

Chimia 52 (1998) 533–538
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ISSN 0009–4293

Supramolecular Approaches to Advanced Materials

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Abstract. Synthetic strategies based upon metal-directed self-assembly or upon the post-functionalization of dendritic and related systems have been used for the preparation of new nanodimensioned metal-containing species. These and related studies on the design of metallomesogens are reported in this paper.

1. Introduction

Our interests lie in the use of supramolecular chemistry, and particularly metallosupramolecular chemistry, for the construction of molecular assemblies with designed and tunable functionality. The target of this work is to build functional molecular machines based upon smaller molecular units which can be studied and perfected in isolation. This article provides an overview of some of the directions which we are taking and shows the methodologies which we have adopted. Whilst the systems discussed fall within the general description of 'advanced materials', individual compounds are identified by keywords such as *supramolecular chemistry, smart materials, molecular recognition, sensors, molecular machines or nanotechnology*.

2. Metallodendrimers

The problems of designing molecular machines are similar in many respects to those encountered with their macroscopic analogues – precision in macroscopic machines translates to chemical purity at the molecular level, concepts of identifiable and discrete components exist in both cases, the real-world factory translates to a chemical reaction. For both macroscopic and microscopic assembly processes, a fundamental question is how the various components are linked together. What are

the molecular analogues of nuts and bolts, of screws and nails, of glue or of welding? Whilst biology provides us with numerous examples of functioning molecular machinery, it has adopted an assembly methodology based upon a large number of weak interactions. Unfortunately, our ability to control intermolecular interactions in artificial systems is not so highly developed, and it is frequently necessary to rely upon covalent linkage of the components. We and others have adopted dendritic substructures as the core of our machines, with a strategy which will allow the introduction of designed functionality at surface or inner generations. The metal centres may be used as an assembly principle, as a required functionality or both. Dendritic systems incorporating metal centres are of considerable current interest *inter alia* as novel magnetic, electronic or photo-optical materials [1–4]. We commence with a short discussion of systems in which a dendritic or branched system provides a structure on which we can 'hang' our desired metal-containing functionality.

2.1. Organometallic Derivatives of Branched Systems – Towards Onion-Shell Compounds

One area of ongoing interest within our group is the incorporation of metal carbonyl clusters into branched systems. The aim is to prepare multigeneration molecules in which layers of metal carbonyl clusters are interspersed by organic spacer groups. In dendritic systems, the higher metal-containing generations will bring the clusters into proximity with one another and one can envisage the facile formation of a spherical metal-containing surface. In this case, the metal is used as functionality rather than as an assembly principle. It is hoped that thermal reactions or treatment with an oxygen plasma will lead to metal-oxide shells.

Our first approaches are indicated in *Scheme 1*. A series of polyalkynes **2** based upon a tetraphenylmethane core **1** have been prepared. The synthetic method is iterative and can be extended to incorporate any desired number of alkyne units. Subsequent reaction with dicobalt octacarbonyl leads to the formation of tetrahedral $\{Co_2C_2\}$ clusters at the site of each of the alkyne functionalities. The compounds are reasonably air-stable, obtained in high yields, and, to date, we have experienced no problems in achieving complete reaction of all of the alkyne units in the precursors **2**. A full representation of the third-generation Co_{24} compound, which has a radius of *ca.* 22 Å, is given in the *Figure*. We are currently extending these studies to higher generations and to studies on the properties of these unusual metal-rich molecular species. Naturally, the compounds **3** are not strictly dendritic, and we are also developing analogous syntheses using reagents **4** and **5** which lead to dendrimers in which branching occurs at each aromatic ring.

As one of the ultimate aims is the formation of metal-oxide spheres, we have also considered multimetallic systems and addressed the question of controlling the stoichiometry of heterometallic systems. In order to do this, we have developed a series of heterotopic ligands which have two separate metal binding sites which will selectively bind different types of metal carbonyl compound. Ligand **6** contains both alkyne and phosphane functionalities which can react with low oxidation-state metal centres. Reaction of **6** with $[M(CO)_5X]$ ($M = Mo$ or W ; $X =$ solvent) results in the clean metallation of the phosphane sites to give **7**. Subsequent reaction with dicobalt octacarbonyl results in clean reaction of the alkyne units to give heteronuclear systems **8** containing both $\{Co_2C_2\}$ and $\{M(CO)_5\}$ groups. No exchange of the original $M(CO)_5$ groups for cobalt carbonyls occurs upon reaction with $Co_2(CO)_8$. Preliminary results indicate that the same methodology may be used to incorporate group-8 metal carbonyl clusters at the *P*-donor site.

2.2. First-Generation Metallodendrimers

The majority of dendrimers are 'organic' – 'organic' refers both to their *chemical character* and to the *type of chemical reaction* used in their synthesis. This most often means molecules composed of C, H and O, in combination with other main-group elements such as N, P, Si or S. Dendrimers are usually prepared by the formation of covalent carbon-carbon or

