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Coordination polymers: polymers, rings and oligomers containing gold(I) centres

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Contents

Abstract

A personal view is given of current research in the synthesis of macromolecules containing linear gold(I) centres. These range from conjugated, rigid-rod polymers to macrocyclic compounds, including novel catenanes and a doubly braided catenane formed in high yield by simple self assembly. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Coordination polymers; Linear gold(I) centres; Catenanes

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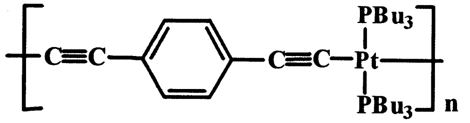
1. Introduction

This article describes the synthesis and characterization of some new types of oligomers, polymers and rings with gold atoms in the backbone. These compounds form a small part of the more general field of metal-containing polymers, which are of interest since they might have unusual optical or electrical properties, with the associated potential applications, or they might be useful as precursors to other materials. It is not possible to give a general review, acknowledging the important contributions of other groups, but it should be noted that many simple gold(I) polymers and oligomers are known, including the simple halogen-bridged gold(I) halides [1], and the sulfur-bridged gold(I) thiolates that have application in chrysotherapy [1,2]. The first part of this review describes gold(I) complexes with strictly linear bridging ligands such as dialkynyl ligands and the related, but neutral, diisocyanide ligands, and it should be noted that similar approaches have been made with other metals. For example, the rigid rod polymers $[Pt(PBu_3)_2(\mu\text{-}C{\equiv}C\text{–}R\text{–}C{\equiv}C\text{–}]_n$ (**1**), R = aryl spacer group, have been reported [3,4], and polymers are now known with Pt–Pt bonds and even Pt_3 cluster units in the backbone as illustrated by **2** and **3**, PP = $Ph_2PCH_2PPh_2$ [5,6]. This article begins by describing rigid-rod polymers containing gold(I) centres and then goes on to explore the impact of allowing greater or lesser amounts of flexibility in the bridging ligands used to make the polymers. Linear ‘molecular wires’ and catenated ‘molecular switches’ may be formed.



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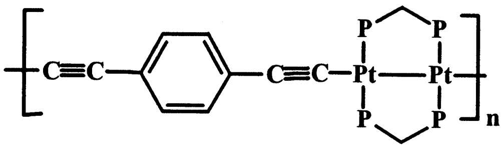

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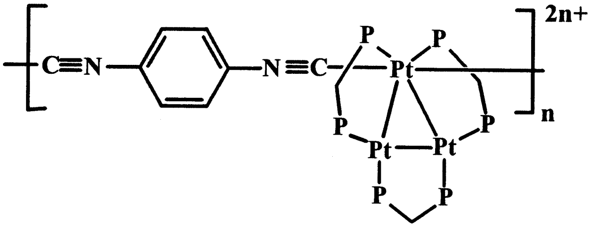

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2. Linear gold(I) oligomers and polymers: diisocyanides and diacetylides or isocyanoacetylides

Gold(I) tends to have a coordination number of two with linear stereochemistry [1], so it is well-suited to form linear rigid-rod polymers. If neutral polymers are to be formed, one neutral ligand L and one anionic ligand X^- are required for each gold(I) centre. Suitable ligands might then include $L–R–X^-$, where R is a linear spacer group, and L might be an isocyanide and X^- an acetylide. Alternatively, one ligand L–R–L and $^-X–R–X^-$ could be used for each two gold(I) centres. Cationic polymers could be prepared if all donors are neutral. Some of the polymers targeted are then shown as **4**–**6**. Since many of these polymers proved to be insoluble, it has been important to prepare model compounds containing only two gold(I) atoms, by using capping monodentate ligands in combination with one bridging ligand, in order to optimise the synthetic methods and to facilitate characterization of the polymers.

$$-\!\!\left[\mathrm{L{-}L{-}Au{-}X{-}X{-}Au}\right]_n\!\!- \qquad \mathbf{4}$$

$$-\!\!\left[\mathrm{L{-}X{-}Au{-}L{-}X{-}Au}\right]_n\!\!- \qquad \mathbf{5}$$

$$-\!\!\left[\mathrm{L{-}L{-}Au{-}L{-}L{-}Au}\right]_n^{2n+}\!\!- \qquad \mathbf{6}$$

The most successful synthetic route to isocyanide(alkynyl)gold(I) complexes is by reaction of oligomeric or polymeric compounds $(AuC{\equiv}CR)_n$, in which the alkynyl ligand bridges by bonding to one gold atom through the σ-donor and to a second gold atom using its π-electrons [7], with an isocyanide ligand. Although the simplest derivative Au_2C_2 has been known for many years, the more stable digold diacetylides $(AuC{\equiv}C–Ar–C{\equiv}CAu)_n$ (**7**), needed for this work were unknown and were prepared according to Eq. (1), B = base, in which the aryl spacer group Ar = 1,4-C_6H_4, 4,4′-$C_6H_4C_6H_4$ or 1,4-(2,5-$Me_2C_6H_2$) [8].

$$2[\mathrm{Me_2SAuCl}] + \mathrm{HCC{-}Ar{-}CCH} + 2\mathrm{B}$$
$$\rightarrow 2\mathrm{Me_2S} + 2\mathrm{BH^+Cl^-} + \{\mathrm{Au{-}C{\equiv}C{-}Ar{-}C{\equiv}C{-}Au}\}_n \qquad (1)$$

Suitable binuclear gold(I) model compounds $[RN{\equiv}CAuC{\equiv}C–Ar–C{\equiv}CAuC{\equiv}NR]$ (**8**) (R = *t*-Bu or Xy = 2,6-dimethylphenyl), and $[RC{\equiv}CAuC{\equiv}N–Ar–N{\equiv}CAuC{\equiv}CR]$ (**9**) (R = *t*-Bu or Ph, Ar = 1,4-C_6H_4, 1,4-(2-MeC_6H_3), 1,4-(2,6-*t*-$Bu_2C_6H_2$), 1,4-(C_6Me_4), 1,4′-(2,6-$Me_2C_6H_2$)$_2$), were then prepared as shown in Eqs. (2) and (3) [8].

