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Supramolecular Chemistry

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Abstract. Metallosupramolecular chemistry makes use of the interaction of organic ligands with metal ions to assemble new structures.

Edwin Constable was born in Edinburgh, Scotland, in 1955. He studied chemistry at the University of Oxford where he completed his D. Phil. in 1980 under the direction of *K. Seddon*. He held a post-doctoral Fellowship working with *J. Lewis* at the University of Cambridge and started his independent research career with a Fellowship from the Commissioners of the Royal Exhibition of 1851. He subsequently held positions as demonstrator and lecturer at the University of Cambridge and accepted his present position as Professor of Inorganic Chemistry at the University of Basel in 1993. He is an associate editor of *Chemical Communications*.

Catherine Housecroft was born in Yorkshire in 1955 and studied chemistry at Durham University where she completed her doctorate in 1979 with *K. Wade*. She was a post-doctoral associate with *T. Fehlner* at the University of Notre Dame and then an Assistant Professor at the University of New Hampshire before accepting a position at the University of Cambridge where she was appointed the first female University lecturer in Chemistry in 1990. She has been a Professor in Basel since 1997 and is regional editor of *Polyhedron*.

Edwin Constable and *Catherine Housecroft* have been married since 1987 and the research group today reflects the fusion of their interests in supramolecular, coordination, organometallic, and theoretical chemistry together with materials science.

For further details of the research interests in the group, see: http://ac.chemie.unibas.ch/ac/ecc.html.

The main emphasis of our research lies in supramolecular chemistry. Our interests cover the full gamut of supramolecular chemistry from biological interactions to materials science. Our principal target at present is to use self-assembly processes for the construction of functional supramolecular systems and a number of examples of this approach will be given.

Helical Metal Complexes

Correctly designed multidentate ligands react with metal ions to build helical complexes (*Scheme 1*) and we have been interested in the factors controlling the formation and properties of such compounds for a number of years. By matching the number and spatial arrangement of donor atoms in the ligand with the favoured coordination numbers and geometries of the metal ions, it is possible to exert a subtle control over the self-assembly. In our studies, we have concentrated upon nitrogen-donor oligopyridine ligands [1]. We have usually used commensurate systems in which the ligand and metal requirements are complementary, as in the formation of a dinuclear double helix from the reaction of two tetradentate oligopyridines with two four-coordinate metal ions such as Cu(I) or Ag(I) (*Fig.*).

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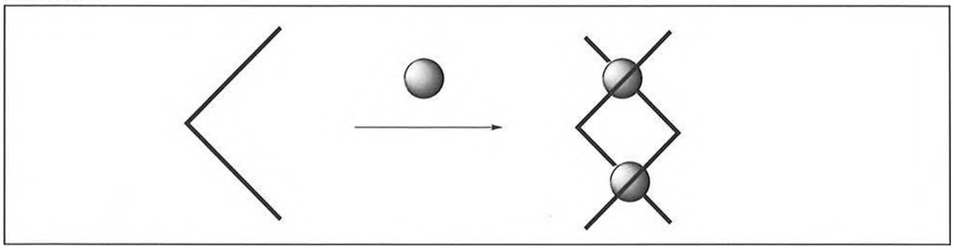
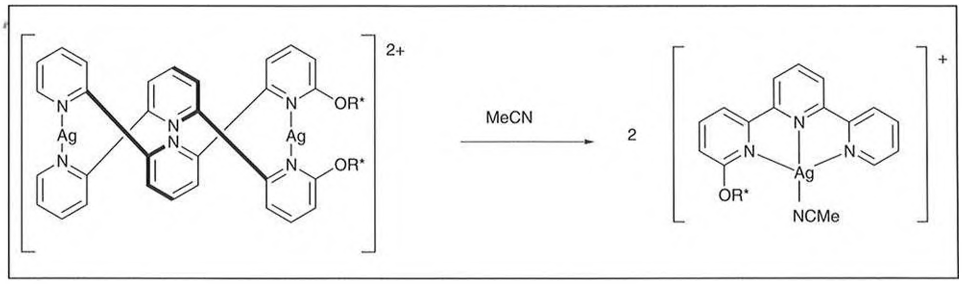
Scheme 1



