# Precious metal polymers: platinum or gold atoms in the backbone 

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The synthesis and characterisation of oligomers and polymers containing gold or platinum atoms in the backbone are reported. The polymers range in structure from the conjugated, rigid-rod type containing linear gold $(\mathrm{I})$ centres to hyperbranched or dendrimeric materials containing octahedral platinum(iv) centres.

## Introduction

This article gives a personal account of the synthesis and characterization of some new types of oligomers and polymers with either platinum or gold atoms in the chain backbone. These 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 or they might be useful as precursors to other materials or as catalyst precursors. There are several known types of linear-chain polynuclear coordination complexes containing platinum or gold, including the stacked, one dimensional conductors or semiconductors $\mathrm{K}_{2} \mathrm{Pt}(\mathrm{CN})_{4} \mathrm{Br}_{0.30} \cdot 3 \mathrm{H}_{2} \mathrm{O},{ }^{1} \quad\left[\mathrm{Pt}\left(\mathrm{NH}_{2} \mathrm{Et}\right)_{4}\right]\left[\mathrm{PtCl}_{2}\left(\mathrm{NH}_{2} \mathrm{Et}_{4}\right] \mathrm{Cl}_{4}\right.$. $4 \mathrm{H}_{2} \mathrm{O}$ and $\mathrm{K}_{4}\left[\mathrm{Pt}_{2}\left(\mathrm{P}_{2} \mathrm{O}_{5} \mathrm{H}_{2}\right)_{4} \mathrm{X}\right] \cdot n \mathrm{H}_{2} \mathrm{O}(\mathrm{X}=\mathrm{Cl}, \mathrm{Br}, \mathrm{I}),{ }^{2}$ and the simple halogen-bridged gold(I) halides. ${ }^{3}$ More recently, rigid rod polymers such as $\left[\mathrm{Pt}\left(\mathrm{PBu}_{3}\right)_{2}(\mu-\mathrm{C} \equiv \mathrm{C}-\mathrm{R}-\mathrm{C} \equiv \mathrm{C}-]_{n} \mathbf{1}(\mathrm{R}=\right.$ aryl spacer group) have been reported. ${ }^{4}$ The dialkynyl ligands, and related but neutral diisocyanide ligands, are particularly well suited to the design of rigid-rod polymers and examples are now known with $\mathrm{Pt}-\mathrm{Pt}$ bonds and even $\mathrm{Pt}_{3}$ cluster units in the backbone as illustrated by 2 and 3, $\mathrm{PP}=\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{PPh}_{2}{ }^{5,6}$ The first part of this article will describe the further development of this field to include gold-containing rigid-rod polymers.



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## Gold-containing oligomers and polymers

Gold(I) tends to have a coordination number of two with linear stereochemistry, ${ }^{3}$ 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 $\mathrm{X}^{-}$are required for each gold(I) centre. Suitable ligands might then include $\mathrm{L}-\mathrm{R}-\mathrm{X}^{-}$, where R is a linear spacer group, and L might be an isocyanide and $\mathrm{X}^{-}$an acetylide. Alternatively, one ligand $\mathrm{L}-\mathrm{R}-\mathrm{L}$ and $-\mathrm{X}-\mathrm{R}-\mathrm{X}^{-}$ could be used for each two gold(I) centres. The general types of polymers targetted 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.

$$
\begin{aligned}
& {[L-L-A u-X-X-A u]_{n}} \\
& {[L-X-A u-L-X-A u]_{n}} \\
& {[L-X-A u-X-L-A u]_{n}}
\end{aligned}
$$

## Diisocyanides, diacetylides and isocyanoacetylides

Since the isocyanide functionality is sensitive to bases, the most successful synthetic route to isocyanide(alkynyl)gold(I) complexes is by reaction of oligomeric or polymeric compounds ( $\mathrm{AuC} \equiv \mathrm{CR})_{n}$, in which the alkynyl ligand bridges by bonding to one gold atom through the $\sigma$ donor and to a second gold atom using its $\pi$ electrons, ${ }^{7}$ with an isocyanide ligand. Although the explosive $\mathrm{Au}_{2} \mathrm{C}_{2}$ has been known for many years, the more stable (CAUTION: but still potentially explosive) digold diacetylides $(\mathrm{AuC} \equiv \mathrm{C}-\mathrm{Ar}-\mathrm{C} \equiv \mathrm{CAu})_{n} 7$ needed for this work were unknown and were prepared according to eqn. (1), $\mathrm{B}=$ base, in which the aryl spacer group $\mathrm{Ar}=1,4-\mathrm{C}_{6} \mathrm{H}_{4}, 4,4^{\prime}-\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{C}_{6} \mathrm{H}_{4}$ or $1,4-\left(2,5-\mathrm{Me}_{2} \mathrm{C}_{6} \mathrm{H}_{2}\right) .{ }^{8}$

$$
\begin{gather*}
2\left[\mathrm{Me}_{2} \mathrm{SAuCl}\right]+\mathrm{HCC}-\mathrm{Ar}-\mathrm{CCH}+2 \mathrm{~B} \\
\downarrow \\
2 \mathrm{Me}_{2} \mathrm{~S}+2 \mathrm{BH}^{+} \mathrm{Cl} l^{-}+\{\mathrm{Au}-\mathrm{C}=\mathrm{C}-\mathrm{Ar}-\mathrm{C} \equiv \mathrm{C}-\mathrm{Au}\}_{n} \tag{1}
\end{gather*}
$$

