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FULL PAPER

The isolation and purification of tris-2,2′-bipyridine complexes of ruthenium(II) containing unsymmetrical ligands

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Monomeric ruthenium(II) complexes $[Ru(L)_3]^{2+}$ containing unsymmetric bipyridine ligands [Where L = 5-methyl-2,2′-bipyridine (L^1), 5-ethyl-2,2′-bipyridine (L^2), 5-propyl-2,2′-bipyridine (L^3), 5-(2-methylpropyl)-2,2′-bipyridine (L^4), 5-(2,2-dimethylpropyl)-2,2′-bipyridine (L^5) or 5-(carbomethoxy)-2,2′-bipyridine (L^6)] have been studied and the meridional and facial isomers isolated by the use of cation-exchange column chromatography (SP Sephadex C-25) eluting with either sodium toluene-4-sulfonate or sodium hexanoate. The relative yield of the facial isomer was found to decrease with increasing steric bulk, preventing the isolation of *fac*-$[Ru(L^5)_3]^{2+}$. The two isomeric forms were characterized by ^{1}H NMR spectroscopy, with the complexes $[Ru(L^{1–3})_3]^{2+}$ demonstrating an unusually large coupling between the H^6 and H^4 protons. Crystals suitable for X-ray structural analysis of $[Ru(L^1)_3]^{2+}$ were obtained as a mixture of the meridional and facial isomers, indicating that separation of this isomeric mixture could not be achieved by fractional crystallisation. The optical isomers of the complex $[Ru(L^3)_3]^{2+}$ were chromatographically separated on SP Sephadex C-25 relying upon the inherent chirality of the support. It is apparent that chiral interactions can inhibit geometric isomer separation using this technique.

Introduction

The development of polynuclear coordination species has been the subject of extensive research due to the large number of potential applications.[1] Of particular interest have been metallo-supramolecular assemblies of the polypyridine complexes of ruthenium(II), osmium(II) and rhodium(III) due to their potential as photoactivated charge separated species.[2–4] As a consequence, there is a vast wealth of literature describing the fascinating synthetic,[5] photophysical[6] and electrochemical[7,8] properties of simple monomeric systems. By the judicious choice of ligands and metal centres the electronic potentials can be controlled to direct electrons towards specific sites for light activated secondary reactions; *i.e.* artificial photosynthesis.[9–12]

In order to bring these individual units together within a larger assembly, it is of considerable importance to be able to control the spatial arrangement of both the ligands and the metal centres in relation to one another. It has been demonstrated that the distance between and the orientation of individual groups within larger assemblies can have small but significant effects on the electrochemistry and on the excited-state lifetimes,[13,14] and consequently their potential use as photosensitisers. The isolation of single isomeric forms also has great implication on the ease of characterisation by NMR spectroscopy and simplifies the art of crystal growth for X-ray structural analysis.

Significant progress has been made in the control of the chirality at the metal centres, using either individually isolated chiral building blocks such as Δ- or Λ- *cis*-$[Ru(bpy)_2(py)_2]^{2+}$ [15] or *cis*-$[Ru(bpy)_2(CO)_2]^{2+}$ [16] among others.[17,18] Far less attention has been paid to the potential of meridional (*mer*) and facial (*fac*) isomerism (Fig. 1). In a typical synthesis, using three unsymmetrically functionalised ligands, a statistical distribution of three parts of the *mer*-isomer will be produced to one of the *fac*-isomer, arising from the potential orientation of the ligands in a stepwise addition to the metal centre. However, due to the steric requirements of the ligand, it is expected that the ratio will be further tipped in favour of the *mer*-form.

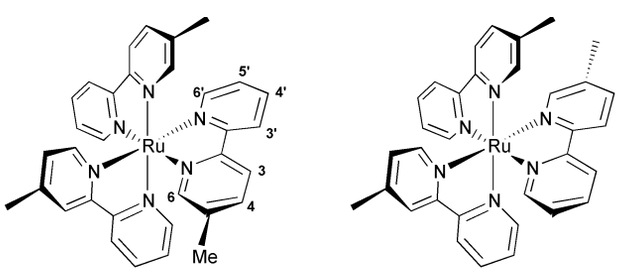

Fig. 1 Schematic illustration of (a) *fac*- and (b) *mer*-$[Ru(L^1)_3]^{2+}$.

The presence of the *mer*/*fac*-isomerism in tris-unsymmetric diimine complexes of ruthenium(II) has been observed in a number of papers, where the individual isomers have been identified by ^{1}H, ^{13}C [19,20] and even ^{99}Ru NMR spectroscopy.[21–23] However the number of examples where such species have been prepared isomerically pure are scarce. Kaim and co-workers have separated, using HPLC methods, the tris-2,2′-azobis-(pyridine) complex of ruthenium(II), demonstrating that the two isomers have different UV–VIS and IR absorbances,[24] while Tresoldi *et al.* isolated the two isomers of $[Rh(bpp)_3]^{3+}$ [bpp = 2,3-bis(2-pyridyl)pyrazine] by column chromatography on alumina.[25] A more comprehensive study of the possibility of separating geometric isomers of unsymmetrically functionalised bipyridine complexes of ruthenium(II) was performed by Rutherford and Keene using the ligand 4-(2,2-dimethylpropyl)-4′-methyl-2,2′-bipyridine.[26] To date however, nobody has described the use of any of these species in the preparation of larger polynuclear assemblies with controlled structural integrity.

Using a similar methodology as that described by Rutherford and Keene, a detailed investigation is described here exploring the possible strengths of cation-exchange chromatography upon 5-functionalised bipyridine ligands. Substitution at the 5-position has not been explored to the same extent as the

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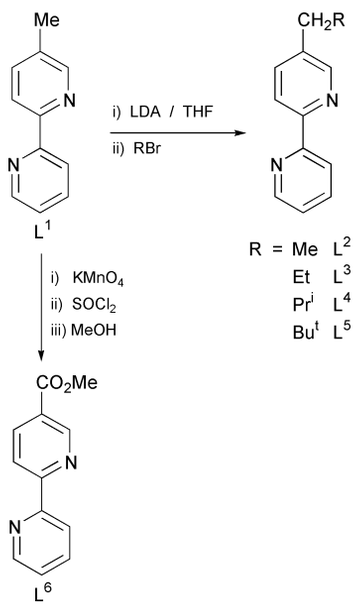
analogous 4-functionalised bipyridine species, probably because of the increased steric constraints which are considered within this study and the commercial availability of 4,4′-dimethyl-2,2′-bipyridine. The orientation of the substituents relative to each other is of considerable interest to us, the *fac*-isomer of 5-functionalised bipyridines provides three groups placed orthogonal. By the use of suitable functionality, the question is posed as to whether these pseudo-octahedral complexes can be used as building blocks for the preparation of larger networks, opening a new route for polynuclear assemblies with controlled geometrical isomerism.

