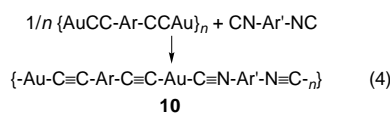


Fig. 1 The intermolecular association present in the solid state structure of $[\text{PhC}\equiv\text{CAuC}\equiv\text{NBu}^2\text{C}_6\text{H}_2\text{N}\equiv\text{CAuC}\equiv\text{CPh}]$ due to (a) π -stacking and (b) $\text{Au}\cdots\text{Au}$ bonding. The $\text{Au}\cdots\text{Au}$ distance is $3.174(1)$ Å.

eqn. (4) (Ar and Ar' are as defined earlier). The polymers are



insoluble, which might have been predicted since intermolecular association through π stacking and/or $\text{Au}\cdots\text{Au}$ 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

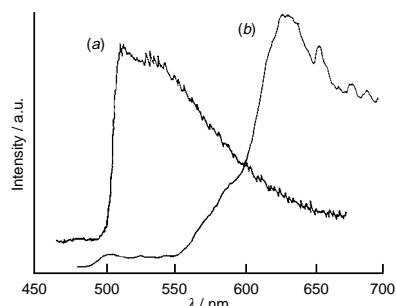


Fig. 2 The emission spectra of $\text{XyNC-Au-CCC}_6\text{H}_4\text{NO}_2-4$, (a) in solution in CH_2Cl_2 and (b) in the solid state, showing the red shift in the solid state. In this case the association in the solid state is due to π -stacking.

when $\text{Au}\cdots\text{Au}$ 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

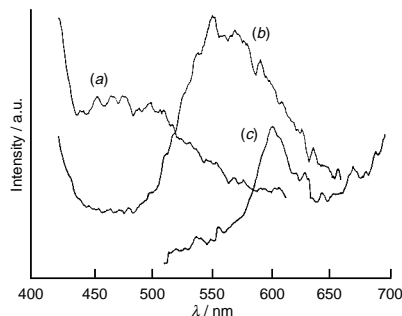
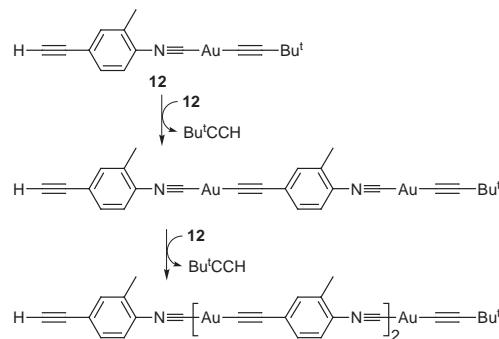


Fig. 3 The solidstate emission spectra of gold(I) complexes showing the red shift with increasing molecular size: (a) $[\text{Bu}^1\text{N}\equiv\text{C-Au-C}\equiv\text{CPh}]$, (b) $\text{XyN}\equiv\text{C-Au-CCC}_6\text{H}_4\text{-C}_6\text{H}_4\text{CC-Au-C}\equiv\text{NXy}$ and (c) $\{ \text{Au-C}\equiv\text{C-C}_6\text{H}_2\text{Me}_2\text{C}\equiv\text{C-Au-C}\equiv\text{NC}_6\text{H}_2\text{Bu}^1 \}_n$

provides evidence for at least some π conjugation in the rigid-rod chains.⁹

The new ligands $4\text{-HC}\equiv\text{CC}_6\text{H}_4\text{N}\equiv\text{C}$ and $4\text{-HC}\equiv\text{C-2-MeC}_6\text{H}_3\text{N}\equiv\text{C}$ bind readily to gold(I) in forming the complexes

such as $[4\text{-HC}\equiv\text{CC}_6\text{H}_4\text{N}\equiv\text{C-Au-Cl}]$ **11** and $[4\text{-HC}\equiv\text{C-2-MeC}_6\text{H}_3\text{N}\equiv\text{C-Au-C}\equiv\text{CBu}^t]$ **12**. The acetylide derivatives such as **12** give weak $\text{Au}\cdots\text{Au}$ bonded association in the solid state [$\text{Au}\cdots\text{Au}$ $3.479(2)$ Å] and form oligomeric complexes $\text{H-(C}\equiv\text{C-Ar-N}\equiv\text{C-Au-)}_n\text{-C}\equiv\text{CBu}^t$ **13** by elimination of Bu^tCCH 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 PMe_3 to give binuclear model complexes such as $[(\text{Me}_3\text{P})\text{Au-C}\equiv\text{C-C}_6\text{H}_2\text{Me}_2\text{-C}\equiv\text{C-Au}(\text{PMe}_3)]$ **14** and this forms loose polymers in the solid state by intermolecular $\text{Au}\cdots\text{Au}$ bonding (Fig. 4).^{9,13}