Suitable binuclear gold(I) model compounds [ $\mathrm{RN} \equiv \mathrm{CAuC} \equiv \mathrm{C}-$ $\mathrm{Ar}-\mathrm{C} \equiv \mathrm{CAuC} \equiv \mathrm{NR}] 8\left(\mathrm{R}=\mathrm{Bu}^{\mathrm{t}}\right.$ or $\mathrm{Xy}=2,6$-dimethylphenyl) and $[\mathrm{RC} \equiv \mathrm{CAuC} \equiv \mathrm{N}-\mathrm{Ar}-\mathrm{N} \equiv \mathrm{CAuC} \equiv \mathrm{CR}] 9\left[\mathrm{R}=\mathrm{Bu}^{\mathrm{t}}\right.$ or Ph , $\mathrm{Ar}=1,4-\mathrm{C}_{6} \mathrm{H}_{4}, \quad 1,4-\left(2-\mathrm{MeC}_{6} \mathrm{H}_{3}\right), \quad 1,4-\left(2,6-\mathrm{Bu}^{\mathrm{t}} \mathrm{C}_{6} \mathrm{H}_{2}\right)$, $1,4-\left(\mathrm{C}_{6} \mathrm{Me}_{4}\right), 1,4^{\prime}-\left(2,6-\mathrm{Me}_{2} \mathrm{C}_{6} \mathrm{H}_{2}\right)_{2}$, were then prepared as shown in eqns. (2) and (3). ${ }^{8}$
$1 / n\{\mathrm{AuCC}-\mathrm{Ar}-\mathrm{CCAu}\}_{n}+2 \mathrm{RNC} \rightarrow[\mathrm{RN} \equiv \mathrm{C}-\mathrm{Au}-\mathrm{C} \equiv \mathrm{C}-\mathrm{Ar}-\mathrm{C} \equiv \mathrm{C}-\mathrm{Au}-\mathrm{C} \equiv \mathrm{NR}]$
$2 / n\{\mathrm{AuCCR}\}_{n}+\mathrm{CN}-\mathrm{Ar}^{\prime}-\mathrm{NC} \rightarrow\left[\mathrm{RC} \equiv \mathrm{C}-\mathrm{Au}-\mathrm{C} \equiv \mathrm{N}-\mathrm{Ar}^{\prime}-\mathrm{N} \equiv \mathrm{C}-\mathrm{Au}-\mathrm{C} \equiv \mathrm{CR}\right]$

While eqns. (2) and (3) indicate that the products are molecular in nature, and this is the case in solution, the compounds associate in the solid state either through $\pi$ stacking between aryl groups of neighbouring molecules ${ }^{9}$ or, more commonly, through intermolecular $\mathrm{Au} \cdots \mathrm{Au}$ bonding. ${ }^{8}$ These weak $\mathrm{Au} \cdots \mathrm{Au}$ interactions, which are known in several other classes of gold(I) complexes, are thought to have strengths of $5-10 \mathrm{kcal} \mathrm{mol}^{-1}$, similar to the strength of hydrogen bonds, and are thought to arise from relativistic London forces. ${ }^{10}$ The association present in crystals of $[\mathrm{PhC} \equiv \mathrm{C}-\mathrm{Au}-$ $\left.\mathrm{C} \equiv \mathrm{NBu}_{2} \mathrm{C}_{6} \mathrm{H}_{2} \mathrm{~N} \equiv \mathrm{C}-\mathrm{Au}-\mathrm{C} \equiv \mathrm{CPh}\right]$ comprises both aryl $\pi$ stacking and $\mathrm{Au} \cdots \mathrm{Au}$ bonding and is shown in Fig. 1.

It was then possible to prepare polymers 10 containing alternating diacetylide and diisocyanide ligands according to


Fig. 1 The intermolecular association present in the solid state structure of $\left[\mathrm{PhC} \equiv \mathrm{CAuC} \equiv \mathrm{NBu}_{2} \mathrm{C}_{6} \mathrm{H}_{2} \mathrm{~N} \equiv \mathrm{CAuC} \equiv \mathrm{CPh}\right.$ ] due to (a) $\pi$-stacking and (b) $\mathrm{Au} \cdots \mathrm{Au}$ bonding. The $\mathrm{Au} \cdots \mathrm{Au}$ distance is 3.174(1) $\AA$.
eqn. (4) ( Ar and $\mathrm{Ar}^{\prime}$ are as defined earlier). The polymers are

$$
\begin{gather*}
1 / n\{\mathrm{AuCC}-\mathrm{Ar}-\mathrm{CCAu}\}_{n}+\mathrm{CN}-\mathrm{Ar} r^{\prime}-\mathrm{NC} \\
\left\{-\mathrm{Au}-\mathrm{C} \equiv \mathrm{C}-\mathrm{Ar}-\mathrm{C} \equiv \mathrm{C}-\mathrm{Au}-\mathrm{C} \equiv \mathrm{~N}-\mathrm{Ar} r^{\prime}-\mathrm{N} \equiv \mathrm{C}-n\right\} \\
10 \tag{4}
\end{gather*}
$$

insoluble, which might have been predicted since intermolecular association through $\pi$ stacking and/or Au $\cdots \mathrm{Au}$ 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 is likely to 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. ${ }^{8}$