Results and discussion

Synthesis

Ligand. A series of unsymmetrical ligands were synthesised (Scheme 1) from 5-methyl-2,2′-bipyridine L^1, prepared by a literature synthesis and further purified by vacuum distillation.[27] Additional functionalisation was achieved, by deprotonation with lithium diisopropylamide (LDA) and subsequent quenching of the carboanion with the appropriate bromoalkane (or methyliodide for ligand L^2) in a similar procedure described for the synthesis of 4-(2,2-dimethylpropyl)-4′-methyl-2,2′-bipyridine.[26] The rate of the nucleophilic attack was found to decrease significantly with the size of the incoming alkane, with the bulky 2-bromo-2-methylpropane requiring several days at room temperature to react and giving a poor yield of L^5.



Scheme 1 Synthetic route to ligands L^1–L^6.

In order to allow further reactions once the ligand has been coordinated to a ruthenium(II) metal centre, (*i.e.* to act as a supramolecular building block), a group needs to be appended that is unreactive during coordination to a metal centre, but can offer subsequent reactivity to create larger assemblies. While aliphatic ligands could potentially be considered, the conditions required to append secondary groups are extreme requiring the use of strong bases. Appended bromo, carboxy and aldehyde groups were also considered, but problems were encountered upon complexation to the metal centre. Many bipyridine ester complexes are known however, and simple base hydrolysis opens up the possibility to add further functionality. 5-(Carbomethoxy)-2,2′-bipyridine L^6 was investigated being the least sterically demanding example. The ligand synthesis was achieved from L^1 *via* a modified literature procedure to 5-carboxy-2,2′-bipyridine.[27] From this the acid chloride was prepared in thionyl chloride and subsequently reacted with dry methanol to give L^6.

Complexes. All of the ligands were coordinated to ruthenium(II) by reaction with $RuCl_3 \cdot xH_2O$ in either ethanol or DMF to give the tris-chelate $[Ru(L)_3]^{2+}$. The complexes were initially purified using cation-exchange chromatography upon SP Sephadex® C-25, eluting with aqueous sodium chloride solution and characterised by elemental analysis, mass spectroscopy and the characteristic UV–VIS absorption spectra. The yields of the products were generally found to be higher in DMF, presumably because of the higher reaction temperature. However, the yields were generally lower than would have been expected, especially with the more sterically hindered ligands. In many of the reactions a brown precipitate was isolated directly from the reaction mixture, which was assumed to be a bis-chelate species indicating that the final ligation step limits the reaction. Difficulties were experienced in the purification of $[Ru(L^5)_3]^{2+}$, with the complex repeatably analyzing for an excess of ammonium hexafluorophosphate despite repeated recrystallisation and repeated passage down a Sephadex LH20 column. It is assumed that the hydrophobic functionality is capable of retaining hydrophobic species.

X-Ray structural analysis of $[Ru(L^1)_3](PF_6)_2$

From a partially resolved fraction taken from a cation-exchange column (described subsequently) crystals of $[Ru(L^1)_3](PF_6)_2$ suitable for X-ray structure determination were obtained from an aqueous methanol mixture. The X-ray structure determination shows the asymmetric unit contains one $[Ru(L^1)_3]$ cation and two PF_6 anions. The $[Ru(L^1)_3]$ cations are arranged into columns within the lattice and involved in weak C–H···π interactions, as observed for $[Ru(bipy)_3](PF_6)_2$.[28,29] The PF_6 anions within the lattice are involved in a significant number of short contacts (2.3–2.9 Å) with the C–H and the methyl moieties of the $[Ru(L^1)_3]$ cations. This is consistent with the formation of C–H···F hydrogen bonds between the cations and anions and in agreement with a database study on organometallic compounds containing fluorinated anions by Braga and co-workers in which they showed that both BF_4 and PF_6 anions can act as hydrogen bond acceptors.[30] They concluded that C–H···F hydrogen bonds to BF_4 and PF_6 anions may be significant in the formation of many crystalline materials.

The average Ru–N bond lengths and N–Ru–N angles correlate with those of published structures[28,29] (selected bond lengths and angles are given in Table 1) The $[Ru(L^1)_3]$ cations are randomly disordered throughout the lattice as a mixture of *mer*- and *fac*-isomers with respect to the relative orientation of the methyl substituents of a single L^1 group. The two conformations refined to 64(1) and 36(1)% respectively, the major conformation is shown in Fig. 2. By examination of the structure, the disorder of the structure can be accounted for by the similarity of the two forms, differing by a single methyl group. The orientation of the rigid cation provides suitable space in the lattice to allow the methyl group to position either side of one of the ligand numbered A. Since the two isomers appear to be isostructural, separation by crystallisation would prove extremely difficult.

Stereochemical explorations and isomer separation

The ratio of the two isomers from a simple statistical analysis should be three *mer* to one *fac*. Direct indication to confirm this by ^{1}H NMR proved impossible because of the complex nature of the spectra of the two isomers with many signals occupying very similar regions of the spectrum. In order to judge the relative percentage of each isomer, separation of the two species was required.

Attempts were initially made to separate the two geometric isomers synthesised using cation-exchange chromatography on Sephadex C25 as has been previously described by Keene and co-workers, eluting with aqueous sodium toluene-4-sulfonate

Table 1 Selected bond lengths (Å) and angles (°) for $[Ru(L^1)_3](PF_6)_2$

Ru(1)–N(1)A	2.055(4)	Ru(1)–N(1)2A	2.063(4)
Ru(1)–N(1)B	2.048(4)	Ru(1)–N(1)2B	2.059(4)
Ru(1)–N(1)C	2.074(5)	Ru(1)–N(1)2C	2.052(4)
N(1)A–Ru(1)–N(1)B	172.24(18)	N(1)B–Ru(1)–N(1)2C	88.66(16)
N(1)A–Ru(1)–N(1)C	91.91(18)	N(1)C–Ru(1)–N(1)2A	97.53(18)
N(1)A–Ru(1)–N(1)2A	79.06(19)	N(1)C–Ru(1)–N(1)2B	170.86(17)
N(1)A–Ru(1)–N(1)2B	94.64(17)	N(1)C–Ru(1)–N(1)2C	78.94(18)
N(1)A–Ru(1)–N(1)2C	96.31(17)	N(1)2A–Ru(1)–N(1)2B	89.98(16)
N(1)B–Ru(1)–N(1)C	94.90(17)	N(1)2A–Ru(1)–N(1)2B	174.15(19)
N(1)B–Ru(1)–N(1)2A	96.33(18)	N(1)2B–Ru(1)–N(1)2C	93.98(19)
N(1)B–Ru(1)–N(1)2B	79.03(17)		

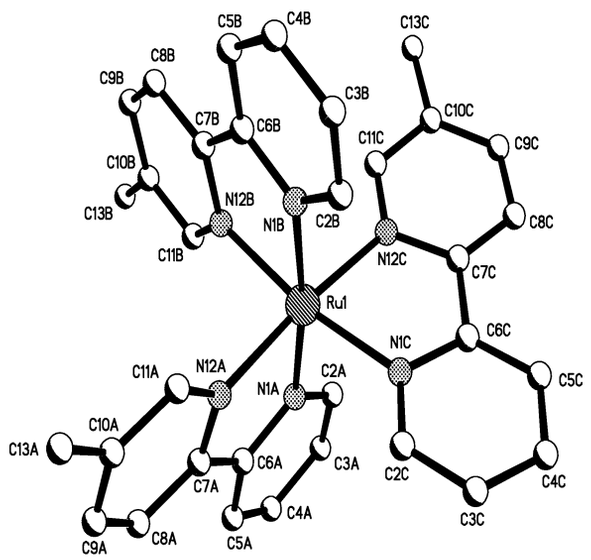


Fig. 2 Molecular connectivity and labeling scheme for the major conformation of the cation. The hydrogen atoms and anions have been removed for clarity.

