

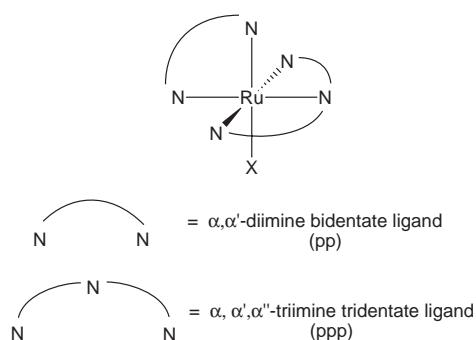
New synthetic route to monocarbonyl polypyridyl complexes of ruthenium: their stereochemistry and reactivity

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A new photochemical synthetic route to species of the type $[\text{Ru}(\text{terpy})(\text{pp})(\text{CO})]^{2+}$ has been elaborated [terpy = 2,2':6',2''-terrapyridine; pp = a bidentate α,α' -diimine ligand such as 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen), 4,4'-dimethyl-2,2'-bipyridine (dmbpy) or 4-(2-methylpropyl)-2,2'-bipyridine (mpbpy)]. For the species $[\text{Ru}(\text{terpy})(\text{mpbpy})(\text{CO})]^{2+}$ containing the new unsymmetrically substituted ligand (mpbpy) the two possible geometric isomers were separated by cation-exchange chromatography. The carbonyl groups can readily be removed and the vacant site substituted with pyridine, triphenylphosphine and chloride, with retention of the stereochemistry at the metal centre. By the correct choice of monodentate ligand at the sixth co-ordination site, the MLCT absorption maximum in the electronic spectra can be shifted by up to 150 nm, and the $\text{Ru}^{\text{III}}-\text{Ru}^{\text{II}}$ redox couple by over 1 V.

Heteroleptic ruthenium complexes of the type $[\text{Ru}(\text{ppp})(\text{pp})\text{X}]^{n+}$ (pp is a bidentate and ppp a tridentate polypyridyl ligand, with the sixth co-ordination site occupied by a wide variety of monodentate species X) have been the subject of considerable and varied research interest. For example, $[\text{Ru}(\text{terpy})(\text{bpy})(\text{H}_2\text{O})]^{2+}$ (terpy = 2,2':6',2''-terrapyridine and bpy = 2,2'-bipyridine) has been long known as the precursor of the ruthenyl ($\text{Ru}^{\text{IV}}=\text{O}$) species $[\text{Ru}(\text{terpy})(\text{bpy})\text{O}]^{2+}$, which has applications as an oxidising agent.¹⁻⁴ Secondly, studies of the oxidative dehydrogenation of complexes such as $[\text{Ru}(\text{terpy})(\text{bpy})(\text{amine})]^{2+}$ (amine = isopropylamine and a number of secondary amines such as piperidine and pyrrolidine) have revealed the stabilisation of unusual imine product species through π -back bonding by the ruthenium(II) metal centre.⁵⁻⁷ As a third example, the complex $[\text{Ru}(\text{terpy})(\text{bpy})(\text{CO})]^{2+}$ has been reported to chemically catalyse the electrochemical reduction of carbon dioxide to methanol.^{8,9}



The co-ordination compounds of ruthenium(II) containing polypyridyl ligands have drawn considerable interest due to their unique photophysical and redox characteristics.¹⁰⁻¹² The versatile series of complexes $[\text{Ru}(\text{ppp})(\text{pp})\text{X}]^{n+}$ was of particular interest to the authors in terms of the possibilities of tuning their photophysical and redox properties by appropriate choice of the monodentate ligand, in the same manner as observed for heteroleptic tris(bidentate) complexes of ruthenium.¹³

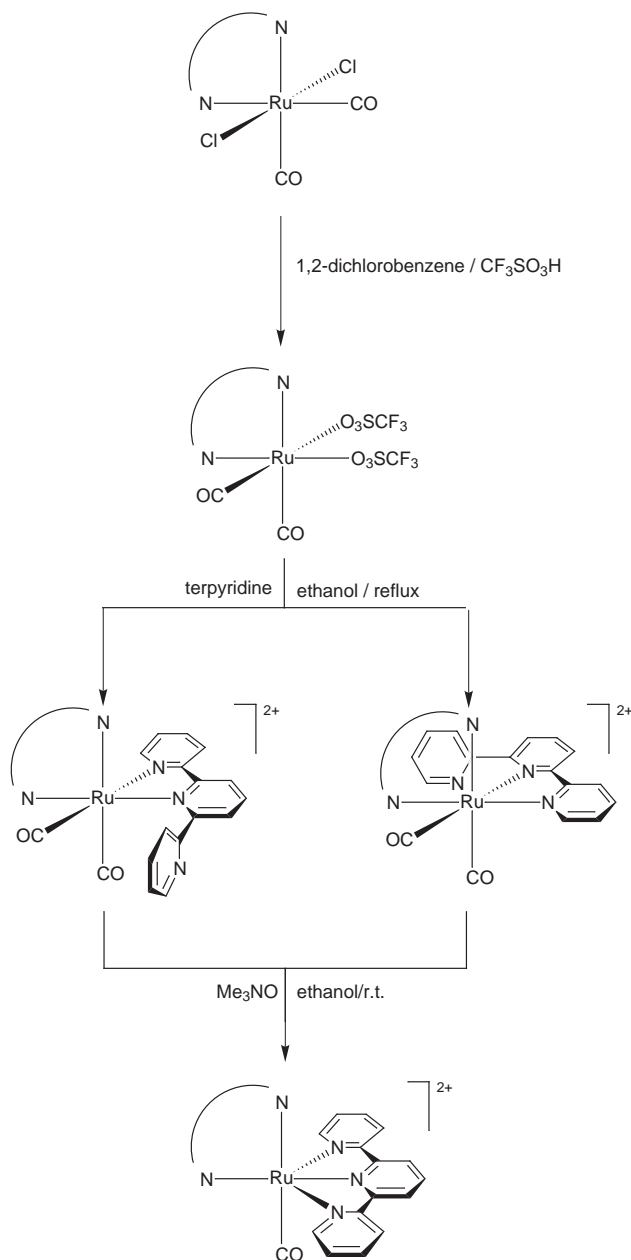
The most common route to the target complexes has been *via* a stepwise ligand addition, applying the tridentate ligand (ppp)

initially to hydrated RuCl_3 to produce complexes of the type $[\text{Ru}(\text{ppp})\text{Cl}_3]$, followed by addition of the bidentate ligand (pp) to give $[\text{Ru}(\text{ppp})(\text{pp})\text{Cl}]^+$.¹⁴ Replacement of the final chloro ligand has then been achieved, either by direct substitution of the new ligand,¹⁴⁻¹⁸ or *via* an intermediate such as the trifluoromethanesulfonato species.^{7,19} However, the method does not always allow access to the desired target complex in good purity or high yield.¹⁸ Alternatively, a versatile synthesis has been demonstrated *via* the nitrosyl species (formed by acidification of the nitro compound which is obtained readily from the chloro precursor) involving its reaction with stoichiometric quantities of azide ion in the presence of the required ligand.²⁰ The technique is based on the facile reaction $\text{Ru}^{\text{II}}-\text{NO}^+ + \text{N}_3^- \longrightarrow \text{N}_2\text{O} + \text{N}_2$, which leaves the co-ordination site available to substitution by a monodentate ligand. Despite the versatility, there are clearly a number of steps involved in the synthetic route.^{6,7,21}

In the light of our earlier studies involving carbonyl complexes as precursors in the synthesis of ruthenium(II) complexes,¹³ we wished to investigate the synthetic utility of carbonyl species of the type $[\text{Ru}(\text{ppp})(\text{pp})(\text{CO})]^{2+}$, on the premise that decarbonylation *via* oxidation using trimethylamine *N*-oxide might provide an alternative route to the $[\text{Ru}(\text{ppp})(\text{pp})\text{X}]^{n+}$ species. However, published routes to the carbonyl species are not trivial either. An example of the direct substitution of a chloro ligand using high pressures and temperatures in the presence of carbon monoxide has been published, but it is not suitable for a large scale synthesis.⁹ An alternative route has been described by Thomas and Fischer²² (Scheme 1) in which the bidentate ligand is added first in the formation of $[\text{Ru}(\text{pp})(\text{CO})_2\text{Cl}_2]$. In an analogous fashion to the method used in the preparation of heteroleptic tris(bidentate ligand) species,¹³ the two chloro ligands were substituted with the more labile trifluoromethanesulfonato ligands, and $[\text{Ru}(\text{pp})(\text{CO})_2(\text{CF}_3\text{SO}_3)_2]$ was then treated with terpyridine to form the complex $[\text{Ru}(\text{terpy})(\text{pp})(\text{CO})_2]^{2+}$, in which the terpyridine adopts a bidentate, rather than the more typical tridentate, co-ordination geometry.²² The desired product may then be produced by the decarbonylation of one of the two carbonyl ligands by the addition of a stoichiometric quantity of Me_3NO .