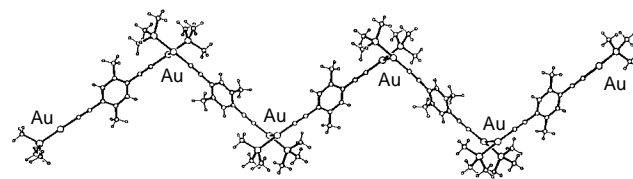


Fig. 4 The intermolecular association through $\text{Au}\cdots\text{Au}$ bonding in the complex $[(\text{Me}_3\text{P})\text{Au-C}\equiv\text{C-C}_6\text{H}_2\text{Me}_2\text{-C}\equiv\text{C-Au}(\text{PMe}_3)]$

The diphosphines $\text{Ph}_2\text{PC}_6\text{H}_4\text{PPh}_2$ or $\text{Pr}^i_2\text{PC}_6\text{H}_4\text{C}_6\text{H}_4\text{PPri}^i_2$ can also give binuclear model complexes such as $\text{PhC}\equiv\text{C-Au-Pr}^i_2\text{PC}_6\text{H}_4\text{C}_6\text{H}_4\text{PPri}^i_2\text{-Au-C}\equiv\text{CPh}$ **15** which has the *anti* conformation with respect to the two P-Au vectors as shown in Fig. 5; the bulky Pr^i groups prevent the formation of

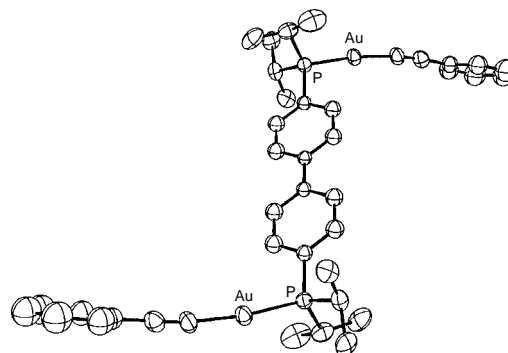


Fig. 5 The *anti* conformation of the two P-Au vectors in $[\text{PhC}\equiv\text{C-Au-Pr}^i_2\text{PC}_6\text{H}_4\text{C}_6\text{H}_4\text{PPri}^i_2\text{-Au-C}\equiv\text{CPh}]$ **15**

intermolecular $\text{Au}\cdots\text{Au}$ bonding in **15**. It is then straightforward to prepare polymers $(\text{Au-C}\equiv\text{C-Ar-C}\equiv\text{C-Au-PR}_2\text{-Ar'-PR}_2\text{-})_n$ **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 $R = Pr^i$ to allow molecular mass determination by GPC. The improved solubility probably arises because the bulky Pr^i groups prevent crosslinking by intermolecular $Au \cdots Au$ 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 $Au \cdots Au$ bonding, as for example in $CH_2(PCy_2-Au-O_2CCF_3)_2$ **17** or $CH_2(PPh_2-Au-C \equiv CBu^t)_2$ **18** shown in Fig. 6.^{14,15} This conformation is

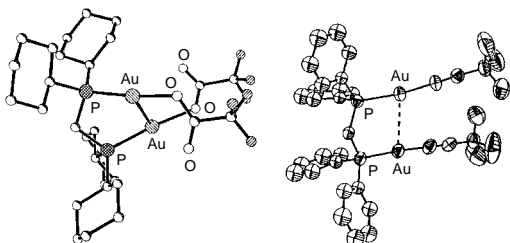


Fig. 6 The *syn* conformation of the two P–Au vectors in $[CH_2(PCy_2-Au-O_2CCF_3)_2]$ **17** and $[CH_2(PPh_2-Au-C \equiv CBu^t)_2]$ **18**

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- $C \equiv NC_6H_4N \equiv C$ is shown in Fig. 7.

