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The Unexpected Preference for the *fac*-Isomer with the Tris(5-ester-substituted-2,2′-bipyridine) Complexes of Ruthenium(II)

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The synthesis of a number of new 2,2′-bipyridine ligands, functionalized with bulky ester side groups, is reported (L2–L8). Their reaction with $[Ru(DMSO)_4Cl_2]$ gives rise to tris-chelate ruthenium(II) metal complexes which show an unusually high proportion of the *fac*-isomer, as judged by ^1H NMR following conversion to the ruthenium(II) complex of 2,2′-bipyridine-5-carboxylic acid methyl ester (L1). The initial reaction appears to have thermodynamic control with the steric bulk of the ligands causing the third ligand to be labile under the reaction conditions used, giving rise to disappointing yields and allowing rearrangement to the more stable facial form. DFT studies indicate that this does not appear to be as a consequence of a metal centered electronic effect. The two isomers of $[Ru(L1)_3](PF_6)_2$ were separated into the two individual forms using silica preparative plate chromatographic procedures, and the photophysical characteristics of the two forms compared. The results appear to indicate that there is no significant difference in both their room temperature electronic absorption and emission spectra or their excited state lifetimes at 77 K.

Introduction

Over the past decade, assemblies containing polypyridine complexes of ruthenium(II), osmium(II), and rhodium(III) have attracted considerable interest.[1] This can be attributed to their unique combination of complex stability, redox activity, and photophysical behavior.[2−4] In particular, they have been considered as probes in the structural elucidation of DNA[5] and received much attention for their potential role in photoactivated energy and electron transfer systems.[6−8] In order to bring these individual units together within a larger assembly designed for a specific task, it is essential to be able to control the spatial arrangement of both the ligands and the metal centers relative to each another. Recent studies have indicated that the interaction of DNA is very dependent on the ligand orientation within dinuclear species.[9,10] Similarly, it has been shown that the distance between, and the orientation of, individual groups within larger assemblies can have small but significant effects on the redox potentials and excited-state lifetimes.[11,12] Consequently, the isolation and study of single isomeric forms is important in the preparation of new functional materials.

Significant progress has been made in the control of metal centered chirality in such species, using enantiopure building blocks such as Δ- or Λ-*cis*-$[Ru(bpy)_2(py)_2]^{2+}$[13] among others,[14−16] but the consideration of geometrical isomerism

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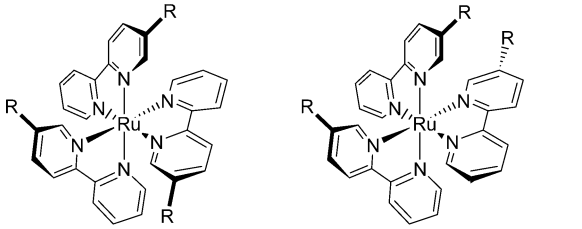

Figure 1. Schematic illustration of the *fac*- and *mer*-tris(bipyridine) complexes of ruthenium(II).

appears to have been the subject of only one detailed study.[17,18] Over the past few years, we have turned our focus on the isolation of isomerically pure tris-chelate complexes containing monofunctionalized 2,2′-bipyridine ligands. These can adopt both the meridional (*mer*-) and facial (*fac*-) isomers (Figure 1). In a typical synthesis, using three identical ligands, a statistical distribution of three parts of the *mer*-isomer will be produced to one of the *fac*-isomer. This ratio arises from the potential orientation of the ligands in a stepwise addition to the metal center. However, due to the steric requirements of the ligand, preceding results indicate that the ratio can be further tipped in favor of the *mer*-form.[19]

Despite the vast wealth of literature examining the polypyridine complexes of ruthenium(II), there are remarkably few studies that have addressed the implications of the stereochemistry upon the photophysical properties of these compounds. A number of di- and trinuclear complexes have been explored giving differing results. The studies performed by Vos and co-workers indicate that there are no differences in the properties of the *meso*- and *rac*-forms of dinuclear species bridged by either 3,5-bis(pyridin-2-yl)-1,2,4-triazole[20] or 1,1′-benzimidazole.[21] However, the studies by Keene indicate small but significant differences in the electrochemical and absorption properties of the *meso*- and *rac*-forms of dinuclear complexes bridged by azobis(2-pyridine),[22] the excited-state lifetimes of a range of diastereoisomers of the trinuclear species bridged by 1,4,5,8,9,12-hexaazatriphenylene,[23] and the intervalence charge transfer frequency in complexes bridged by 2,3-bis(2-pyridyl)-1,4-benzoquinoxaline.[24] Further, there is good evidence that the orientation of a donor/acceptor pair around a $[Ru(bipy)_3]^{2+}$ chromophore appears to affect the lifetime of the resulting charge separated state.[25] However, the question remains: Are there differences in the photophysical properties of *mer*-/ *fac*-isomers of simple monomeric species of $[Ru(L1)_3]^{2+}$ (where L1 is 2,2′-bipyridine-5-carboxylic methyl ester)? Such a unit could potentially be the building block of larger supramolecular assemblies since the three bipyridine chelates bear suitable groups to allow further substitution.[26] In order to assess its suitability for the preparation of polynuclear structures, it is important to understand the properties of the individual components.

Using a similar methodology to that described by Keene et al.,[18] we have recently demonstrated that cation-exchange chromatography can be used in the separation of the *mer*- and *fac*-isomers of a range of 5-substituted-2,2′-bipyridines.[19] However, deesterification and chiral resolution on the ion-exchange resin hampered the isolation of significant quantities of isomerically pure $[Ru(L1)_3]^{2+}$. In an alternative strategy, the *fac*-isomer has been isolated by forming a tripodal podand ligand, and subsequent disconnection of the three arms to give the free *fac*-isomer in a method similar to that described by Weizmann et al.[27] giving the complex *fac*-$[Ru(L1)_3]^{2+}$. The isolation of the *mer*-isomer proved to be more problematic. Following our previous observation that large bulky groups favor the formation of the *mer*-isomer,[19] we discuss here the possibility of using this effect in the preparation of *mer*-$[Ru(L1)_3]^{2+}$ and examine the photophysical properties of both the *mer*- and *fac*-isomers.

Experimental Section

Instrumentation. ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX 300 and DRX500 using the solvent as an internal reference, electronic spectra were recorded on a Perkin-Elmer Lambda 800 spectrophotometer, and emission spectra were recorded on a Perkin-Elmer LS55 spectrofluorimeter having adjusted the sample concentration giving the UV−vis absorption of the MLCT band to 0.1. Emission quantum yields (Φ_{em}'s) were calculated by using $[Ru(bipy)_3](PF_6)_2$ as a standard in acetonitrile (0.062).[28,29] Microanalyses and EI mass spectroscopy were performed by ASEP, The School of Chemistry, The Queen's University of Belfast. The LSI-MS (FAB) and electron impact mass spectroscopy was performed by the EPSRC mass spectroscopy service, The University of Wales, Swansea, U.K. Lifetime measurements were recorded by Dr. W. R. Browne at The School of Chemistry, The Queen's University of Belfast, using previously described experimental methods.[30]

Materials. All starting materials were used as received from the supplier. Laboratory grade solvents were used unless otherwise specified. Tetrahydrofuran (THF) and toluene were distilled under N_2 from potassium and sodium, respectively. SP-Sephadex C25 and Sephadex LH20 were used for chromatographic purification of the metal complexes. Dichlorotetrakis(dimethyl sulfoxide) ru-

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thenium(II)[31] and 2,2′-bipyridine-5-carboxylic acid[19] were prepared via literature procedures.