$$1/n\ \{\mathrm{AuCC{-}Ar{-}CCAu}\}_n + 2\mathrm{RNC}$$
$$\rightarrow [\mathrm{RN{\equiv}C{-}Au{-}C{\equiv}C{-}Ar{-}C{\equiv}C{-}Au{-}C{\equiv}NR}]\ (\mathbf{8}) \qquad (2)$$

$$2/n\ \{\mathrm{AuCCR}\}_n + \mathrm{CN{-}Ar'{-}NC} \rightarrow [\mathrm{RC{\equiv}C{-}Au{-}C{\equiv}N{-}Ar'{-}N{\equiv}C{-}Au{-}C{\equiv}CR}]\ (\mathbf{9}) \qquad (3)$$

The products are molecular in nature but they associate in the solid state either through π-stacking between aryl groups of neighbouring molecules or, more commonly, through intermolecular Au···Au bonding [8,9]. These weak Au···Au interactions, which are known in several other classes of gold(I) complexes, are thought to have strengths from 5–10 kcal mol^{-1}, similar to the strength of hydrogen bond, and are thought to arise from relativistic London forces [10]. The association present in crystals of [$PhC{\equiv}C{-}Au{-}C{\equiv}N{-}t{-}Bu_2C_6H_2{-}N{\equiv}C{-}Au{-}C{\equiv}CPh$] comprises both aryl π-stacking and Au···Au bonding and is shown in Fig. 1.

It was then possible to prepare polymers, **10**, containing alternating diacetylide and diisocyanide ligands according to Eq. (4) (see above for definitions of Ar and Ar′). The polymers are insoluble, as predicted since intermolecular association through π-stacking and/or Au···Au bonding will lead to effective crosslinking of the linear rigid-rods into a three-dimensional network. Though each individual interaction is likely to be weak, the combination of many interactions for each polymer chain can give strong crosslinking leading to insolubility. The polymers are therefore characterised only in the solid state by elemental analysis and by comparison of spectroscopic data with those of the well-characterised model compounds [8].

$$\begin{aligned}&1/n\ \{AuCC{-}Ar{-}CCAu\}_n + CN{-}Ar'{-}NC\\&\rightarrow \{{-}Au{-}C{\equiv}C{-}Ar{-}C{\equiv}C{-}Au{-}C{\equiv}N{-}Ar'{-}N{\equiv}C{-}\}_n]\ (\mathbf{10})\end{aligned} \tag{4}$$

One interesting property of these gold(I) complexes is that they are emissive at room temperature either in the solid state or in solution [9,11]. The emission is

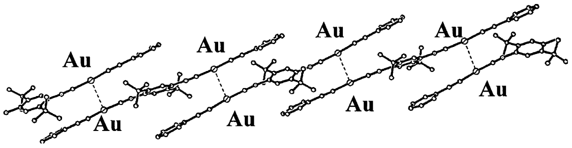


Fig. 1. The intermolecular association present in the solid state structure of [$PhC{\equiv}CAuC{\equiv}N{-}tBu_2C_6H_2{-}N{\equiv}CAuC{\equiv}CPh$] due to Au···Au bonding [Au···Au = 3.174(1) Å].

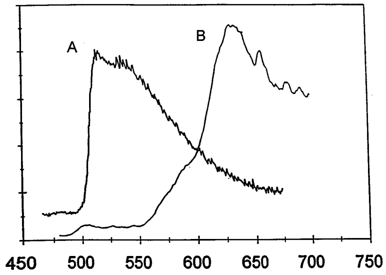


Fig. 2. The emission spectra of $XyNC{-}Au{-}CCC_6H_4{-}4{-}NO_2$; (A) in solution in CH_2Cl_2 and (B) in the solid state, showing the red shift in the solid state.

strongly red-shifted in the solid compared to solution state as illustrated in Fig. 2, particularly when Au···Au bonding or π-stacking is present in the solid state structures. In addition, there is a red shift in the emission and a decrease in emission intensity as the molecules increase in size, as illustrated for the solid state spectra shown in Fig. 3, and this provides evidence for at least some π-conjugation in the rigid-rod chains [9].

The new ligands 4-$HC{\equiv}CC_6H_4N{\equiv}C$ and 4-$HC{\equiv}C$-2-$MeC_6H_3N{\equiv}C$ bind readily to gold(I) in forming the complexes such as [4-$HC{\equiv}CC_6H_4N{\equiv}C$–Au–Cl] (**11**), and [4-$HC{\equiv}C$-2-$MeC_6H_3N{\equiv}C$–Au–C≡C-*t*-Bu] (**12**). The acetylide derivatives such as **12** give a weak Au···Au bonded association in the solid state (Au···Au = 3.479(2) Å) and form oligomeric complexes H-(C≡C–Ar–N≡C–Au–)$_n$–C≡C-*t*-Bu (**13**), by elimination of *t*-BuCCH as illustrated in Scheme 1 [12]. The oligomers tend to precipitate from solution when $n = 4–6$ and then no further chain growth occurs.

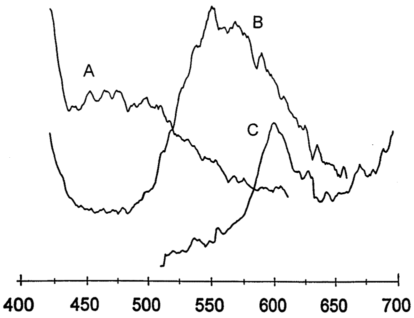
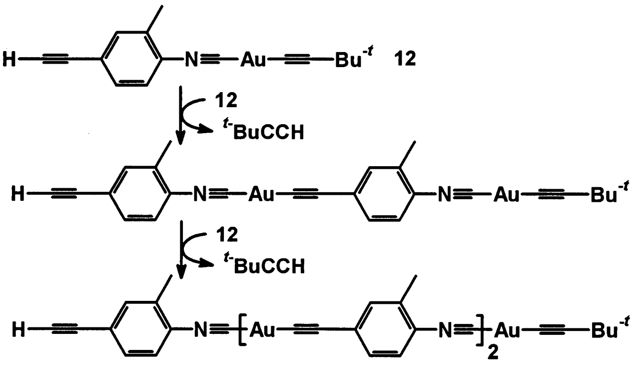


Fig. 3. The solid-state emission spectra of gold(I) complexes: (A) [*t*-BuN≡C–Au–C≡CPh]; (B) [XyN≡C–Au–CCC_6H_4–C_6H_4CC–Au–C≡NXy] and (C) [{Au–C≡C–$C_6H_2Me_2$–C≡C–Au–C≡N–C_6H_2(*t*-Bu_2)–N≡C}$_n$]. There is a red shift with increasing molecular size.



Scheme 1.