The present paper reports a new direct photosynthetic route to polypyridyl ruthenium(II) complexes of the type $[\text{Ru}(\text{tridentate ligand})(\text{bidentate ligand})(\text{CO})]^{2+}$, and their use as precursors in synthesis of other $[\text{Ru}(\text{ppp})(\text{pp})\text{X}]^{n+}$ species.

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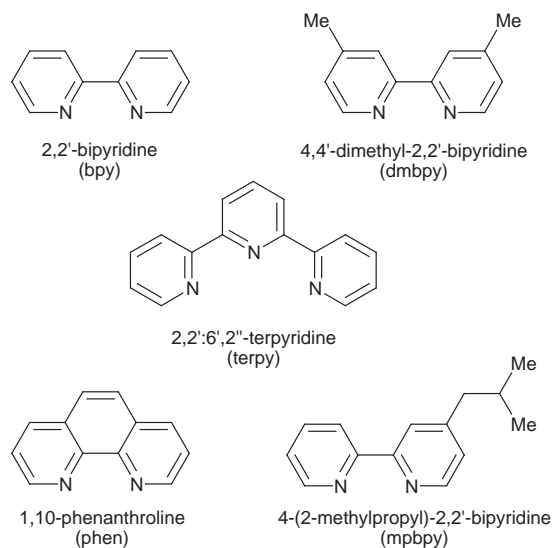


Scheme 1 Published synthetic route for the preparation of $[\text{Ru}(\text{ppp})(\text{pp})(\text{CO})]^{2+}$; ²² r.t. = room temperature

Results and Discussion

The two complexes $[\text{Ru}(\text{terpy})(\text{bpy})(\text{CO})]^{2+}$ and $[\text{Ru}(\text{terpy})(\text{phen})(\text{CO})]^{2+}$ (phen = 1,10-phenanthroline) were synthesized by the route described by Thomas and Fischer²² (Scheme 1). Using the same method the complex $[\text{Ru}(\text{terpy})(\text{dmbpy})(\text{CO})]^{2+}$ (dmbpy = 4,4'-dimethyl-2,2'-bipyridine) was also prepared. Proton NMR data [in $(\text{CD}_3)_2\text{SO}$] of the previously reported complexes have been published, although the assignment of the peaks was not made. In the current study the intermediate dicarbonyl species $[\text{Ru}(\text{terpy})(\text{pp})(\text{CO})_2]^{2+}$ all gave spectra considerably more complex than those previously reported.²² With a bidentate terpyridine ligand there are two possible geometric isomers, each possessing C_1 point group symmetry, which are likely to be present in unequal proportions due to steric considerations. This was clearly demonstrated in the ¹H NMR spectrum of the complex $[\text{Ru}(\text{terpy})(\text{dmbpy})(\text{CO})_2]^{2+}$ which showed four methyl signals, indicating the presence of both forms in the isolated product. In a previous study of analogous species $[\text{Ru}(\text{terpy})(\text{phen})(\text{CO})_2]^{2+}$ ²² the ¹H NMR spectrum reported was significantly simpler. An X-ray structural deter-

mination of a crystal isolated as the protonated salt $[\text{Ru}(\text{Hterpy})(\text{phen})(\text{CO})_2][\text{BF}_4]_3$ characterised it as the isomer which would be likely to be the more stable on the basis of steric interactions: presumably in that instance only the single isomer was obtained on crystallisation.²²



The ¹H NMR spectra of the monocarbonyl complexes $[\text{Ru}(\text{terpy})(\text{pp})(\text{CO})][\text{PF}_6]_2$ were considerably simpler than those of the dicarbonyl species. Upon co-ordination of the third ligation site of the terpyridine the resulting complex possesses C_s symmetry with the plane coincident with the bidentate ligand, orthogonally intersecting the terpyridine ligand. Using ¹H-¹H COSY NMR techniques in conjunction with the relative integration of the peaks, in a manner similar to that described by Gerli *et al.*⁴ in the interpretation of the spectrum for the complex $[\text{Ru}(\text{terpy})(\text{bpz})\text{Cl}]^+$ (bpz = 2,2'-bipyrazine), it was possible completely to assign the spectra for each of the complexes, leading to the data given in Table 1. Several significant points are noted. For each of the complexes the resonances of the terpyridine ligand (rings C and D) have similar chemical shifts, with the integration clearly identifying their signals. The two rings of the bidentate ligand have a significantly different environment: ring A lies *trans* to the terpyridine, while ring B lies *trans* to the carbonyl ligand. Assignment may be made by considering the aromatic anisotropy experienced by proton H6 for each ring: in ring A this proton lies over the carbonyl group, and experiences no effect from an adjacent aromatic group. However, ring B lies over ring D of the terpyridine ligand, and as a consequence experiences a large ring current (anisotropy) so that it is considerably more shielded (upfield) than ring A (typically over 2 ppm). Similar effects, although smaller, are observed on the other protons of each ring, where the relative connectivities were assigned using COSY techniques.

If the bidentate ligand is unsymmetrical, as in mpbpy, additional stereochemical complexity is introduced as there are two possible geometrical isomers in the final product, one with the functional group on ring A the other with it on ring B.

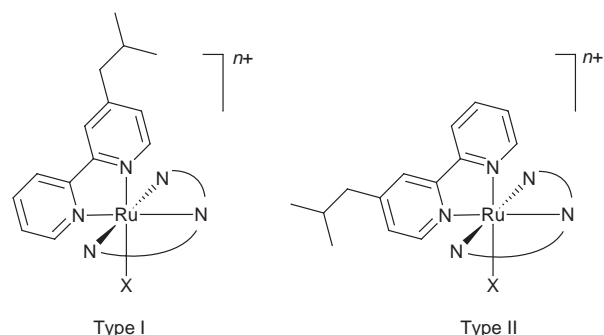
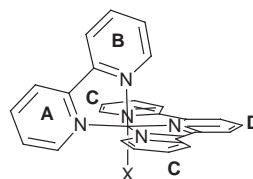


Table 1 300 MHz ^1H NMR Data [δ (J/Hz)] for the complexes (all salts are PF_6^- in CD_3CN)^a



