

Novel oligopyridines for metallosupramolecular chemistry

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Abstract: The use of oligopyridines in metallosupramolecular chemistry will be exemplified and the use of these readily available ligands for the building of a variety of types of assembly will be illustrated.

Introduction

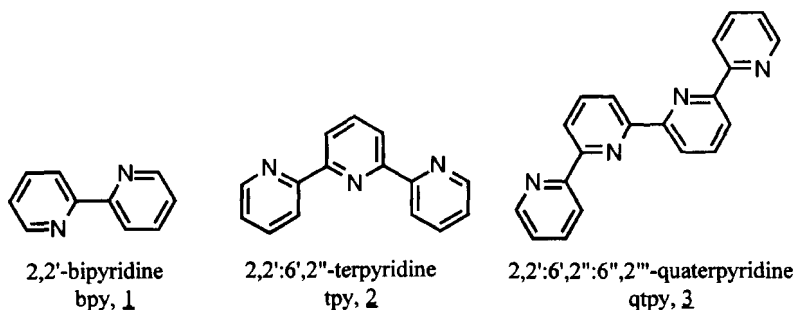
Metallosupramolecular chemistry is concerned with the use of metal ions to control the assembly of appropriate molecular components containing metal-binding domains. The advantages of the methodology lie in the remarkable topological, topographical and stereochemical control which may be achieved as a consequence of the specific coordination requirements of particular metal ions. Although a variety of metal-binding domains have been used, the oligopyridines have proved to be particularly popular choices. The purpose of this article is to give an overview of the power of the metal-based assembly method.

What is metallosupramolecular chemistry?

Supramolecular chemistry is 'chemistry beyond the molecule, bearing on the organized entities of higher complexity that results from the association of two or more chemical species held together by intermolecular forces' (1). The basic tenets of *metallosupramolecular* chemistry are now repeated here (2). Transition metal ions have characteristic and preferred coordination numbers (the number of ligands or donor atoms bonded to the metal) and coordination geometries (the spatial arrangements of the ligands and donor atoms in space). These characteristics may be matched with the inherent bonding properties of polydentate ligands (the number, type and spatial distribution of donor atoms). These ligands may contain one or more metal-binding domains. The assembly process is coded by the acceptor properties of the metal ions (size, coordination number and coordination geometry) and the donor properties of the ligand (number and spatial arrangement of donor atoms). Using this basic model, it is possible to build a wide range of novel and useful assemblies.

