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Remarkable Effect of 4-Substituted 2,2′-Bipyridine Ligands on the Stereochemistry of Ruthenium(II) Complexes

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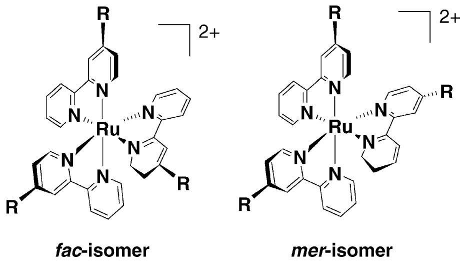
$[RuL_3](PF_6)_2$ complexes containing 4-alkoxycarbonyl-substituted unsymmetrical bipyridine ligands (L) have been obtained exclusively as the *fac* isomers by simple reaction of L with ruthenium(III) chloride in ethylene glycol under microwave irradiation. The position of the alkoxycarbonyl group on the pyridine ring and its transesterification by ethylene glycol were found critical for stereocontrol during ruthenium coordination.

Introduction

Ruthenium(II) complexes with 2,2′-bipyridine ligands constitute a huge field of research because of their stability, interesting redox and photochemical properties and applications in several areas.[1,2] With unsymmetrical 2,2′-bipyridine ligands, the homoleptic complexes $[RuL_3]^{2+}$ can be present in more than one isomeric form (Figure 1), making the analysis and design of multicomponent structures more problematic. For many applications, particularly for supramolecular chemistry, the complexes have to be available as single isomers.[3] Considerable progress has been made in the control of the Δ or Λ configurations,[4] but the geometric isomerism giving the *fac*/*mer* pairs has traditionally received far less attention. From purely statistical considerations, a 1:3 *fac*/*mer* ratio should be expected, and it has been observed in a number of cases, but it can be modified by several parameters. It is known that the statistical preference for the *mer* isomer can be increased by steric effects of the substituent.[5] Further insight in this area has recently came from Fletcher and co-workers with their studies on complexes with 5-substituted-2,2′-bipyridines.[5–8]



***fac*-isomer** ***mer*-isomer**

Figure 1. *fac* and *mer* isomers in RuL_3 complexes.

On the other hand, elegant preorganisations of the three ligands prior to complexation have been realised to direct the coordination towards the *fac* isomer. Some tripodal tris(bipyridine) ligands have been designed and reported to exclusively yield the *fac* isomer after hydrolysis to remove the tether.[6,9] Despite this promising approach, the *fac*/*mer* mixtures obtained generally have to be resolved by using tedious chromatographic techniques sometimes inducing *fac*-to-*mer* isomerisations.[10] From these studies, it is clear that electronic effects play an important role in stereochemical control. Indeed, the thermodynamically favoured arrangement should place each more electron-withdrawing pyridine ring of a given ligand at a *trans* position to the more electron-releasing one of the other ring, according to the so called *trans*-influence.[11]

From this result, it could be anticipated that binding the ester substituent to C-4 instead of C-5 should induce even greater electronic effects on the coordinating pyridine nitrogen atoms and thus enhance the formation of the *fac* isomer. Calculated Hückel charges (Figure 2) support the superior electron-withdrawing effect of the ester at C-4 on pyridine nitrogen electronegativity. In addition, the substituent at C-4 generates weaker steric effects, also auguring lower amounts of the *mer* isomer.

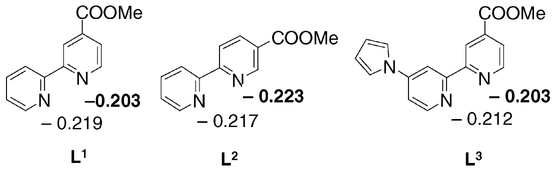


Figure 2. Ligands used in this work and the corresponding Hückel charges on the pyridine nitrogen atoms.