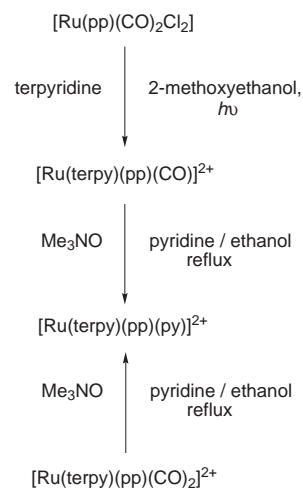
Complex	pp ring A				pp ring B				terpy ring C				terpy ring D		pyridine			aliphatic			
	H3	H4	H5	H6	H2	H4	H5	H6	H3	H4	H5	H6	H3	H4	H2	H3	H4	CH ₂	CH	CH ₃	
[Ru(terpy)(bpy)(CO)] ²⁺	8.64 (8.1)	8.38 (7.8)	7.94 (5.7)	9.56 (5.7)	8.49 (8.1)	8.07 (7.6)	7.33 (5.7)	7.22 (5.7)	8.46 (8.1)	8.13 (8.0)	7.42 (5.7)	7.72 (4.7)	8.60 (7.8)	8.53 (8.1)							
[Ru(terpy)(dmbpy)(CO)] ²⁺	8.49	2.72 ^b (7.8)	7.76 (7.6)	9.35 (5.7)	8.34	2.41 ^b (7.6)	7.14 (5.7)	7.02 (5.7)	8.44 (7.9)	8.13 (7.8)	7.43 (7.7)	7.71 (5.7)	8.58 (8.1)	8.51 (8.1)							
[Ru(terpy)(phen)(CO)] ²⁺	8.34 (9.0)	8.95 (8.1)	8.27 (5.2)	9.89 (3.8)	8.21 (9.0)	7.64 <i>c</i>	7.64 <i>c</i>	8.59 7.1	8.52 (8.1)	8.05 (8.1)	7.25 (5.7)	7.54 (5.7)	8.71 (8.1)	8.63 (7.2)							
<i>cis</i> - [Ru(terpy)(mpbpy)(CO)] ²⁺	8.64 (8.1)	8.37 (8.0)	7.92 (5.7)	9.54 (5.7)	8.31	—	7.13 (5.7)	7.06 (5.7)	8.45 (8.1)	8.13 (8.0)	7.43 (5.7)	7.72 (5.7)	8.59 (8.0)	8.52 (7.9)				2.50 (6.7)	1.86 (6.7)	0.81 (6.7)	
<i>trans</i> - [Ru(terpy)(mpbpy)(CO)] ²⁺	8.47	—	7.71 (5.7)	9.38 (5.7)	8.48 (8.1)	8.06 (7.9)	7.31 (5.6)	7.20 (5.7)	8.45 (8.1)	8.13 (7.9)	7.43 (5.7)	7.71 (5.7)	8.59 (7.6)	8.54 (7.9)				2.87 (7.6)	2.19 <i>c</i>	1.07 (6.7)	
[Ru(terpy)(bpy)(py)] ²⁺	8.66 <i>c</i>	8.29 (7.9)	7.81 (7.9)	8.65 <i>c</i>	8.39 (8.6)	7.81 <i>c</i>	7.06 (5.7)	7.25 (5.7)	8.42 (8.1)	8.01 (7.9)	7.39 (5.3)	7.77 (5.5)	8.51 (8.6)	8.18 (8.1)	7.67 (6.7)	7.19 (6.4)	7.76 <i>c</i>				
[Ru(terpy)(dmbpy)(py)] ²⁺	8.51	2.72 ^b (7.8)	7.66 (4.8)	8.47 (6.2)	8.25	2.36 ^b (7.9)	6.88 (5.7)	7.04 (5.7)	8.41 (8.1)	8.00 (7.9)	7.40 (5.5)	7.77 (4.8)	8.50 (8.1)	8.16 (8.1)	7.65 (6.2)	7.17 (6.7)	7.75 (7.6)				
[Ru(terpy)(phen)(py)] ²⁺	8.34 (9.1)	8.86 (8.3)	8.18 (8.6)	9.07 (5.2)	8.16 (9.1)	8.37 (8.3)	7.40 (5.3)	7.62 (6.0)	8.43 (7.7)	7.96 (8.0)	7.25 (8.0)	7.60 (6.7)	8.56 (8.1)	8.34 (8.3)	7.83 (6.0)	7.24 <i>c</i>	7.80 (7.6)				
<i>cis</i> - [Ru(terpy)(mpbpy)(py)] ²⁺	8.68 (8.1)	8.28 (7.6)	7.80 (5.7)	8.65 (5.7)	8.25	—	6.87 (5.7)	7.09 (6.2)	8.45 (8.1)	8.00 (7.9)	7.39 (5.7)	7.77 (4.8)	8.54 (8.1)	8.17 (8.1)	7.67 (5.3)	7.18 (6.9)	7.75 (7.6)	2.51 (7.2)	1.82 (7.0)	0.78 (6.7)	
<i>trans</i> - [Ru(terpy)(mpbpy)(py)] ²⁺	8.50	—	7.64 (6.2)	8.50 (4.8)	8.39 (8.1)	7.79 (8.0)	7.04 (7.6)	7.23 (5.7)	8.42 (8.1)	8.01 (7.9)	7.40 (5.3)	7.76 (5.3)	8.52 (8.1)	8.17 (8.1)	7.67 (6.2)	7.18 (5.2)	7.67 (7.6)	2.89 (7.6)	2.11 <i>c</i>	1.08 (6.9)	
[Ru(terpy)(dmbpy)(PPh ₃)] ²⁺	8.51	2.67 ^b (7.8)	7.41 (6.2)	9.06 (6.2)	8.30	2.36 ^b (7.9)	6.75 (6.0)	6.92 (5.8)	8.10 (8.1)	7.88 (7.9)	7.65 (5.2)	7.84 (5.2)	8.08 (8.1)	7.97 (8.1)	6.86 ^d (8.8)	7.18 ^d (8.1)	7.38 ^d (6.2)				
[Ru(terpy)(dmbpy)Cl] ²⁺	8.44	2.73 (7.8)	7.77 (5.7)	9.98 (5.7)	8.15	2.31 (7.9)	6.76 (5.7)	7.06 (5.7)	8.35 (8.1)	7.85 (7.9)	7.26 (5.3)	7.66 (5.2)	8.46 (8.1)	8.04 (8.1)							

^a When pp is bpy or the unfunctionalised side of L, H3 and H6 are doublets, H4 and H6 are doublets of doublets. When pp is dmbpy or the substituted side of L, H3 is a singlet, H5 and H6 are doublets of doublets. When pp is phen (an unorthodox numbering scheme is assumed to correlate with bpy), H3, H4 and H6 are doublets, H5 is a doublet of doublets. ^b The shift quoted for the H4 proton for the methyl substituent. ^c The coupling constants were unobtainable, due to the overlying of several peaks. ^d Protons for the PPh₃ group.

In view of our previous success with cation-exchange chromatographic techniques in the separation of stereoisomers of mononuclear and oligonuclear species based on tris(bidentate ligand) metal centres, it was of interest to know whether similar methods might be applied to the separation of these two isomers.^{23–32} For this purpose the ligand 4-(2-methylpropyl)-2,2'-bipyridine (mpbpy) was synthesized by the lithiation of 4-methyl-2,2'-bipyridine and subsequent reaction with 2-bromopropane. The new ligand was obtained as a viscous oil, which proved extremely soluble in most organic solvents. Using previously reported methods^{13,29} it was possible to prepare the complex $[\text{Ru}(\text{mpbpy})(\text{CO})_2\text{Cl}_2]$ in reasonable yield. However during the next step of the synthesis the isolation of the bis(trifluoromethanesulfonato) complex $[\text{Ru}(\text{mpbpy})(\text{CF}_3\text{SO}_3)_2(\text{CO})_2]$ proved difficult as the precipitation by diethyl ether from 1,2-dichlorobenzene solution was rendered difficult by the excellent solubility induced by the appended isopropyl substituent. The crude product was isolated by removal of the solvent using vacuum distillation, and it was used without further purification. Subsequent reaction with terpyridine provided a pale brown solid in tolerable yield (45%). Infrared spectroscopy confirmed that there were two peaks in the carbonyl stretch region ($\tilde{\nu}_{\text{CO}} = 2092$ and 2040 cm^{-1}), consistent with previously reported species.¹³ Proton NMR spectroscopy proved of marginal use since there are theoretically four possible geometric isomers, all of which appeared to be present in the aliphatic region of the spectrum for the reaction products (see Experimental section). Similarly, four signals were observed for the downfield shifted H6a proton of the bpy moiety (at δ 9.16, 9.04, 8.90 and 8.88) leading to the same conclusions. However, attempts selectively to decarbonylate one of the carbonyl groups proved difficult, as the second was removed with remarkable ease. Consequently an alternative synthetic route was required.

