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Stereochemistry and polymetallic ligand-bridged molecular assemblies

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Contents

Abstract

There have been many recent developments in synthetic methodologies for polymetallic ligand-bridged molecular assemblies, encouraged by the prospect that such materials have potential application to photochemical molecular devices. The assemblies have involved

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ruthenium(II) metal centers, which are invariably octahedral. However, the synthetic advances have often occurred without consideration of the problem of stereochemical ambiguity in the products. The present review examines this uncertainty and ways in which it may be addressed. In particular, it assesses approaches to the pre-determination of the stereochemistry of polynuclear assemblies incorporating Ru(II) and related centers [e.g. Os(II)] by the use of precursors with an established geometry, and the use of chromatographic techniques in the separation of stereoisomeric mixtures. Some of our own work is elaborated, where we have been able to separate stereoisomers of chromophore-quencher complexes and of dinuclear and trinuclear ligand-bridged species. Additionally, the review summarizes our preliminary studies of their physical properties as a function of the spatial arrangement of the components.

1. Introduction

1.1. Mimicry of photosynthetic systems

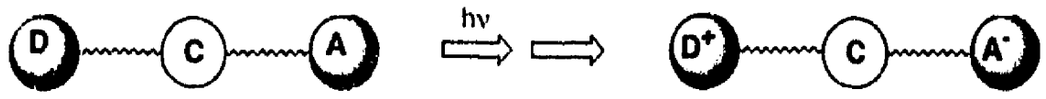
The concept of controlled molecular architecture – and emergence of the "nanometer technology" – has developed from an increasingly intimate understanding of properties at a molecular level. One example of its application is the rational design of supramolecular assemblies which form the basis of materials to be used in photochemical molecular devices (PMDs). Following light absorption, such materials may perform a variety of functions; e.g. conversion of light energy to chemical or electrical energy, light-activated molecular switches, etc. Artificial photosynthesis is but one obvious goal.

In nature, the process of photosynthesis originates with light-promoted electronic excitation within the "antenna system" of an organism. In a series of short range, rapid electron-transfer steps, physically-separated reducing and oxidizing centers are created which have lifetimes sufficient that subsequent chemical reactivity may take place (the reduction of carbon dioxide to carbohydrates and the oxidation of water to oxygen, respectively) [1,2]. Such an organism must necessarily contain (inter alia) two essential components: light absorbers ("chromophores") which harvest light energy allowing electronic excitation, as well as electron- and energy-transfer agents ("quenchers") which rapidly relay the absorbed electronic energy away from the chromophore to an appropriate site in the system for utilization. Further, for a photosynthetic system an additional component is also required, namely catalytic sites, at which the chemical reactions occur.

The three components are contained within an enzyme matrix which controls the spatial relationships between them and, together with the trans-membrane nature of some of the relay processes, limit the reactivity pathways. However, the precise manner in which the enzyme structure effects processes such as electron transfer remains a subject of conjecture [3].

A key issue is the rapid physical separation of the excited electron from the chromophore, and a number of elegant model studies of this process have been undertaken, albeit they are limited because the linkages between the components are covalent [4–8]. The overall principle of such studies is represented below, where

a chromophore (C) is attached to redox-active groups (quenchers). In the case where an electron donor (D) and an electron acceptor (A) are involved, the initial D–C–A species absorbs light energy and forms an excited state D–*C–A, which produces the redox charge-separated state D^+–C–A^- by a series of electron transfer steps.



As an exemplar of such studies, the work of Gust, Moore and coworkers is cited, where photoexcitation of a carotenoid–porphyrin–diquinone tetrad (represented C–P–Q_A–Q_B) gives rise to the charge-separated state $C^{\cdot+}$–P–Q_A–$Q_B^{\cdot-}$, rationalized via a series of electron transfers between adjacent groups(Fig. 1)[9]. In these particular studies, the components are actually mimics of the natural system – the porphyrin as the chromophore with the carotenoid and quinone moieties being donor- and acceptor-quencher functionalities, respectively. More extended (pentad C–P_1–P_2–Q_A–Q_B) systems of the same type have also been investigated [10].

Attention is also drawn to the elegant bis(porphyrin) systems of Sauvage and coworkers [11,12] which model the function of the "reaction center" in the photosynthetic process.

Ultimately, chemical reactions in any photosynthetic scheme are multi-electron processes, although in the chromophore only one electron is excited per photon absorbed. The simultaneous supply of several electrons is achieved by the use of "antenna" systems which funnel electrons to a reaction site. To achieve artificial photosynthesis, the same elements of spatial and charge separation must occur within synthesized molecules. Although the precise chemical reactions will differ from those in the natural systems, they necessarily remain multi-electron in character, so that the artificial molecular assembly ("supramolecule") will also require several sites for light absorption and electron excitation, and be designed so that the photo-

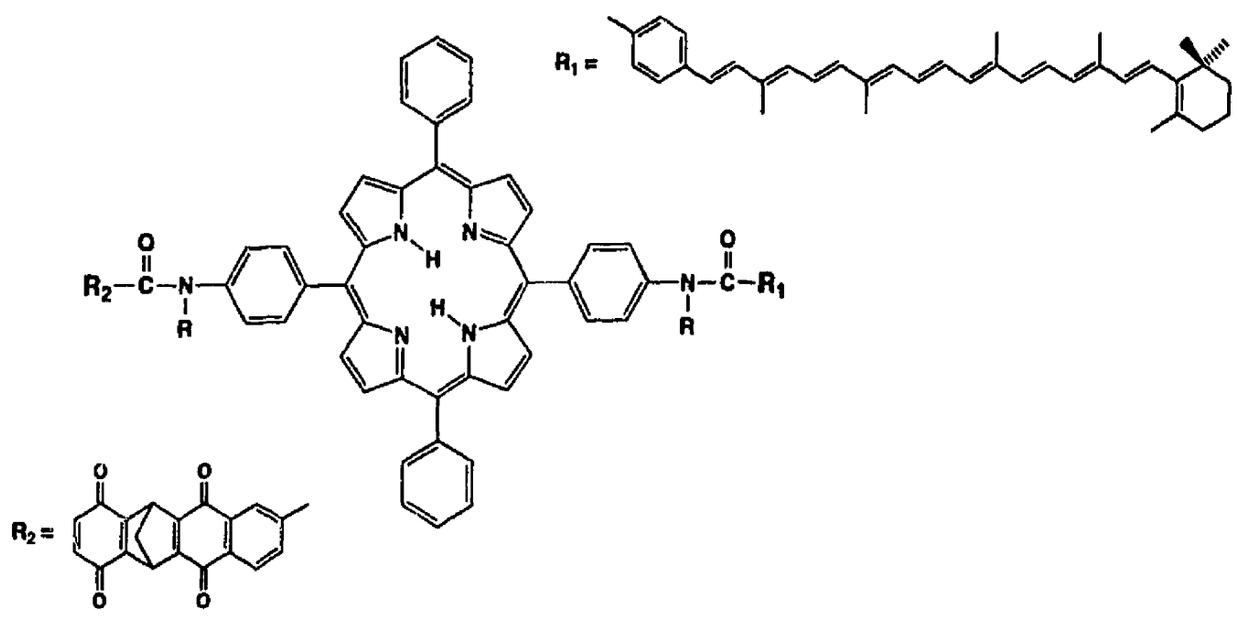
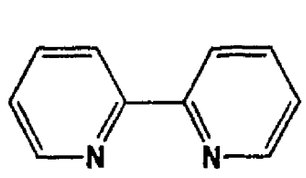


Fig. 1. Chromophore-quencher tetrad C–P–Q_A–Q_B [9].

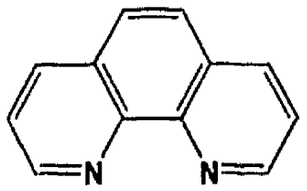
induced electron transfer relay is directed to a spatially-separated chemically reactive (catalytic) site.

1.2. Electron and energy transfer in polymetallic assemblies

Polymetallic molecules, appropriately constructed, could conceivably provide the basis for such a supramolecular system [13,14]. For the required building blocks, mononuclear transition metal complexes of the d^6 metal centers ruthenium(II), osmium(II) and rhenium(I) with polypyridyl ligands {e.g. bpy = 2,2′-bipyridine and phen = 1,10-phenanthroline and their analogues} are of particular interest as precursors because of their extensive (and well studied!) photochemistry [15]. Of these, the ruthenium compounds have received most attention, as the synthetic versatility of osmium is comparatively limited and rhenium species tend to lack broad-band absorption in the visible spectral region.



bpy = 2,2'-bipyridine



phen = 1,10-phenanthroline

The capacity for variation of the photophysical, spectral and redox characteristics by ligand control is extensive, and this has been well documented for homoleptic and bis(heteroleptic) complexes of ruthenium(II) with bidentate polypyridyl ligands [15]. As alluded to previously [15], with 200 bidentate ligands (pp), there are 200 homoleptic possibilities $[Ru(pp)_3]^{2+}$, $\sim 4 \times 10^4$ bis(heteroleptic) $[Ru(pp)_2(pp')]^{2+}$ species and $\sim 1.3 \times 10^6$ tris(heteroleptic) complexes $[Ru(pp)(pp')(pp'')]^{2+}$: our recent reports of the synthesis of a range of tris(heteroleptic) complexes of ruthenium [16–19] and osmium [20] have served to emphasize this particularly attractive aspect of versatility in the utilization of such species as building blocks for polynuclear assemblies.

Over the last decade, significant developments have occurred in synthetic schemes for a wide range of ligand-bridged polymetallic assemblies. It is not intended to exhaustively review the area, as only a portion is of particular relevance to the subsequent discussion. However, it is noted that there is a recent comprehensive review [21] addressing the synthesis and physical properties (electrochemical and photophysical) of such complexes, and the reader is directed to that work for additional information.

The nature of the bridging moiety may have a significant influence on the properties of a polynuclear assembly. It can promote strong coupling between the centers or be effectively insulating (or anything in between). It can be flexible or it can rigidly control the spatial relationship between the attached metal centers. In terms of coupling, the concept of a "supramolecular" assembly implies that the individual components will substantially retain their individual characteristics. Very strong coupling is not consistent with this requirement, although the study of systems in

which the coupling may be systematically varied is valuable in developing our understanding of intramolecular electron and energy transfer processes that occur in polymetallic assemblies following light absorption.

The consequence of flexibility (or at least lack of rigidity) within the bridge is that the geometry of the assembly is uncertain, both in terms of the distance by which the metal centers are separated as well as their relative orientations. Under these circumstances, any theoretical treatment of electron or energy transfer is rendered difficult. Additionally, since in any applications of these materials such transfers will be over long distances and directional, the uncertainty is limiting. Such directional control, which is a feature of the framework provided by the enzyme matrix in natural systems, can only be developed when there is rigidity in the bridge and the stereochemical features of the component metal centers themselves are known and controlled.

Given these restrictions, one should note the advantages and limitations of some of the polynuclear assemblies which have been developed.

Initially, mention should be made of the self-assembled polymetallic species in which metal centers {tetrahedral such as Ag(I) or Cu(I) [22–28]; octahedral such as Fe(II), Co(II), Co(III), Ni(II), Ru(II) [24,29–31]} have been used as linking points for long chain polypyridyl ligands, forming double and triple strand helicate structures. While the helicates themselves are rod-like, there have also been examples of extending the principle to 2D structures [32–36]. The concept is extremely elegant, but is not entirely relevant to the present discussion of stereochemical variation in polynuclear species induced by tris(bidentate) ligation at octahedral centers: while such a coordination mode may be present in helicate structures, the only stereoisomeric ambiguity is the chirality which is in turn generally controlled by the helicity.

Polymetallic helical configurations are also included in the intermediate species in the formation of molecular composite knots [37], but as the Cu(I) centers involved are tetrahedral, these complexes are not germane to this review. It is primarily in cases where metal centers in a polynuclear assembly possess octahedral coordination that their individual (rather than collective) stereochemistries are of fundamental concern.

In such assemblies, simple bridges such as CN^- will produce mainly chain-like structures [38]. There is also a range of bridges, using the α,α′-diimine ligating motif in polypyridyl species, which may produce extended polynuclear systems, but in which there is considerable flexibility because of the possibility of bond rotation in the link (e.g. phenyl, polyphenyl or alkynyl) between the ligating groups [39–49]. There are a number of dendrimers (including the so called "star-burst" and "arboral" structures) which may be put in the same category [50–53].

On the other hand, there are a number of bridges which possess sufficient rigidity to meet the criteria specified above in terms of controlling the molecular framework. As one example in this category, a series of assemblies containing up to twenty-two metal centers have been reported by the Italian groups headed by Denti and Balzani [54–68]. The syntheses involve what has been termed a "complexes as ligands" technique: this methodology dates back to early syntheses of dinuclear ligand-bridged species [69,70], but has been developed for the larger oligomers using either a convergent or divergent approach [21].

One of this series is the decanuclear species, which has been synthesized in homo- or hetero-metallic forms containing Ru(II) and/or Os(II) [56]. From photophysical studies it demonstrates that energy transfer may be directed from a number of peripheral sites (M_p) to a single central site (M_c), whereas in other cases energy is transferred in the opposite direction(Fig. 2)[56].

Structural control within such polymetallic molecules is paramount since the type and arrangement of metal centers greatly influences energy migration patterns [21,71]. But despite an extensive and rapidly growing literature on the synthesis and electronic characteristics of such compounds [21], the issue of the effects of stereo-isomerism on those properties, while receiving occasional tacit acknowledgement, has rarely been addressed. An understanding of such aspects seems fundamental: photo-promoted intramolecular electron or energy transfer between chromophoric and catalytic sites are essential processes in artificial assemblies designed as photo-chemical molecular devices, and they will be spatially dependent. The assembly is required to provide the molecular framework which is a feature associated with the enzyme matrix in natural systems, and which controls the directional qualities of the transfer processes.

The redox charge separation described earlier in organic systems occurs also in metal-containing species, in which a metal center functions as the chromophore (**C**) and the redox active groups (**D** and **A**) are attached to the ligands. Although many examples are now known [21], two of the original examples are chosen to illustrate

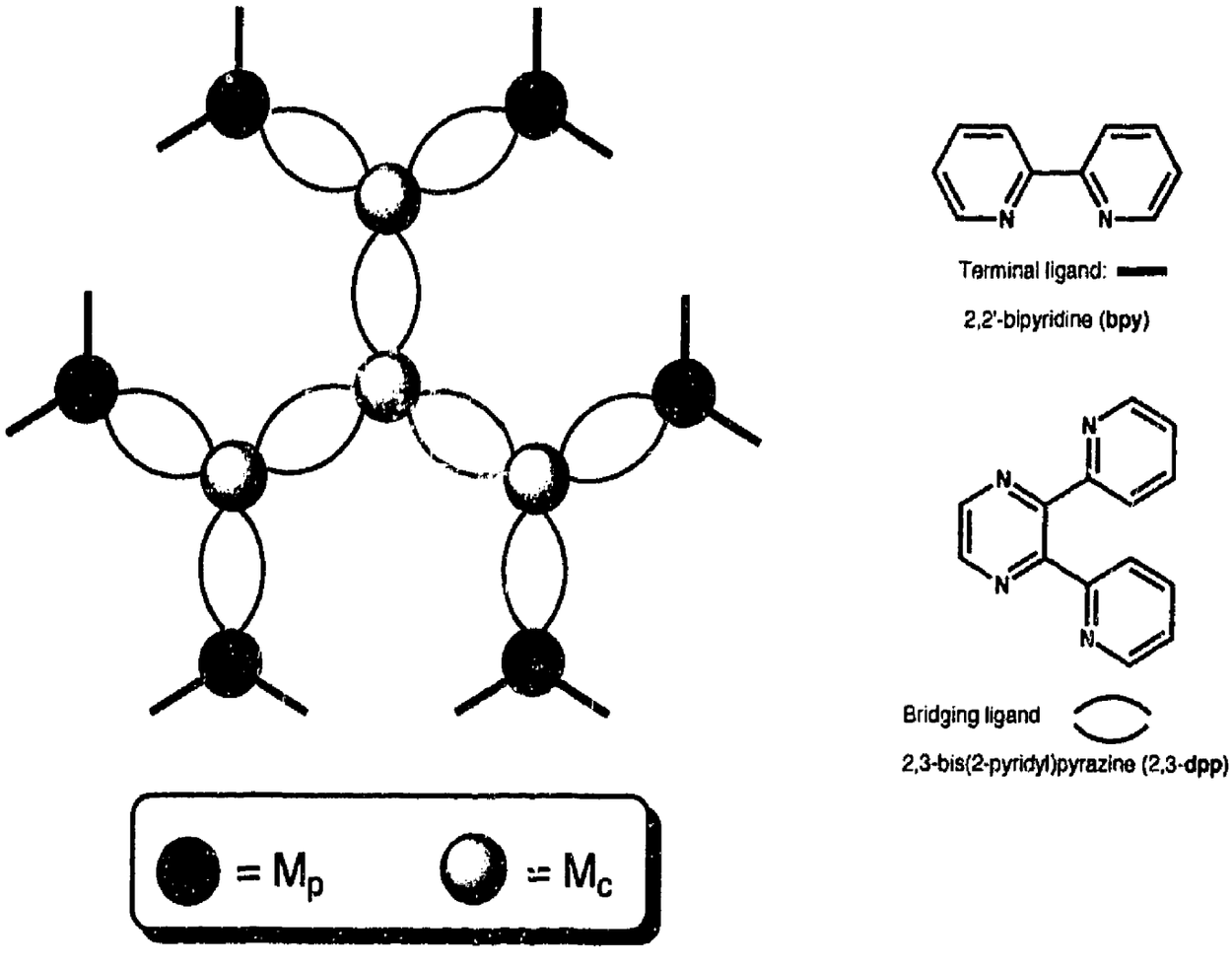


Fig. 2. The decanuclear species $[Ru_{10}(dpp)_9(bpy)_{12}]^{20+}$ [56].