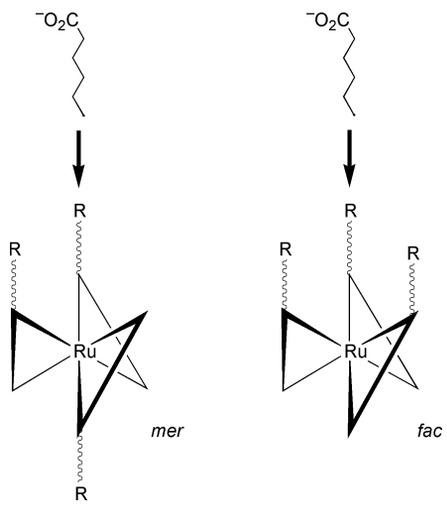


Fig. 3 Schematic illustration of the possible difference in hydrophobic interactions between the complexes $[Ru(L^{1\text{–}5})_3]^{2+}$ with hexanoate.

solution (0.15 mol dm^{-3}).[31,32] While there was clear indication that the complexes of ligands L^1 and L^2 were separable, an effective column length of over 8 m was required. As a consequence aqueous sodium hexanoate (0.125 mol dm^{-3}) was considered, having been shown previously to have a suitable hydrophobic interaction with polypyridine complexes of ruthenium(II).[31] With ligands L^1 and L^2 the effective column length required to separate the isomers was reduced to 5 and 3 m respectively. While ligands L^3 and L^4 were both separated rapidly upon the column within 2 m.

In each case the isomer travelling fastest on the cation-exchange column was tentatively assigned as the *fac*-isomer (being expected in smaller quantities), as the colour of the band on the column was considerably less intense than the following product and consequently less concentrated. With ligands L^1 and L^2, the approximate ratio of products obtained from the column were three parts *mer* to one of *fac*. However, using the more sterically demanding ligands L^3 and L^4, the ratio was significantly increased, while none of the *fac*- isomer of ligand L^5 was observed.

With these aliphatic isomers, a greater differentiation of the two isomeric forms is observed with the hexanoate rather than the toluene-4-sulfonate anion. Since the *fac*-isomer had a greater rate of passage through the column, the association with the anion must be greater, reducing the effective charge on the complex, when compared to the *mer*-isomer. This can be justified by a simple consideration of the structure of the complexes (Fig. 3). In the *fac*-isomers, the three hydrophobic groups are all aligned along the three-fold axis of the pseudo-octahedral structure. As a consequence it provides a hydrophobic pocket to receive the aliphatic tail of the hexanoate. In the *mer*-isomer, the three functional groups are not aligned as well, with two of the functional groups diametrically opposed (*trans*) to each other, and so the hydrophobic cavity is not as pronounced, hence provides a poorer interaction with the aliphatic anion. The toluene-4-sulfonate, allows for additional π-stacking interactions with the pyridine rings, which negates the interaction with the three functional groups, and so the differentiation of the two geometric forms is much less pronounced.

The ruthenium(II) complex of ester ligand L^6 proved a little more difficult to separate. While resolution of two isomers was achieved using sodium hexanoate after 6 m, the isolation of the products from the eluent mixture proved to be impossible. It is assumed that either the hexanoate associates too well with the cation to allow exchange of the anion (such as PF_6^-, or BPh_4^-) from the aqueous solution preventing both precipitation and extraction into methylene chloride. Alternatively, it is possible that the basicity of the eluent has facilitated deesterification and the zwitterionic complex can not be extracted or precipitated from aqueous solution. Using aqueous sodium toluene-4-sulfonate solution (0.15 mol dm^{-3}), significant broadening of the band on the column was observed. However, after an effective 10 m column length complete separation had not been achieved. By systematically removing the front and tail of the band, two different products were isolated. The slower moving fraction was subsequently identified as the *fac*-isomer, contrary to the results observed with the aliphatic isomers.

The separation of the ester functionalised complex L^6 appeared to be contrary to the above hypothesis, however the carboxyl groups do not provide a good hydrophobic cavity, and so the differentiation of the two geometric forms must rely upon a different structural feature. The preliminary studies indicate that the *mer*-isomer has the most favourable interactions with both toluene-4-sulfonate and hexanoate anions. Further studies are required to rationalise the nature of these.

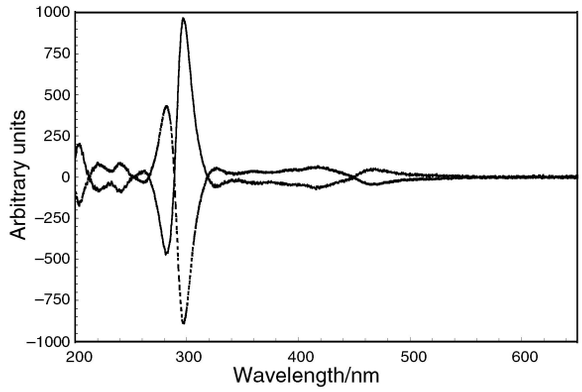


Fig. 4 Circular dichroism spectrum of Λ- (——) and Δ-$[Ru(L^3)_3]^{2+}$ (----).

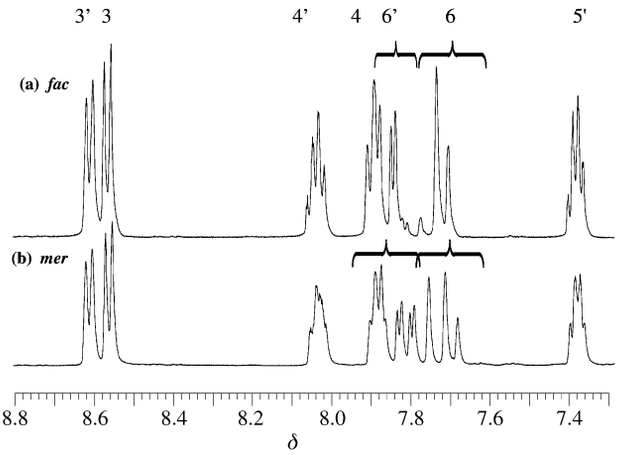


Fig. 5 ^{1}H NMR spectra (500 MHz, 25 °C, d_6-acetone) of (a) *fac*- and (b) *mer*-$[Ru(L^1)_3](PF_6)_2$.