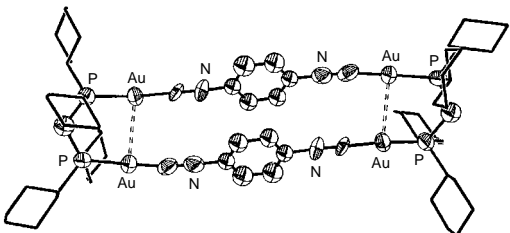


Fig. 7 The structure of the cationic ring complex **20** ($R = Cy$ and $Ar = 1,4-C_6H_4$)

It is also possible to use mixed phosphine–acetylide donors in forming polymers of gold(I). Thus the ligands $Ph_2PC \equiv CH$ and $Pr^i_2PC \equiv CH$ 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

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- $(HC \equiv C)_2C_6H_3Me-5$ yields digold(I) model complexes 1,3- $(L-Au-C \equiv C)_2C_6H_3Me-5$ **22** ($L =$ phosphine, phosphite or isocyanide ligand) which form ribbon structures in the solid state through $Au \cdots Au$ bonding as seen in Fig. 8.¹⁷

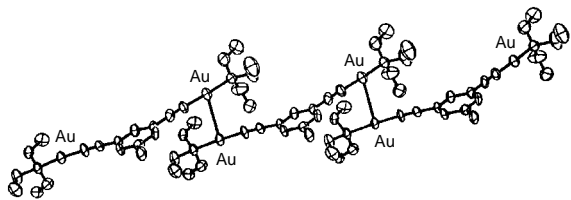
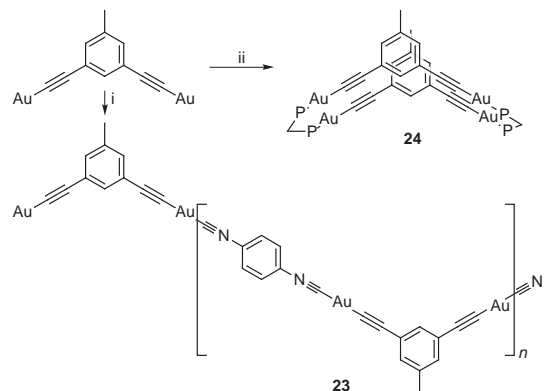


Fig. 8 The intermolecular association through $Au \cdots Au$ bonding in the complex $[1,3-(L-Au-C \equiv C)_2C_6H_3Me-5]$ [$L = P(OMe)_3$]

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



Scheme 2 Reagents: i, $C_6H_4(CN)_2$; ii, $Ph_2PCH_2PPh_2$

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 $Au \cdots Au$ 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 $Au \cdots Au$ bonding (Fig. 9). With all bridging ligands,

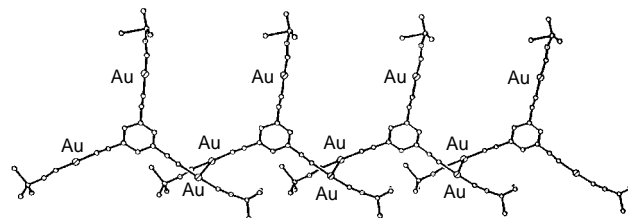
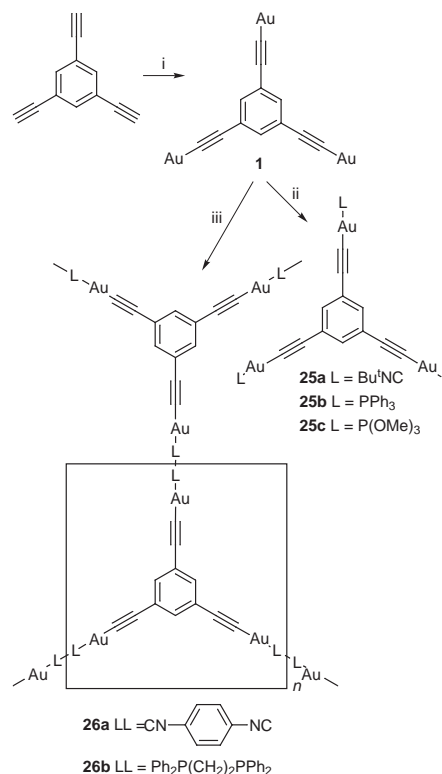


Fig. 9 The intermolecular association through $Au \cdots Au$ bonding in the complex $[1,3,5-(L-Au-C \equiv C)_3C_6H_3]$ ($L = Bu^tNC$)