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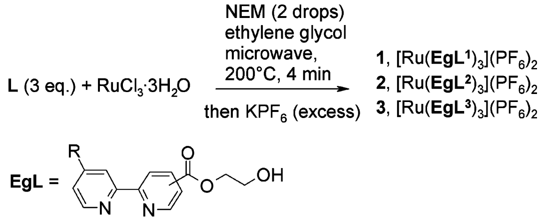
Results and Discussion

Ligands L^1, L^2 and L^3 were prepared in acceptable yields through Stille cross-couplings[12–16] between 2-(tributylstannyl)pyridine or 4-(1*H*-pyrrol-1-yl)-2-(tributylstannyl)pyridine[14] and the appropriate 2-chloro-(methoxycarbonyl)pyridine. Ligand L^2 was prepared for purposes of comparison.[5]

With the ligands in hand and following our previous studies,[12] we prepared the homoleptic Ru^{II} complexes by microwave irradiation of a mixture of ruthenium(III) chloride and the appropriate amount of ligand L in ethylene glycol in the presence of *N*-ethylmorpholine (NEM) as reducing agent (Scheme 1). After four minutes of irradiation (250 W, reflux at 200 °C), the expected dark red solutions (as a result of MLCT absorption) were obtained. After work-up, complexes **1**–**3** were obtained as red solids. The structural analyses were carried out directly on crude products to obtain the exact isomer compositions after the reaction.



Scheme 1. Preparation of complexes **1**–**3**.

The ^1H NMR spectrum of complex **1** was found to be clean (Figure 3). In the aliphatic region, three signals at δ = 4.47, 3.85 and 3.06 ppm integrating at a ratio of 2:2:1, respectively, were observed. This pattern was consistent with a hydroxyethyl ester moiety resulting from complete transesterification of the ligand by the solvent. Such a transesterification had already been detected elsewhere, but little detail was given.[17] More striking was the aromatic region, which showed the presence of seven main reso-

