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Precious Metal Polymers

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Summary: The synthesis and properties of polymers containing precious metal centres in the backbone are described. Polymers with labile transition metal centres can be prepared by ring-opening polymerization of macrocycles, and examples are given with silver, gold and palladium as the metal centres. In some cases, the polymers can be further organized by using ligands with hydrogen bonding substituents, and self-assembly into sheet or network structures can then occur. Secondary bonding between inorganic centres can also lead to ordered self-assembly. Bicyclic precursors can ring open to form either chains or sheets.

Keywords: bis(pyridine) ligands; diphosphine; gold; palladium; silver

Introduction

There is intense interest in the synthesis and properties of metal-containing polymers.[1] Such polymers may be broadly classified as those having metallic units appended to the polymer backbone or those with metal atoms incorporated into the backbone. Polymers with peripheral metal complexes are most commonly synthesised by functionalization of an organic polymer or by polymerization of an organic monomer with a peripheral metal-containing unit. Two examples are shown in Figures 1 and 2. Figure 1 shows how poly(4-vinylpyridine) can be functionalized by the addition of diphoshinedigold(I) fragments.[2] Short chain diphosphines such as $Ph_2PCH_2CH_2PPh_2$ tend to form intrachain links whereas longer chain diphosphines give a greater degree of interchain crosslinks. With shorter chain diphosphines, the gold(I) centers may be close enough together to form a secondary aurophilic attraction as indicated by the broken bond in Figure 1. Figure 2 shows how a vinyl monomer containing an organoplatinum(IV) unit can be polymerized to give a polymer with pendant organometallic units.[3] A polymer having the same functionality can be prepared by adding the platinum unit by oxidative addition after polymerization as shown in Figure 2.

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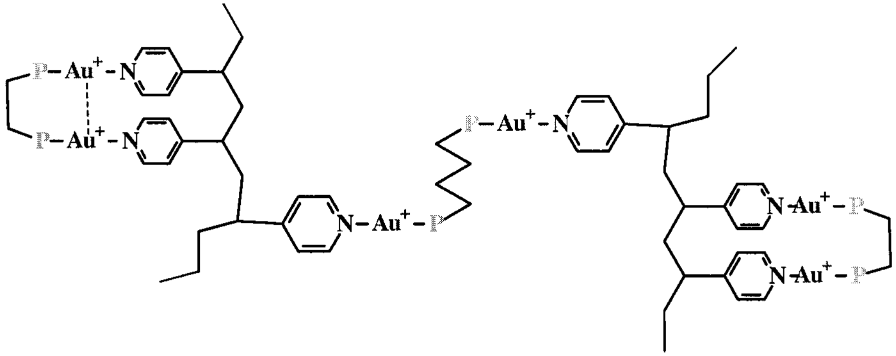


Figure 1. Poly-4-vinylpyridine functionalized with diphosphinedigold(I) units.

