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Substitutionally inert complexes as chiral synthons for stereospecific supramolecular syntheses

Frederick M. MacDonnell *, Mahn-Jong Kim, Swamy Bodige

Department of Chemistry and Biochemistry, The University of Texas, Arlington, TX 76019, USA

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Abstract

An overview of the synthesis of diastereomerically and enantiomerically pure metallodendrimers illustrates the use of chiral, non-racemic ruthenium(II)–trisphenanthroline complexes as synthons for supramolecular synthesis. Derivitization of the substitutionally inert Δ and Λ enantiomers of $[Ru(phen)_3]^{2+}$ with coupling functions along the ligand periphery permits the construction of multimetallic assemblies without disturbing the stereochemistry at the chiral metal center. Specifically, 1,10-phenanthroline-5,6-dione and 1,10-phenanthro-

* Corresponding author. Tel.: +1-817-272-2972; fax: +1-817-272-5445.
E-mail address: macdonn@uta.edu (F.M. MacDonnell)

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line-5,6-diamine are used because they retain the C_2 symmetry of the metal complex along the metal–bidentate ligand axis. The ring-forming condensation reaction between these two ligands leads to a symmetric, rigid, and planar tetrapyrido[3,2-a:2′,3′-c:3″,2″-h:2″,3″j]phenazine (tpphz) bridge between stereocenters. This strategy has been demonstrated previously with the stereospecific syntheses of three isomeric Ru dimers and four isomeric tetramers. Selective oxidation of these smaller oligonuclear structures (dimers and tetramers) results in the formation of peripheral dione functions at the 5 and 6 positions of the phenanthroline which is required for next generation dendrimer growth. Reactions of these new core molecules with $[Ru(phen)_2(diamine)]^{2+}$ yields the dendritic hexanuclear, $[((phen)_2Ru(tpphz))_2Ru(tpphz)Ru((tpphz)(Ru(phen)_2)_2]^{20+}$ (**Ru$_6$**), and decanuclear, $[(((phen)_2Ru(tpphz))_2Ru(tpphz))_3Ru]^{20+}$ (**Ru$_{10}$**), dendrimers, some of which have been prepared in enantiopure form.

Keywords: Diastereomer; Enantiomer; Metallodendrimers; Supramolecular syntheses

1. Introduction

Octahedral coordination of transition metal ions with polypyridyl ligands is one of the most common structural motifs observed in supramolecular chemistry [1]. Supramolecular assemblies constructed from octahedrally coordinated metal–tris chelate complexes, such as $[Ru(phen)_3]^{2+}$ or $[Ru(bpy)_3]^{2+}$ (where phen is 1,10-phenanthroline and bpy is 2,2′-bipyridine), necessarily incorporate either Λ or Δ

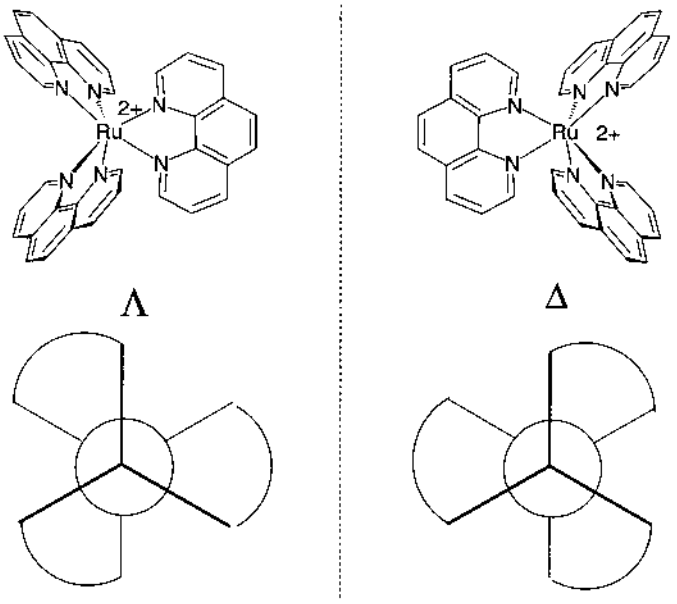

Fig. 1. Fischer projections of the enantiomers of the D_3 symmetric $[Ru(phen)_3]^{2+}$ cation.

enantiomeric forms of the complex, drawn schematically in Fig. 1. Obviously such units introduce chirality at the local level and when multiple chiral centers are linked-diastereomers are formed [2,3]. If the bipyridine or phenanthroline ligands are asymmetrically substituted (i.e. no longer C_2 symmetric), even more isomers are obtained due to the formation of *mer* and *fac* isomers. Extensive use has been made of the ruthenium–trisdiimine complex as a basic structural component in dendrimers, oligomers, and coordination polymers [4,5]. Much of this work has been done without control of the local ruthenium stereochemistry due to the lack of viable synthetic routes and therefore most of the compounds reported are actually complicated mixtures of diastereomers.

We [6,7] and others [8–19] have developed several new methods for stereospecific syntheses of supramolecular structures incorporating $[Ru(diimine)_3]^{2+}$ structural units (for an excellent review see [2]). By using such methods, it is now possible to topologically organize these building blocks into precisely-defined functional arrays (supramolecular species) in a manner which is well suited to take full advantage of their electrochemical, photophysical, and stereochemical properties. For example, chiral $[Ru(diimine)_3]^{2+}$ building blocks may be used as components to build large and functional arrays for chiral molecular recognition, light-energy conversion processes, information storage and/or molecular sensors. Dendritic arrays, in particular, offer attractive architectures because their antenna-like structures are well-suited for light-harvesting functions as well as having deep molecular clefts which may serve as endoreceptor sites for host–guest chemistry.