3. Introducing a bend: compounds with diphosphines and diacetylides or phosphinoacetylides

Diphosphines cannot give strictly linear rigid-rod compounds since there will be a tetrahedral angle at each phosphorus atom. The question then arises as to whether these ligands will give polymers at all, since ring formation is also possible.

The digold(I) diacetylides described above can be capped with monodentate phosphine ligands such as PMe_3 to give binuclear model complexes such as $[Me_3P–Au–C\equiv C–C_6H_2Me_2–C\equiv C–Au–PMe_3]$ (**14**), and this forms loose polymers in the solid state by intermolecular Au···Au bonding (Fig. 4) [9,13]. The diphosphines $Ph_2P–C_6H_4–PPh_2$ or i-$Pr_2P–C_6H_4–C_6H_4–P$–i-Pr_2 can also give binuclear model complexes such as $PhC\equiv C–Au$–i-$Pr_2P–C_6H_4–C_6H_4–P$–i-$Pr_2–Au–C\equiv CPh$ (**15**), which has the *anti* conformation with respect to the two P–Au vectors as shown in Fig. 5; the bulky *i*-Pr groups prevent the formation of intermolecular Au···Au bonding in **15**. It is then straightforward to prepare polymers $(Au–C\equiv C–Ar–C\equiv C–Au–PR_2–Ar'–PR_2–)_n$ (**16**), incorporating both diphosphine and diacetylide bridges. It is likely that the *anti* conformation of the P–Au vectors in **15** is maintained in these polymers, which are sufficiently soluble when R = *i*-Pr to allow molecular weight determination by GPC. The improved solubility probably arises because the bulky *i*-Pr groups prevent crosslinking by intermolecular Au···Au bonding.

It is possible to tailor the system to give rings instead of polymers. Thus, ligands $R_2PCH_2PR_2$ give digold complexes in which the *syn* conformation of the two P–Au vectors is preferred so as to allow intramolecular Au···Au bonding, as for example in $CH_2(PCy_2–Au–\ O_2CCF_3)_2$ (**17**), or $CH_2(PPh_2–Au–C\equiv C$–t-$Bu)_2$ (**18**), shown in

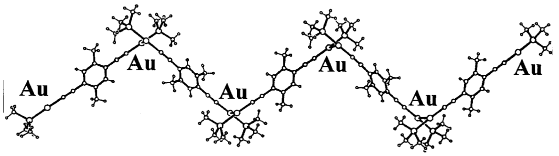


Fig. 4. Association through Au···Au bonding in $[Me_3P–Au–C\equiv C–C_6H_2Me_2–C\equiv C–Au–PMe_3]$.

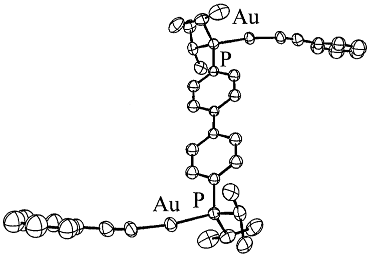


Fig. 5. The *anti* conformation of the P–Au vectors in $[PhC\equiv C–Au$–i-$Pr_2P–C_6H_4–C_6H_4–P$–i-Pr_2–$Au–C\equiv CPh]$ (**15**).

Fig. 6 [14,15]. This conformation is maintained on reaction of **17** with rigid rod bridging ligands and so large rings are formed in $[CH_2(PR_2–Au–C\equiv C–Ar–C\equiv C–Au–PR_2)_2CH_2]$ (**19**), or $[CH_2(PR_2–Au–C\equiv N–Ar–N\equiv C–Au–PR_2)_2CH_2]^{4+}$ (**20**). The structure of the complex **20** with R = cyclohexyl and the bridging ligand 1,4-$C\equiv N–C_6H_4–N\equiv C$ is shown in Fig. 7.

It is also possible to used mixed phosphine-acetylide donors in forming polymers of gold(I). Thus the ligands $Ph_2PC\equiv CH$ and *i*-$Pr_2PC\equiv CH$ form model complexes $HC\equiv CPR_2–Au–Cl$ which, on treatment with base, can eliminate HCl to give the polymers $[\{R_2PC\equiv C–Au–\}_n]$ (**21**) [16].

4. Increasing the bend: compounds with angular diacetylides or triacetylides

In the complexes with diphosphines or phosphinoacetylides, the chains are not strictly linear because of the tetrahedral angle at phosphorus, yet polymers can still be formed in preference to the alternative ring structures. What will happen if another angle is introduced in the diacetylide bridge? The dialkyne 1,3-$(HC\equiv C)_2$-5-MeC_6H_3 yields digold(I) model complexes 1,3-$(L–Au–C\equiv C)_2$–5-MeC_6H_3 (**22**), L = phosphine, phosphite or isocyanide ligand, which form ribbon structures in the solid state through Au···Au bonding as seen in Fig. 8 [17].

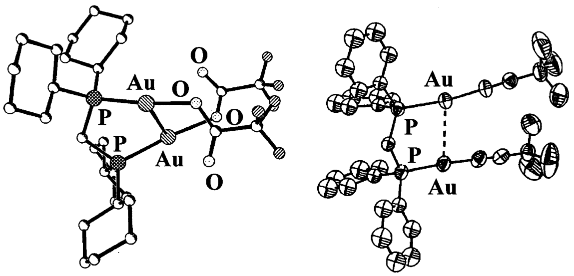


Fig. 6. The *syn* conformation of the P–Au vectors in $[CH_2(PCy_2–Au–O_2CCF_3)_2]$ (**17**), and $[CH_2(PPh_2–Au–C\equiv C–t\text{-}Bu)_2]$ (**18**).

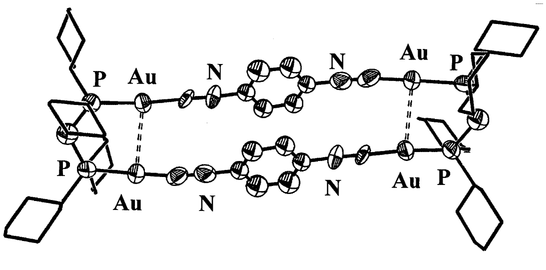


Fig. 7. The structure of the cationic ring complex **20**, R = Cy and Ar = 1,4-C_6H_4.

Kinked polymers such as **23** are formed when linear diisocyanide ligands are used but, if the neutral bridging ligand is also non-linear, then ring structures such as **24** are formed instead (Scheme 2) [17].