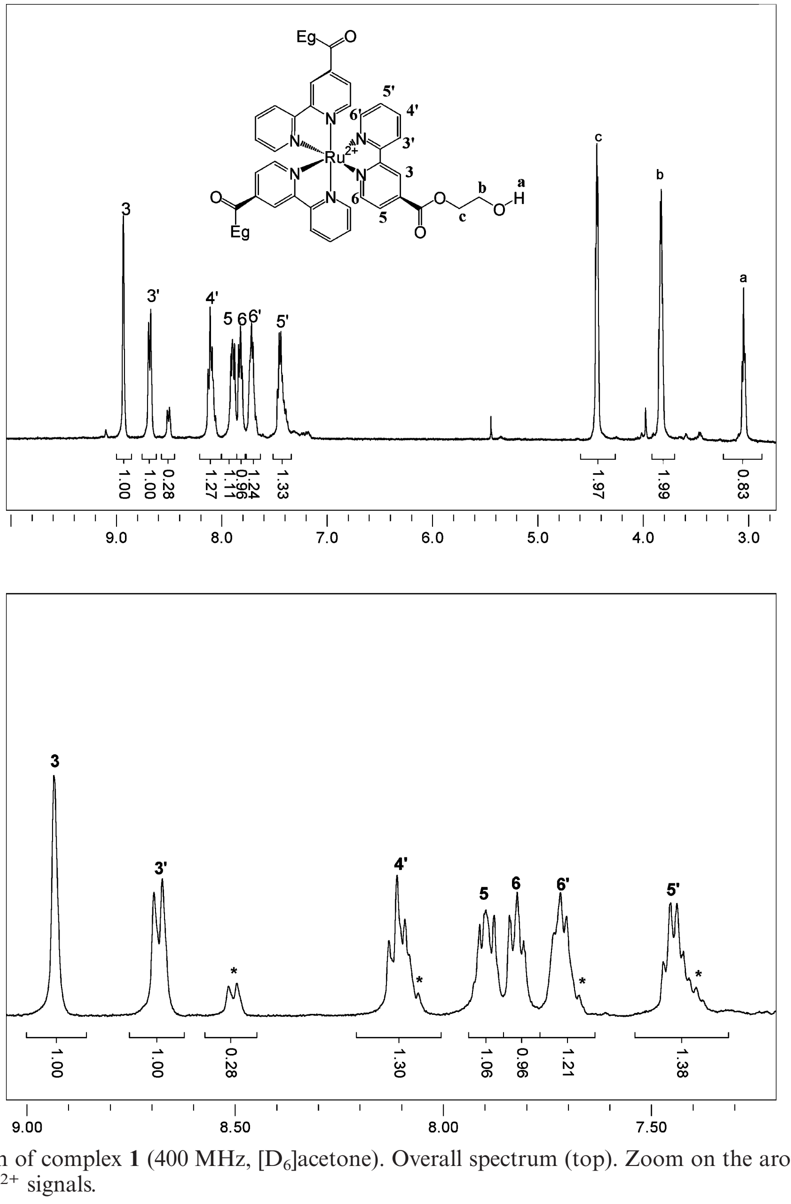


Figure 3. ^1H NMR spectrum of complex **1** (400 MHz, [D$_6$]acetone). Overall spectrum (top). Zoom on the aromatic region (bottom). The asterisks indicate $[Ru(bpy)_3]^{2+}$ signals.

nances assigned to pyridine protons. Such equivalence of the three ligands coordinated to the Ru atom indicates that the complex was present exclusively as the C_3-symmetric *fac* isomer, because in the *mer* isomer (C_1 symmetry) each ligand should give rise to an independent set of signals, and therefore the spectrum would be much more complicated (theoretically, 21 pyridine signals, probably with some overlap). The small doublet at δ = 8.52 ppm was attributed to one resonance of $[Ru(bpy)_3]^{2+}$ (the other being masked by complex **1**) arising from decarboxylation of the ligands under microwave irradiation, as already reported elsewhere.[17] The signals of $[Ru(bpy)_3]^{2+}$ were clearly assigned by adding a sample of this complex prepared separately into the NMR tube containing **1**. Other partially decarboxylated intermediates that could have potentially formed, such as $[RuEgL^1(bpy)_2]^{2+}$ or $[Ru(EgL^1)_2bpy]^{2+}$, were not observed to the NMR limit of detection. Except this side product, the spectrum clearly showed the major non-decarboxylated complex **1** with completely symmetrical *fac* geometry.

In order to compare this selectivity with published data, the microwave irradiation in ethylene glycol was repeated with ligand L^2, which bears the carboxylate group at the 5-position. After work-up, complex **2** was analysed by ^{1}H NMR (Figure 4). By comparing the spectrum with those of the published analogue,[7] it was found that also a mixture of the *mer* and *fac* isomers was present as clearly evidenced by the two doublets at δ = 8.65 and 8.73 ppm in a ratio consistent with published results. Moreover, the aliphatic region showed clearly that the ligand had been transesterified again by ethylene glycol and that a mixture of isomers (only three signals should be expected for the *fac* isomer) were present. It seems that the carboxylate group at C-4 instead of C-5 exclusively directed the coordination towards the *fac* isomer.

Finally, complex **3** was examined. The ^{1}H NMR spectrum of complex **3** was very clean (Figure 5). Only traces of an impurity were detected, which was identified as the complex with the fully decarboxylated ligand by comparison with the spectrum of an authentic sample that we had previously prepared.[11] Interestingly, much less decarboxylation was obtained than in complex **1**. In the aliphatic region, three resonances at δ = 4.48, 4.11 and 3.88 ppm integrating at a ratio of 2:1:2, respectively, were observed; they correspond to the transesterified ligands. The aromatic region was very clean: there were only eight sharp resonances that were assigned to the six pyridine protons and the two sets of pyrrole protons. Such equivalence of the three ligands coordinated to the Ru atom again indicated that the complex was present exclusively as the C_3-symmetric *fac* isomer. The *mer* isomer (C_1 symmetry) should theoretically give rise to up to 18 pyridine signals.

To gain further insight into this selectivity, we changed the reaction conditions used for the formation of **3**, namely, the solvent and the method of heating (Table 1).