It was observed that the yellow complexes of the type $[\text{Ru}(\text{pp})(\text{CO})_2\text{Cl}_2]$ darkened in colour when exposed to direct sunlight, possibly indicating a decarbonylation, consistent with earlier reports where photoactivation of the same species has been used in the substitution of a second bidentate ligand.³³ Consequently a new photochemical route was investigated for the direct addition of a triply co-ordinated terpyridine ligand. Solutions of the precursor complexes $[\text{Ru}(\text{pp})(\text{CO})_2\text{Cl}_2]$ in 2-methoxyethanol with a slight excess of terpyridine under argon gave the desired complexes in tolerable yield after a total of approximately 18 h exposure to direct tropical sunlight. It was observed that the reaction also proceeded after exposure to a UV lamp, but required considerably longer reaction times. The resulting mixture was filtered to remove the starting product (or possible intermediates in the reaction), and the solvent removed under reduced pressure. The crude reaction products were then purified by cation-exchange chromatography on SP Sephadex C-25 support, eluting with aqueous 0.2–0.3 mol dm⁻³ sodium toluene-4-sulfonate solution (containing 10% acetone in the case of complexes incorporating mpbpy, to improve solubility in water). A minor fast-moving red band was tentatively assigned as the by-product $[\text{Ru}(\text{terpy})(\text{pp})\text{Cl}]^+$, but was not typically obtained in sufficient yield to facilitate complete characterisation. The following major pale yellow band was then collected, and found to be the desired product in 15–25% yield after isolation as the hexafluorophosphate salt. This was closely followed by another minor brown-red band, again never obtained in large quantities but tentatively assigned as an aqua species. Proton NMR spectra for all the target complexes were in agreement with those for the same complexes prepared by the more traditional method.

The complex $[\text{Ru}(\text{terpy})(\text{mpbpy})(\text{CO})]^{2+}$, prepared by the photolytic decarbonylation described above, was obtained as an approximate 50% mixture of the two possible geometric isomers. Separation of these two species was achieved using



Scheme 2 New photosynthetic route for the synthesis of $[\text{Ru}(\text{ppp})(\text{pp})(\text{CO})]^{2+}$

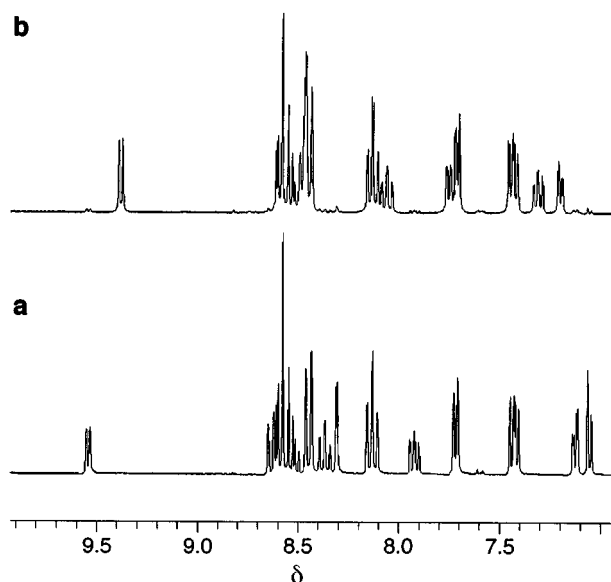


Fig. 1 Proton NMR (CD_3CN , 300 MHz) spectra of the complexes (a) *cis*- $[\text{Ru}(\text{terpy})(\text{mpbpy})(\text{CO})][\text{PF}_6]_2$ and (b) *trans*- $[\text{Ru}(\text{terpy})(\text{mpbpy})(\text{CO})][\text{PF}_6]_2$

cation-exchange chromatography by passage down a long column (SP Sephadex C-25; approximately 2 m in length), eluting with aqueous sodium toluene-4-sulfonate solution (0.3 mol dm⁻³) containing 10% ethanol. The two pale yellow bands were collected and isolated as the hexafluorophosphate salts. Both isomers demonstrated distinctly different patterns in their ¹H NMR spectra (Fig. 1). Using ¹H–¹H COSY NMR techniques, in conjunction with the relative integration of the peaks, it was again possible to assign all the resonances (Table 1). The signals for the terpyridine rings were all consistent with the assignments of the analogous complexes containing symmetrical ligands (discussed previously). The first band down the column had the substituted ring at position B, since the proton H6 exhibited a chemical shift of δ 7.06, while the same proton resonates at δ 9.38 for the second band in accordance with its assignment to ring A. Hence the first band off the column is assigned as the one which has the functionalised pyridyl *trans* to the carbonyl ligand and *cis* to terpyridine (Type I), while the second fraction has the functionalised pyridyl *cis* to the carbonyl and *trans* to the terpyridine (Type II). Similar arguments can be made using the methylene proton signals, leading to the same conclusions.

For the monocarbonyl complexes $[\text{Ru}(\text{terpy})(\text{pp})(\text{CO})]^{2+}$ to be of synthetic utility the carbonyl moiety has to be readily

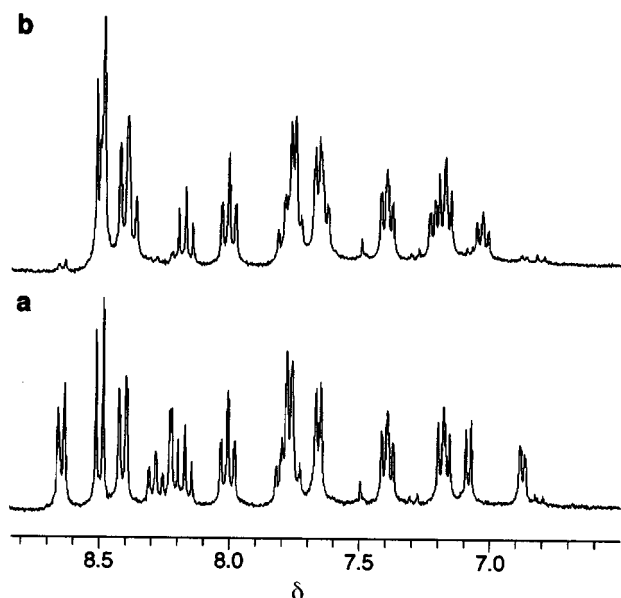


Fig. 2 Proton NMR (CD_3CN , 300 MHz) spectra of the complexes (a) *cis*- $[\text{Ru}(\text{terpy})(\text{mpbpy})(\text{py})](\text{PF}_6)_2$ and (b) *trans*- $[\text{Ru}(\text{terpy})(\text{mpbpy})(\text{py})](\text{PF}_6)_2$

removed and replaced with the desired target ligand. By addition of a large excess of Me_3NO to $[\text{Ru}(\text{terpy})(\text{pp})(\text{CO})]^{2+}$ in refluxing ethanol an immediate change from yellow-orange to dark red was observed as the carbonyl was removed and replaced by a solvent ligand. For characterisation, pyridine was subsequently added and the mixture refluxed for up to 8 h, giving a cherry red solution. Only one major product was observed during purification by cation-exchange chromatography.