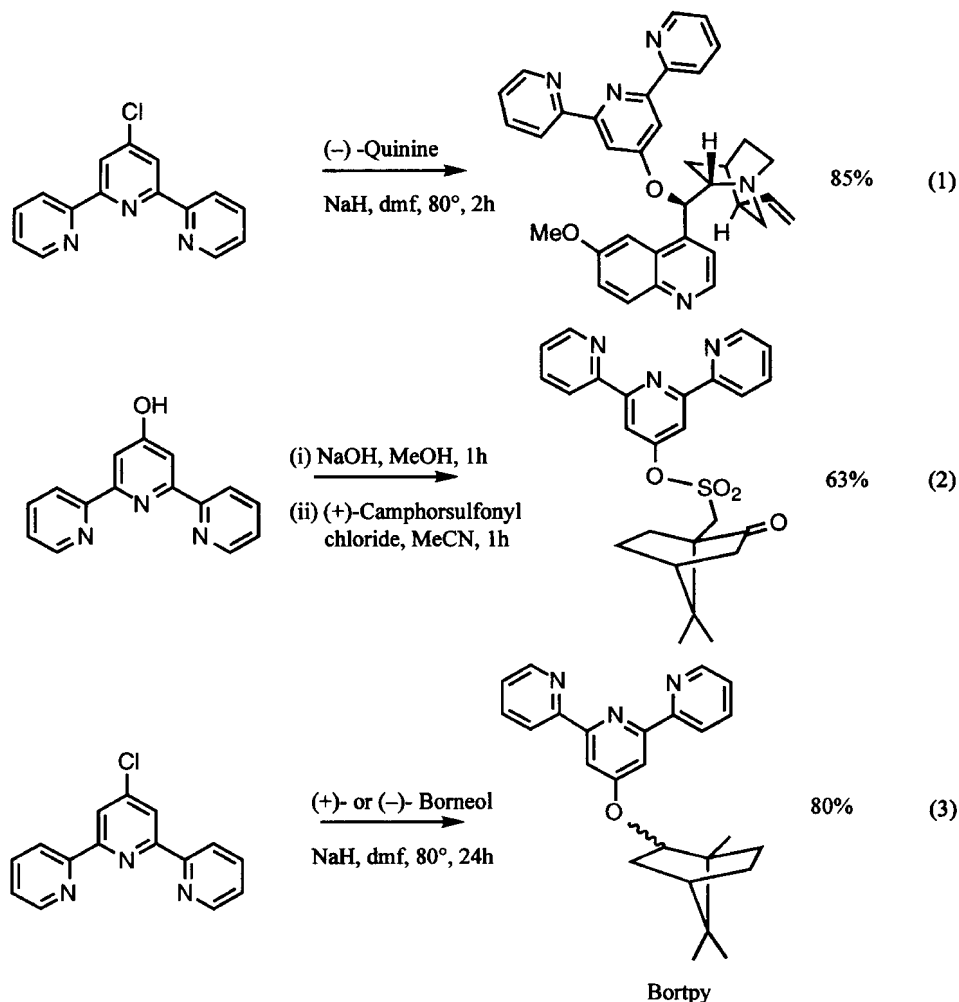
The oligopyridines

This article is concerned with the use of the prototypical oligopyridines as components of metallosupramolecular systems. These ligands are bpy (1), tpy (2) and qtpy (3). There is a number of reasons for the widespread use of such ligands. They are readily available with a variety of substituents, and their complexes are thermodynamically and often kinetically stable. Furthermore, complexes are readily formed with most metal ions in a variety of oxidation states. We have discussed previously the reasons which have lead us (3) and others (4) to adopt the tpy metal-binding domain as a building block in supramolecular chemistry.



Substituted 2,2':4',6''-terpyridines as metal-binding domains

The ease of synthesis of 4'-substituted 2,2':6',2''-terpyridines (5) has meant that we have concentrated upon this structural motif. Although the $[\text{Ru}(\text{tpy})_2]^{2+}$ structural unit is not normally luminescent in fluid solution at room temperature, we have demonstrated that useful photoactivity may be obtained in two ways. The introduction of strongly electron-withdrawing substituents, such as SO_2Me , yields complexes with photophysical properties reminiscent of $[\text{Ru}(\text{bpy})_3]^{2+}$ (6) whilst luminescent *substituents* such as 9-anthryl, give ligand-centred properties which may be modified or lost upon coordination (7).



One of the reasons we adopted the $[\text{M}(\text{tpy})_2]$ motif was the fact that it was achiral, in contrast to $[\text{M}(\text{bpy})_3]$. However, we have recently addressed questions of chirality and have shown that chiral substituents, derived from the chiral pool, may readily be incorporated into the 4'-position of a tpy ligand (Eqs. 1 - 3) (8). These reactions occur without racemisation and each of these chiral ligands has been structurally characterised and the absolute configuration confirmed. The aim of these studies was the detection of chiral discrimination within the diastereomeric complexes that could be formed. However, the site of chirality is relatively remote from the metal-binding domain and we observe no differences between the ^1H NMR spectra of diastereomeric pairs of complexes such as $[\{(+)\text{-Bortpy}\}\text{Ru}\{(-)\text{-Bortpy}\}]^{2+}$ and $[\{(-)\text{-Bortpy}\}\text{Ru}\{(-)\text{-Bortpy}\}]^{2+}$. We are currently preparing a second generation of ligands in which the chiral substituents are attached to the 6-position of the tpy ligand.

As a part of our programme aimed at the synthesis of molecular machines we have recently introduced a variety of redox-functionalised oligopyridines bearing ferrocenyl substituents (9). In the most recent extension of this program, we have probed the introduction of main group and transition metal clusters as substituents. Our original attempts to prepare carboranyl-substituted free ligands were attended by low yields (0 - 10%), but the solid state structures of the species so obtained were sufficiently interesting that we searched for improved synthetic routes (10). For example, compound **4** formed a lattice in which the planar tpy domains formed stacks and the hydrophobic carboranyl substituents formed channels (Fig. 1).