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Scheme 1

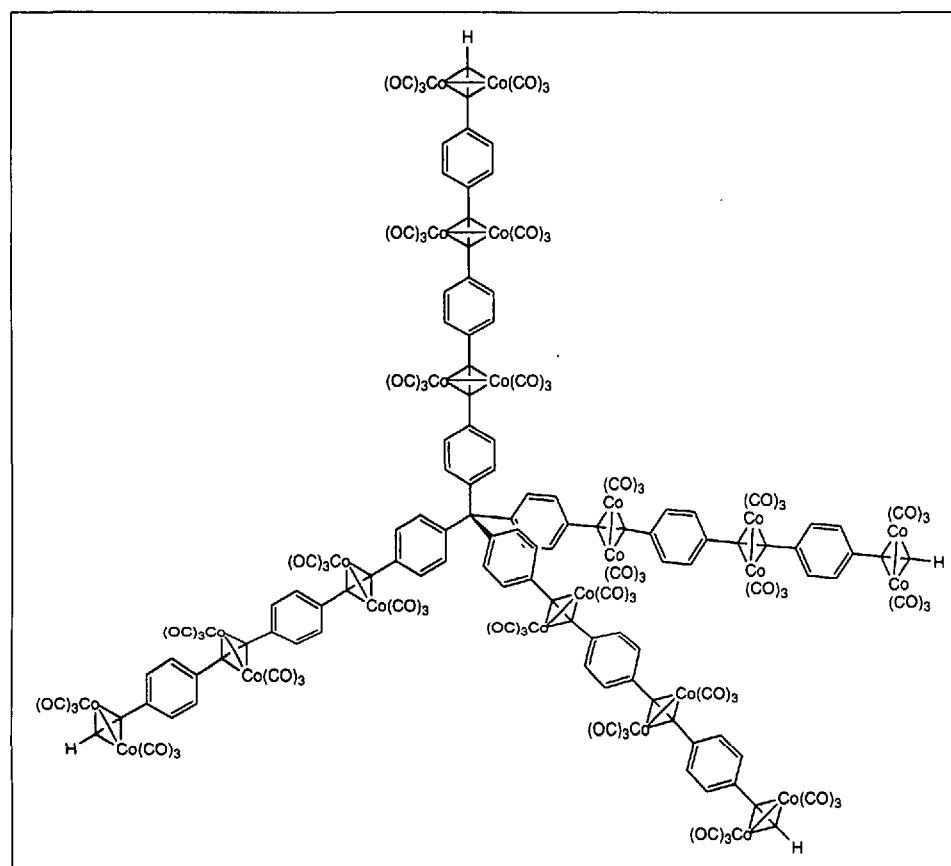
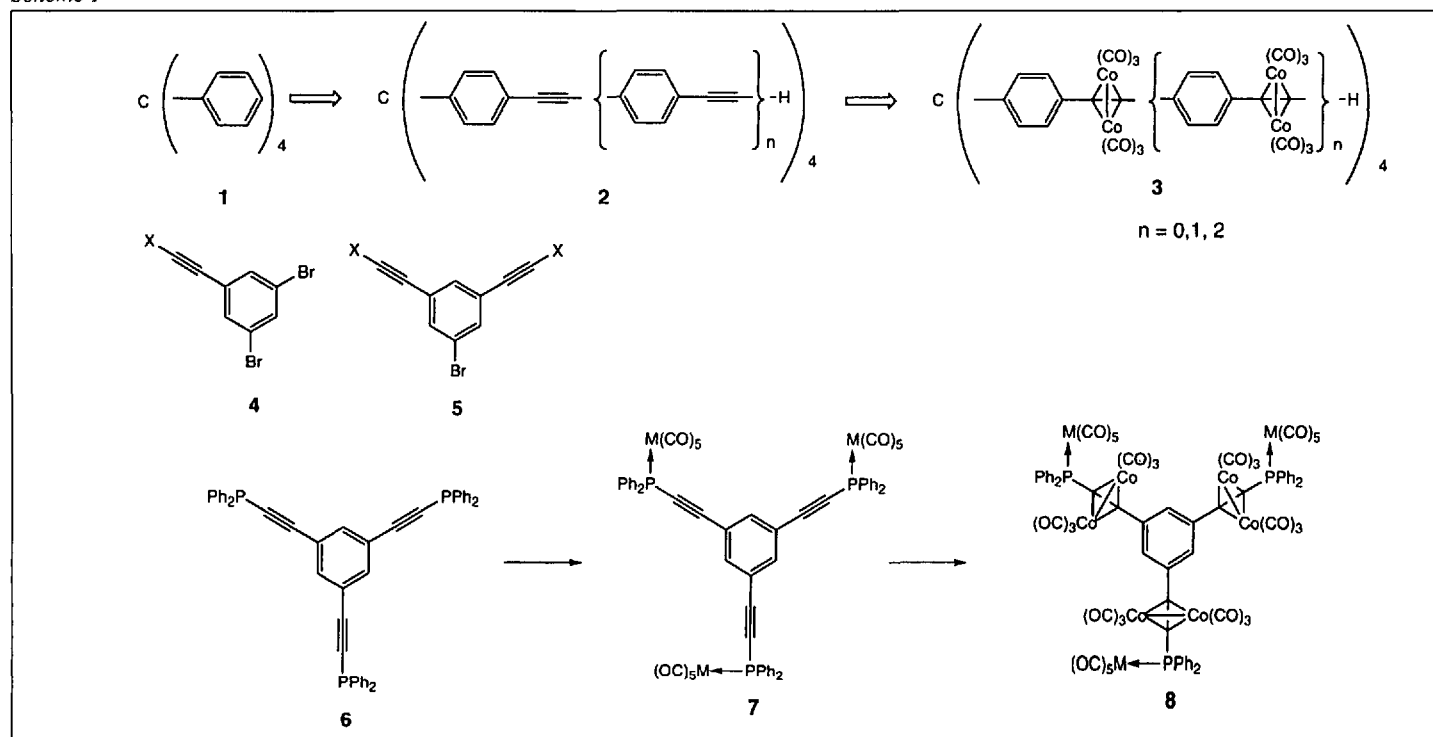


Figure. A representation of the Co_{24} species obtained from the reaction of the third-generation polyalkyne with dicobalt octacarbonyl

carbon-heteroatom bonds. For monodispersed species, the same reactions must occur repeatedly and with high efficiency. Covalent bonds involving carbon are kinetically stable and have significant energy barriers for their formation.