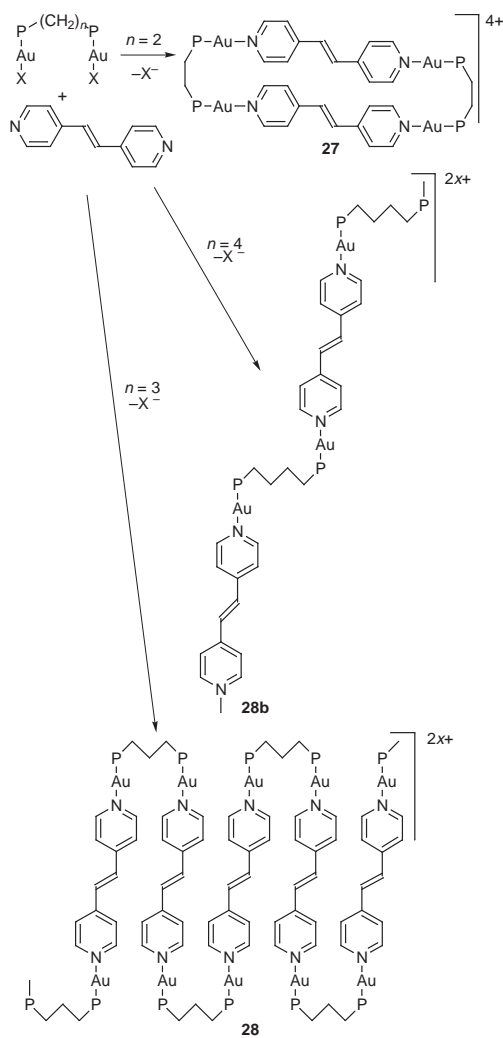
whether the strictly linear diisocyanides or angular diphosphines, insoluble polymers **26** are formed (Scheme 3).¹⁸



Scheme 3 Reagents: i, $[AuCl(SMe_2)]$, $NaOAc$; 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 $(\text{CH}_2)_n(\text{PPh}_2)_2$ and a more labile linear bridging ligand *trans*-1,4-bis(pyridyl)-ethene. 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 large rings to polymers at some point in the series (Scheme 4). Further, the polymers could reversibly cleave to smaller fragments in solution owing to the lability of the pyridine donors and this might allow crystallisation and so to full structural characterisation of the polymers.¹⁹



Scheme 4 X = CF_3CO_2 , P = PPh_2

With $(\text{CH}_2)_2(\text{PPh}_2)_2$, the ring structure $[\text{Au}_4(\mu\text{-Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2(\mu\text{-NC}_5\text{H}_4\text{CH}=\text{CHC}_5\text{H}_4\text{N})_2]^{4+}$ **27** is preferred as shown in Fig. 10 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 .¹⁹

The switch to a polymeric structure $[\{\text{Au}_2[\mu\text{-Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2](\mu\text{-NC}_5\text{H}_4\text{CH}=\text{CHC}_5\text{H}_4\text{N})\}_n]^{2n+}$ **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 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. 11(b)].¹⁹

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

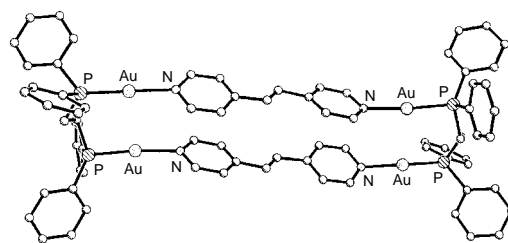


Fig. 10 The structure of the cationic ring complex $[\text{Au}_4(\mu\text{-Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2(\mu\text{-NC}_5\text{H}_4\text{CH}=\text{CHC}_5\text{H}_4\text{N})_2]^{4+}$

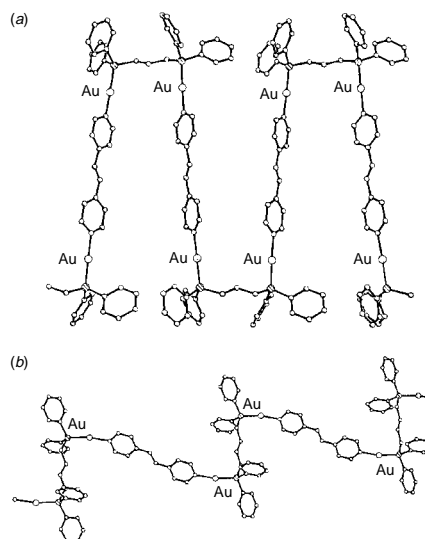


Fig. 11 The structures of the cationic polymer chains $[\{\text{Au}_2[\mu\text{-Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2](\mu\text{-NC}_5\text{H}_4\text{CH}=\text{CHC}_5\text{H}_4\text{N})\}_n]^{2n+}$; (a) $n = 3$; (b) $n = 4$