Although we eventually obtained acceptable yields of carboranyl substituted compounds by the assembly of the carborane directly in the complex from the reaction of decaborane with the ruthenium(II) complexes of acetylene-substituted tpy ligands 5 (Eq. 4), the properties of these complexes proved to be somewhat disappointing. In particular, the remote carboranyl substituent was found to have no influence upon the redox properties of the ruthenium centre.

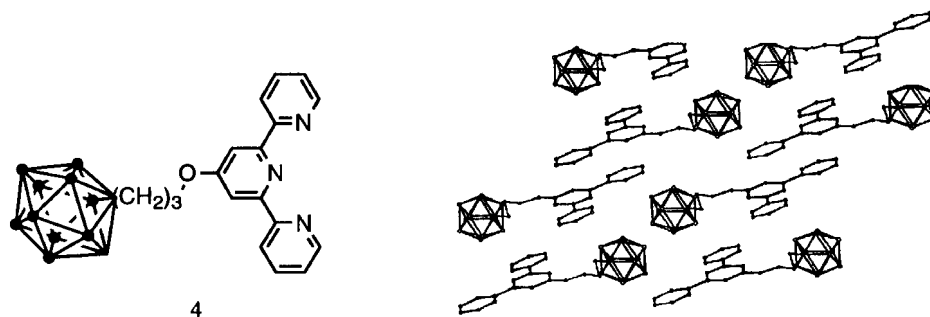
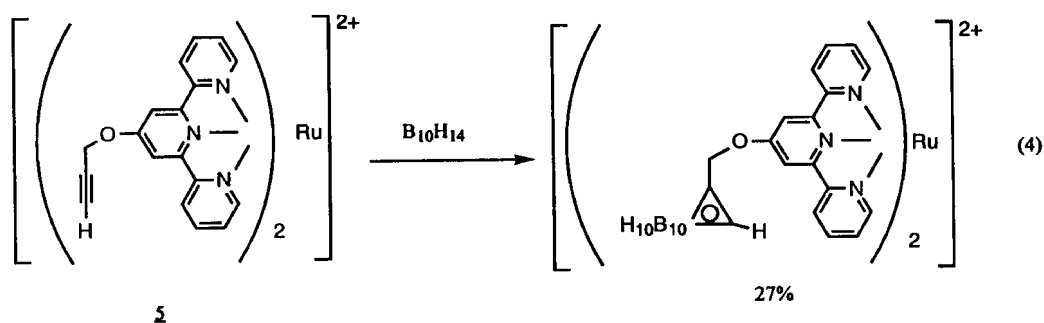
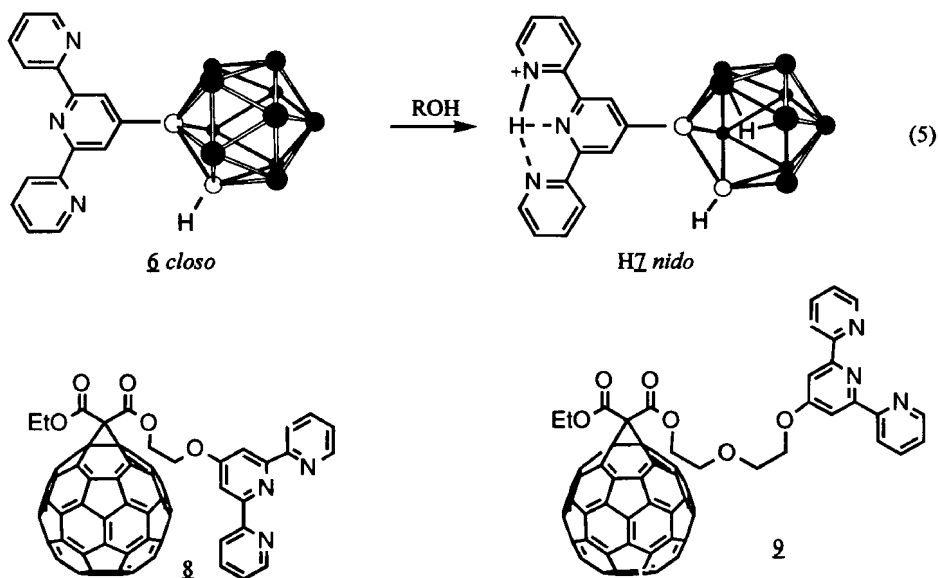