In metallodendrimers, growth steps involving metal donor-atom interactions

or the metal-activated reaction of a *coordinated ligand* as opposed to carbon-carbon or carbon-heteroatom bond formation offer a valuable alternative methodology. The methodology is based on the thermodynamic and kinetic features of coordinate bond formation as opposed to covalent bond formation. In particular, the

chelate effect will be used to ensure that metallodendrimers are both thermodynamically and kinetically stable. A judicious choice of metal centre allows kinetic control over the reaction.

We have developed metallodendrimers based upon 2,2'-bipyridine (bpy) or 2,2':6',2''-terpyridine (tpy) metal-binding motifs. The assembly process is illustrated in the formation of the first-generation triruthenium complex **10** in high yield from the tris(tpy) ligand **9** simply by heating with $[\text{Ru}(\text{tpy})\text{Cl}_3]$ (Scheme 2). The reaction of **9** with labile metal ions such as Fe^{II} results in the formation of highly coloured, but very sparingly soluble, polynuclear complexes. These latter species are randomly cross-linked polymers and oligomers of stoichiometry $[\text{M}(\mathbf{9})_{0.67}]_2\text{X}_2$, but their insolubility precludes further purification and characterisation. The difficulties encountered in the synthesis of ligands such as **9**, combined with their insolubility, lead us to consider new approaches.

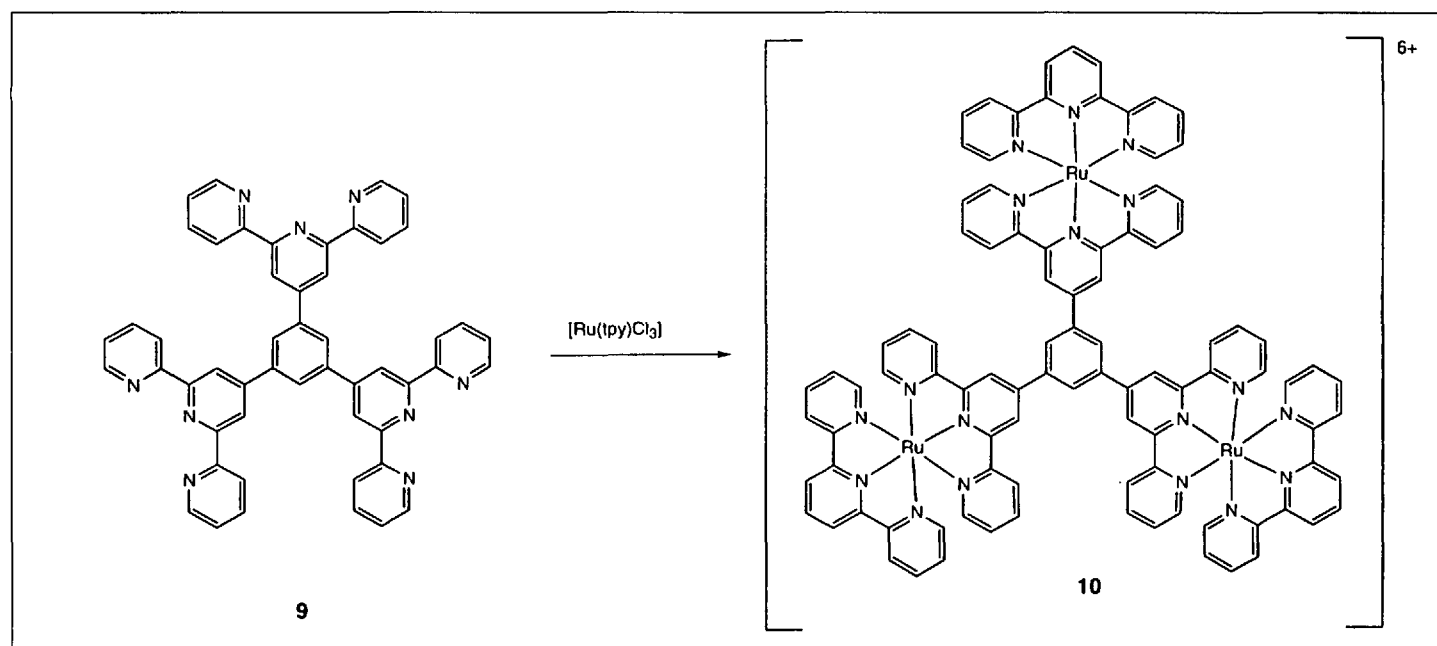
We now use pentaerythritol $\text{C}(\text{CH}_2\text{OH})_4$ as a cheap and readily available starting point. Compound **11** contains four tetrahedrally distributed tpy domains, and reaction with $[\text{Ru}(\text{tpy})\text{Cl}_3]$ gives the expected first-generation tetranuclear complex $[\{(\text{tpy})\text{Ru}\}_4(\mathbf{11})\}^{8+}$ in excellent yields. Pendant functionality may readily be introduced at the surface generation by the use of $[\text{Ru}(\text{Xtpy})\text{Cl}_3]$ in the metallation step, and the 40-boron first-generation *ortho*-carbaboranyl-functionalised metallodendrimer **12** is a typical example of such a compound (Scheme 3).