Scheme 2



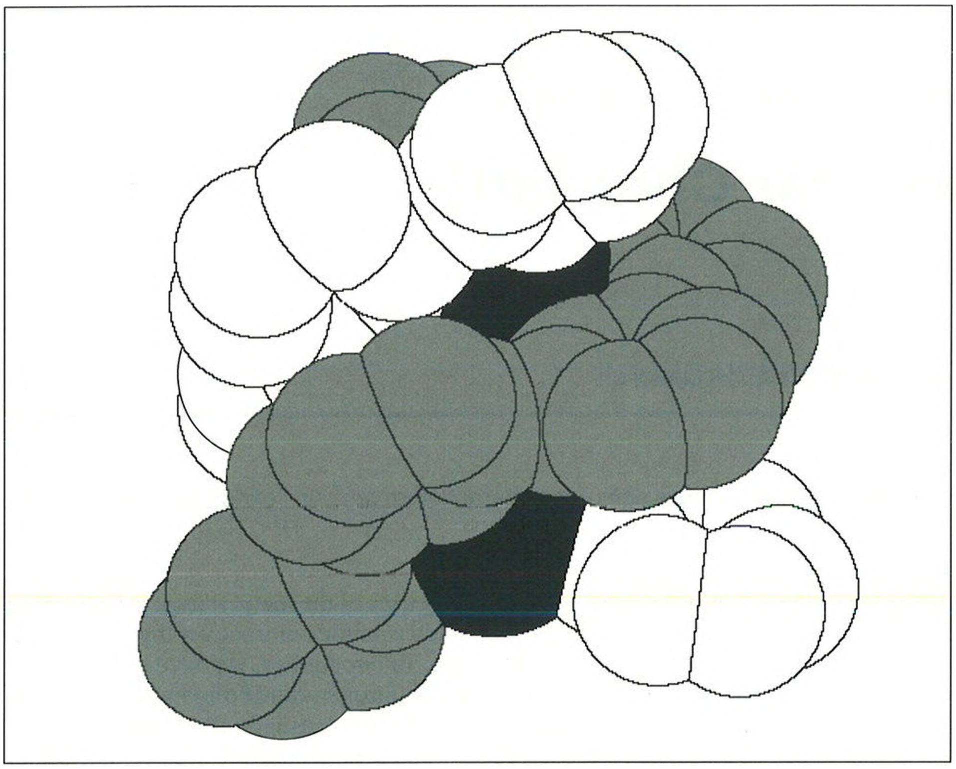
