Stereochemistry in Tris(bidentate ligand)ruthenium(II) Complexes containing Unsymmetrical Polypyridyl Ligands

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The synthesis and stereochemistry of monomeric ruthenium(II) complexes containing the unsymmetrical bidentate ligand pmbipy [4-(2,2-dimethylpropyl)-4'-methyl-2,2'-bipyridine] have been studied. In the complexes $[Ru(dmbipy)(pmbipy)(CO)_2]^{2+}$ (dmbipy is the symmetrical bidentate ligand 4,4'-dimethyl-2,2'-bipyridine) and $[Ru(pmbipy)_2(CO)_2]^{2+}$, the geometric isomers (two and three, respectively) have been identified and characterized by NMR techniques, and one isomer of each species has been isolated in a pure form by fractional recrystallization. The dicarbonyl species have both been used as precursors for the synthesis of $[Ru(dmbipy)(pmbipy)_2]^{2+}$ by a decarbonylation process: under certain conditions, the conversion was shown to take place with retention of the stereochemical relationship of the two ligands in the dicarbonyl precursor. Mixtures of the three geometric isomers of $[Ru(dmbipy)(pmbipy)_2]^{2+}$ were separated by cation-exchange chromatography, and the isomers characterized by NMR techniques. The complex $[Ru(pmbipy)_3]^{2+}$ was synthesized, and the two geometric isomers separated and characterized in a similar manner.

We have recently reported the utilization of a synthetic methodology for tris(heteroleptic) complexes of ruthenium(II),[1,2] which has allowed access to an extended range of compounds with increased complexity of formulation and stereochemistry. The scheme is based on the sequential addition of three bidentate polypyridyl ligands (L^1, L^2 and L^3) to the oligomer $[\{Ru(CO)_2Cl_2\}_n]$.[3-6] By incorporating potentially bridging ligands, such as 2,2'-bipyrimidine (bipym) or 2,3-bis(2-pyridyl)pyrazine (bpypz), the method may be extended to the synthesis of dinuclear (and higher nuclearity) species.[7]

Such polymetallic 'supramolecular' assemblies have evoked considerable attention because of the possibility of achieving redox charge separation within them following light absorption—with the consequent potential application to the harvesting of light energy and its conversion to chemical fuels.[8] Polypyridyl complexes of ruthenium, osmium and rhenium have been primary targets for the component centres of such assemblies because of the capacity for controlled variation of their ground and excited state properties, redox potentials, and electron and energy transfer characteristics.[9] A number of recent reports have described the spectral, photophysical and electrochemical behaviour of assemblies including such centres with nuclearities of 2–22.[10-13]

An important issue which has received little attention in these studies is that of the spatial relationship of the metal centres within the molecular assemblies, which may profoundly effect energy (and electron) migration patterns. This in turn depends on the stereochemical identity (chiral and geometric) of the component metal centres.

There have been few studies of stereoisomerism of monomeric ruthenium(II) centres with unsymmetrical ligands. For complexes of the type $[Ru(L^4)_3]^{2+}$ (L^4 is an unsymmetrical bidentate ligand), the existence of *fac* and *mer* geometric isomers has been recognized from ^1H and ^{13}C NMR studies of complexes where L^4 = unsymmetrically substituted derivatives of 2,2'-bipyridine and 1,10-phenanthroline,[14,15] 2,2'-azopyridine,[16] and 2-(2-pyridyl)thiazole and 2-(2-pyrazinyl)thiazole.[17] Similary, ^{99}Ru NMR spectroscopy has been used to identify the presence of both geometric isomers in analogous complexes where L^4 = 1-(2-pyridyl)-3,5-dimethylpyrazole,[18] 2-(2-pyridyl)oxazole[19] and 2,3-bis(2-pyridyl)pyrazine.[20] In only one report has the separation of such stereoisomers been claimed, using HPLC techniques, in the species $[Ru(apy)_3]^{2+}$ (two geometric isomers) and $[Ru(apy)_2(bipy)]^{2+}$ (two of the three possible geometric isomers) [bipy = 2,2'-bipyridine, apy = 2,2'-azopyridine].[16]

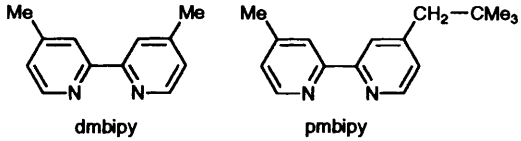
For ligand-bridged dinuclear species containing polypyridyl bidentate ligands, there is even greater paucity in reported examples of stereoisomerism. Hua and von Zelewsky[21] prepared single isomers of two dinuclear species using optically resolved mononuclear precursors, and the diastereoisomers of a range of such dimers have been separated within our own work.[7]

We are undertaking a detailed stereochemical study of monomeric tris(bidentate ligand)ruthenium(II) complexes, and the polynuclear species derived from them, with the ultimate aim of stereochemical control of metal centres in polynuclear assemblies.

Using our synthetic methodology, the dicarbonyl species $[Ru(L^1)(L^2)(CO)_2]^{2+}$ are key precursors in the syntheses of mono- and poly-nuclear systems, and we report here investigations of the mononuclear $[Ru(L^1)(L^2)(CO)_2]^{2+}$ and $[Ru(L^1)(L^2)_2]^{2+}$ systems where the two ligands L^1 and L^2 are the symmetrical ligand dmbipy [4,4'-dimethyl-2,2'-bipyridine] and the unsymmetrical ligand pmbipy [4-(2,2-dimethylpropyl)-4'-methyl-2,2'-bipyridine].

Results and Discussion

Synthesis of 4-(2,2-*Dimethylpropyl*)-4'-*methyl*-2,2'-*bipyridine* (*pmbipy*).—The ligand pmbipy was synthesized by reaction of 2-bromo-2-methylpropane with the mono anion of 4,4'-dimethyl-2,2'-bipyridine (dmbipy) (formed by its reaction with one mole equivalent of the hindered base lithium diisopropylamide). The nucleophilic substitution stage was found to be



very slow, presumably due to the steric bulk of the *tert*-butyl substituent and the relatively poor leaving-group capabilities of Br^-. A minor yield of the disubstituted species was also obtained, but was separated from the required product by chromatographic procedures.

The ^1H and ^{13}C NMR spectral details for pmbipy are given in the Experimental section. The protons at the 3- and 5-positions of the pyridyl ring containing the neopentyl substituent are shielded (upfield) relative to those on a pyridyl ring containing a methyl group, due to the increased inductive effects of the neopentyl group. The assignment of the 5- and 6- (and 5'- and 6'-) positions to the two pairs of doublets for each ring were based on the deshielding effects of the nitrogen atoms. Peak assignments were determined by XHCORRD (CX-H shift correlation with ^1H decoupling in F1 domain), DEPT (distortionless enhancement by polarization transfer) and proton decoupling techniques.