Using similar procedures under the same conditions (excess of Me_3NO with pyridine in ethanolic solution) the dicarbonyl complexes $[\text{Ru}(\text{terpy})(\text{bpy})(\text{CO})_2]^{2+}$, $[\text{Ru}(\text{terpy})(\text{dmbpy})(\text{CO})_2]^{2+}$ and $[\text{Ru}(\text{terpy})(\text{phen})(\text{CO})_2]^{2+}$ yielded the same products $\{[\text{Ru}(\text{terpy})(\text{pp})(\text{py})]^{2+}\}$ as the monocarbonyl species; the identity of the products was confirmed by ^1H NMR spectroscopy. Consequently, the intermediate monodecarbonylation is not a prerequisite to obtaining target compounds, eliminating a delicate step from the reported reaction sequence.

To confirm the retention of stereochemistry at the metal centre upon the removal and subsequent replacement of the carbonyl moiety by an alternative monodentate ligand, the two geometric isomers of the complex $[\text{Ru}(\text{terpy})(\text{mpbpy})(\text{CO})]^{2+}$ were treated separately. Using reaction conditions similar to those described, the carbonyl ligand was exchanged for pyridine in the presence of a large excess of Me_3NO in refluxing ethanol. Following purification of the complexes by cation-exchange chromatography and isolation of the products as the hexafluorophosphate salts, the complexes were characterised by ^1H NMR studies. As illustrated in Fig. 2, the two reactions yielded clearly different complexes, each uncontaminated by the other isomer. By comparison with the spectra for similar complexes, full assignment was made (Table 1). It is clear that no scrambling of the ligand positions is observed during the reaction, since the relative positions of the chelate ligands are the same for both the reactants and products. This is in contrast with the decarbonylation of the complex $[\text{Ru}(\text{bpy})_2(\text{CO})]^{2+}$, where slight scrambling is observed at temperatures greater than 40°C .³⁴

Species of the type $[\text{Ru}(\text{pp})(\text{pp})(\text{CO})]^{2+}$ can be used as a precursor to a wide variety of complexes, which display a great variety of electrochemical and photophysical characteristics. For example, the carbonyl ligand of the complex $[\text{Ru}(\text{terpy})(\text{bpy})(\text{CO})]^{2+}$ was replaced with triphenylphosphine, chloride ion and thiocyanate ion using similar conditions as described for the analogous pyridine complex. The former two ligands

Table 2 Comparison of electrochemical and spectroscopic data for complexes of the type $[\text{Ru}(\text{terpy})(\text{pp})\text{X}]^{n+}$

Complex	Electrochemical potentials ($\text{Ru}^{\text{III}}-\text{Ru}^{\text{II}}$) ^a E_p/V ($\Delta E_p/\text{mV}$) vs. SCE	Electronic spectrum (MLCT) $\lambda_{\text{max}}^b/\text{nm}$
$[\text{Ru}(\text{terpy})(\text{dmbpy})\text{Cl}]^+$	0.75 (100)	506
$[\text{Ru}(\text{terpy})(\text{dmbpy})(\text{PPh}_3)]^{2+}$	1.35 (80)	438
$[\text{Ru}(\text{terpy})(\text{dmbpy})(\text{CO})]^{2+}$	1.89 (120)	364
$[\text{Ru}(\text{terpy})(\text{dmbpy})(\text{py})]^{2+}$	1.19 (110)	470
$[\text{Ru}(\text{terpy})(\text{bpy})\text{Cl}]^+$	0.81 (70)	502
$[\text{Ru}(\text{terpy})(\text{bpy})(\text{py})]^{2+}$	1.26 (130)	467
$[\text{Ru}(\text{terpy})(\text{phen})(\text{py})]^{2+}$	1.24 (100)	462
$[\text{Ru}(\text{terpy})(\text{bpy})(\text{PhCN})]^{2+}$	1.33 ^c	448 ^{c,d}
$[\text{Ru}(\text{terpy})(\text{bpy})(4,4'\text{-bpy})]^{2+}$	1.23 ^e	466 ^{d,e}
$[\text{Ru}(\text{terpy})(\text{bpy})(\text{H}_2\text{O})]^{2+}$	1.08 ^c	476 ^{c,d}
$[\text{Ru}(\text{terpy})(\text{bpy})(\text{NH}_3)]^{2+}$	1.02 ^c	482 ^{c,d}

^a In MeCN , $0.1 \text{ mol dm}^{-3} \text{NBu}_4\text{PF}_6$, sweep rate 0.2 V s^{-1} . ^b Recorded in MeCN at room temperature unless otherwise stated. ^c Taken from ref. 5. ^d In aqueous solution. ^e Taken from ref. 35.

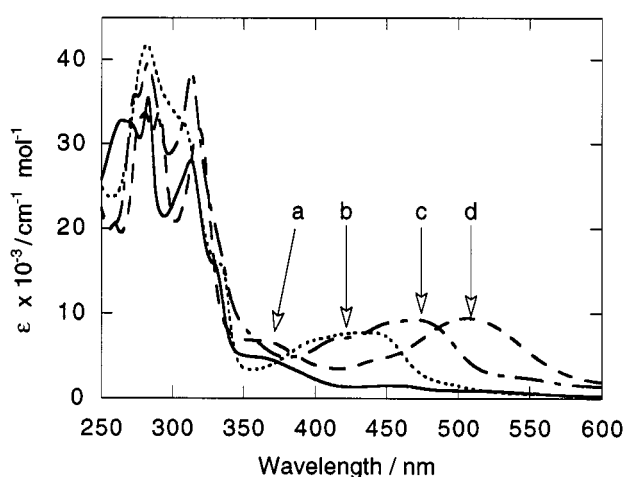


Fig. 3 Electronic absorption spectra of $[\text{Ru}(\text{terpy})(\text{bpy})\text{X}]^{n+}$ as the PF_6^- salt in MeCN : X = CO (a), pyridine (b), PPh_3 (c) or Cl^- (d)

produced single products which were purified and fully characterised using the techniques previously described. However, the complex $[\text{Ru}(\text{terpy})(\text{bpy})(\text{SCN})]^{2+}$ contained two isomers, which possess some interesting photochemical behaviour which is currently under investigation in our laboratory.

The electronic spectra of polypyridyl complexes of ruthenium(II) demonstrate an intense absorption band in the visible region, attributed to unresolved metal-to-ligand charge transfers (MLCT) from the metal centre to the π^* level of the terpyridine and bipyridine ligands. The identity of the ligand X at the sixth co-ordination site in the complexes of the type $[\text{Ru}(\text{pp})(\text{pp})\text{X}]^{n+}$ can dramatically influence the position of this absorption, as demonstrated by the complexes synthesized in this work (see Table 2 and Fig. 3), with the difference between absorption for the mono-chloro and -carbonyl species being almost 150 nm. Since the lowest ligand π^* level is unlikely to be affected by the identity of X in this sequence, the hypsochromic (blue) shift in the MLCT absorption is ascribed to variations in the metal d_π level.¹³ This is consistent with the observation that the $\text{Ru}^{\text{III}}-\text{Ru}^{\text{II}}$ redox couple is shifted by over 1 V in changing X from a chloro to a carbonyl ligand.

With the correct choice of ligands, it should be possible to synthesize complexes of the type $[\text{Ru}(\text{pp})(\text{pp})\text{X}]^{2+}$ with tuned spectral and redox characteristics, depending upon the electronic characteristics of the monodentate X ligand. As a first approximation our results correlate with the electrochemical parametrisation of Lever,³⁶ which gives a reasonable indication of the effect that the ligand will transfer to the complexes'

physical behaviour. With the ability to tune the MLCT at the metal centre, similar systems are envisaged for the control of long-lived donor–acceptor charge-separated species.

