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New tricks for an old ligand: cyclometallated and didentate co-ordination of 2,2′:6′,2″-terpyridine to ruthenium(II)

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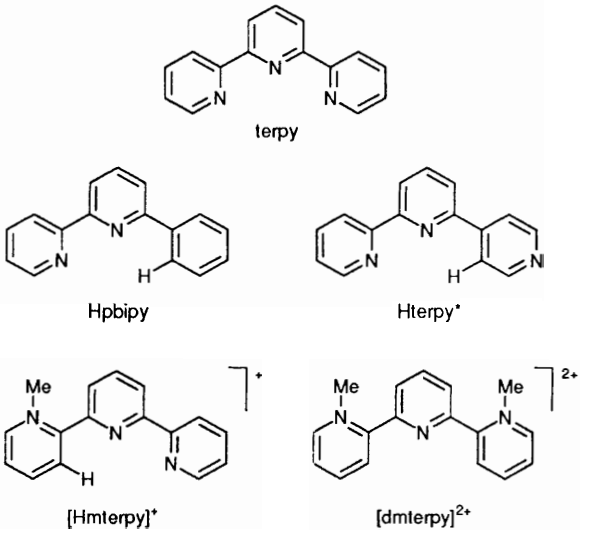
Monomethylation of 2,2′:6′,2″-terpyridine (terpy) afforded the *N*-methyl-2,2′:6′,2″-terpyridinium cation, [Hmterpy]$^+$. With one of the terminal pyridine ring nitrogen atoms thus protected, it co-ordinates to ruthenium(II) either as a didentate *N*,*N*′-donor giving [Ru(terpy)(Hmterpy-*N*,*N*′)Cl][PF_6]$_2$, or as a cyclometallating terdentate ligand giving [Ru(terpy)(mterpy-*N*,*N*′,*C*)][PF_6]$_2$, depending upon the reaction conditions. Both complexes have been fully characterised by spectroscopic and electrochemical methods, and the crystal structures of [Ru(terpy)(mterpy-*N*,*N*′,*C*)][BF_4]$_2$·2MeCN and [Ru(terpy)(Hmterpy-*N*,*N*′)Cl][PF_6]$_2$·2MeCN determined.

Compounds incorporating mono-[1] or poly-pyridyl[2] binding sites continue to attract much interest, both for their fundamental co-ordination behaviour and their use as multinucleating bridging ligands in supramolecular chemistry. Cyclometallating analogues of oligopyridine ligands, in which one or more pyridine ring nitrogen is replaced by a carbon donor atom, have also attracted interest.[3–7] The archetypal example is 2-phenylpyridine, which co-ordinates as an *N*,*C*-donor analogue of bipyridine, and has been extensively studied.[3] Terdentate cyclometallating ligands are exemplified by 6-phenyl-2,2′-bipyridine (Hpbipy)[5] and 2,2′:6′,4″-terpyridine (Hterpy*),[6] and may all be thought of as *N*,*N*′,*C*-donor analogues of 2,2′:6′,2″-terpyridine. Cyclometallation affects the redox and photophysical properties of the resulting complexes to a much greater extent than does attachment of substituents to the ligand backbone, and the incorporation of a cyclometallating ligand into multinuclear complexes can have the effect of enhancing the interactions between the metal centres.[8,9]

2,2′-Bipyridine (bipy) usually co-ordinates to a single metal centre as a didentate *N*,*N*-donor ligand.[10] Occasionally, a cyclometallated *N*,*C*-binding mode is adopted.[11] It can also be made to act as a cyclometallating *N*,*C*-donor ligand if one of the nitrogen atoms is quaternised and hence prevented from co-ordinating;[12] this can also result in monodentate *N*-donor co-ordination.[13] Rarely, bipy is also observed to bridge two metal centres.[14] Similarly, 2,2′:6′,2″-terpyridine (terpy) favours terdentate co-ordination,[15] but didentate binding can be achieved by co-ordination to a metal centre possessing a strong preference for co-ordination of only two further donor atoms because there are only two vacant (or substitution labile) co-ordination sites: thus, [Ru(bipy)$_2$Cl$_2$] reacts with terpy to give octahedral [Ru(bipy)$_2$(terpy-*N*,*N*′)]$^{2+}$.[16] Some complexes containing didentate terpy ligands have been shown by ^{1}H NMR spectroscopy to exhibit a 'tick-tock' fluxional process involving the terpy ligand in which the central pyridyl ring is always co-ordinated and the terminal rings are alternately co-ordinated or pendant.[17] Recently, small amounts of [Ru(Rterpy)(Xterpy-*N*,*N*′)Cl]$^+$ complexes (Rterpy = 4′-substituted 2,2′:6′,2″-terpyridines) were isolated as by-products of the synthesis of [Ru(Rterpy)$_2$]$^{2+}$ from [Ru(Rterpy)Cl$_3$] and Rterpy.[18] These complexes are, however, rather photolabile with respect to rearrangement to give [Ru(Rterpy)$_2$]$^{2+}$, especially in the case of R = H.