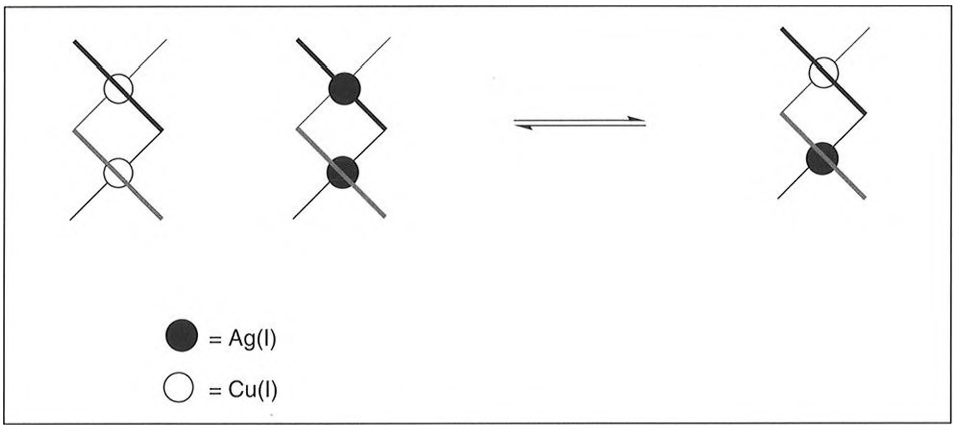
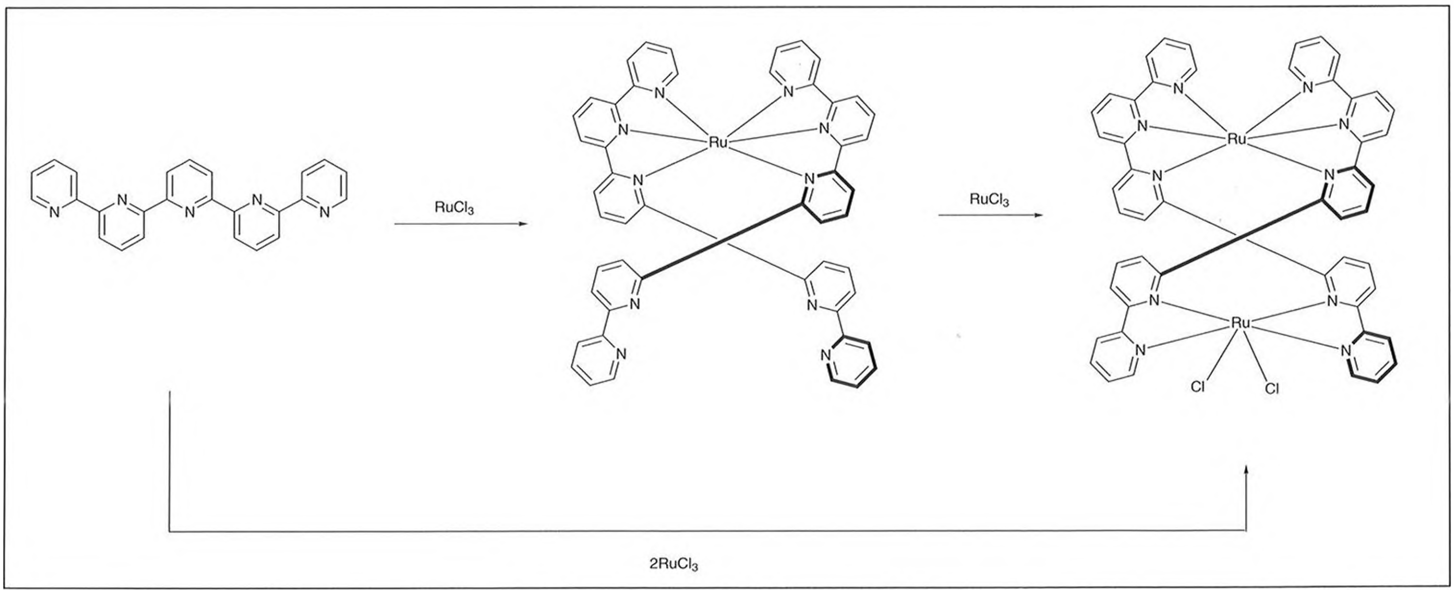