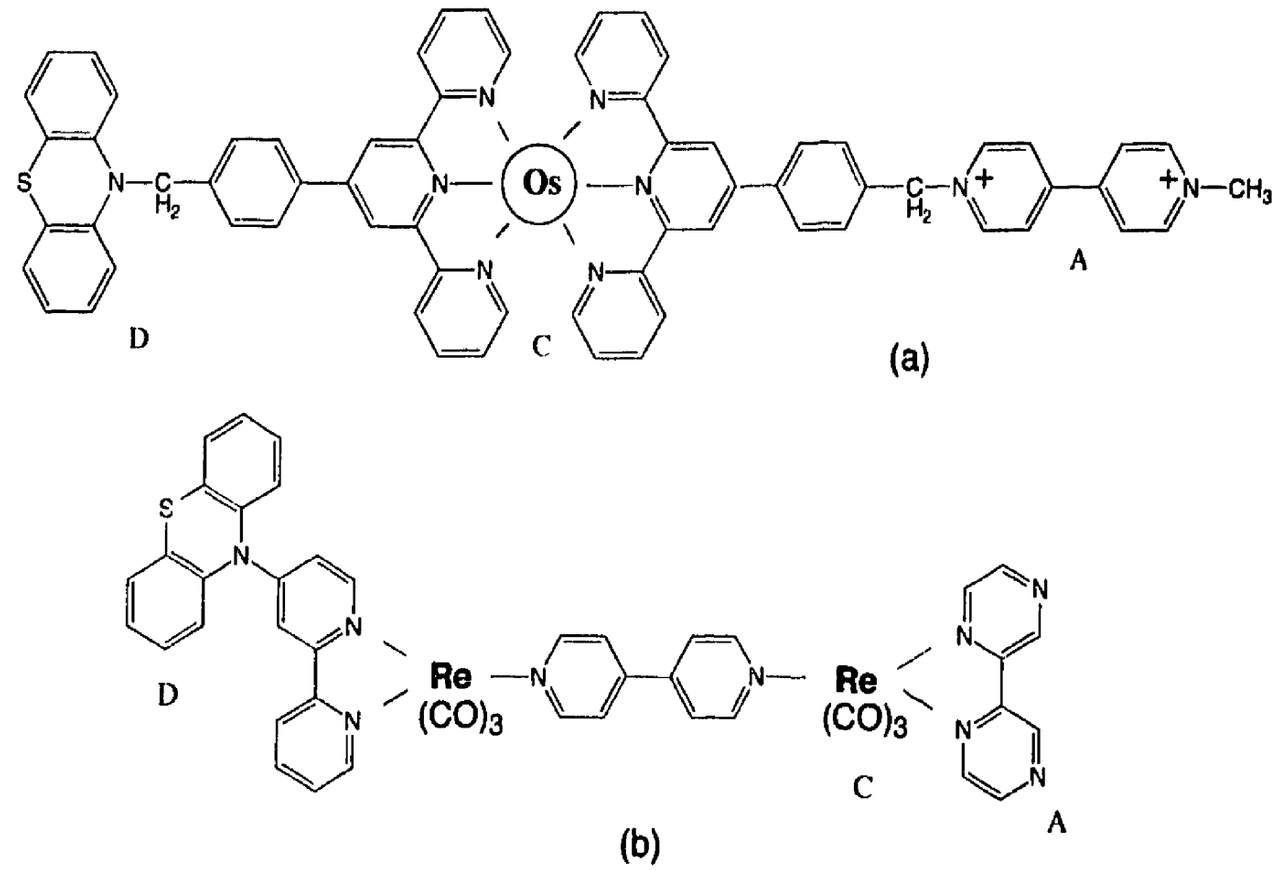


Fig. 3. Chromphore-quencher complexes exhibiting redox charge separation [72,73].

the point (Fig. 3). In system (a), following photoexcitation at the osmium center (**C**) to produce the metal-to-ligand charge transfer (MLCT) state, a sequence of redox quenching processes occur in which the donor phenothiazine (**D**) is oxidized and the acceptor 4,4′-bipyridium functionalization (**A**) reduced, forming the charge-separated state, D^+–C–$A^{\cdot -}$ [72]. Similarly in (b), charge separation can be achieved across a bridge between two metal centers: following photoexcitation of the Re^I–bpz chromophore (bpz=2,2′-bipyrazine) to form the MLCT excited state, the ultimate product has the donor phenothiazine as a radical cation and the bpz ligand as a radical anion [73]. In both of these cases, there are no isomeric uncertainties about the target molecules, but that has been an exception rather than the norm in the systems investigated.

2. Stereochemistry in polymetallic assemblies

2.1. The "stereochemical problem"

Stereoisomerism is possible in systems containing octahedral metal centers with bidentate ligands [74]. When the ligands are symmetrical (C_2 symmetry), chiral forms (Δ and Λ enantiomers) exist for the tris(bidentate) species, whereas for a bis(bidentate) complex there are geometric isomers (*cis/trans*) as well as enantiomers of the *cis* form. When ligands are non-symmetrical, extra geometrical isomerism occurs. In polynuclear species based on such centers, the stereoisomeric possibilities

increase exponentially with the number of metal centers. In such cases, the samples obtained under normal synthetic conditions will be a mixture of stereoisomers in an uncertain ratio – a product described by von Zelewsky as possessing a "fuzzy stereochemistry" [75].

A number of examples may be given involving systems where studies have been undertaken on the physical properties of isolated species which clearly have a number of stereochemical possibilities. The following cases are discussed as they are representative but are also particularly relevant to our subsequent approach to the "stereochemical problem".

In their studies of charge-separated excited states in mono-nuclear complexes containing ligands with donor- and acceptor-quencher functionalities, Elliot and coworkers have investigated the system $[Ru(44PTZ)_2(423DQ^{2+})]^{4+}$ [76,77]. An examination of stereoisomerism in such a system reveals that there are four geometric isomers, shown in Fig. 4 (**A** represents the bipyridinium acceptor quencher, and **D** the phenothiazine donor quencher). A similar number of isomers are possible in $[Ru(bpy\text{-}AQ)_2(bpy\text{-}PTZ)]^{2+}$, studied by Meyer et al. [78]. In both the above systems [77,78], the possible existence of geometric isomers was acknowledged, although there was no evidence for more than one isomer – or if more than one isomer was present there was no evidence of differences in their characteristics.

A number of examples of ligand-bridged oligomeric species have been reported

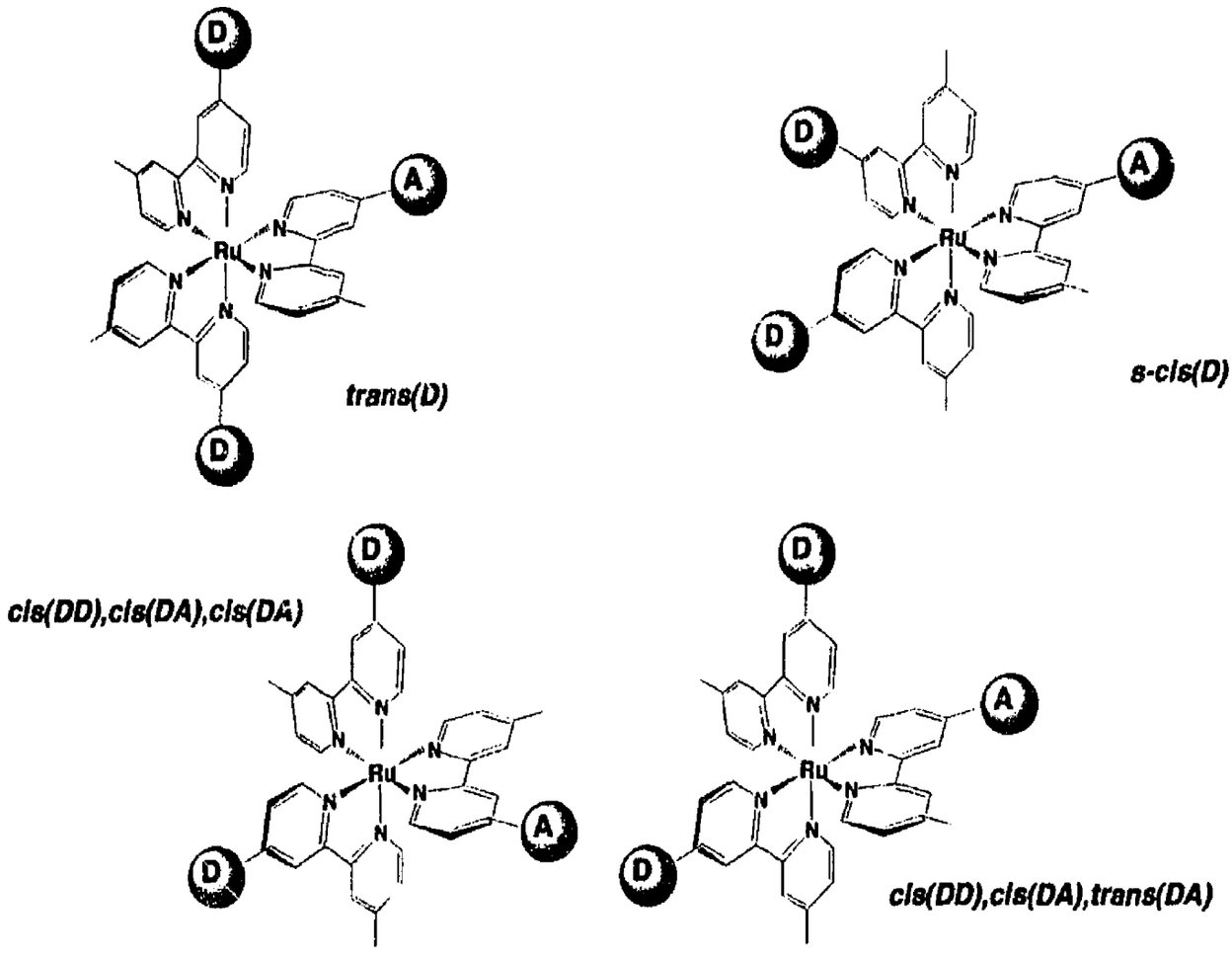
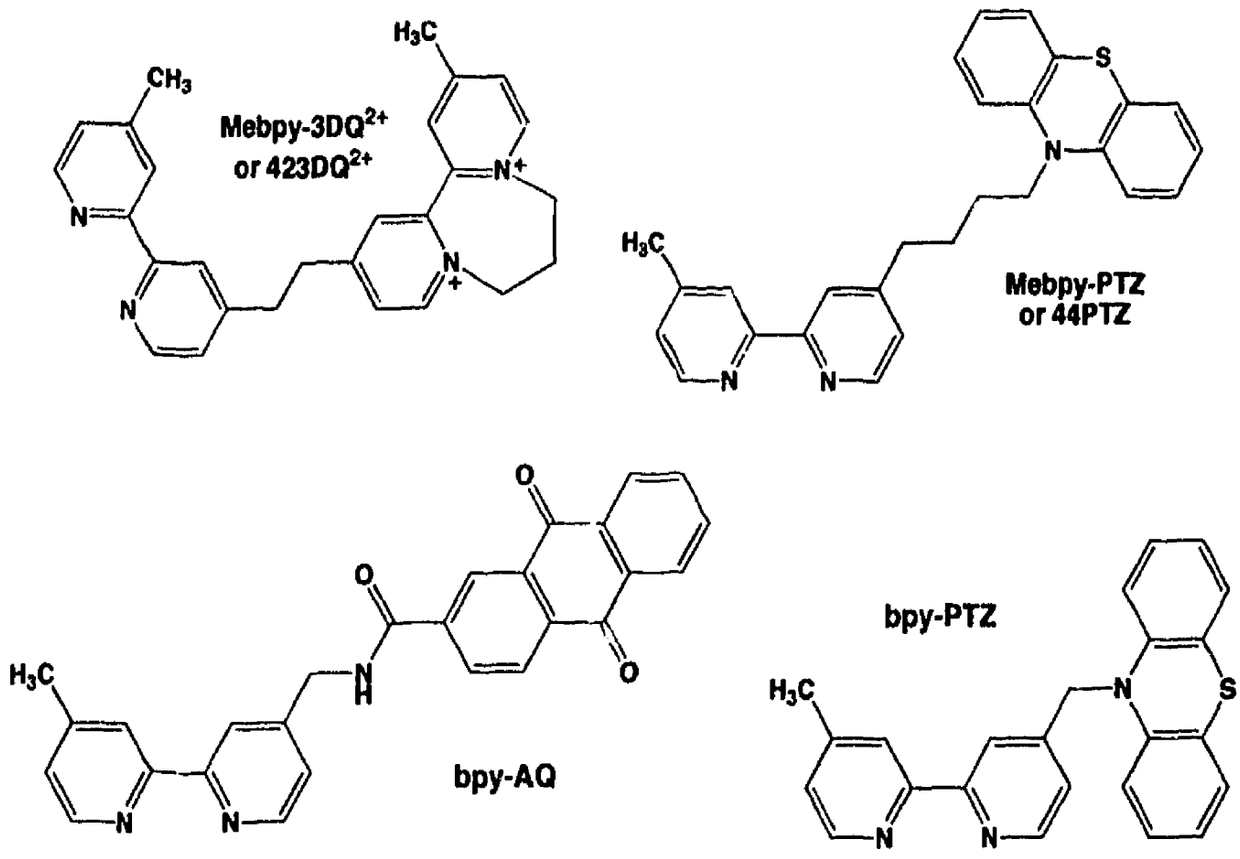


Fig. 4. Geometric isomers in a general $[Ru(bpy\text{-}D)_2(bpy\text{-}A)]^{2+}$ complex.



by Denti, Balzani and coworkers [54–68], as well as examples from other laboratories [21].

Of these oligomers, the decanuclear species mentioned earlier (Fig. 2) has been reported in which the bridging ligand is 2,3-bis(2-pyridyl)pyrazine (2,3-dpp) and terminal ligands 2,2-bipyridine (bpy) [56]. In such an assembly, since the internal metal centers (M_c) are $[Ru(2,3\text{-dpp})_3]^{2+}$ moieties, they all can exhibit *mer/fac* geometrical isomerism as 2,3-dpp in non-symmetrical. In addition, all ten metal centers may be chiral. As a result of this, there are in fact 6,144 diastereoisomers of this species – each with an enantiomeric form! While it is unlikely that all these stereoisomers would be represented in a synthesized mixture, it emphasizes the point that the stereochemistry of such systems is very complicated. Furthermore, the presence of a plethora of stereoisomers complicates the characterization of the complex by techniques such as NMR, the interpretation of which is rendered extremely difficult as the diastereoisomeric complexes have non-equivalent NMR spectra [58,79]. It also implies that the electrochemical and photophysical data measured represent an average of the various forms.

As another example, a study was presented by Brewer and coworkers on the electrochemical and photophysical properties of the trinuclear species $[\{Ru(bpy)_2\}_2\{Os(2,3\text{-dpp})_2Cl_2]^{4+}$ [80]. In this complex the bridging Os center may adopt a *cis(Cl)* or *trans(Cl)* geometry, and since the 2,3-dpp ligand is non-symmetrical, the *cis(Cl)* form has three geometric isomers and the *trans* isomer two. All the *cis* isomers may have chiral forms, as well as both ruthenium centers. As a result, there are actually sixteen possible diastereoisomers, all but two of which have enantiomeric forms. Of course, the full complement may not necessarily exist. However, in the representations in Fig. 5, the stereochemistry in such a linear

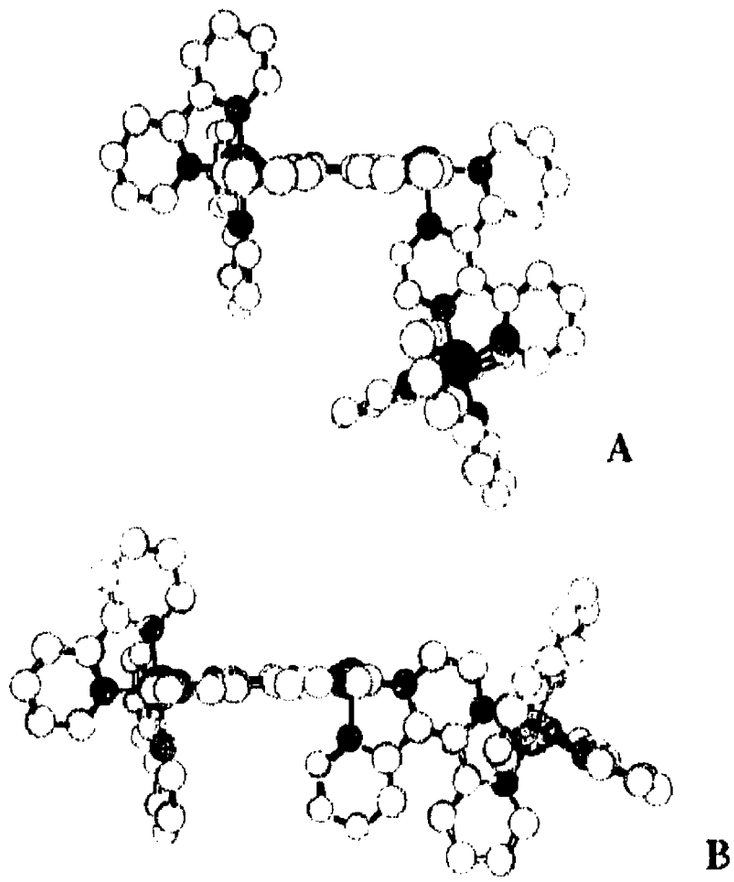


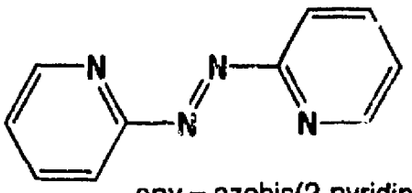
Fig. 5. Chem 3D® representation of diastereoisomers of $[\{Ru(bpy)_2\}_2\{Os(2,3\text{-}dpp)_2Cl_2\}]^{4+}$ (H atoms omitted for clarity) [80].

trinuclear species may be very different for a relatively small change – the species shown are both Δ(Ru)Δ(Os)Δ(Ru) forms, and differ only in that the geometric arrangement about the Os center is *cis(Cl)/cis(pyrazine)* and *cis(Cl)/trans(pyrazine)*, shown below as **A** and **B** respectively. The consequences on the relative disposition of the two "terminal" ruthenium centers is quite profound.