The pentaerythritol building blocks allow us to prepare 'real' dendrimers with multiple branching points. The ligand **13** possesses a tpy domain but also possesses three hydroxy groups – in other words, **13** is simply an Xtpy ligand ($X = \text{OCH}_2\text{C}(\text{CH}_2\text{OH})_3$) and, as expected, it forms an adduct $[\text{Ru}(\mathbf{13})\text{Cl}_3]$ with ruthenium trichloride. The key species for the formation of dendrimers is **14**, $[\{(\mathbf{13})\text{Ru}\}_4(\mathbf{11})]^{8+}$, which is simply a surface generation Xtpy-functionalized species ($X = \text{OCH}_2\text{C}(\text{CH}_2\text{OH})_3$) prepared by the reaction of **11** with $[\text{Ru}(\mathbf{13})\text{Cl}_3]$. However, the X-functionality incorporates three nucleophilic hydroxy groups which can react with suitable electrophiles. At this

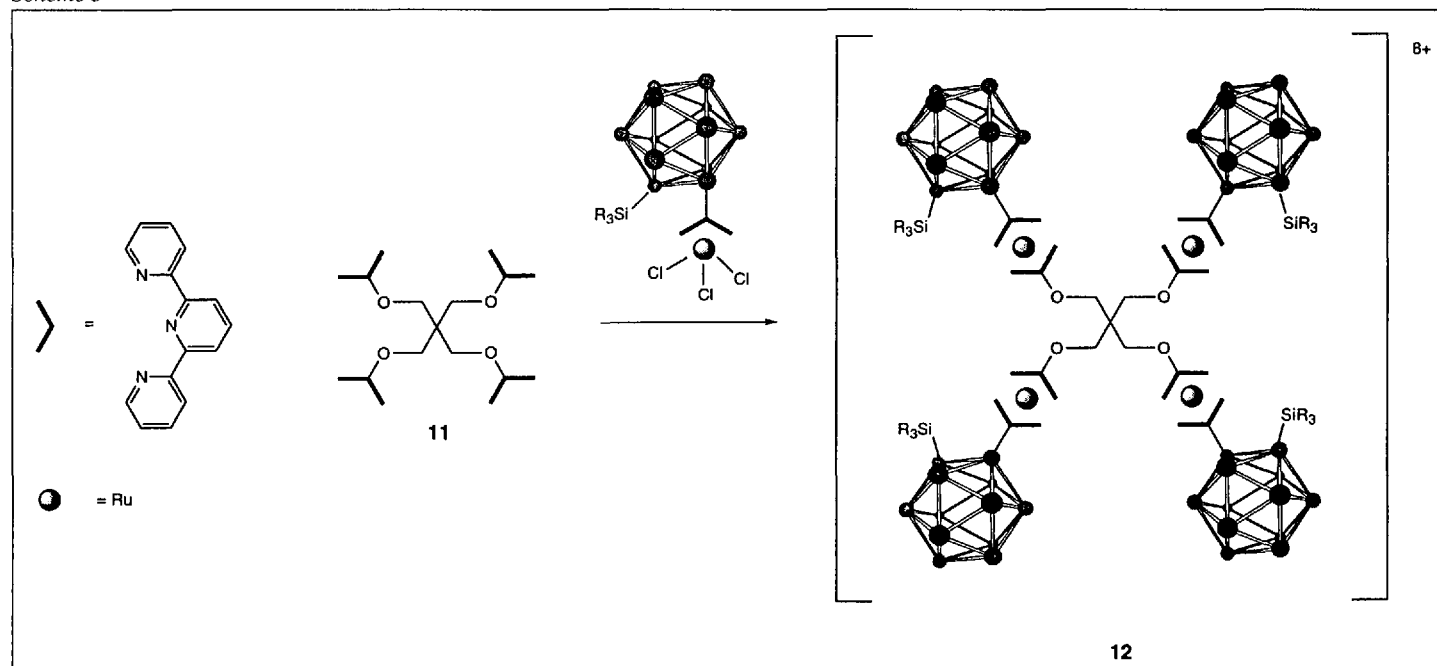
point, we used a trick that we learnt a number of years ago. 4-Halopyridines are weakly electrophilic, but their electrophilicity may be dramatically enhanced by coordination to a transition-metal ion. The positive charge of the metal ion is transmitted to the 4-position and nucleophilic displacement of halide is facile. This observation allows us to directly incorporate $[\text{Ru}(\text{tpy})_2]$ units into **14**. The complex cation $[(\text{tpy})\text{Ru}(\text{Cltpy})]^{2+}$ possesses a 4'-chloro-2,2':6',2''-terpyridine ligand in which the electrophilic character is enhanced by coordination. Reaction of $[(\text{tpy})\text{Ru}(\text{Cltpy})][\text{PF}_6]_2$ with $[\{(\mathbf{13})\text{Ru}\}_4(\mathbf{11})]^{8+}$ yields the expected hexadecanuclear complex **15** (Scheme 4). The sim-

plicity of this approach is remarkable, and the success relies upon the *in situ* synthesis of four new **11** ligands. Through a relatively short sequence of reactions using readily available starting materials, a soluble, isomerically pure and monodispersed Ru_{16} complex has been prepared. We are currently investigating subsequent growth reactions and the photophysical and redox properties of these high-nuclearity metallodendrimers. The molecules are remarkably soluble, can be purified by conventional chromatographic methods and give well-resolved $^1\text{H-NMR}$ spectra, even though the Ru_{16} species **15** $[\text{PF}_6]_{32}$ has a molecular mass of 14 362 and a diameter of over 50 Å.