Ligand Synthesis. All ligands were prepared by a similar route.

2,2′-Bipyridine-5-carboxylic Acid Phenyl Ester (L2). 2,2′-Bipyridine-5-carboxylic acid (0.421 g, 2.01 mmol) was refluxed in thionyl chloride (30 mL) for 1 h. The thionyl chloride was removed under reduced pressure, and the pale yellow solid was dried in vacuo for 2.5 h. The resulting solid was dissolved in dry toluene (or THF) (50 mL) and triethylamine (2 mL) to which was added phenol (0.297 g, 3.16 mmol). This mixture was refluxed for 4 h and stirred for a further 16 h at room temperature. The organic solution was then washed with water (80 mL) and dried over anhydrous magnesium sulfate. The solvent was then removed in vacuo, and the resulting pale beige solid was dried in vacuo for an hour. The crude product was recrystallized from acetone/water. Yield 0.154 g, 27%. Found: C, 71.11; H, 4.46; N, 8.95%. $C_{17}H_{12}N_2O_2 \cdot 0.5(H_2O)$ requires C, 71.57; H, 4.59; N, 9.82. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.26 (2H, d, J = 7.5 Hz, PhH^2), 7.30 (1H, d, J = 7.5 Hz, PhH^4), 7.39 (1H, dd, J = 4.8 and 7.6 Hz, bipy $H^{5'}$), 7.46 (2H, dd, J = 7.5 and 7.5 Hz, PhH^3), 7.88 (1H, dd, J = 8.0 and 7.6 Hz, bipy$H^{4'}$), 8.53 (1H, d, J = 8.0 Hz, bipy$H^{3'}$), 8.58 (2H, m, bipyH^3 and bipyH^4), 8.74 (1H, d, J = 4.8 Hz, bipy$H^{6'}$), 9.44 (1H, s, bipyH^6). ^{13}C: δ 164.0 (COO), 160.1 (Q), 155.1 (Q), 151.0 (CH), 150.7 (PhQ), 149.5 (CH), 138.5 (CH), 137.1 (CH), 129.6 (2PhH), 126.2 (PhH), 125.3 (Q), 124.7 (CH), 122.1 (CH), 121.6 (2PhH), 120.7 (CH). E.I-MS m/z 277 $[M]^+$.

2,2′-Bipyridine-5-carboxylic Acid (3,4-Dimethyl-phenyl) Ester (L3). The crude product was recrystallized from methanol. Yield 34%. Found: C, 72.92; H, 5.23; N, 8.68%. $C_{19}H_{16}N_2O_2 \cdot 0.5(H_2O)$ requires: C, 72.83; H, 5.47; N, 8.94. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.36 (3H, s, Me), 2.38 (3H, s, Me), 6.98 (1H, d, J = 8.1 Hz, PhH^6), 7.03 (1H, s, PhH^2), 7.19 (1H, d, J = 8.1 Hz, PhH^5), 7.38 (1H, dd, J = 4.8 and 7.4 Hz, bipy $H^{5'}$), 7.87 (1H, dd, J = 7.9 and 7.4 Hz, bipy$H^{4'}$), 8.52 (1H, d, J = 7.9 Hz, bipy$H^{3'}$), 8.56 (2H, m, bipyH^3 and bipyH^4), 8.73 (1H, d, J = 4.8 Hz, bipy$H^{6'}$), 9.42 (1H, s, bipyH^6). ^{13}C: δ 164.6 (COO), 160.3 (Q), 155.4 (Q), 151.4 (CH), 149.8 (CH), 148.9 (PhQ), 138.9 (CH), 138.5 (PhQ), 137.5 (CH), 134.9 (PhQ), 130.9 (PhH), 125.7 (Q), 125.0 (PhH), 122.9 (PhH), 122.4 (CH), 121.0 (CH), 119.0 (CH), 20.3 (Me), 19.7 (Me). ES-MS m/z 304 $[M]^+$.

2,2′-Bipyridine-5-carboxylic Acid (2,6-Dimethyl-phenyl) Ester (L4). The crude product was recrystallized from methanol. Yield 30%. Found: C, 70.84; H, 5.46; N, 8.27%. $C_{19}H_{16}N_2O_2$ requires: C, 70.79; H, 5.63; N, 8.69. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.27 (6H, s, Me), 7.16 (3H, m, PhH^{3-5}), 7.42 (1H, dd, J = 4.7 and 7.4 Hz, bipy $H^{5'}$), 7.91 (1H, dd, J = 7.9 and 7.4 Hz, bipy$H^{4'}$), 8.61 (1H, d, J = 7.9 Hz, bipy$H^{3'}$), 8.64 (2H, m, bipyH^3 and bipyH^4), 8.78 (1H, d, J = 4.6 Hz, bipy$H^{6'}$), 9.53 (1H, s, bipyH^6). ^{13}C: δ 162.9 (COO), 159.8 (Q), 154.6 (Q), 150.7 (CH), 149.2 (CH), 147.8 (PhQ), 138.3 (CH), 136.9 (CH), 129.9 (PhQ), 128.5 (PhH), 125.9 (PhH), 124.6 (Q), 124.4 (CH), 121.8 (CH), 120.5 (CH), 16.1 (Me). ES-MS m/z 304 $[M]^+$.

2,2′-Bipyridine-5-carboxylic Acid (Naphthalen-2-yl) Ester (L5). The crude product was recrystallized from dichloromethane/acetone. Yield 36%. Found: C, 77.02; H, 4.77; N, 8.45%. $C_{21}H_{14}N_2O_2$ requires: C, 77.30; H, 4.32; N, 8.58. ES-MS m/z 327 $[MH]^+$. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38 (1H, dd, J = 4.8 and 7.6 Hz, bipy $H^{5'}$), 7.40 (1H, dd, J = 2.2 and 9.0 Hz, naH^3), 7.56−7.50 (2H, m, naH^6, naH^7), 7.75 (1H, d, J = 2.2 Hz, naH^1), 7.91−7.77 (3H, m, naH^5, naH^8, bipy$H^{4'}$), 7.94 (1H, d, J = 9.0 Hz, naH^4), 8.55 (1H, d, J = 7.9 Hz, bipy$H^{3'}$), 8.61 (2H, m, bipyH^3 and bipyH^4), 8.75 (1H, d, J = 4.8 Hz, bipy$H^{6'}$), 9.49 (1H, s, bipyH^6). ^{13}C: δ 164.2 (COO), 160.2 (Q), 155.5 (Q), 151.1 (CH), 149.5 (CH), 148.3 (naQ), 138.6 (CH), 137.1 (CH), 133.9 (naQ), 131.7 (naQ), 129.6 (naH), 127.9 (naH), 127.8 (naH), 126.7 (naH), 125.9 (naH), 125.3 (Q), 124.7 (CH), 122.1 (CH), 121.0 (naH), 120.7 (CH), 118.7 (naH).

