

The isolation and secondary functionalisation of *fac*-tris-2,2'-bipyridine complexes of ruthenium(II)†

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fac-Ruthenium(II) tris-(5-carboxy-2,2'-bipyridine) has been synthesised as a single geometric isomer for the first time, and proves to be a good 'building-block' to introduce new functionality with retention of the isomeric integrity.

The tris-2,2'-bipyridine complexes of ruthenium(II) have become one of the most widely studied transition metal species due to their unique physical behaviour.^{1,2} It is these properties that have led to their application in supramolecular chemistry, both as a lumiphore in molecular sensors and the photoactive centre in light induced charge-separated species.^{1,3} However, the ability to construct multi-component molecular architectures is frustrated by isomeric considerations. To build a unique structure the stereochemistry of the individual components must be controlled.⁴ To this end, considerable progress has been achieved in the development of enantiomerically pure building-blocks possessing either a Δ or Λ metal configuration.^{5,6} Far less attention has been paid to the issue of *mer/fac*-isomerism in such species.

In a recent paper, we described the isomeric separation of a range of tris(5-functionalised-2,2'-bipyridine) complexes of ruthenium(II) by cation ion-exchange chromatography.⁷ In keeping with the statistical expectation, the combination of three ligands to one metal favours the *mer*-form, being three times more likely than the corresponding *fac*-isomer. This preference for the *mer*-isomer is further enhanced by steric interactions leading to poor yields of the *fac*-form. To realise isomerically pure *fac*-functionalised building-blocks for the development for larger molecular structures we report here an alternative synthetic strategy leading to the single geometric isomer.

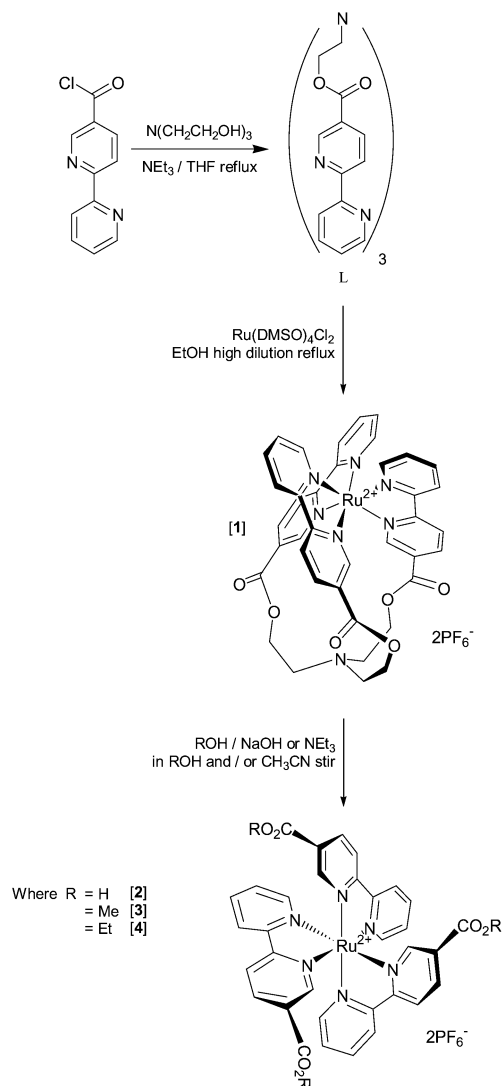
To orient the three functional groups along the C_3 -axis found in the *fac*-isomer (Scheme 1), the three bidentate units must be preorganised prior to complexation to the metal centre. This can potentially be achieved by tethering the three bipyridyls together and consequently preventing formation of the *mer*-isomer. A number of such tripodal tris-bipyridine ligand systems have previously been reported^{8–11} but none of them allow simple disconnection of the tether to offer the further inclusion of additional functional groups. To overcome this, ester linkages were chosen where simple base hydrolysis could potentially be used to liberate the desired *fac*-tris-chelate complex.