If a third acetylide link is added as in 1,3,5-$(HC{\equiv}C)_3C_6H_3$, the gold derivatives can in principle form more complex network polymers either through intermolecular Au···Au bonding or through the use of bridging ligands. The capped complexes 1,3,5-$(L{-}Au{-}C{\equiv}C)_3C_6H_3$, (**25**), are found to form one-dimensional ribbon structures in the solid state with one gold atom not taking part in Au···Au bonding (Fig. 9). With all bridging ligands, whether the strictly linear diisocyanides or angular diphosphines, insoluble polymers, **26**, are formed (Scheme 3) [18].

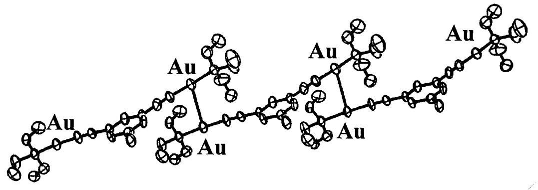
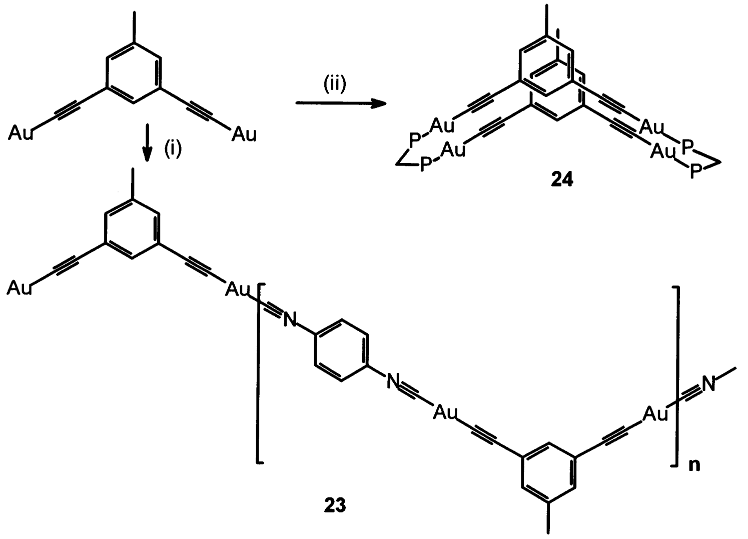


Fig. 8. The intermolecular association through Au···Au bonding in the complex $[1,3\text{-}(L{-}Au{-}C{\equiv}C)_2\text{-}5\text{-}MeC_6H_3]$, $L = P(OMe)_3$.



Scheme 2.

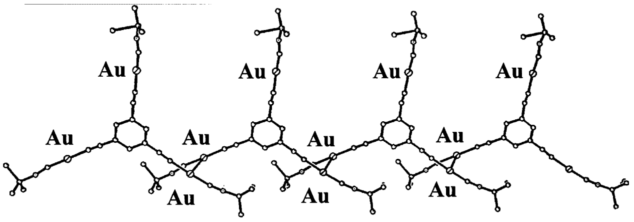
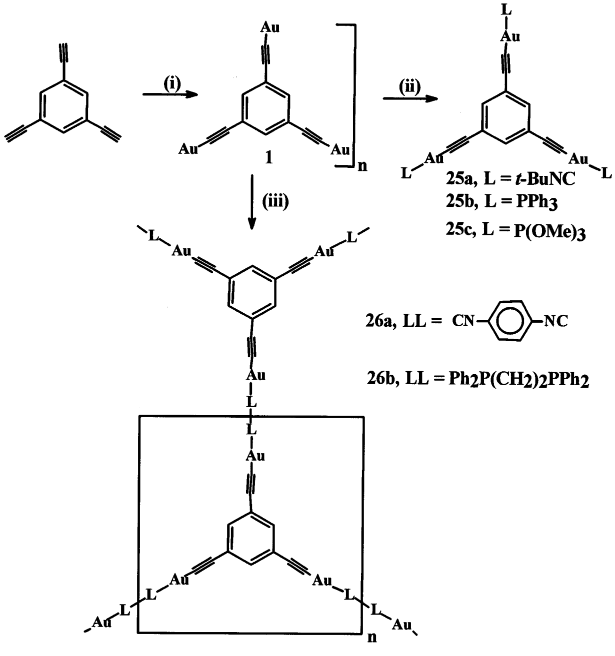


Fig. 9. The intermolecular association through Au···Au bonding in the complex [1,3,5-(L–Au–C≡C)$_3$C$_6$H$_3$], L = *t*-BuN≡C.

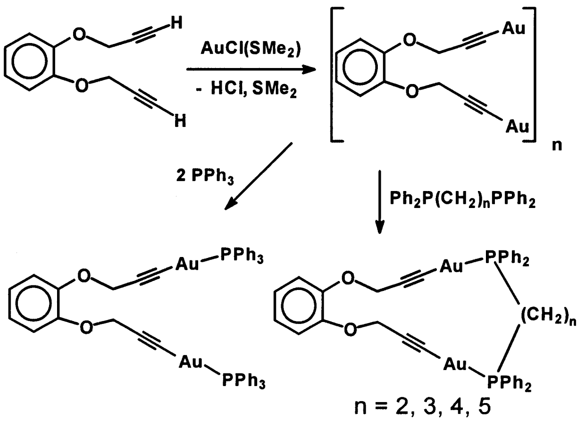


Scheme 3.

5. Catenanes and double catenanes: compounds with diphosphines and flexible diacetylides

If a flexible diacetylide is used in this chemistry, it is easy to form ring complexes. For example, digold(I) derivatives of the acetylides formed from *o*-, *m*- or *p*-$C_6H_4(OCH_2CCH)_2$ and diphosphines all form simple ring complexes as shown in Scheme 4 for the *ortho* derivatives and Fig. 10 for selected *meta* and *para* derivatives [19].

As the ring size is increased, the cavity size becomes large enough to allow catenation. Thus, based on the dialkyne $Me_2C(C_6H_4OCH_2CCH)_2$, the digold(I) complex with $Ph_2P(CH_2)_nPPh_2$ is a simple ring when $n = 2$, exists in solution as an



Scheme 4.