2,2′-Bipyridine-5-carboxylic Acid (Undec-2-yl) Ester (L6). The crude product was purified by Soxhlet extraction into hexane, followed by column chromatography eluting with DCM/2% MeOH, isolating the major fraction by evaporation of the solvent. Yield 12.5%. Found: C, 74.54; H, 8.59; N, 8.45%. $C_{22}H_{30}N_2O_2$ requires: C, 74.57; H, 8.47; N, 7.90. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.89 (6H, m, CH_3), 1.33 (12H, m, CH_2), 1.67 (4H, m, CH_2), 5.19 (1H, m, CH), 7.36 (1H, dd, J = 4.7 and 7.5 Hz, bipy$H^{5'}$), 7.85 (1H, dd, J = 8.0 and 7.5 Hz bipy$H^{4'}$), 8.42 (1H, d, J = 8.3 Hz, bipyH^4), 8.46 (1H, d, J = 8.3 Hz, bipy$H^{3'}$), 8.50 (1H, d, J = 8.2 Hz, bipyH^3), 8.71 (1H, d, J = 4.8 Hz, bipy$H^{6'}$), 9.27 (1H, s, bipyH^6). ^{13}C: δ 164.0 (COO), 158.2 (Q), 154.1 (Q), 149.4 (CH), 148.3 (CH), 136.9 (CH), 136.0 (CH), 125.2 (Q), 123.4 (CH), 120.8 (CH), 119.4 (CH), 74.8 (CH), 33.0 (CH_2), 30.7 (CH_2), 23.9 (CH_2), 21.5 (CH_2), 12.9 (CH_3). ES-MS m/z 355 $[M]^+$.

2,2′-Bipyridine-5-carboxylic Acid (Adamantan-1-yl-methyl) Ester (L7). The crude product was purified by recrystallization from hexane. Yield 22%. Found: C, 74.46; H, 6.77; N, 7.94%. $C_{22}H_{24}N_2O_2$ requires: C, 75.83; H, 6.94; N, 8.04. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.63−1.88 (12H, m, CH_2), 2.04 (3H, m, CH), 3.98 (2H, s, OCH_2), 7.37 (1H, dd, J = 4.8 and 7.3 Hz, bipy$H^{5'}$), 7.86 (1H, dd, J = 7.6 and 7.9 Hz, bipy$H^{4'}$), 8.42 (1H, dd, J = 8.3 Hz, bipyH^4), 8.48 (1H, d, J = 7.9 Hz, bipy$H^{3'}$), 8.52 (1H, d, J = 8.3 Hz, bipyH^3), 8.72 (1H, d, J = 4.7 Hz, bipy$H^{6'}$), 9.31 (1H, s, bipyH^6). ^{13}C: δ 165.8 (COO), 159.7 (Q), 154.3 (Q), 150.8 (CH), 149.8 (CH), 138.4 (CH), 137.5 (CH), 126.5 (Q), 124.9 (CH), 122.2 (CH), 120.9 (CH), 75.21 (OCH_2), 39.4 (3ACH), 37.2 (3ACH), 33.6 (Q), 28.1 (3CH). ES-MS m/z 349 $[M]^+$.

2,2′-Bipyridine-5-carboxylic Acid (Adamantan-2-yl) Ester (L8). The crude product was purified by recrystallization from methanol. Yield 24%. Found: C, 73.51; H, 6.80; N, 8.41%. $C_{21}H_{22}N_2O_2 \cdot 0.5(H_2O)$ requires: C, 73.46; H, 6.58; N, 8.38. ^{1}H NMR (300MHz, $CDCl_3$): 1.61−1.92 (10H, m, CH), 2.08 (2H, m, CH), 3.49 (2H, m, CH), 5.25 (1H, m, OCH), 7.37 (1H, dd, J = 4.7 and 7.6 Hz, bipy$H^{5'}$), 7.85 (1H, dd, J = 7.6 and = 8.0 Hz, bipy$H^{4'}$), 8.44 (1H, dd, J = 8.3 Hz, bipyH^4), 8.48 (1H, d, J = 8.0 Hz, bipy$H^{3'}$), 8.52 (1H, d, J = 8.3 Hz, bipyH^3), 8.72 (1H, dd, J = 4.7 Hz, bipy$H^{6'}$), 9.34 (1H, s, bipyH^6). ^{13}C: δ 163.6 (COO), 158.2 (Q), 154.1 (Q), 149.5 (CH), 148.4 (CH), 136.9 (CH), 136.0 (CH), 125.6 (Q), 123.4 (CH), 120.8 (CH), 119.5 (CH), 77.1 (OCH_2), 37.7 (CH_2), 36.7 ($2CH_2$) 33.9 (CH), 32.4 ($2CH_2$), 27.7 (CH), 27.4 (CH), 27.3 (CH). ES-MS m/z 334 $[M]^+$.

Complex Synthesis. All complexes were prepared by a similar route.

$[Ru(L2)_3](PF_6)_2$. To a refluxing ethanolic (60 mL) solution of L2 (51 mg, 0.185 mmol) and silver nitrate (100 mg) was added $Ru(DMSO)_4Cl_2$ (25.5 mg, 0.0527 mmol) in small portions over an hour. The reaction mixture refluxed for a further 3 h. Sodium chloride (5 mg) was added, and the brown-orange mixture was filtered. The solvent was removed in vacuo and the dark residues dissolved in water (50 mL). Ammonium hexafluorophosphate (50 mg) was added giving the product as a dark red precipitate, which was collected by filtration. (Further purification if required was achieved by recrystallization from acetone/water and passage down a Sephadex LH20 column eluting with acetone.) Yield 61.6 mg, 96%. Found: C, 45.73; H, 3.33; N, 6.96%. $C_{51}H_{36}F_{12}N_6O_6P_2Ru \cdot 0.5(NH_4PF_6) \cdot 4(H_2O)$ requires: C, 45.80; H, 3.17; N, 6.82. LSI-MS: $[M - PF_6]$ 1075, $[M - 2PF_6]$ 930.

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$[Ru(L3)_3](PF_6)_2$. Yield 88%. Found: C, 50.76; H, 4.04; N, 6.02. $C_{57}H_{48}F_{12}N_6O_6P_2Ru \cdot 0.5(H_2O)$ requires: C, 50.75; H, 3.96; N, 6.23. LSI-MS: $[M - PF_6]$ 1159, $[M - 2PF_6]$ 1015.

$[Ru(L4)_3](PF_6)_2$. Yield 40%. Found: C, 52.24; H, 3.82; N, 5.98%. $C_{57}H_{48}F_{12}N_6O_6P_2Ru$ requires: C, 52.50; H, 3.71; N, 6.44. LSI-MS: $[M - PF_6]$ 1159, $[M - 2PF_6]$ 1015.

