

New Stepwise Approach to Inert Heterometallic Triple-Stranded Helicates

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The new tripodal fac-functionalized building block, fac-ruthenium(II) tris-(5-hydroxymethyl-2,2'-bipyridine), has been synthesized as a single geometric isomer and used as starting point in the isolation of a kinetically inert heterometallic helicate by the stepwise inclusion of additional 2,2'-bipyridine chelating groups followed by a second metal ion. This stepwise synthetic methodology gives access to a new range of chiral nanoscale structures inaccessible by traditional self-assembly procedures.

Hundreds of helical single-, double-, and triple-stranded metallosupramolecular systems containing two or more metal ions, commonly known as *helicates*, have in recent years appeared in the literature.¹ Such complexes have been pivotal in the development of self-assembly processes for the fabrication of nanoscale complexes.² Yet the predictive control over the resulting structure remains in its infancy, having only mastered with reliability the macroscopic features such as the number of metal ions and ligand strands. As a result the majority of helicates are homometallic¹ because of the difficulty in simultaneously coordinating two different cations. This can be overcome by choosing a ligand system with two dissimilar metal-binding sites (i.e., *heterotopic* ligands).³ However, the requirements to fine-tune both the ligand structure and the reaction conditions can make isolation of the targeted product difficult.

We show here that in moving to a *stepwise* methodology, two or more metals can be introduced selectively, giving simple access to heterometallic complexes with *homotopic* ligands. To achieve this, the first metal must be kinetically inert, such as the tris-diimine complexes of ruthenium(II).⁴ Two heteronuclear ruthenium(II) helicates have been pre-

pared via a self-assembly route,⁵ yet this cation is not normally appropriate to such processes. The isolation of multicomponent complexes with inert metal chelates is frustrated by the isomeric possibilities.⁶ Not only must the metal centered chirality be considered, but also the mer/fac isomerism.⁷ Statistically, the combination of three ligands and one metal favors the mer isomer, but to prepare a helicate, the fac isomer is required. This can be achieved by preorganizing the three functional groups along the C_3 axis prior to complexation, as initially demonstrated by Weizman et al.⁸ and more recently by ourselves.⁹ Tethering of the three chelating groups together and the subsequent disconnection after the introduction of the metal ion allows the fac trischelate complex to be isolated alone.

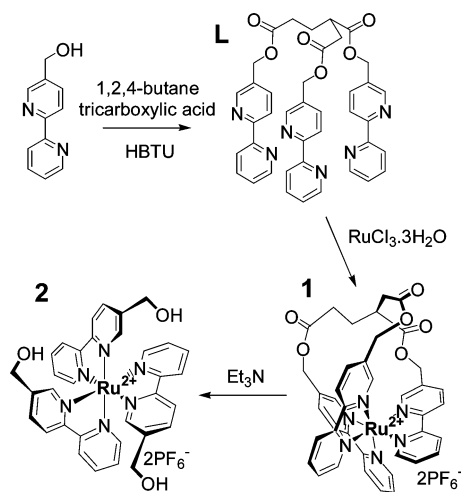
5-Hydroxymethyl-2,2'-bipyridine was prepared by a literature procedure,¹⁰ but subsequent attempts to connect three of these units to tripodal tricarboxylic acids proved problematic. Initially, C_3 symmetric systems, such as (bis-carboxyethyl-amino)-propionic acid and 1,3,5-benzenetricarboxylic acid, were investigated, but ester formation proved to be difficult. After we reluctantly moved to a C_1 symmetric system, HBTU-mediated coupling of the alcohol with commercially available 1,2,4-butane tricarboxylic acid was found to give the tethered ligand **L** (Scheme 1) in a 69% yield and high purity. This was subsequently reacted with $RuCl_3 \cdot 3H_2O$ to give the cage-like complex **1** in a 54% yield, as the hexafluorophosphate salt. ¹H NMR spectroscopy con-

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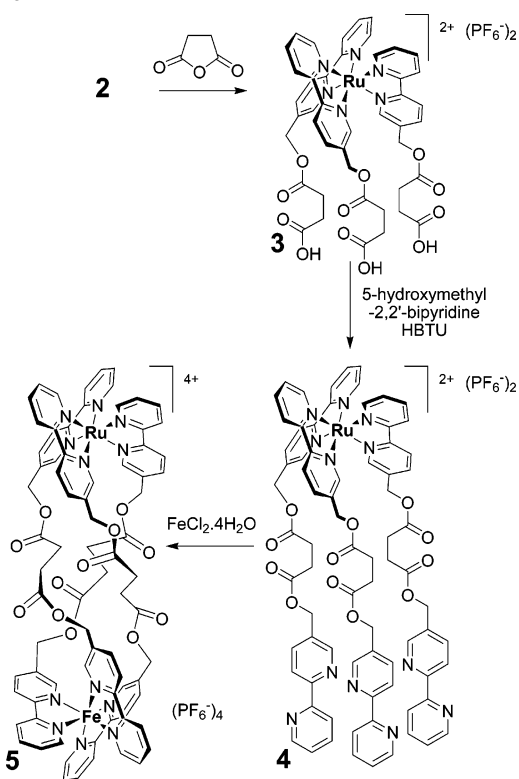
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Scheme 1