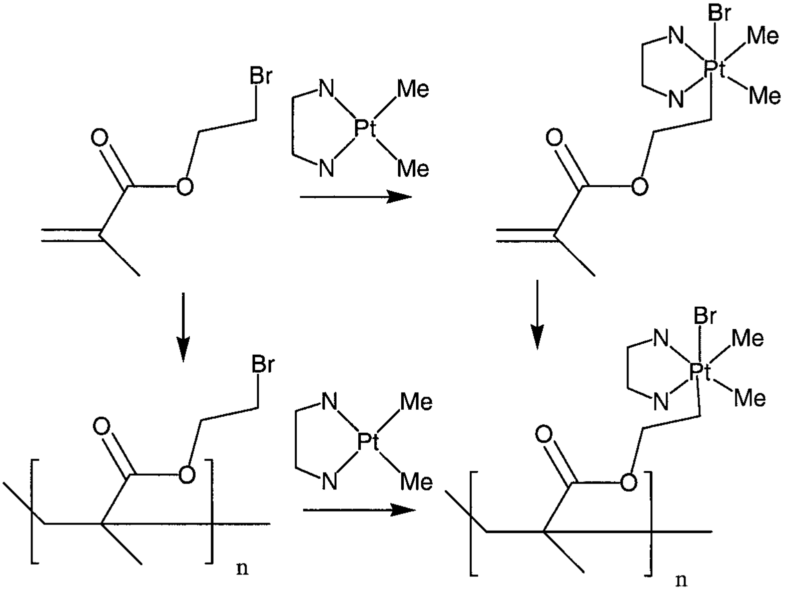
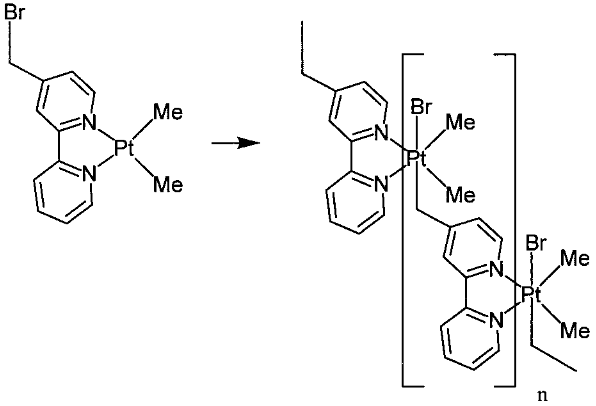


Figure 2. Two routes to synthesis of organoplatinum polymers (NN = 2,2'-bipyridine).

This article is concerned with the synthesis of polymers with transition metal atoms in the backbone. Three mechanisms of polymerization have been studied as detailed below.

Addition Polymerization

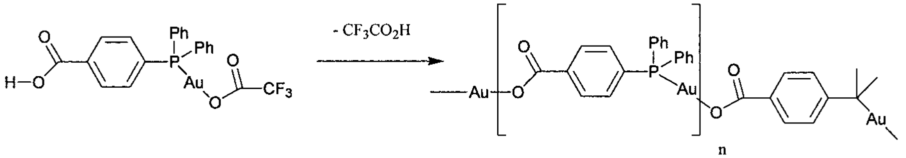
The first method involves addition polymerization at a metal center. An example involving oxidative addition as the propagation step is shown in equation (1).[4]



(1)

Condensation Polymerization

Several examples of condensation oligomerization or polymerization have been found.[5,6] A recent example is shown in equation (2). The product polymer can be crystallized and forms a double-stranded polymer. The polymer strands are held together by aurophilic attractions in the solid state as shown in Figure 3.



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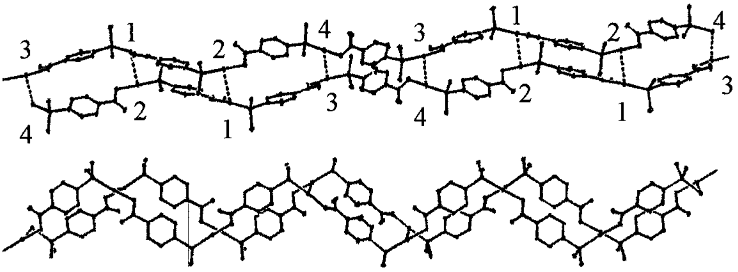


Figure 3. Two views of the double stranded polymer of equation 1, with only the *ipso* carbon atoms of the phenyl groups shown. The aurophilic bonds are shown as dashed lines.

Ring-Opening Polymerization

Recent advances have been made in designing strained ring complexes that can easily undergo ring-opening polymerization, in which ring strain is relieved. Several examples have been discovered in gold(I) chemistry. For example, the dithiolate complex with bridging *trans*-bis(diphenylphosphino)ethylene exists as a macrocycle in solution but crystallizes as the ring-opened polymer, whose structure is shown in Figure 4.[7] The individual chains are associated through weak interchain attractions between AuS groups as shown in Figure 4.