Several tripodal ligand systems were initially explored by the condensation of 5-chlorocarbonyl-2,2'-bipyridine with a number of trialcohols including 1,3,5-tris(hydroxymethyl)benzene and 1,1,1-tris(hydroxymethyl)ethane. Triethanolamine was eventually chosen giving the ligand L (Scheme 1) as it was obtained in reasonable yield (62%) and high purity.‡ The ligand L was subsequently reacted with Ru(DMSO)₄Cl₂ under high dilution conditions in ethanol to give the cage like complex **1**. This was purified by cation-exchange chromatography on Sephadex SP C25 to remove contamination by undesirable

oligomeric species. The product was isolated in 85% yield as the hexafluorophosphate salt.§

The ¹H NMR spectrum of complex **1** demonstrated the desired C_3 -symmetry expected for the *fac*-isomer. Of particular note are the four methylene protons on the tether each of which shows a unique diastereotopic signal. Upon standing in a protic solvent complex **1** was however observed to decompose, presumably by the desired ester hydrolysis to the tris-acid **2**. This was confirmed by stirring complex **1** in 0.1 M aqueous NaOH solution giving the tris-acid **2** in quantitative yield. Characterisation of **2** was confirmed by LSIMS MS and ¹H NMR spectroscopy consisting entirely of the target C_3 -symmetric *fac*-isomer.§

In order to demonstrate the generality of the tether removal procedure, a series of transesterifications were attempted by



Scheme 1

† Electronic supplementary information (ESI) available: Table S1: Spectral data for 1–5. Fig. S1: ¹H NMR spectrum of **5**. See <http://www.rsc.org/suppdata/cc/b2/b202886g/>

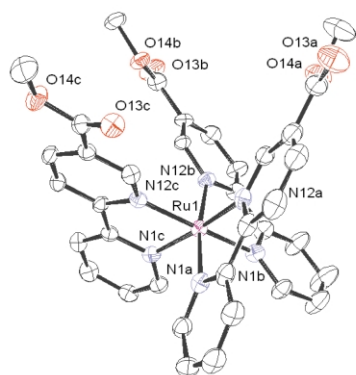


Fig. 1 The structure of the cation of **3** with ellipsoids at 50% probability. Hydrogen atoms, anions and water of crystallisation have been deleted for clarity.

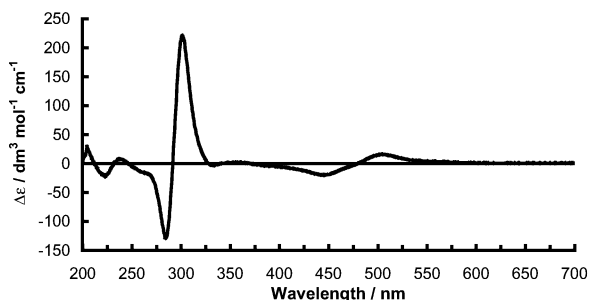


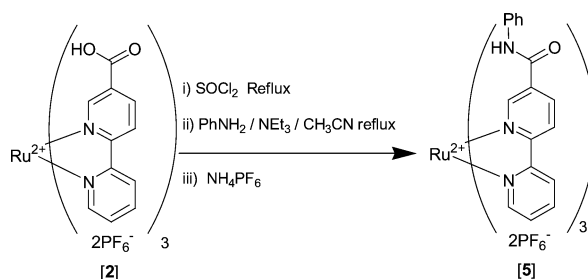
Fig. 2 Circular dichroism spectrum of Δ -**1** (CH_3CN : 1×10^{-4} M).

reacting complex **1** with methanol and ethanol in the presence of triethylamine. Species **3** and **4** were isolated in good yield as the hexafluorophosphate salts and purified on Sephadex LH20. As with the acid **2**, the ^1H NMR spectra of **3** and **4** illustrate that all three of the ligands are chemically equivalent indicating the C_3 -symmetry expected for the *fac*-isomer. § The structural integrity was confirmed by the comparison of the ^1H NMR spectrum of *fac*-**3** with the previously published spectrum of this isomer isolated by separation from a mixture of *mer*- and *fac*-**3**.⁷ By implication, the tether removal gives complete retention of the metal centred geometrical isomerism.