Synthetic Methodology for Complexes.—Ruthenium complexes containing bidentate polypyridyl ligands, $[Ru(L^1)(L^2)(L^3)]^{2+}$, were synthesized by sequential addition of the ligands to the oligomer $[\{RuCl_2(CO)_2\}_n]$.[1-6]

The first step in this procedure was the addition of the first ligand (L^1) producing $[Ru(L^1)(CO)_2Cl_2]$, with the geometry *cis*-$(CO)_2$,*trans*-Cl_2.[2,22,23] The substitution of the second ligand (L^2) initially requires the replacement of chloride by trifluoromethanesulfonate ligands (which are superior leaving groups), and is achieved by reaction of the dichloro complex with trifluoromethanesulfonic acid in 1,2-dichlorobenzene solution.[24] The addition of L^2 to $[Ru(L^1)(CO)_2(CF_3SO_3)_2]$ [which has been assigned the geometry *cis*-$(CO)_2$,*cis*-$(CF_3SO_3)_2$][2,3,5] was performed in absolute ethanol at reflux yielding the dicarbonyl complex *cis*-$[Ru(L^1)(L^2)(CO)_2]^{2+}$. The final stage of the synthesis involved the decarbonylation of the $[Ru(L^1)(L^2)(CO)_2]^{2+}$ species by trimethylamine *N*-oxide in the presence of the third polypyridyl ligand (L^3) using 2-methoxyethanol as a solvent.

In the present instance, the major target complex was $[Ru(dmbipy)(pmbipy)_2]^{2+}$, which may be formed by either of two routes depending on the order of the sequential addition: *viz.* by addition of dmbipy to $[Ru(pmbipy)_2(CO)_2]^{2+}$ in the final decarbonylation step, or alternatively by addition of pmbipy to $[Ru(dmbipy)(pmbipy)(CO)_2]^{2+}$. There are stereochemical implications of syntheses of the target from these alternate dicarbonyl precursors.

Stereochemical Considerations and Characterization of Isomers.—For the complex $[Ru(dmbipy)(pmbipy)_2]^{2+}$ there are three possible geometric isomers based on the relative orientation of the two neopentyl groups (R). The two isomers in which the neopentyl groups bear a *cis* relationship to each other are differentiated by the fact that **II** has higher symmetry (sym-*cis*: point group C_2) than **III** (unsym-*cis*: C_1). For the two precursor dicarbonyl species, $[Ru(dmbipy)(pmbipy)(CO)_2]^{2+}$ has two possible geometric forms **IV** and **V**, and $[Ru(pmbipy)_2(CO)_2]^{2+}$ three **VI**–**VIII** {which are analogous to those for the target $[Ru(dmbipy)(pmbipy)_2]^{2+}$ species}.

Experimentally, the dicarbonyl complex $[Ru(dmbipy)(pmbipy)(CO)_2]^{2+}$ formed two geometric isomers (**IV** and **V**), which were separated by fractional recrystallization from ethanolic solution (**IV** being the less soluble) and identified by ^1H NMR spectroscopy (Table 1). The assignment of the *tert*-butyl signals at δ 1.05 and 0.88 to **IV** and **V**, respectively, is based on the upfield shift of protons orientated above the plane of an adjacent pyridyl ring, from which they experience an out-of-plane ring current effect. The integration of these two peaks indicates an isomer ratio **IV**:**V** of 1:1, which suggests there are no stereochemical or electronic preferences under the described reaction conditions and the orientation of attachment is predominantly statistical.

The complete assignment of the spectra of these isomers was based on such ring current effects.[17,25,26] The consequence of the ring currents generated by the aromatic rings is a shielding effect of up to 2 ppm on protons lying above the plane of an adjacent ring. The magnitude of this shift diminishes in protons more distant from the nitrogen: the difference in chemical shifts for the H^3 protons is only 0.1–0.2 ppm. A further effect which influences the chemical shifts of the aromatic protons is the inductive effects of the neopentyl substituent. This is observed in the resonances of the H^3 protons: in **V** the protons H^{3a} and H^{3b} have equivalent positions relative to the carbonyl substituents, but differ in their proximity to a neopentyl or methyl group (respectively), and H^{3a} is shifted upfield 0.11 ppm relative to H^{3b}. A similar shift is present in **IV** (compare H^{3a} and $H^{3'b}$). A similar effect is also observed with the H^5 protons.

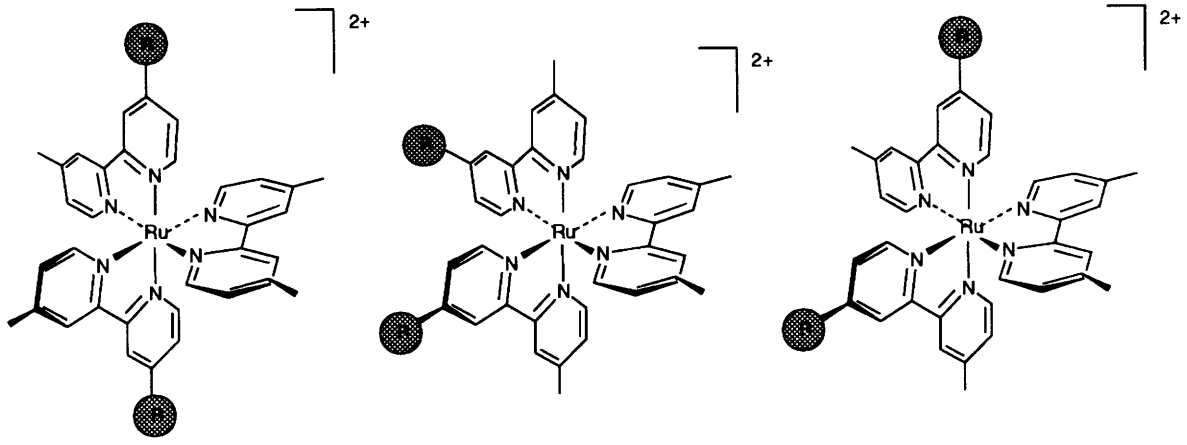
Similarly, the ^1H NMR assignments of the three isomers of $[Ru(pmbipy)_2(CO)_2]^{2+}$ were based on the upfield shift observed on protons lying above the plane of an adjacent ring and the upfield inductive effect of the neopentyl substituent group. Separation of isomer **VI** was achieved by fractional recrystallization from ethanol of an isomeric mixture. The other two isomers could not be completely separated, but were identified and characterized by ^1H NMR spectroscopy (Table 1). In **VI**, both neopentyl-substituted pyridyl rings are *cis* to the two carbonyl groups, while in **VIII** only one neopentyl-substituted pyridyl ring is *cis* to the two carbonyl groups. For **VII** each neopentyl-substituted ring is *trans* to a carbonyl ligand. The three possible isomers were assigned and their relative proportions determined using the *tert*-butyl singlet ^1H NMR resonance. The *tert*-butyl signal at δ 1.05 is the most downfield *tert*-butyl resonance and is assigned to isomer **VI** as the *tert*-butyl groups on rings a and b experience no ring current effects from adjacent ligands. The differences between isomers **VII** and **VIII** are more subtle as the neopentyl-substituted pyridyl rings are orientated over the plane of the adjacent ligand and therefore both experience ring current effects. The integration of the *tert*-butyl signals at δ 1.05, 0.85 and 0.88 (2.6:1.0:1.1) does not give the isomer ratio directly since there are two *tert*-butyl environments in isomer **VIII**. By assuming that the resonance at δ 0.85 corresponds to **VII**, the isomer ratio can be determined as **VI**:**VII**:**VIII** = 1.5:1:2.2. This analysis is consistent with the ratio based on the resonances arising from the H^6,$H^{6'}$ protons, as well as similar calculations based on the methylene and methyl resonances.