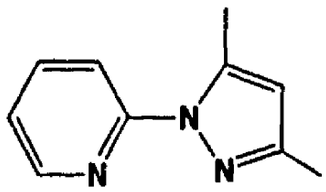
2.2. *Stereochemistry in ruthenium complexes with bidentate ligands*

Although an extensive literature exists on the synthesis of mononuclear complexes of ruthenium(II), there have been few studies of stereoisomerism. When non-symmetrical bidentate ligands are involved, for complexes of the type $[Ru(ab)_3]^{2+}$ the existence of *fac* and *mer* geometric isomers has been recognized from ^1H and ^{13}C NMR studies of complexes where ab = non-symmetrically-substituted derivatives of 2,2-bipyridine and 1,10-phenanthroline [81,82], azobis(2-pyridine) [83], and 2-(2-pyridyl)thiazole and 2-(2-pyrazyl)thiazole [84]. Similarly, ^{99}Ru NMR has been used to identify the presence of both geometric isomers in analogous complexes where ab = 1-(2-pyridyl)-3,5-dimethylpyrazole [85], 1-methyl-2-(2-pyridyl)imidazole, 2-(2-pyridyl)oxazole, 2-(2-pyridyl)thiazole and 2-(2-pyridyl)selenazole [86], and 2,3-bis(2-pyridyl)pyrazine [87]. Prior to our own work [88,89], there were few reports claiming the separation of such stereoisomers. Using HPLC techniques, separations were achieved for the species $[Ru(apy)_3]^{2+}$ (two geometric isomers) and $[Ru(apy)_2(bpy)]^{2+}$ (two of the three possible geometric isomers) {bpy = 2,2'-

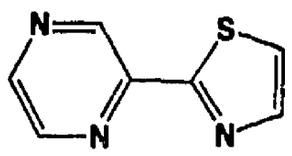
bipyridine; apy = azobis(2-pyridine)} [83]. Structures of *mer*-$[Ru(apy)_3]^{2+}$ and *cis,trans,cis*-$[Ru(apy)_2Cl_2]$ have also been published {the order of specification of the geometry being acido ligand (Cl^-); py; azo} [90]. More recently, the separation of geometric isomers has been reported for complexes of substituted pyrazolylpyridine ligands [91].



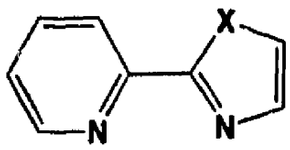
apy = azobis(2-pyridine)



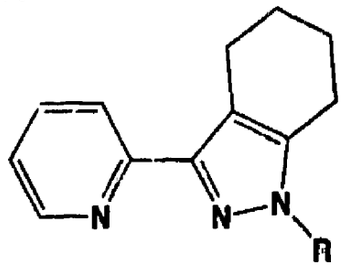
1-(2-pyridyl)-3,5-dimethylpyrazole



2-(2-pyrazyl)thiazole



X = N-Me: 1-methyl-2-(2-pyridyl)imidazole
X = O: 2-(2-pyridyl)oxazole
X = S: 2-(2-pyridyl)thiazole
X = Se: 2-(2-pyridyl)selenazole



1-substituted-3-(2-pyridinyl)-4,5,6,7-tetrahydroindazoles

Three isomers of $[Ru(pap)_2Cl_2]$ and/or $[Ru(tap)_2Cl_2]$ have been isolated [92,93], and the structures of the *cis–trans–cis*- and *cis–cis–cis*-$[Ru(pap)_2Cl_2]$ [94] and *cis–trans–cis*-$[Ru(pap)_2N_3)]$ [95] forms determined. The *cis–trans–cis, cis–cis–cis and trans–trans–trans* geometric isomers of $[Ru(npap)_2Cl_2]$ have been separated [96] and the stereochemical course investigated of the reactions of $[Ru(pap)_2Cl_2]$ and $[Ru(npap)_2Cl_2]$ species with H_2O/OH^- [97,98], and of the reaction of $[Ru(pap)_2(OH_2)_2]^{n+}$ and $[Ru(tap)_2(OH_2)_2]^{2+}$ to form $[Ru(pap)_2B_2]^{2+}$/ $[Ru(tap)_2B_2]^{2+}$ (B is a bidentate ligand) [99]. *Cis* and *trans* isomers of $[Ru(L)_2Cl_2]$ (where L are aryl(2-pyridylmethylene)amine Schiff-base ligands) have also been reported [100].

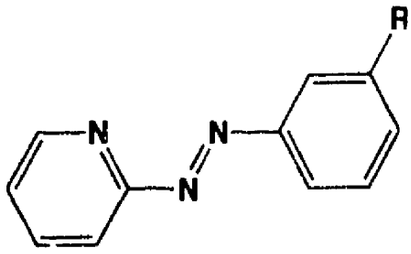
In terms of the separation of chiral forms of such molecules, the resolution of $[Ru(pp)_3]^{2+}$ [101,102], $[Ru(phen)_2(py)_2]^{2+}$ [103] and $[Os(pp)_3]^{2+}$ [104,105] (pp = phen and bpy) was achieved many decades ago.

As far as dinuclear complexes are concerned, very little stereochemical information has been available. In a number of cases, there have been claims for absolute preferences for one diastereoisomeric forms over another [83,106] and linkage isomerism has been shown in species involving the 3,4-bis(2-pyridyl)-1,2,4-triazolate (bpt) ligand (below) as a bridge [107–109]. Our own studies on the stereochemistry of ligand-bridged dimers, and those of von Zelewsky and coworkers [110,111] will be discussed in more detail below.

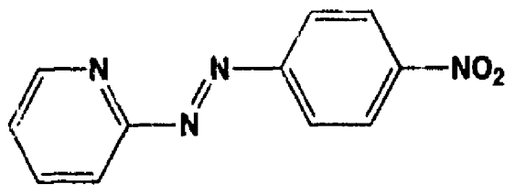
2.3. *Addressing the "stereochemical problem"*

2.3.1. *Using tridentate ligands.*

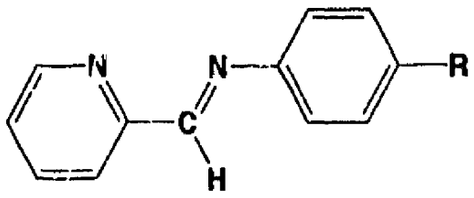
The stereochemical problem may be avoided by the use of tridentate ligands of the type 2,2′:6′,2″-terpyridine (tpy), which coordinate in a meridional fashion about



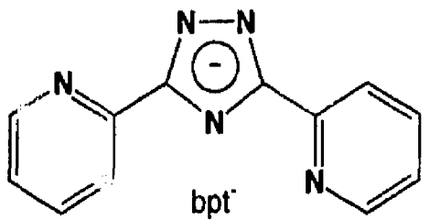
R = H: pap = 2-(phenylazo)pyridine
R = CH_3: tap = 2-(3-tolylazo)pyridine



npap = 2-{(4-nitrophenyl)azo}pyridine



R = H, CH_3, or Cl



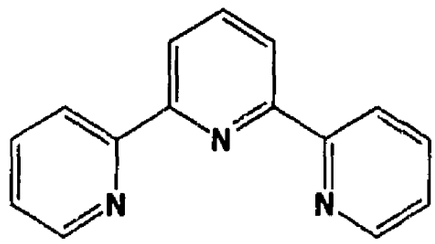
bpt⁻

an octahedral metal center creating an achiral species of the type $[M(tpy)_2]^{n+}$ [21,39,40]. However, it should be noted that there are a number of consequences of this approach. Firstly, the lifetime of the ^{3}MLCT excited state of $[Ru(tpy)_2]^{2+}$ is some 3–4 orders of magnitude shorter at room temperature in solution than for $[Ru(bpy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$, and unlike the latter complexes $[Ru(tpy)_2]^{2+}$ does not luminesce [112–116]. This is a consequence of faster radiationless deactivation through a ^{3}MC (metal-centered) state, brought about by the weaker field strength in $[Ru(tpy)_2]^{2+}$ because of the geometric requirements of the coordinated tpy ligand and resultant distortion from the strictly octahedral environment [117,118]. At 77 K, this path is unavailable, and the luminescence and emission lifetime of $[Ru(tpy)_2]^{2+}$ is comparable with that of $[Ru(bpy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$ [119]. It has been shown that the lifetime of the $[Ru(tpy)_2]^{2+}$ chromophore is significantly increased by the incorporation of electron-withdrawing substituents at the 4′-position [39,120–122].

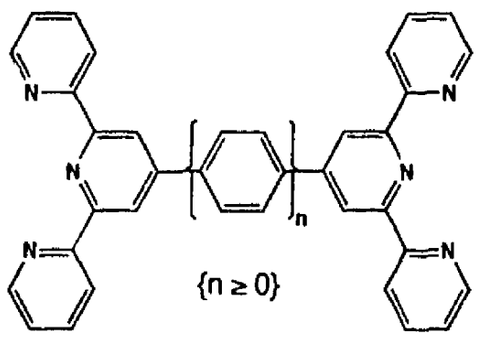
The second consequence is that in order to avoid further stereoisomerism (geometric), any bridging must occur through the 4′-positions of the tpy ligands, which for $[Ru(tpy)_2]^{2+}$ species have a mutually *trans* arrangement – any polynuclear species involving bridging ligands based on tpy-type ligands is therefore necessarily linear or rod-like.

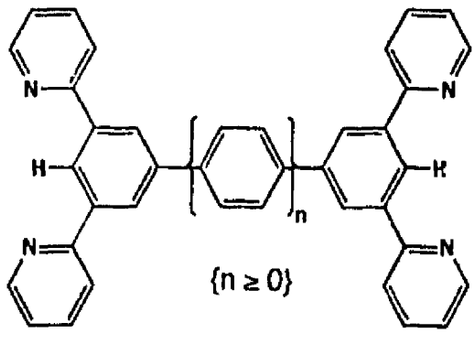
Sauvage and coworkers have also examined the cyclometallated analogue on the basis that the higher σ-donating properties of the cyclometallating ligand allows some control of the spectroscopic and redox characteristics [42,43,123].

The use of these ligands and ligand-bridges has allowed a development of the



tpy = 2,2':6',2"-terpyridine



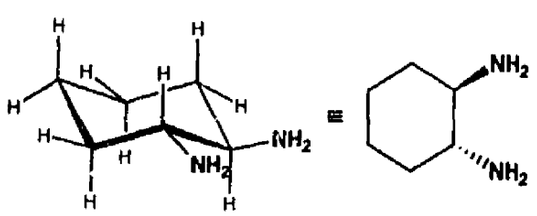


understanding of aspects of intramolecular electron and energy transfer processes [39–43,123]. However, to comprehend fully the consequences of the spatial relationship of the component metal centers on these processes – and maximize the ability to vary the characteristics of the coordination environment of those centers – the use of tris(bidentate) species is ultimately required. And therein lies a challenge.

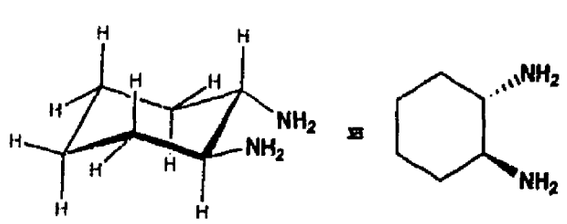
2.3.2. *Chiral building blocks and the "Chiragens"*

Two separate approaches have been taken to this task by von Zelewsky and coworkers [75].

In the first, an enantiomerically pure chiral building block was sought which could be used to produce mono- and dinuclear species of predetermined stereochemistry. The complexes $[Ru(phen)_2(py)_2]^{2+}$ and $[Ru(bpy)_2(py)_2]^{2+}$ (conveniently resolved by conventional diastereoisomer formation using the O,O'-dibenzoyltartrate anion) were found to undergo stereoretentive substitution of the two monodentate pyridine ligands [110,111,124]. This important property was shown by reaction of either Δ- or Λ-$[Ru(pp)_2(py)_2]^{2+}$ (pp = bpy or phen) with the chiral bidentate ligand (R,R)-1,2-diaminocyclohexane (or its enantiomer) to give pure diastereoisomeric products [111].



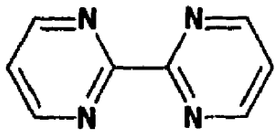
RR-diaminocyclohexane
RR-dach



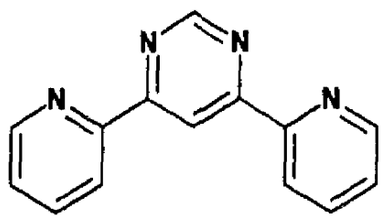
SS-diaminocyclohexane
SS-dach

These chiral precursors were used to synthesize dinuclear species $[\{Ru(pp)_2\}_2(\mu\text{-BL})]^{4+}$ (pp = bpy or phen; BL = bridging ligands 2,2-bipyrimidine

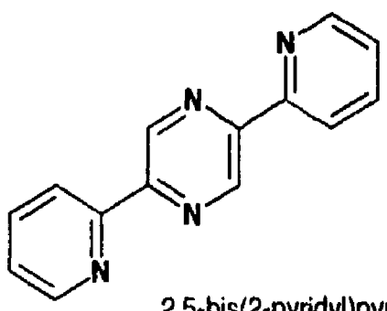
{bpm}, 2,5-bis(2-pyridyl)pyrazine {2,5-dpp} or 4,6-bis(2-pyridyl)pyrimidine {4,6-dppm}) with predetermined stereochemistry [110,111]. In these cases the *meso*-(ΔΛ) diastereoisomer and the enantiomers (ΔΔ and ΛΛ) of the *rac* diastereoisomer were separately synthesized and their stereochemical integrity confirmed using ^{1}H NMR and CD methods.



2,2'-bipyrimidine
bpm

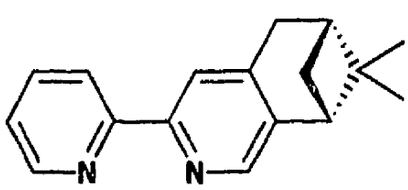


4,6-bis(2-pyridyl)pyrimidine
4,6-dppm



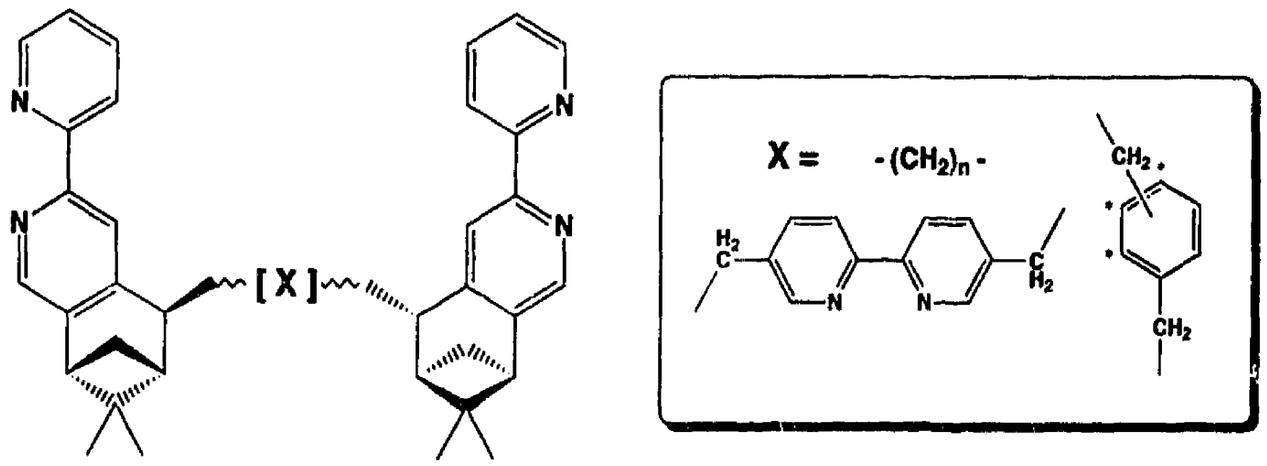
2,5-bis(2-pyridyl)pyrazine
2,5-dpp

The principle of the second strategy was to impose a chiral disposition about the metal center of a precursor, which in turn would promote the stereoselective synthesis of oligomers derived from it. Such ligands, called "Chiragens", are based on [4,5]-pineno-2,2'-bipyridine, which are derived from the naturally occurring chiral species (−)-myrtenal [125,126]. [4,5]-Pineno-2,2'-bipyridine is chiral, and undergoes regioselective deprotonation whereby two such moieties may be linked by a spacer to give the "Chiragen" series of ligands. The linkage may be an alkyl chain {denoted CG[n]; n=0, 3, 4–7} [124–127], bpy {denoted CG[bpy]} [127] or *o*-, *m*- or *p*-xylendiyl {denoted CG[*o*/*m*/*p*-xyl]} [129–131]. The Chiragens CG[n] where $n \geq 4$ show stereospecific coordination to octahedral metal centers ruthenium and osmium [126], and the same ligands have been used to control the stereochemistry of the general species of the type [Ru(CG[n])Cl$_2$] and [Os(CG[n])X$_2$]$^{m+}$ (X=Cl$^-$, m=0; X=DMSO, m=2) [131,132], which may be used as precursors in syntheses of higher nuclearity assemblies. They have also been used to produce helicate species with predetermined chirality [129]. The ligands CG[n] (n=0, 3) and the CG[bpy] do not coordinate as tetradentate ligands: however, they coordinate to a metal center in a bidentate manner and therefore are potential bridges. They have been incorporated in di- or trinuclear species: in such systems stereospecificity was observed, but was induced by the chirality of the metal centers involved [128].