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 strongly red shifted in the solid compared to solution state as illustrated in Fig. 2, particularly


Fig. 2 The emission spectra of $\mathrm{XyNC}-\mathrm{Au}-\mathrm{CCC}_{6} \mathrm{H}_{4} \mathrm{NO}_{2}-4$, (a) in solution in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ and (b) in the solid state, showing the red shift in the solid state. In this case the association in the solid state is due to $\pi$-stacking.
when $\mathrm{Au} \cdots \mathrm{Au}$ bonding or $\pi$ 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


Fig. 3 The solidstate emission spectra of gold(I) complexes showing the red shift with increasing molecular size: (a) $\left[\mathrm{Bu}^{\mathrm{t}} \mathrm{N} \equiv \mathrm{C}-\mathrm{Au}-\mathrm{C} \equiv \mathrm{CPh}\right]$, (b) $\mathrm{XyN} \equiv \mathrm{C}-\mathrm{Au}-\mathrm{CCC}_{6} \mathrm{H}_{4}-\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{CC}-\mathrm{Au}-\mathrm{C} \equiv \mathrm{NXy}$ ] and (c) $\{\mathrm{Au}-\mathrm{C} \equiv \mathrm{C}-$ $\left.\left.\mathrm{C}_{6} \mathrm{H}_{2} \mathrm{Me}_{2} \mathrm{C} \equiv \mathrm{C}-\mathrm{Au}-\mathrm{C} \equiv \mathrm{NC}_{6} \mathrm{H}_{2} \mathrm{Bu}^{\mathrm{t}}\right) \mathrm{N} \equiv \mathrm{C}\right\}_{n}$
provides evidence for at least some $\pi$ conjugation in the rigidrod chains. ${ }^{9}$
The new ligands $4-\mathrm{HC} \equiv \mathrm{CC}_{6} \mathrm{H}_{4} \mathrm{~N} \equiv \mathrm{C}$ and $4-\mathrm{HC} \equiv \mathrm{C}-$ $2-\mathrm{MeC}_{6} \mathrm{H}_{3} \mathrm{~N} \equiv \mathrm{C}$ bind readily to gold(I) in forming the complexes
such as $\left[4-\mathrm{HC} \equiv \mathrm{CC}_{6} \mathrm{H}_{4} \mathrm{~N} \equiv \mathrm{C}-\mathrm{Au}-\mathrm{Cl}\right] \quad 11$ and $[4-\mathrm{HC} \equiv \mathrm{C}-$ $\left.2-\mathrm{MeC}_{6} \mathrm{H}_{3} \mathrm{~N} \equiv \mathrm{C}-\mathrm{Au}-\mathrm{C} \equiv \mathrm{CBu}^{\mathrm{t}}\right]$ 12. The acetylide derivatives such as $\mathbf{1 2}$ give weak $\mathrm{Au} \cdots \mathrm{Au}$ bonded association in the solid state $[\mathrm{Au} \cdots \mathrm{Au} 3.479(2) \AA$ A and form oligomeric complexes $\mathrm{H}-(\mathrm{C} \equiv \mathrm{C}-\mathrm{Ar}-\mathrm{N} \equiv \mathrm{C}-\mathrm{Au}-)_{n}-\mathrm{C} \equiv \mathrm{CBu}^{\mathrm{t}} 13$ by elimination of ButCCH on heating as illustrated in Scheme 1.12 The oligomers tend to precipitate from solution when $n=4-6$ and then no further chain growth occurs.


Scheme 1

## Diphosphines, diacetylides and 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 $\mathrm{PMe}_{3}$ to give binuclear model complexes such as $\left[\left(\mathrm{Me}_{3} \mathrm{P}\right) \mathrm{Au}-\mathrm{C} \equiv \mathrm{C}\right.$ $\left.\mathrm{C}_{6} \mathrm{H}_{2} \mathrm{Me}_{2}-\mathrm{C} \equiv \mathrm{C}-\mathrm{Au}\left(\mathrm{PMe}_{3}\right)\right] \mathbf{1 4}$ and this forms loose polymers in the solid state by intermolecular $\mathrm{Au} \cdots \mathrm{Au}$ bonding (Fig. 4). ${ }^{9,13}$


Fig. 4 The intermolecular association through $\mathrm{Au} \cdots \mathrm{Au}$ bonding in the complex $\left[\left(\mathrm{Me}_{3} \mathrm{P}\right) \mathrm{Au}-\mathrm{C} \equiv \mathrm{C}-\mathrm{C}_{6} \mathrm{H}_{2} \mathrm{Me}_{2}-\mathrm{C} \equiv \mathrm{C}-\mathrm{Au}\left(\mathrm{PMe}_{3}\right)\right]$
The diphosphines $\mathrm{Ph}_{2} \mathrm{PC}_{6} \mathrm{H}_{4} \mathrm{PPh}_{2}$ or $\mathrm{Pr}_{2}{ }_{2} \mathrm{PC}_{6} \mathrm{H}_{4} \mathrm{C}_{6} \mathrm{H}_{4} \mathrm{PPr}^{\mathrm{i}}{ }_{2}$ can also give binuclear model complexes such as $\mathrm{PhC} \equiv \mathrm{C}-\mathrm{Au}-$ $\operatorname{Pr}^{\mathrm{i}}{ }_{2} \mathrm{PC}_{6} \mathrm{H}_{4} \mathrm{C}_{6} \mathrm{H}_{4} \mathrm{PPr}^{\mathrm{i}}{ }_{2}-\mathrm{Au}-\mathrm{C} \equiv \mathrm{CPh} 15$ which has the anti conformation with respect to the two $\mathrm{P}-\mathrm{Au}$ vectors as shown in Fig. 5; the bulky $\operatorname{Pr}^{i}$ groups prevent the formation of