The three isomers of the target complex $[Ru(dmbipy)(pmbipy)_2]^{2+}$ were separated by cation-exchange chromatography, and their ^1H NMR spectra are shown in Fig. 1 and detailed in Table 2. The resonances of the protons attached to the C^3 position of the pyridyl rings are the most downfield of the aromatic protons due to in-plane ring current effects. If adjacent to a neopentyl group there is an upfield shift by ≈ 0.14 ppm relative to the protons adjacent to a methyl group. This same effect is also observed for the protons attached to the C^5 positions of the rings. The inductive effect of the neopentyl group has only a very small influence (0.02 ppm) on protons attached at the C^6 positions.

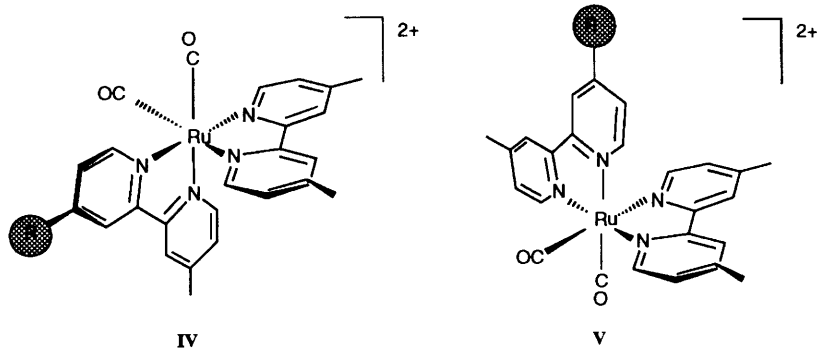
The protons at the C^6 positions do appear to have very slight ring current effects, depending on whether they are positioned over a methyl- or neopentyl-substituted ring. Hence, for the two more symmetrical isomers of $[Ru(dmbipy)(pmbipy)_2]^{2+}$ (*trans* and sym-*cis*) there are three environments, two of which coincide in the *trans* isomer.

The symmetry of these two isomers is also evident in the protons attached at C^5. The two protons adjacent to a neopentyl group (the upfield signal) are in one environment in each of the isomers, although that environment differs between the two isomers. These two protons have different environments in the unsym-*cis* isomer.

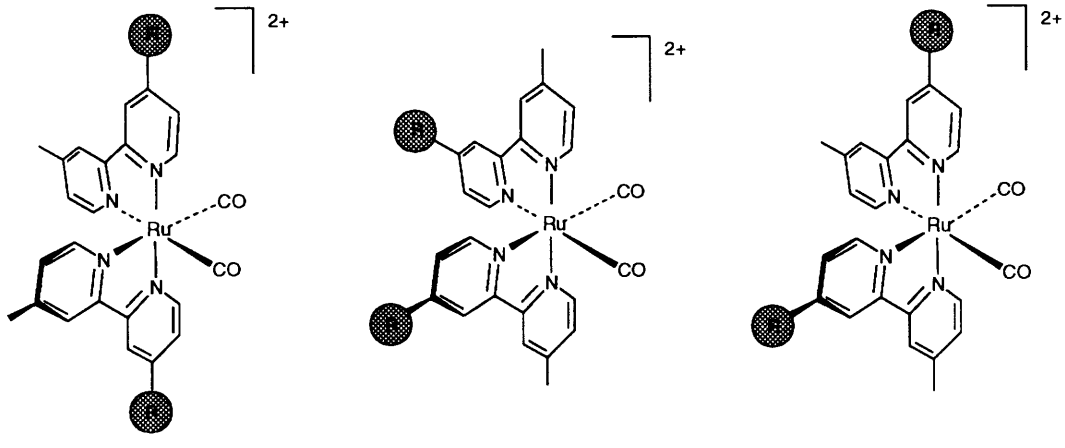
The singlet resonance arising from the *tert*-butyl group appears at δ 0.90 for the sym-*cis* isomer and at δ 0.93 for the other two isomers. The *tert*-butyl signals of $[Ru(dmbipy)_2$-



I *trans* (R) II sym-*cis* (R) III unsym-*cis* (R)



IV V



VI *trans* (R) VII sym-*cis* (R) VIII unsym-*cis* (R)

$(pmbipy)]^{2+}$ and *fac*-$[Ru(pmbipy)_3]^{2+}$ are also observed at δ 0.93. In *mer*-$[Ru(pmbipy)_3]^{2+}$ there are two peaks at δ 0.90 (two protons) and 0.93 (one proton). There are two different *cis* environments in $[Ru(dmbipy)(pmbipy)_2]^{2+}$ (exemplified in the sym-*cis* and unsym-*cis* isomers) and it appears that the *tert*-butyl resonance occurs at δ 0.93 except in the particular *cis* environment found in the sym-*cis* isomer. In the *mer*-$[Ru(pmbipy)_3]^{2+}$ species, two of the *tert*-butyl groups are in such a juxtaposition and hence the ratio of peaks at δ 0.90 and 0.93 is 2:1. Interestingly, in the complex $[Ru(dpbipy)_3]^{2+}$ [dpbipy is the symmetrically disubstituted neopentyl ligand 4,4′-bis(2,2-dimethylpropyl)-2,2′-bipyridine], all the *tert*-butyl groups would display this special relationship, and the ^1H NMR spectrum does indeed show one resonance at δ 0.90.[27]

The two geometric isomers of $[Ru(pmbipy)_3]^{2+}$ were separated by cation-exchange chromatography, and the ^1H NMR spectra are shown in Fig. 2, and the peak positions are rationalized by the arguments used above for the $[Ru(dmbipy)(pmbipy)_2]^{2+}$ analogues (Table 2). The higher symmetry of the *fac*- (**IX**; point group C_3) compared with the *mer*-isomer (**X**; point group C_1) is clearly evident from the spectra [Fig. 2(*b*) and 2(*a*), respectively].