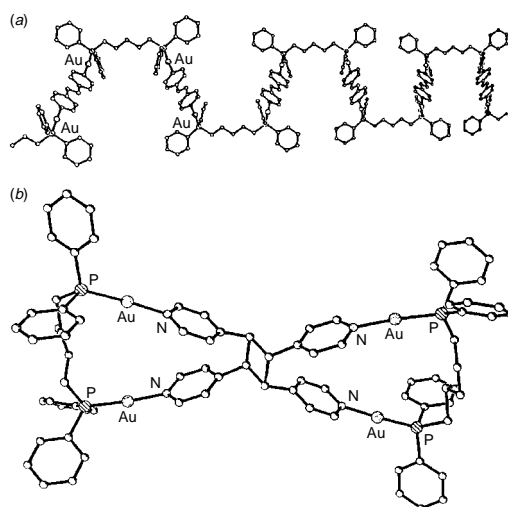
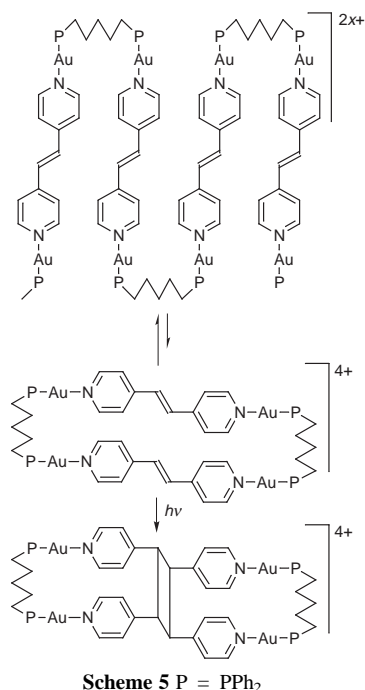


Fig. 12 The structures of the helical (a) cationic polymer chains $[\{\text{Au}_2[\mu\text{-Ph}_2\text{P}(\text{CH}_2)_5\text{PPh}_2](\mu\text{-NC}_5\text{H}_4\text{CH}=\text{CHC}_5\text{H}_4\text{N})\}_n]^{2n+}$, and of the cyclobutane ring form (b)

are polymers **28c**, 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) ethene 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 **28d** (Fig. 13) whose structure is similar to that of **28b**, having *anti* conformation of adjacent P–Au vectors but with the long (CH₂)₆ chain partly folded back on itself.¹⁶

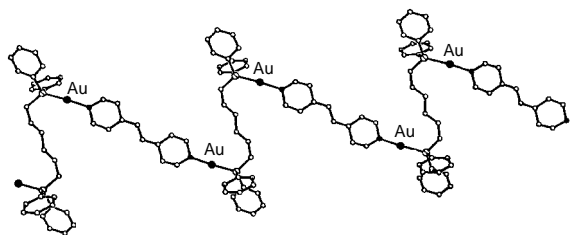


Fig. 13 The structure of the cationic polymer chain $[\{Au_2[\mu\text{-}Ph_2P(CH_2)_6PPh_2](\mu\text{-}NC_5H_4CH=CHC_5H_4N)\}_n]^{2n+}$

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*-Ph₂PCH=CHPPh₂ or [Fe(η^5 -C₅H₄PPh₂)₂]; the structure of the polymer **29** prepared from the latter ligand is shown in Fig. 14 and has the stretched polymer form with *anti*