Figure. *The double-helical complex shown here is formed in a self-assembly reaction of Cu(I) salts with 2,2':6',2":6",2'''-quaterpyridine*

Scheme 3



Scheme 4



However, we have recently found that interesting dynamic behaviour results when incommensurate donor sets are used. A typical example is seen in the reaction of tridentate ligands with Ag(I), which usually favours four-coordination, when an equilibrium is set up between mononuclear non-helical and dinuclear double-helical complexes (*Scheme 2*) [2].

More recently, we have extended these studies to covalently linked systems based upon two pentadentate ligand domains which form dinuclear non-helical complexes with Co(II) but dinuclear double-helical 'hair-pin' complexes with other transition-metal ions. It is possible to use the dynamic behaviour of these systems to selectively prepare heterodinuclear complexes (*Scheme 3*) [3].

Although our preferred methodology relies upon self assembly, it is possible to use kinetically inert metal centres to build up species in a step-wise manner to give information about intermediates. A typical example is seen in the Ru(II) system presented in *Scheme 4*, where the mononuclear prehelicate is pre-organized for the formation of a dinuclear double helicate [3].

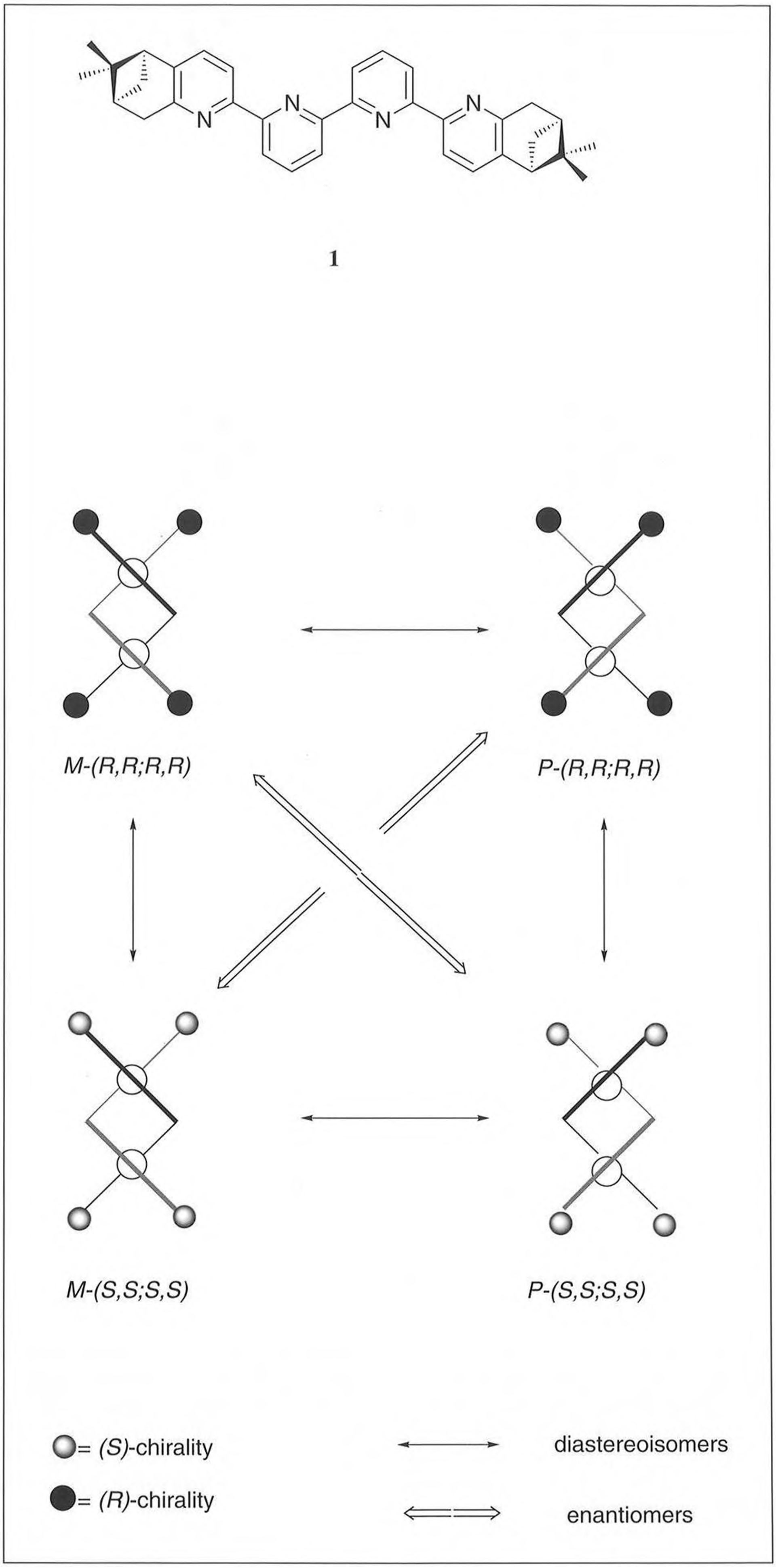
Chiral Complexes

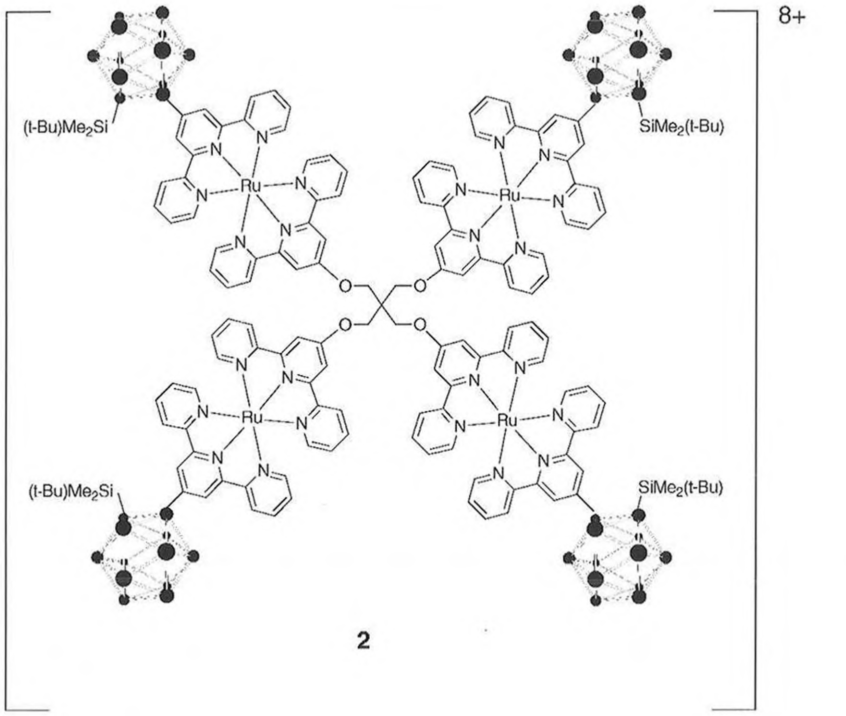