We have recently reported on the rapid and efficient construction of diastereomerically pure (dp) and enantiomerically pure (ep) ruthenium dimers [7] and tetramers [6] using chiral, non-racemic $[Ru(phenanthroline)_3]^{2+}$ derivatives as molecular building blocks. These supramolecules are highly symmetric, luminescent and easily characterized despite their nanoscopic dimensions. We now report the extension of this chemistry to construct hexanuclear and decanuclear dendritic assemblies which contain large well-defined, chiral molecular clefts as well as intriguing luminescent properties.

2. Substitutionally-inert complexes as chiral synthons

The most direct way to ensure stereochemical control in supramolecular assemblies is to start with stereochemically well-defined monomers. One approach is to start with enantiopure complexes, such as Δ or Λ $[Ru(phen)_3]^{2+}$, which are coordinatively saturated and substitutionally inert. In order to use these complexes as chiral molecular building blocks or chiral synthons, synthetic methods must be developed to functionalize the ligand periphery in a manner which ultimately provides a way to bridge monomers. We have focused on the use of symmetrically functionallized phenanthroline ligands, 1,10-phenanthroline-5,6-dione (phendione) and 1,10-phenanthroline-5,6-diamine (phendiamine) which can undergo a condensation reaction while coordinated to form a tpphz bridge between monomers, as shown in Fig. 2. In related work, the groups of Lehn and Torr have shown that

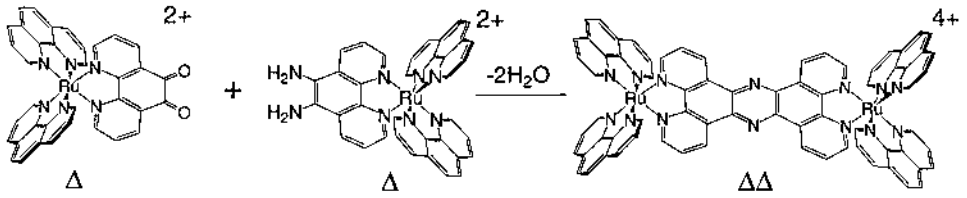

Fig. 2. Condensation reaction between coordinated phendione and phendiamine.

peripheral halogen and/or ethynyl functional groups on the chiral $[Ru(phen)_3]^{2+}$ core can form dp and ep phenylene or acetylene bridged assemblies [11–18].

We contrast this approach with the more common use of enantiopure complexes such as Δ or Λ *cis*-$[Ru(diimine)_2L_2]$ as chiral synthons. As shown in Fig. 3, reaction of these complexes with multitopic bridging ligands such as HAT [14] directly yields the diastereomerically pure (dp) and enantiomerically pure (ep) multimetallic products. While appealing, in that thermodynamically favorable chelation reactions are used to form the bridge, this approach suffers two important limitations. First, only one chelating site per ruthenium is available for bridging—limiting the types of supramolecular structures that are accessible. For example, dendrimers constructed in this manner must rely solely on the multitopic ligand to serve as the branch site even though the metal center provides a natural branching site. However, it should be noted that the use of chiral chelating ligands (so called chiragens) which are predisposed to form a specific enantiomer, can overcome this difficulty [20]. Second, the labile monodentate ligands in *cis*-$[Ru(diimine)_2L_2]$ are tightly bound and difficult to displace, frequently resulting in low yields (ca. 30%).

By comparison, the yields for the formation of the tpphz bridge, discussed previously, typically exceeds 90%. Furthermore, because each phenanthroline ligand may be modified at up to six sites along the periphery (excluding positions 2 and 9 due to steric reasons), there is flexibility in the types of supramolecular structures that may be obtained. Fig. 4 shows two examples. At the top, the formation of a dp and ep linear trimer is shown whereas formation of a dp and ep

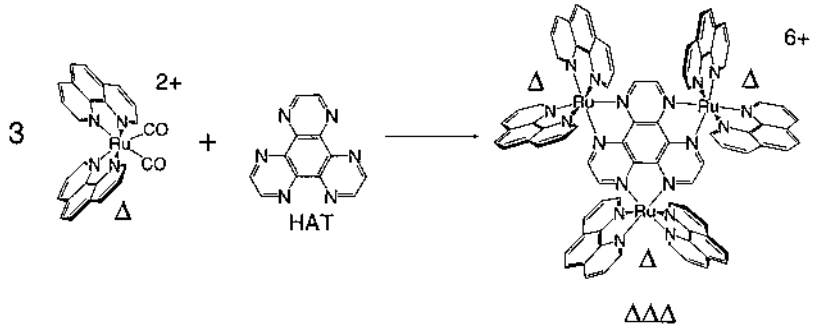

Fig. 3. Stereospecific syntheses using substitutionally labile complexes.