The fraction of $[Ru(L^3)_3]^{2+}$, identified as the *mer*-isomer, was repeatably passed down the cation-exchange column eluted with 0.125 mol dm^{-3} sodium hexanoate over the period of several days. Once an effective column length of 12 m had been achieved, two resolved bands of equal intensity were observed. Preliminary ^{1}H NMR studies indicated that the two products were identical. By comparison of the two circular dichroism spectra of the two fractions, the isomer has separated into the two enantiomers (Fig. 4). Since the anion is achiral, the chirality of the polydextrose Sephadex support must be responsible for the chiral induction. While similar behaviour has been observed with dinuclear species eluted with sodium toluene-4-sulfonate,[32] this is the first instance where it has been observed using sodium hexanoate with a mononuclear species.

While the use of cation-exchange chromatography on a Sephadex support for the separation of geometric isomers of thermodynamically stable transition metal bipyridine complexes appears to be possible, the efficacy of the procedure can be reduced due to the inherent chirality of the support itself. After repeated passage down the column, the enantiomeric resolution will shadow the desired delicate geometric separation and as in the case of $[Ru(L^6)_3]^{2+}$ could potentially prevent complete separation of the two geometric isomers.

^{1}H NMR studies

The analysis of the ^{1}H NMR spectra of the *fac*-isomers is relatively straightforward arising from the C_3 symmetry (Fig. 1). As a consequence the three ligands are all equivalent giving rise to seven aromatic signals. The *mer*-isomers on the other hand possess C_1 symmetry, with all three of the ligands inequivalent, potentially giving rise to 21 aromatic signals. However, due to the similarity of the signals many of these occupy very similar regions of the spectrum. By the use of ^{1}H correlation spectroscopy (COSY), signals were isolated into individual ring systems (Table 2).

The complex *fac*-$[Ru(L^1)_3](PF_6)_2$ [Fig. 5(a)] shows the ^{1}H NMR spectrum expected, with seven aromatic signals. A point worthy of note however is that H^6 was not the expected tight doublet, but had a strong coupling to H^4, of 20 Hz. Similar behaviour was also observed upon the unfunctionalised pyridine ring, with an unusually large coupling between $H^{6'}$ and $H^{4'}$. These couplings appear to be solvent independent, being observed in deuterated acetone, acetonitrile and DMSO. An analogous coupling was also present in the complex of L^2 and to a lesser extent with L^3. As the size of the aliphatic functionality increased to that of L^4 the effect disappeared, and was not present in the ester functionalised complex *fac*-$[Ru(L^6)_3](PF_6)_2$.

The complex *mer*-$[Ru(L^1)_3](PF_6)_2$ [Fig. 5(b)] has a remarkably similar spectrum to that of the *fac*-isomer. Only the signals assigned as H^6 and $H^{6'}$ showed any significant difference in their chemical shifts as a consequence of slight ring current effects depending on whether they are positioned over a methyl or an unsubstituted ring. In the *fac*-isomer, all three of the H^6 protons are positioned over the methylpyridine rings, causing a stronger upfield position. While the $H^{6'}$ are all positioned over unsubstituted pyridine systems, causing a relative downfield position. With the *mer*-isomer, one H^6 is over a methylpyridine ring, giving a signal similar to that of the *fac*-isomer (Fig. 1), while two are over unsubstituted pyridine systems giving rise to a larger signal downfield of H^6. A similar argument can be given to account for the order of the signals of $H^{6'}$ and the three signals for the methyl groups. The system is however made more complex by exceptional couplings between H^6 and H^4, and $H^{6'}$ and $H^{4'}$, as observed in the *fac*-isomer.

The spectra for the complexes *mer*-$[Ru(L^{2\text{–}5})_3](PF_6)_2$ demonstrate similar behaviour to that of *mer*-$[Ru(L^1)_3](PF_6)_2$, however, as the aliphatic chain length increases, the splitting between the three sets of signals for each ligand system becomes more apparent. In the complex of L^2, the H^3 and H^4 are partially resolved, while ligand L^5 has 21 independent identifiable aromatic signals. H^3 and $H^{3'}$ show significant differences in their relative position, and yet do not experience ring currents of adjacent aromatic groups. As a consequence, the σ-electron donation from the aliphatic groups must play a significant role in the relative position of all of the aromatic signals. The three bipyridine ligands are identical, only their relative orientation differs, with respect to the groups situated *trans* to each coordinated pyridine group through the ruthenium(II) centre. The electron donating groups increase the Lewis basicity of the pyridine groups. This has a consequence upon the other coordinated groups giving rise to a difference in the chemical shifts observed. While the connectivity of the three ring systems was established using ^{1}H-COSY techniques, analysis of the relative peak position is unduly complex and identification of individual ring systems was not achieved.

fac-$[Ru(L^6)_3](PF_6)_2$ demonstrates a significantly different ^{1}H NMR spectrum [Fig. 6(a)] to that of the other ligands considered. As a consequence of the electron-withdrawing nature of the ester substituent, the functionalised pyridine ring has chemical shifts significantly downfield of those of the other complexes examined, with a more typical coupling between H^6 and H^4 observed (1.4 Hz).

mer-$[Ru(L^6)_3](PF_6)_2$ has a spectrum with great similarity to that of the analogous *fac*-isomer. However, the three sets of ligand signals offer a significant difference in their chemical shifts. In particular the $H^{5'}$ signals are completely resolved into three sets of multiplets [Fig. 6(b)]. This large difference in the three ligand environments is not only a consequence of the strong intraligand electronic effects developed from the attached carbonyl function, but also the interligand effects of the carbonyl group to orthogonal ring systems. The strength of this latter effect appears to be considerable, by comparison

Table 2 ^{1}H NMR chemical shifts (δ_H) (and coupling constants J/Hz) for *fac*- and *mer*-$[Ru(L)_3]^{2+}$ (L^1–L^6)