$[Ru(L5)_3](PF_6)_2$. Yield 58%. Found: C, 52.39; H, 3.70; N, 6.26%. $C_{63}H_{42}F_{12}N_6O_6P_2Ru \cdot 0.5NH_4PF_6$ requires: C, 52.13; H, 3.06; N, 6.27. LSI-MS: $[M\text{-}2PF_6]$ 1079/1080.

$[Ru(L6)_3](PF_6)_2$. Yield 38%. Found: C, 51.12; H, 5.48; N, 6.35%. $C_{66}H_{90}F_{12}N_6O_6P_2Ru \cdot 0.5NH_4PF_6$ requires: C, 51.6; H, 5.99; N, 5.93. LSI-MS: $[M + Na]^+$ 1478, $[M - PF_6]$ 1310, $[M - 2PF_6]$ 1165.

$[Ru(L7)_3](PF_6)_2$. Yield 23%. Found: C, 55.41; H, 5.07; N, 5.85%. $C_{66}H_{72}F_{12}N_6O_6P_2Ru$ requires: C, 55.19; H, 5.05; N, 5.78. LSI-MS: $[M - PF_6]$ 1291, $[M - 2PF_6]$ 1146.

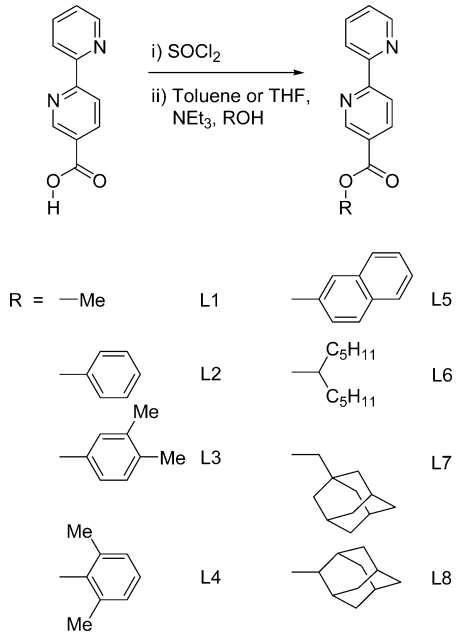
$[Ru(L8)_3](PF_6)_2$. Yield 55%. Found: C, 54.50; H, 6.24; N, 5.78%. $C_{63}H_{66}F_{12}N_6O_6P_2Ru\ 2(C_3H_6O)\cdot(H_2O)$ requires: C, 54.80; H, 5.17; N, 6.06. LSI-MS mass spec: $[M - PF_6]$ 1249, $[M - 2PF_6]$ 1104.

All Complexes Were Converted to $[Ru(L1)_3](PF_6)_2$ via the Same Route. For example, $[Ru(L4)_3](PF_6)_2$ (20 mg, 15.3 μmol) was stirred in methanol (10 mL) and triethylamine (1 mL) for 24 h. The solvent was removed and the complex passed down a Sephadex LH20 column eluting with methanol. Following removal of the solvent, the complex was isolated as a red-brown solid. Yield 10.4 mg, 66%. The complex was characterized by ^{1}H NMR giving a mixture of the two isomers similar to those described previously.[19] Isomeric separation of $[Ru(L1)_3](PF_6)_2$ was achieved using preparative thick layer plate silica chromatography, eluted with a 20% aqueous DMF solution saturated with ammonium chloride. (R_f of *mer*-isomer 0.62. R_f of *fac*-isomer 0.43.)

Alternative Reaction Conditions Used in the Preparation of $[Ru(L1)_3](PF_6)_2$ via $[Ru(L5)_3](PF_6)_2$. Identical reagents to those used in the preparation of $[Ru(L5)_3](PF_6)_2$ were employed, using a variety of solvent mixtures and temperatures: (a) with 22% benzene in ethanol at reflux, (b) with 50% toluene in ethanol at reflux, (c) ethylene glycol at 70 °C, (d) ethylene glycol at 100 °C, and (e) ethylene glycol at 130 °C. When prepared in ethylene glycol, the reaction mixture was passed through a cation-exchange SP Sephadex C25 column eluted with 0.1 M aqueous sodium 4-toluenesulfonate to remove the organic solvent. The crude product from each reaction was isolated by the addition of ammonium hexafluorophosphate and extracted into dichloromethane and converted to the methyl ester $[Ru(L1)_3](PF_6)_2$ without further purification in (a) 20%, (b) 86%, (c) 30%, (d) 52%, and (e) 32% overall yield.

Density Functional Calculations. The geometry optimization and total energy calculations were performed on $[Ru(L1)_3]^{2+}$ using the SIESTA code.[32] The standard DFT supercell approach with GGA-PBE[33] functional is implemented, and the Kohn−Sham wave function is expanded with localized basis sets. In the calculations, Troullier−Martins norm-conserving pseudopotentials were used for all the elements. In the Ru pseudopotential, the semicore states (4s, 4p) are included. For all the atoms except the O, double-ζ-polarization (DZP) split valence basis set is employed, and the semicore states of Ru are represented by single-ζ-polarization (SZP). For the O atoms, triple-ζ-polarization (TZP) split valence basis set is used for the 2p orbital, and double-ζ-polarization (DZP) split valence basis set is used for the 2s orbital. The energy cutoff for the real space grid is 150 Ry, and the localization radii of the basis functions were determined from an energy shift of 0.01 eV. The calculated energy difference between the two isomeric forms is extremely small (0.04 eV), in favor of the *fac*-isomer.

Scheme 1. Synthesis of Ligands L1−L8



The single-point energy calculations on the two isomeric forms optimized from SIESTA were also performed using Gaussian03.[34] The hybrid B3LYP exchange-correlation functional[35−38] and the 3-21+G* basis set were used. The calculated energy difference between the two isomeric forms in the gas phase is very small (0.09 eV), in favor of the *fac*-isomer. The solution effects were estimated according to the PCM method,[39] as implemented in Gaussian03. The calculated solvation energy difference is 0.09 eV in water and ethanol, in favor of the *mer*-isomer in both cases.

Results and Discussion

Synthetic Results. Following a standard procedure described previously,[19] a range of ligands L2−L8 was prepared from 2,2′-bipyridine-5-carboxylic acid via the acid chloride using the appropriate alcohols (Scheme 1). The yields were

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observed to be significantly lower than expected. In particular, the bulky aliphatic ligands L6−L8 proved extremely difficult to isolate and purify as the compounds appeared to undergo rapid deesterification upon exposure to water and decomposed in attempts to purify with silica chromatography. Attempts were made to isolate additional compounds formed from a range of other secondary and tertiary alcohols (such as 2-methyl-2-propanol), but without success. While similar species are known, substituted at the 4 and 4′-bipyridine positions,[40] it appears that the preparation of bulky aliphatic esters at the 5 position is more problematic and the products are vulnerable to hydrolysis.