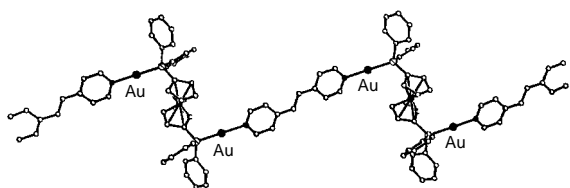


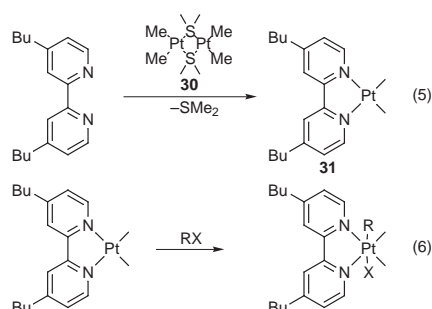
Fig. 14 The structure of the cationic polymer chain $[\{Au_2[\mu\text{-}Fe(C_5H_4PPh_2)_2](\mu\text{-}NC_5H_4CH=CHC_5H_4N)\}_n]^{2n+}$

conformation of adjacent P–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'-di-*tert*-butyl-2,2'-bipyridine onto a dimethylplatinum(II) centre by displacement of weakly bound Me₂S ligands from [Pt₂Me₄(μ -SMe₂)₂] **30** to give **31**,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.

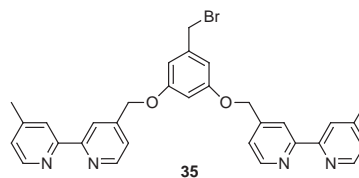
Linear chain platinum polymers

The oxidative addition of 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'-bipyridine, 4-BrCH₂-4'-Me-2,2'-(C₅H₄N)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

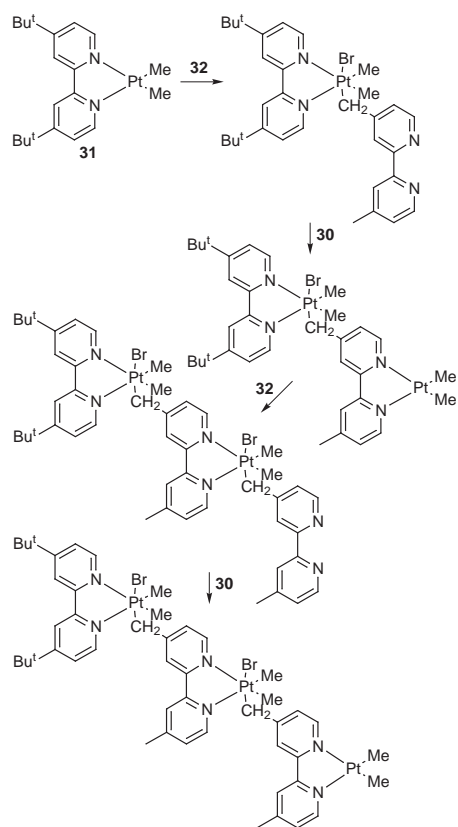
A simple self-assembly of a platinum containing polymer occurs on reaction of **32** with **30** as shown in Scheme 7. Displacement of the Me₂S ligands from **30** gives the platinum(II) monomer **33** which undergoes polymerisation by intermolecular oxidative addition.²³

Dendrimeric platinum polymers

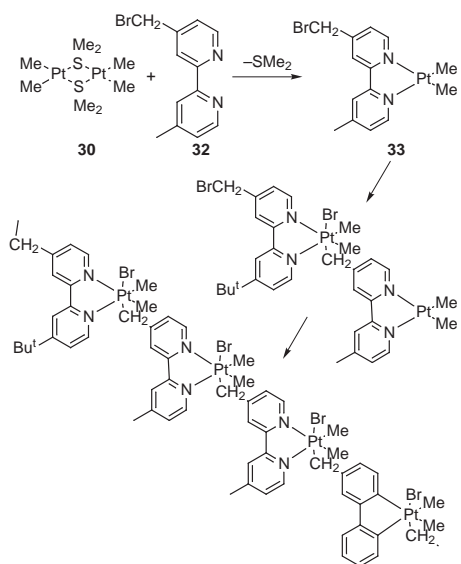
To make a dendrimer, it is necessary to introduce a branch in each generational growth step.²⁴ This requires at least a trifunctional reagent having two alkyl halide and one bipyridine or one alkyl halide and two bipyridine units as present in **34** and **35** respectively. The first successful synthesis is a convergent



method based on the reagent **34** (Scheme 8). Reagent **34** can add to 2 equiv. of **31** to give the diplatinum(IV) complex **36**, which