Entries 1–2 show that the heating mode (microwave or thermal) does not affect the outcome of the reaction. In contrast, switching the solvent from ethylene glycol to dmf (and hence avoiding transesterification) prevented us from isolating the expected red product, but the neutral purple dichlorido complex (entries 3 and 4), as assessed by NMR and mass spectrometry, was obtained. The pure dichlorido product was obtained by microwave irradiation (entry 3) but not by thermal heating. Finally, other solvents with a boiling point similar to ethylene glycol were employed (entries 5 and 6), but only intractable mixtures were obtained. The complexation was also investigated at lower temperatures in ethylene glycol, butanol or ethanol (entries 7–9), in which case only the dichlorido complex, but no homoleptic complex **3**, was detected. Interestingly, the ligands were not transesterified, thus it appeared that such a reaction could occur only at high temperatures (near 200 °C). In summary, we were able to obtain the tris(chelate) complexes of ruthe-

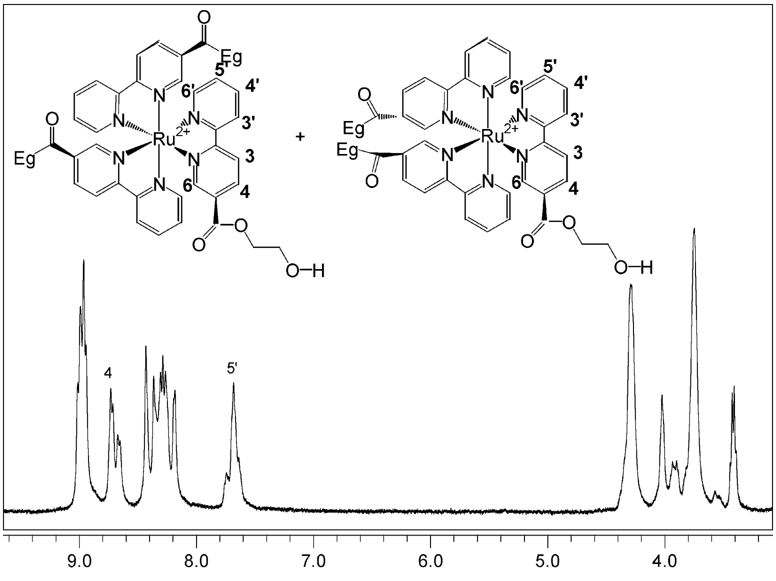


Figure 4. ^{1}H NMR spectrum of complex **2** (400 MHz, [D$_6$]acetone).

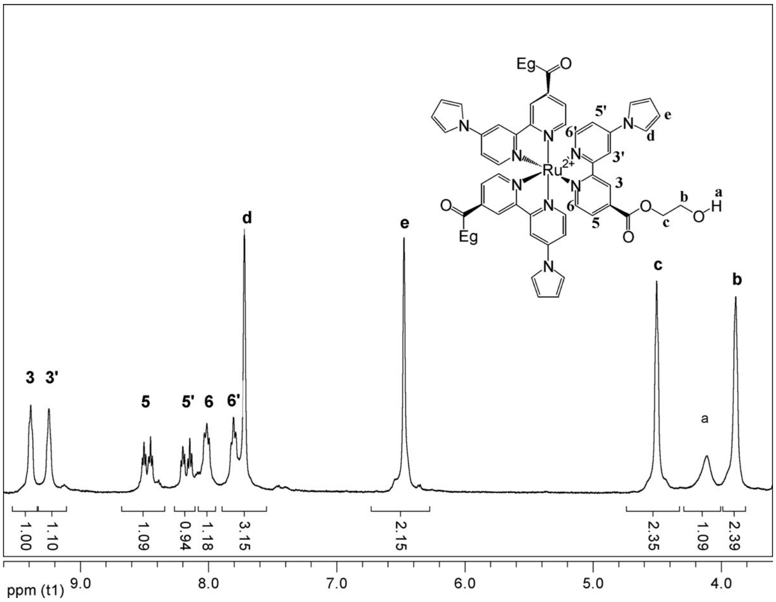


Figure 5. ^{1}H NMR spectrum of complex **3** (400 MHz, [D$_6$]acetone).