A chiragen based on the "dipineno" precursor has also been developed {designated superchiragen[0] or SGS[0]} and shows similar behavior to its CG[0] analogue [127,128].

In terms of the overall aims, by imposing stereochemistry on the primary building

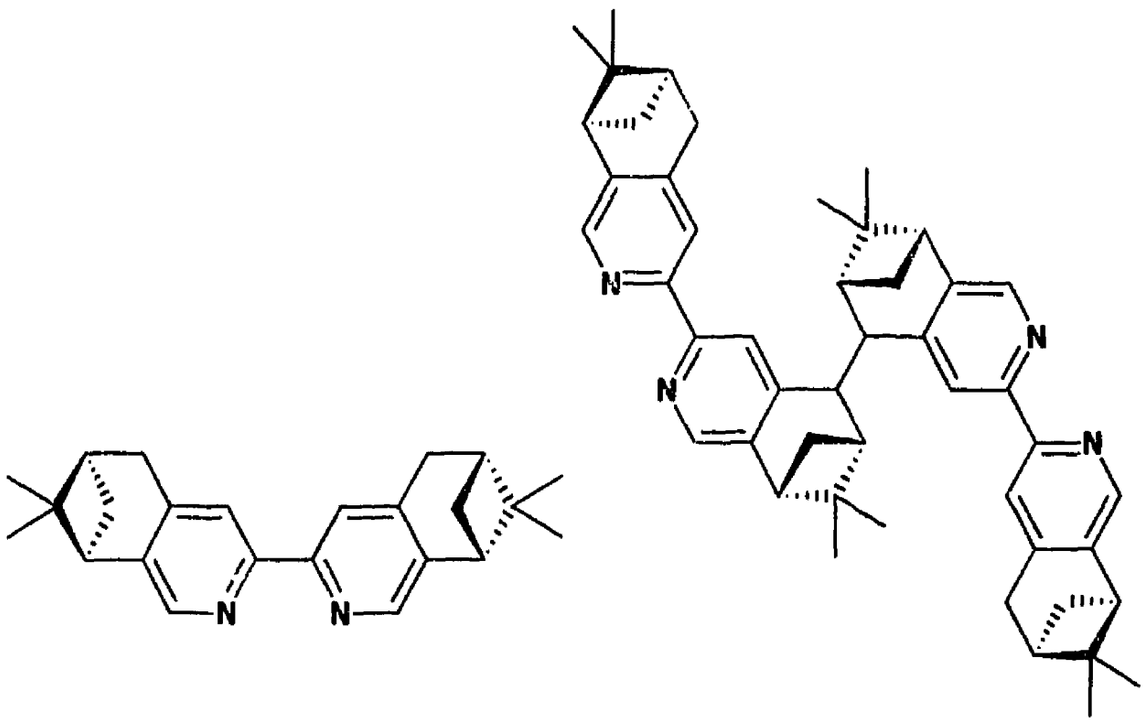


block of an assembly the "Chiragen" approach seeks to maintain stereoselectivity in the addition of further components. Furthermore, since that stereoselectivity appears to be complete, the chances of photoisomerization are minimized so that the stereochemistry is retained during photochemical processes.

The negative aspect of the approach is that since the Chiragen occupies four coordination positions about the metal center, the opportunity for versatility in terms of the coordination environment is limited.

2.3.3. *Other examples of stereoselective synthesis*

There are a limited number of other recent examples of controlled stereochemistry which reflect a burgeoning interest in the topic. For example, there have been a number of examples involving condensations of chiral monomers containing the 1,10-phenanthroline-5,6-dione ligand to form bridged complexes of predetermined stereochemistry. Lincoln and Nordén [133] have used this methodology to produce ΔΔ-[{Ru(phen)$_2$}$_2$(dppz(11-11′)dppz}]$^{4+}$ (Fig. 6) using resolved [Ru(phen)$_2$-



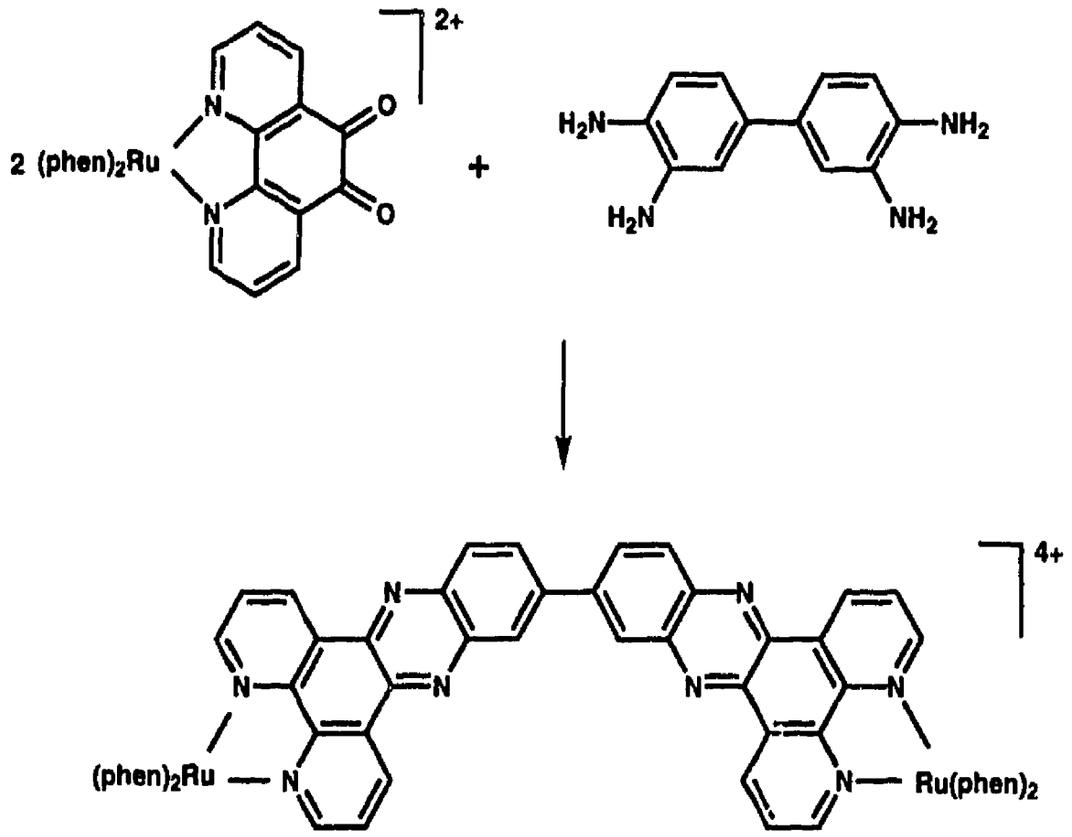


Fig. 6. Stereoselective synthesis of diastereoisomers [{Ru(phen)$_2$}$_2$(dppz(11-11')dppz)]$^{4+}$ [133].

(phen-5,6-dione)]$^{2+}$ [134] as the precursor. In a similar manner, Lehn and coworkers [135] have reported the complex shown in Fig. 7, in which the stereochemistry of the two ruthenium centers is predetermined by the use of the same Δ- or Λ-[Ru(phen)$_2$(1,10-phenathroline-5,6-dione)]$^{2+}$ precursor: Again in a related system, MacDonnell and Bodige have used resolved precursors to form a single diastereoisomer of the tpphz-bridged dimer (Fig. 8) [136]:

Tor and coworkers [137] have reported the use of the Hua and von Zelewsky precursor [111] to produce chiral complexes of functionalized phen ligands, which may be subsequently linked to form dimers with predetermined stereochemistry (Fig. 9).

Additionally, Kane-Maguire and coworkers [138] have recently reported the resolution of *cis*-[Ru(phen)$_2$(CH$_3$CN)$_2$]$^{2+}$, which may be used as a chiral

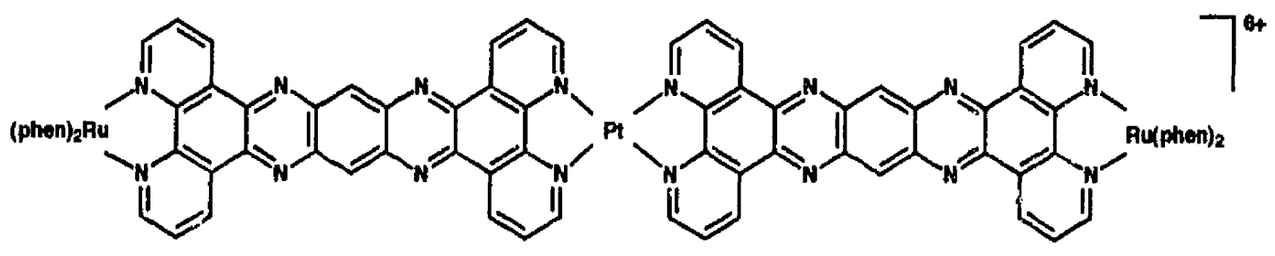


Fig. 7. Stereoselective synthesis of diastereoisomers of trimetallic species [135].

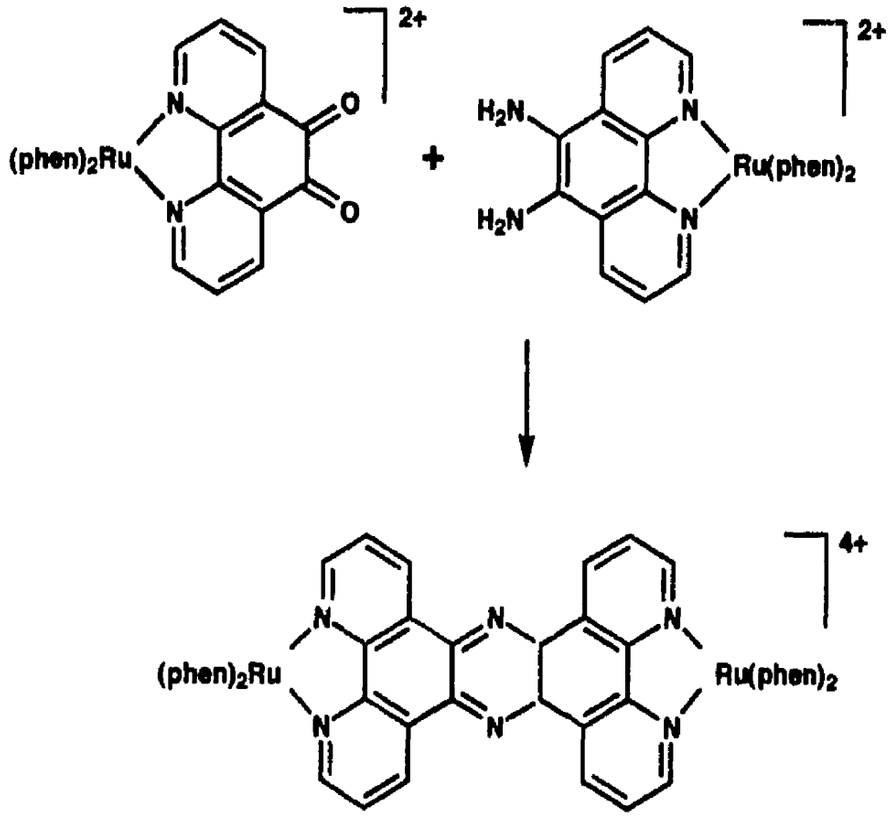


Fig. 8. Stereoselective synthesis of diastereoismers of $[\{Ru(phen)_2\}_2\{\mu\text{-tpphz}\}]^{4+}$ [136].

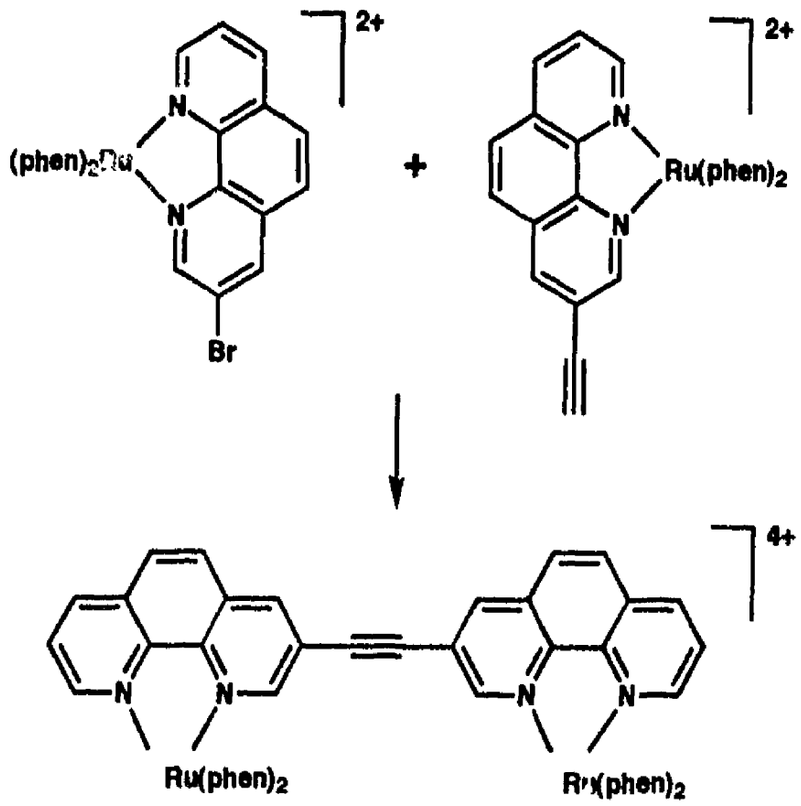


Fig. 9. Stereoselective synthesis of diastereoismers of alkyne-bridged dinuclear species [137].

precursor for further synthesis, including chiral neutral species such as *cis*-$[Ru(phen)_2X_2]$ ($X=CN^-$, Cl^-) which are difficult to obtain by other means.

While these examples show the increasing appreciation of the problem, they do not offer a general approach to its solution.

3. Stereochemistry and polynuclear assemblies

3.1. The synthesis of tris(heteroleptic) complexes

In our own approach to the stereochemical problem, we have attempted to honor three aims. Firstly, the use of metal centers in polynuclear assemblies was considered important because it provides the ability to control the photophysical and spectral characteristics of the chromophore component, as well as the redox properties (a feature important in controlling intramolecular electron and energy transfer following light absorption), and such versatility may only be achieved by the use of bidentate ligands. The second necessity was that the centers must have a substantial level of photoinertness. For complexes containing pyridyl-type ligands low levels of photolability are known [139], and in cases where stereoisomerism is possible photoisomerization and photoracemization have been reported, particularly in cases where monodentate ligands are involved [101,140,141]. In the case of the "Chiragen" ligands, one of the attractive features was that since the chiral ligand imposed a stereoselectivity on its attachment to the metal center, photoracemization would be minimized [131]. It is worth noting however from our studies that tris(heteroleptic) species proved to be at least 10^2–10^3 times more photoinert than the $[Ru(bpy)_3]^{2+}$ archetype, [17] and despite concerns to the contrary [131], we have not observed photolability in the $[Ru(pp)_2(CO)_2]^{2+}$ species.

The synthetic methodology we have used for the heteroleptic tris(bidentate)-ruthenium(II) complexes is based on the sequential addition of the polypyridyl ligands to the oligomeric precursor $[Ru(CO)_2Cl_2]_n$, as summarized in Fig. 10 [16,17].