Stereochemical Aspects of the Decarbonylation Reaction.— There are two paths by which the target complex [Ru-

Table 1 ^{1}H NMR chemical shifts (δ_H) for $[Ru(L^1)(L^2)(CO)_2]^{2+}$ in CD_3CN solution

Complex	Isomer	Ligand[a]	H^3	$H^{3'}$	H^{5}[b]	$H^{5'}$[b]	H^{6}[b]	$H^{6'}$[b]	H^7	$H^{7'}$	H^8	H^{10}
$[Ru(dmbipy)(pmbipy)(CO)_2]^{2+}$	**IV**	a	8.31	8.34	7.66	7.29	8.88	7.18	2.47	—	2.85	1.05
		b	8.31	8.42	7.29	7.71	7.18	8.86	2.47	2.68	—	—
	V	a	8.20	8.46	7.24	7.71	7.19	8.86	—	2.68	2.65	0.88
		b	8.31	8.42	7.29	7.71	7.19	8.86	2.47	2.68	—	—
$[Ru(pmbipy)_2(CO)_2]^{2+}$	**VI**	a	8.31	8.34	7.67	7.30	8.89	7.17	—	2.48	2.85	1.05
		b	8.31	8.34	7.67	7.30	8.89	7.17	—	2.48	2.85	1.05
	VII	a	8.20	8.47	7.25	7.72	7.20	8.87	—	2.68	2.65	0.85
		b	8.20	8.47	7.25	7.72	7.20	8.87	—	2.68	2.65	0.85
	VIII	a	8.31	8.34	7.67	7.30	8.89	7.17	—	2.48	2.85	1.05
		b	8.20	8.47	7.25	7.72	7.19	8.87	—	2.68	2.65	0.88

[a] See Experimental section. [b] Doublet, J 5 Hz.

Table 2 ^{1}H NMR chemical shifts (δ_H) for $[Ru(L^1)(L^2)(L^3)]^{2+}$ in CD_3CN solution

Complex	Isomer	H^3	$H^{3'}$	$H^{3''}$	H^5	$H^{5'}$	H^6	$H^{6'}$	$H^{6''}$	H^7	H^8	H^{10}
$[Ru(dmbipy)(pmbipy)_2]^{2+}$	*trans* **I**	8.21[a]	8.35	8.31	7.15[b]	7.19[b]	7.51[b]	7.49[b]	—	2.51	2.67	0.93
	sym-*cis* **II**	8.20[a]	8.35	8.32	7.12[c]	7.20[d]	7.51[b]	7.53[b]	7.50[b]	2.51	2.67	0.90
	unsym-*cis* **III**	8.21[a]	8.35	8.31	7.15[d]	7.20[d]	7.50[d]	—	—	2.51	2.67	0.93
$[Ru(pmbipy)_3]^{2+}$	*fac* **IX**	8.21	8.35	—	7.15[b]	7.19[b]	7.49[b]	7.52[b]	—	2.51	2.67	0.93
	mer **X**	8.22	8.35	8.20	7.13[d]	7.20[d]	7.51[d]	—	—	2.51	2.67	0.90, 0.93
$[Ru(dmbipy)_2(pmbipy)]^{2+}$		8.21	8.35	8.31	7.13[b]	7.19[b]	7.50[d]	—	—	2.50	2.66	0.93

[a] Doublet, J 1.5 Hz. [b] Doublet, J 5 Hz. [c] Doublet of doublets, J 1.5 and 5 Hz. [d] Multiplet.

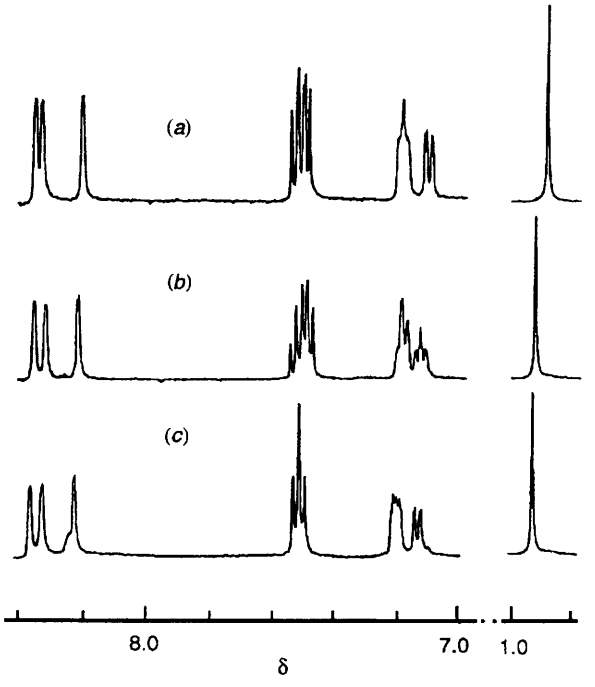


Fig. 1 Proton NMR spectra (300 MHz, CD_3CN) of the geometric isomers of $[Ru(dmbipy)(pmbipy)_2]^{2+}$: (*a*) sym-*cis* (**II**); (*b*) unsym-*cis* (**III**); (*c*) *trans* (**I**)

$(dmbipy)(pmbipy)_2]^{2+}$ may be obtained from the dicarbonyl precursors, equations (1) and (2). It is clear that if the

$$[Ru(dmbipy)(pmbipy)(CO)_2]^{2+} \xrightarrow[Me_3NO,pmbipy]{MeOCH_2CH_2OH} [Ru(dmbipy)(pmbipy)_2]^{2+} \quad (1)$$

$$[Ru(pmbipy)_2(CO)_2]^{2+} \xrightarrow[Me_3NO,dmbipy]{MeOCH_2CH_2OH} [Ru(dmbipy)(pmbipy)_2]^{2+} \quad (2)$$