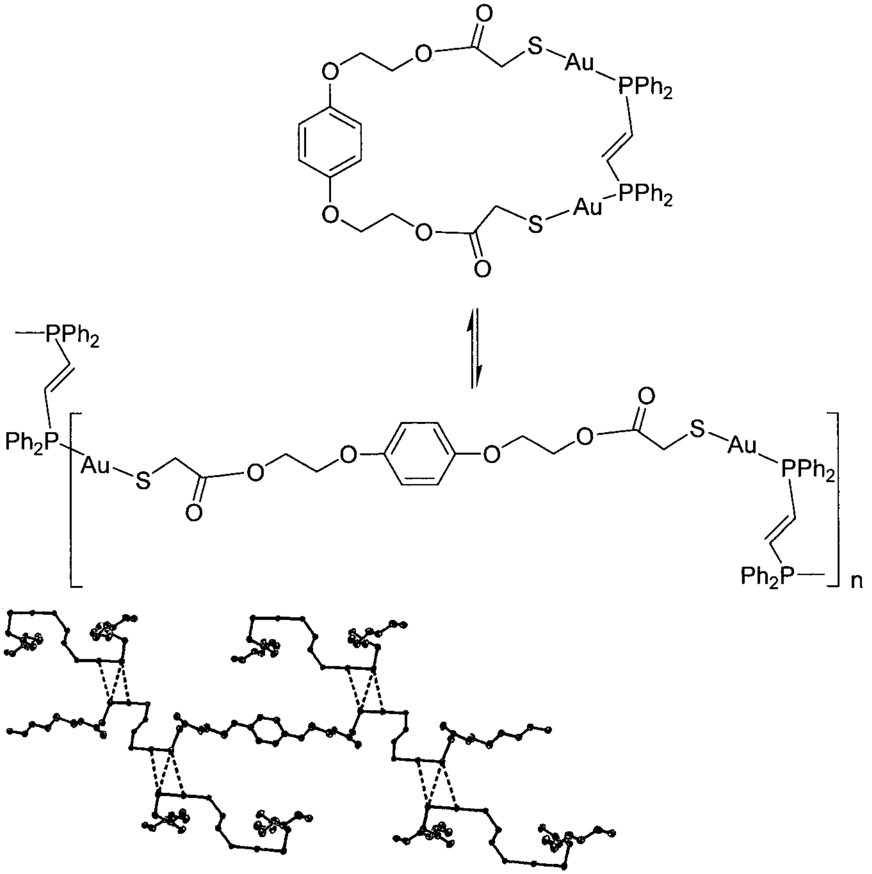


Figure 4. The structure of the dithiolate(diphosphine)digold(I) polymer. The dashed lines indicate weak interchain bonds and the phenyl groups of the diphosphine are omitted for clarity.

An example of a bis(pyridine) complex of gold(I) thatcan ring open is shown in Figure 5. When the diphosphine is $Ph_2PCH_2CH_2PPh_2$, the complex exists in solution as a mixture of the macrocycle and the ring-opened oligomer. Crystallization then yields the unusual 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.[8]