Fig. 1 Packing of 4 in the crystal



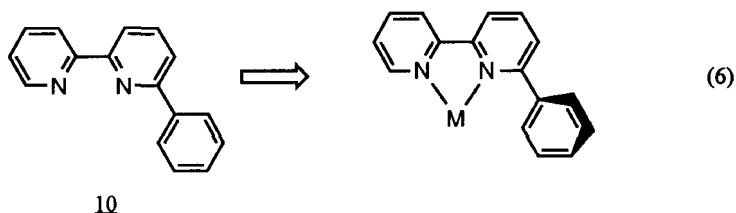
This problem was eventually circumvented by the attachment of the carborane directly to the tpy in ligand 6. In this case, the ruthenium(II)/(III) potential of the complex $[\text{Ru}(\text{6})_2][\text{PF}_6]_2$ was found to be affected by the cluster substituent, and more importantly the chemistry of the carborane was also affected by the presence of the tpy or the metal. Although the free ligand was stable in non-protic solvents, reaction with alcohols resulted in a decapping and the formation of a zwitterionic *nido* species H7 (Eq. 5). A similar decapping to give a *nido* ligand also occurs with the coordinated ligand. The change from the neutral *closo*



ligand 6 to the anionic *nido* ligand in $[\text{Ru}(\text{7})_2]$ results in a change in the ruthenium(II)/(III) redox potential of about 200 mV (11). In the most recent extension of this work, we have introduced all-carbon fullerene clusters as substituents and are currently probing the properties of the metal complexes of ligands such as 8 and 9 (12).

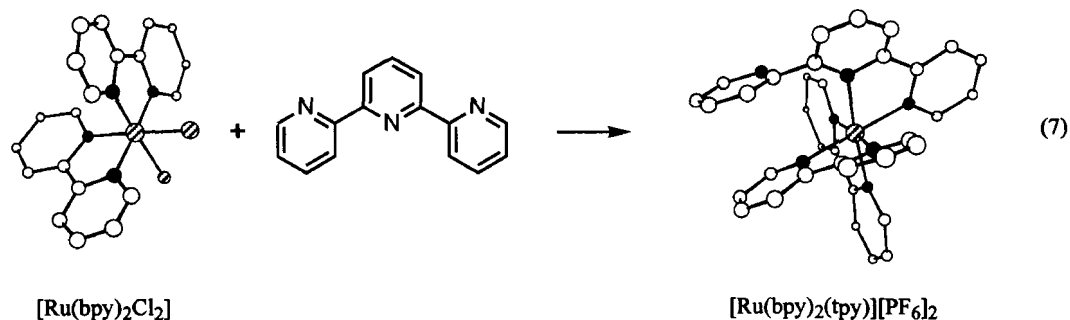
Hypodentate ligands and helication

Up to this point, we have assumed that a tpy ligand will act as a tridentate N_3 -donor to a metal centre. Recently, we began to question this assumption in the pursuit of helical coordination compounds. From studies of the coordination behaviour of ligands such as **10** we showed that when a non-coordinated aryl ring was directly attached to a coordinated ring, there was a significant ($60 - 90^\circ$) twisting about the interannular C-C bond, as indicated in Eq. 6 (13).



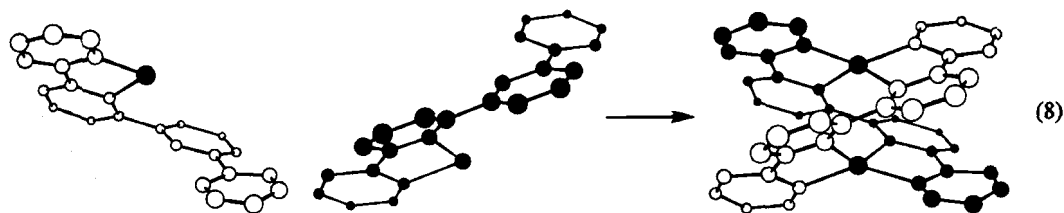
We wondered if it would be possible to persuade a tpy ligand to act as a didentate N_2 -donor and set out to determine the requirements for such a *hypodentate* bonding mode. The approach adopted was very simple: we used a kinetically inert ruthenium(II) centre with a preference for six coordination which already had two didentate bpy ligands attached. Reaction with tpy presented the metal with a total number of donor atoms ($2+2+3$) greater than the favoured coordination number of the metal of six. The result was the formation of the complex $[\text{Ru}(N,N'\text{-bpy})_2(N,N'\text{-tpy})]^{2+}$ containing a didentate hypodentate tpy ligand (Eq. 7) (14). Similar complexes were obtained when the tpy was replaced by substituted derivatives. The methodology is general. For example, the reaction of $[\text{Ru}(\text{tpy})\text{Cl}_3]$ with qtpy presents a total of $3+4 = 7$ donor atoms to the six coordinate ruthenium(II) centre and the consequence is the formation of the complex $[\text{Ru}(\text{tpy})(\text{qtpy})]^{2+}$ which contains a tridentate tpy ligand and a tridentate hypodentate qtpy.