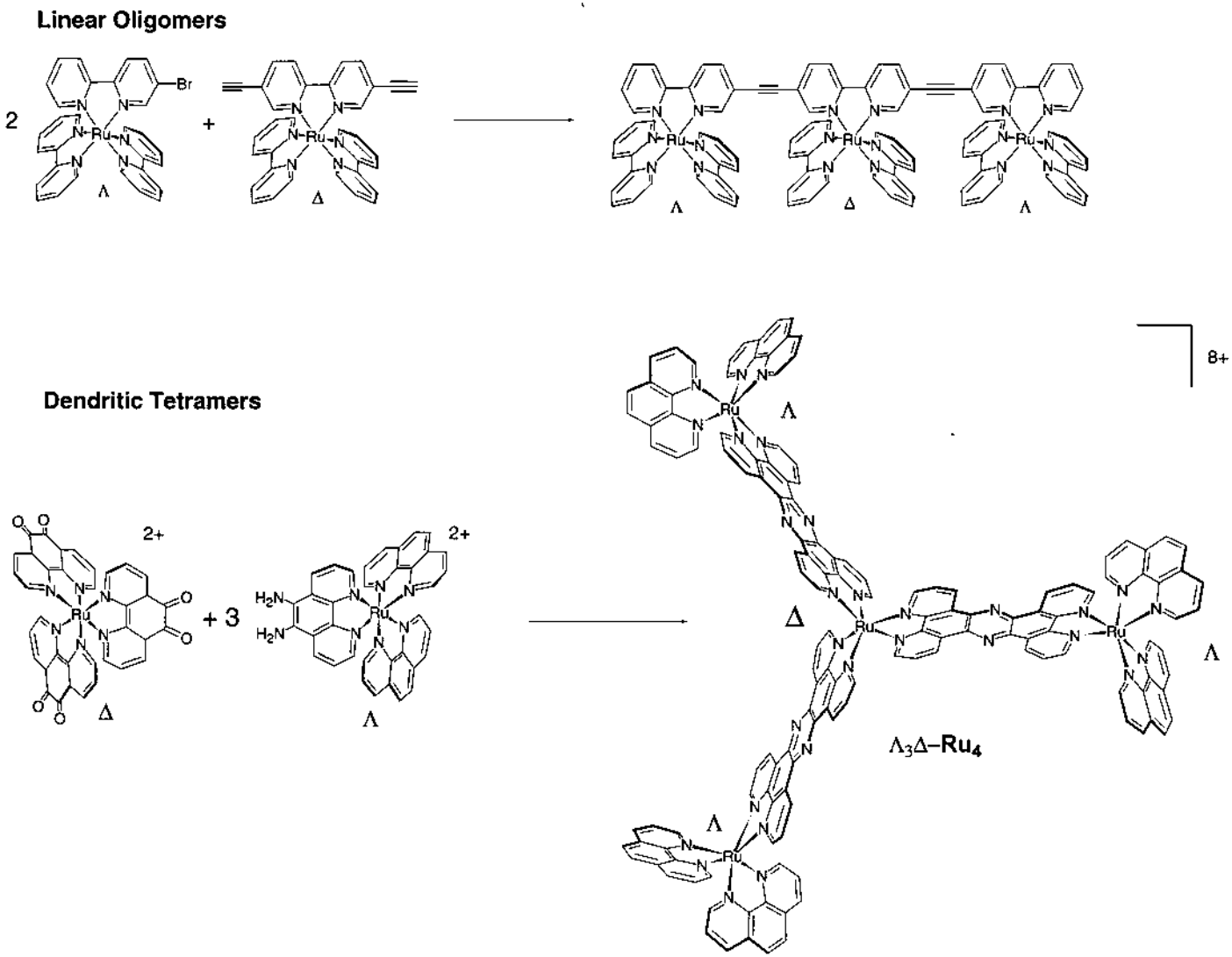

Fig. 4. Linking of substitutionally inert metal complexes using peripheral functional groups.

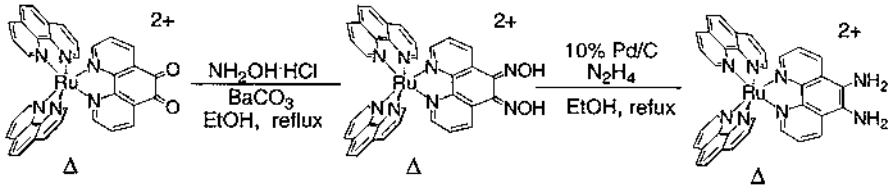

Fig. 5. Conversion of coordinated phendione to phendiamine.

metal centered dendritic tetramer (**Ru_4**) structure is shown below. Both reactions use substitutionally inert synthons and are obtained in good yield. As seen from the **Ru_4** structure, it is possible to use the trigonal symmetry of the monomers as natural branching sites for dendritic assemblies.

The six substutionally-inert chiral synthons, that we have focused on, are the enantiomers of the C_2 symmetric complexes Δ- and Λ-$[Ru(phen)_2(phendione)]^{2+}$, Δ- and Λ-$[Ru(phen)_2(phendiamine)]^{2+}$ and the D_3 symmetric Δ- and Λ-$[Ru(phendione)_3]^{2+}$ (enantiomers of the latter two are shown in Fig. 4). These derivatives were chosen because they retain as many symmetry elements of the D_3 symmetric parent complex, $[Ru(phen)_3]^{2+}$, as possible. Disubstitution of the phenanthroline ligand at adjacent to positions 5 and 6 along the C_2 axis retains the local symmetry. Coupling along this axis with the symmetric tpphz bridges retains many of the symmetry elements in the final structures. The bridging reaction between stereocenters has additional desirable characteristics. The reaction is simple, does not require anaerobic or anhydrous conditions and is irreversible.