Fig. 5 The anti conformation of the two $\mathrm{P}-\mathrm{Au}$ vectors in $[\mathrm{PhC} \equiv \mathrm{C}-\mathrm{Au}-$ $\left.\mathrm{Pr}_{2}{ }_{2} \mathrm{PC}_{6} \mathrm{H}_{4} \mathrm{C}_{6} \mathrm{H}_{4} \mathrm{PPr}^{\mathrm{i}}{ }_{2}-\mathrm{Au}-\mathrm{C} \equiv \mathrm{CPh}\right] 15$
intermolecular $\mathrm{Au} \cdots \mathrm{Au}$ bonding in 15. It is then straightforward to prepare polymers $\left(\mathrm{Au}-\mathrm{C} \equiv \mathrm{C}-\mathrm{Ar}-\mathrm{C} \equiv \mathrm{C}-\mathrm{Au}-\mathrm{PR}_{2}-\mathrm{Ar}^{\prime}-\mathrm{PR}_{2}-\right)_{n}$ 16 incorporating both diphosphine and diacetylide bridges. It is likely that the anti conformation of the $\mathrm{P}-\mathrm{Au}$ vectors in $\mathbf{1 5}$ is
maintained in these polymers, which are sufficiently soluble when $\mathrm{R}=\operatorname{Pr}^{i}$ to allow molecular mass determination by GPC. The improved solubility probably arises because the bulky Pr ${ }^{\mathrm{i}}$ groups prevent crosslinking by intermolecular $\mathrm{Au} \cdots \mathrm{Au}$ bonding.

It is possible to tailor the system to give rings instead of polymers. Thus, ligands $\mathrm{R}_{2} \mathrm{PCH}_{2} \mathrm{PR}_{2}$ give digold complexes in which the syn conformation of the two $\mathrm{P}-\mathrm{Au}$ vectors is preferred so as to allow intramolecular $\mathrm{Au} \cdots \mathrm{Au}$ bonding, as for example in $\mathrm{CH}_{2}\left(\mathrm{PCy}_{2}-\mathrm{Au}-\mathrm{O}_{2} \mathrm{CCF}_{3}\right)_{2} 17$ or $\mathrm{CH}_{2}\left(\mathrm{PPh}_{2}-\mathrm{Au}-\right.$ $\left.\mathrm{C} \equiv \mathrm{CBu}^{\mathrm{t}}\right)_{2} \mathbf{1 8}$ shown in Fig. 6. ${ }^{14,15}$ This conformation is


Fig. 6 The syn conformation of the two $\mathrm{P}-\mathrm{Au}$ vectors in $\left[\mathrm{CH}_{2}\left(\mathrm{PCy}_{2}-\mathrm{Au}-\right.\right.$ $\left.\left.\mathrm{O}_{2} \mathrm{CCF}_{3}\right)_{2}\right] \mathbf{1 7}$ and $\left[\mathrm{CH}_{2}\left(\mathrm{PPh}_{2}-\mathrm{Au}-\mathrm{C} \equiv \mathrm{CBut}_{2}\right] \mathbf{1 8}\right.$
maintained on reaction of 17 with rigid-rod bridging ligands and so large rings are formed in $\left[\mathrm{CH}_{2}\left(\mathrm{PR}_{2}-\mathrm{Au}-\mathrm{C} \equiv \mathrm{C}-\mathrm{Ar}-\mathrm{C} \equiv \mathrm{C}-\mathrm{Au}-\right.\right.$ $\left.\left.\mathrm{PR}_{2}\right)_{2} \mathrm{CH}_{2}\right] \quad 19$ or $\left[\mathrm{CH}_{2}\left(\mathrm{PR}_{2}-\mathrm{Au}-\mathrm{C} \equiv \mathrm{N}-\mathrm{Ar}-\mathrm{N} \equiv \mathrm{C}-\mathrm{Au}-\right.\right.$ $\left.\left.\mathrm{PR}_{2}\right)_{2} \mathrm{CH}_{2}\right]^{4+}$ 20. The structure of the complex 20 with $\mathrm{R}=$ cyclohexyl and the bridging ligand $1,4-\mathrm{C} \equiv \mathrm{NC}_{6} \mathrm{H}_{4} \mathrm{~N} \equiv \mathrm{C}$ is shown in Fig. 7.