Table 1. Variation of reaction parameters for the preparation of **3**.[a]

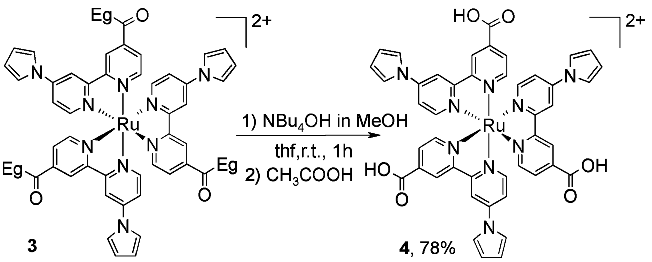
Entry	Conditions	Product, yield
1	$HO(CH_2)_2OH$, microwaves, 4 min, 200 °C	**3**, 82%
2	$HO(CH_2)_2OH$, Δ, 12 h, 200 °C	**3**, 84%
3	dmf, microwaves, 8 min, 160 °C	$[Ru(L^3)_2Cl_2]$, 68%
4	dmf, Δ, 12 h, 160 °C	$[Ru(L^3)_2Cl_2]$, in complex mixture
5	$MeO(CH_2CH_2O)_3Me$, microwaves, 10 min, 210 °C	complex mixture[b]
6	$CH_3(CH_2)_7OH$, microwaves, 10 min, 200 °C	complex mixture[b]
7	$HO(CH_2)_2OH$, microwaves, 4 min, 100 °C	$[Ru(L^3)_2Cl_2]$, 55%
8	$CH_3(CH_2)_3OH$, microwaves, 10 min, 120 °C	$[Ru(L^3)_2Cl_2]$, 40%
9	CH_3CH_2OH, microwaves, 10 min, 80 °C	$[Ru(L^3)_2Cl_2]$, 39%

[a] Reactions performed with 60 μmol $RuCl_3{\cdot}xH_2O$ and 0.19 mmol L^3 in 5 mL solvent. [b] Intractable mixture from which no product could be characterised.

nium only with ethylene glycol, as in our previous reports. The precise reason for that still remains a question, but it is possible that the combination of the polarity, high boiling point and good solubilising properties of ethylene glycol made it an ideal solvent to prepare the complexes. Another important factor is the ability of ethylene glycol to form hydrogen bonds with the nitrogen atoms of the bipyridine ligands. We hypothesise that hydrogen-bond interactions between the OH groups of the solvent (and/or those with the transesterified ligand) and the nitrogen atoms of the pyridine part of the ligands could help the third ligand to coordinate the ruthenium. At present, however, we do not know whether the transesterification of the ligand is only a secondary reaction or if it plays a major role in the complexation and in determining the isomer ratio.

To explain the selectivity, one hypothesis is that, due to hydrogen-bond interactions with the solvent, there is an organising effect such that the second and third incoming ligands give rise to the exclusive formation of the *fac* isomer. However, this should also lead to stereocontrol with **2**, which is clearly not the case. Another conceivable explanation is that, during the complexation, there is a rearrangement of the ligands, yielding the thermodynamically more stable *fac* configuration.[7] This explanation assumes that there is some kinetic lability of at least one of the ligands, which is supported by the high temperature of the synthesis (200 °C) and by the fact that the ligands have a strong electronic dissymmetry. This is especially pronounced for L^3, in which the ring bearing the pyrrole is a much better σ-donor and much worse π-acceptor than the ring with the carboxylate. These electronic effects are in agreement with the reports by Keene and co-workers, who studied the coordination of an unsymmetrical bipyridine ligands bearing two electron-donor substituents. With a methyl group and a neopentyl group on the 4- and 4′-positions, respectively, a mixture of the *fac* and *mer* isomers was always obtained.[18]

Finally, we verified that the ethylene glycolate chain in complex **3** could be easily removed to release the free carboxylic functions in order to obtain new donor–acceptor homoleptic complexes for TiO_2 sensitisation. Treatment of **3** with a methanol solution of NBu_4OH followed by acidification gave complex **4** in good yield (Scheme 2).



Scheme 2. Deprotection of esters in complex **2** (the PF_6 anion was omitted for clarity).