2.1. Preparation of the chiral synthons

The synthesis and resolution of these chiral synthons is a relatively simple process. As shown in Fig. 5, enantiopure $[Ru(phen)_2(phendiamine)]^{2+}$ is synthesized from enantiopure $[Ru(phen)_2(phendione)]^{2+}$ in two steps [21]. First, coordinated phendione is converted to the dioxime by reaction with $NH_2OH{\cdot}HCl$ in refluxing ethanol in the presence of $BaCO_3$. Next, the dioxime is reduced by catalytic reduction (Pd) with hydrazine hydrate in EtOH to yield the coordinated diamine. The stereochemistry about the ruthenium is unaffected as shown by the similarity of both the sign and magnitude of the CD spectra of the product if resolved Δ- (or Λ)-$[(phen)_2Ru(phendione)]^{2+}$ is used as starting material. The resolution of $[Ru(phen)_2(phendione)]^{2+}$ by diastereotopic precipitation with arsenyl-tartrate salts has already been reported [22].

Efforts to directly resolve the chiral synthon $[Ru(phendione)_3]^{2+}$ has thus far not been successful. Fortunately, an alternate route exists in which coordinated phenanthroline ligands can be derivatized without racemization of the overall metal complex. Gillard and Hill [23] have reported that Δ-$[Ru(phen)_3]^{2+}$ may be directly

oxidized to Δ-$[Ru(phendione)_3]^{2+}$ at 100°C in a solution of sulfuric acid, nitric acid and sodium bromide (as a catalyst) *with retention of the stereochemistry*! In fact, it appears that the reactivity of coordinated phenanthroline ligands is largely unaffected by the presence of the metal ion or actually enhanced in some cases. The oxidation of phenanthroline to phenanthroline-5,6-dione is known to be more facile when the ligand is coordinated to a transition metal [23,24]. Torr and coworkers have reported several heretofore unknown phenanthroline derivatives whose preparation actually requires coordination of the ligand [25]. Because we have made extensive use of the ligand oxidation reaction (vide infra), we have carefully examined the stereochemical outcome and come to similar conclusions [26].

2.2. Stereospecific syntheses of dimers and tetramers

As shown in Fig. 2, coupling between $[Ru(phen)_2(phendione)]^{2+}$ and $[Ru(phen)_2(phendiamine)]^{2+}$ gives a dimer. The strength of this approach is highlighted by the simplicity of the multimetallic syntheses. By using enantiopure synthons, the two D_2 symmetric ΛΛ-**Ru_2** and ΔΔ-**Ru_2** enantiomers and the C_{2h} symmetric, *meso* complex, ΔΛ-**Ru_2** are synthesized directly [7]. The related complex, ΔΛ-$[(bpy)_2Ru(tpphz)Ru(bpy)_2](NO_3)_4$, has been crystallized and analyzed by X-ray crystallography [27]. This dimer has a internuclear Ru–Ru distance of 12.7 Å and shows a slight twist in the tpphz bridge in the otherwise rigid structure.

Coupling between three $[Ru(phen)_2(phendiamine)]^{2+}$ and $[Ru(phendione)_3]^{2+}$ yields the tetranuclear structure also shown in Fig. 4. Because all three C_2 axes of the $[Ru(phendione)_3]^{2+}$ synthon are symmetrically substituted the dendritic tetramer captures the full symmetry of the building blocks. The propeller shaped tetramers ($\Delta_3\Delta$-**Ru_4**, $\Delta_3\Lambda$-**Ru_4**, $\Lambda_3\Delta$-**Ru_4**, and $\Lambda_3\Lambda$-**Ru_4**) are all both dp and ep and represent all of the D_3 symmetric isomers possible for the tetramer [6].

Since neither the individual synthons nor the bridges allow any significant conformational isomerism, the overall structure is fixed and the relative position of the individual chiral centers as well as the overall topochemistry of the products is easily determined. For the tetramer, we calculate the peripheral Ru to Ru distance at 23 Å and estimate the an overall diameter of 3.4 nm for the large pinwheel shaped isomers. The bridge is also conjugated, and should favor some degree of electronic communication between the various chromophores and redox centers with the overall structure. In fact, recent studies of the luminescent properties have shown that the bridges somewhat insulate the individual metal centers [28–30].

2.3. Dimers and tetramers as core molecules for dendrimers

In order to build larger structures from the 'core' structures of dimers and tetramers, the 'terminal' phenanthroline groups of these molecules must be further functionallized. Typical dendritic syntheses utilize protecting groups at certain growth sites to prevent cross-linking reactions during generational growth reactions. In our system, the unfunctionallized phenanthroline ligands can act as protected phendiones which are 'deprotected' by selective oxidation. As depicted in

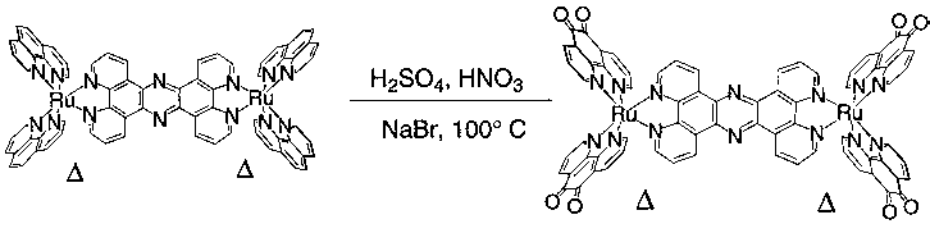

Fig. 6. Selective oxidation of ruthenium dimer.