Conclusion

Complexes of the type $[\text{Ru}(\text{ppp})(\text{pp})(\text{CO})]^{2+}$ can act as versatile precursors for the synthesis of complexes with greatly differing redox and photophysical characteristics, *via* the substitution of the carbonyl ligand with a suitable monodentate species. The decarbonylation procedure appears to be quite general, and proceeds with retention of the stereochemistry at the metal centre. Using this methodology, several complexes have been synthesized, and have demonstrated that the choice of monodentate ligand can be used to tune the electrochemical and photophysical characteristics. The published preparation of the monocarbonyl species is complex, and a considerably more simple photochemical procedure has been developed, giving a direct route to the carbonyl complex. The cation-exchange chromatographic methods for separating isomers of ruthenium(II) complexes developed within this laboratory have proved to be applicable in the separation of geometric forms of complexes $[\text{Ru}(\text{ppp})(\text{pp})(\text{CO})]^{2+}$ (where pp is unsymmetric), demonstrated by the separation of both geometric isomers of the complex $[\text{Ru}(\text{terpy})(\text{mpbpy})(\text{CO})]^{2+}$.

Experimental

Instrumentation

Proton NMR spectra were recorded on a Bruker Aspect AM300 spectrometer using the solvent as an internal reference, ^1H – ^1H COSY spectra on a Varian Unity Inova-500 spectrometer in CD_3CN solutions, electronic absorption spectra on a Varian CARY 5E spectrophotometer and IR spectra using a Perkin-Elmer 16000 series FTIR spectrophotometer with the samples prepared in Nujol mulls and placed between NaCl plates. Microanalyses were carried out within the department using a Carlo Erba EA 1108 CHNS analyser. Cyclic voltammetric measurements were made in acetonitrile solutions containing 0.1 mol dm^{-3} tetra-*n*-butylammonium hexafluorophosphate (Fluka) as supporting electrolyte with a platinum disc working electrode, and a Ag–Ag⁺ reference electrode using a BAS 100A Electrochemical Analyzer. At the end of each experiment ferrocene was added as an internal standard, and the peak potentials corrected to the SCE (E_3 of ferrocene–ferrocenium +0.400 V relative to SCE).³⁷

Materials

2,2'-Bipyridine, 4,4'-dimethyl-2,2'-bipyridine, 1,10-phenanthroline, 2,2':6',2''-terpyridine, sodium toluene-4-sulfonate (all Aldrich), 2-methoxyethanol and triphenylphosphine (both Fluka), lithium chloride (Aldrich), lithium diisopropylamide (1.5 M, Aldrich), and ruthenium trichloride hydrate (Strem) were used as received without further purification. Laboratory grade solvents were used unless otherwise specified. Tetrahydrofuran (BDH) was distilled under N_2 from sodium wire with benzophenone as an indicator. Trifluoromethanesulfonic acid (3M), 1,2-dichlorobenzene (Aldrich) and pyridine (Aldrich) were freshly distilled as required. Trimethylamine *N*-oxide (Aldrich) was sublimed (120 °C under vacuum) prior to use. SP-Sephadex C-25 and Sephadex LH20 (Amrad Pharmacia Biotech) were used for chromatographic purification of the metal complexes.

4-Methyl-2,2'-bipyridine was prepared *via* a Kröhnke synthesis from 2-acetylpyridine (99+%; Aldrich);^{38,39} the polymer $[\{\text{Ru}(\text{CO})_2\text{Cl}_2\}_n]^{13}$ the complexes $[\text{Ru}(\text{pp})(\text{CO})_2\text{Cl}_2]$ (pp = bpy, dmbpy or phen; method B),¹³ $[\text{Ru}(\text{dmbpy})(\text{CO})_2(\text{CF}_3\text{SO}_3)_2]^{13}$ and $[\text{Ru}(\text{pp})(\text{terpy})(\text{CO})]^{2+}$ (pp = bpy or phen)²² were prepared following literature syntheses.

Ligand synthesis

4-(2-Methylpropyl)-2,2'-bipyridine. A solution of 4-methyl-2,2'-bipyridine (0.580 g, 3.41 mmol) in dry thf (25 cm³) was cooled to below –40 °C under argon, and a large excess of LiNPr_2 (20 cm³) added over 30 min. After stirring at –40 °C for 3 h a large excess of 2-bromopropane (5 cm³, 53 mmol) was added in dry thf (20 cm³), and the reaction allowed to warm slowly to room temperature while stirring overnight. The reaction was quenched with water (2 cm³), and the solvent removed *in vacuo*. After the addition of a saturated aqueous solution of sodium hydrogencarbonate (10 cm³), the mixture was extracted with dichloromethane (3 × 30 cm³). The organic phase was dried over magnesium sulfate and filtered. Following the removal of the solvent, the brown residue was purified first by column chromatography on silica gel with hexane–ethyl acetate–triethylamine (14:6:1) as eluent collecting the first band, then again on silica gel eluted with chloroform–methanol (50:1), collecting the first band. Following removal of the solvent, the product was obtained as a yellow oil, yield 0.485 g (67%) (Found: C, 78.4; H, 8.0; N, 13.1. $\text{C}_{14}\text{H}_{16}\text{N}_2$ requires C, 79.2; H, 7.6; N, 13.2%). NMR (CDCl_3 , 300 MHz): ^1H , δ 8.63 (1 H, d, *J* 5.0, H6'), 8.50 (1 H, d, *J* 5.0, H6), 8.35 (1 H, d, *J* 7.7, H3'), 8.16 (1 H, s, H3), 7.74 (1 H, dd, *J* 7.7, 7.7, H4'), 7.23 (1 H, dd, *J* 5.0, 7.8, H5'), 7.04 (1 H, d, *J* 5.0, H5), 2.51 (2 H, d, *J* 7.1, CH_2), 1.94 (1 H, m, CH) and 0.88 (6 H, d, *J* 6.6 Hz, CH_3); ^{13}C , δ 156.2 (C2'), 155.7 (C2), 151.6 (C4), 149.0 (C6'), 148.8 (C6), 136.8 (C4'), 124.6 (C5'), 123.5 (C5), 121.6 (C3'), 121.1 (C3), 44.7 (CH_2), 29.5 (CH) and 22.2 (CH_3).

Complex syntheses

Dicarbonyl(4,4'-dimethyl-2,2'-bipyridine)(2,2':6',2''-terpyridine)ruthenium(II) hexafluorophosphate, $[\text{Ru}(\text{terpy})(\text{dmbpy})(\text{CO})_2][\text{PF}_6]_2$. The complex $[\text{Ru}(\text{dmbpy})(\text{CO})_2(\text{CF}_3\text{SO}_3)_3]$ (250 mg, 0.391 mmol) and 2,2':6',2''-terpyridine (109 mg, 4.68 mmol) were heated at reflux in absolute ethanol (15 cm³) for 2 h. The solvent was removed and the brown residue taken up in hot water (50 cm³). The aqueous solution was filtered through Celite, and washed with additional hot water (3 × 20 cm³). A solution containing saturated aqueous potassium hexafluorophosphate was added to the filtrate resulting in a pale precipitate. The residue was stored at 4 °C overnight and the product was collected by filtration and dried *in vacuo* to give a pale cream solid, yield 182 mg (54%) (Found: C, 41.4; H, 2.6; N, 8.1. $\text{C}_{29}\text{H}_{23}\text{F}_{12}\text{N}_5\text{O}_2\text{P}_2\text{Ru}$ requires C, 40.3; H, 2.7; N, 8.1%). IR: $\tilde{\nu}_{\text{CO}}/\text{cm}^{-1}$ (Nujol) 2089 and 2037. NMR (CD_3CN , 300 MHz): ^1H (aliphatic), δ 2.72 (3 H, s, CH_3), 2.64 (3 H, s, CH_3), 2.47 (3 H, s, CH_3) and 2.41 (3 H, s, CH_3).