Scheme 6

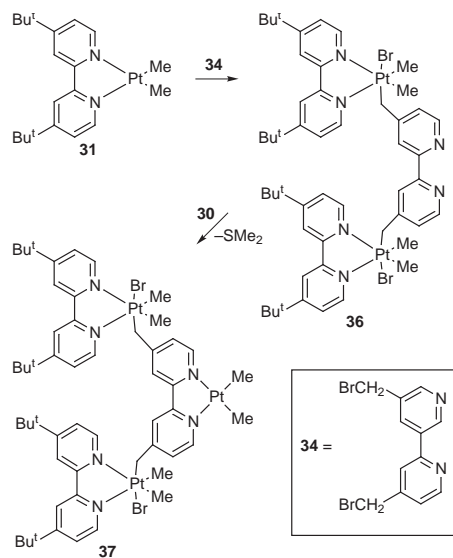


Scheme 7

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 Pt₇ 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 **34** 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

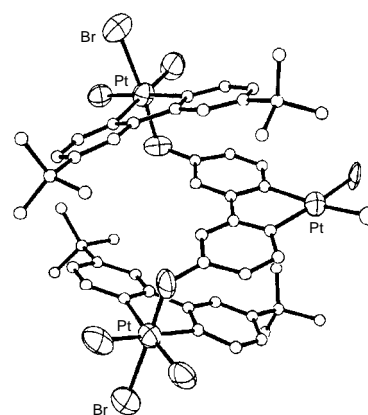
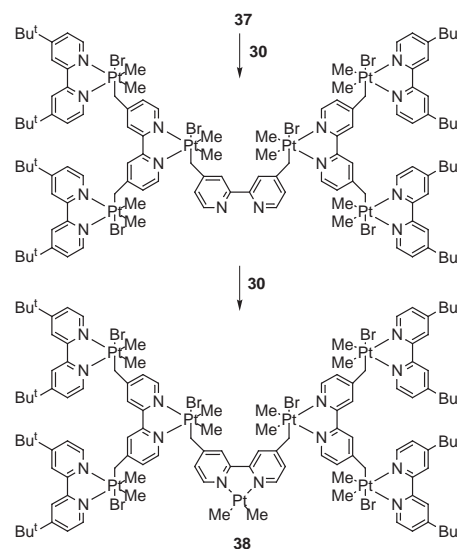
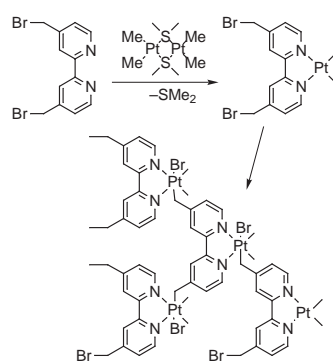