Helices are inherently chiral and may be left- or right-handed. Our studies of helicates have led to a more general interest in chiral compounds. In particular, we have been designing chiral ligands which will give rise to diastereoisomeric excesses or fully diastereoselective formation of left or right-handed helicates (*Scheme 5*). With ligands such as **1**, essentially complete diastereoselectivity is achieved. It turns out that the key interactions are between the chiral auxiliaries and the oligopyridine core of the second ligand rather than between the chiral substituents as we had originally expected [3]. In the course of these studies, we have prepared a large number of chiral ligands which we are currently investigating as chiral auxiliaries for catalysis and as stereogenic components for the preparation of chiral dendrimers and starburst compounds.

Dendrimers and Starburst Complexes

In addition to using self-assembly to bring reaction components together, we have also embarked on a programme of utilizing dendrimer and starburst compounds as cores for the support of func-

Scheme 5





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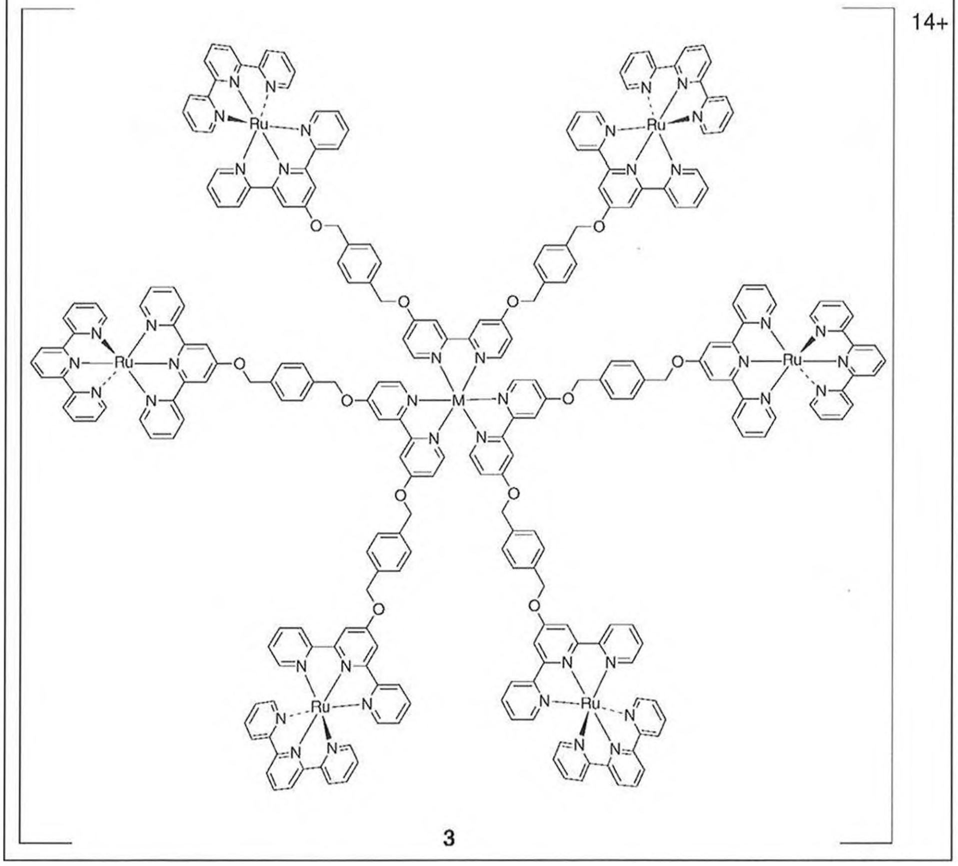

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tionality [4]. A typical example is seen in the tetranuclear complex **2** which is used as a support for four carborane substituents [5]. This complex represents an approach to the preparation of borane-rich dendrimers which might have application in neutron-capture therapy.