Carbonyl(4,4'-dimethyl-2,2'-bipyridine)(2,2':6',2''-terpyridine)ruthenium(II) hexafluorophosphate, $[\text{Ru}(\text{terpy})(\text{dmbpy})(\text{CO})][\text{PF}_6]_2$. The complex $[\text{Ru}(\text{terpy})(\text{dmbpy})(\text{CO})_2][\text{PF}_6]_2$ (80 mg, 93 μmol) was dissolved in absolute ethanol, and the solution deaerated for 30 min with N_2 . Trimethylamine *N*-oxide (9.1 mg, 120 μmol) was added and the reaction stirred at room temperature for 2 h, during which the colour visibly darkened. The solvent was removed *in vacuo* at room temperature, and the product recrystallised from acetone–ethanol to give a dark yellow solid, yield 47.3 mg (61%) (Found: C, 38.9; H, 2.6; N, 7.9. $\text{C}_{28}\text{H}_{23}\text{F}_{12}\text{N}_5\text{O}_2\text{P}_2\text{Ru}\cdot 0.2\text{HPF}_6$ requires C, 38.5; H, 2.6; N, 8.0%). IR: $\tilde{\nu}_{\text{CO}}/\text{cm}^{-1}$ (Nujol) 1991. ^1H NMR data given in Table 3.

***trans*-Cl-*cis*-CO- $[\text{Ru}(\text{mpbpy})(\text{CO})_2\text{Cl}_2]$.** A solution of mpbpy (307 mg, 1.45 mmol) in AR methanol (15 cm³) was deaerated for 30 min with N_2 . To this was added $[\{\text{Ru}(\text{CO})_2\text{Cl}_2\}_n]$ (300 mg, 1.30 mmol) and the mixture refluxed for 2.5 h. The volume was reduced to 5 cm³, and the precipitate collected by filtration. The yellow product was recrystallised from hot methanol in subdued light. A second harvest was obtained by recrystallising the residues, total yield 381 mg (66%) (Found: C, 43.7; H, 3.8; N,

6.2. $C_{16}H_{16}Cl_2N_2O_2Ru$ requires C, 43.7; H, 3.7; N, 6.4%. IR: $\tilde{\nu}_{CO}/cm^{-1}$ (Nujol) 2057 and 1983. 1H NMR ($CDCl_3$, 300 MHz): δ 9.16 (1 H, d, J 5.0, H6'), 9.01 (1 H, d, J 5.5, H6), 8.20 (1 H, d, J 7.7, H3'), 8.07 (1 H, dd, J 8.0, 8.0, H4'), 8.0 (1 H, s, H3), 7.62 (1 H, dd, J 5.0, 7.7, H5'), 7.41 (1 H, d, J 6.0, H5), 2.63 (2 H, d, J 7.1, CH_2), 1.96 (1 H, m, CH) and 0.94 (6 H, d, J 6.6 Hz, CH_3).

Dicarbonyl[4-(2-methylpropyl)-2,2'-bipyridine](2,2':6',2''-terpyridine)ruthenium(II) hexafluorophosphate, [Ru(terpy)-(mpbp)(CO) $_2$][PF $_6$] $_2$. The complex [Ru(mpbp)(CO) $_2$ Cl $_2$] (204 mg, 464 μ mol) was heated to 110 °C in nitrogen-purged 1,2-dichlorobenzene (50 cm 3). To this was added trifluoromethanesulfonic acid (0.15 cm 3) and the mixture heated for 1.5 h. The solvent was distilled off under vacuum giving a pale cream solid, which was dissolved in nitrogen-purged 95% aqueous ethanol (30 cm 3). To this was added 2,2':6',2''-terpyridine (150 mg, 640 μ mol) and the mixture refluxed for 3 h. The solvent was removed, and the brown residue extracted with hot water, filtered and the product precipitated with potassium hexafluorophosphate. After cooling to 4 °C the pale product was collected by filtration, washed with water and dried *in vacuo*, yield 236 mg (45%) (Found: C, 44.5; H, 3.6; N, 7.7. $C_{31}H_{27}F_{12}N_5O_2P_2Ru \cdot 3C_3H_6O$ requires C, 44.1; H, 3.9; N, 7.0%). IR: $\tilde{\nu}_{CO}/cm^{-1}$ (Nujol) 2092 and 2040. NMR (CD_3CN , 300 MHz): 1H (aliphatic), δ 0.81, 0.83, 0.94 and 0.99 (d, J 6.7, CH_3), 2.59, 2.62, 2.79 and 2.86 (d, J 7.6 Hz, CH_2).

Photochemical synthesis of [Ru(pp)(terpy)(CO)][PF $_6$] $_2$. In a typical experiment [Ru(pp)(CO) $_2$ Cl $_2$] (0.250 mmol) and 2,2':6',2''-terpyridine (260 mmol) were suspended in 2-methoxyethanol (50 cm 3) and deaerated with argon. The flask was sealed and placed outside in direct sunlight. A change from pale yellow to dark red was observed after a short time. After a total of 18 h in direct sunlight the solvent was removed. The brown residues were dissolved in water, and the solutions filtered (typically removing 10–20 mg of yellow starting material). The crude product was precipitated by the addition of saturated potassium hexafluorophosphate solution to give a dark brown solid, which was extracted with dichloromethane. Following removal of the solvent under reduced pressure the crude product was converted into the chloride salt by metathesis with LiCl in acetone solution. The precipitate was collected by filtration through Celite and extracted with water. The aqueous solution (50 cm 3) was introduced onto a SP Sephadex C-25 column (dimensions 30 \times 400 mm), and eluted with aqueous 0.2 mol dm $^{-3}$ sodium toluene-4-sulfonate solution containing 10% acetone, collecting the pale yellow band between the two dark red fractions. The product was isolated by the addition of saturated KPF $_6$ solution and extraction with dichloromethane (3 \times 50 cm 3), followed by removal of the solvent and drying *in vacuo*. Further purification was by passage down a short Sephadex LH20 column (eluted with 50% methanol–acetone), to remove the excess of inorganic salts. Yields and characterisation are given in Table 3.

Separation of *cis/trans*-[Ru(terpy)(mpbp)(CO)][PF $_6$] $_2$. The mixture of the geometric isomers of [Ru(terpy)(mpbp)(CO)] $^{2+}$ (75 mg) was converted into the chloride salt as outlined above, and the products reintroduced onto a SP Sephadex C-25 column (dimensions 20 mm \times 2 m). The compounds are extremely pale in colour, and consequently it was necessary to use new cation exchanger for this procedure. On elution with aqueous 0.25 mol dm $^{-3}$ sodium toluene-4-sulfonate solution containing 10% acetone, two bands separated after passage down 1 m of the support. The two isomers were collected separately, and isolated by the addition of saturated KPF $_6$ solution and extraction with dichloromethane (3 \times 20 cm 3). The solvent was removed under reduced pressure. The excess of inorganic salts was removed by 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*. Yields and characterisations are given in Table 3.

[Ru(pp)(terpy)(py)][PF $_6$] $_2$. In a typical experiment [Ru(pp)(terpy)(CO)][PF $_6$] $_2$ (1.5 mmol) was dissolved in absolute ethanol (5 cm 3) and Me $_3$ NO (15 mmol) added, whereupon the solution changed rapidly to a dark red. It was brought to reflux and after 5 min pyridine (200 μ l) was added and the reaction mixture refluxed for 6 h. After cooling, the cherry red solution was diluted with water (100 cm 3) and introduced onto a SP Sephadex C-25 column (dimensions 20 \times 400 mm), and eluted with 0.4 mol dm $^{-3}$ sodium chloride solution, collecting the major red fraction. The product was isolated by the addition of saturated KPF $_6$ solution and extraction with dichloromethane (3 \times 20 cm 3). The solvent was removed under reduced pressure. The excess of inorganic salts was removed by 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*. Yields and characterisations are given in Table 3.