Fig. 6, oxidation of the dimer by a mixture of sulfuric acid–nitric acid and NaBr catalyst selectively converts the 5 and 6 positions on all four 1,10-phenanthrolines to form coordinated 1,10-phenanthroline-5,6-diones. This reaction is remarkably effective with an isolated yield of 76% and retention of stereochemistry as determined from CD. The crude product is sufficiently clean, as revealed by NMR analyses, to be used directly for further dendritic growth. The ^{1}H-NMR spectrum of the oxidized dimer is shown in Fig. 7. Assignments were made with the assistance of COSY data and by comparison to the unoxidized dimer and $[Ru(phendione)_3]^{2+}$. Only 9 aromatic peaks are observed which is what is expected for a D_2 ($\Delta\Delta$ and $\Lambda\Lambda$) or C_{2h} ($\Delta\Lambda$) symmetric molecule. Oxidation of **Ru$_4$** under similar conditions yields $[((phendione)_2Ru(tpphz))_3Ru]^{8+}$ in 72% yield, also in remarkably pure form.

The oxidation reaction requires harsh reaction conditions which leads to the question of whether the chiral centers are racemized under these conditions. As

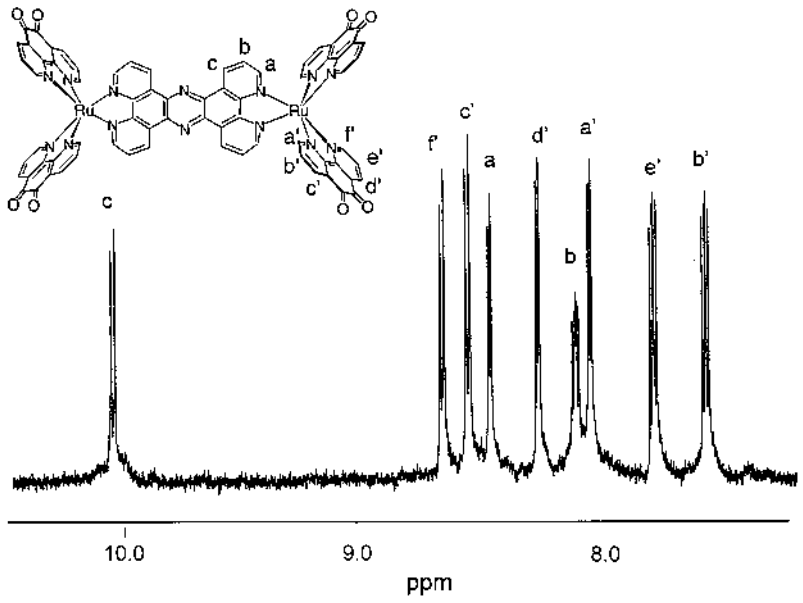

Fig. 7. ^{1}H-NMR of oxidized **Ru$_2$**$[PF_6]_2$ in CD_3CN.

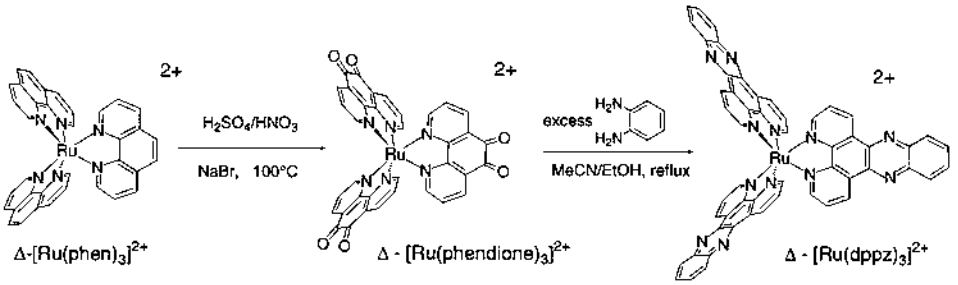

Fig. 8. Conversion of Δ-$[Ru(phen)_3]^{2+}$ to Δ-$[Ru(dppz)_3]^{2+}$.

mentioned previously, oxidation of $[Ru(phen)_3]^{2+}$ to $[Ru[phendione)_3]^{2+}$ was reported by Gillard and Hill to occur with retention of stereochemistry, however this conclusion was based solely on CD data [23]. Similarly, the dinuclear and tetranuclear products both exhibit cotton effects appropriate in sign and magnitude to what may be expected by comparison with starting material and $[Ru[phendione)_3]^{2+}$, but this method is only semi-quantitative.

In order to obtain a better analysis of the stereochemical outcome of these reactions, we examined a model system by NMR analysis using chiral lanthanide shift reagents [26]. Enantiopure $[Ru(phen)_3]^{2+}$ was oxidized to yield $[Ru[phendione)_3]^{2+}$ which, in turn, was further derivatized by reaction with excess 1,2-diaminobenzene to form the dichloromethane-soluble $[Ru(dppz)_3]^{2+}$ complex, as shown in Fig. 8. This complex having been both oxidized and then reacted to form peripheral phenazine rings clearly models the conditions the larger complexes are exposed to. The $[Ru(dppz)_3]Cl_2$ complex also showed good solubility in dichloromethane, which is required for in the NMR-chiral shift technique first described by Barton and Nowick [31]. We calibrated the NMR experiment with $[Ru(phen)_3]Cl_2$ samples of known optical purity and were able to detect the presence of as little as 5% of the minor isomer. When Δ-$[Ru(dppz)_3]^{2+}$, prepared as described above, was examined none of the minor isomer was detected. We conclude that little to no racemization (less than 5%) occurs under these conditions and by inference, none occurs for the reactions of the larger complexes.