From a methanolic solution, crystals of **3** suitable for X-ray structural analysis were obtained as the hexafluorophosphate salt. ¶ Fig. 1 illustrates the cation, with the metal coordinated to the six pyridyl nitrogens [2.045(5)–2.069(4) Å] of the three bidentate ligands in a distorted octahedral arrangement. The most important feature of the structure is the *cis*-arrangement of each of the three ester groups with respect to the ruthenium(II) centre. As a consequence, the cationic species presents the *fac*-isomer confirming the ^1H NMR studies.

In keeping with our previously published results,⁷ 20 mg of complex **1** was separated into the Δ and Λ stereoisomers on Sephadex SP C25 cation-exchange resin eluted with an aqueous solution of sodium (–)-*O,O'*-dibenzoyl-L-tartrate. The two isolated enantiomers demonstrated strong Cotton effects, (Fig. 2), which did not appear to change significantly upon de-esterification to **2**. As with the retention of geometrical integrity on removal of the tether, the metal centred chirality is also preserved provided that excessive exposure to light or high temperatures are avoided.

The three carboxylic acid groups presented by complex **2** offer new opportunities to allow the introduction of a great variety of new functionalities with a unique orientation. In addition to the preparation of esters, the synthesis of amides allows an alternative synthetic route for the preparation of supramolecular architectures with the advantage that they are less susceptible to acid and base hydrolysis than complexes **3** and **4**. By refluxing **2** in thionyl chloride, the triacyl chloride was prepared and reacted without isolation with aniline to prepare the triphenylamide **5** in reasonable yield (60%) as the



Scheme 2

hexafluorophosphate salt (Scheme 2). Characterisation by ^1H NMR spectroscopy again indicated the C_3 -symmetry of the *fac*-isomer (ESI, Fig. 1S). § This complex is directly analogous to the species previously published by Uppadine *et al.*, with the C_2 -symmetric 5,5'-diamide-2,2'-bipyridine ligands which have demonstrated considerable potential as anion sensors.¹²

In conclusion, we have developed a method of synthetically isolating *fac*-tris(asymmetrically substituted bipyridine) complexes of ruthenium(II) and demonstrated that these can be subsequently reacted to form both esters and amides with retention of isomeric integrity of the complex. This structurally controlled building-block offers considerable potential in the preparation of new supramolecular species with a structurally controlled architecture. Studies are currently in progress to use complex **2** in the synthesis of kinetically inert helicates, while complex **5** offers exciting possibilities as a molecular sensor.

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Notes and references

‡ Characterisation of L: Found C: 64.41, H: 5.10, N: 12.70. Calc. for $\text{C}_{30}\text{H}_{33}\text{O}_6\text{N}_7 \cdot 2\text{CH}_3\text{OH}$: C: 64.81, H: 5.44, N: 12.90%, ^1H NMR (500 MHz, CDCl_3) δ 3.00 (2H, t, J 5.6 Hz), 4.37 (2H, t, J 5.6 Hz), 7.17 (1H, dd, J 4.7, 7.4 Hz), 7.63 (1H, dd, J 7.4, 8.2 Hz), 8.18 (1H, d, J 8.2 Hz, bipyH⁴), 8.24 (1H, d, J 8.2 Hz), 8.26 (1H, d, J 8.2 Hz), 8.51 (1H, d, J 4.7 Hz), 9.05 (2H, s).

§ A table of ^1H NMR data provided in the ESI†.

¶ Crystal data: $\text{C}_{36}\text{H}_{31}\text{F}_{12}\text{N}_6\text{O}_{6.5}\text{P}_2\text{Ru}$, $M = 1042.68$, monoclinic, space group = $P2_1/n$, $a = 11.9005(17)$, $b = 20.520(3)$, $c = 16.710(3)$ Å, $\beta = 96.937(2)^\circ$, $V = 4050.8(10)$ Å³, $Z = 4$, $\mu = 0.577$ mm⁻¹, $T = 153(2)$ K, $F(000) = 2092$, 29541 reflections measured in angle range $3 < 2\theta < 57^\circ$, 8716 independent reflections, 570 parameters, final parameters were $wR2 = 0.1249$ and $R1 = 0.0585$ [$I > 2\sigma(I)$]. CCDC reference number 183067. See <http://www.rsc.org/suppdata/cc/b2/b202886g/> for crystallographic data in CIF or other electronic format.

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