Attempts were made to coordinate each of the ligands to ruthenium(II) by gently refluxing them in ethanol with $[Ru(DMSO)_4Cl_2]$ (where DMSO is dimethyl sulfoxide) in the presence of silver nitrate. The crude reaction mixtures were filtered, giving a red-brown solution. Following removal of the solvent, the product was precipitated from water with ammonium hexafluorophosphate and the product passed down a Sephadex LH20 column, eluting with acetone and recrystallizing from water/acetone several times. The yields were disappointingly low in each case (with the exception of the complex formed from L2). It appears that the bulky substituents hinder the reaction from going to completion. This was further confirmed by the presence of purple-brown species, typical of complexes possessing only two of the desired ligands surrounding the metal center. These byproducts were removed during the purification. Second, the compounds appear to be very susceptible to hydrolysis in the presence of water, leading to species bearing free acid groups that could not be extracted from aqueous solution. The identity of each new complex was confirmed by elemental analysis. Unsurprisingly, the complexes were observed to retain water despite prolonged drying in vacuo. The presence of the carbon rich ester groups was clearly apparent in the CHN analyses. Similarly, LSI mass spectrometry indicated the presence of each of the complexes by the appropriate ruthenium-bearing cluster less one hexafluorophosphate anion, $[M - PF_6]^+$.

Attempts were made to characterize each of the complexes by ^{1}H NMR spectroscopy. However, the resulting spectra proved to be complex, particularly in the aromatic region. The presence of two isomers was apparent in each case (Figure 2a). While the *fac*-isomers each possess C_3-symmetry (with all three ligands being chemically equivalent), the *mer*-isomer has C_1-symmetry (with each ligand giving rise to an independent set of signals). Consequently, little information could be obtained from the spectra. To overcome the problems in determining the relative *mer*/*fac* isomeric ratio, each of the complexes were converted to the methyl ester L1 by stirring overnight at room temperature in methanol/triethylamine. The two isomeric forms of the complex $[Ru(L1)_3]^{2+}$ have previously been described,[19,26] and so the peaks pertaining to them can be identified and integrated leading to the relative ratio of the two products. This was achieved by examining the $H^{5'}$ (7.50−7.65 ppm) and the methyl signals (3.65−3.70 ppm). The area enclosed by the signal pertaining to the most downfield *mer* proton was used to indicate the proportion of the adjacent overlying region of the spectrum that arose from the protons of the *fac*-isomer (Figure 2a,b). Due to the nature of the spectra, and the closeness of the peaks, the accuracy of the experiments (±10%) was not ideal. However, a significant deviation from the expected behavior was observed.

In previous studies, we have observed that transesterification to give *fac*-$[Ru(L1)_3](PF_6)_2$ proceeded with complete retention of the metal centered stereochemistry.[26] However, in order to demonstrate this to be the case with the examples under consideration in this study, the relative isomeric ratio of both the complexes $[Ru(L3)_3](PF_6)_2$ and $[Ru(L7)_3](PF_6)_2$ was estimated to be 3:2.6 and 3:1.7, respectively, by integration of the bipyridine $H^{5'}$ protons. Subsequent comparison with the resulting methyl ester complex $[Ru(L1)_3](PF_6)_2$ indicated that the ratios remained the same (Figure 2a,b and Table 1).

The expected statistical ratio of the two isomers, assuming a stepwise addition of ligands without them rearranging during the synthesis, should be 3 *mer* to 1 *fac*. The ^{1}H NMR spectrum for the complex $[Ru(L1)_3](PF_6)_2$ prepared directly from the ligand L1 prove this to be the case (Table 1).[19] Similarly, the isomeric mixture resulting from the phenyl ester L2 exhibited the same ratio. However, as the steric bulk of the ligands was increased by the inclusion of two methyl substituents on the phenolic group (L3 and L4), the quantity of the *fac*-isomer present in the sample became significantly larger than theory would suggest. Upon increasing the size of the ligand with a naphthyl group (L5), a 1:1 ratio of the two isomers was observed. A similar result was found for the bulky aliphatic substituents with ligands L6, L7, and L8 giving rise to a disproportionately high quantity of the *fac*-isomer.

Discussion of the Synthetic Procedures. The initial assumption had been that the use of the more sterically demanding ester substituents would give rise to the *mer*-isomer, as previously observed in alkyl substituted systems.[19] This does not appear to be the case in the systems described here and could give a possible insight into the mechanism for the bipyridine ligand substitution reaction.

With the inclusion of large hydrophobic groups, the initial interpretation of the results was that the ligands are forming a micellular aggregation in the ethanolic solution, encouraged by the possibility of π-stacking interactions in the case of ligand L5.[41] Thus, the ligands with their polar bipyridine units pointing into the bulk solution would be prearranged in the correct orientation to form the *fac*-isomer, leading to the disproportional ratio observed. In order to confirm this hypothesis, the reaction conditions were changed. To remove possible π-stacking interactions in the bulk solution, and to reduce the possibility of micelle formation, the reaction with ligand L5 was performed under virtually identical conditions, but including either 22% benzene or 50% toluene in the