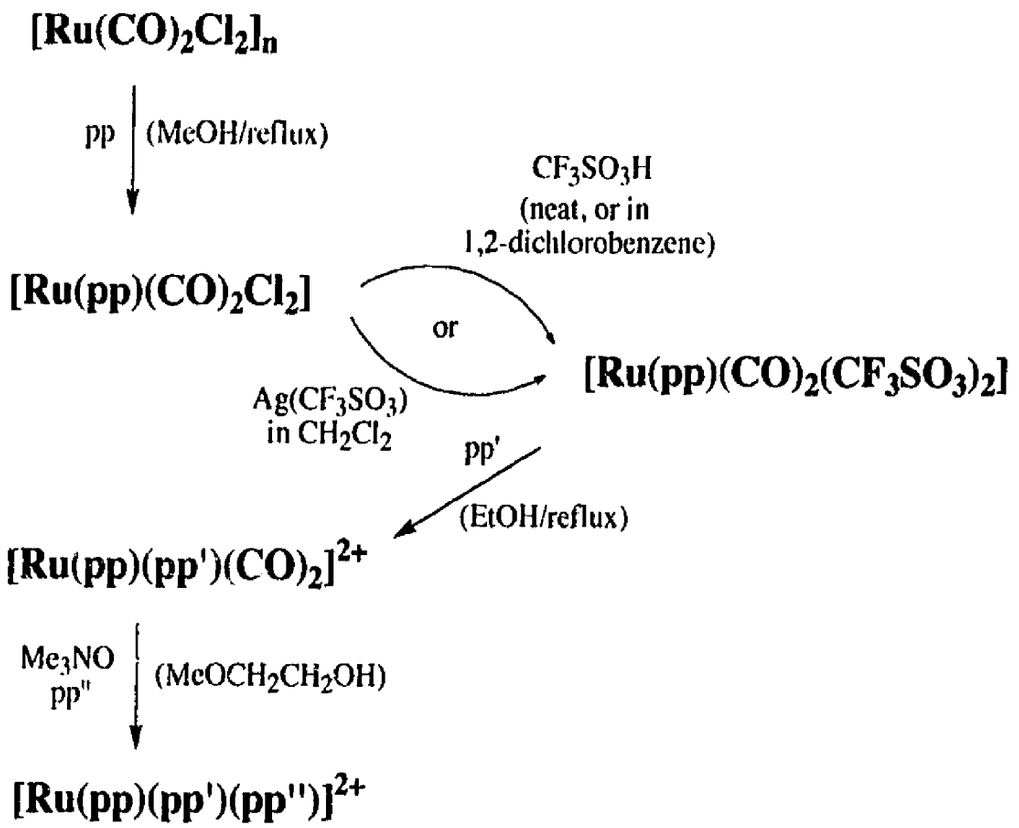


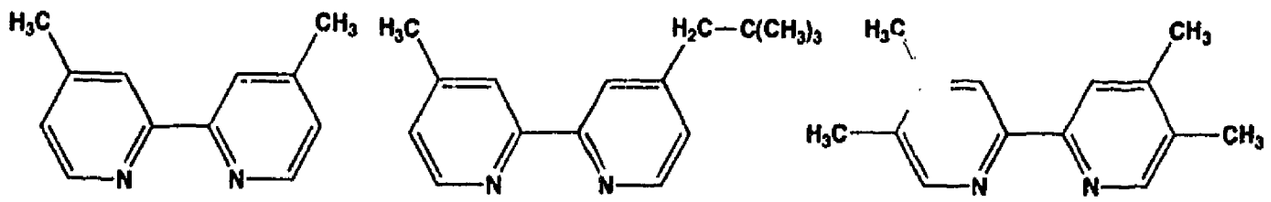
Fig. 10. Synthetic scheme for heteroleptic tris(bidentate)ruthenium(II) complexes [17].

Preliminary details of the scheme were reported earlier [142–147]. We have also recently reported a related synthetic route to produce heteroleptic tris(bidentate)osmium(II) analogues [20].

3.2. Stereochemical considerations

From a stereochemical point of view, the penultimate complex in the scheme, viz. the species $[Ru(pp)(pp')(CO)_2]^{2+}$, is pivotal as such a bis(bidentate) species is closely stereochemically related to the final product and it is at this final stage that the stereochemistry may be controlled. We undertook two separate but interrelated studies of the stereochemistry of this decarbonylation process.

In the first, the formation of the species $[Ru(Me_2bpy)(pmb)_2]^{2+}$ was studied in detail [88]. In this complex, 4,4′-dimethyl-2,2′-bipyridine (Me_2bpy) is a symmetrically-substituted ligand, and 4-methyl-4′-*neo*-pentyl-2,2′-bipyridine (pmb) is non-symmetrically substituted. The target complex in such a case has three possible geometric isomers, shown below. In terms of the synthetic scheme, there are of course two alternative approaches: the target complex can be obtained by either reaction of Me_2bpy with $[Ru(pmb)_2(CO)_2]^{2+}$ (which has three geometric isomers exactly analogous to the target), or by reaction of pmb with $[Ru(Me_2bpy)(pmb)(CO)_2]^{2+}$, which has two geometric forms. Figs. 11–13



Clearly, in the first case, if stereochemical integrity were retained in the decarbonylation process, then a direct conversion of each of the dicarbonyl isomers to the

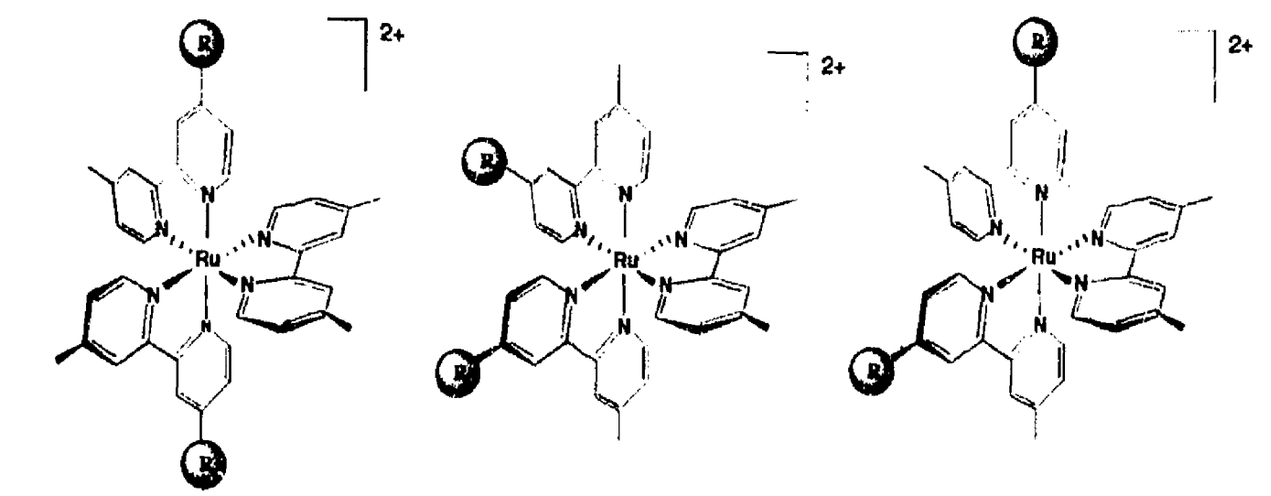


Fig. 11. Geometric isomers of $[Ru(pmb)_2(Me_2bpy)]^{2+}$ (R = *neo*-pentyl-).

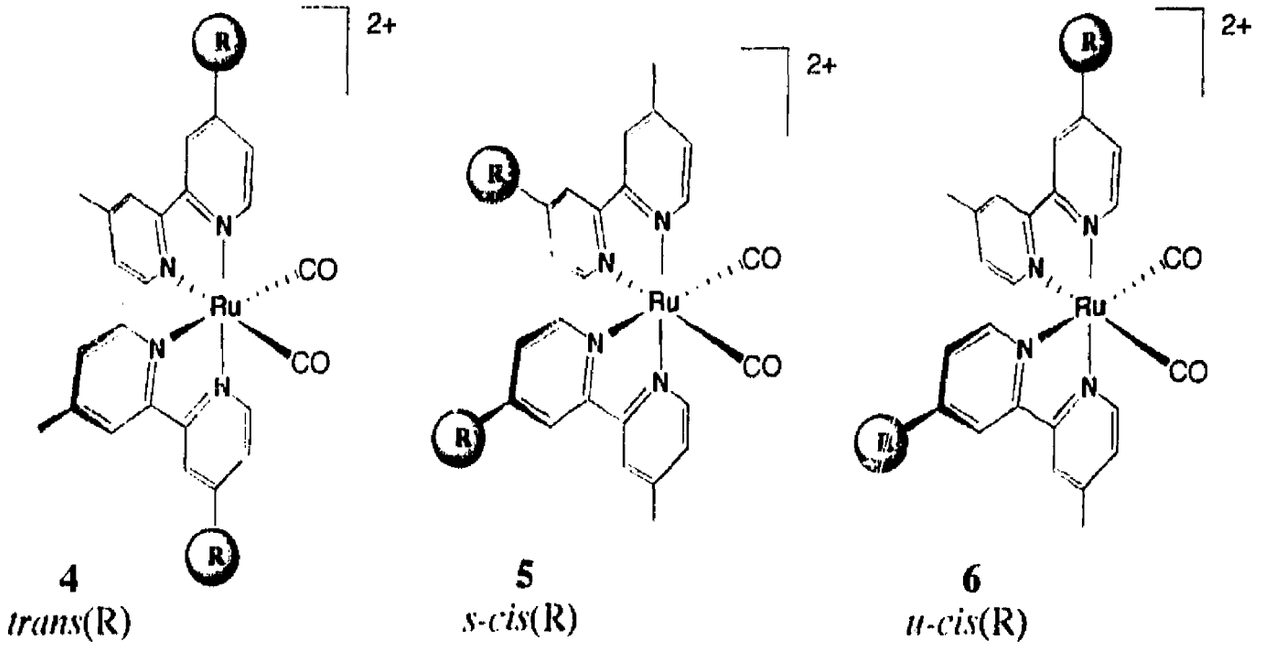


Fig. 12. Geometric isomers of $[Ru(pmb)_2(CO)_2]^{2+}$.

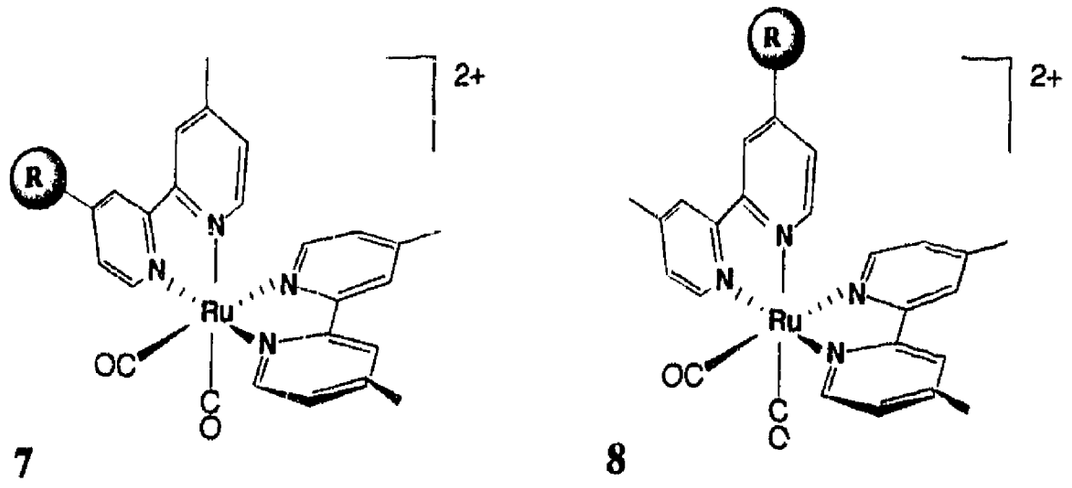


Fig. 13. Geometric isomers of $[Ru(pmb)(Me_2bpy)CO)_2]^{2+}$.

corresponding isomer of the target complex would be expected. In the second case, the addition of the second pmb ligand to either of the two geometric isomers of the dicarbonyl species could occur in two ways and so two isomers would be obtained in each case. Within our studies, the respective dicarbonyl complexes were separated into their geometric isomers and the stereochemical course of the final reaction studied. In the decarbonylation reactions, the dicarbonyl species was reacted with excess trimethylamine *N*-oxide (TM*NO*) in the presence of the third bidentate ligand. Initial studies used refluxing 2-methoxyethanol as the solvent, but careful investigations revealed that a small amount (~5%) of ligand scrambling occurred under those conditions: however, if the reaction was performed at ≤40 °C, then the stereochemical integrity of the dicarbonyl species was completely retained in the manner shown in Fig. 14 [88].

In the second study, the chiral integrity of the dicarbonyl species was observed during the decarbonylation process [147]. This work involved two separate but

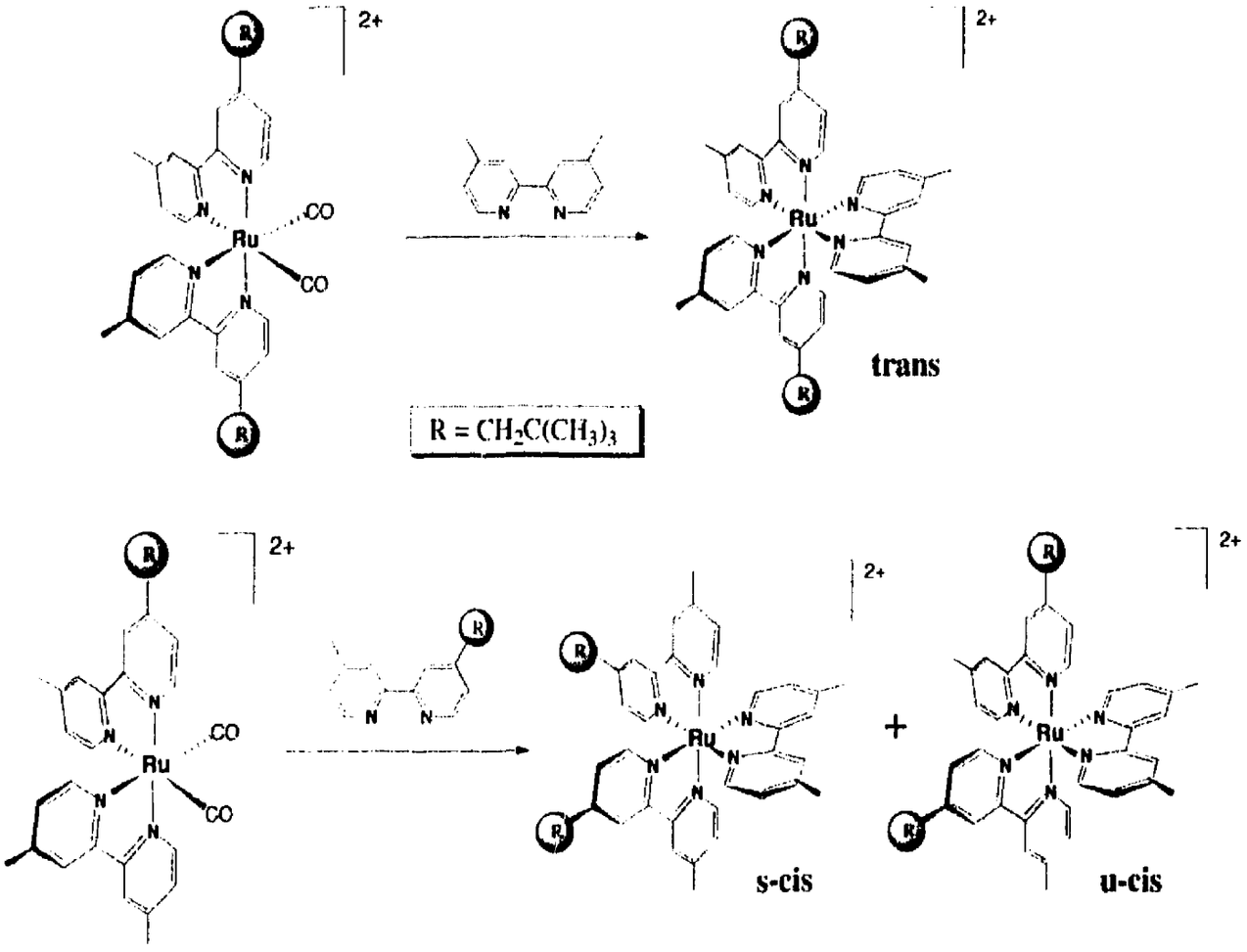


Fig. 14. Stereochemical course of the decarbonylation reactions of $[Ru(pmb)_2(CO)_2]^{2+}$ with Me_2bpy, and of $[Ru(pmb)(Me_2bpy)(CO)_2]^{2+}$ with Me_2bpy [88].

significant parts. The $[Ru(pp)(pp')(CO)_2]^{2+}$ precursor is chiral and may be resolved into Δ and Λ enantiomers. This was achieved for the cases where pp = pp' = bpy (or phen), with chiral integrity being established unequivocally by the use of ^1H NMR studies with chiral lanthanide shift reagents. The chiral $[Ru(pp)_2(CO)_2]^{2+}$ forms were then reacted under decarbonylation conditions with a third pp ligand to produce the corresponding $[Ru(pp)_3]^{2+}$ complexes, for which the chiral forms are well characterized [101,102]. The results were totally analogous with those for the $[Ru(Me_2bpy)(pmb)_2]^{2+}$ study, and showed total retention of chirality at temperatures ≤ 40 °C, with ~5% racemization at 120 °C.

The chiral dicarbonyl species may also be used as a precursor for dinuclear species. The synthetic methodology may be used to prepare dinuclear complexes if the dicarbonyl precursor is reacted with a complex $[Ru(pp)(pp')('pp'')]^{2+}$ in which one of the ligands in the tris(bidentate) species is a potential bridging ligand, such as 2,2'-bipyrimidine. This has been referred to earlier as the "complexes as ligands" approach to oligomer synthesis. In the present instance, the tris(bidentate) complex $[Ru(Me_4bpy)_2(bpm)]^{2+}$ {Me_4bpy = 4,4',5,5'-tetramethyl-2,2'-bipyridine) was resolved by cation exchange column chromatogaphy (see below) and one enantiomer reacted with a chiral form of $[Ru(phen)_2(CO)_2]^{2+}$ under decarbonylation conditions. At a temperature ≤ 40 °C, it was found that the one single diastereoisomer of the dinuclear species $[(Me_4bpy)_2Ru(bpm)Ru(phen)_2]^{4+}$ was obtained(Fig. 15).