In order to force terpy to adopt a novel *N*,*N*′,*C* cyclometallating binding mode we have protected one of the terminal pyridine ring nitrogen atoms by quaternisation giving the *N*-methyl-2,2′:6′,2″-terpyridinium cation Hmterpy$^+$. We describe herein the syntheses, spectroscopic properties and crystal structure of the cyclometallated complex [Ru(terpy)(mterpy-*N*,*N*′,*C*)][X]$_2$ (X = PF_6 **1** or BF_4 **1a**) and of the non-metallated complex [Ru(terpy)(Hmterpy-*N*,*N*′)Cl][PF_6]$_2$ **2**.



Experimental

Proton NMR spectra were recorded on JEOL GX270, Lambda 300, or GX400 spectrometers, UV/VIS spectra on a Perkin-Elmer Lambda 2 instrument and fast atom bombardment (FAB) mass spectra on a VG Autospec instrument, with 3-nitrobenzyl alcohol as matrix. Electrochemical measurements were made with an EG&G PAR 273A potentiostat, using platinum-bead working and auxiliary electrodes and a saturated calomel electrode (SCE) as reference. The measurements were performed using acetonitrile distilled over calcium hydride, with 0.1 mol dm^{-3} [NBu^n_4][PF_6] as supporting electrolyte. Ferrocene was added at the end of each experiment as an internal reference, and all redox potentials are quoted *vs.* the ferrocene–ferrocenium couple. 2,2′:6′,2″-Terpyridine[19] and [Ru(terpy)Cl$_3$][20] were prepared by the literature methods.

Preparations

***N*-Methyl-2,2′:6′,2″-terpyridinium hexafluorophosphate, [Hmterpy][PF$_6$].** 2,2′:6′,2′-Terpyridine (0.233 g, 1.00 mmol) and [Me$_3$O][BF$_4$] (0.148 g, 1.00 mmol) were heated to reflux in dichloromethane (15 cm^3) for 2 h. On cooling, the yellow suspension was extracted with water (2 × 20 cm^3). An excess of aqueous [NH$_4$][PF$_6$], together with a few drops of aqueous ammonia, were added to the combined yellow aqueous extracts. Concentration *in vacuo* afforded a pale pink microcrystalline solid which was filtered off, recrystallised from aqueous acetone with added aqueous ammonia, and dried *in vacuo* (0.225 g, 57%). FAB mass spectrum: *m*/*z* 248, [*M* − PF$_6$]$^+$ (Found: C, 48.5; H, 3.5; N, 10.7. Calc. for C$_{16}$H$_{14}$F$_6$N$_3$P: C, 48.9; H, 3.6; N, 10.7%). ^{1}H NMR (CD$_3$CN, 270 MHz): δ 8.79 (dd, 1 H, H^6), 8.73 (dd, 1 H, H$^{6''}$), 8.69 (dd, 1 H, H$^{5'}$), 8.62 (ddd, 1 H, H^4), 8.41 (dd, 1 H, H$^{3''}$), 8.23 (dd, 1 H, H$^{4'}$), 8.17 (dd, 1 H, H^3), 8.08 (ddd, 1 H, H^5), 7.93 (ddd, 1 H, H$^{4''}$), 7.82 (dd, 1 H, H$^{3'}$), 7.47 (ddd, 1 H, H$^{5''}$) and 4.34 (s, 3 H, Me).