Using a combination of self-assembly and building blocks based upon kinetically inert complexes, we have developed a series of heptanuclear starburst complexes such as **3**. These complexes are of interest as they allow us to probe the degree of interaction between adjacent metal centres with a great deal of precision [6].

In related studies, we have developed multinuclear starburst systems in which a polyalkyne core-molecule is post-functionalized by reaction with $Co_2(CO)_8$ to generate multiple Co_2C_2 clusters, an example of a 24-metal starburst is seen in **4** [7].

Currently, derivatives of **4** which have dendritic rather than starburst structures are being investigated with a view to the preparation of new metal-oxide phases and nanostructures.

Biofunctionalized Supramolecules

Recently, we have embarked upon the functionalization of mononuclear and multinuclear dendritic complexes with bioactive substituents. The aim is to investigate the effect that the appended metal-containing functionality has upon the molecular recognition of the biological component with a long-term view to using metal ions as on-off switches or to deliver biomolecules. At present, we have a series of complexes functionalized with oligonucleotides [8], oligopeptides, and oligosaccharides. Ruthenium-functionalized oligonucleotide derivatives are being investigated as photoactivated endonucleases for complementary sequences.

Initial results with these biofunctionalized systems are extremely encouraging and indicate that significant modification of the biological response is possible. As an example, complexes of the sugar-functionalized ligand **5** are not hydrolysed by glucosidases which hydrolyse the free ligand.

Photocatalysis

One of our long-standing interests lies in the use of ruthenium or other transition-metal photocatalysts for the storage or conversion of light energy. Multinuclear metallodendrimers can function as antenna molecules and be used for the collection of light and subsequent energy- or electron-transfer to acceptors. The majority of systems are based upon 2,2'-bipyridine (bpy) ligands. Since the stereogenic properties of $\{M(bpy)_3\}$ centres are not ideal, we have systematically investigated the use of 2,2':6',2"-terpyridine (tpy) $\{Ru(tpy)_2\}$ motifs for such applications. Although $[Ru(tpy)_2]^{2+}$ salts are essentially non-luminescent in fluid solution at room temperature, we have shown that the introduction of electron-withdrawing substituents onto the tpy [8] results in a lengthening of the excited-state lifetime and that ligands such as **6** give ruthenium complexes with lifetimes comparable to

$[M(bpy)_3]^{2+}$ salts [9]. We are currently preparing new antenna systems incorporating thienyl spacers. This work and related studies are in collaboration with the groups of *V. Balzani* and *F. Barigelletti* in Bologna.

Concurrently, we are also involved in the design of new mononuclear photocatalysts with functionality which will allow absorption to metal-oxide surfaces as part of an ongoing collaboration with *M. Graetzel* (EPFL).

Other areas of interest include the formation of molecular polygons, photoactivated molecular machines, metallomesogens, and catalysis.

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[1] E.C. Constable, 'Comprehensive Supramolecular Chemistry', Vol. 9, Ed. J.-M. Lehn, Pergamon, 1996, p. 213.

[2] G. Baum, E.C. Constable, D. Fenske, C.E. Housecroft, T. Kulke, *Chem. Commun* **1998**, 2659.

[3] G. Baum, E.C. Constable, D. Fenske, C.E. Housecroft, T. Kulke, *Chem. Eur. J.*, in press.

[4] E.C. Constable, *Chem. Commun.* **1997**, 1073; E.C. Constable, C.E. Housecroft, *Chimia* **1998**, *52*, 533.