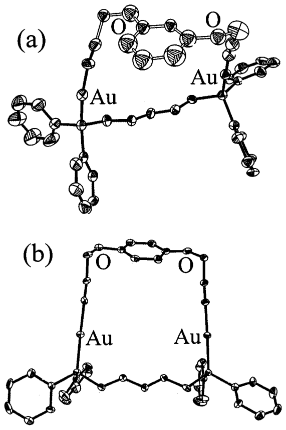
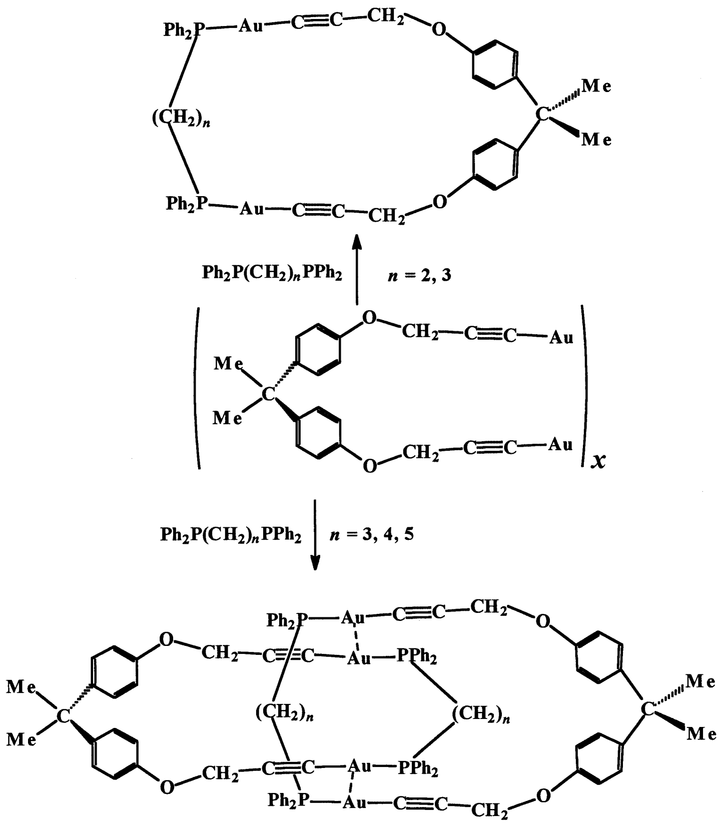


Fig. 10. The structures of [$C_6H_4(OCH_2CCAu)_2\{\mu\text{-}Ph_2P(CH_2)_5PPh_2\}$]. (a) *meta* derivative and (b) *para* derivative.

equilibrium between ring and catenane when $n = 3$, and exists as a catenane only when $n = 4$ or 5 (Scheme 5). The catenane when $n = 3$ contains short Au···Au contacts but not when $n = 4$ (Fig. 11) [20].

The most interesting discovery is that changing the hinge atom X in the compounds $X(C_6H_4OCH_2CCH)_2$ can lead to major changes in the gold(I) chemistry. Thus, in reactions with $Ph_2P(CH_2)_4PPh_2$, the products are simple rings when $X = O$ or S, the [2] catenane when $X = Me_2C$ and a novel double braid catenane when $X = C_6H_{10}$ (cyclohexylidene). The double braid catenane self-assembles very selectively from eight components in high yield. The structure of this remarkable complex is shown in Fig. 12. It undergoes an interesting switching motion in solution as shown by variable temperature ^1H and ^{31}P NMR spectroscopy (Fig. 13) [20].



Scheme 5.

Another interesting complex is formed from the bis(alkyne) $(CH_2OC_6H_4-OCH_2CCH)_2$, which forms a simple ring complex with $Ph_2P(CH_2)_4PPh_2$, but the cavity is large enough for two rings to associate in the solid state through Au···Au bonding and with a phenyl group of one ring penetrating the cavity of the other as shown in Fig. 14 [19].

6. Cationic chains and rings: compounds with diphosphine and bis(pyridyl) ligands

The principles determining if rings or polymers would be formed were now understood in general terms but the detailed structures of the polymers could not be determined since they could not be crystallised. To overcome this problem, gold(I) complexes were formed using flexible diphosphine ligands $(CH_2)_n(PPh_2)_2$ and a more labile linear bridging ligand *trans*-1,4- bis(pyridyl)ethylene. It was argued that the intramolecular Au···Au bonding interactions would decrease progressively with increasing n and so the preferred structure would switch from the

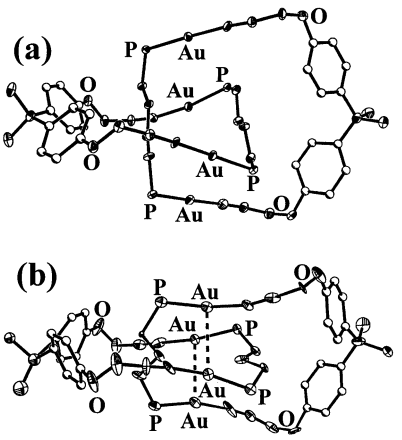


Fig. 11. Structures of the [2]-catenanes $[Me_2C(C_6H_4OCH_2CCAu)_2\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}]_2$. (a) $n = 4$ and (b) $n = 3$. Phenyl groups are omitted for clarity.

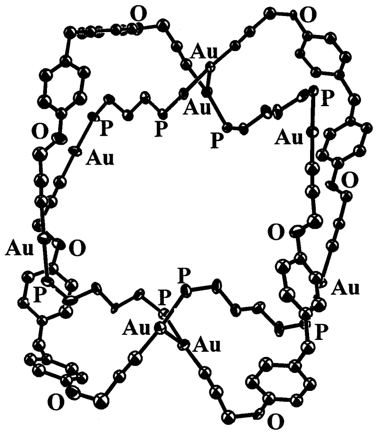


Fig. 12. Structure of the double braid [2]-catenane $[\{C_6H_{10}(C_6H_4OCH_2CCAu)_2\{\mu\text{-}Ph_2P(CH_2)_4PPh_2\}\}_2]_2$. The phenyl groups and omitted and only the *ipso*-carbons of the cyclohexylidene groups are shown.

large rings to polymers at some point in the series (Scheme 6). Further, the polymers could reversibly cleave to smaller fragments in solution due to the lability of the pyridine donors and this might allow crystallisation and so the full structural characterisation of the polymers [21].

With $(CH_2)_2(PPh_2)_2$, the ring structure $[Au_4(\mu\text{-}Ph_2PCH_2CH_2PPh_2)_2(\mu\text{-}NC_5H_4CH{=}CHC_5H_4N)_2]^{4+}$, (**27**), is preferred as shown in Fig. 15 but the Au···Au distance of 3.625(3) Å indicates very weak Au···Au bonding and no significant Au···Au attraction is expected for higher values of n [21].