Fig. 7 The structure of the cationic ring complex 20 ( $\mathrm{R}=\mathrm{Cy}$ and $\mathrm{Ar}=1,4-$ $\mathrm{C}_{6} \mathrm{H}_{4}$ )

It is also possible to use mixed phosphine-acetylide donors in forming polymers of gold(I). Thus the ligands $\mathrm{Ph}_{2} \mathrm{PC} \equiv \mathrm{CH}$ and $\operatorname{Pr}_{2}{ }_{2} \mathrm{PC} \equiv \mathrm{CH}$ form model complexes $\mathrm{HC} \equiv \mathrm{CPR}_{2}-\mathrm{Au}-\mathrm{Cl}$ which, on treatment with base, can eliminate HCl to give the polymers $\left\{\mathrm{R}_{2} \mathrm{PC} \equiv \mathrm{C}-\mathrm{Au}-\right\}_{n} 21 .{ }^{16}$

## Angular diacetylides and 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 an angle is introduced in the diacetylide bridge? The dialkyne $1,3-(\mathrm{HC} \equiv \mathrm{C})_{2} \mathrm{C}_{6} \mathrm{H}_{3} \mathrm{Me}-5$ yields digold(I) model complexes $1,3-(\mathrm{L}-\mathrm{Au}-\mathrm{C} \equiv \mathrm{C})_{2} \mathrm{C}_{6} \mathrm{H}_{3} \mathrm{Me}-522(\mathrm{~L}=$ phosphine, phosphite or isocyanide ligand) which form ribbon structures in the solid state through $\mathrm{Au} \cdots \mathrm{Au}$ bonding as seen in Fig. 8. ${ }^{17}$


Fig. 8 The intermolecular association through $\mathrm{Au} \cdots \mathrm{Au}$ bonding in the complex $\left[1,3-(\mathrm{L}-\mathrm{Au}-\mathrm{C} \equiv \mathrm{C})_{2} \mathrm{C}_{6} \mathrm{H}_{3} \mathrm{Me}-5\right]\left[\mathrm{L}=\mathrm{P}(\mathrm{OMe})_{3}\right]$

Kinked polymers such as $\mathbf{2 3}$ are formed when linear diisocyanide ligands are used but, if the neutral bridging ligand
is also non-linear, then ring structures such as $\mathbf{2 4}$ are formed instead (Scheme 2). ${ }^{17}$


Scheme 2 Reagents: i, $\mathrm{C}_{6} \mathrm{H}_{4}(\mathrm{CN})_{2}$; ii, $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{PPh}_{2}$
If a third acetylide link is added as in $1,3,5-(\mathrm{HC} \equiv \mathrm{C})_{3} \mathrm{C}_{6} \mathrm{H}_{3}$, the gold derivatives can in principle form more complex network polymers either through intermolecular $\mathrm{Au} \cdots \mathrm{Au}$ bonding or through the use of bridging ligands. The capped complexes $1,3,5-(\mathrm{L}-\mathrm{Au}-\mathrm{C} \equiv \mathrm{C})_{3} \mathrm{C}_{6} \mathrm{H}_{3} 25$ are found to form one-dimensional ribbon structures in the solid state with one gold atom not taking part in $\mathrm{Au} \cdots \mathrm{Au}$ bonding (Fig. 9). With all bridging ligands,


Fig. 9 The intermolecular association through $\mathrm{Au} \cdots \mathrm{Au}$ bonding in the complex $\left[1,3,5-(\mathrm{L}-\mathrm{Au}-\mathrm{C} \equiv \mathrm{C})_{3} \mathrm{C}_{6} \mathrm{H}_{3}\right]\left(\mathrm{L}=\mathrm{Bu}^{\mathrm{t}} \mathrm{N} \equiv \mathrm{C}\right)$
whether the strictly linear diisocyanides or angular diphosphines, insoluble polymers 26 are formed (Scheme 3). ${ }^{18}$


Scheme 3 Reagents: i, [ $\left.\mathrm{AuCl}\left(\mathrm{SMe}_{2}\right)\right], \mathrm{NaOAc}$; ii, 3L; iii, 1.5 L-L

Rings and polymers 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. A series of experiments was carried out next using flexible diphosphine ligands $\left(\mathrm{CH}_{2}\right)_{n}\left(\mathrm{PPh}_{2}\right)_{2}$ and a more labile linear bridging ligand trans-1,4-bis(pyridyl)ethene. It was argued that the intramolecular $\mathrm{Au} \cdots \mathrm{Au}$ bonding interactions would decrease progressively with increasing $n$ and so the preferred structure would switch from the large rings to polymers at some point in the series (Scheme 4). Further, the polymers could reversibly cleave to smaller fragments in solution owing the lability of the pyridine donors and this might allow crystallisation and so to full structural characterisation of the polymers. ${ }^{19}$