As a result of these observations, we realised that the control of hypodentate bonding modes was a key step in the formation of double-helical complexes. The basic strategy for the formation of a double-helical complex involves the interaction of a ligand thread containing two n -dentate metal binding domains with a metal ions with a preference for a coordination number of $2n$ (15). The twisting of the ligand thread is most

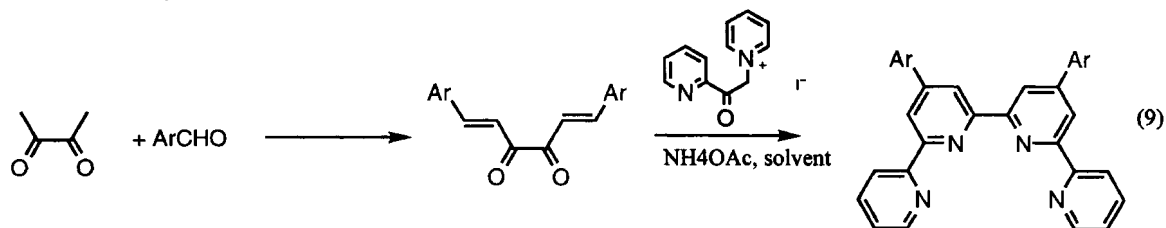


simply controlled if it occurs about the interannular C-C bond between two aromatic groups - and this was exactly the type of twisting that we had seen between bonded and non-bonded aromatic groups.

We can now apply this coding to the ligand qtpy. The four nitrogen donor atoms of qtpy cannot all coordinate to a single tetrahedral metal centre. At most, two of the nitrogens can bind in the putative intermediate shown in cartoon form at the left hand side of Eq. 8. If we analyse this species in a little more detail, we have a ligand thread with two available donor atoms and a metal ion with two vacant coordination sites. Two thread could come together to form a dinuclear double helix, as shown in Eq. 8. This is exactly what happen in practice, and dinuclear double-helical compounds result from the reaction of qtpy with silver(I) or copper(I) salts (16)



Recently, we have made an extended study of the effects of substituents on the ligand upon this helication process. The presence of a wide variety of substituents does not effect the formation of the double helices upon reaction of the ligands with copper(I) or silver(I). In particular, we have introduced a convenient new method for the formation of a variety of 4',4''-diaryl-substituted compounds from cheap and readily available starting materials, as indicated in Eq. 9 (17).



Another question which we have been addressing relates to directionality within the double helical complexes. If a ligand thread has a 'head' and a 'tail' end, then the formation of the double-helical complex could result in the formation of head-to-head (HH) or head-to-tail (HT) isomers (Fig. 2). The sense of directionality was readily introduced by the design of asymmetrically substituted qtpy ligands, with the most convenient synthetic strategies leading to 4- or 4,4'-substituted species. Molecular modelling studies indicated that there might be a preference for the HT isomer and preliminary studies showed that an excess of one of the two isomers was indeed formed upon reaction of asymmetric qtpy ligands with copper(I), although it was not possible to confirm whether the HH or HT isomer was the dominant species (18). Very recently, we have determined the crystal structure of the complex formed from the reaction of **11** with copper(I); it appears that only the HH isomer is formed (Fig. 3) (19). The reasons for this selectivity are not yet clear!