2.4. Stereospecific syntheses dendritic hexamers and decamers

Figs. 9 and 10 show the products (**Ru_6** and **Ru_{10}**) obtained from the reaction of the oxidized dimer (**Ru_2**) and tetramer (**Ru_4**) with a slight stoichiometric excess (3.4 equivalents) of $[Ru(phen)_2(phendiamine)]^{2+}$. At this point, only the two homochiral enantiomers of **Ru_6** have been isolated, $\Delta_4\Delta_2$-**Ru_6** and $\Lambda_4\Lambda_2$-**Ru_6**. The decamer has only been prepared as a mixture from racemic starting materials. Both supramolecules have been characterized by NMR and MALDI–TOF or electrospray mass spectrometry [32].

The convenient **Ru_6** and **Ru_{10}** notation obscures the fact that the former complex is actually a $+12$ cation and the latter is a $+20$ cation. Both complexes have been

isolated as the hexafluorophosphate salts and the chloride salts. Both complexes show good solubility in acetonitrile and DMSO (for the PF_6^- salts) and in water and methanol (for the Cl^- salts). The crude complex is relatively pure; the main impurity being the appearance of the dimer (**Ru_2**) which is a known side product in these types of reactions [6]. Size exclusion chromatography using lipophillic sephadex (LH-20) with water—MeCN eluent is all that is required to isolate the pure product.

The ^{1}H-NMR spectrum of $\Lambda_4\Lambda_2$-**Ru_6** is shown in Fig. 11. The most striking feature of the spectrum is the simplicity which is what is expected for the D_2 symmetric dendrimer. Inspection of the structure of **Ru_6** reveals that three symmetrically non-equivalent sets of aromatic protons for the tpphz ligands should be observed for the complex. These sets are labled in Fig. 11 as (Ha, Hb, Hc), (Ha′, Hb′, Hc′) and (Ha″, Hb″, Hc″) and are expected as doublets in a 1:2:2 ratio. The tpphz hydrogens (i.e. Hc, Hc′, Hc″) located *para* to the imine nitrogens are usually observed downfield, well-separated from the remaining aromatic protons, and easily assigned. In this region, we clearly observe two doublets of equal intensity at 9.94 and 10.03 ppm. The third doublet of lesser intensity is observed at 10.06 ppm, however apparently half of this doublet is buried under a larger peak. Starting from these three doublets, most of the remaining peaks can be assigned with the aid of COSY data and by comparison with smaller 'model' complexes (i.e. $[Ru(phen)_3]^{2+}$, **Ru_2**, **Ru_4**). It should be noted that the resolution of the NMR experiment is not sufficient to clearly observe two separate peaks for (Ha and Ha′) and (Hb and Hb′). This is not surprising considering the local similarity of the two environments. However, COSY data clearly indicates that the peaks are simply overlapping and are coupled to Hc and Hc′ downfield. Although the **Ru_{10}** complex has not yet been prepared in dp and ep form, the ^{1}H-NMR data is also quite simple and completely consistent with the proposed structure. As was observed for the dimers and tetramers, diastereomers of **Ru_6** are not distinguishable by NMR.

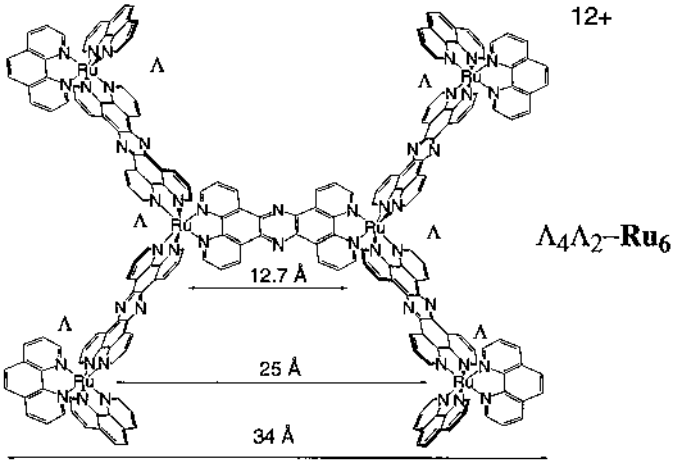

Fig. 9. Drawing of stereochemically pure hexanuclear dendrimer (**Ru_6**).