Conclusions

In summary, we have shown that the introduction of a 4-alkoxycarbonyl substituent in 2,2′-bipyridine allowed stereocontrol of coordination and formation of the *fac*-homoleptic $[RuL_3]^{2+}$ complexes in ethylene glycol. To the best of our knowledge, this is the first time that the *fac* isomer has been prepared as a single product by using disconnected bipyridine ligands. This process is an important step towards the controlled design of well-defined supramolecular architectures. The evaluation of complex **4** as sensitiser in photovoltaic cells is under investigation and will be reported in due course. The preparation of other unsymmetrical ligands with different electronic properties and their corresponding complexes is also progressing in order to gain further insight into the origin of the exclusive preference for the *fac* isomer.

Experimental Section

Preparation of Complexes 1–3: The typical procedure for complexes **1**–**3** is as follows: Ligand $\mathbf{L^3}$ (53.1 mg, 0.19 mmol), $RuCl_3{\cdot}3H_2O$ (15.69 mg, 0.06 mmol) and two drops of *N*-ethylmorpholine were suspended in ethylene glycol (5 mL), and the mixture was heated under reflux for 14 h or alternatively irradiated in the CEM discover microwave oven (250 W, 200 °C, 4 min). Once cold, the orange solution was poured into a saturated aqueous solution of KPF_6 (25 mL) and left in the refrigerator for 5–6 h. The red solid formed was filtered and washed with water, toluene and diethyl ether. The solid obtained was dissolved in the minimum amount of acetonitrile, poured into water (25 mL) and left to precipitate in the refrigerator. After filtration and washing (water, toluene, diethyl ether), the product was obtained as a dark red solid. Yield: 65 mg (82%). ^1H NMR (400 MHz, $[D_6]$acetone): $\delta = 9.40$ (br. s, 1 H), 9.25 (br. s, 1 H), 8.46 (dd, $J = 10.4$ and 6.0 Hz, 1 H), 8.16 (dd, $J = 12.4$ and 6.4 Hz, 1 H), 8.02 (dd, $J = 5.8$ Hz and 1.5 Hz, 1 H), 7.82 (dd, $J = 6.0$ and 1.6 Hz, 1 H), 7.72 (s, 2 H), 6.47 (s, 2 H), 4.48 (br. s, 2 H), 4.12 (br. s, 1 H), 3.89 (br. s, 2 H) ppm. MS (ESI): *m*/*z* = 1174.0 $[M - PF_6]^+$, 514.6 $[M - 2PF_6]^{2+}$. $C_{51}H_{45}F_{12}N_9O_9P_2Ru{\cdot}H_2O$ (1337.15): calcd. C 45.77, H 3.54, N 9.43; found C 46.02, H 3.75, N 9.18.

Preparation of $[Ru(HCOOL^2)_3]_2(PF_6)_2$ (4): Complex **3** (13.19 mg, 0.01 mmol) was dissolved in thf (5 mL), and the mixture was sonicated until complete dissolution. A solution of NBu_4OH in methanol (0.2 mL of a 0.1 M solution) was then added; a precipitate formed instantaneously, and the suspension was stirred for one hour at room temperature. Water (5 mL) was then added to dissolve the precipitate. The solvent thf was then evaporated under reduced pressure, and the pH of the aqueous phase was adjusted to 3 by using glacial acetic acid. The precipitate formed was then left in the refrigerator for 5–6 h. The red solid was then collected by filtration and washed with water, diethyl ether and dried overnight under reduced pressure to yield **4** as a red solid (9.30 mg, 78%) in pure form. ^1H NMR (400 MHz, $[D_6]$DMSO): $\delta = 9.35$ (br. s, 1 H), 9.09 (br. s, 1 H), 7.93 (s, 2 H), 7.60–7.80 (m, 4 H), 6.42 (s, 2 H) ppm. MS (ESI): *m*/*z* = 896.1 $[M - 2PF_6 - H]^+$. $C_{45}H_{33}F_{12}N_9O_6P_2Ru{\cdot}2H_2O$ (1222.10): calcd. C 44.19, H 3.05, N 10.31; found C 43.82, H 2.79, N 10.62.

Supporting Information (see footnote on the first page of this article): Experimental procedures and additional spectroscopic characterisation.

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