***N*,*N*″-Dimethyl-2,2′:6′,2″-terpyridinedium hexafluorophosphate, [dmterpy][PF$_6$]$_2$.** 2,2′:6′,2″-Terpyridine (0.100 g, 0.43 mmol) and iodomethane (1 cm^3, excess) were heated to reflux in toluene (10 cm^3) for 20 h. On cooling, the reaction mixture was extracted with water (2 × 20 cm^3). An excess of aqueous [NH$_4$][PF$_6$] was added to the combined aqueous extracts, which were concentrated *in vacuo* to precipitate the product. This was filtered off, washed with water, and recrystallised from aqueous acetonitrile to afford an off-white microcrystalline solid (0.100 g, 42%). FAB mass spectrum: *m*/*z* 408, [*M* − PF$_6$]$^+$; 262, [*M* − 2PF$_6$]$^+$; and 248, [*M* − Me − 2PF$_6$]$^+$ (Found: C, 36.9; H, 3.4; N, 7.9. Calc. for C$_{17}$H$_{17}$F$_{12}$N$_3$P$_2$: C, 36.9; H, 3.1; N, 7.6%). ^{1}H NMR (CD$_3$CN, 300 MHz): δ 8.77 (dd, 2 H, H^6), 8.64 (ddd, 2 H, H^4), 8.40 (dd, 1 H, H$^{4'}$), 8.16 (dd, 2 H, H^3), 8.11 (ddd, 2 H, H^5), 8.04 (dd, 2 H, H$^{3'}$) and 4.24 (s, 6 H, Me).

[Ru(terpy)(mterpy-*N*,*N*′,*C*)][PF$_6$]$_2$ 1. The complex [Ru(terpy)Cl$_3$] (0.060 g, 0.14 mmol) and AgBF$_4$ (0.082 g, 0.42 mmol) were heated at reflux in acetone (10 cm^3) for 1.5 h. The dark solution was filtered through Celite to remove precipitated AgCl, and the filtrate concentrated to dryness. The salt [Hmterpy][PF$_6$] (0.080 g, 0.20 mmol) and dimethylformamide (20 cm^3) were added, and the resulting solution was heated to 130 °C for 5 h. On cooling, water (50 cm^3) and an excess of [NH$_4$][PF$_6$] were added. The dark pink precipitate was filtered off, washed with water, dissolved in the minimum volume of acetonitrile and chromatographed over flash-grade silica using MeCN–saturated aqueous KNO$_3$–water (14:2:1) as the eluent. The main pink product band was collected as fractions of 10 cm^3, and the compositions of these were determined by thin-layer chromatography. Those later fractions containing an impurity of the slightly slower-moving orange [Ru(terpy)$_2$]$^{2+}$ were discarded. The clean fractions were combined, and water and an excess of [NH$_4$][PF$_6$] were added. Reduction in volume afforded a red-black precipitate, which was filtered off and recrystallised from aqueous acetonitrile (0.013 g, 11%). FAB mass spectrum: *m*/*z* (^{102}Ru) 727, [*M* − PF$_6$]$^+$; 581, [*M* − 2PF$_6$]$^+$; and 567, [*M* − Me − 2PF$_6$]$^+$ (Found: C, 42.9; H, 2.9; N, 9.7. Calc. for C$_{31}$H$_{24}$F$_{12}$N$_6$P$_2$Ru: C, 42.7; H, 2.8; N, 9.6%). ^{1}H NMR (CD$_3$CN, 300 MHz): δ 8.74 (dd, 1 H, H$^{3B/5B}$), 8.67 (dd, 1 H, H$^{5B/3B}$), 8.65 (d, 2 H, H^{3E}), 8.53 (dd, 1 H, H^{3A}), 8.42 (dd, 2 H, H^{3D}), 8.22 (m, 2 H, H^{4E}, H^{4B}), 7.95 (m, 2 H, H^{4A}, H^{4C}), 7.82 (ddd, 2 H, H^{4D}), 7.52 (dd, 1 H, H^{6A}), 7.28 (dd, 2 H, H^{6D}), 7.20 (ddd, 1 H, H^{5A}), 7.08 (m, 3 H, H^{6C}, H^{5D}), 6.95 (dd, 1 H, H^{5C}) and 4.61 (s, 3 H, Me).

The tetrafluoroborate salt [Ru(terpy)(mterpy-*N*,*N*′,*C*)][BF$_4$]$_2$ **1a** was obtained quantitatively by concentration of a sample of **1** in aqueous acetonitrile containing an excess of NaBF$_4$.