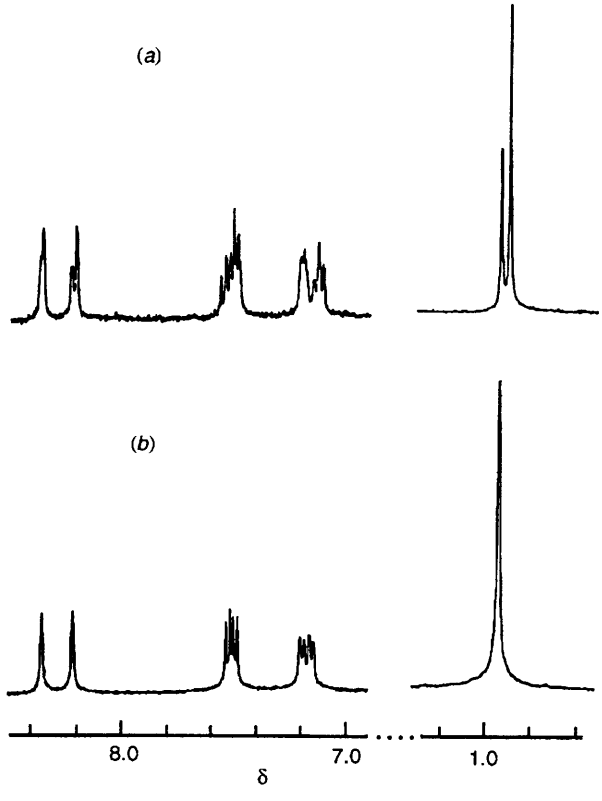
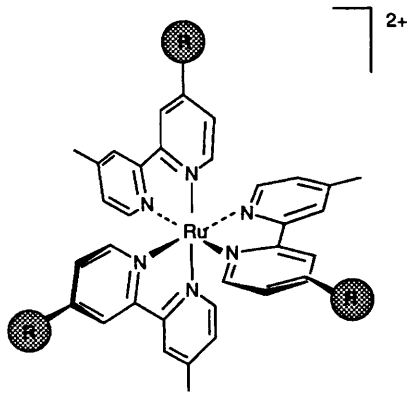
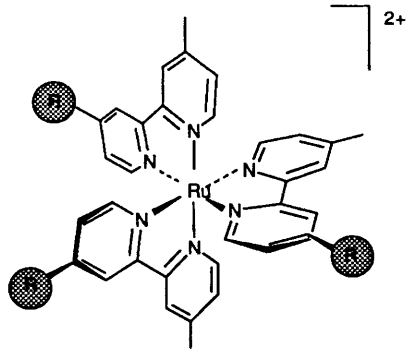


Fig. 2 Proton NMR spectra (300 MHz, CD_3CN) of the geometric isomers of $[Ru(pmbipy)_3]^{2+}$: (*a*) *mer* (**X**); (*b*) *fac* (**IX**)

decarbonylation process occurs so that the relative geometry of the two ligands in the dicarbonyl precursors is retained, the transformation of each form of $[Ru(pmbipy)_2(CO)_2]^{2+}$ would produce the corresponding geometric isomer of $[Ru(dmbipy)(pmbipy)_2]^{2+}$ (*i.e.* **VI** ⟶ **I**, **VII** ⟶ **II**, **VIII** ⟶ **III**). On the other hand, the decarbonylation reactions of each



fac **IX**



mer **X**

isomer of $[Ru(dmbipy)(pmbipy)(CO)_2]^{2+}$ in the presence of pmbipy would produce two isomers of the target complex $[Ru(dmbipy)(pmbipy)_2]^{2+}$, *i.e.* **IV** ⟶ **II** + **III** (because the neopentyl group must remain *cis* to the two positions of substitution) and **V** ⟶ **I** + **III**.

In previous applications of the synthetic methodology,[1-6] the incorporation of the third bidentate ligand was achieved by decarbonylation of $[Ru(L^1)(L^2)(CO)_2]^{2+}$ by Me_3NO in the presence of L^3 in refluxing 2-methoxyethanol solution. In the present studies, it was possible to determine the stereochemical course of this reaction, by use of specific geometric isomers of the $[Ru(pmbipy)_2(CO)_2]^{2+}$ and $[Ru(dmbipy)(pmbipy)(CO)_2]^{2+}$ precursors with an assessment of the isomeric distribution in the $[Ru(dmbipy)(pmbipy)_2]^{2+}$ product.

These studies indicated that at the higher temperatures associated with refluxing 2-methoxyethanol, there was some loss of stereochemical integrity and ligand scrambling during the decarbonylation process. However at lower temperatures, reactions left for a longer period underwent the decarbonylation and substitution to produce the product in which the stereochemical and ligand integrity were maintained, although the yields were lower.

By reacting a 1 : 1 mixture of **IV** and **V** with pmbipy at room temperature, the three isomers of $[Ru(dmbipy)(pmbipy)_2]^{2+}$ were obtained in the ratio **I**:**II**:**III** = 1:1:2. This represents a sum of the conversion **V** ⟶ **I** + **III** and **IV** ⟶ **II** + **III**, and is consistent with retention of stereochemistry in the reaction. Under the same conditions, the reaction of **IV** alone realized a 1 : 1 mixture of **II** and **III**, which clearly indicates the retention of the stereochemical relationship of the ligands in $[Ru(dmbipy)(pmbipy)(CO)_2]^{2+}$ during its subsequent reaction.

The reaction of **VI** with dmbipy at room temperature under decarbonylation conditions realized only isomer **I** of the product $[Ru(dmbipy)(pmbipy)_2]^{2+}$. Interestingly, when the same reaction was performed under reflux, scrambling was evident and the other isomers [sym-*cis* (16%) and unsym-*cis* (2%)] were detected, as well as the species $[Ru(dmbipy)_2(pmbipy)]^{2+}$ (3%).

Tris[4-(2,2-*dimethylpropyl*)-4′-*methyl*-2,2′-*bipyridine*]-*ruthenium*(II), $[Ru(pmbipy)_3]^{2+}$.—In the course of these studies, the complex $[Ru(pmbipy)_3]^{2+}$ was synthesized and chromatographically separated into its two possible geometric isomers, which were characterized by ^1H NMR spectroscopy. This complex has been reported previously,[28] but isomeric forms were not considered. There is only one literature reference[16] of the complete separation of isomers of a complex of the type $[Ru(L^4)_3]^{2+}$.

Conclusion

The synthesis and characterization of the geometric isomers of $[Ru(dmbipy)(pmbipy)(CO)_2]^{2+}$ and $[Ru(pmbipy)_2(CO)_2]^{2+}$, and of the $[Ru(dmbipy)(pmbipy)_2]^{2+}$ product formed from their decarbonylation, have been achieved. Examination of the stereochemistry of the addition of this final ligand in a decarbonylation step have revealed that under certain reaction conditions the stereochemical relationship of the ligands in the dicarbonyl precursors is maintained in the process.

These results have a number of important consequences. Dicarbonyl species of this type may be used in the construction of polymetallic molecular assemblies,[7] and the present observations raise the possibility of predetermination of the spatial relationship of metal centres by the use of dicarbonyl species of specific geometry. The further aspect of chiral control has also been investigated in our laboratory.[29] In addition, it is noted that in previous studies of complexes incorporating quencher-functionalized ligand substituents, charge-separated excited states have been reported without consideration of the spatial effects within the possible geometric isomers.[30] Studies of the present type, in which such redox-active groups replaced the model neopentyl substituents, would allow an assessment of the spatial dependence of such processes on the relationship of such groups within isomeric forms of the same molecule. An alternative approach[31] has been taken to this problem by the attachment of redox-active groups to the separated isomers of tris(bidentate ligand)ruthenium(II) complexes containing carboxylato-substituted ligands of the 2,2′-bipyridine type. A collaborative photophysical study of the spatial dependence of electron and energy transfer processes within such isomeric species will be undertaken,[31] and reported subsequently.