Scheme 2



Scheme 3



Compound **13** also allows us access to what we call 'zeroth'-generation dendrimers such as $[\text{Ru}(\mathbf{13})_2]^{2+}$. This compound is really just an $[\text{Ru}(\text{Xtpy})_2]^{2+}$ species which has six surface hydroxy groups, and we are currently using variations on the methodology described above to form homo- and heterometallic metallodendrimers.

2.3. Branched Systems through Metal-Activated Reactions

We have already seen the utility of metal activation of organic components in the *in situ* synthesis of ligands, and we have extended this approach to the preparation of a whole variety of multinuclear complexes. In the example given above, we have used the reaction of a mononuclear complex containing a single electrophilic site. It occurred to us that the approach could be extended to complexes with multiple electrophilic sites. This we have done, and a typical example is seen in the reaction of $[\text{Ru}(\text{Cl}_2\text{bpy})_3]^{2+}$ ($\text{Cl}_2\text{bpy} = 4,4'$ -dichloro-2,2'-bipyridine) with HOtpy (= 4'-hydroxy-2,2':6',2''-terpyridine). The complex $[\text{Ru}(\text{Cl}_2\text{bpy})_3]^{2+}$ possesses six electrophilic sites and the complex **16** is obtained in good yield (Scheme 5). Although **16** contains six tpy metal-binding functionalities, reaction with $[\text{Ru}(\text{tpy})\text{Cl}_3]$ leads to a mixture of complexes containing between four and seven metal centres.

On this occasion, steric interactions at the periphery hinder the growth reaction of the outer metal-containing generation. Introduction of a 1,4-phenylene spacer between the bpy and tpy domains overcomes this problem.

Perhaps one of the most spectacular examples is seen in the synthesis of **19** from trinuclear precursors. Although coordination of a nucleophile to a metal ion usually decreases its nucleophilicity, such complexes can still react with very good electrophiles. We had previously demonstrated that ruthenium complexes of HOtpy reacted with benzyl halides to give *O*-benzylated derivatives and simply extended this reaction to multinuclear complexes of HOtpy. Compound **17** possesses six electrophilic bromomethyl groups which reacted smoothly with the trinuclear complex **18** which contains a nucleophilic hydroxy group. The octadecanuclear complex **19** was isolated by conventional chromatography and fully characterised by conventional methods (Scheme 6).

Complex **19** and many related multinuclear species were found to adsorb to metal-oxide surfaces, and we have embarked on the spectroscopic investigation of the materials formed. Optical waveguide light spectroscopy (OWLS) indicates that monolayers are formed and that the di-

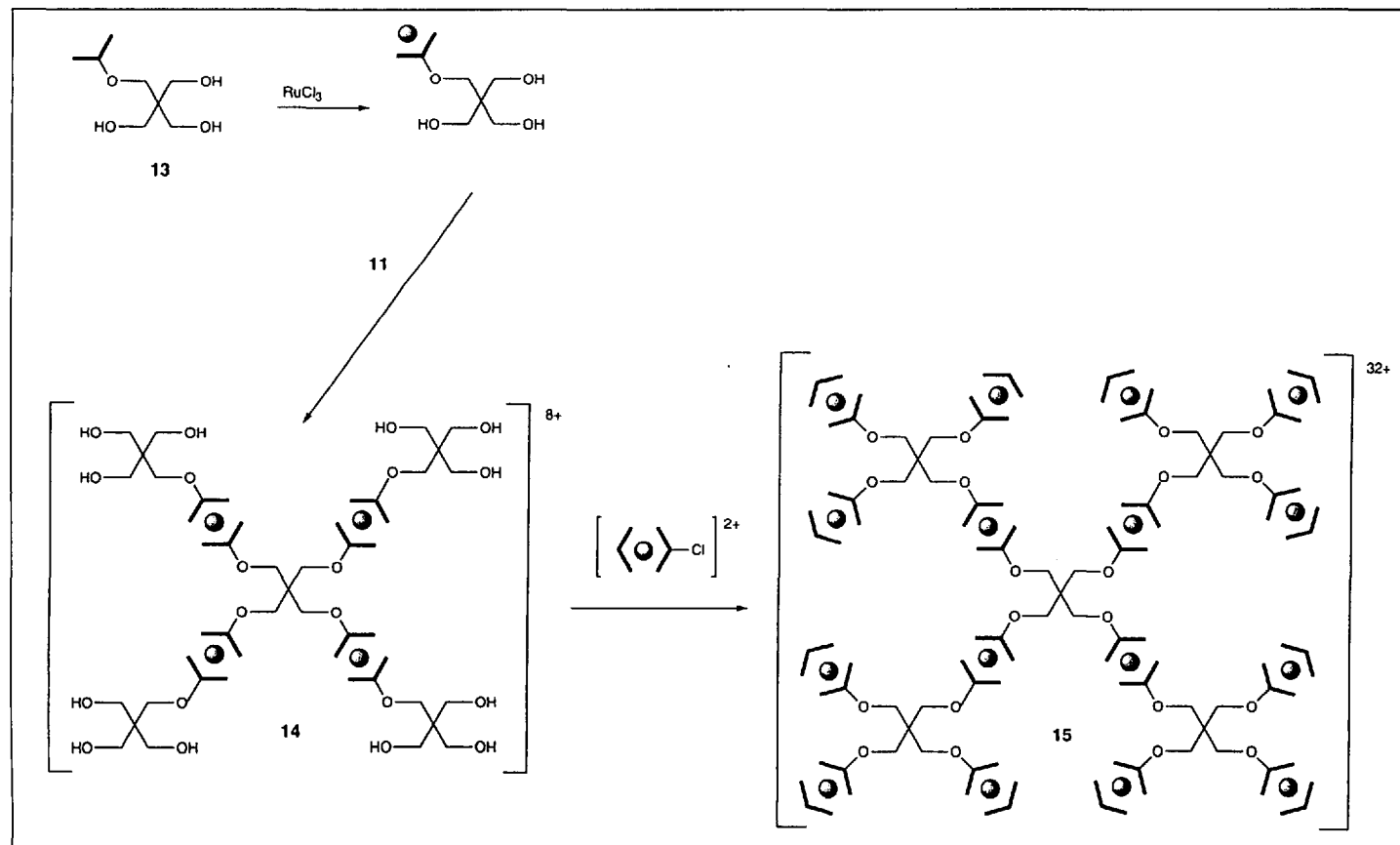
mensions of the adsorbed species closely resemble those calculated for the cations. The dimensions of the polynuclear dendritic cations correspond reasonably well with those obtained from STM studies on monolayers of the complexes on gold surfaces. Further surface and photophysical studies on the adsorbed species are underway.