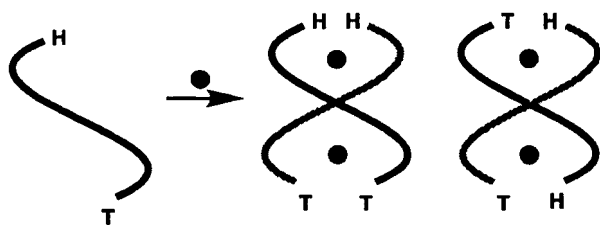


Fig. 2 The formation of HH and HT isomers of a double helix

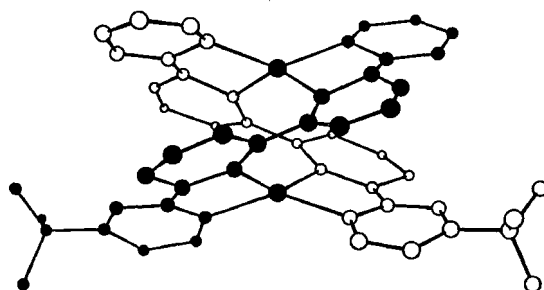


Fig. 3 The structure of the HH complex $[\text{Cu}_2(\mathbf{11})_2]^{2+}$

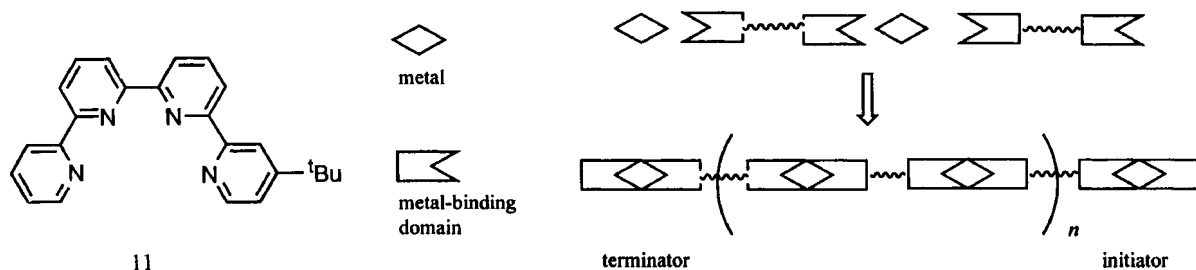
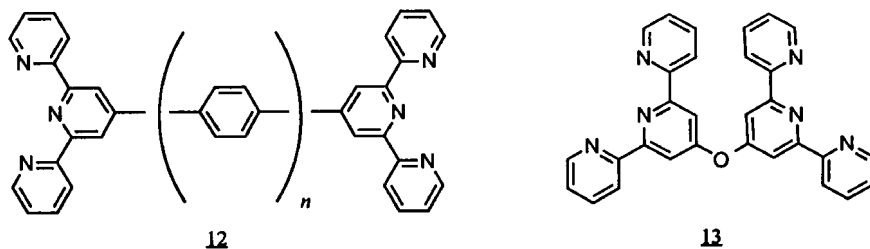


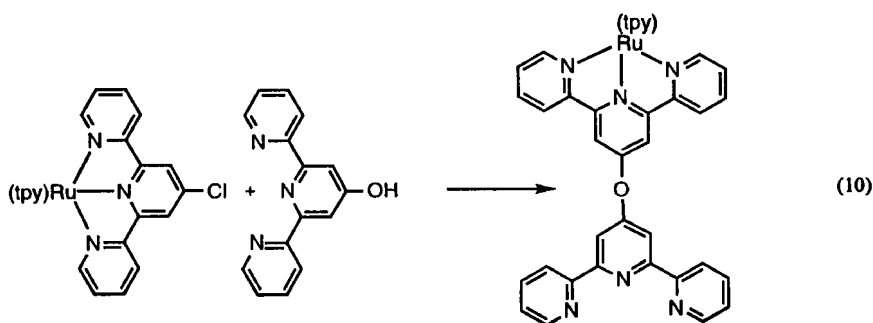
Fig. 4 The coordination oligomer approach to self-assembly

The assembly of coordination polymers and oligomers

The tpy metal-binding domain has proved to be particularly versatile in the assembly of coordination polymers and oligomers. The key to this approach is the design of multinucleating ligands which contain two or more tpy metal-binding domains. Our strategy is reminiscent of a copolymerisation, in which two separate monomers, metal ion and the ligand with multiple tpy domains, are brought together. The analogy may be extended even further. The simple mononucleating 4'-substituted tpy ligands which we discussed earlier are now seen to be terminator or initiator ligands. The strategy is shown in pictorial form for a ligand containing two tpy domains in Fig. 4 (20).