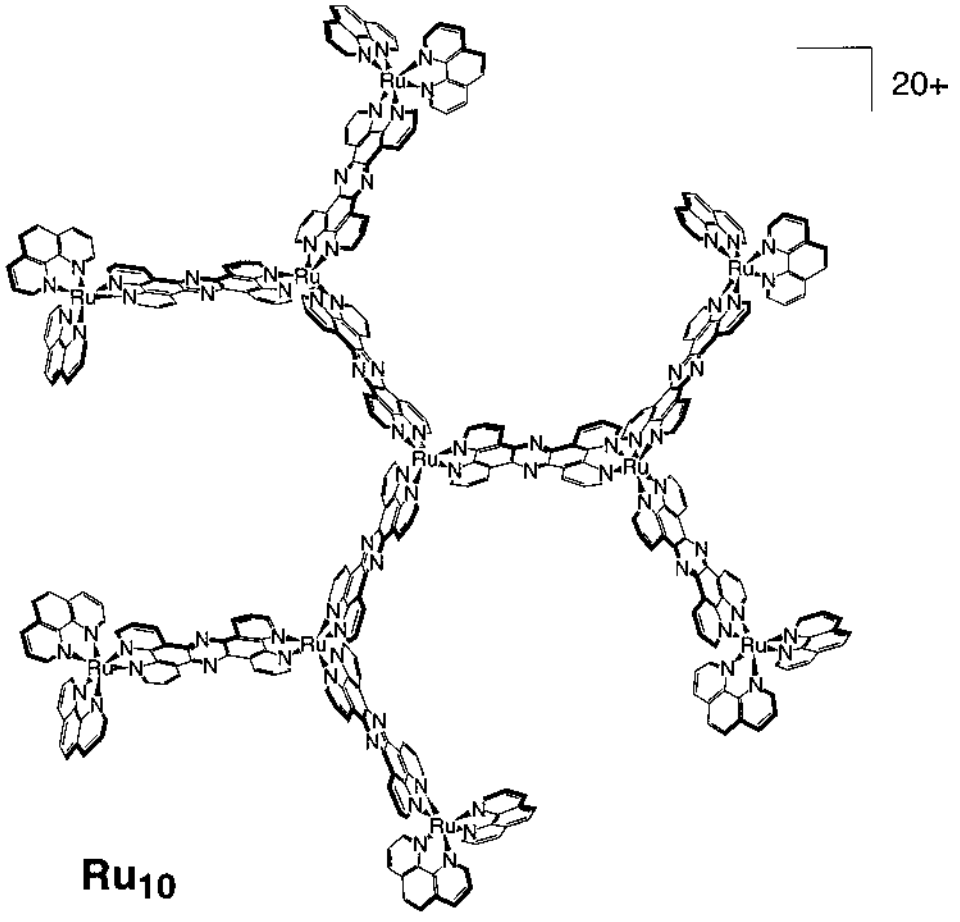

Fig. 10. Drawing of decanuclear dendrimer (**Ru_{10}**).

Electrospray mass spectrometry has been performed on both **Ru_6** and **Ru_{10}**. In both cases, parent ion peaks were observed for **Ru_6** at m/z 997 [**Ru_6**$-5PF_6^-]^{5+}$, 807 [**Ru_6**$-6PF_6^-]^{6+}$, 670 [**Ru_6**$-7PF_6^-]^{7+}$ and **Ru_{10}** at m/z 1216 [**Ru_{10}**$-7PF_6^-]^{7+}$, 1047 [**Ru_{10}**$-8PF_6^-]^{8+}$, 914 [**Ru_{10}**$-9PF_6^-]^{9+}$, 808 [**Ru_{10}**$-10PF_6^-]^{10+}$, 721 [**Ru_{10}**$-11PF_6^-]^{11+}$ which corroborates the NMR characterization of the dendrimers. Electrospray mass spectrometry has been used successfully as the primary characterization for decanuclear ruthenium dendrimers where stereochemical control was lacking [33].

The absorption, luminescent and circular dichroism data at 23°C for the hexamer and decamer as well as the monomers, dimer and tetramer in deaerated acetonitrile are displayed in Table 1. The absorption spectra of the multinuclear complexes exhibit intense ligand-centered (LC) bands in the UV region ($\varepsilon \sim 10^6$ M^{-1} cm^{-1}) and intense metal-to-ligand charge-transfer (MLCT) bands in the visible region (ε in

the range 100 000–250 000 M^{-1} cm^{-1}). All the complexes are luminescent in acetonitrile solution at room temperature (λ_{max} in the range 600–720 nm) and at 77 K (data not shown), except $[Ru(phendione)_3]^{2+}$ which is luminescent only at 77 K. For **Ru_2** and **Ru_4** the extinction coefficient and Cotton effect are approximately proportional to the total number (and stereochemical configuration for CD) of ruthenium chromophores within the structure (i.e. roughly $\times 2$ and $\times 4$ times the absorption and CD observed for $[Ru(phen)_3]^{2+}$]. Luminescence emission maxima are red-shifted relative to the monomers but are at relatively high energy (720 nm) compared to other luminescent ruthenium polypyridine dendrimers [5].

The hexamer and decamer continue the trend, although the extinction coefficients observed are somewhat higher than would be predicted by simple comparison with $[Ru(phen)_3]^{2+}$. The emission maxima for both are observed at ca. 720 nm. Energy-transfer from the central chromophore to an emmiting state on the peripheral complexes was observed in the tetramer, **Ru_4** [28,30]. It will be especially interesting to see how the decanuclear structure affects the photophysical properties of this assembly as it contains three non-symmetry equivalent Ru sites. Detailed investigations into the electronic structure and properties of the **Ru_6** and **Ru_{10}** complexes are underway in collaboration with a group at the University of Messina.

Some conclusions may be drawn from the CD data (Table 1). The homochiral **Ru_6** complexes gave intense Cotton effects for the enantiomers that were equal in intensity but opposite in sign as expected. This data supports the conclusion that little to no racemization is occurring in the construction of these dendritic complexes.