[Ru(terpy)(Hmterpy-*N*,*N*′)Cl][PF$_6$]$_2$ 2. The complex [Ru(terpy)Cl$_3$] (0.055 g, 0.12 mmol), [Hmterpy][PF$_6$] (0.055 g, 0.14 mmol) and *N*-methylmorpholine (one drop) were heated at reflux in methanol (10 cm^3) for 3 h. The reaction mixture was cooled and the crude product precipitated by addition of an excess of aqueous [NH$_4$][PF$_6$]. The precipitate was collected on Celite, washed with water, dissolved in the minimum volume of acetonitrile, and chromatographed as for **1** above. Orange [Ru(terpy)$_2$]$^{2+}$ was eluted first and discarded. The desired product was eluted as the second, main, purple-brown band, and collected as fractions whose purities were checked by TLC. Those that were clean were combined and precipitated by addition of an excess of aqueous [NH$_4$][PF$_6$]. The solid was filtered off and recrystallised from aqueous acetonitrile, affording **2** as a purple-brown powder (0.014 g, 12%). FAB mass spectrum: *m*/*z* (^{102}Ru) 763, [*M* − PF$_6$]$^+$, 618, [*M* − 2PF$_6$]$^+$; and 603, [*M* − Me − 2PF$_6$]$^+$ (Found: C, 40.7; H, 2.7; N, 9.2. Calc. for C$_{31}$H$_{25}$ClF$_{12}$N$_6$P$_2$Ru: C, 41.0; H, 2.8; N, 9.3%). ^{1}H NMR (CD$_3$CN, 400 MHz); δ 10.17 (dd, 1 H, H^{6A}), 8.85 (dd, 1 H, H^{3A}), 8.72 (dd, 1 H, H^{3B}), 8.38 (ddd, 1 H, H^{4A}), 8.32 (m, 3 H, H^{3D}, H^{3F}, H^{6C}), 8.15 (m, 2 H, H^{3E}, H^{5E}), 8.10 (ddd, 1 H, H^{4C}), 8.05 (dd, 1 H, H^{4B}), 8.00 (m, 2 H, H^{4D}, H^{4F}), 7.94 (ddd, 1 H, H^{5A}), 7.87 (ddd, 1 H, H^{5C}), 7.82 (dd, 1 H, H^{4E}), 7.78 (dd, 1 H, H$^{6D/6F}$), 7.62 (dd, 1 H, H$^{6F/6D}$), 7.38 (m, 2 H, H^{5D}, H^{5F}), 7.14 (dd, 1 H, H^{5B}), 6.84 (dd, 1 H, H^{3C}) and 2.87 (s, 3 H, Me).

Crystallography

Red-black block-shaped crystals of complex **1a**·2MeCN and purple-black block-shaped crystals of **2**·2MeCN were grown by diffusion of diethyl ether vapour into acetonitrile solutions of [Ru(terpy)(mterpy-*N*,*N*′,*C*)][BF$_4$]$_2$ and [Ru(terpy)(Hmterpy-*N*,*N*′)Cl][PF$_6$]$_2$, respectively. Suitable crystals were mounted on glass fibres with Superglue.

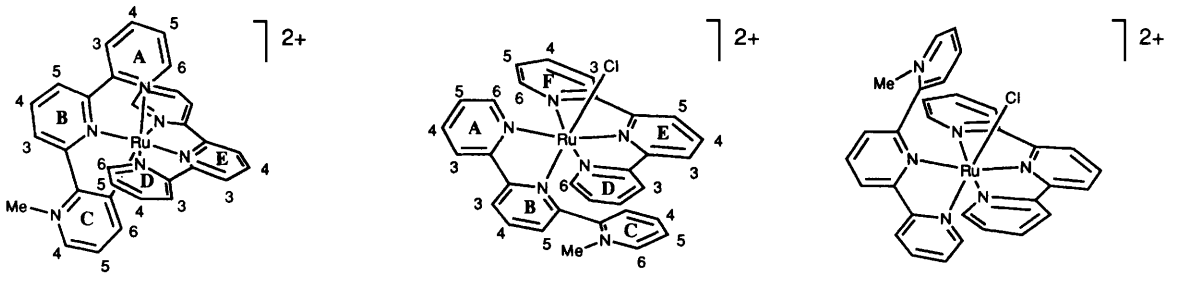
Data were collected using a Siemens SMART three-circle diffractometer with a CCD area detector (graphite-monochromatised Mo-Kα X-radiation, $\bar{\lambda}$ = 0.710 73 Å). Data were collected for Lorentz and polarisation effects, and for absorption effects by an empirical method based on multiple measurements of equivalent data. Details of the crystal parameters, data collection and refinement are in Table 1. The structures were solved by conventional heavy-atom or direct methods (SHELXTL)[21] and were refined by the full-matrix least-squares method on all F^2 data (SHELXL 93)[21] using a Silicon Graphics Indigo R4000 computer. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters. Selected bond lengths and angles are in Tables 2 and 3, and inter-ring torsion angles in Table 4. The only problem was that in complex **2**·2MeCN one of the two hexafluorophosphate anions was badly disordered. The disorder was modelled by allowing five of the F atoms to have two alternative positions with site occupancies of 0.5 in each position; the sixth F atom and the P atom refined successfully in fixed positions with unit site occupancy.