Scheme 2



firmed the low symmetry, with seven broad aromatic signals and the diastereotopic methylene protons adjacent to the bipyridines presenting as three overlapping AB patterns. After it was stirred overnight in the presence of triethylamine, the ^1H NMR spectrum became noticeably sharper with a single AB quartet at 4.46 ppm indicating C_3 symmetry. The identity of the resulting fac triol complex **2** was confirmed by ES-MS with the characteristic $[\text{M} - \text{PF}_6]^+$ and $[\text{M} - 2\text{PF}_6]^{2+}$ peaks.

Esterification of the three hydroxyl groups presented by complex **2** offers opportunities to build up new polynuclear complexes (Scheme 2). The reaction of **2** with succinic anhydride gave complex **3**, bearing three free fac-orientated carboxylic acid groups, in a quantitative yield. The subsequent reaction with 5-hydroxymethyl-2,2'-bipyridine using HBTU coupling introduced three new chelating groups in a

74% yield. The resulting complex, **4**, can be viewed as a precursor to a range of *heterometallic homotopic* helicates. It is noteworthy that if the ligand of complex **4** alone were to be mixed with metal ions in an attempted self-assembly procedure, a wide variety of complexes would be anticipated given the ligand's flexibility. Without the adoption of this stepwise procedure, the isolation of heterometallic species cannot be achieved.

The formation of an $\text{Ru}^{\text{II}}-\text{Fe}^{\text{II}}$ complex was achieved by stirring complex **4** with $[\text{Fe}(\text{H}_2\text{O})_4\text{Cl}_2]$. A dark red solid was isolated in a quantitative yield from the reaction by precipitation with NH_4PF_6 . The ES-MS gave the expected $[\text{M} - 4\text{PF}_6]^{4+}$, $[\text{M} - 3\text{PF}_6]^{3+}$, and $[\text{M} - 2\text{PF}_6]^{2+}$ peaks, and microanalysis indicated the retention of 3 molecules of water in the solid state. The majority of the bipyridine signals for the two metals are concurrent in the ^1H NMR spectrum (Figure 1). However, the H^6 signals are sufficiently distinct to show that the isolated product is a mixture of both the rac (homochiral) and meso forms (Figure 2),¹ with the signals for both metal centers being split into two sets of approximately equal intensity. This is also apparent in the methylene and ethylene linkages where a manifold of diastereotopically coupled signals are observed with the introduction of the second metal ion. It is noted that the ligand is not sufficiently rigid for the ruthenium center to direct the helicity at the second metal coordination site in this case.

The electronic spectra of **5** approximates to the sum of the two metallic components with the ligand-centered absorptions being about twice as intense as the two mono-metallic species. The metal-to-ligand charge transfer (MLCT) band shows a significant shoulder at 520 nm assigned as the Fe^{II} to bipyridyl excitation, in addition to the expected Ru^{II} MLCT at 453 nm. From the emission spectrum, a quantum yield of 0.030 is observed, approximately half of that for $[\text{Ru}(\text{bipy})_3](\text{PF}_6)$ (0.062),¹¹ implying that the emission is either unaffected by the second metal center or is weakly quenched, presumably, by an electron exchange mechanism leading to formation of $[\text{Fe}(\text{bipy})_3]^{3+}$. Similarly, the electrochemistry of **5**, shows the presence of two metal centers. The initial $\text{Fe}^{\text{II/III}}$ couple is observed at +1.08 V followed by the $\text{Ru}^{\text{II/III}}$ couple at +1.27 V against a SCE.¹² As is typical of the polypyridyl complexes of Fe^{II} , the $\text{Fe}^{\text{II/III}}$ couple is completely irreversible, leading to the loss of the metal ion, and so the second $\text{Ru}^{\text{II/III}}$ oxidation most likely pertains to complex **4**. A series of six ligand reductions are also observed with varying degrees of reversibility.

The ^1H NMR spectrum of complex **5** indicates the presence of both the meso and rac diastereoisomers. To demonstrate that a true helicate can be isolated, an attempt to separate these diastereoisomers was undertaken using cation-exchange chromatography.¹³ After an effective column length of 1 m, two distinct bands could be observed. The faster-moving narrow band was removed (**5a**), and the second fraction (**5b**) recycled on the column. While this second band