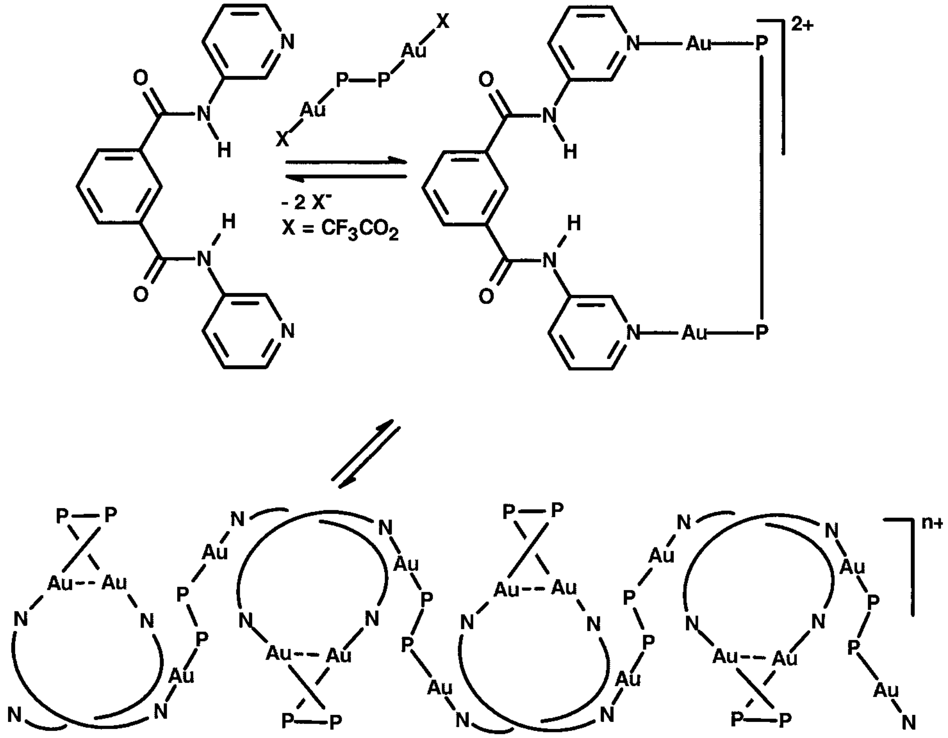


Figure 5. Ring-opening polymerizationof a cationic bis(pyridine)digold(I) macrocycle.

In this example the amide groups of the ligand are not involved in interchain hydrogen bonding but, in other cases, such bonding can occur and can lead to supromolecular association of the polymer chains to give duplexes, or sheet or network structures. An example is shown in Figure 6, in which the supramolecular structure formed through interchain hydrogen bonding is a network structure.[8]

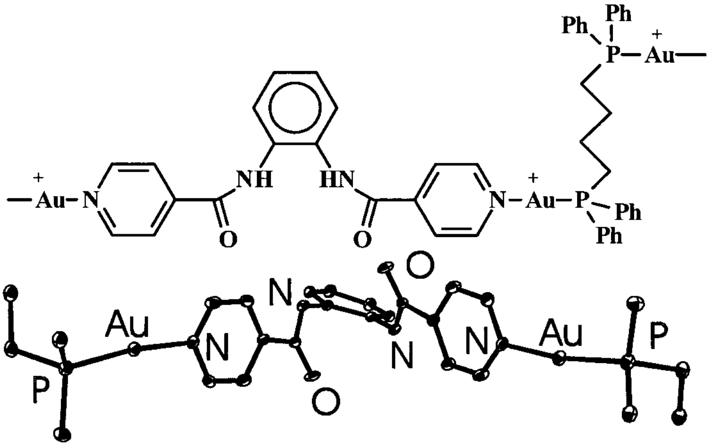
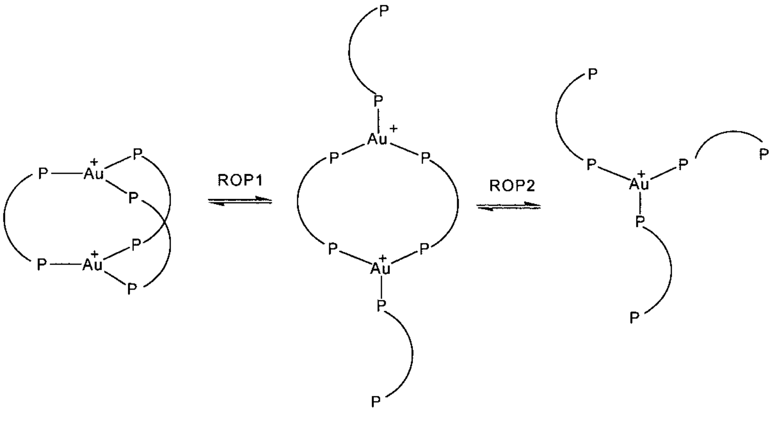


Figure 6. The repeat unit in the polymer chain of a cationic gold(I) polymer. The chains are crosslinked through interchain NH..O=C hydrogen bonding to give a supramolecular network structure.