Our first approaches to the bridging ligands involved compounds of type **12** in which the metal-binding domains are linked by a variable number of 1,4-phenylene spacers (21). More recently, we have introduced a new generation of bridging ligands in which ether linkages connect the two tpy domains. The parent ligand is botpy **13** which may be prepared directly from the reaction of 4'-chlorotpy with 4'-hydroxytpy under standard Williamson conditions (22). Although the yields of **13** were high, the reaction conditions were harsh (several days in boiling dmf) and we have now developed a powerful new *in situ* method of ligand synthesis. We have shown previously that the coordination of a 4'-chlorotpy ligand to a metal ion activates the chlorine towards nucleophilic displacement (23). If the attacking nucleophile is 4'-hydroxytpy, then this results in the generation of a botpy ligand. This strategy is illustrated in Eq. 10 and



has been developed into a divergent step-wise procedure, as illustrated in Figs. 5 and 6. In these Figs. the tpy is represented by a half circle. Although this methodology works well for the assembly of the di- and trinuclear species indicated in Figs. 5 and 6, it is not possible to extend it indefinitely. For example, in the reaction of the dinuclear product in Fig. 5 with a further equivalent of tpy attack at the C-O bond is competitive with that at the C-Cl bond. Naturally, higher nuclearity complexes may be obtained if the bridging ligand system contains more than two tpy domains, and ligand **14** has been useful in this respect (24). However, in the final analysis, it was clear that we required a suite of *different* coupling methods if we were going to develop a truly convergent approach to the formation of high-nuclearity metallodendrimers and polymers.

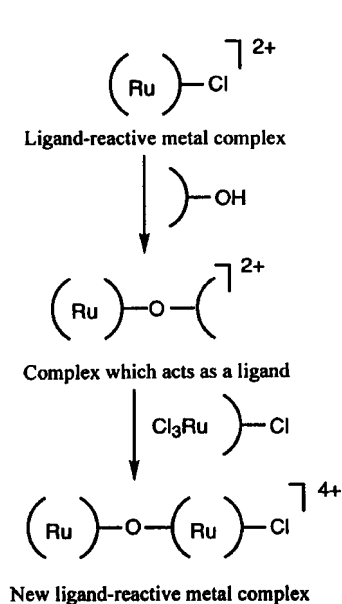


Fig. 5 Divergent synthesis of dinuclear species

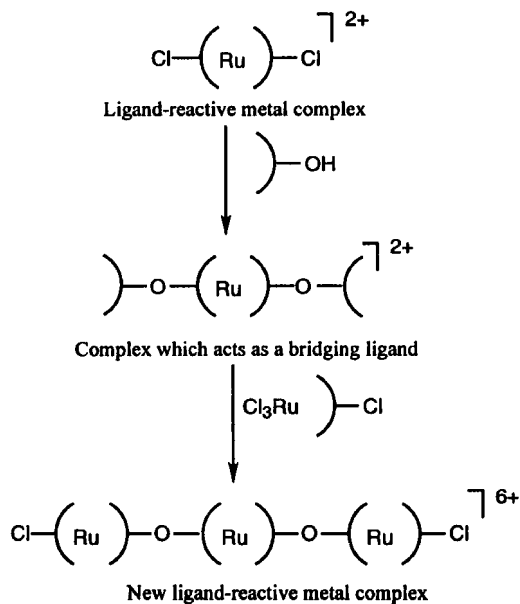
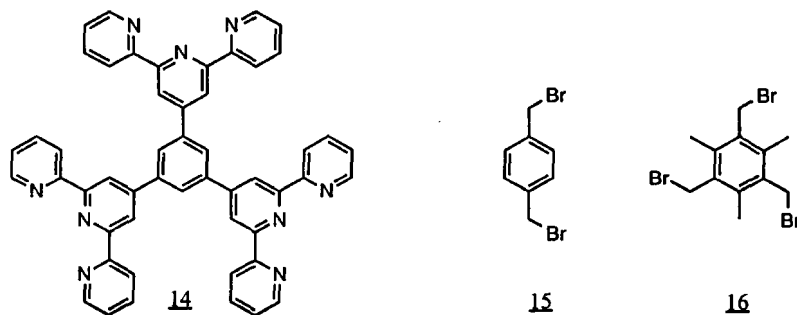


Fig. 6 Divergent synthesis of trinuclear species



The new strategy that we adopted is an inversion of that described for the *in situ* synthesis of **13**. For the synthesis of **13** we used the reaction of a coordinated electrophile with a nucleophile to form the new ligand. We now use the reaction of a coordinated 4'-hydroxytyty nucleophile with an electrophile such as **15** or **16** (25). An application of this methodology are presented in Fig. 7, and shows the preparation of hexanuclear and nonanuclear species.