Scheme $4 \mathrm{X}=\mathrm{CF}_{3} \mathrm{CO}_{2}, \mathrm{P}=\mathrm{PPh}_{2}$
With $\left(\mathrm{CH}_{2}\right)_{2}\left(\mathrm{PPh}_{2}\right)_{2}$, the ring structure $\left[\mathrm{Au}_{4}(\mu-\right.$ $\left.\left.\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{CH}_{2} \mathrm{PPh}_{2}\right)_{2}\left(\mu-\mathrm{NC}_{5} \mathrm{H}_{4} \mathrm{CH}=\mathrm{CHC}_{5} \mathrm{H}_{4} \mathrm{~N}\right)_{2}\right]^{4+} 27$ is preferred as shown in Fig. 10 but the $\mathrm{Au} \cdots \mathrm{Au}$ distance of 3.625 (3) A indicates very weak $\mathrm{Au} \cdots \mathrm{Au}$ bonding and no significant $\mathrm{Au} \cdots \mathrm{Au}$ attraction is expected for higher values of $n .{ }^{19}$
The switch to a polymeric structure $\left[\left\{\mathrm{Au}_{2}[\mu-\right.\right.$ $\left.\left.\left.\mathrm{Ph}_{2} \mathrm{P}\left(\mathrm{CH}_{2}\right)_{n} \mathrm{PPh}_{2}\right]\left(\mu-\mathrm{NC}_{5} \mathrm{H}_{4} \mathrm{CH}=\mathrm{CHC}_{5} \mathrm{H}_{4} \mathrm{~N}\right)\right\}_{n}\right]^{2 n+} \quad 28$ occurs when $n=3$ and the polymer 28a has an interesting sinusoidal conformation as shown in Fig. 11(a), since the conformation of adjacent $\mathrm{P}-\mathrm{Au}$ vectors is syn. There is then a switch to the anti conformation of $\mathrm{P}-\mathrm{Au}$ vectors when $n=4$, such that a more stretched polymer chain is formed in 28b [Fig. 11(b)]. ${ }^{19}$

An interesting case occurs when $n=5$, since three different structural forms have been crystallised (Fig. 12). Two of these


Fig. 10 The structure of the cationic ring complex $\left[\mathrm{Au}_{4}(\mu-\right.$ $\left.\left.\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{CH}_{2} \mathrm{PPh}_{2}\right)_{2}\left(\mu-\mathrm{NC}_{5} \mathrm{H}_{4} \mathrm{CH}=\mathrm{CHC}_{5} \mathrm{H}_{4} \mathrm{~N}\right)_{2}\right]^{4+}$

(b)


Fig. 11 The structures of the cationic polymer chains $\left[\left\{\mathrm{Au}_{2}[\mu-\right.\right.$ $\left.\left.\left.\mathrm{Ph}_{2} \mathrm{P}\left(\mathrm{CH}_{2}\right)_{n} \mathrm{PPh}_{2}\right]\left(\mu-\mathrm{NC}_{5} \mathrm{H}_{4} \mathrm{CH}=\mathrm{CHC}_{5} \mathrm{H}_{4} \mathrm{~N}\right)\right\}_{n}\right]^{2 n+}$; (a) $n=3$; (b) $n=4$



Fig. 12 The structures of the helical (a) cationic polymer chains [\{ $\mathrm{Au}_{2}[\mu-$ $\left.\left.\left.\mathrm{Ph}_{2} \mathrm{P}\left(\mathrm{CH}_{2}\right)_{5} \mathrm{PPh}_{2}\right]\left(\mu-\mathrm{NC}_{5} \mathrm{H}_{4} \mathrm{CH}=\mathrm{CHC}_{5} \mathrm{H}_{4} \mathrm{~N}\right)\right\}_{n}\right]^{2 n+}$, and of the cyclobutane ring form (b)
are polymers $\mathbf{2 8 c}$, one of which has the sinusoidal conformation as in 28a but the other has a conformation intermediate between syn and anti and the resulting chain adopts a helical structure [Fig. 12(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. 12(b)]. Further study showed
that 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 $5 .{ }^{16}$


The complex with $n=6$ proved to be a stretched polymer $\mathbf{2 8 d}$ (Fig. 13) whose structure is similar to that of $\mathbf{2 8 b}$, having anti conformation of adjacent $\mathrm{P}-\mathrm{Au}$ vectors but with the long $\left(\mathrm{CH}_{2}\right)_{6}$ chain partly folded back on itself. ${ }^{16}$


Fig. 13 The structure of the cationic polymer chain $\left[\left\{\mathrm{Au}_{2}[\mu-\right.\right.$ $\left.\left.\left.\mathrm{Ph}_{2} \mathrm{P}\left(\mathrm{CH}_{2}\right)_{6} \mathrm{PPh}_{2}\right]\left(\mu-\mathrm{NC}_{5} \mathrm{H}_{4} \mathrm{CH}=\mathrm{CHC}_{5} \mathrm{H}_{4} \mathrm{~N}\right)\right\}_{n}\right]^{2 n+}$

The polymers 28 are not conjugated since there is a saturated carbon chain in the diphosphine ligands. However, conjugated polymers can be prepared by using the diphosphine ligands trans $-\mathrm{Ph}_{2} \mathrm{PCH}=\mathrm{CHPPh}_{2}$ or $\left[\mathrm{Fe}\left(\eta^{5}-\mathrm{C}_{5} \mathrm{H}_{4} \mathrm{PPh}_{2}\right)_{2}\right]$; the structure of the polymer 29 prepared from the latter ligand is shown in Fig. 14 and has the stretched polymer form with anti


Fig. 14 The structure of the cationic polymer chain $\left[\left\{\mathrm{Au}_{2}[\mu-\right.\right.$ $\left.\left.\left.\mathrm{Fe}\left(\mathrm{C}_{5} \mathrm{H}_{4} \mathrm{PPh}_{2}\right)_{2}\right]\left(\mu-\mathrm{NC}_{5} \mathrm{H}_{4} \mathrm{CH}=\mathrm{CHC}_{5} \mathrm{H}_{4} \mathrm{~N}\right)\right\}_{n}\right]^{2 n+}$
conformation of adjacent $\mathrm{P}-\mathrm{Au}$ vectors. This polymer, as a pressed disc, converts from being an insulator to a semiconductor when doped with iodine, partial oxidation of ferrocene to ferricenium centres is thought to be a likely rationalisation of this observation. ${ }^{16}$

In conclusion, it is now possible to tailor the structures of gold(I) compounds with bridging ligands to give either rings or polymers. The polymers have interesting structures and preliminary studies indicate the possibility of optical and electronic properties based on the conjugation along the chains.