The switch to a polymeric structure $[\{Au_2(\mu\text{-}Ph_2P(CH_2)_nPPh_2)(\mu\text{-}NC_5H_4CH{=}CHC_5H_4N)\}_n]^{2n+}$ (**28**), occurs when $n = 3$ and the polymer **28a** has an

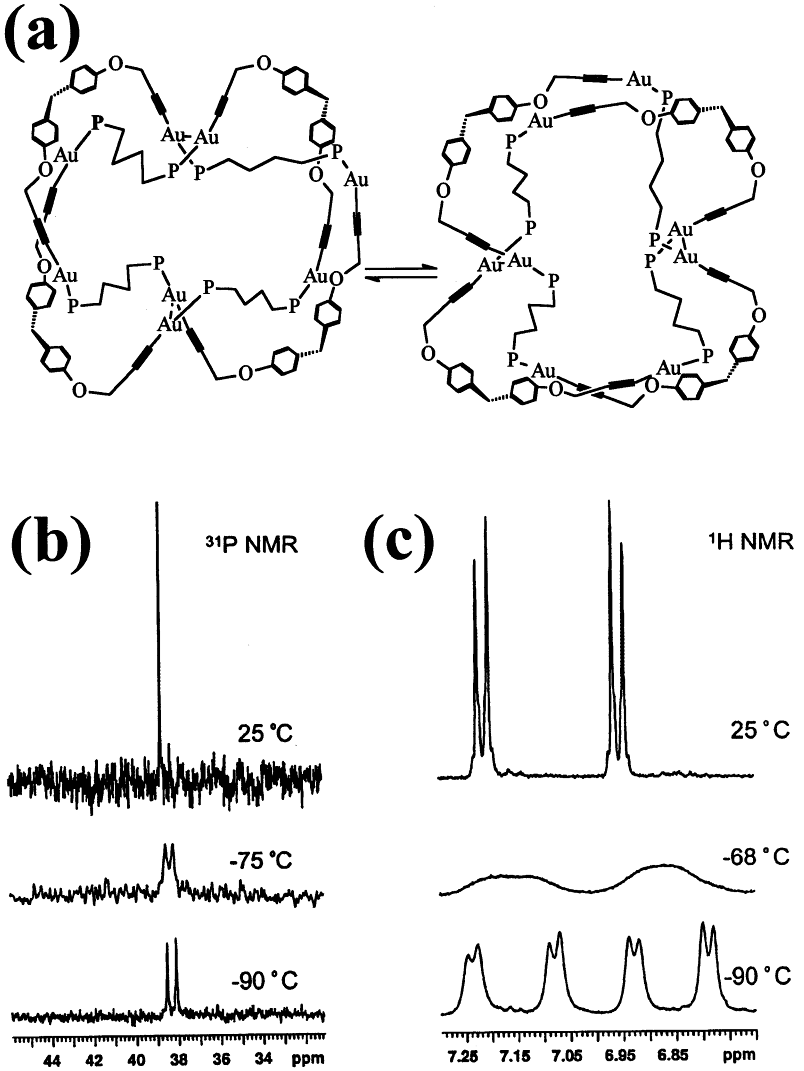


Fig. 13. The molecular switching in the double braid catenane. (a) The proposed mechanism, and the variable temperature NMR spectra; (b) ^{31}P NMR and (c) ^{1}H NMR of the C_6H_4 protons.

interesting sinusoidal conformation as shown in Fig. 16(a), since the conformation of adjacent P–Au vectors is *syn*. There is then a switch to the *anti* conformation of P–Au vectors when $n = 4$, such that a more stretched polymer chain is formed in **28b** (Fig. 16(b)) [21].

An interesting case occurs when $n = 5$, since three different structural forms were crystallised (Fig. 17). Two of these are polymers **28c**, one of which has the sinusoidal conformation as in **28a** but the other has a conformation intermediate

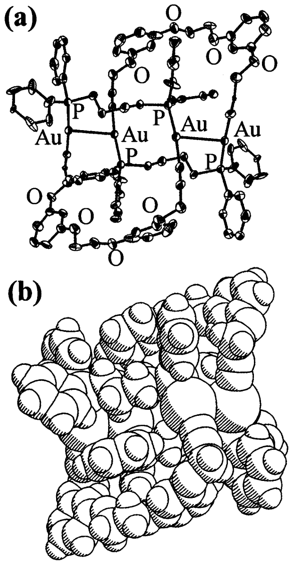
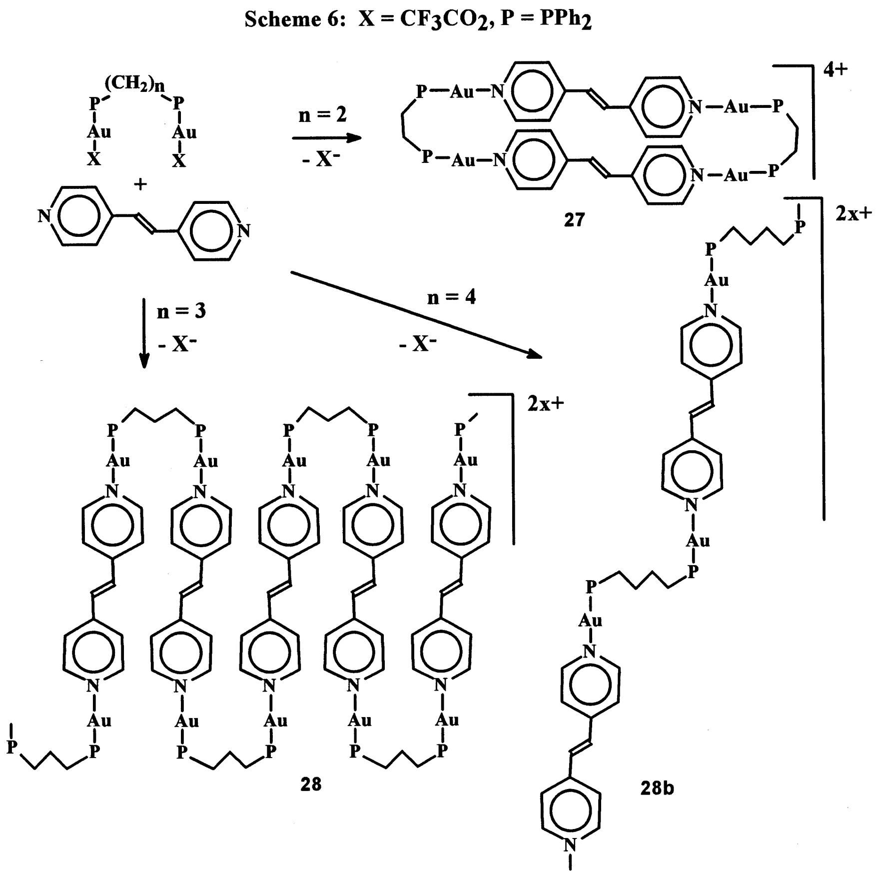