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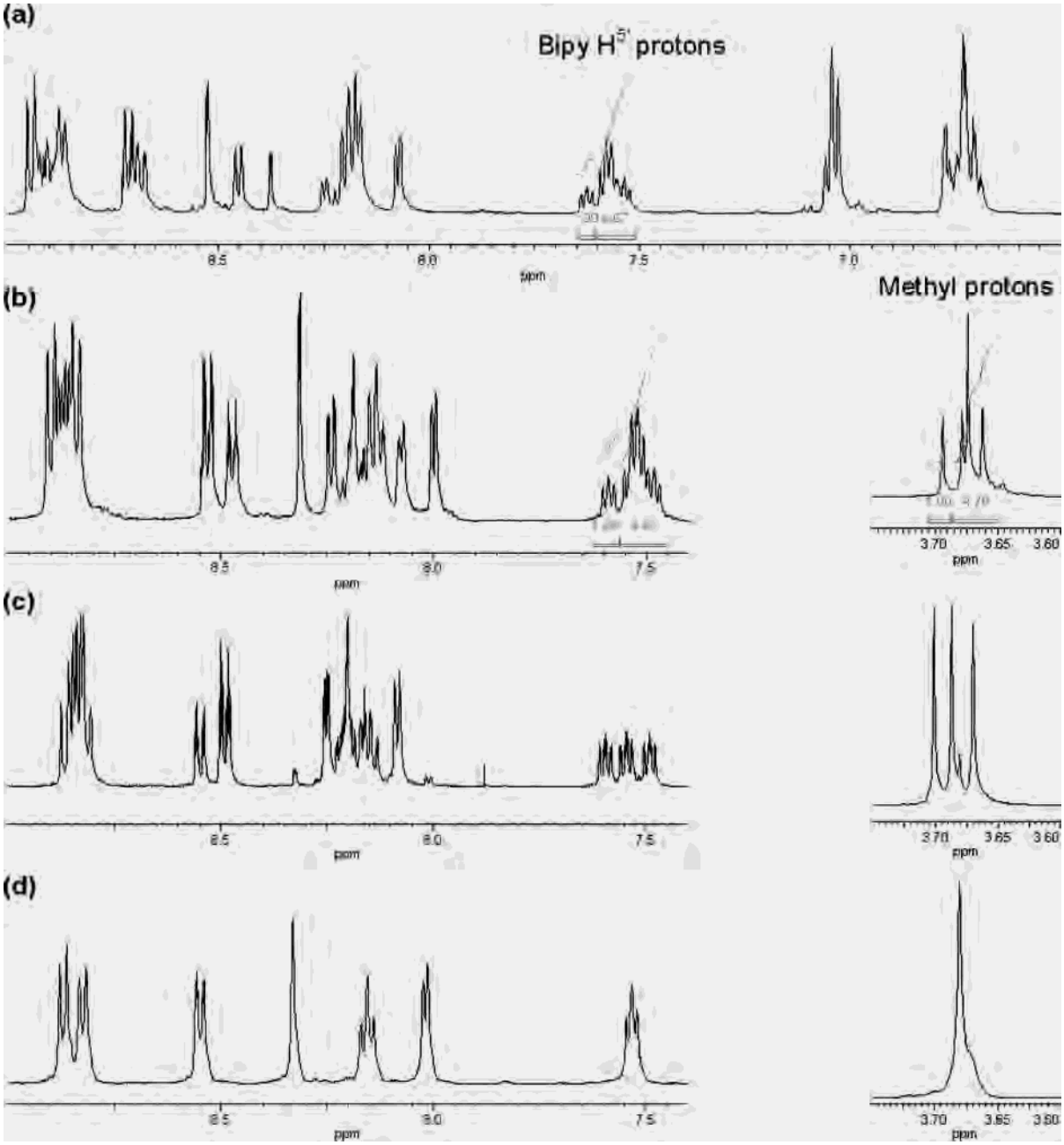

Figure 2. ^{1}H NMR spectra of (a) $[Ru(L3)_3](PF_6)_2$, (b) $[Ru(L1)_3](PF_6)_2$ (derived from $[Ru(L3)_3](PF_6)_2$), (c) *mer*-$[Ru(L1)_3](PF_6)_2$, and (d) *fac*-$[Ru(L1)_3](PF_6)_2$ (500 MHz, 25 °C, d_6-acetone).

ethanolic solution. In both cases, the yield was notably smaller than anticipated, with a large quantity of the brown/purple di-chelated complex removed upon purification. The isomeric ratio (3:2.4 ± 0.3) (Table 1) of the two products, identified following conversion to the complex $[Ru(L1)_3](PF_6)_2$, again showed a significantly enhanced quantity of the *fac*-isomer. Consequently, it would be reasonable to assume that the ligands are not preorganizing themselves prior to the complexation reaction, but at a later stage.

Alternatively, the unusual preference for the *fac*-isomer may be due to ligand rearrangement following initial complex formation. The bonding between the chelating 2,2′-bipyridine chelate and the low spin d^6 ground state ruthenium(II) center is considered to be extremely strong, strengthened by π-back-donation to the π^* ligand orbitals.[42] The inclusion of substituents in the 6 and 6′ and to a lesser extent the 5 and 5′ positions, however, are known to cause destabilization of the tris-chelate complexes due to imposed steric constraints.[43] In the ligands under investigation, the inclusion of bulky substituents appears to hinder the complexation of the final ligand, giving rise to the low yields. In addition, complex $[Ru(L5)_3](PF_6)_2$ was noted to decompose upon prolonged standing, implying that the tri-chelate complex is unstable with respect to ligand dissociation. Since there appears to be a kinetic lability, it is possible that one of the ligands could temporarily dissociate, and then recombine in a thermodynamically more stable configuration. To investigate

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Table 1. The Effect on the *mer*/*fac* Isomeric Ratio of Using Bulky Substituents in the Formation of the Complex $[Ru(L1)_3](PF_6)_2$

isolated complex	conditions/solvent used in the synthesis of the complex prior to conversion to $[Ru(L1)_3](PF_6)_2$[a]	isomeric *mer* to *fac* ratio following conversion to $[Ru(L1)_3](PF_6)_2$ (error ± 0.3)
$[Ru(L1)_3](PF_6)_2$	at reflux in ethanol	3:1.0
$[Ru(L2)_3](PF_6)_2$	at reflux in ethanol	3:1.0
$[Ru(L3)_3](PF_6)_2$	at reflux in ethanol	3:2.0
$[Ru(L4)_3](PF_6)_2$	at reflux in ethanol	3:3.0
$[Ru(L5)_3](PF_6)_2$	at reflux in ethanol	3:3.0
$[Ru(L5)_3](PF_6)_2$	in ethylene glycol 70 °C	3:0.9
$[Ru(L5)_3](PF_6)_2$	in ethylene glycol 100 °C	3:2.3
$[Ru(L5)_3](PF_6)_2$	in ethylene glycol 130 °C	3:2.3
$[Ru(L5)_3](PF_6)_2$	at reflux in 22% benzene/ethanol	3:2.5
$[Ru(L5)_3](PF_6)_2$	at reflux in 50% toluene/ethanol	3:2.1
$[Ru(L6)_3](PF_6)_2$	at reflux in ethanol	3:1.3
$[Ru(L7)_3](PF_6)_2$	at reflux in ethanol	3:1.6
$[Ru(L8)_3](PF_6)_2$	at reflux in ethanol	3:1.9

[a] All complexes were converted to $[Ru(L1)_3](PF_6)_2$ after initial isolation by stirring in methanol at room temperature in the presence of triethylamine.

this possibility, the formation of $[Ru(L5)_3](PF_6)_2$ was attempted at three different temperatures in ethylene glycol (Table 1). At 70 °C, the theoretical 3 *mer* to 1 *fac* ratio was detected (Table 1), and so presumably at this temperature the ligand does not undergo significant ligand dissociation. As the same experiment is attempted at higher temperatures (100° and 130 °C), the relative ratio of the *fac*-isomer increases significantly indicating ligand reorientation has occurred. It is surprising that carrying the reaction out in refluxing ethanol (78 °C) gave the unusually high proportion of the *fac*-isomer, while the use of ethylene glycol at 70 °C gave the expected ratio. It would thus appear that solvent itself plays an important role in the reaction, either by stabilizing an intermediate or due to the difference in polarity.