Experimental

Measurements.—The NMR studies [^1H and ^{13}C NMR, XHCORRD (optimized for J 138 Hz), DEPT and decoupling experiments] were performed on a Bruker Aspect AM300 NMR spectrometer in CD_3CN solutions. Infrared spectra were measured using a Perkin-Elmer 1600 series FTIR spectrophotometer with samples prepared in Nujol mulls and placed between NaCl plates. Electronic spectra (in acetonitrile solutions) were obtained using a Hewlett Packard HP 89532K UV/VIS spectrophotometer. Microanalyses were carried out by Chemical & Micro Analytical Services Pty. Ltd. (Belmont, Victoria, Australia).

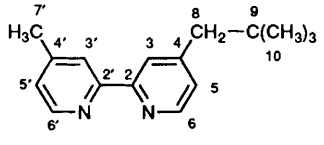
Materials.—The compounds 4,4′-dimethyl-2,2′-bipyridine (Aldrich), 2-bromo-2-methylpropane (Aldrich), butyllithium (Aldrich), $RuCl_3 \cdot 3H_2O$ (Strem), 2-methoxyethanol (Aldrich) and formic acid (BDH, 90%) were used as received without further purification. Laboratory grade solvents were used unless otherwise specified.

Diisopropylamine (Aldrich) was distilled under nitrogen and stored over 5 Å molecular sieves. Tetrahydrofuran (BDH) was doubly distilled under nitrogen from sodium wire with benzophenone as an indicator. Trifluoromethanesulfonic acid

(3 mol dm^{-3}) and 1,2-dichlorobenzene (Aldrich) were freshly distilled as required. Standardization of butyllithium was performed by titrating against 2,2,2'-trimethylpropionanilide (Aldrich). The oligomer $[\{Ru(CO)_2Cl_2\}_n]$ was synthesized by the method established in the literature.[2,32]

Thin-layer chromatography was conducted on Kiesegel 60 H F_{254} plates (Merck). Kieselgel 60 H (Merck) was used for vacuum column chromatography.[33] Sephadex LH-20 and SP-Sephadex C-25 (Pharmacia) were used for chromatographic purification of metal complexes by exclusion and cation-exchange techniques respectively.

Ligand Syntheses.—4-(2,2-*Dimethylpropyl*)-4'-*methyl*-2,2'-*bipyridine* (*pmbipy*). The reaction was carried out under an inert atmosphere of dry nitrogen at −78 °C. 4,4'-Dimethyl-2,2'-bipyridine (dmbipy; 5 g, 0.027 mol) was dried under vacuum at 60 °C overnight then dissolved in freshly distilled thf (150 cm^3). Lithium diisopropylamide (1.1 equivalents) was formed *in situ* by reacting LiBu (24.27 cm^3, 1.116 mol dm^{-3}) with diisopropylamine (3.8 cm^3) in thf (20 cm^3). The lithium diisopropylamide mixture was stirred for *ca.* 1.5 h, and the dmbipy solution added dropwise over 1 h. The resultant deep red-purple solution was allowed to stir for an additional 1 h prior to transfer by cannula to another vessel containing 2-bromo-2-methylpropane (12.49 cm^3, 5 equivalents) in thf (20 cm^3). This mixture was stirred for 1 h, warmed to room temperature and stirred for 3 d, during which time the colour changed from red through green to yellow. The reaction mixture was quenched with distilled water (100 cm^3), extracted into diethyl ether (50 cm^3) and dichloromethane (3 × 50 cm^3), and the combined organic extracts dried over anhydrous sodium sulfate and the solvent removed. Purification was accomplished by vacuum column chromatography using silica gel [eluent: 50% ethyl acetate–light petroleum (b.p. 40–60 °C)]. Thin-layer chromatography of the procedure using the same solvent showed three spots with R_f values of 0.04, 0.38 and 0.78 corresponding to the three compounds dmbipy, pmbipy and bpbipy. The pure product pmbipy was isolated as a yellow oil, yield 2.14 g, 37%. NMR (CD_3CN): ^1H, δ 8.50 (1 H, d, *J* 4.85,



pmbipy

H^6), 8.48 (1 H, d, *J* 4.9, $H^{6'}$), 8.25 (1 H, s, $H^{3'}$), 8.18 (1 H, s, H^3), 7.20 (1 H, d, *J* 5.1, $H^{5'}$), 7.16 (1 H, d, *J* 4.9 Hz, H^5), 2.61 (2 H, s, H^8), 2.42 (3 H, s, $H^{7'}$), 0.93 (9 H, s, H^{10}); ^{13}C, δ 156.9 ($C^{2'}$), 156.3 (C^2), 150.5 ($C^{4'}$), 149.9 ($C^{6'}$), 149.4 (C^6), 149.2 (C^4), 126.7 (C^5), 125.6 ($C^{5'}$), 123.5 (C^3), 122.4 ($C^{3'}$), 49.9 (C^8), 32.2 (C^9), 29.5 (C^{10}), 21.2 ($C^{7'}$).

Complex Syntheses.—*Dicarbonyldichloro*(4,4'-*dimethyl*-2,2'-*bipyridine*)*ruthenium*(II), $[Ru(dmbipy)(CO)_2Cl_2]$. A solution of the ligand dmbipy (2.5 g, 13.6 mmol) in AR methanol (25 cm^3) was deaerated for 30 min before the addition of $[\{Ru(CO)_2Cl_2\}_n]$ (1.55 g, 6.8 mmol). The mixture was refluxed for 1.5 h with vigorous stirring and the precipitate collected on cooling. The yellow product was recrystallized from boiling methanol in subdued light, yield 1.96 g, 70% (Found: C, 37.5; H, 2.10; N, 7.2%. $C_{14}H_{14}Cl_2N_2O_2Ru$ requires C, 37.5; H, 2.10; N, 7.3%). IR: $\tilde{\nu}_{max}/cm^{-1}$ (Nujol) 2060 and 1988 (CO). NMR: $\delta_H(CD_3CN)$ 8.96 (2 H, d, *J* 5, H^6), 8.29 (2 H, s, H^3), 7.54 (2 H, d, *J* 5 Hz, H^5), 2.57 (6 H, s, CH_3).