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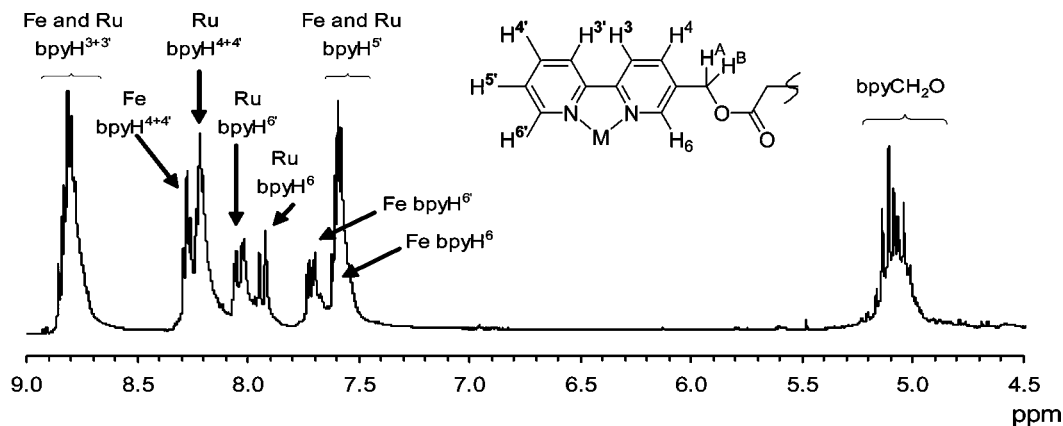


Figure 1. ^1H NMR spectrum of **5** in acetone- d_6 22 °C.

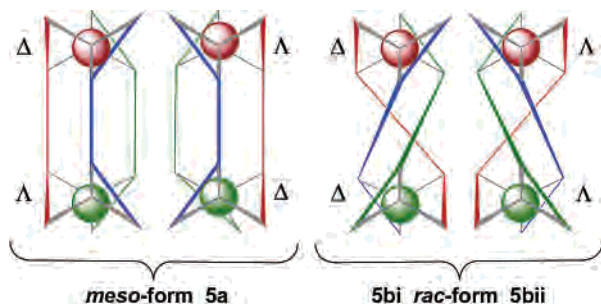


Figure 2. Isomeric components of complex **5**.

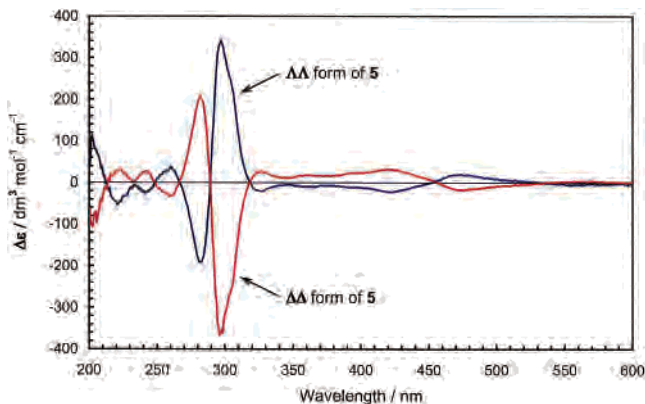


Figure 3. CD spectra for $\Delta\Delta$ - and $\Lambda\Lambda$ -**5** (CH_3CN at 298 K).

did not resolve completely into two distinct bands after 4 m of travel, the front (**5bi**) and back (**5bii**) thirds were collected separately and analyzed by UV–vis and circular dichroism (CD) spectroscopy. As anticipated, all of the collected fractions demonstrate identical visible absorption spectra. When the UV–vis spectra were used to adjust for the concentration, the differential extinction coefficients in the CD measurements could be determined. Importantly, the first band did not demonstrate an appreciable Cotton effect leading to its assignment as the meso form (**5a**, Figure 2),

composed of an enantiomeric pair (Δ -Ru– Λ -Fe and Λ -Ru– Δ -Fe). Because of the structural similarities between the two metal environments, it is extremely unlikely that this pair of enantiomers could be separated using the techniques currently available to us. The two isolated fractions from the second band (**5bi** and **5bii**) however have extremely strong Cotton effects, with the two fractions demonstrating equal and opposite differential extinction coefficients (Figure 3), typical of an enantiomeric pair of dinuclear helicates. By comparison of the π – π^* transitions (at approximately 300 nm) to those of complexes with a known configuration, the faster-moving fraction (**5bi**) is tentatively assigned as the $\Delta\Delta$ form, while the slower band (**5bii**) the $\Lambda\Lambda$ form.¹⁴ The solutions used for the spectroscopic measurements did not appear to decrease in CD signal intensity upon standing in solution over a period of several weeks, signifying that the complexes are stable to racemization or conversion to the meso form under normal laboratory conditions.

In conclusion, we have demonstrated the isolation of a new tripodal fac-orientated ruthenium(II) building block and shown that this can be used in the systematic isolation of helicates. Crucially, we have shown that, by introducing the second metal ion in the final step, the selective formation of a heterometallic helicate can be achieved, despite having two identical coordination environments, in good overall yield. In future studies, we intend to exploit this new methodology in the isolation of a range of new heterometallic helicates with potentially interesting photophysical properties.

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Supporting Information Available: Experimental details and physical characterization of all products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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