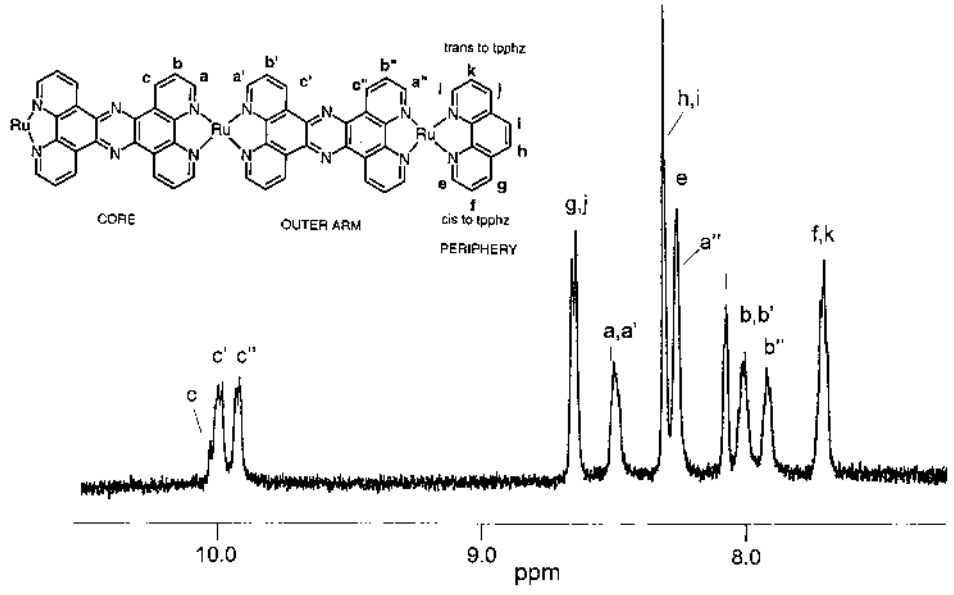

Fig. 11. ^{1}H-NMR Spectrum of **Ru_6**$[PF_6]_{12}$ in CD_3CN.

Table 1
Absorption, luminescence and circular dichroism properties in acetonitrile deaerated solution at 298 K

Complex	Absorption λ_{max}, nm (ε, M^{-1} cm^{-1})[a]	Luminescence λ_{em} (nm)	CD $\lambda_{min/max}$[b], (Mol. CD)
Mononuclear complexes			
Λ-$[Ru(phen)_3]^{2+}$	442 (19 200)	604[c]	467 (+21)
Λ-$[(phen)_2$	434 (14 800)	625	459 (+13)
$Ru(phendione)]^{2+}$			
Λ-$[(phen)_2$	455 sh (15 200)	650	470 (+17)
$Ru(phendiamine)]^{2+}$			
Λ-$[Ru(phendione)_3]^{2+}$	417 (14 700)	No emission	453 (+10)
Dinuclear complexes			
$\Delta\Delta$-**Ru_2**	439 (36 500)	710	470 (−36)
$\Lambda\Lambda$-**Ru_2**	438 (35 500)	710	470 (+36)
$\Lambda\Delta$-**Ru_2**	439 (38 100)	710	–
Tetranuclear complexes			
$\Delta_3\Delta$-**Ru_4**	439 (86 000)	718	476 (−73)
$\Lambda_3\Delta$-**Ru_4**	439 (78 000)	715	466 (+36)
$\Delta_3\Lambda$-**Ru_4**	441 (76 000)	720	466 (−38)
$\Lambda_3\Lambda$-**Ru_4**	439 (85 000)	718	475 (+68)
Hexanuclear complexes			
$\Delta_2\Delta_4$-**Ru_6**	440 (136 000)	720	475 (−104)
$\Lambda_2\Lambda_4$-**Ru_6**	440 (136 000)	720	477 (+117)
Decanuclear complexes			
Ru_{10} (mixture)	440 (228 000)	720	–

[a] Only the lowest energy maximum or shoulder is given.
[b] $\lambda_{max/min}$ for the lowest energy transition.
[c] Data from reference [34,35].

2.5. Dendritic supramolecular architecture

The hexamers and decamers are truly nanoscopic and, like their smaller predecessors, are both conformationally rigid molecules. The homochiral hexamers (all Λ and all Δ) have diameters estimated at 4.6 nm and retain the D_2 symmetry of the core molecule. The decamer is composed of 448 non-hydrogen atoms (not including the anions) with a diameter of 5.3 nm. Preparation of this molecule from chiral synthons will yield nanostructures with perfect D_3 symmetry.

Unlike before with the dimers and tetramers, stereochemical composition is expected to result in large changes in the topochemistry which are only beginning to be revealed. Molecular modeling calculations show that adjacent rutheniums must have an alternating Δ then Λ then Δ (and so on) stereochemical composition to keep the molecule approximately planar. As can be seen in the drawings for both **Ru_6** and **Ru_{10}**, if the molecule remains planar then steric crowding may prevent

further dendritic growth. Models also indicate that large homochiral structures will no longer be flat but instead twist out of the plane defined by the core-suggesting even larger structures may be accessible.

From inspection, it is obvious that both **Ru$_6$** and **Ru$_{10}$** have deep molecular clefts which are defined by the dendritic arms of the complex. In fact, due to the structure both complexes have multiple molecular clefts which are topologically identical and due to the rigid structure-precisely defined. Ultimately, it is hoped that these molecular clefts may serve as 'binding pockets' or 'endoreceptor sites' for chiral recognition. The fact that we can tune the stereochemistry of these sites as well as possibly couple a binding event with a physical response such as the luminescence intensity only adds to their promise.

3. Summary

We have described a conceptually simple yet but powerful synthetic methodology for the construction of diasteromerically and enantiomerically pure supramolecular assemblies. The 'substitutionally-inert chiral synthon' approach centers on the use of enantiopure $[Ru(phen)_3]^{2+}$ derivatives as the fundamental molecular building blocks for supramolecular syntheses. By working with enantiopure monomers, the multimetallic products are both dp and ep which both simplifies characterization and provides unique topochemical control. These coupling reaction along the ligand periphery provide a simple route to assemble these chiral synthons into conformationally rigid, nanoscopic structures with precisely defined architectures. Dendritic tetramers, hexamers and decamers as well as dp and ep dimers have been assembled using this method and demonstrate its utility.

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