Dicarbonyldichloro[4-(2,2-*dimethylpropyl*)-4'-*methyl*-2,2'-*bipyridine*]*ruthenium*(II), $[Ru(pmbipy)(CO)_2Cl_2]$. The pmbipy compound was synthesized and purified in an analogous manner to the corresponding dmbipy complex in 81% yield (Found: C, 46.0; H, 4.30; N, 5.9. $C_{18}H_{20}Cl_2N_2O_2Ru$ requires C, 46.2; H, 4.30; N, 6.0%). IR: $\tilde{\nu}_{max}/cm^{-1}$ (Nujol) 1981 and 2047 (CO). NMR: $\delta_H(CD_3CN)$ 8.98 (1 H, d, *J* 5, H^6), 8.95 (1 H, d, *J* 5, $H^{6'}$), 8.33 (1 H, s, $H^{3'}$), 8.21 (1 H, s, H^3), 7.54 (1 H, d, *J* 5, $H^{5'}$), 7.51 (1 H, d, *J* 5 Hz, H^5), 2.75 (2 H, s, H^8), 2.57 (3 H, s, $H^{7'}$), 0.98 (9 H, s, H^{10}).

Dicarbonyl(4,4'-*dimethyl*-2,2'-*bipyridine*)*bis*(*trifluoromethanesulfonato*)*ruthenium*(II), $[Ru(dmbipy)(CO)_2(CF_3SO_3)_2]$. This complex was synthesized by a method based on that of Sullivan *et al.*[24] in which $[Ru(dmbipy)(CO)_2Cl_2]$ (750 mg, 1.82 mmol) in 1,2-dichlorobenzene (200 cm^3) was deaerated with dry nitrogen for 30 min, resulting in a cloudy yellow solution. Trifluoromethanesulfonic acid (0.5 cm^3) was added dropwise by syringe (platinum needle) and the solution heated to 120 °C for 1.5 h. The mixture was cooled to 0 °C and the product precipitated by the addition of diethyl ether (200 cm^3). The mixture was allowed to stir for 1 h, and the complex collected by vacuum filtration under nitrogen and washed with diethyl ether (2 × 5 cm^3), cold distilled water (2 × 5 cm^3) and diethyl ether (2 × 5 cm^3), yield 990 mg, 85%. IR: $\tilde{\nu}_{max}/cm^{-1}$ (Nujol) 2099 and 2027 (CO), 1031, 893, 574 and 516 ($CF_3SO_3^-$).

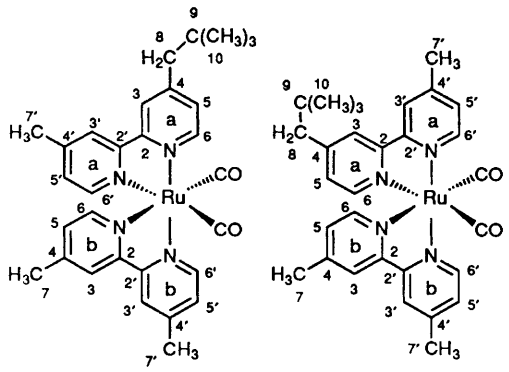
Dicarbonyl[4-(2,2-*dimethylpropyl*)-4'-*methyl*-2,2'-*bipyridine*]*bis*(*trifluoromethanesulfonato*)*ruthenium*(II), $[Ru(pmbipy)(CO)_2(CF_3SO_3)_2]$. The pmbipy compound was synthesized in a similar manner to the dmbipy complex, with the exception that the 1,2-dichlorobenzene was distilled off prior to precipitation with diethyl ether. Yield was 55%. IR: $\tilde{\nu}_{max}/cm^{-1}$ (Nujol) 2033 and 2095 (CO), 1028, 895, 574 and 518 ($CF_3SO_3^-$).

Dicarbonylbis(4,4'-*dimethyl*-2,2'-*bipyridine*)*ruthenium*(II) *hexafluorophosphate dihydrate*, $[Ru(dmbipy)_2(CO)_2][PF_6]_2 \cdot 2H_2O$. The complex $[Ru(dmbipy)(CO)_2(CF_3SO_3)_2]$ (780 mg, 1.21 mmol) was added to a deaerated solution of dmbipy (590 mg, 2.45 mmol) in absolute ethanol (30 cm^3) and the mixture was refluxed for 1.5 h. The ethanol was removed on the rotary evaporator and the black residue extracted with boiling water (50 cm^3) and filtered. The complex was precipitated from the filtrate by addition of KPF_6 and the mixture stored at 4 °C overnight. The cream complex was collected, and washed with cold distilled water and diethyl ether. The solid was recrystallized from ethanol–acetone, yield 714 mg, 75%. The complex was purified by cation-exchange chromatography (SP-Sephadex C-25, 0.2 mol dm^{-3} NaCl eluent): the cation was precipitated from the eluent by the addition of solid KPF_6, and the resultant solid filtered off and washed with water (20 cm^3) and diethyl ether (20 cm^3) (Found: C, 38.1; H, 2.90; N, 6.7. $C_{26}H_{24}F_{12}N_4O_2P_2Ru$ requires C, 38.3; H, 2.95; N, 6.9%). IR: $\tilde{\nu}_{max}/cm^{-1}$ (Nujol) 2087 and 2034 (CO). NMR: $\delta_H(CD_3CN)$ 8.86 (2 H, d, *J* 5, H^6), 8.43 (2 H, s, H^3), 8.30 (2 H, s, $H^{3'}$), 7.72 (2 H, d, *J* 5, H^5), 7.30 (2 H, d, *J* 5, $H^{5'}$), 7.19 (2 H, d, *J* 5 Hz, $H^{6'}$), 2.67 (6 H, s, CH_3), 2.47 (6 H, s, CH_3').

Dicarbonyl(4,4'-*dimethyl*-2,2'-*bipyridine*)[4-(2,2-*dimethylpropyl*)-4'-*methyl*-2,2'-*bipyridine*]*ruthenium*(II) *hexafluorophosphate dihydrate*, $[Ru(dmbipy)(pmbipy)(CO)_2][PF_6]_2 \cdot 2H_2O$. The mixed bipyridine complex was synthesized and purified (90% yield) in an analogous manner to $[Ru(dmbipy)_2(CO)_2][PF_6]_2$, by the substitution of pmbipy into $[Ru(dmbipy)(CO)_2(CF_3SO_3)_2]$ (Found: C, 39.7; H, 3.55; N, 6.0. $C_{30}H_{36}F_{12}N_4O_4P_2Ru$ requires C, 39.7; H, 4.00; N, 6.2%). IR: $\tilde{\nu}_{max}/cm^{-1}$ (Nujol) 2099 and 2053 (CO).

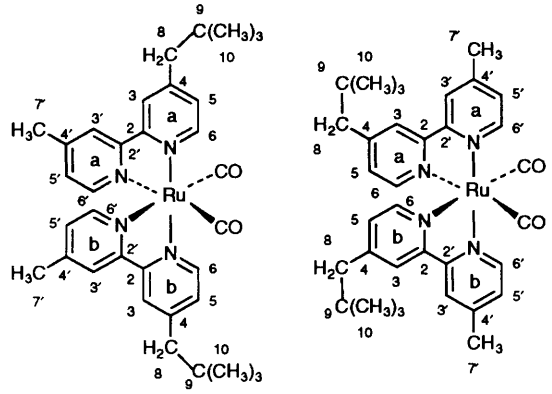
The crude product was found to be a mixture of two isomers (**IV** and **V**). By fractional recrystallization from ethanol, the less soluble isomer (**IV**) could be obtained in pure form. The ^1H NMR shifts (in CD_3CN solution) of the two isomers are given in Table 1 (numbering scheme shown below).