Alternative method for [Ru(pp)(terpy)(py)][PF $_6$] $_2$. In a typical experiment [Ru(pp)(terpy)(CO) $_2$][PF $_6$] $_2$ (20 μ mol) was dissolved in absolute ethanol (50 cm 3) and Me $_3$ NO (0.20 mmol) added, whereupon the solution changed rapidly to a dark red. It was brought to reflux and after 5 min pyridine (5 cm 3) was added and the reaction mixture refluxed for 8 h. After cooling, the cherry red solution was diluted with water (100 cm 3). Purification was identical to that described above. Yields and characterisation are given in Table 3.

[Ru(terpy)(dmbpy)(PPh $_3$)][PF $_6$] $_2$. The complex [Ru(terpy)(bpy)(CO)][PF $_6$] $_2$ (50 mg, 61.8 μ mol) was dissolved in absolute ethanol (5 cm 3) and Me $_3$ NO (200 mg, 267 μ mol) added. The solution was brought to reflux and after 5 min triphenylphosphine (2 g, 7.5 mmol) was added and the reaction mixture refluxed for 12 h. After cooling, the cherry red solution was diluted with water (100 cm 3) and introduced onto a SP Sephadex C-25 column (dimensions 20 \times 400 mm) and eluted with 0.2 mol dm $^{-3}$ sodium toluene-4-sulfonate solution containing 20% acetone, collecting the major red fraction. The product was isolated by the addition of saturated KPF $_6$ solution, and extraction with dichloromethane (3 \times 20 cm 3). The solvent was removed under reduced pressure. The excess of inorganic salts was removed by 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*. Yields and characterisations are given in Table 3.

[Ru(terpy)(dmbpy)Cl][PF $_6$] $_2$. The complex [Ru(terpy)(dmbpy)(CO)][PF $_6$] $_2$ (42 mg, 52.0 μ mol) was dissolved in absolute ethanol (5 cm 3) and Me $_3$ NO (180 mg, 240 μ mol) added. The solution was brought to reflux and after 5 min a large excess of lithium chloride (5 g) was added and the reaction mixture refluxed for 12 h. After cooling, the dark red solution was diluted with water (100 cm 3), filtered under gravity and the crude product precipitated with a saturated aqueous solution of ammonium hexafluorophosphate. This was dissolved in a 20% acetone–water mixture and introduced onto a SP Sephadex C-25 column (dimensions 20 \times 400 mm), eluted with aqueous 0.4 mol dm $^{-3}$ sodium chloride solution, collecting the major red fraction. The product was isolated by the addition of saturated KPF $_6$ solution and extraction with dichloromethane (3 \times 20 cm 3). The solvent was removed under reduced pressure. The excess of inorganic salts was removed by passage through a short Sephadex LH20 column (eluted with 50% methanol–acetone), and the product isolated by removal of the solvent and drying *in vacuo*. Yields and characterisations are given in Table 3.

Table 3 Analytical and spectroscopic data for the complexes

Complex	Yield (%)	Analysis			Formula	Expected			IR ^a ν̄(CO)/ cm ⁻¹	Electronic spectral data ^b λ _{max} (±2)/nm (ε × 10 ⁻³ /cm ⁻¹ mol ⁻¹)					
		Found	Found	Found		Expected	Expected	Expected							
[Ru(terpy)(bpy)(CO)] ²⁺	21	41.6	2.9	8.0	C ₂₆ H ₁₉ F ₁₂ N ₅ OP ₂ Ru·1.5C ₃ H ₆ O	41.9	3.4	7.6	1996	368 (sh) (4.8)	330 (sh) (18.9)	314 (30.8)	283 (39.7)	263 (36.9)	
[Ru(terpy)(dmbpy)(CO)] ²⁺	24	43.1	3.7	6.9	C ₂₈ H ₂₃ F ₁₂ N ₅ OP ₂ Ru·2.5C ₃ H ₆ O	43.4	3.9	7.1	1999	364 (sh) (4.8)	329 (sh) (15.8)	313 (27.8)	283 (35.5)	264 (32.8)	
[Ru(terpy)(phen)(CO)] ²⁺	16	44.3	3.3	7.2	C ₂₈ H ₁₉ F ₁₂ N ₅ OP ₂ Ru·2.5C ₃ H ₆ O	44.4	3.5	7.2	1990	386 (sh) (5.1)	329 (20.5)	314 (25.9)	282 (41.4)	271 (48.9)	230 (47.8)
<i>cis</i> -[Ru(terpy)(mpbpy)(CO)] ²⁺	12 ^c	43.6	4.1	7.1	C ₃₀ H ₂₇ F ₁₂ N ₅ OP ₂ Ru·2C ₃ H ₆ O ^d	44.1	4.0	7.1	1992	368 (sh) (5.2)	330 (sh) (14.9)	310 (27.1)	283 (34.0)	272 (30.7)	230 (sh) (25.6)
<i>trans</i> -[Ru(terpy)(mpbpy)(CO)] ²⁺	12 ^c				<i>d</i>				1995	364 (sh) (4.8)	331 (sh) (15.9)	314 (28.3)	283 (36.4)	264 (35.3)	234 (sh) (25.8)
[Ru(terpy)(bpy)(py)] ²⁺	98 (73) ^e	41.8	2.8	9.8	C ₃₀ H ₂₄ F ₁₂ N ₆ P ₂ Ru	41.9	2.9	10.0		467 (10.1)	415 (sh) (7.1)	312 (40.2)	287 (39.0)	274 (34.2)	242 (28.6)
[Ru(terpy)(dmbpy)(py)] ²⁺	98 (79) ^e	43.5	3.3	8.4	C ₃₂ H ₂₈ F ₁₂ N ₆ P ₂ Ru	43.3	3.2	9.5		470 (9.3)	416 (sh) (7.1)	313 (38.3)	282 (39.5)	274 (25.8)	243 (25.9)
[Ru(terpy)(phen)(py)] ²⁺	92 (75) ^e	43.5	2.8	9.1	C ₃₂ H ₂₄ F ₁₂ N ₆ P ₂ Ru	43.5	2.7	9.5		462 (9.8)	410 (sh) (8.6)	312 (37.8)	264 (60.5)	226 (50.8)	
<i>cis</i> -[Ru(terpy)(mpbpy)(py)] ²⁺	98	47.4	5.4	7.8	C ₃₄ H ₃₂ F ₁₂ N ₆ P ₂ Ru·3C ₃ H ₆ O	47.4	4.6	7.7		468 (8.4)	417 (sh) (6.5)	313 (33.5)	283 (34.5)	274 (30.7)	243 (23.9)
<i>trans</i> -[Ru(terpy)(mpbpy)(py)] ²⁺	98	47.4	5.0	7.6	C ₃₄ H ₃₂ F ₁₂ N ₆ P ₂ Ru·3C ₃ H ₆ O	47.4	4.6	7.7		471 (7.9)	420 (sh) (5.3)	313 (37.3)	284 (38.2)	274 (35.3)	242 (30.4)
[Ru(terpy)(dmbpy)(PPh ₃)] ²⁺	77	51.1	3.9	6.0	C ₄₅ H ₃₈ F ₁₂ N ₅ P ₃ Ru·1.5C ₃ H ₆ O	51.3	4.0	6.0		438 (7.8)	396 (sh) (6.7)	334 (15.7)	307 (sh) (32.7)	282 (41.7)	228 (58.6)
[Ru(terpy)(dmbpy)Cl] ⁺	52	45.6	4.0	9.8	C ₂₇ H ₂₃ ClF ₆ N ₅ PRu·H ₂ O	45.2	3.6	9.8		506 (9.4)	368 (sh) (6.6)	318 (31.8)	291 (33.7)	281 (33.6)	239 (31.1)

^a In Nujol, all bands strong. ^b In acetonitrile at 25 °C. ^c Total yield of synthesis 24%. ^d Microanalysis for the *cis/trans* isomeric mixture (prior to separation). ^e Yield from the dicarbonyl analogue [Ru(terpy)(pp)(CO)₂]²⁺.

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