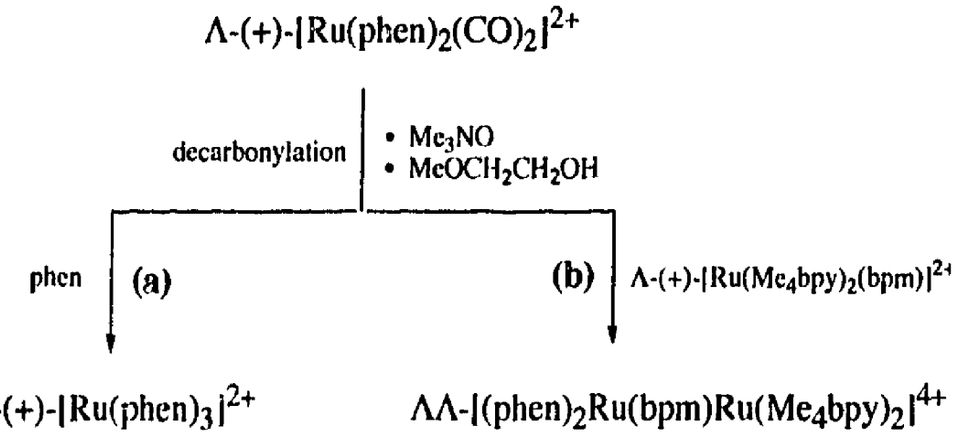


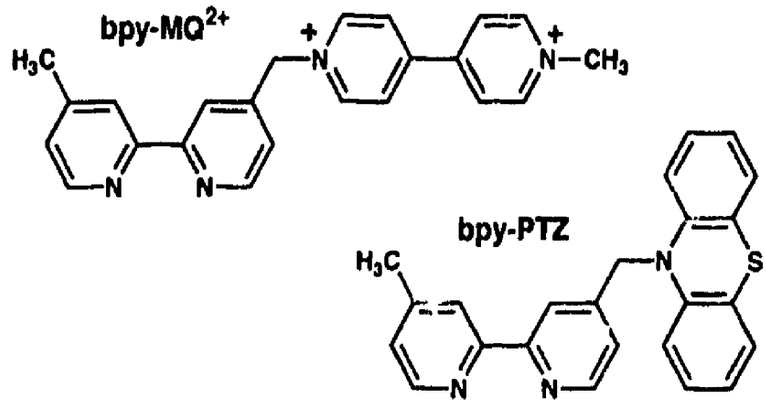
Fig. 15. Stereochemical course of decarbonylation reactions [147].

The conclusions are extremely significant. The synthetic methodology allows the extensive and controlled variation of the coordination environment of individual metal centers, and therefore of the spectral, photophysical and redox characteristics. But in addition, since the stereochemical integrity of the dicarbonyl precursor is maintained in the decarbonylation reaction, the stereochemistry may be predetermined in mononuclear and oligonuclear species by appropriate choice of the stereochemistry of the precursor. We have exploited our methodology to control the stereochemistry of ligand-bridged polymetallic assemblies, and as well as to probe the effect of the spatial relationship of the component metal centers on intramolecular electron and energy transfer within them. A number of examples are summarized below.

3.2.1. Example – a mononuclear chromophore-quencher system

Previous studies on chromophore-quencher complexes (see above) have probed the characteristics of the charge-separated state as a function of the distance of separation of the donor and acceptor groups, and the nature of the rigidity and electronic character of the bridging groups between them. However, the dependence of the electron transfer process on their stereochemical relationship has not been investigated. In some cases, the systems have been deliberately chosen to avoid this spatial ambiguity [39], while other studies of this type have investigated target compounds composed of a mixture of stereoisomers [76–78]. While the existence of the stereoisomers has been acknowledged [77,78], we are not aware of any report of the isolation of stereoisomers of a mononuclear species containing a single donor and a single acceptor functionality.

The combination of the synthetic methodology for tris(heteroleptic) complexes [17] and the confirmation of retention of stereochemical integrity during the final decarbonylation step of our scheme [88,147] allowed the isolation of a species of this type. Using variations on the earlier techniques, we have isolated the four geometric isomers of the system $[Ru(Me_2bpy)(bpy\text{-}MQ^{2+})(bpy\text{-}PTZ)]^{4+}$ (Fig. 16) {Me_2bpy = 4,4′-dimethyl-2,2′-bipyridine; bpy-MQ^{2+} = ((4′-methyl-2,2′-bipyridin-4-yl)methyl)-1′-methyl-4,4′-bipyrinediium cation; bpy-PTZ = [(4′-methyl-2′,2-bipyridin-4-yl)methyl]phenothiazine} [89].



A variation in the methodology described earlier [17] was required to avoid the sensitivity of the PTZ functionality to oxidation by the decarbonylation agent TMNO. Firstly, the bpy-MQ^{2+} ligand was added to the $[Ru(Me_2bpy)(CO)_2(CF_3SO_3)_2]$ precursor. As with the pmb system, [88] the presence of the non-symmetrically-substituted bidentate ligand in $[Ru(Me_2bpy)(bpy\text{-}MQ^{2+})(CO)_2]^{4+}$ induces geometrical isomerism in its complexes: **9A** contains the MQ^{2+} substituent in a *cis/trans* orientation with respect to both carbonyl ligands, whereas in **9B** it has a *cis/cis* orientation (Fig. 17). Fractional crystallization allowed substantial but not complete separation of the geometric forms, but the separation – and the avoidance of the problem of the sensitivity of the PTZ grouping in the decarbonylation process – was achieved via an extra step introduced into the previously reported synthetic scheme [17]. The decarbonylation of **9** with TM*N*O was undertaken in the presence of pyridine (py) to produce $[Ru(Me_2bpy)(bpy\text{-}MQ^{2+})(py)_2]^{4+}$ (**10**), which was readily separated into geometric isomers by cation exchange chromatography. Such bis(pyridine) species are known to react with a third bidentate polypyridyl ligand with stereochemical retention of configuration [111].

The stereochemical consequences of the reactions of **10A** and **10B** with bpy-PTZ are shown in Fig. 18: **10A** results in a *trans*-**11**+*cis(2)*-**11** mixture and **10B** produces *cis (1)*-**11**+*cis(3)*-**11**. The two pairs of isomeric mixtures of $[Ru(Me_2bpy)(bpy\text{-}MQ^{2+})(bpy\text{-}PTZ)]^{4+}$ were separated by cation-exchange chromatography, giving the four isomers which were characterized by NMR spectroscopic techniques.

The physical characteristics of the isomers have been investigated. No significant differences were observed between the electronic absorption spectra of stereoisomers, or in their electrochemical behavior. Initial photophysical studies suggest differences are observed between the four geometric forms of the complex $[Ru(Me_2bpy)(bpy\text{-}MV^{2+})(bpy\text{-}PTZ)]^{4+}$: the lifetimes of the charge-separated state for all the *cis* isomers are different (while of the same order), with the behavior of the *trans* isomer being distinct. These details will be reported shortly [89].

3.2.2. Example – a dinuclear system with an α-azodiimine bridge

The stereochemistry of the dinuclear species $[(pp)(pp')Ru(BL)Ru(pp'')(pp''')]^{4+}$ (where pp=pp′ and pp″=pp‴; BL is a bridging ligand) has been examined [79,110,111,147]. For all such dimeric species, there are two diastereoisomeric forms, comprised of the enantiomeric pairs ΔΔ/ΛΛ and ΔΛ/ΛΔ. In cases where the coordina-

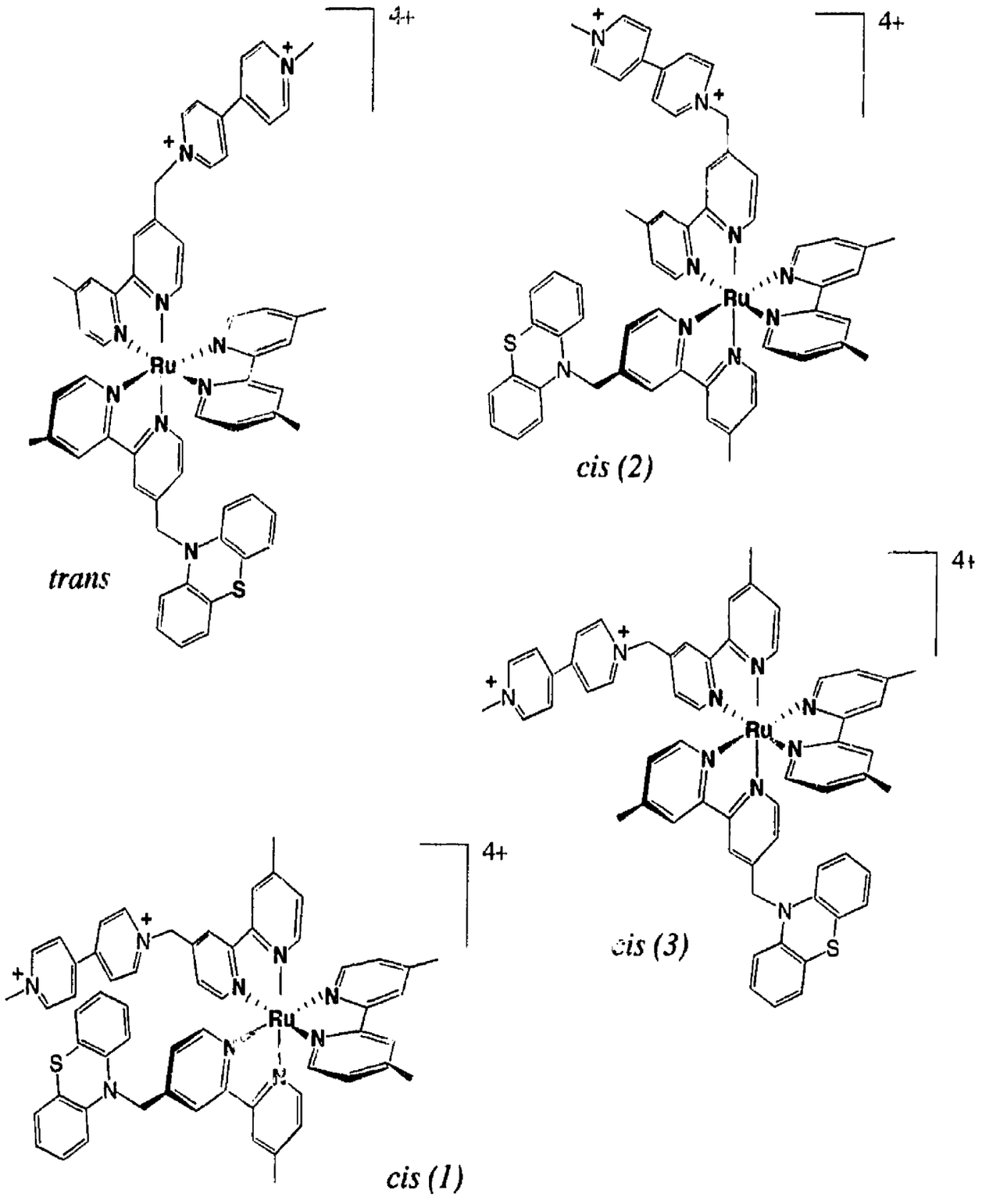


Fig. 16. Geometric isomers of the system $[Ru(Me_2bpy)(bpy\text{-}MQ^{2+})(bpy\text{-}PTZ)]^{4+}$ [89].

tion environment of the metal centers is equivalent (i.e. pp=pp′=pp″=pp‴), the ΔΛ and ΛΔ forms are identical (i.e. a *meso* form).

There is a significant difference between the *rac* and *meso* diastereoisomers as the terminal polypyridyl ligands "above" and "below" the plane of the bridging ligand bear a significantly different relationship. For the complexes where the axes of the "bites" of the two bidentate moities of the bridging ligand (BL) are linear (e.g. bpm) or have a stepped parallel relationship (e.g. apy), the terminal polypyridyl ligands "above" and "below" the plane of the bridging ligand are approximately parallel

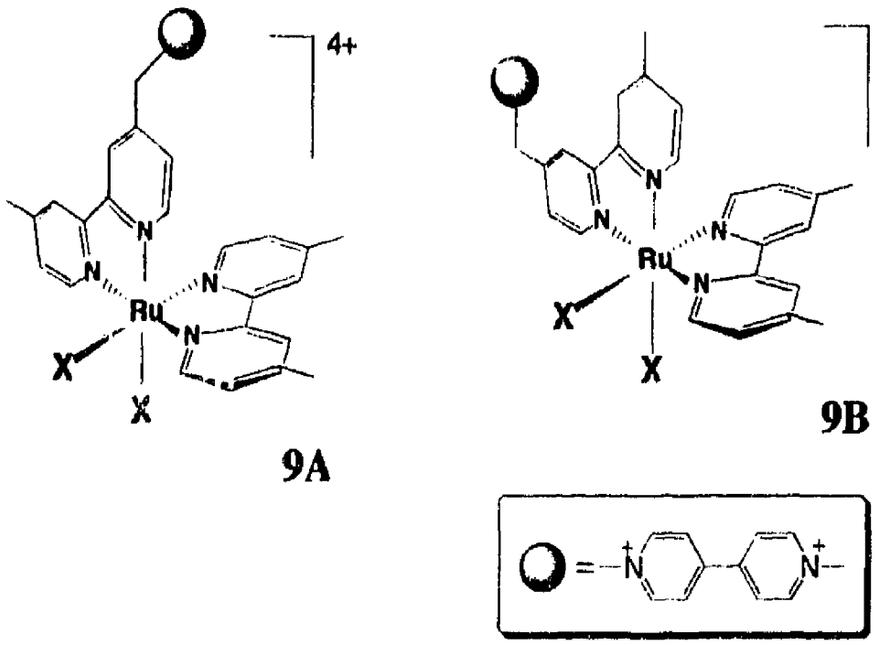
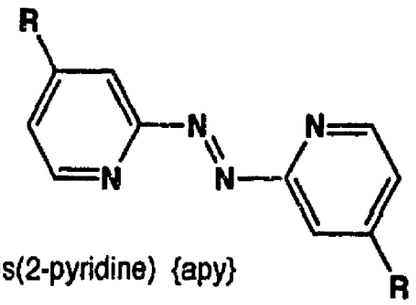


Fig. 17. Geometric isomers of the system $[Ru(Me_2bpy)(bpy\text{-}MQ^{2+})X_2]^{4+}$ {X=CO (**9**) or X=py (**10**)} [89].

in the ΔΔ/ΛΛ form, whereas they are perpendicular in the ΔΛ/ΛΔ stereoisomer. This is shown in a schematic manner in Fig. 19. It should be noted that if the relationship of the axes of the two "bites" are angular (e.g. 2,3-dpp, HAT), the above description is reversed.

We have separated the diastereoisomers for a range of dinuclear complexes by cation-exchange chromatography [79], and the synthesis of predetermined diastereoisomers of a selection of dinuclear species has been achieved using chiral precursors [110,111,147].



R = H: azobis(2-pyridine) {apy}

= CH_3: azobis(4-methyl-2-pyridine) {mapy}

To probe the stereochemical effects in dinuclear species, we chose to investigate the series of complexes $[(pp)_2Ru(BL)Ru(pp')_2]^{2+}$, where pp/pp' were the terminal ligands bpy or Me_2bpy, and the bridging ligand BL was of the α-azodiimine type (apy or mapy) [148].