Dicarbonylbis[4-(2,2-*dimethylpropyl*)-4'-*methyl*-2,2'-*bipyridine*]*ruthenium*(II) *hexafluorophosphate hydrate*, $[Ru(pmbipy)_2(CO)_2][PF_6]_2 \cdot H_2O$. The crude complex was synthesized and purified (62% yield) in an analogous manner to that described for $[Ru(dmbipy)_2(CO)_2][PF_6]_2$, by the substitution of pmbipy into $[Ru(pmbipy)(CO)_2(CF_3SO_3)_2]$ (Found: C, 43.2; H, 4.30; N, 5.8. $C_{34}H_{42}F_{12}N_4O_3P_2Ru$ requires C, 43.2; H, 4.50; N, 5.9%). IR: $\tilde{\nu}_{max}/cm^{-1}$ (Nujol) 2096 and 2042 (CO).

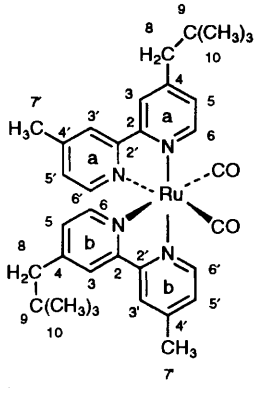


IV V

The crude product was found to be a mixture of three isomers (**VI**, **VII** and **VIII**), which were separated by fractional recrystallization from ethanol. The ^{1}H NMR shifts (in CD_3CN solution) of the three isomers are given in Table 1 (numbering scheme shown below).



VI VII



VIII

(4,4'-Dimethyl-2,2'-bipyridine)bis[4-(2,2-dimethylpropyl)-4'-methyl-2,2'-bipyridine]ruthenium(II) *hexafluorophosphate dihydrate*, $[Ru(dmbipy)(pmbipy)_2][PF_6]_2 \cdot 2H_2O$. As an exemplar of the synthetic method, $[Ru(dmbipy)(pmbipy)(CO)_2]$ (30 mg, 0.034 mmol) and pmbipy (24 mg, 0.1 mmol) were dissolved in 2-methoxyethanol (10 cm^3) and deaerated with dry nitrogen for 20 min. An excess of trimethylamine *N*-oxide (7 mg, 0.1 mmol) was added and the reaction refluxed for 3 h, during which time the solution changed from yellow to bright orange. The alternative for the reaction was that the solution was maintained at room temperature for 36 h. In both cases, the solvent was removed on the rotary evaporator, the residue dissolved in water, and the product precipitated from the filtered solution by the addition of KPF_6. This mixture was stored at 4 °C overnight, and the product collected by vacuum filtration, sorbed onto a column of SP-Sephadex C-25 cation exchanger, and eluted with 0.2 mol dm^{-3} NaCl. The single band was collected, KPF_6 added, and the orange cation extracted into dichloromethane (3 × 50 cm^3), which was dried over anhydrous sodium sulfate. The solvent was removed, the residue dissolved in water and the product re-precipitated with KPF_6. After storage at 4 °C overnight, the solid was collected by vacuum filtration, washed with diethyl ether and air dried. Yield 25 mg, 70% at reflux; 7 mg, 20% at room temperature (Found: C, 48.6; H, 4.65; N, 7.9. $C_{44}H_{56}F_{12}N_6O_2P_2Ru$ requires C, 48.4; H, 5.15; N, 7.7%). UV/VIS: λ_{max}/nm (CH_3CN) 210 (ε/dm^3 mol^{-1} cm^{-1} 79 600), 250 (25 400), 258 (24 000), 288 (70 600), 426 (sh), 458 (12 000).

The isomers were separated by cation exchange chromatography on SP-Sephadex C-25 using 0.125 mol dm^{-3} sodium toluene-4-sulfonate as the eluent.[7] The hexafluorophosphate salts were isolated by precipitation from the eluent by addition of KPF_6, and the suspension extracted using dichloromethane. The ^{1}H NMR shifts (in CD_3CN solution) of the three isomers are given in Table 2.

Bis(4,4'-dimethyl-2,2'-bipyridine)[4-(2,2-dimethylpropyl)-4'-methyl-2,2'-bipyridine]ruthenium(II) *hexafluorophosphate*, $[Ru(dmbipy)_2(pmbipy)][PF_6]_2$. The complex was synthesized in 57% yield in an analogous manner to that described for $[Ru(dmbipy)(pmbipy)_2][PF_6]_2$, by reaction of pmbipy with $[Ru(dmbipy)_2(CO)_2]^{2+}$ under decarbonylation conditions (Found: C, 48.2; H, 4.30; N, 8.3. $C_{40}H_{44}F_{12}P_2N_6Ru$ requires C, 48.1; H, 4.45; N, 8.4%). UV/VIS: λ_{max}/nm (MeCN) 208 (ε/dm^3 mol^{-1} cm^{-1} 84 000), 250 (25 000), 258 (23 300), 288 (84 200), 426 (sh), 458 (15 300). The ^{1}H NMR shifts (in CD_3CN solution) are given in Table 2.

Tris[4-(2,2-dimethylpropyl)-4'-methyl-2,2'-bipyridine]ruthenium(II) *hexafluorophosphate*, $[Ru(pmbipy)_3][PF_6]_2$. The complex was synthesized using an adaption of a procedure published previously,[34,35] *via* $[Ru(dmf)_6]^{2+}$ (dmf = *N*,*N*-dimethylformamide) as precursor. Yield: 25% (Found: C, 51.5; H, 4.80; N, 7.2. $C_{48}H_{60}F_{12}N_6P_2Ru$ requires C, 51.8; H, 5.45; N, 7.6%). UV/VIS: λ_{max}/nm (MeCN) 210 (ε/dm^3 mol^{-1} cm^{-1} 70 100), 250 (21 000), 258 (19 600), 288 (66 000), 426 (sh), 458 (12 000).

The isomers were separated by cation-exchange chromatography on SP-Sephadex C-25 using 0.125 mol dm^{-3} sodium toluene-4-sulfonate as the eluent.[7] The hexafluorophosphate salts were isolated by precipitation from the eluent by addition of KPF_6, and the suspension extracted using dichloromethane. The ^{1}H NMR shifts (in CD_3CN solution) of the two isomers are given in Table 2.

Acknowledgements

We are grateful to Mr. Laurie Kelso and Mr. Joe Treadway for useful discussions on aspects of the work, and the Australian Research Council for financial support.

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Received 23*rd May* 1994; *Paper* 4/03028A