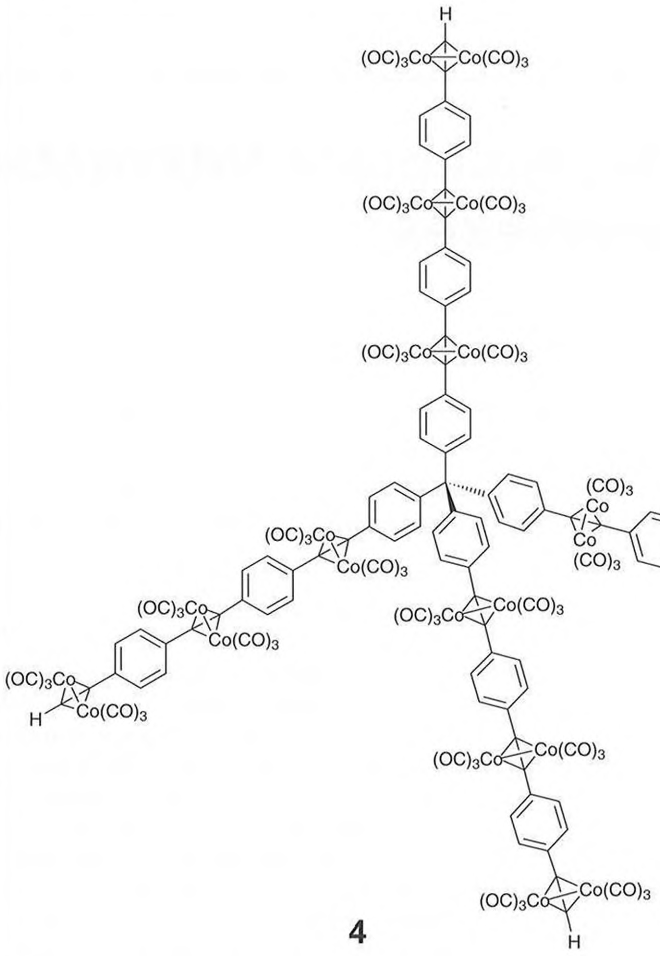
[5] D. Armspach, M. Cattalini, E.C. Constable, C.E. Housecroft, D. Phillips, *Chem. Commun.* **1996**, 1823.

[6] E.C. Constable, P. Harverson, *Chem. Commun.* **1996**, 33; *Inorg. Chim. Acta.* **1996**, *252*, 9; *Polyhedron*, in press; E.C. Constable, P. Harverson, M. Oberholzer, *Chem. Commun.* **1996**, 1821.

[7] E.C. Constable, O. Eich, C.E. Housecroft, L.A. Johnston, *Chem. Commun.* **1998**, 2661.

[8] E.C. Constable, A.M.W. Cargill Thompson, N. Armaroli, V. Balzani, M. Maestri, *Polyhedron* **1992**, *11*, 2707; M. Maestri, N. Armaroli, V. Balzani, E.C. Constable, A.M.W. Cargill Thompson, *Inorg. Chem.* **1995**, *34*, 2759.

[9] N. Armaroli, F. Barigelletti, E.C. Constable, S. Encinas, E. Figgemeier, L. Flamigni, C.E. Housecroft, E.R. Schofield, J.G. Vos, *Chem. Commun.*, in press.



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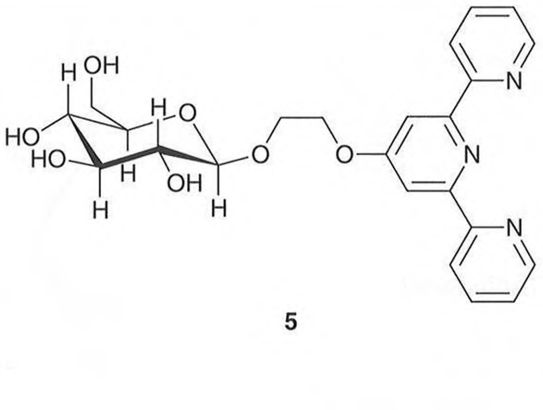

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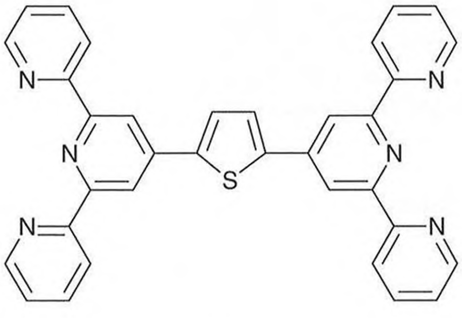

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