The bridging ligand affects the degree of metal–metal interaction in di- and oligonuclear complexes as it determines the distance and relative orientation of the metal centers, and influences through-space electronic coupling and the degree of through-bond communication (via ligand–metal orbital overlap) [14,149]. Ligands possessing the azo functionality have extremely low-lying π* orbitals and are strongly π-accepting [83,92,96,150–153]. Moreover, dinuclear complexes in which ligands

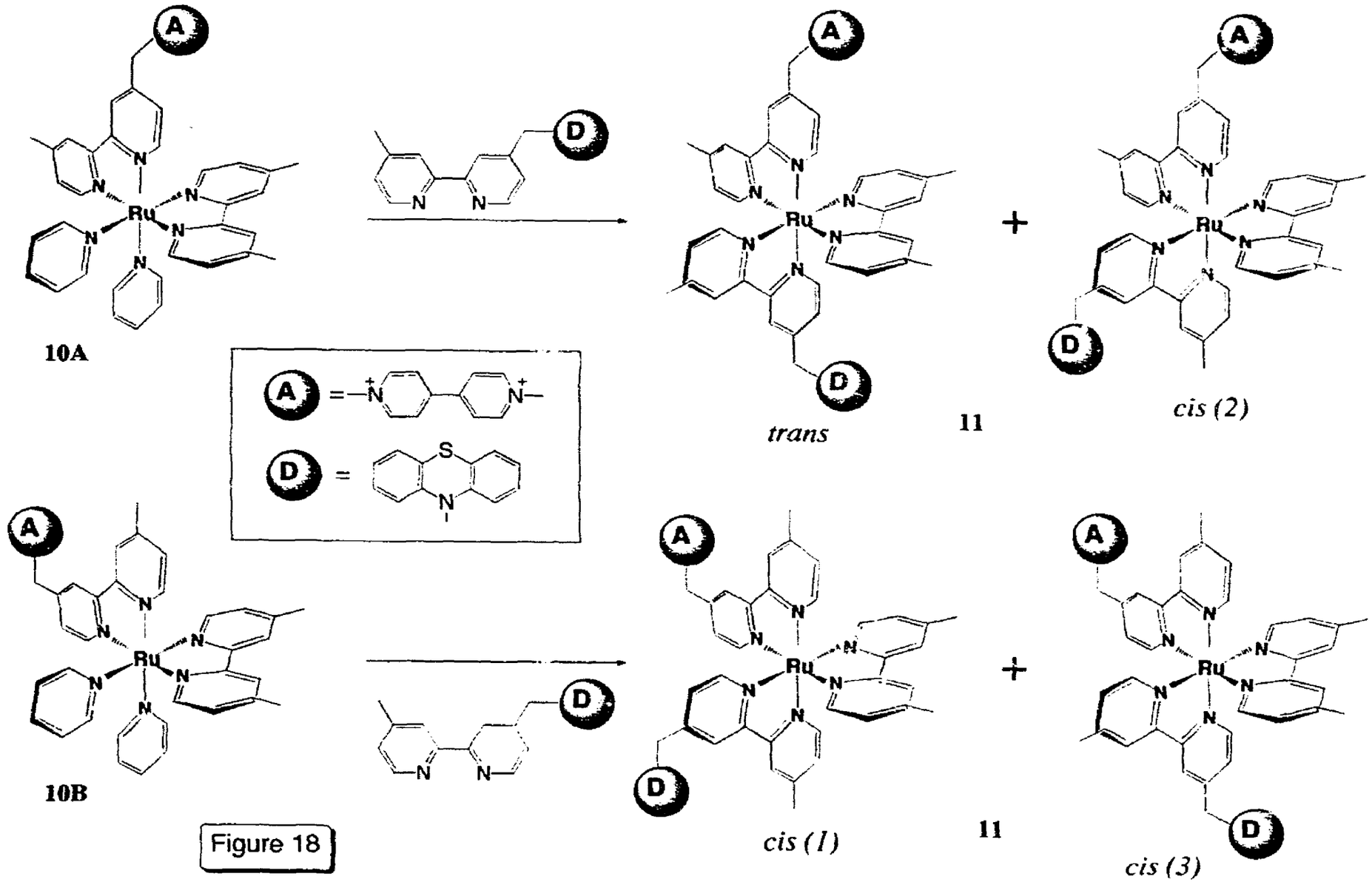


Fig. 18. Stereochemical course of the reactions of the geometric isomers (**10A** and **10B**) of $[Ru(Me_2bpy)(bpy\text{-}MQ^{2+})(py)_2]^{4+}$ with bpy-PTZ. [89].

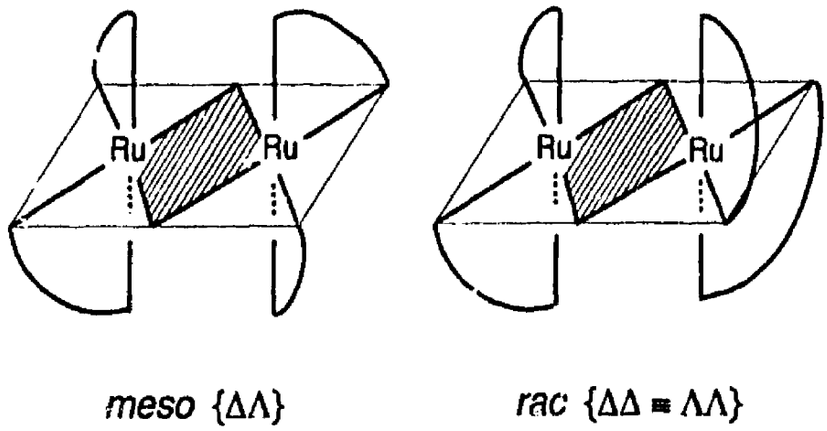


Fig. 19. Schematic representation of the diastereoisomeric forms of the dinuclear ligand-bridged species $[\{Ru(pp)_2\}_2(BL)]^{4+}$ {pp=a symmetrical bidentate ligand; BL=a symmetric bridging ligand (shown hatched) in which the axes of the two "bites" are linear}.

such as azobis(2-pyridine) function as the bridge have comproportionation constants (K_c) in excess of 10^8 for the di-ruthenium case, and hence exhibit a very high degree of metal–metal interaction [83,149,150,154,155]. Bridging ligands of this type also are found to enhance the structural differences between the diastereoisomers of such dinuclear species, because of the stepped-parallel (as opposed to linear) orientation of the axes of the bidentate chelating ligand functions in the apy-type bridging groups(Fig. 20).

The two diastereoisomeric forms were readily separated by cation-exchange chromatography, the relative ease of separation being rationalized in terms of the pronounced stereochemical differences in the relative orientation of the terminal ligands induced by the α-azodiimine bridging ligands.

Previous studies of α-azodiimine-bridged dinuclear compounds suggested that only one diastereoisomer was observed [83]: there were differences in the synthesis

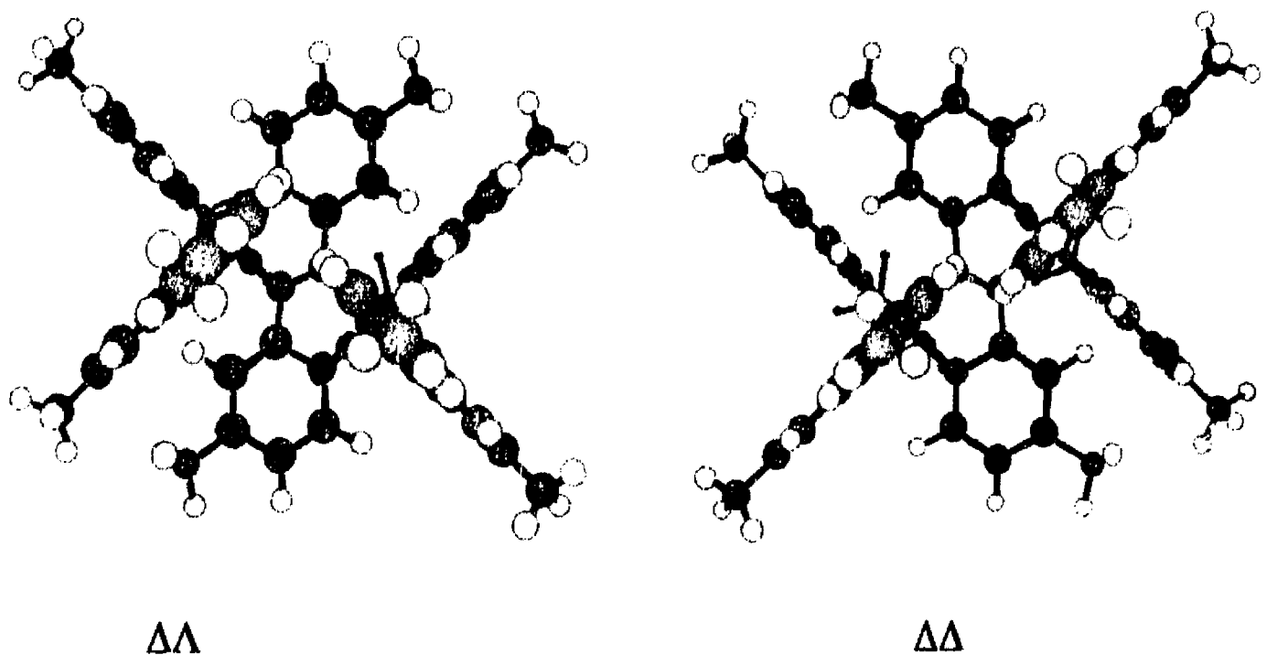


Fig. 20. CHEM 3D® representations of the diastereoisomeric forms of $[\{Ru(Me_2bpy)_2\}_2(\mu\text{-mapy})]^{4+}$ [148].

conditions in the two studies, but our work clearly shows the presence of both isomers [148].

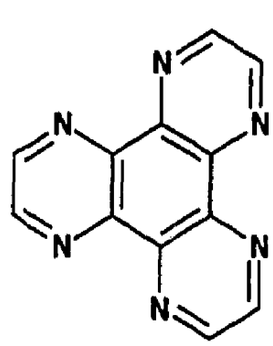
The diastereoisomers show differences in their physical characteristics. For example, during the chromatographic separation there was a noticeable difference in the color of the diastereoisomers on the column – the first band eluted (*meso*) was dark emerald-green and the second band (*rac*) olive-green for all five dinuclear compounds involving the α-azodiimine bridging ligands. The absorption spectra of the complexes showed intense bands in the UV region, with bands in the visible region (assigned as arising from MLCT transitions) at ca. 380 and 770 nm: for the two diastereoisomers of $[\{Ru(bpy)_2\}_2(\mu\text{-apy})]^{4+}$ there was a red shift of ~7 nm in the *rac* compared with the *meso* form in the absorption arising from the lowest energy $d(Ru)\rightarrow\pi^*(\mu\text{-apy})$ transition. The stereochemistry also affected the $d(Ru)\rightarrow\pi^*(bpy)$ transition; a shoulder at 400 nm in the *meso* isomers was enhanced in the *rac* isomers. We are not aware of other reports of a significant difference in such physical properties of ligand-bridged diastereoisomers.

The differences were also reflected in the electrochemical properties of the diastereoisomers. Although the effects were relatively small, in all the α-azodiimine bridged complexes, the oxidative couples were shifted to more positive potentials and the reductive couples to more negative potentials for the *rac* (ΔΔ/ΛΛ) forms relative to the *meso* (ΔΛ) diastereoisomers. Additionally, the separation between the two metal-centered oxidations ($\Delta E_{1/2ox}$) was consistently larger for the *rac* form. This implies a slightly greater degree of metal–metal communication for one stereochemical form over the other, and we believe this to be the first observation of stereochemical influences on the electron transfer properties within dinuclear metallic complexes.

Similar differences may be even more clearly demonstrated in a related dinuclear complex, $[\{(bpy)_2Ru\}_2(\mu\text{-dpa})]^{4+}$ {dpa = 2,3-bis(2-pyridyl)-1,4-diaazaanthracene}. In this case, the separation of the oxidation waves of the two metal centers is greater {$E_{1/2}$ = 1.17 and 1.32 V cf. 1.14 and 1.32 V} for the *meso* diastereoisomer (in which the terminal ligands of the different metal centers are parallel), indicating differences in the communication induced by the stereochemistry (Fig. 21) [156].

3.2.3. Example – mono-, di- and tri-nuclear complexes of the HAT ligand

We have also investigated the stereochemistry of complexes containing the bridging ligand 1,4,5,8,9,12-hexaazatriphenylene (HAT) [157]: This ligand has three sites for bidentate ligation to a metal center, and may serve as a bidentate ligand in mononuclear species or as a ligand bridge in di- and tri-nuclear species. Examples are



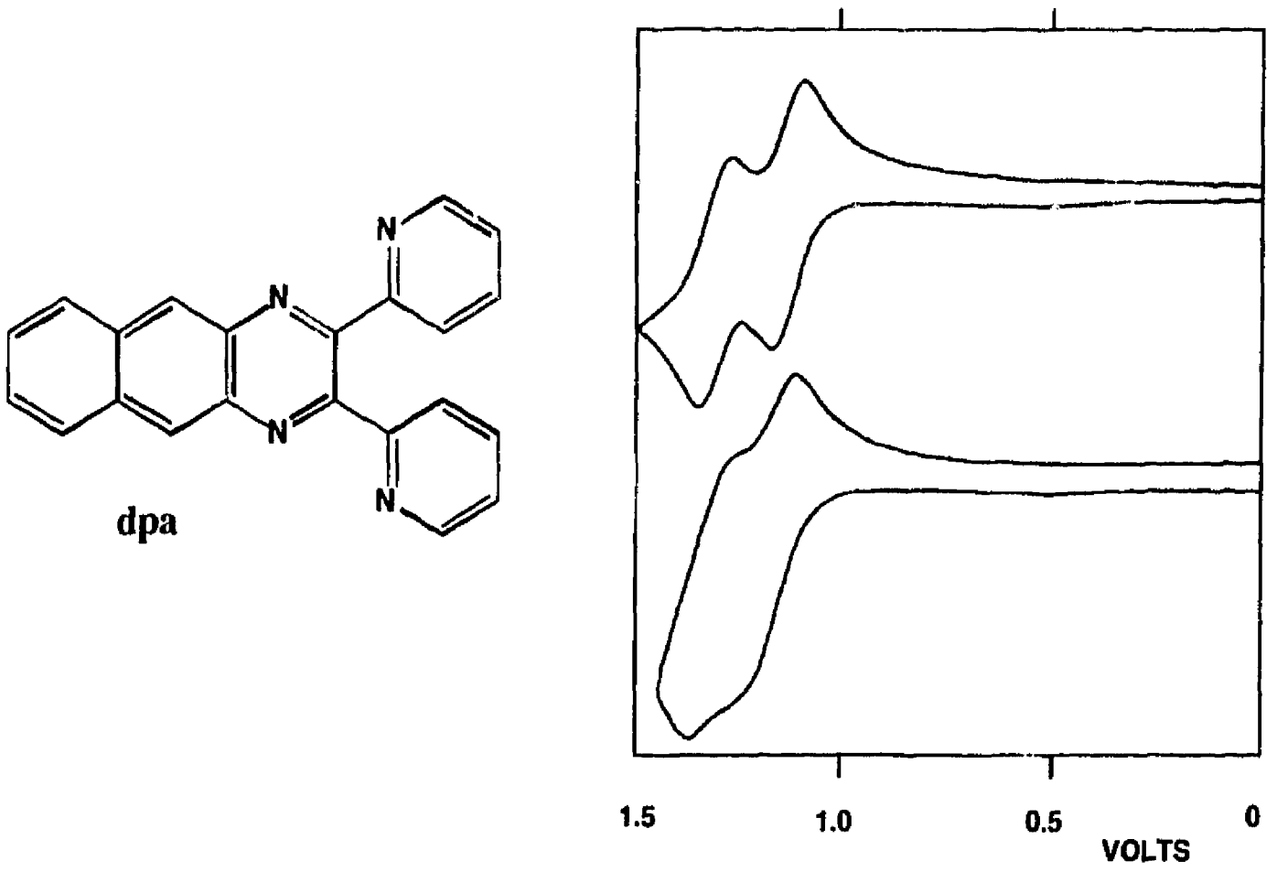


Fig. 21. Cyclic voltammetry of $[\{(bpy)_2Ru\}_2(\mu\text{-dpa})]^{4+}$ (CH_3CN/0.1 M $[(C_4H_9)_4]ClO_4$ solution vs Ag/Ag^+) [156].

known in each of these categories, and studies have addressed synthetic strategies for homonuclear and heteronuclear species [158–162], photophysical properties [159,161–165] and interaction with biological species such as DNA [166–169]. In all these studies, the problem of stereoisomerism within the species of each nuclearity has not been elaborated, although it has been acknowledged [165].

The development of synthetic methodologies using stereoisomerically pure building blocks [88,147] and chromatographic techniques [79] have enabled us to isolate individual diastereoisomers (and their corresponding enantiomeric pairs) in homonuclear and heteronuclear complexes involving HAT as the bridging ligand [157,170]. This stereochemical control has allowed an investigation into the effect of stereoisomerism on physical properties such as their electrochemical and photophysical characteristics [157], and the interaction with chiral assemblies such as DNA. These investigations had previously been limited because stereoisomerically pure complexes have not been available

Our investigations of the mono-, di- and tri-nuclear complexes are discussed in succession below. The separated diastereiosomers – and when appropriate, enantiomers – have all been isolated, and were characterized by ^1H NMR spectroscopy (including studies involving the chiral lanthanide-induced shift reagent [Eu(tfc)$_3$]), CD spectra and ORD measurements).

In general, the separation of stereoisomers was achieved using cation exchange chromatographic techniques. The mononuclear complexes $[Ru(pp)_2(HAT)]^{2+}$ (HAT = bpy or phen) were resolved into enantiomeric forms using an eluent with a

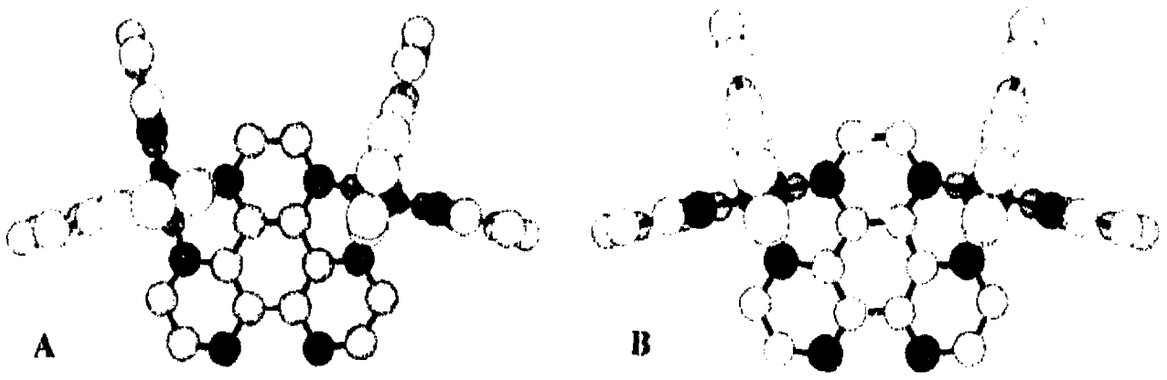


Fig. 22. Chem 3D® representation of diastereoisomeric forms of $[\{Ru(bpy)_2\}_2(\mu\text{-HAT})]^{4+}$: (A) *rac*- {ΔΔ (≡ΛΛ)}; (B) *meso*- {ΛΔ}. Hydrogen atoms are omitted for clarity.

chiral anion (see below). The dinuclear complexes $[\{Ru(pp)_2\}_2(\mu\text{-HAT})]^{4+}$ were chromatographically separated into the *rac* (ΔΔ/ΛΛ) and *meso* (ΔΛ) diastereoisomeric forms, and the *rac* form was resolved by the same technique using a chiral eluent. In a similar manner, the homometallic trinuclear complexes $[\{Ru(pp)_2\}_3(\mu\text{-HAT})]^{6+}$ were chromatographically separated into the heterochiral ($\Delta^2\Lambda/\Lambda^2\Delta$) and homochiral ($\Delta^3/\Lambda^3$) diastereoisomeric forms (determined by NMR spectroscopy), and the Δ^3/Λ^3 diastereoisomer was subsequently resolved using a chiral eluent (Figs. 22 and 23).