Complete atom coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

Results and Discussion

Methylation of terpyridine

Methylation of terpy to give *N*-methyl-2,2′:6′,2″-terpyridinium salts proved not to be entirely straightforward. No reaction was observed to occur between terpy and an excess of iodomethane in methanol at reflux. There was likewise no significant reaction between terpy and a stoichiometric amount of MeI using either butan-1-ol or toluene as the solvent, at a variety of



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Scheme 1 Representation of cyclometallated $[Ru(terpy)(mterpy\text{-}N,N',C)]^{2+}$ and of the two possible isomers of non-metallated $[Ru(terpy)(Hmterpy\text{-}N,N')Cl]^{2+}$, including atom numbering schemes used in ^1H NMR assignments

temperatures, despite the reaction of equimolar quantities of 2,2′-bipyridine and MeI in butan-1-ol at reflux being reported to favour the formation of the monomethylated product.[13] Use of an excess of MeI in butan-1-ol at reflux afforded a mixture of *N*-methyl-2,2′:6′,2″-terpyridinium iodide and *N*,*N*″-dimethyl-2,2′:6′,2″-terpyridinedium diiodide, while significant quantities of unreacted terpy remained in the mother-liquor. The use instead of toluene as the solvent resulted in the exclusive formation of the diiodide, which was converted into the hexafluorophosphate salt by anion metathesis and characterised.

Clean *N*-methyl-2,2′:6′,2″-terpyridinium hexafluorophosphate was obtained in 57% yield by the reaction of equimolar quantities of terpy and trimethyloxonium tetrafluoroborate in dichloromethane at reflux for 2 h, followed by extraction into water, precipitation with an excess of aqueous $[NH_4][PF_6]$, and recrystallisation from aqueous acetone. During the recrystallisation step a few drops of aqueous ammonia were added to ensure that the $[Hmterpy][PF_6]$ was not protonated as a result of hydrolysis of the $[NH_4][PF_6]$. Longer reaction times did not increase the yield, while use of an excess of $[Me_3O][BF_4]$ was found to result in the product being contaminated with the bis(methylated) product. The positive-ion FAB mass spectrum of $[Hmterpy][PF_6]$ exhibited a main fragment at *m*/*z* 248 ascribable to the cationic fragment $[Hmterpy]^+$. The ^1H NMR spectrum in CD_3CN solution exhibited 11 aromatic resonances ascribable to the protons on the three, non-equivalent, pyridine rings. In addition, a singlet integrating to 3 H at δ 4.34 results from the methyl protons. The aromatic resonances were assigned by comparison with the simpler spectrum of $[dmterpy][PF_6]_2$ and by studying the coupling interactions. Typically for both free and co-ordinated pyridine rings in 2,2′:6′,2″-terpyridine ligands, $^3J(H^3H^4) \approx {}^3J(H^4H^5) \approx 7.5$–8.0 and $^3J(H^5H^6) \approx 5.5$–6.0 Hz.

Syntheses of complexes

There are two possible ways in which *N*-methyl-2,2′:6′,2″-terpyridinium hexafluorophosphate may be expected to react with $[Ru(terpy)Cl_3]$ (Scheme 1). It could either adopt a cyclometallating tridentate bonding mode giving $[Ru(terpy)(mterpy\text{-}N,N',C)]^{2+}$ **I** or co-ordinate as a didentate *N*,*N*-donor ligand to give a complex of the form $[Ru(terpy)(Hmterpy\text{-}N,N')Cl]^{2+}$, in which the sixth co-ordination site at the ruthenium is occupied by a chloride. Furthermore, in the latter case two isomeric forms may be envisaged, one in which the pendant, quaternised pyridine ring lies next to the central pyridine ring of the other co-ordinated terpy (**II**), and one in which it lies next to the chlorine (**III**), though only complexes of type **II** have been reported.[5,6,22] Whether the cyclometallated complex, non-metallated complex, or a mixture of the two is formed on treating a potentially terdentate cyclometallating ligand with $[Ru(terpy)Cl_3]$ depends largely on the solvent used for the reaction. However, the effect of a particular solvent system varies from ligand to ligand, and one that favours the cyclometallation of one ligand may result in a mixture of products being formed if a different ligand is used.[5–7,22]