The observation that these compounds adsorbed onto metal oxide surfaces has also led to a collaboration with the group of Prof. Michael Grätzel, and we are currently designing new tpy ligands for attaching photoactive ruthenium and rhodium complexes to titanium-dioxide surfaces.

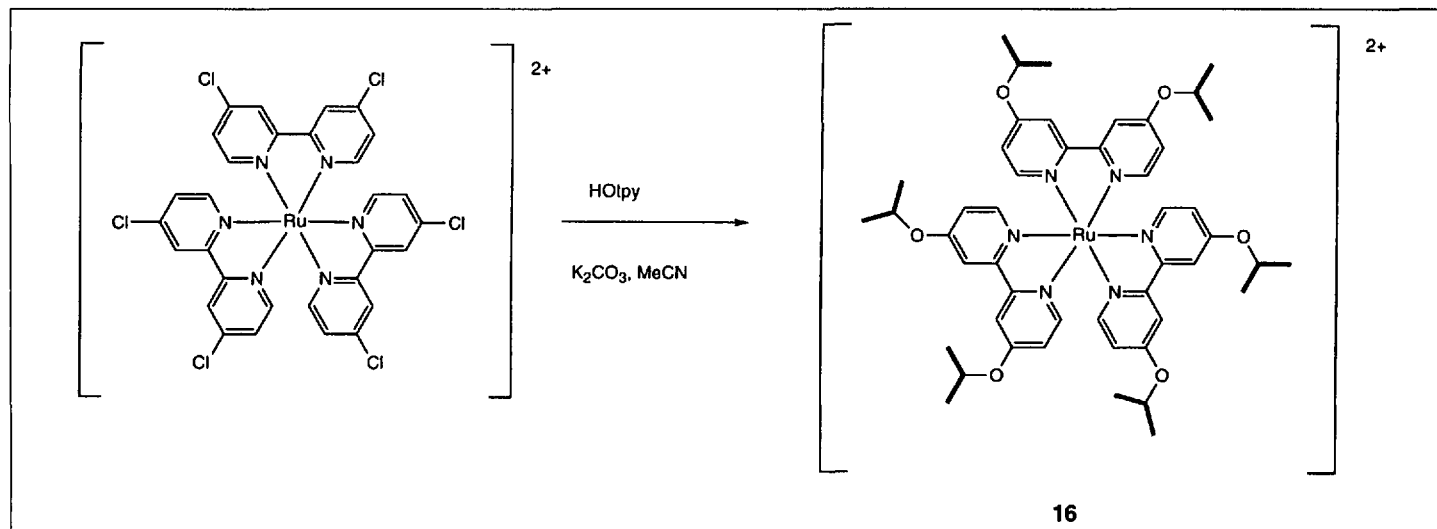
3. Metallomesogens

There is currently significant interest in metallomesogens. The inclusion of metal centres into liquid-crystalline phases leads to several important structural and physical modifications associated with their colour, magnetism and polarisability. Coloured metallomesogens would have applications in electrooptical displays, which currently use pleochroic dyes as guests in a liquid-crystal host material, although many of the guest dyes are photochemically unstable. Paramagnetic mesophases

