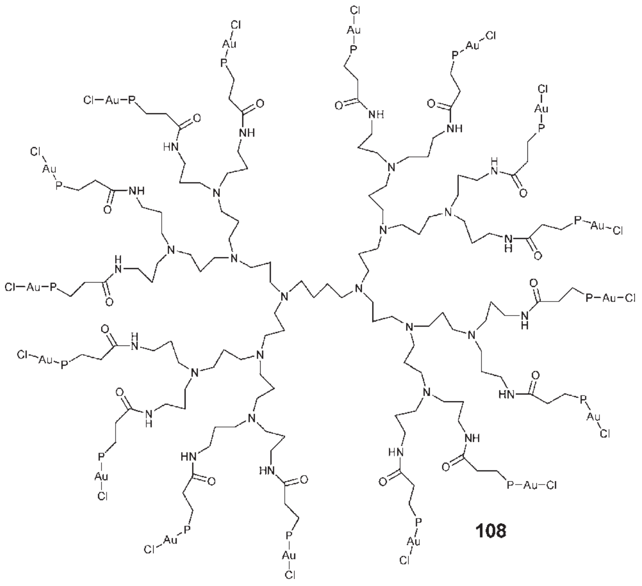
If further branches are added at each nitrogen atom with each generation, then the number of surface gold atoms increases rapidly. Compound **108** is derived from a polyamine dendrimer by conversion of the terminal $-NH_2$ groups to $-NHC(=O)CH_2CH_2PPh_2$ groups and then to $-NHC(=O)CH_2CH_2PPh_2AuCl$ groups by binding AuCl units to all of the terminal phosphine groups. Compound **108** contains 16 AuCl units, and the next generation contains 32 AuCl units. There are likely to be NH···O=C hydrogen bonds between amide groups and Au···Au aurophilic bonds between some of the surface gold(I) centres in these dendrimers.[37]



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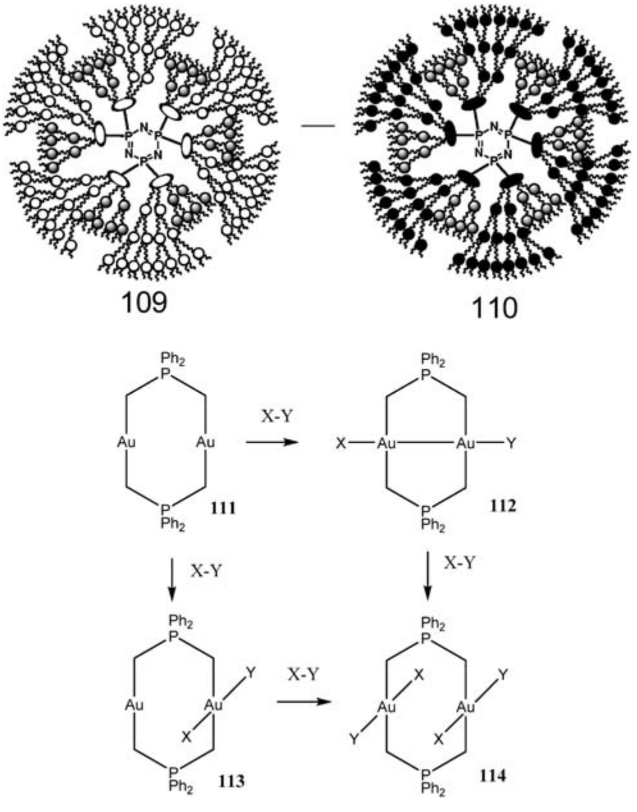
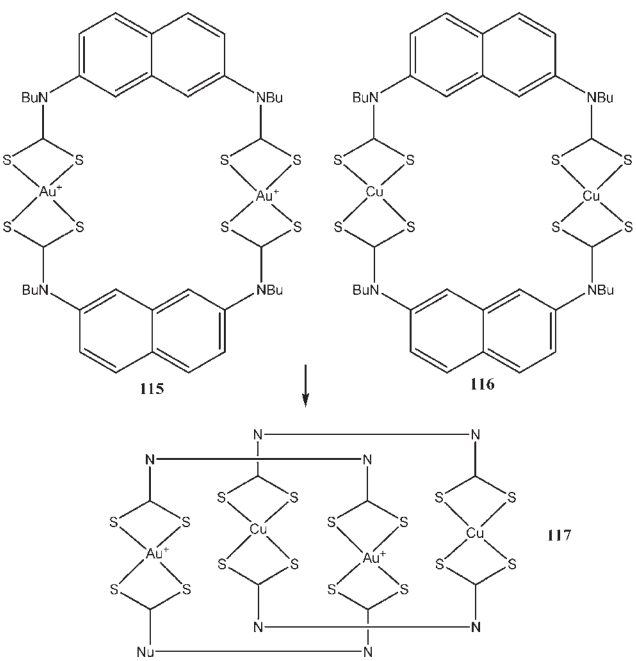
In another strategy, dendrimers containing P=N–P=S, P = N–P=N–P=S and $-PR_2$ units have been prepared and AuCl units were then added to the phosphine sulfide or phosphine donor groups. In the representations in Scheme 32, **109** represents a precursor dendrimer and **110** represents the dendrimer saturated by addition of 90 AuCl units. In these representations, open circles represent $CH_2-PPh_2=N-P=S$ units and open ovals represent $CH_2-PPh_2=N-P=N-P=S$ units, while the closed circles and ovals represent the corresponding units in which the P=S groups are converted to P=S–Au–Cl groups. It can be seen that, in these compounds, AuCl units can be added at both surface and internal sites of the dendrimer. By using related strategies, dendrimers containing thousands of gold atoms have been prepared. The compounds can be further derivatized by replacement of the chloride ligands on gold(I) by metal carbonyl and other anions. It has also been possible to reduce gold complexes in the pores of dendrimers to give dendrimers containing encapsulated gold nanoparticles.[37]