In the case of $[Hmterpy][PF_6]$, the use of methanol with *N*-methylmorpholine added as a reducing agent results in the non-metallated product **2** being favoured. Use of various aqueous ethanol and aqueous methanol systems typical of those that have previously been used to favour cyclometallation afforded mixtures of products that would have proved difficult to separate chromatographically owing to the similarities in charges and masses of the cyclometallated and non-metallated complexes. The cyclometallated complex **1** was eventually prepared by treating the starting material $[Ru(terpy)Cl_3]$ with 3 equivalents of $AgBF_4$ to abstract the co-ordinated chlorides prior to reaction with $[Hmterpy][PF_6]$,[23] thereby preventing the formation of complex **2** in which a chloride is retained. The yields of pure **1** and **2** were disappointingly low, largely because $[Ru(terpy)_2]^{2+}$ was produced in each case as a significant by-product from scrambling of the $[Ru(terpy)Cl_3]$, and this was difficult to separate chromatographically from the desired products. The actual amounts of **1** and **2** that we isolated pure were therefore considerably less than the amounts actually formed during the reactions. In addition, the reaction performed in methanol with *N*-methylmorpholine resulted in partial reduction of $[Ru(terpy)Cl_3]$ to metallic ruthenium.

Both complexes were satisfactorily characterised by FAB mass spectra, which showed peaks corresponding to the loss of both one and two $[PF_6]^-$ counter ions. Partial elemental analysis data were also in accord with the proposed formulations.

Crystal structures of complexes 1a and 2

Several attempts were made to grow crystals of complex **1** suitable for X-ray crystallography, though in all cases the crystals that were obtained diffracted very poorly. Anion metathesis of a sample of **1** with an excess of $NaBF_4$ in aqueous acetonitrile afforded $[Ru(terpy)(mterpy\text{-}N,N',C)][BF_4]_2$ **1a**, crystals of which proved much more suitable for X-ray analysis. The solid-state structure of **2** was also determined.

The structures of the complex cations are depicted in Figs. 1 and 2, respectively. The asymmetric unit of **1a**·2MeCN contains two crystallographically independent complex units and four MeCN molecules. The two independent complex cations are similar, with only relatively minor differences in bond lengths, angles and ring torsion angles between them. The pseudo-octahedral ruthenium centre is in an N_5C co-ordination environment from one terpy ligand and one deprotonated, cyclometallated (mterpy) ligand. The two terdentate ligands are approximately mutually perpendicular. The three aromatic rings of each ligand are nearly coplanar; the torsion angles between rings are in Table 4. As is usual for terpy ligands bound to ruthenium(II) centres in the conventional terdentate manner,

Table 1 Crystallographic data for complexes **1a**·2MeCN and **2**·2MeCN

Complex	**1a**·2MeCN	**2**·2MeCN
Formula	$C_{35}H_{30}B_2F_8N_8Ru$	$C_{35}H_{31}ClF_{12}N_8P_2Ru$
M	837.36	990.14
System, space group	Tetragonal, $P4_1$	Orthorhombic, *Pbca*
a/Å	12.3582(13)	14.440(5)
b/Å	12.3582(13)	29.286(8)
c/Å	47.573(9)	18.300(4)
U/Å^3	7265(2)	7739(4)
Z	8	8
D_c/g cm^{-3}	1.531	1.700
μ/mm^{-1}	0.511	0.655
F(000)	3376	3968
T/K	173(2)	293(2)
Crystal size/mm	0.4 × 0.3 × 0.1	0.5 × 0.3 × 0.3
2θ range for data collection/°	4.6–50	3.6–46.5
Reflections collected (total, independent, R_{int})	33 552, 12 705, 0.050	28 801, 5548, 0.036
Data, restraints, parameters	12 700, 13, 979	5545, 42, 570
Final $R1$, $wR2$[a,b]	0.067, 0.154	0.057, 0.159
Weighting factors[b]	0.0367, 22.0790	0.0723, 32.6367
Largest peak, hole/e Å^{-3}	+0.535, −0.638	+1.106, −0.753

[a] Structure was refined on F_o^2 using all data; the value of R_1 is given for comparison with older refinements based on F_o with a typical threshold of $F \geqslant 4\sigma(F)$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$ where $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [\max(F_o^2,0) + 2F_c^2]/3$.