## Platinum-containing oligomers and polymers

The synthesis of oligomers or polymers with platinum atoms in the backbone is based on the two simple reactions shown in eqns. (5) and (6). The first is a ligand substitution of a diimine

ligand such as $4,4^{\prime}$-di-tert-butyl-2, $2^{\prime}$-bipyridine onto a dimethylplatinum(II) centre by displacement of weakly bound $\mathrm{Me}_{2} \mathrm{~S}$ ligands from $\left[\mathrm{Pt}_{2} \mathrm{Me}_{4}\left(\mu-\mathrm{SMe}_{2}\right)_{2}\right] \mathbf{3 0}$ to give $\mathbf{3 1},{ }^{20}$ while the second involves oxidative addition of an alkyl halide to the platinum(II) centre of 31, a reaction which occurs easily for primary alkyl halides and is tolerant to a wide range of functional groups. ${ }^{21}$ Both reactions occur in almost quantitative yield and so are ideal for multistep syntheses as described below.

## Linear chain platinum polymers

The oxidative addition to platinum(II) of alkyl halides containing polymerisable substituents can lead to polymers with organoplatinum(IV) substituents as side chains, ${ }^{22}$ but the key to making polymers with platinum atoms in the backbone is to use alkyl halides with a bipyridine substituent. Thus, the oxidative addition of a bromomethyl derivative of $2,2^{\prime}$-bipyridine, $4-\mathrm{BrCH}_{2}-4^{\prime}-\mathrm{Me}-2,2^{\prime}-\left(\mathrm{C}_{5} \mathrm{H}_{4} \mathrm{~N}\right)_{2}$ 32, to 31 gives a platinum(Iv) complex with a free bipyridine group, which can then coordinate to a second dimethylplatinum unit, and repetition of the sequence can give oligomers with platinum atoms in the backbone as shown in Scheme $6 .{ }^{23}$

A simple self-assembly of a platinum containing polymer occurs on reaction of $\mathbf{3 2}$ with $\mathbf{3 0}$ as shown in Scheme 7. Displacement of the $\mathrm{Me}_{2} \mathrm{~S}$ ligands from 30 gives the platinum (II) monomer 33 which undergoes polymerisation by intermolecular oxidative addition. ${ }^{23}$

## Dendrimeric platinum polymers

To make a dendrimer, it is necessary to introduce a branch in each generational growth step. ${ }^{24}$ This requires at least a trifunctional reagent having two alkyl halide and one bipyridine or one alkyl halide and two bipyridine units as present in $\mathbf{3 4}$ and 35 respectively. The first successful synthesis is a convergent

method based on the reagent 34 (Scheme 8). Reagent 34 can add to 2 equiv. of $\mathbf{3 1}$ to give the diplatinum(Iv) complex 36, which


Scheme 6


Scheme 7
can then add a dimethylplatinum(II) group to the free bipyridine to regenerate a reactive platinum(II) centre in 37, whose structure is shown in Fig. $15 .{ }^{25}$

Now repetition of the cycle using 37 and 34 gives a $\mathrm{Pt}_{7}$ dendrimer 38 (Scheme 9). One more generation can be grown, but the reactive platinum(II) centre, which is formed at the centre of the molecule in a convergent synthesis, becomes increasingly sterically congested with each generation and eventually the oxidative addition step fails. ${ }^{25}$

The self-assembly of a hyperbranched polymer with platinum atoms in the backbone is readily achieved by reaction of $\mathbf{3 4}$ with 30. The first step is ligand substitution to give the platinum(II) complex, which then undergoes polymerisation by intermolecular oxidative addition (Scheme 10). ${ }^{25}$


Scheme 8


Fig. 15 The structure of the $\mathrm{Pt}^{I V}{ }_{2} \mathrm{Pt}^{\mathrm{II}}$ complex 37



Scheme 9

A divergent method for dendrimer growth is based on the reagent 35 , which contains one bromomethyl group and two bipyridine groups. With this system, the reactive platinum(II)


Scheme 10
centres are formed at the periphery of the dendrimer and it is easy to introduce a different metal in the outer generation as shown in Scheme 11, using as a source of dimethylpalladium units the complex $\left[\mathrm{Pd}_{2} \mathrm{Me}_{4}(\mu \text {-pyridazine })_{2}\right] 39 .{ }^{26}$


Scheme 11

Stars and exotic molecules based on polyfunctional cores
Polyfunctional cores are useful for facilitating the rapid growth of complex molecules. Two useful core molecules for platinum oligomers are $\mathbf{4 0}$ and $\mathbf{4 1}$. The synthesis of a $\mathrm{Pt}_{9}$ dendrimer by



Scheme 12
use of the core reagent $\mathbf{4 0}$ and the dendrimer reagent $\mathbf{3 4}$ is shown in Scheme $12 .{ }^{26}$
The core reagent $\mathbf{4 1}$ is useful for assembling four molecules which contain one platinum(II) centre each, including simple molecules like 31 or the more complex linear or dendrimeric molecules prepared in Schemes 6, 8 and $9.23,25,27$ An example is shown in Scheme 13 and the most complex example so far prepared is the $\mathrm{Pt}_{28}$ dendrimer shown in Fig. 16 and formed by coupling four $\mathrm{Pt}_{7}$ dendrimer units 38 to the tetrafunctional core.