Double Ring-Opening Polymerization

A polycyclic transition metal complex can undergo multiple ring-opening and this can also lead to formation of unusual structures. The first ROP gives a chain structure and the second gives a sheet.



The structures of two such reactions are shown in Figures 7 and 8. The one-dimensional chain compound is formed when the diphosphine PP = *trans*-$Ph_2PCH{=}CHPPh_2$ and is shown in Figure 7. It contains alternating ring and chain sections, like a chain-link fence.[10]

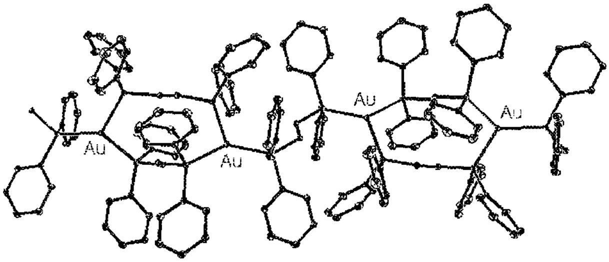


Figure 7. The chain link fence structure formed by single ring-opening polymerization (trifluoroacetate anions are not shown).

The double ring-opening polymerization occurs when the the diphosphine PP = $Ph_2P(CH_2)_4PPh_2$ and the structure is shown in Figure 8 (left).[10] The anions in this case are $[Au(CN)_2]^-$ and two of them are present in each giant ring. This is a honeycomb structure with the gold atoms having trigonal planar stereochemistry. A similar double ring opening is observed with silver(I) when the the diphosphine PP = $Ph_2P(CH_2)_6PPh_2$ and the structure is shown in Figure 8 (right).[11] In this case, the trifluoacetate anions also coordinate to silver(I), which therefore has distorted tetrahedral stereochemistry. In this case, the structure is a puckered sheet with alternate anions coordinated on either side of the plane of the sheet structure.

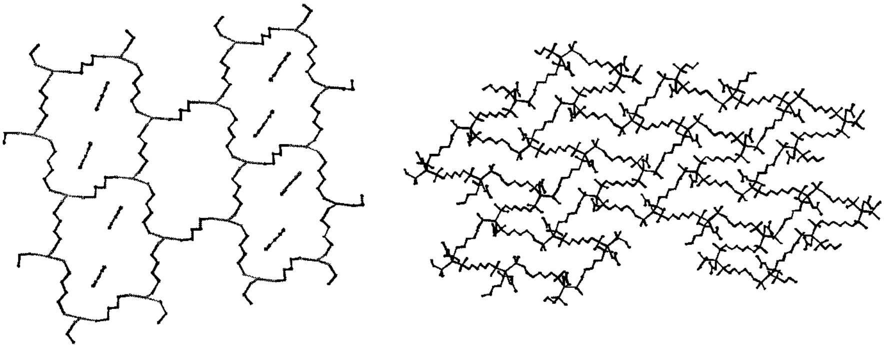


Figure 8. The honeycomb (left) and puckered sheet (right) structures (phenyl groups omitted).

Conclusion

Ring-opening polymerization is shown to be a very powerful method for the synthesis of polymeric, sheet and network structures. Further structural complexity and ordering may be obtained by using interchain aurophilic attractions or hydrogen bonding. These synthetic advances should prove useful in the design of functional molecular materials.

Acknowledgments

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