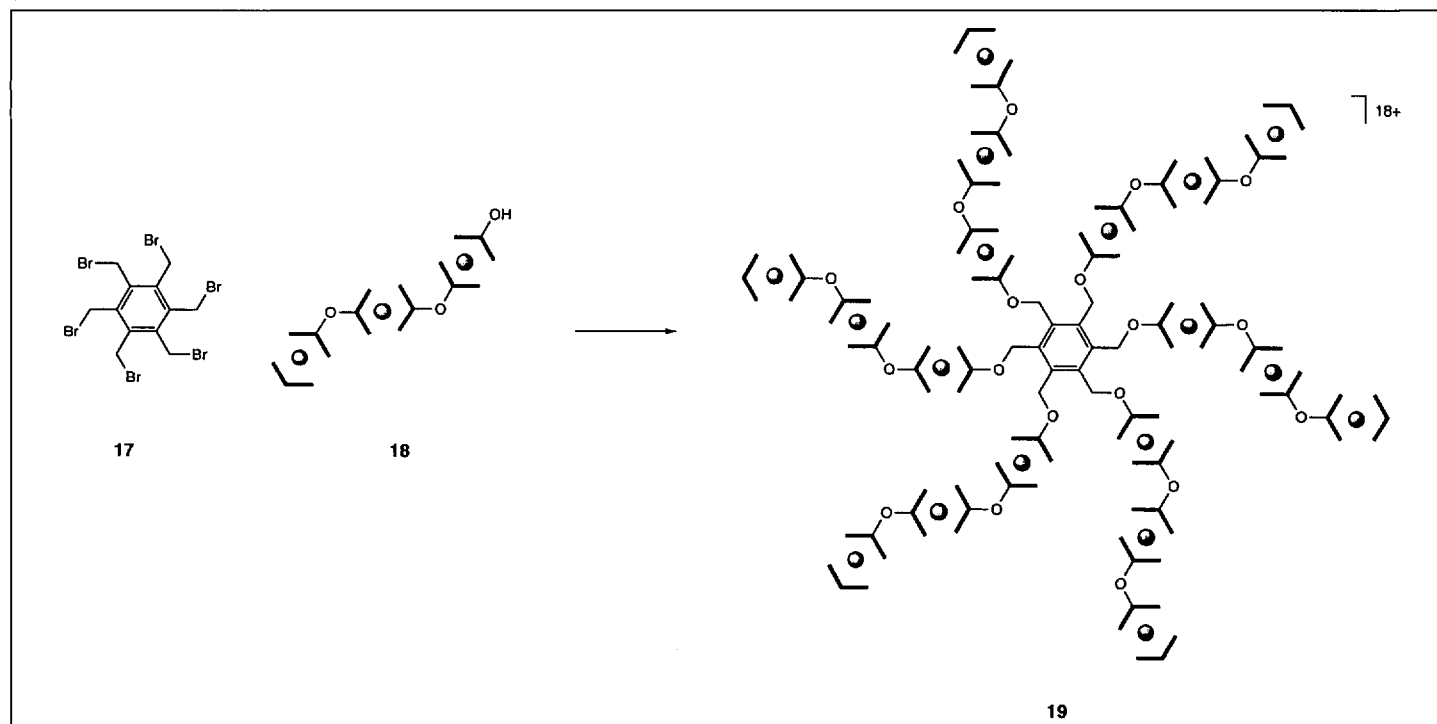
Scheme 4



Scheme 5



Scheme 6



might be switchable between isotropic and aligned states by external magnetic fields. Polarisability of electron density is one of the most important characteristics of molecules that form liquid crystals and is closely linked with properties like birefringence, dielectric constants and the thermal stability of liquid-crystal phases, and metal complexes have a high density of polarizable electrons and should be effective in promoting mesomorphic behaviour and extending the temperature range of liquid-crystalline phases.

In this context, we have prepared a series of oligopyridine ligands which have long-chain alkyl or cholesteryl substituents and are investigating both the free organic molecules and their complexes. The 4'-substituted tpy ligands **20** and **21**

are typical of those prepared in this work and are readily obtained from the reaction of Cltpy with the appropriate alcohol in basic conditions. The ligands are obtained in excellent yields and have the low melting points that might be expected. Ligand **20** showed fully reversible behaviour upon passing through the melting point (104°) when studied by DSC, although a significant and repeatable hysteresis of 23° was observed on the cooling cycle. No evidence of a mesophase was obtained. The cholesteryl ligand **21** is rather more interesting; DSC shows a broad melting peak at $145\text{--}152^\circ$ but shows no recrystallisation process upon cooling to 40° , suggesting that a glassy phase is formed. A rather interesting observation, for which we have no explanation at present, is associated

with the thermodynamics of the melting process: for **20** a typical value of $\Delta_{\text{fus}}H$ is 92.8 kJ mol^{-1} , whereas for the cholesteryl derivative **21** $\Delta_{\text{fus}}H$ is only 10.7 kJ mol^{-1} . The value of $\Delta_{\text{fus}}S$ for **21** of 25.6 J mol^{-1} also anomalously low. Studies of the metal complexes of these ligands are underway.

A second series of ligands **22–24** were also prepared and these appear to be more promising. The cholesteryl ligand **24** shows fully reversible melting/recrystallisation behaviour on DSC, but the other two ligands show some additional features. Both ligands show phase transitions below their melting points and show two recrystallisation peaks in their cooling curves. Upon melting, the ligands show a cloudy phase before the clearing point is reached. These

ligands might show a very small temperature range mesophase between the melting and clearing points. The lower temperature processes are almost certainly crystal phase transitions. Once again, studies on the metal complexes are underway.

4. Molecular Wires

Another essential component of any molecular machine is a 'wire' through which electronic information may be transmitted. Numerous conjugated aromatic systems have been proposed in this context, some of the most successful of which are based upon polythienyl or polyalkyne units. Our approach has been the covalent linking of the molecular wire to the metal binding groups to optimise electronic interactions. We have previously used poly-

phenylene spacers between oligopyridine domains, and we have now developed a series of pyridines and oligopyridines linked by oligothieryl spacer groups. A first generation of photoactive devices such as **25** based upon thienyl-spaced tpy domains have been prepared. In such compounds, electron- or energy-transfer from ruthenium to osmium is expected after irradiation within the ruthenium MLCT absorption, and the photophysical properties are currently under investigation in collaboration with the group of Prof. *Francesco Barigelletti* in Bologna.