Complex	H^3	H^4	H^6	$H^{3'}$	$H^{4'}$	$H^{5'}$	$H^{6'}$	CH_2	$CH_{2/1}$	CH_3
fac-$[Ru(L^1)_3]^{2+}$	8.55 (8.3)	7.86 (5.5, 20.4)	7.71 (15.2)	8.59 (8.1)	8.03 (6.9, 13.5)	7.39 (6.0, 12.0)	7.88 (8.3)			2.10
fac-$[Ru(L^2)_3]^{2+}$	8.59 (8.4)	7.90 m	7.69 (20.2)	8.62 (8.0)	8.04 (7.4, 7.5)	7.40 (5.9, 7.3)	7.90 m		2.44 (7.5)	0.95 (7.5)
fac-$[Ru(L^3)_3]^{2+}$	8.62 (8.1)	7.92 (8.1)	7.67	8.59 (8.3)	8.05 (7.6, 8.0)	7.40 5.8, 7.4)	7.89 (5.5)	2.46 (7.30)	1.35 m	0.60 (6.9)
fac-$[Ru(L^4)_3]^{2+}$	8.61 (8.6)	7.94 (8.4)	7.60	8.63 (8.5)	8.06 (7.9, 7.7)	7.42 (5.8, 7.5)	7.91 (5.5)	2.29 (7.2)	1.63 m	0.65, 0.61 (6.7/6.7)
fac-$[Ru(L^6)_3]^{2+}$	8.87 (8.6)	8.54 (8.5)	8.32	8.82 (8.1)	8.15 (7.8, 7.6)	7.52 (6.0, 7.7)	8.00 (5.6)			3.68
mer-$[Ru(L^1)_3]^{2+}$	8.69 (8.4)	8.04 (8.1)	7.85[a]	8.75 (8.2)	8.18 m	7.53 m	7.95 (5.6)			2.10
	8.69 (8.4)	8.04 (8.1)	7.87[a]	8.75 (8.2)	8.18 m	7.53 m	7.98 (5.0)			2.09[b]
	8.69 (8.4)	8.04 (8.1)	7.91[a]	8.75 (8.2)	8.18 m	7.53 m	8.02 (6.0)			2.09[b]
mer-$[Ru(L^2)_3]^{2+}$	8.74 (8.4)	8.09 m	7.80[a]	8.76 (8.1)	8.21 m	7.57 m	8.02 (5.6)		2.45 (7.5)	0.93 (7.5)
	8.73 (8.3)	8.09 m	7.84[a]	8.76 (8.1)	8.19 m	7.56 m	8.02 (5.6)		2.45 (7.5)	0.91 (7.5)
	8.74 (8.4)	8.10 m	7.87[a]	8.76 (8.1)	8.18 m	7.55 m	8.04 (5.6)		2.45 (7.5)	0.91 (7.5)
mer-$[Ru(L^3)_3]^{2+}$	8.60 (8.2)	7.91 (7.5)	7.68	8.64 (8.1)	8.06 m	7.40 m	7.89 (5.0)	2.39	1.35	0.59[b] (7.2)
	8.59 (8.3)	7.91 (7.5)	7.66	8.64 (8.1)	8.06 m	7.40 m	7.89 (5.0)	2.39	1.35	0.59[b] (7.2)
	8.60 (8.2)	7.93 (7.5)	7.68	8.64 (8.1)	8.06 m	7.41 m	7.91 (4.9)	2.39	1.35	0.59[b] (7.2)
mer-$[Ru(L^4)_3]^{2+}$	8.67 (8.0)	7.99 (8.3)	7.60	8.73 (8.1)	8.15 m	7.50 m	7.90 (5.3)	2.33 m	1.57 m	0.60, 0.50 (m, 6.6)
	8.66 (8.3)	7.98 (8.5)	7.64	8.73 (8.1)	8.15 m	7.50 m	7.97 (5.2)	2.33 m	1.57 m	0.60, 0.50 (m, 6.6)
	8.69 (8.1)	7.99 (8.3)	7.71	8.71 (8.0)	8.15 m	7.49 m	8.03 (5.4)	2.26 m	1.57 m	0.60, 0.48 (m, 6.6)
mer-$[Ru(L^5)_3]^{2+}$	8.61 (7.7)	7.89 (7.8)	7.54	8.66 (8.1)	8.06 m	7.42 m	7.90 (5.6)		2.10	0.54
	8.60 (7.7)	7.87 (7.8)	7.68	8.66 (8.1)	8.06 m	7.42 m	7.90 (5.6)		2.10	0.52
	8.61 (7.7)	7.89 (7.8)	7.73	8.64 (7.8)	8.06 m	7.42 m	7.96 (5.4)		2.07	0.51
mer-$[Ru(L^6)_3]^{2+}$	8.85 (8.4)	8.49 (8.5)	8.21	8.85 (8.4)	8.25 (7.8, 8.0)	7.60 (5.6, 7.7)	8.11 (5.6)			3.69
	8.85 (8.4)	8.49 (8.5)	8.25	8.84 (8.5)	8.20 (7.6, 7.9)	7.55 (5.6, 7.7)	8.17 (5.5)			3.68
	8.86 (8.6)	8.55 (8.5)	8.26	8.82 (8.0)	8.15 (7.8, 8.0)	7.49 (5.6, 7.6)	8.09 (5.6)			3.67

[a] Possibly as a doublet, of 10–20 Hz, but three peaks overlying each other prevents isolation. [b] The peak is composed of several resolved doublets, of similar frequency.

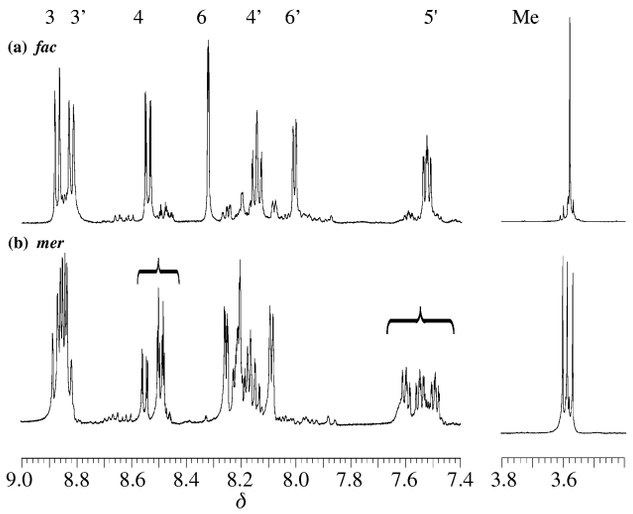


Fig. 6 ^{1}H NMR spectra (500 MHz, 25 °C, d_6-acetone) of (a) *fac*- and (b) *mer*-$[Ru(L^6)_3](PF_6)_2$.

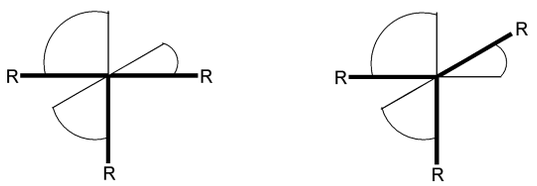


Fig. 7 Possible synthetic route to new supramolecular building blocks.

of the spectrum of the *mer*-isomer to that of the *fac*-isomer. As with the previous systems, a consideration of the relative position of the H^6 and $H^{6'}$ signals is instructive. In the *fac*-isomer, the signal for H^6 is downfield relative to all of the H^6 signals of the *mer*-complex. In the former, the functionalised ring experiences a cooperative effect of the three ester moieties acting solely upon each other. Due to the electronegativity of the oxygen atom, the proton signals for these three rings are all deshielded. In the *mer*-isomer, one functionalised ring is adjacent to a carbonyl function, while the other two are adjacent to unsubstituted pyridine systems. As a result, the deshielding effect on the rings with appended ester groups is less pronounced. A similar set of arguments are possible to explain the reason for the upfield shift demonstrated by the signal for $H^{6'}$.