Considering the evidence, it would appear that the *fac*-isomers of $[Ru(L3-L8)_3]^{2+}$ are thermodynamically more stable than the corresponding *mer*-forms. Purely on steric grounds, CPK modeling studies indicate this not to be the case. In a recent paper, Tamayo et al. describe the isolation and exploration of a number of *mer*- and *fac*-isomers of a number of cyclometalated pyridyl tris-chelates of iridium and clearly demonstrate the stability of the *fac*-form arising from an electronic effect.[44] In the present study, the *fac*-isomer places the three carbonyl bearing pyridyl groups *cis* to each other. Since the carbonyl groups are electron withdrawing, the three pyridyl groups bearing these functions would become better π-acceptors than the unsubstituted pyridyl groups. Theoretically, it could be argued that the most stable arrangement would place the three substituted ligands *trans* to the unfunctionalized heterocyclic rings (*trans*-influence).[45] If this were the case, it might be expected that there would be a significant difference in the N−Ru bond lengths of the two differing pyridyl groups. Examination of the data in the previously published X-ray structural analysis[24] of *fac*-

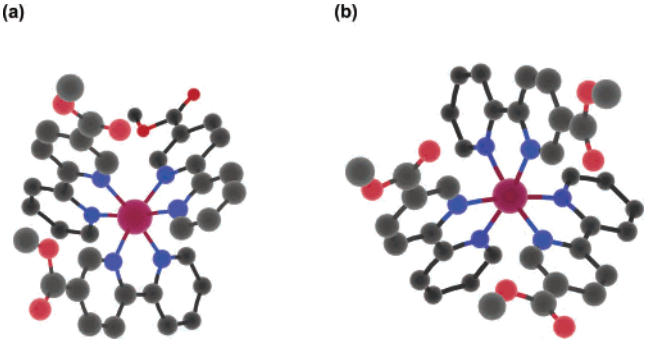

Figure 3. The DFT minimized structure of (a) *mer*-$[Ru(L1)_3]^{2+}$ and (b) *fac*-$[Ru(L1)_3]^{2+}$.[46] (Structures available as PDB files in Supporting Information.)

$[Ru(L1)_3]^{2+}$ indicates that all six of the bond lengths are lying in the range 2.042−2.070 Å with no systematic variation. If there is a difference, it appears to be within the experimental error involved in the structural determination.

DFT Calculations. In order to explore if there is a significant energy difference in the electronic configuration of the two isomeric forms, density functional theory calculations using the SIESTA code[32] were performed on the complex cations *mer*- and *fac*-$[Ru(L1)_3]^{2+}$. The resulting structures (Figure 3) were compared to the previously reported X-ray crystallographic study of $[Ru(L1)_3](PF_6)_2$.[26] The DFT calculation gave the average Ru−N bond to be 2.092 Å compared to the experimental length of 2.056 Å. The average N−Ru−N chelate angle also gave a good correlation between the calculated and experimental structures (78.8° and 78.7°, respectively). The calculated relative energy difference between the two isomeric forms is small (0.04 eV), in favor of the *fac*-isomer (Figure 3b), being consistent with the experimental observations. Similar DFT gas-phase calculations using Gaussian03[34] yielded similar results in favor of the *fac*-isomer. In order to explore if the solvent plays a significant role in differential stability of the two complexes, the effects of both ethanol and water were estimated according to the PCM method implemented in Gaussian03. While the *mer*-isomer appeared to be the more stable, the difference between the two was so small as to have little effect on the overall stability of the system involved. Consequently, the studies indicate that the size of the relative energy difference between the two isomeric forms is extremely small and it is unlikely to account for the unusually high experimental preference for the *fac*-isomer as observed.

From the modeling studies, the only significant difference between the two structures appears to be the size of the dipole moments of the two complexes: 9.08 D for the *fac*-isomer in the gas phase, and 3.44 D for the *mer*-form. These are further enhanced in the water containing models to 13.9 and 5.5 D, respectively. This is also apparent from examining the structure of complexes: the *fac*-isomer has the three functional groups placed toward one face of the pseudo-octahedral geometry, while the *mer*-isomer places two electron withdrawing carbonyl groups in opposition.

Isomeric Preference. With the bulky groups, the complexes appear to be thermally unstable, permitting the ligands

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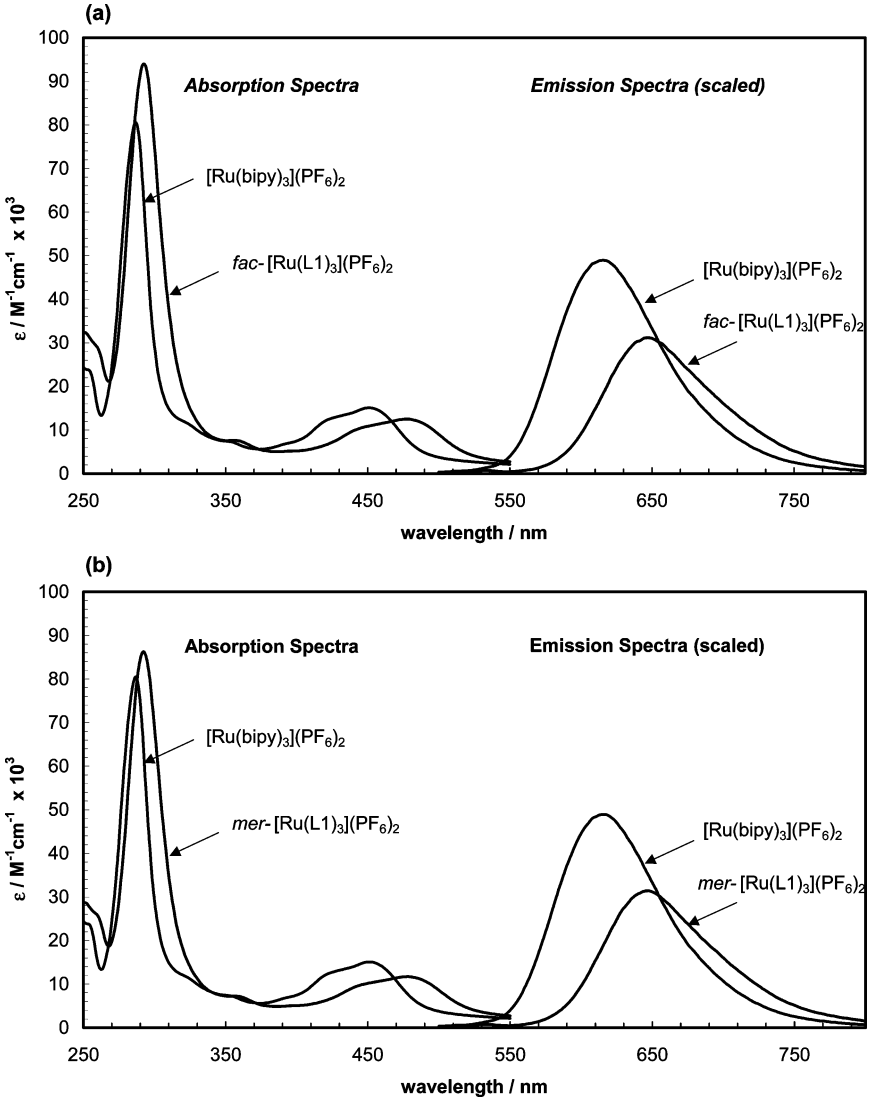

Figure 4. UV−vis absorption and emission spectra of (a) *fac*-$[Ru(L1)_3](PF_6)_2$ and (b) *mer*-$[Ru(L1)_3](PF_6)_2$ recorded under a normal atmosphere, 298 K in acetonitrile.

to rearrange to a more thermodynamically stable configuration, in this case the *fac*-isomer. Since this is the case, it is conceivable that the transesterification reaction used to convert $[Ru(L)_3]^{2+}$ to $[Ru(L1)_3]^{2+}$ does not proceed with the retention of the metal centered stereochemical integrity. However, it appears that this reaction proceeds rapidly, removing the offending bulky groups giving a stable product. Second, this derivatization occurs at room temperature, and it appears that reaction conditions over 70 °C are required to cause the ligand rearrangement justifying the experimental procedures used.