Fig. 14. Structure of the associated dimer formed by the complex $[(\text{-}CH_2OC_6H_4OCH_2CCAu)_2\{\mu\text{-}Ph_2P(CH_2)_4PPh_2\}]$. (a) The molecular structure and (b) the space filling diagram, showing the interpenetrating but uncatenated rings.

between *syn* and *anti* and the resulting chain adopts a helical structure (Fig. 17(a)). In most of the structurally characterised polymers, the chains pack parallel to one another but the helical polymer has chains that cross over one another while running in mutually perpendicular directions. The third structural form with $n = 5$ proved to be a novel ring structure with a central cyclobutane ring formed by a $2 + 2$ cycloaddition reaction of two bis(pyridyl)ethylene ligands (Fig. 17(b)). This form was only obtained when crystallisation was carried out in the open laboratory and it is thought to be formed by a photochemical cyclisation of small amounts of ring structure present in equilibrium with the chain forms as shown in Scheme 7 [21].

The complex with $n = 6$ was shown to be a stretched polymer **28d** (Fig. 18(a)) whose structure is similar to that of **28b**, having *anti* conformation of adjacent P–Au vectors but with the long $(CH_2)_6$ chain partly folded back on itself [21]. In this case, the corresponding silver complex has also been characterized; the structure is similar but with co-ordinated trifluoroacetate ions so that each silver(I) centre is trigonal rather than linear (Fig. 18(b)) [22].

The polymers **28** are not conjugated since there is a saturated carbon chain in the diphosphine ligands. However, conjugated polymers were prepared by using the diphosphine ligands *trans*-$Ph_2PCH{=}CHPPh_2$ or $[Fe(\eta^5\text{-}C_5H_4PPh_2)_2]$; the structure of the polymer **29** prepared from the ferrocene-based ligand is shown in Fig. 19 and has the stretched polymer form with *anti* conformation of adjacent P–Au vectors. This polymer, as a pressed disc, converts from being an insulator to a semiconduc-



Scheme 6.

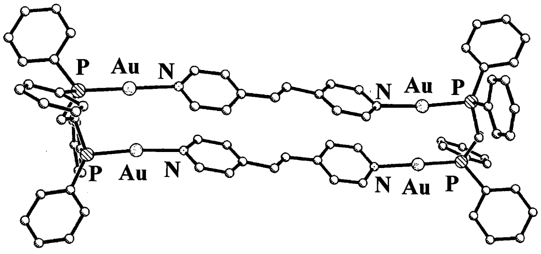


Fig. 15. The structure of the cationic ring complex $[Au_4(\mu\text{-}Ph_2PCH_2CH_2PPh_2)_2(\mu\text{-}NC_5H_4CH{=}CHC_5H_4N)_2]^{4+}$.

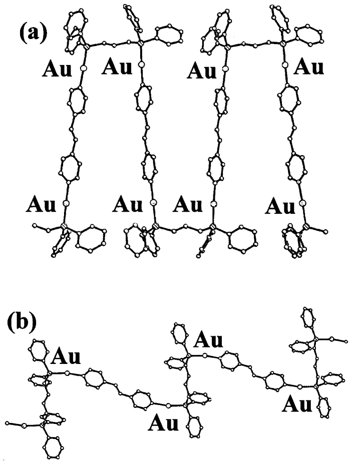


Fig. 16. The structures of the cationic polymer chains $[\{Au_2(\mu\text{-}Ph_2P(CH_2)_nPPh_2)(\mu\text{-}NC_5H_4CH{=}CHC_5H_4N)\}_n]^{2n+}$; (a) $n = 3$; (b) $n = 4$.

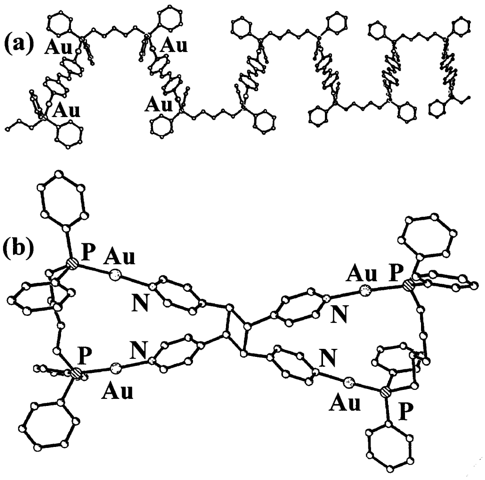
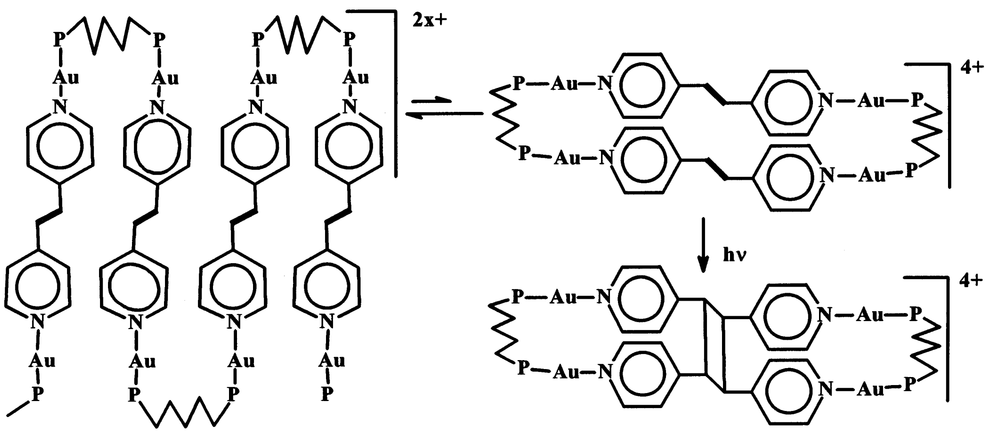


Fig. 17. The structures of (a) the helical cationic polymer chains $[\{Au_2(\mu\text{-}Ph_2P(CH_2)_5PPh_2)(\mu\text{-}NC_5H_4CH{=}CHC_5H_4N)\}_n]^{2n+}$, and (b) of the cyclobutane ring form.

tor when doped with iodine – partial oxidation of ferrocene to ferricenium centres is thought to be a likely rationalisation of this observation [16].