The potential construction of supramolecular building blocks

As discussed previously, polypyridine complexes of ruthenium(II) have been widely used to add photophysical function in supramolecular assemblies. In order to ensure that structural integrity can be maintained, careful consideration of the individual monomeric species is required. From this study, it is apparent that geometric isomers can be separated into the two forms. In theory, the two discussed isomers can potentially be viewed as rigid building blocks (Fig. 7), bringing a controlled architecture to supramolecular structures such as dendrimers. The *mer*-isomer is effectively T-shaped while the *fac*-isomer with its three-fold symmetry and three orthogonal functional groups can be viewed as a corner piece to a molecular cube, or an end unit to a helical structure. Further, with each unit being chiral and enantiomeric separation using cation-exchange methods discussed previously, further structural control can be envisaged in the development of interesting new materials.

To create larger assemblies, suitable groups to facilitate further functionalisation are required. Simple attempts to prepare ruthenium complexes with the ligands 5′-bromomethyl-2,2′-bipyridine and 5-(2,2′-bipyridine)carbaldehyde were initially considered, however these ligands proved to be impossible to coordinate to the transition metal. To overcome this problem, the ligand L^6 was successfully coordinated to the metal centre and separation of the *mer*/*fac*-isomers attempted. In order to demonstrate further functionality can be achieved, the separated complexes were deesterified under basic conditions to yield the acid. Unfortunately, the improved water solubility has as yet prevented characterisation, although it has been assumed that the metal centre stereochemistry is maintained. Similarly, the resolved esters were reacted in thionyl chloride to give the tris-acid chloride complex. While this species appeared to readily react with several amines, insufficient quantities of the products were isolated to facilitate characterisation. Because of the problems of isomeric separation of the ester-functionalised system $[Ru(L^6)_3]^{2+}$, it is apparent that this preparative route is not sufficient to allow appreciable quantities of these two potential new building-blocks to be prepared and explored. Alternative synthetic approaches to overcome this problem are currently being explored.

Conclusions

The isolation of several new *fac*- and *mer*-isomers of 5-functionalised-2,2′-bipyridine complexes has been achieved using cation-exchange chromatography, using either sodium hexanoate or toluene-4-sulfonate. However, the isolation of the two forms of the complexes appears to be hindered, especially in the species taking a longer passage down the column, by the simultaneous chiral resolution induced by the polydextrose support. As expected, the increasing steric bulk of the appended group has a significant effect on the ratio of the *fac* to *mer* isomers. With an appended butyl group, only the *mer* isomer was isolated. As a consequence a planned synthesis of this isomer can be considered by the use of large bulky groups. However, due to the statistical and steric considerations a route to the *fac*-isomer using this method does not appear to be practical as the separation of a mixture of products appears to be extremely inefficient.

Experimental

Instrumentation

^{1}H and ^{13}C NMR spectra were recorded on a Brüker DPX 300 and DRX500 using the solvent as an internal reference, electronic spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer, circular dichroism (CD) spectra were recorded on a Jasco J-720 spectropolarimeter and normalised to the electronic spectra. Microanalyses and EI mass spectroscopy were performed by A.S.E.P., The School of Chemistry, The Queen′s University of Belfast. The LSIMS(FAB) and mass spectroscopy was performed by the EPSRC mass spectrometry Service, The University of Wales, Swansea.

Materials

Lithium diisopropylamide 2.0 M in cyclohexane (LDA; Aldrich) and ruthenium trichloride hydrate (Johnson Matthey) were used as received without further purification. Laboratory grade solvents were used unless otherwise specified. Tetrahydrofuran and diethylether (BDH) were distilled under N_2 from potassium and sodium respectively with benzophenone as an indicator. SP-Sephadex C-25 (Aldrich) and Sephadex LH20 (Fluka) were used for chromatographic purification of the metal complexes. 5-Methyl-2,2′-bipyridine (L^1) was prepared *via* a Kröhnke synthesis from 2-acetylpyridine (99+%; Aldrich).[33]

Ligand synthesis

The aliphatically substituted ligands L^2–L^5 were synthesised following a modified literature method.[26] In a typical reaction a solution of 5-methyl-2,2′-bipyridine (0.500 g, 2.94 mmol) in dry THF (50 cm^3) (or diethylether) was cooled to below −40 °C

under nitrogen and a large excess of LDA (6.0 cm^3, 12 mmol) added over 30 min. After stirring at −40 °C for 3 h, a large excess of the appropriate bromoalkane (16 mmol) (or methyl-iodide in the preparation of L^2) was added in dry THF (20 cm^3) and the reaction allowed to slowly warm to room temperature while stirring overnight. The reaction was quenched with water (1–2 cm^3) and the solvent removed *in vacuo*. After the addition of a saturated aqueous solution of sodium hydrogen carbonate (10 cm^3), the mixture was extracted with dichloromethane (3 × 30 cm^3). The organic phase was dried over magnesium sulfate and filtered. Following the removal of the solvent, the brown residue was purified firstly by column chromatography on silica gel with dichloromethane–methanol (50 : 1), collecting the first band as a yellow oil.

5-Ethyl-2,2′-bipyridine (L^2). Yield 86% (Found: C, 75.60; H, 6.83; N, 13.17. $C_{12}H_{12}N_2 \cdot 1/3H_2O$ requires C, 75.76; H, 6.71; N, 14.72%), EIMS: *m*/*z* 184 [M^+]. NMR ($CDCl_3$, 300 MHz): ^{1}H, δ 8.67 (1 H, d, *J* 4.2 Hz, H$^{6'}$), 8.53 (1 H, s, H^6), 8.37 (1 H, d, *J* 8.0 Hz, H$^{3'}$), 8.32 (1 H, d, *J* 8.1 Hz, H^3), 7.79 (1 H, dd, *J* 7.8, 7.8 Hz, H$^{4'}$), 7.65 (1 H, d, *J*.8.1 Hz, H^4), 7.17 (1 H, d, *J* 4.7, 7.3 Hz, H$^{5'}$), 2.74 (2 H, q, *J* 7.6 Hz, CH_2), 1.29 (3 H, t, *J* 7.6 Hz, CH_3); ^{13}C, δ 156.1 (Cq), 153.9 (Cq), 149.1 (CH), 148.9 (CH), 139.5 (Cq), 136.8 (CH), 136.2 (CH), 123.5 (CH), 120.8 (CH), 120.7 (CH), 25.9 (CH_2), 15.2 (CH_3).