I should like to take this opportunity to heartily thank all of the talented co-workers who have been involved in the projects over the years. Their names are to be found in the references below. I should also like to thank the various funding agencies and companies who have given support: S.E.R.C., Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung, University of Basel, University of Cambridge, Royal Society, Unilever, Ciba-Geigy, Johnson Matthey and the European Community. Part of this work represents an ongoing three centre collaboration between our group and the groups of Professor Jean-Pierre Sauvage (Strasbourg) and those of Professors Vincenzo Balzani and Francesco Barrigelletti (Bologna).

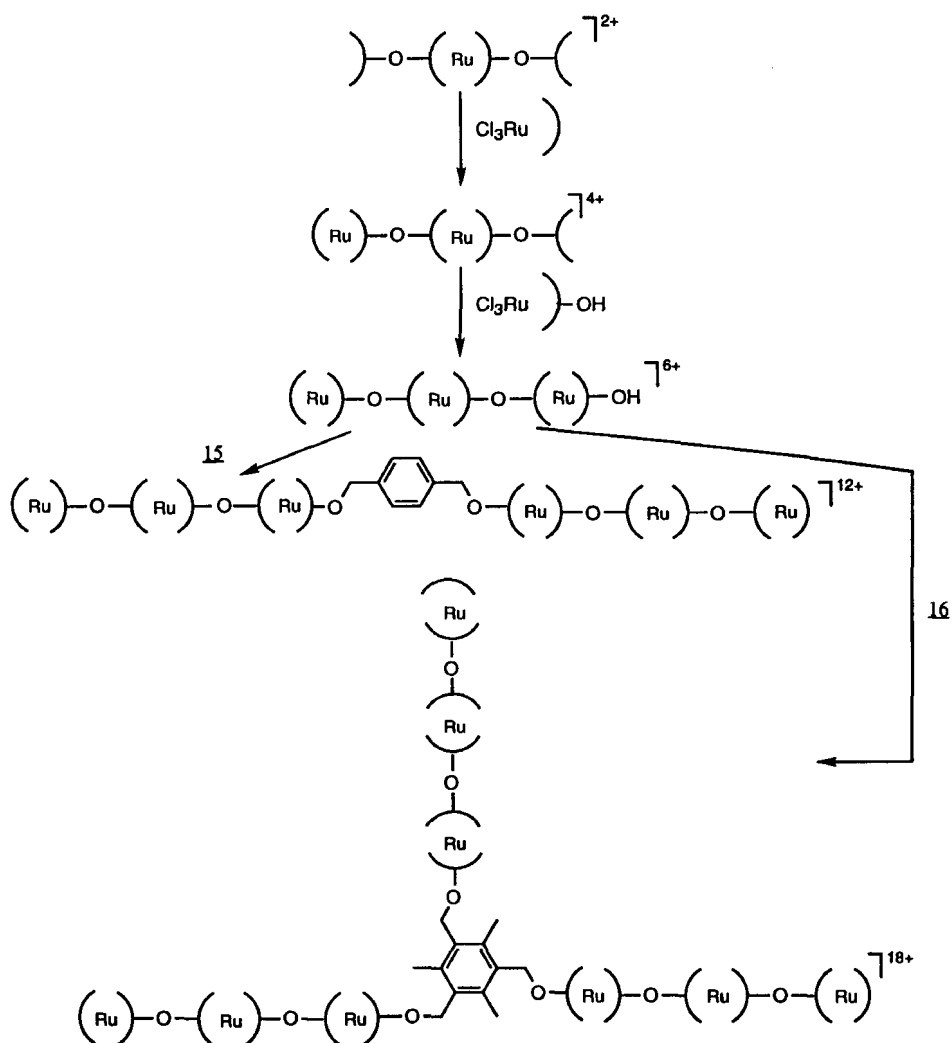


Fig. 7 A new convergent methodology for the synthesis of high nuclearity metallodendrimers

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