Finally, it is found that the bridging ligand 4,4′-bipyridine has a greater tendency to form rings rather than polymers compared to *trans*-bis(4-pyridyl)ethylene. Thus, the complexes $[Au_{2x}(L\text{–}L)_x\{Ph_2P(CH_2)_nPPh_2\}_x]^{2x+}$, with $n = 3$ or 5, exist as rings with $x = 2$ when L–L = 4,4′-bipyridine, but as polymers with $x = \infty$ when L–L = *trans*-bis(4-pyridyl)ethylene (compare Fig. 20 with Fig. 16 Fig. 17) [22].



Scheme 7.

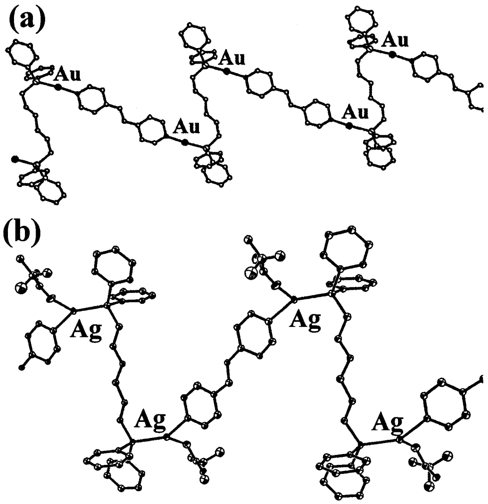


Fig. 18. The structure of the cationic polymer chains (a) $[\{Au_2(\mu\text{-}Ph_2P(CH_2)_6PPh_2)(\mu\text{-}NC_5H_4CH{=}CHC_5H_4N)\}_n]^{2n+}$ and (b) $[\{Ag_2(O_2CCF_3)_2(\mu\text{-}Ph_2P(CH_2)_6PPh_2)(\mu\text{-}NC_5H_4CH{=}CHC_5H_4N)\}_n]$.

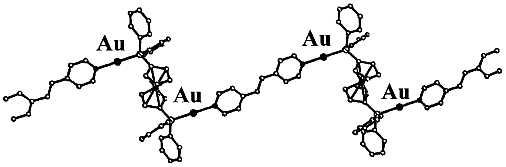


Fig. 19. The structure of the cationic polymer chain $[\{Au_2(\mu\text{-}Fe(C_5H_4PPh_2)_2)(\mu\text{-}NC_5H_4CH{=}CHC_5H_4N)\}_n]^{2n+}$.

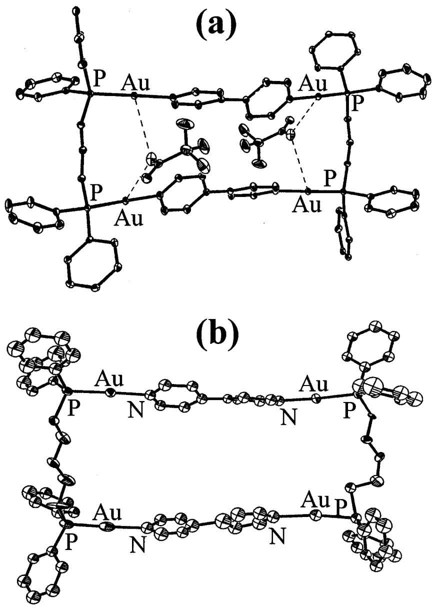


Fig. 20. Structures of the gold(I) ring complexes $[\{Au_2(\mu\text{-}Ph_2P(CH_2)_nPPh_2)(\mu\text{-}NC_5H_4C_5H_4N)\}_2]^{4+}$: (a) with $n = 3$, with two weakly coordinated trifluoroacetate anions shown, and (b) with $n = 5$.

7. Conclusions

It is now possible to tailor the structures of gold(I) compounds with bridging ligands to give either rings or polymers, depending on the degree of flexibility of the bridging ligands and sometimes on secondary bonding forces such as aryl–aryl or gold–gold attractions. The polymers have interesting structures and preliminary studies indicate the possibility of optical and electronic properties based on the conjugation along the chains (molecular wires), while the rings may self-assemble to give catenanes or double braid catenanes (molecular switches).

In the future, it will be necessary to learn how to control the self-assembly so that complex device-like structures can be prepared simply and easily by using the Au···Au attractive forces. Polymers of neutral rings $[S(C_6H_4OCH_2CCAu)_2(\mu\text{-}Ph_2PCCPPh_2)]$ can be assembled to give one-dimensional chains [20], and cationic rings $[Au_2(\mu\text{-}Ph_2P(CH_2)_5PPh_2)]^{2+}$ can be connected by anionic $[Au(CN)_2]^-$ links to give kinked chains [22], as shown in Fig. 21. Ultimately, it is desirable to connect the molecular wires and switches.

Acknowledgements

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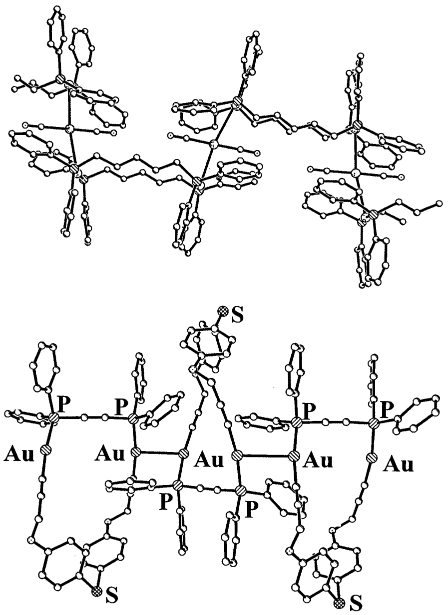

Fig. 21. Structures of $\{[Au_2(\mu\text{-}Ph_2P(CH_2)_5PPh_2)_2][Au(CN)_2]\}_n^{n+}$

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