An unplanned bonus with some of these ligands was the ability to selectively form molecular squares such as **26** upon reaction with square-planar metal complexes. This compounds are formed in excellent yield through self-assembly processes upon reaction of the thienyl-spaced ligand

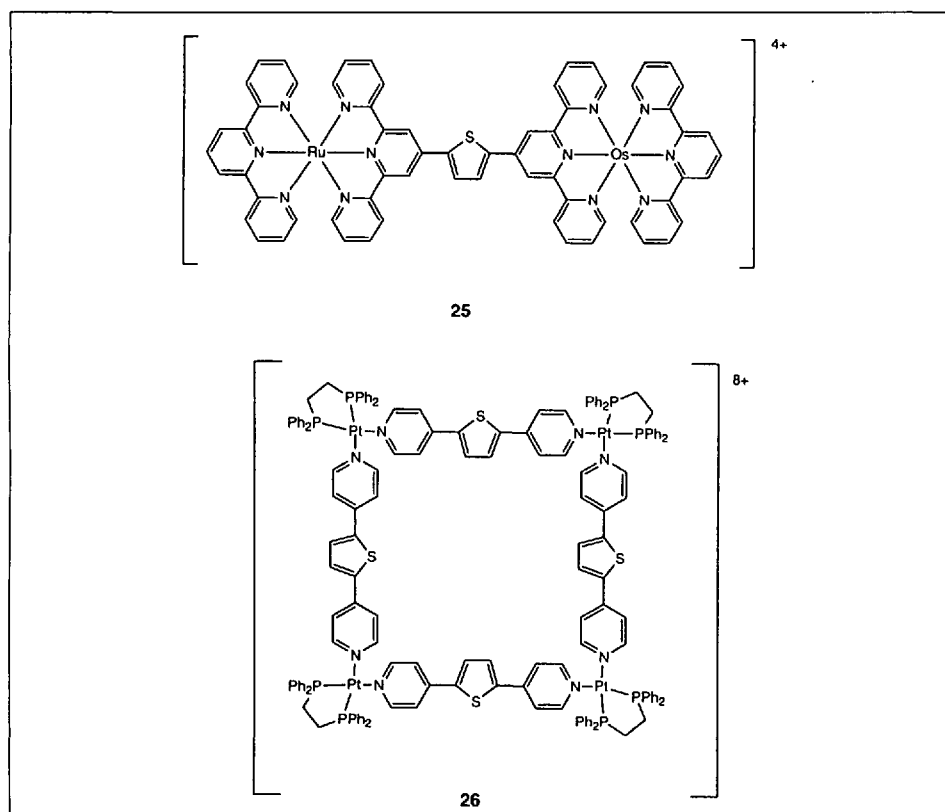
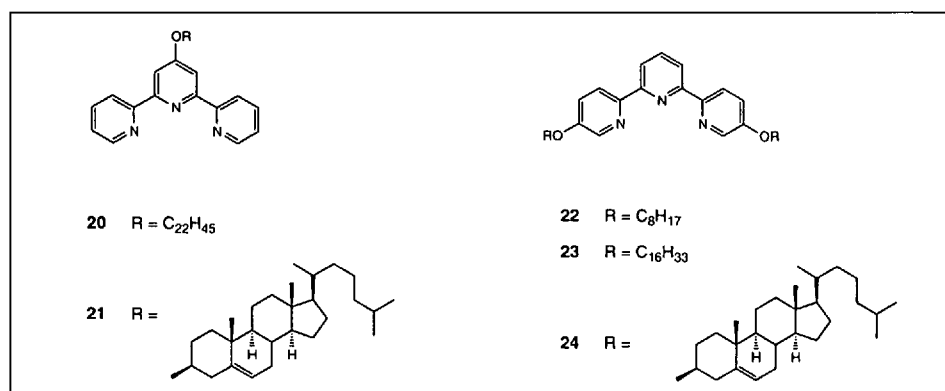
with appropriate platinum(II)-dppf complexes. We are currently considering the consequences of enhanced electronic communication between metal centres in such compounds!

5. Summary

This very short article has served to highlight some of the areas in which we are active. The emphasis of our work is synthetic and is at the interface of inorganic and organic chemistry. Much of the art lies in the design of the organic components, with the metal-directed self-assembly often coming as something of an anticlimax in the final stage. The majority of the work described is directed towards novel electronic materials [5], artificial photosynthetic systems [6] and new metal-containing mesogens [7].

As always, the major thanks go to the co-workers who have been involved in this work; for the work discussed, our thanks go in particular to Dr. *Dominique Armspach*, Dr. *Paul Bowyer*, *Marco Cattalini*, *Oliver Eich*, Dr. *Peter Harverson*, Dr. *Lesley Johnston*, Dr. *Bénédicte Krattinger*, Dr. *Martin Oberholzer*, Dr. *David Phillips*, *Ingo Poleschak*, *Chantal Schmitt* and *Emma Schofield*. We also gratefully acknowledge our ongoing collaborations with Dr. *Jeremy Ramsden* and Profs. *Vincenzo Balzani*, *Francesco Barigelletti*, *Dieter Fenske*, *Michael Grätzel*, *Hans-Jörg Güntherodt*, *Mauro Maestri* and *J. Fraser Stoddart* and would particularly like to thank the University of Basel and the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung* for financial support.

Received: July 20, 1998



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