The precise nature of the rearrangement and enhanced isolation of the *fac*-isomer remains ambiguous. In a polar solvent such as ethanol, it is conceivable that the appended organic functionalities could form a hydrophobic pocket. To explore this phenomenon further, it would be necessary to attempt the reaction in a variety of solvents possessing a wide variation in polarities. However, the ligands' susceptibilities to de-esterification and the poor solubility of the complexes in organic solvents prevent such a detailed analysis. As an alternative explanation, the observations could arise from the *fac*-isomer possessing greater interactions between the counteranions than with the *mer*-isomer. Such behavior has been observed between similar species and organic anions,[19] and it is known that anions will bind along the C_3-axis of structurally similar difunctionalized tris-chelate complexes.[47,48]

Isomeric Separation of $[Ru(L1)_3](PF_6)_2$. Following the isolation of $[Ru(L1)_3](PF_6)_2$ and an estimation of the relative isomeric ratios of the two components, it is evident that the use of bulky substituents will not give isomerically pure *mer*-isomer. To attempt a comparative study of the photophysical properties of the two forms, it was necessary to separate the mixtures of both isomers. In our previous studies, this had been achieved through the repeated passage of the mixture through an SP Sephadex C25 cation exchange column, eluting with aqueous sodium hexanoate solution.[19] However,

(46) Diagram prepared from a PDB file using *Chem. 3D*, version 5.0; Cambridge Soft: Cambridge, MA, 1999.
(47) Uppadine, L. H.; Drew, M. G. B.; Beer, P. D. *Chem. Commun.* **2001**, 291−292.
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Table 2. Photophysical Properties in CH_3CN at 298 K

	absorption LC		absorption MLCT		emission		
complex	$\lambda_{max} \pm 2$ nm	$10^{-3}\,\epsilon$ $dm^3\,mol^{-1}\,cm^{-1}$	$\lambda_{max} \pm 2$ nm	$10^{-3}\,\epsilon$ $dm^3\,mol^{-1}\,cm^{-1}$	$\lambda_{max} \pm 2$ nm	$\Phi_{em} \pm 5\%$	$\tau \pm 5$ ns[a]
fac-$[Ru(L1)_3](PF_6)_2$	292	86.5	477	13.4	647	0.040	179
mer-$[Ru(L1)_3](PF_6)_2$	292	89.5	477	14.2	647	0.040	188

[a] Recorded in acetonitrile as a glass matrix at 77 K.

the separation had proved to be less than ideal, as the competing enantiomeric separation (induced by the chiral nature of the dextran support) had prevented complete separation of the two geometrical components. However, as an indication of the purity of the complex $[Ru(L1)_3](PF_6)_2$, silica TLC, eluting with a water/DMF mixture, demonstrated two very distinct spots. As a consequence, preparative plate chromatography allowed the isolation of the *fac*- and *mer*-isomers in reasonable purity (Figure 2c,d). Since such a great difference in R_f values for the two complexes was observed, it is a good indication that the two forms have very different dipole moments (as indicated by the DFT studies), with the *mer*-isomer travelling faster on the plate.

Photophysical Characterization. Following isolation of the *mer*- and *fac*-$[Ru(L1)_3](PF_6)_2$, it was possible to explore the photophysical properties of the two isomers. To the authors' knowledge, there has been no comparative study of the emissive properties of the *mer*- and *fac*-geometrical isomers of this type. The electronic absorption spectra for the two isomers (Figure 4 and Table 2) did not show any significant difference, with the ligand centered absorptions at 292 nm and the characteristic metal-to-ligand band at 447 nm both within the experimental error (±2 nm). Both these absorptions are red shifted with respect to $[Ru(bipy)_3](PF_6)_2$ as a consequence of the electron withdrawing nature of the carbonyl groups.[3] Similarly, the emission spectra of the two isomers appeared to be remarkably similar with the maximum at 647 nm. The emission quantum yields are lower than that for the parent complex $[Ru(bipy)_3](PF_6)_2$, and the excited state lifetimes at 298 K were not sufficiently long-lived to be recorded. However, at 77 K lifetimes for both of the isomers were obtained (188 ns for *mer*-$[Ru(L1)_3](PF_6)_2$ and 179 ns for *fac*-$[Ru(L1)_3](PF_6)_2$). These are short by comparison to that of $[Ru(bipy)_3](PF_6)_2$ and are in keeping with similar species possessing electron withdrawing carbonyl functionalities. However, within the confinement of the experimental error, there does not appear to be a significant difference between the two isomers.

The results indicate that the ligand orientation around the metal center does not significantly affect the general photophysical properties of the complex. Despite the difference in dipole moments for the two isomers, this does not translate to the photophysical behavior. It can therefore be concluded that the differences in the ground and excited state energy levels are not significantly affected by the ligand orientation around the metal centers in complexes of this type, as would be anticipated by the DFT studies.

Conclusions

The premise for this work was the isolation of the *mer*-isomer of $[Ru(L1)_3](PF_6)_2$ by considering the inclusion of bulky ester functions. However, it appears that, upon increasing the steric bulk, a disproportionately large ratio of the *fac*-isomer can be formed. The precise nature of this effect is ambiguous, but it appears to be as a consequence of the increased lability of the ligands. To our knowledge, this is the first time a possible "pseudo-*trans*-influence" has been observed in the preparation of tris(bipyridine) complexes of ruthenium(II). Separation of the two isomers of $[Ru(L1)_3]^{2+}$ has been achieved using a simple and reproducible technique opening up the possibilities of isolating reasonable quantities of the *mer*-isomer. Since the smaller substituents give this structural motif in the best yields, this study shows that the best synthetic approach to isomerically pure *mer*-$[Ru(L1)_3]^{2+}$ is probably through direct combination of L1 with the ruthenium cation, and then removal of the 25% *fac*-isomer using preparative plate chromatography. Finally, a comparative photophysical investigation of both a *mer*- and *fac*-isomer of a ruthenium(II) tris-chelated complex indicates there to be no significance difference between the two structural forms. The consideration of the polypyridine complexes of ruthenium(II) as individual components in larger supramolecular architectures appears to be a continuing trend. Through this study, we have demonstrated that the individual isomers can be separated into pure compounds, suitable for the construction of larger species of known architecture easing the problems of characterization and structural integrity.

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Supporting Information Available: Molecular structures in PDB format. This material is available free of charge via the Internet at http://pubs.acs.org.

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