5-Propyl-2,2′-bipyridine (L^3). Yield 84% (Found: C, 77.89; H, 7.47; N, 13.09. $C_{13}H_{14}N_2 \cdot 1/6H_2O$ requires C, 77.58; H, 7.18; N, 13.92%). EIMS: *m*/*z* 198 [M^+]. NMR ($CDCl_3$, 300 MHz): ^{1}H, δ 8.67 (1 H, d, *J* 4.2 Hz, H$^{6'}$), 8.50 (1 H, s, H^6), 8.36 (1 H, d, *J* 8.0 Hz, H$^{3'}$), 8.31 (1 H, d, *J* 8.1 Hz, H^3), 7.80 (1 H, dd, *J* 7.6, 7.8 Hz, H$^{4'}$), 7.63 (1 H, d, *J*.8.1 Hz, H^4), 7.23 (1 H, d, *J* 4.8, 7.5 Hz, H$^{5'}$), 2.65 (2 H, q, *J* 7.6 Hz, CH_2), 1.66 (2 H, m, CH_2) 0.97 (3 H, t, *J* 7.4 Hz, CH_3); ^{13}C, δ 155.3 (Cq), 153.1 (Cq), 148.3 (CH), 148.1 (CH), 137.0 (Cq), 135.8 (2 × CH), 127.2 (CH), 122.4 (CH), 119.7 (CH), 33.8 (CH_2), 22.9 (CH_2), 18.1 (CH_3).

5-(2-Methylpropyl)-2,2′-bipyridine (L^4). Yield 60% (Found: C, 77.37; H, 7.60; N, 12.79. $C_{14}H_{16}N_2 \cdot 1/4H_2O$ requires C, 77.56; H, 7.67; N, 12.92%). EIMS: *m*/*z* 212 [M^+]. NMR ($CDCl_3$, 300 MHz): ^{1}H, δ 8.62 (1 H, d, *J* 5.0 Hz, H$^{6'}$), 8.45 (1 H, s, H^6), 8.31 (1 H, d, *J* 7.7 Hz, H$^{3'}$), 8.22 (1 H, d, *J* 8.0 Hz, H^3), 7.78 (1 H, dd, *J* 7.5, 7.5 Hz, H$^{4'}$), 7.41 (1 H, d, *J*.8.0 Hz, H^4), 7.24 (1 H, d, *J* 5.0, 7.8 Hz, H$^{5'}$), 2.45 (2 H, d, *J* 7.2 Hz, CH_2), 1.84 (1 H, m, CH) 0.85 (6 H, d, *J* 6.6 Hz, CH_3); ^{13}C, δ 156.6 (Cq), 154.2 (Cq), 150.2 (CH), 149.5 (CH), 137.8 (CH), 137.4 (Cq), 137.2 (CH), 123.7 (CH), 121.1 (CH), 120.9 (CH), 42.5 (CH_2), 30.4 (CH), 22.6 (CH_3).

5-(2,2-Dimethylpropyl)-2,2′-bipyridine (L^5). Yield 50% (Found: C, 78.21; H, 8.18; N, 12.38. $C_{15}H_{18}N_2 \cdot 1/5H_2O$ requires C, 78.36; H, 8.07; N, 12.18%). EIMS: *m*/*z* 226 [M^+]. NMR ($CDCl_3$, 300 MHz): ^{1}H, δ 8.67 (1 H, d, *J* 4.2 Hz, H$^{6'}$), 8.46 (1 H, s, H^6), 8.37 (1 H, d, *J* 8.0 Hz, H$^{3'}$), 8.30 (1 H, d, *J* 8.1 Hz, H^3), 7.80 (1 H, dd, *J* 7.6, 7.8 Hz, H$^{4'}$), 7.59 (1 H, d, *J*.8.1 Hz, H^4), 7.28 (1 H, d, *J* 5.3, 7.8 Hz, H$^{5'}$), 2.55 (2 H, s, CH_2), 0.94 (9 H, s, CH_3); ^{13}C, δ 155.2 (Cq), 152.8 (Cq), 149.7 (CH), 148.1 (CH), 141.5 (Cq), 137.6 (CH), 135.9 (CH), 122.4 (CH), 119.8 (CH), 119.1 (CH), 46.0 (CH_2), 29.9 (Cq), 28.2 (CH_3).

5-Carboxy-2,2′-bipyridine. 5-Methyl-2,2′-bipyridine (8.75 g, 51.45 mmol) was mixed with water (60 ml) and 35 g of $KMnO_4$ was added in 7 portions over 7 h, heated initially at 70 °C for 3 h and then at 90 °C for the subsequent 4 h. The mixture was filtered hot through Celite® and washed with hot water (3 × 50 ml). The pale pink solution was then slowly acidified (dropwise) with 1 M HCl to obtain a while precipitate at pH *ca.* 4–5. The precipitate was collected by filtration and dried *in vacuo*. Further adjustment of the pH allowed second and third fractions to be obtained. Yield 4.20 g, 38%. Characterisation in keeping with published results. Melting point 217–220 °C.[34]

5-(Carbomethoxy)-2,2′-bipyridine (L^6). 5-Carboxy-2,2′-bipyridine (0.20 g, 1.0 mmol) was refluxed in thionyl chloride (30 ml) for 3 h. The thionyl chloride was removed under reduced pressure and the yellow solid dried *in vacuo* for 3 h. This was dissolved in dry THF (30 ml) to which was added triethylamine (2 ml) followed by methanol dried over molecular sieves (5 ml) and stirred for 16 h. The solvent was removed and the solid suspended in water (50 ml) and extracted into dichloromethane (3 × 30 ml). The organic layer was dried over magnesium sulfate and the solvent removed *in vacuo* to give a white solid. Yield 0.202 g, 94% (Found: C, 62.60; H, 4.66; N, 11.83. $C_{12}H_{10}N_2O_2 \cdot H_2O$ requires C, 62.06; H, 5.21; N, 12.06%). EIMS: *m*/*z* 214 [M]$^+$, 183 [M − OMe]$^+$, 155 [M−CO_2Me]$^+$, NMR ($CDCl_3$, 300 MHz): ^{1}H, δ 9.27 (1 H, s, H^6), 8.72 (1 H, d, *J* 4.4 Hz, H$^{6'}$), 8.51 (1 H, d, *J* 8.1 Hz, H^3), 8.48 (1 H, d, *J* 8.1 Hz, H$^{3'}$), 8.41 (1 H, d, *J*.8.2 Hz, H^4), 7.85 (1 H, dd, *J* 7.8, 7.8 Hz, H$^{4'}$), 7.36 (1 H, d, *J* 4.8,7.8 Hz, H$^{5'}$), 3.98 (2 H, s, CH_3), ^{13}C, δ 164.8 (CO_2), 158.5 (Cq), 154.0 (Cq), 149.5 (CH), 148.4 (CH), 137.0 (CH), 136.1 (CH), 124.6 (Cq), 123.5 (CH), 120.9 (CH), 119.5 (CH).