Scheme 13


Fig. 16 Proposed structure of the $\mathrm{Pt}_{28}$ dendrimer

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## Notes and References

1 J. R. Ferraro and J. M. Williams, in Introduction to Synthetic Electrical Conductors, Academic Press, New York, 1987, p. 139.
2 R. J. H. Clark, in Lower-Demensional Systems and Molecular Electronics, ed. R. M. Metzger, P. Day and G. C. Papavassilion, Plenum, New York, 1991, p. 263.
3 R. J. Puddephatt, The Chemistry of Gold, Elsevier, Amsterdam, 1978.
4 (a) J. Lewis, M. S. Khan, A. K. Kakkar, B. F. G. Johnson, T. B. Marder, H. B. Fyfe, F. Wittman, R. H. Friend and A. E. Dray, J. Organomet. Chem., 1992, 425, 165; (b) S. J. Davies, B. F. G. Johnson, M. S. Khan and J. Lewis, J. Chem. Soc., Chem. Commun., 1991, 187.
5 M. J. Irwin, G. Jia, J. J. Vittal and R. J. Puddephatt, Organometallics, 1996, 15, 5321.
6 A. M. Bradford, E. Kristof, M. Rashidi, D.-S. Yang, N. C. Payne and R. J. Puddephatt, Inorg. Chem., 1994, 33, 2355.

7 D. M. P. Mingos, J. Yau, S. Menzer and D. J. Williams, Angew. Chem., Int. Ed. Engl., 1995, 34, 1894.
8 M. J. Irwin, G. Jia, N. C. Payne and R. J. Puddephatt, Organometallics, 1996, 15, 51.
9 M. J. Irwin, J. J. Vittal and R. J. Puddephatt, Organometallics, 1997, 16, 3541.

10 J. Li and P. Pyykko, Chem. Phys. Lett., 1992, 197, 586.
11 (a) C.-M. Che, H.-K. Yip, W.-C. Lo and S.-M. Peng, Polyhedron, 1994, 13, 887; (b) V. W.-W. Yam and S. W.-K. Choi, J. Chem. Soc., Dalton Trans., 1996, 4227.
12 G. Jia, N. C. Payne, J. J. Vittal and R. J. Puddephatt, Organometallics, 1993, 12, 4771.
13 G. Jia, R. J. Puddephatt, J. D. Scott and J. J. Vittal, Organometallics, 1993, 12, 3565
14 G. Jia, R. J. Puddephatt and J. J. Vittal, J. Organomet. Chem., 1993, 449, 211.

15 N. C. Payne, R. Ramachandran and R. J. Puddephatt, Can. J. Chem., 1995, 73, 6.
16 M. J. Irwin, L. M. Rendina, J. J. Vittal and R. J. Puddephatt, Chem. Commun., 1996, 1281; M. J. Irwin, PhD thesis, University of Western Ontario, 1997.
17 M.-A. McDonald, H. A. Jenkins and R. J. Puddephatt, unpublished work; M.-A. McDonald, MSc Thesis, University of Western Ontario, Canada, 1997.
18 M. J. Irwin, Lj. Manojlovic-Muir, K. W. Muir, R. J. Puddephatt and D. S. Yufit, Chem. Commun., 1997, 219.

19 M. J. Irwin, J. J. Vittal, G. P. A. Yap and R. J. Puddephatt, J. Am. Chem. Soc., 1996, 118, 13101.
20 J. D. Scott and R. J. Puddephatt, Organometallics, 1983, 2, 1643.
21 L. M. Rendina and R. J. Puddephatt, Chem. Rev., 1997, 97, 1735.
22 S. Achar, R. J. Puddephatt and J. D. Scott, Polyhedron, 1996, 15, 2363; Can. J. Chem., 1996, 74, 1983; S. Achar, J. D. Scott, J. J. Vittal and R. J. Puddephatt, Organometallics, 1993, 12, 4592; S. Achar, J. D. Scott and R. J. Puddephatt, Organometallics, 1992, 11, 2325.
23 S. Achar and R. J. Puddephatt, Organometallics, 1995, 14, 1681.
24 N. Ardoin and D. Astruc, Bull. Soc. Chim. Fr., 1995, 132, 875.
25 S. Achar, J. J. Vittal and R. J. Puddephatt, Organometallics, 1996, 15, 43; S. Achar and R. J. Puddephatt, Angew. Chem., Int. Ed. Engl., 1994, 33, 847.
26 G.-X. Liu and R. J. Puddephatt, Organometallics, 1996, 15, 5257.
27 S. Achar and R. J. Puddephatt, J. Chem. Soc., Chem. Commun., 1994, 1895.

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