4. Macrocycles, catenanes, oligomers and polymers in gold(II) and gold(III) chemistry

Most gold(II) compounds are formed by oxidative addition to macrocyclic digold(I) complexes and so they are naturally formed within a ring structure (Scheme 32), but there has not yet been a concerted attempt to develop polymers or larger macrocycles from these compounds. There may be an equilibrium between digold(II) and mixed oxidation state gold(I)–gold(III) complexes. Scheme 32 illustrates chemistry based on phosphine ylides as bridging ligands, but several other systems are known, and guanidinate and formamidinate derivates may give particularly short Au(II)–Au(II) distances. Complex **111** can act as a precursor to gold(II)–gold(II) complexes **112** (*e.g.* X = Cl, Y = CCl_3), gold(I)–gold(III) complexes **113** (*e.g.* X = Y = Me), and gold(III)–gold(III) complexes **114** (*e.g.* X = Y = Cl).[2,38]



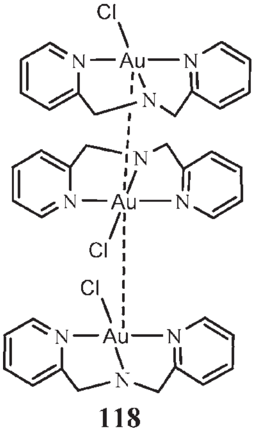
Scheme 32 (a) Dendrimers containing P=S (**109**, open circles) and P=S–Au–Cl units (**110**, closed circles). (b) Cyclic Au(I)Au(I), Au(II)Au(II), Au(I)Au(III) and Au(III)Au(III) complexes.



Scheme 33 A digold(III) macrocycle and a rare mixed-metal [2]catenane.

There are some very elegant macrocyclic gold(III) dithiocarbamate complexes, such as **115** in Scheme 33, which contains cationic gold(III) centres. This complex reacts with the corresponding neutral copper(II) complex **116** to form a mixed metal [2]catenane derivative **117**. The key to success in forming the [2]catenane selectively was to maximise the favourable bonding interactions between acceptor gold(III) and donor copper(II) centres by adjusting the size of the spacer groups.[39]

The polymer chemistry of gold(III) is not well-developed but there are some supramolecular polymers. For example, the cationic amidogold(III) complex can pack in columns in **118** or form a polymer **119** by alternate Au(III)···Au(I) aurophilic bonds and secondary Cl···Au(III) bonds.[39]



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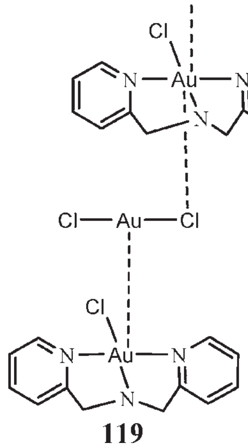

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5. Conclusions

The above examples illustrate how gold chemistry is an important component in the rapid recent developments in the field of inorganic and organometallic macrocycles, polymers and molecular materials. The dynamic coordination chemistry and preference for linear stereochemistry of gold(I) has allowed the formation of crystalline polymers and network materials, whose structures can be determined to provide a firm foundation for further development. The use of chiral ligands can give polymers with high stereoselectivity. Dynamic ring-opening polymerization is a particularly useful method for the synthesis of polymers, and both sheet and network structures. The ability of gold to form aurophilic attractions, which can be used alone or in combination with hydrogen bonding and other secondary bonding interactions, provides a tool for increasing the dimensionality of ring and polymer structures or to form supramolecular materials by self-assembly processes. Berthelot's comment in 1860 that "*la chimie cree son propre objet*" is well illustrated by the creative syntheses described above. The gold centres have useful properties for photonics and catalysis, so these synthetic advances should prove useful in the design of functional molecular materials.

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