Complex syntheses

The ruthenium(II) complexes of ligands L^1–L^6 were synthesised by similar reactions in either DMF or ethanol. In a typical reaction a solution of 5-ethyl-2,2′-bipyridine (120 mg, 0.65 mmol) and $RuCl_3 \cdot xH_2O$ (38.6 mg, 0.15 mmol) were dissolved in DMF (30 ml) and heated at 100 °C for 16 h. The mixture was cooled, diluted with water (150 ml) and added to SP Sephadex® C-25 cation-exchange support. Once the complex was entirely loaded on the product was eluted with 0.3 M aqueous sodium chloride solution, collecting the orange–red fraction. The product was reclaimed from the brine solution, by the addition of saturated aqueous ammonium hexafluorophosphate solution and subsequent extraction with dichloromethane (5 × 50 ml) and dried *in vacuo*. Yield 86.7 mg. (Samples for microanalysis were further crystallized from acetone–water and passed down an Sephadex® LH20 column, eluted with a 50% methanol–acetone mixture.)

[Ru(L^1)$_3$](PF$_6$)$_2$. Yield 62% (prepared in ethanol) [Found: C, 45.53; H, 3.98; N, 7.83. $C_{33}H_{30}N_6RuP_2F_{12} \cdot 2(CH_3)_2CO$ requires C, 46.02; H, 4.16; N, 8.26%]. LSIMS: *m*/*z* 757 [M − PF_6]$^+$, 616 [MH − 2PF_6]$^+$. UV–VIS absorption (MeCN): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 253 (29600), 289 (80400), 448 (12000).

[Ru(L^2)$_3$](PF$_6$). Yield 75% (prepared in DMF) (Found: C, 45.84; H, 3.92; N, 8.54. $C_{36}H_{36}N_6RuP_2F_{12}$ requires C, 45.82; H, 3.92; N, 8.91%). LSIMS: *m*/*z* 799 [M − PF_6]$^+$, 654 [MH − 2PF_6]$^+$. UV–VIS absorption (MeCN): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 252 (31700), 290 (88000), 447 (12600).

[Ru(L^3)$_3$](PF$_6$). Yield 65% (prepared in DMF) (Found: C, 47.70; H, 4.62; N, 7.75. $C_{39}H_{42}N_6RuP_2F_{12}$ requires C, 47.52; H, 4.29; N, 8.54%). LSIMS: *m*/*z* 841 [M − PF_6]$^+$, 695 [MH − 2PF_6]$^+$. UV–VIS absorption (MeCN): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 252 (29300), 290 (84200), 447 (12700).

[Ru(L^4)$_3$](PF$_6$). Yield 94% (prepared in DMF) (Found: C, 47.40; H, 4.48; N, 7.24. $C_{42}H_{48}N_6RuP_2F_{12} \cdot 2H_2O$ requires C, 47.42; H, 4.92; N, 7.90%). LSIMS: *m*/*z* 883 [M − PF_6]$^+$, 738 [MH − 2PF_6]$^+$. UV–VIS absorption (MeCN): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 252 (30900), 290 (91300), 446 (14100).

$[Ru(L^5)_3](PF_6)$. Yield 54% (prepared in ethanol) (Found: C, 48.38; H, 4.84; N, 8.17. $C_{45}H_{54}N_6RuP_2F_{12}\cdot\frac{1}{4}NH_4PF_6$ requires C, 48.66; H, 4.99; N, 7.88%). LSIMS: *m*/*z* 925 $[M - PF_6]^+$, 780 $[MH - 2PF_6]^+$. UV–VIS absorption (MeCN): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 253 (29600), 290 (88600), 447 (13200).

$[Ru(L^6)_3](PF_6)$. Yield 62% (prepared in ethanol) (Found: C, 40.91; H, 2.97; N, 7.80. $C_{36}H_{30}N_6O_6RuP_2F_{12}\cdot H_2O$ requires C, 41.11; H, 3.07; N, 7.99%). LSIMS: *m*/*z* 888 $[M - PF_6]^+$, 873 $[M - (PF_6 + CH_3)]^+$, 742 $[MH - 2PF_6]^+$, 729 $[MH - (2PF_6 + CH_3)]^+$. UV–VIS absorption (MeCN) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 251 (30500), 290 (94800), 477 (11300).

Separation of *mer*/*fac*-isomers. The mixture of the geometric isomers (typically 70–100 mg) were converted to the chloride salt by metathesis with LiCl in acetone solution and the solid collected by filtration on Celite®. The red solid was extracted with water and the resulting solution introduced onto a SP Sephadex C-25 column (dimensions 26 mm × 1.6 m). Eluent flow was regulated by use of a peristaltic pump. On elution of 0.125 mol dm^{-3} sodium hexanoate (0.15 mol dm^{-3} sodium toluene-4-sulfonate with ligand L^6), the intense red band was typically repeatedly passed through the column until separation was clearly observed. The material was collected from the column and a saturated aqueous solution of NH_4PF_6 added to the resulting orange solution and extracted with dichloromethane (3 × 20 cm^3). The solvent was removed under reduced pressure. Excess inorganic salts were removed by the passage through a short Sephadex LH20 column (eluted with 50% methanol–acetone) and the product isolated by removal of the solvent and dried *in vacuo*. ^{1}H NMR data is given in Table 2.

X-Ray structural analysis

Data were collected a Bruker-AXS SMART diffractometer using the SAINT-NT software [35] with graphite monochromated Mo-Kα radiation. A crystal was mounted on to the diffractometer at low temperature under dinitrogen at *ca.* 120 K. Crystal stability was monitored and there were no significant variations (< ± 2%). Cell parameters were obtained from 400 accurately centred reflections in range 3–50°. ω–θ scans were employed for data collection and Lorentz and polarisation corrections and empirical absorption corrections were applied.

The structure was solved using direct methods and refined with the SHELXTL version 5.0 and SHELXL-98 program packages [36] and the non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen-atom positions were added at idealised positions and a riding model with fixed thermal parameters ($U_{ij} = 1.2U_{eq}$ for the atom to which they are bonded ($1.5U_{eq}$ for CH_3)), was used for subsequent refinements. The function minimised was $\Sigma[w(|F_o|^2 - |F_c|^2)]$ with reflection weights $w^{-1} = [\sigma^2|F_o|^2 + (g_1P)^2 + (g_2P)]$ where $P = (\text{max. } |F_o|^2 + 2|F_c|^2)/3$.

Crystal data for $[Ru(L^1)_3](PF_6)_2$. $M = 901.64$, monoclinic, space group $P2_1$, $a = 10.5990(15)$, $b = 13.5789(18)$, $c = 13.3087(18)$ Å, $\beta = 105.815(3)°$, $U = 1842.9(4)$ Å^3, $Z = 2$, $\mu = 0.607$ mm^{-1}, $R_{int} = 0.0704$, transmission range (max, min.) = 0.848, 0.759. A total of 14232 reflections were measured for the angle range $3 < 2\theta < 57°$ and 8088 independent reflections were used in the refinement. The final parameters were $wR2 = 0.1328$ and $R1 = 0.0509$ [$I > 2\sigma^1$].

CCDC reference number 166368.

See http://www.rsc.org/suppdata/dt/b1/b104365j/ for crystallographic data in CIF or other electronic format.

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