The resolution of the $\Delta^2\Lambda/\Lambda^2\Delta$ diastereoisomer could not be achieved chromatographically, but the two forms were isolated by separately reacting resolved ΔΔ and ΛΛ forms of $[\{Ru(pp)_2\}_2(\mu\text{-HAT})]^{4+}$ with *rac*-$[Ru(pp)_2Cl_2]$ resulting in the two diastereoisomeric complexes $\Delta^3/\Delta^2\Lambda$ and $\Lambda^3/\Lambda^2\Delta$, respectively. These diastereoisomeric mixtures were separated by cation exchange chromatography, thus realizing the $\Delta^2\Lambda$ and $\Lambda^2\Delta$ forms. Since the absolute configuration of the precursor complex $[\{Ru(bpy)_2\}_2(\mu\text{-HAT})]^{4+}$ was known, the absolute configuration assignments of $\Delta^2\Lambda$- and $\Lambda^2\Delta$-$[\{Ru(bpy)_2\}_3(\mu\text{-HAT})]^{6+}$ could be made. We have used the same methodology to isolate the stereoisomers of mixed Ru/Os trinuclear systems [170].Fig. 24

Cyclic voltammetry was performed on the separated diastereoisomers, *rac*- and *meso*-$[\{Ru(pp)_2\}_2(\mu\text{-HAT})]^{4+}$, and homochiral- and heterochiral-$\{Ru(pp)_2\}_3$-

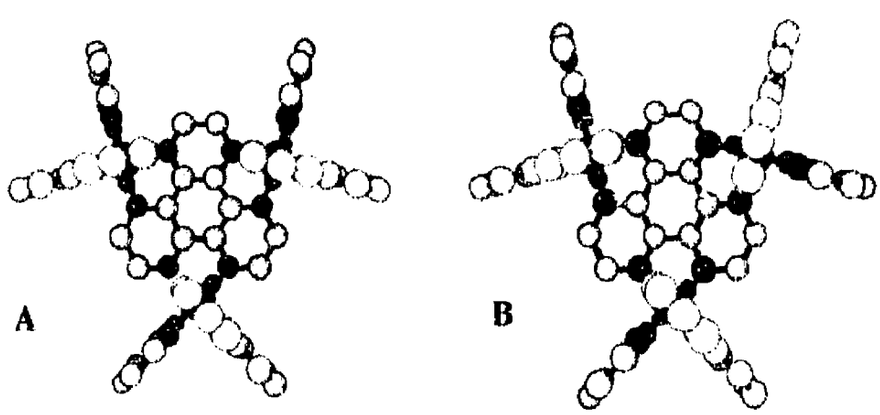


Fig. 23. Chem 3D® representation of diastereoisomeric forms of $[\{Ru(bpy)_2\}_3(\mu\text{-HAT})]^{6+}$: (A) heterochiral {ΔΔΛ}; (B) homochiral {ΔΔΔ (≡ΛΛΛ)}. Hydrogen atoms are omitted for clarity.

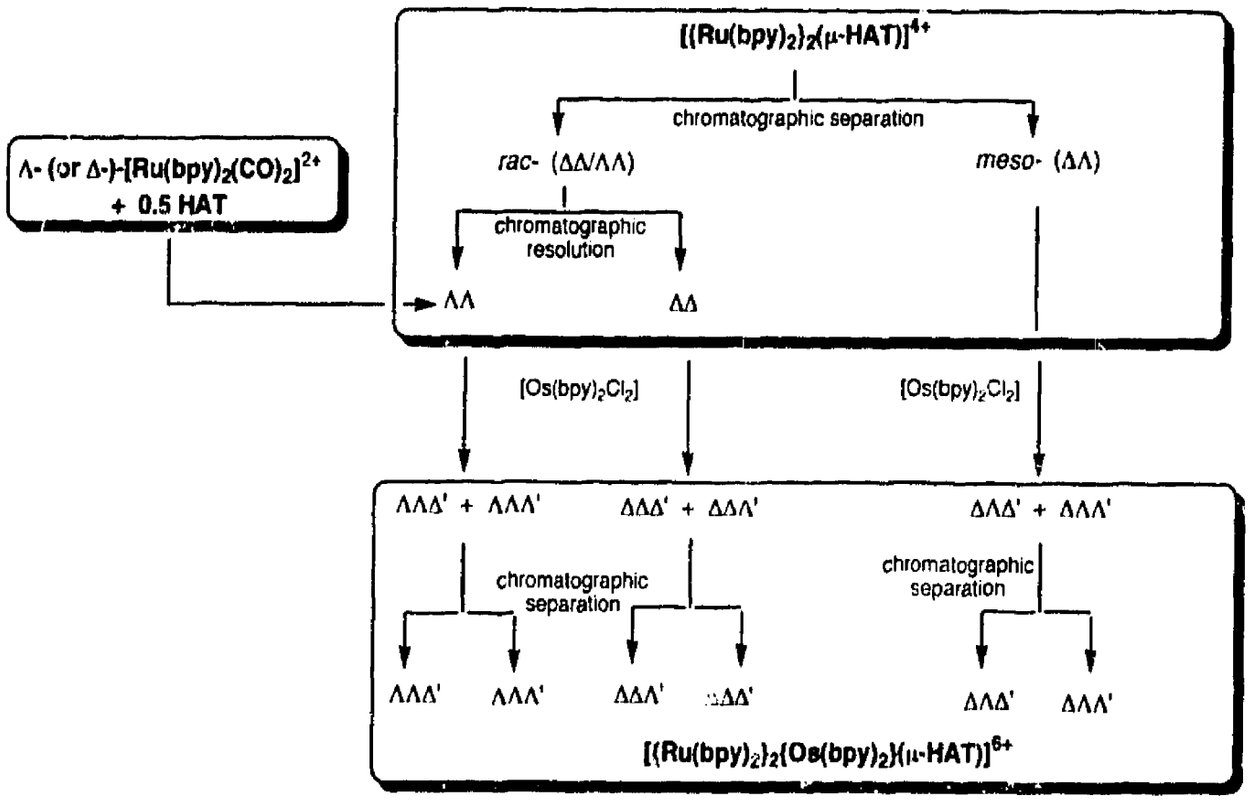


Fig. 24. Synthetic methodology for stereoisomers of $[\{Ru(bpy)_2\}_2\{Os(bpy)_2\}(\mu\text{-HAT})]^{6+}$ [170].

$(\mu\text{-HAT})]^{6+}$ (where pp = bpy or phen). The one-electron reversible oxidation waves are directly correlated with the number of coordinated metal centers [158,164], suggesting significant metal–metal electronic communication which is a characteristic of conjugated bridging ligands [171]. Comparisons of the metal–metal interaction between the second and third metal oxidation process indicated a 40 mV increase (stronger interaction) in the homochiral-$[\{Ru(phen)_2\}_3(\mu\text{-HAT})]^{6+}$ over the heterochiral-$[\{Ru(phen)_2\}_3(\mu\text{-HAT})]^{6+}$ diastereoisomer.

No significant differences were observed between the electronic absorption spectra of the diastereoisomers in the present study.

Initial photophysical results have been undertaken on these systems. For the dinuclear species at room temperature, the relative luminescence quantum yields and the emission lifetimes showed a significant drop for the *meso* compared with the *rac* diastereisomers. Moreover in a glass at low temperature (77 K), the luminescence of the lifetimes of the trinuclear heteronuclear diastereoisomer were slightly shorter than those of the homonuclear form. No significant differences were detected at room temperature in the diastereoisomeric forms of the trinuclear compounds.

3.3. Stereochemistry – does it make any difference?

There have been numerous assertions that stereochemistry will have little influence on physical properties in circumstances where mixtures of isomers were investigated [56,150]. It is apparent for these first studies of this question that the stereochemistry does influence the electronic transitions and the inter-metal communication. It would be the normal expectation that such variations would become more significant as

the size of the assembly grew, and we are currently investigating oligomers of higher nuclearity to clarify this issue.

Moreover, there have been several assertions that the use of tris(bidentate) building blocks for polynuclear assemblies will inevitably lead to a stereochemical complexity which is intractable [21,39,40]. Perhaps it is premature to impose such judgement at this point of time.

3.4. Chromatographic techniques

The chromatographic separation of stereoisomers forms an essential part of our study. The mechanism deserves some comment in the present context. Our studies of these processes are at an advanced stage and will be published in the near future [172,173].

While the technique is based on a cation exchange mechanism (SP-Sephadex C25 support), the mode of separation is profoundly influenced by a differential association between the components of the mixture and the anion of the eluent. This effect has been studied previously [174–176], particularly in relation to the separation of stereoisomers of cobalt(III) complexes containing polyamine ligands. In those instances, the association of different geometric isomers with appropriate anions via hydrogen bonding [177] was regarded as the prime operative mechanism. Optical resolution of racemates to the enantiomers has also been achieved using eluents with chiral anions, although the Sephadex support itself is chiral and is not without participation in such separations [174,175].

For the present polypyridyl complexes, the rate of elution – even for species with high charges – is rapid in the presence of certain anions by comparison with (e.g.) Cl^-, indicating that there is an association which lowers the effective charge of the complex. In addition, in these circumstances where the association is present, separations of mononuclear complexes of the same charge but different ligand composition, geometric isomers of mononuclear species, and diastereoisomeric di- and oligonuclear complexes is achieved. Clearly, the different species undergo differential association with certain anions leading to chromatographic separation in their presence. Additionally, enantiomers of mono- and oligonuclear complexes can be separated, on the basis of differential association with chiral anions and/or because of the involvement of the chiral support [172,173].

The precise nature of the associations is currently under investigation. For species containing polypyridyl ligands, a hydrogen bonding mechanism is unlikely. In our early studies involving the separation of diastereoisomeric forms of dinuclear species, toluene-4-sulfonate was used on the instinctive notion that an aromatic ion might undergo π-stacking with the diastereosiomer in which the terminal ligands were parallel (rather than orthogonal). While separation was indeed achieved, the order of elution indicated that preferential association occurred with the diastereoisomer in which the terminal rings were orthogonal. Further, the effect does not actually require an aromatic anion, and any alkyl carboxylate where $n>4$ shows an association and allows a chromatographic separation. Our studies indicate that the association appears to have components involving both π-stacking and specific hydrophobic

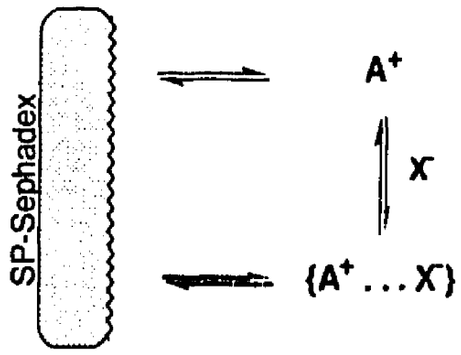


Fig. 25. Proposed mechanism for influence of anions on cation exchange processes.

interactions, as confirmed by NMR studies of the interaction of the anions and the substrates [172,173].

Studies of these chromatographic processes over the temperature range 5–50 °C reveal a temperature dependence [172,173]: since the equilibria directly involving the support are likely to have small activation energies [178], it is clear that the association equilibrium is fundamental in the process. NMR titration studies of the anions with diastereoisomeric forms of dinuclear complexes indicate differences in the association constants between pairs of diastereoisomers in dinuclear systems, so that the separations occur as a result of the association processes (Fig. 25).

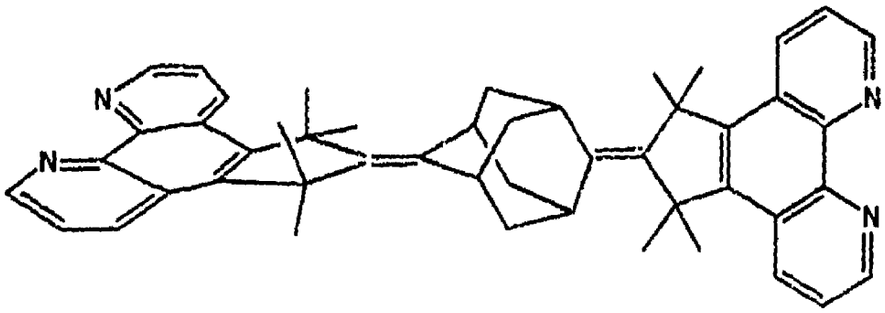
We have been able to routinely resolve mononuclear, dinuclear and trinuclear complexes into their enantiomers using eluents with chiral anions [147,157,179]. The optical resolutions undoubtedly occur by similar differential associations. Again the nature of that association is uncertain at this point: interestingly, a crystal structure of Δ-[Ru(bpy)$_2$(py)$_2$]{(−)-O,O′-dibenzoyl-L-tartrate}12.H$_2$O clearly demonstrates a specific packing of benzoyl groups of the anion between the bpy planes and py rings of the cation, allowing differential interaction of the chiral anion with enantiomers of the cation [180].

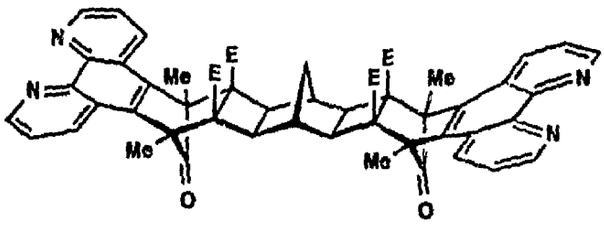
4. Stereochemistry and polynuclear assemblies – the past, present and future

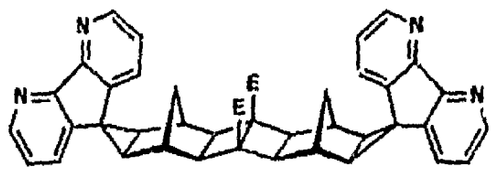
There has been a major recent surge in the methodologies of synthetic chemistry of polymetallic assemblies, and also in the design of ligands and bridges required to meet specific requirements of electronic and spatial characteristics appropriate to their potential application. Polypyridyl ligands have a special importance in these developments – particularly in combination with the d^6 metal centers Ru(II), Os(II) and Re(I) – and a fundamental tenet of the work described above is that ultimately versatility is enhanced significantly by the use of bidentate ligands, although the requirement is not exclusive.

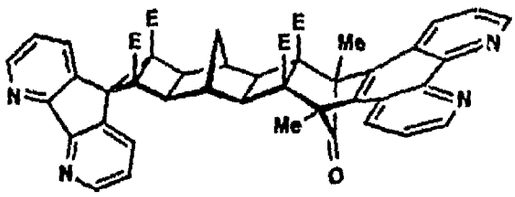
However, that condition is associated with the spectre of a proliferation of isomeric possibilities. Accordingly, a particular interest would be the symmetric functionalization of a bidentate ligating motif (such as 1,10-phenanthroline and 4,5-diazafluorene). There are recent examples of such methodologies in bridged species with adamantane-linked phen and daf ligands of C_{2v} symmetry {daf=4,5-diazafluorene}

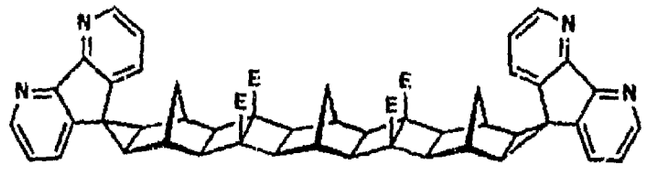
[181–183], and the linking of the same groupings by norbonane-based "molrac" bridges (C_s symmetry) [184]. Both developments herald an ability to meet the symmetry restriction in a rigid bridge system yet provide a linkage with versatility in terms of electronic characteristics and the physical separation between ligating groups.











There are other consequences of the present stereochemical studies that have not been addressed in this review. There has been much recent interest in the intercalation of metal complexes into nucleotides such as DNA, and there is a relevance in terms both for their use as photoprobes and also in the design of chemotherapeutic drugs [14,185,186]. The biological activity of polypyridyl complexes of iron and ruthenium, and the stereochemical component of such interactions, have in fact been known for decades [187]. The consequences of the much wider range of complexes of this type which have now been synthesized is tantalizing, but their stereochemistry is certain to be critical in this context.

As a final reflection, it should be remembered that the synthetic techniques for large polymetallic assemblies have been acquired relatively recently (over the last decade), and in a sense this has been associated with the simultaneous development of appropriate techniques for characterization – particularly in mass spectrometry. The earlier construction of large organic assemblies was underpinned by a clear understanding of the stereochemistry of the tetrahedral carbon atom. This is not the case in coordination chemistry: over the last two or three decades the understanding and control of the stereochemistry of octahedral and tetrahedral metal centers has not always attracted attention at the cutting edge of research in inorganic chemistry. The contrast should be heeded – unless the synthetic developments are accompanied by an understanding of the detailed stereochemistry, then the products

will often remain incompletely characterized and be mixtures of stereoisomers that possess very different spatial orientations of components. The utilization of the new materials may well be critically dependent on the control of component geometry in a supramolecular assembly.

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