Fig. 15 The structure of the Pt^{IV}₂Pt^{II} complex **37**



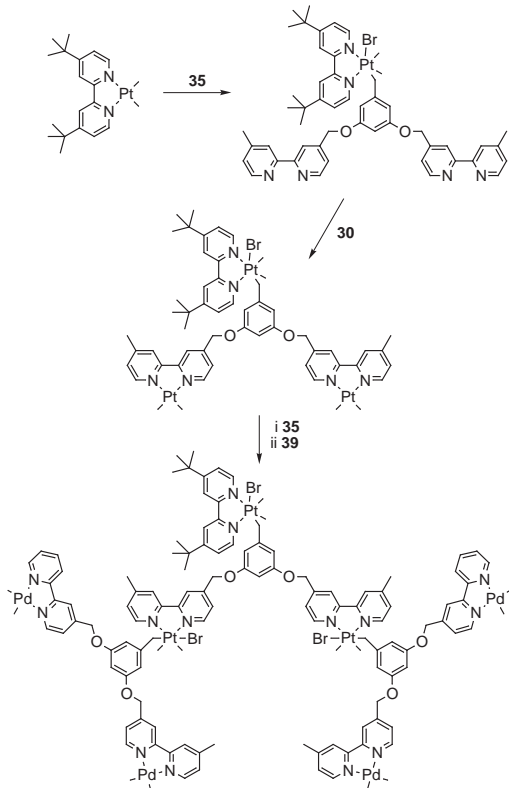
Scheme 9

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

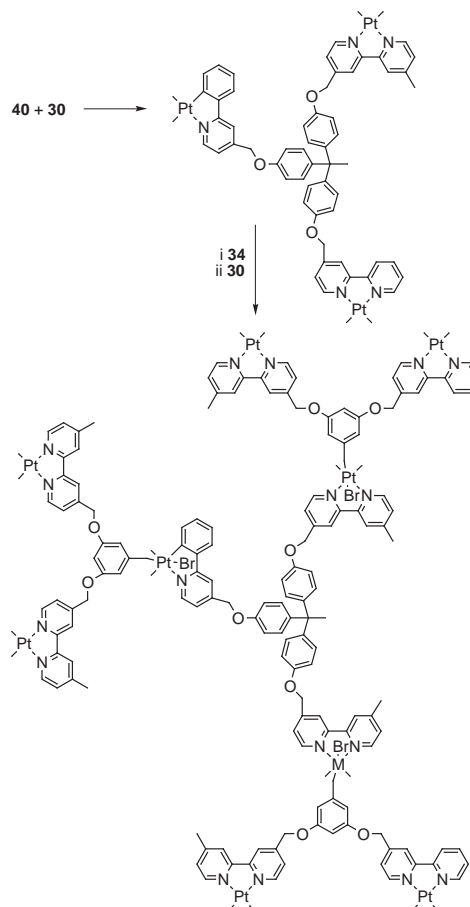
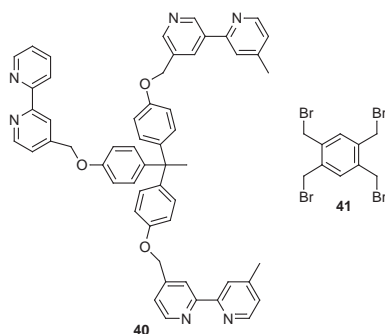
centres are formed at the periphery of the dendrimer and it is easy to introduce a different metal in the outer generation as shown in Scheme 11, using as a source of dimethylpalladium units the complex $[\text{Pd}_2\text{Me}_4(\mu\text{-pyridazine})_2]$ **39**.²⁶



Scheme 11

Stars and exotic molecules based on polyfunctional cores

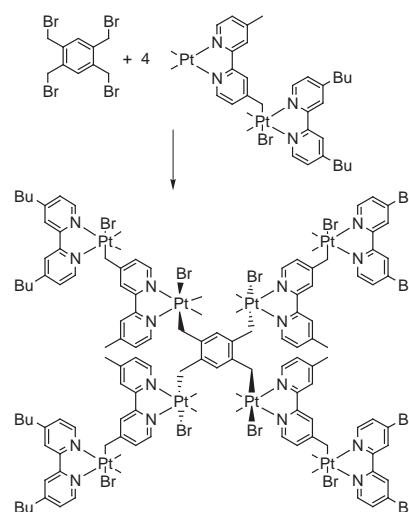
Polyfunctional cores are useful for facilitating the rapid growth of complex molecules. Two useful core molecules for platinum oligomers are **40** and **41**. The synthesis of a Pt_9 dendrimer by



Scheme 12

use of the core reagent **40** and the dendrimer reagent **34** is shown in Scheme 12.²⁶

The core reagent **41** 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 Pt_{28} dendrimer shown in Fig. 16 and formed by coupling four Pt_7 dendrimer units **38** to the tetrafunctional core.



Scheme 13

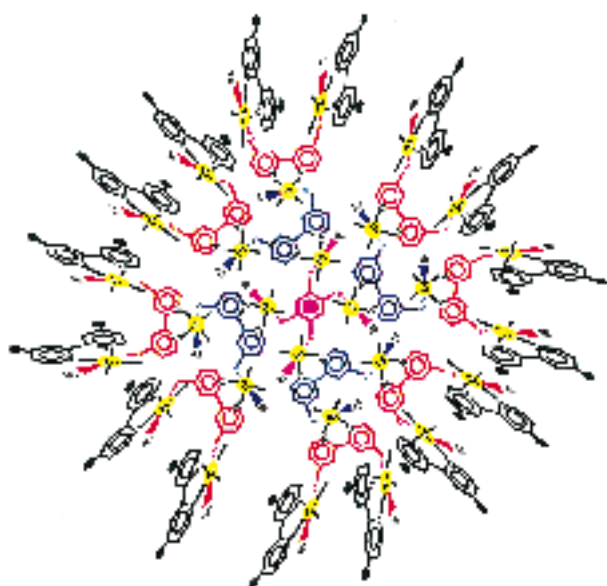


Fig. 16 Proposed structure of the Pt₂₈ dendrimer

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