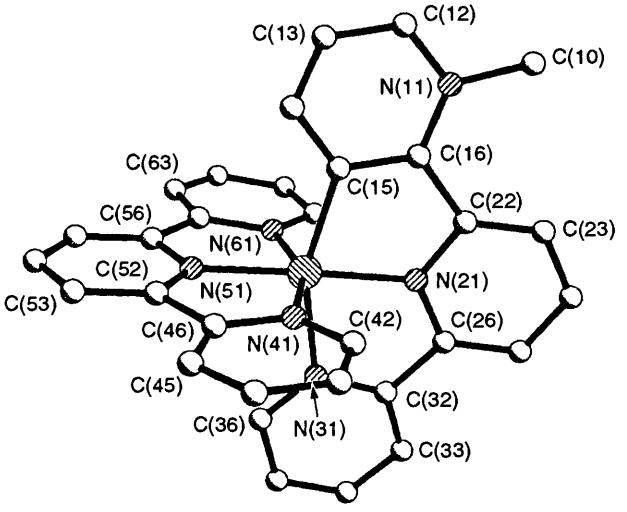

Fig. 1 Crystal structure of one of the two independent cations of complex **1a**

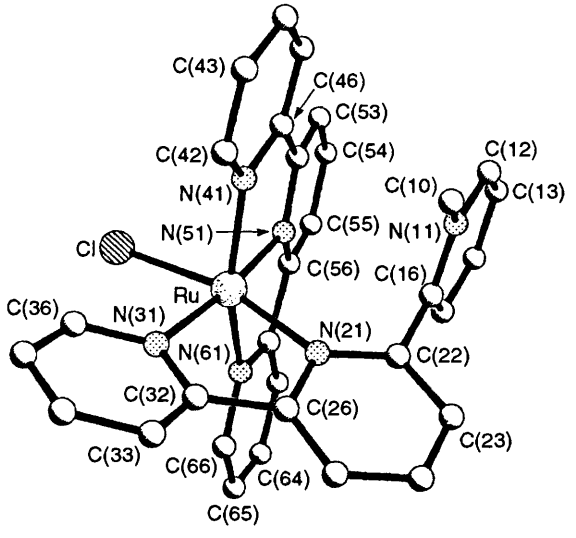

Fig. 2 Crystal structure of the cation of complex **2**

the Ru–N bonds to the central pyridyl rings are shorter than those to the terminal pyridyl rings (Table 3).[20,24] The ruthenium–donor atom distances for the cyclometallated (mterpy) ligand are similar to those involving the terpy ligand. Considering that there are significant differences in some of the bond lengths between the two independent cations, which must result from crystallographic packing effects, we feel that it is inappropriate to draw any conclusions as to the effect of cyclometallation on these bond lengths.

No crystallographically characterised complexes directly comparable to **1a** were found in the literature, though we have recently reported cyclometallated complexes of 6-(2-dimethylaminophenyl)-2,2′-bipyridine and 2-(2- dimethylaminophenyl)-1,10-phenanthroline.[7] In addition, Sauvage and co-workers have crystallographically characterised a dinuclear ruthenium complex [(mpterpy)Ru(tpbp)Ru(mpterpy)][PF_6]$_2$ [mpterpy = 4′-(4-methylphenyl)-2,2′:6′,2″-terpyridine] incorporating the bis(cyclometallating) *N*,*C*,*N*′-donor ligand 3,3′,5,5′-tetra(2-pyridyl)biphenyl (H_2tpbp).

The cation of complex **2** (Fig. 3) has the expected pseudo-octahedral structure of type **II** discussed above. The [Hmterpy]$^+$ ligand acts as a didentate *N*,*N*′-donor, with a torsion angle of 18.2° between the two co-ordinated pyridine rings. The pendant methylated pyridyl ring (ring 1) makes an angle of 94° with ring 2. This pendant ring also lies stacked approximately parallel with the central ring (ring 5) of the terpy ligand; the short graphitic-type contacts between these rings lie in the range 3.04–3.53 Å. Comparable π-stacking interactions are common in other ruthenium(II) polypyridyl complexes.[16,24] The terpy ligand adopts the conventional terdentate bonding mode with the three pyridine rings being essentially coplanar; the inter-ring torsion angles are in Table 4. As for **1a** above, the N atom of the central pyridine ring forms a shorter bond to the Ru atom than those of the two terminal pyridine rings. The sixth co-ordination site is occupied by a chloride. The only other structurally characterised complex containing a ruthenium(II) centre surrounded by a donor set comprising a terpy, a bipy unit and a co-ordinated Cl$^-$ is the asymmetric dinuclear complex [Ru_2(qpy)(terpy)$_2$Cl][PF_6]$_3$ (qpy = 2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine).[24] Complex **2** is stabilised as a result of the non-co-ordinated pyridine ring nitrogen atom being methylated. The complex [Ru(terpy)-(Hterpy-*N*,*N*′)Cl]$^+$, in which the nitrogen is unprotected, readily rearranges to give [Ru(terpy)$_2$]$^{2+}$.[18]

^{1}H NMR spectra

The ^{1}H NMR spectrum of complex **1** shows that in solution the cation posesses a plane of symmetry, with the result that the

Table 2 Selected bond lengths (Å) and angles (°) for complex **1a**

Ru(1)–N(51)	1.988(12)	Ru(2)–N(81)	1.930(12)
Ru(1)–N(21)	1.989(10)	Ru(2)–N(111)	1.992(10)
Ru(1)–C(15)	2.030(9)	Ru(2)–C(105)	2.069(9)
Ru(1)–N(41)	2.062(7)	Ru(2)–N(71)	2.080(8)
Ru(1)–N(61)	2.070(7)	Ru(2)–N(91)	2.081(6)
Ru(1)–N(31)	2.113(7)	Ru(2)–N(121)	2.095(8)
N(51)–Ru(1)–N(21)	177.5(3)	N(81)–Ru(2)–N(111)	178.3(3)
N(51)–Ru(1)–C(15)	101.5(3)	N(81)–Ru(2)–C(105)	101.8(3)
N(21)–Ru(1)–C(15)	79.8(3)	N(111)–Ru(2)–C(105)	79.5(3)
N(51)–Ru(1)–N(41)	79.0(3)	N(81)–Ru(2)–N(71)	79.4(4)
N(21)–Ru(1)–N(41)	98.8(3)	N(111)–Ru(2)–N(71)	99.5(4)
C(15)–Ru(1)–N(41)	90.6(3)	C(105)–Ru(2)–N(71)	92.6(3)
N(51)–Ru(1)–N(61)	79.4(3)	N(81)–Ru(2)–N(91)	79.5(3)
N(21)–Ru(1)–N(61)	102.8(3)	N(111)–Ru(2)–N(91)	101.6(3)
C(15)–Ru(1)–N(61)	93.2(3)	C(105)–Ru(2)–N(91)	91.1(3)
N(41)–Ru(1)–N(61)	158.4(3)	N(71)–Ru(2)–N(91)	158.9(3)
N(51)–Ru(1)–N(31)	100.7(3)	N(81)–Ru(2)–N(121)	100.0(3)
N(21)–Ru(1)–N(31)	78.0(3)	N(111)–Ru(2)–N(121)	78.7(3)
C(15)–Ru(1)–N(31)	157.8(4)	C(105)–Ru(2)–N(121)	158.2(4)
N(41)–Ru(1)–N(31)	94.2(3)	N(71)–Ru(2)–N(121)	90.3(3)
N(61)–Ru(1)–N(31)	90.4(3)	N(91)–Ru(2)–N(121)	94.0(3)

Table 3 Selected bond lengths (Å) and angles (°) for complex **2**

Ru–N(51)	1.969(5)	Ru–N(31)	2.069(5)
Ru–N(41)	2.073(5)	Ru–N(61)	2.087(4)
Ru–N(21)	2.108(4)	Ru–Cl	2.398(1)
N(51)–Ru–N(31)	173.2(2)	N(51)–Ru–N(41)	79.4(2)
N(31)–Ru–N(41)	96.0(2)	N(51)–Ru–N(61)	79.1(2)
N(31)–Ru–N(61)	105.6(2)	N(41)–Ru–N(61)	158.5(2)
N(51)–Ru–N(21)	108.0(2)	N(31)–Ru–N(21)	77.3(2)
N(41)–Ru–N(21)	96.2(2)	N(61)–Ru–N(21)	88.4(2)
N(51)–Ru–Cl	83.62(13)	N(31)–Ru–Cl	91.71(14)
N(41)–Ru–Cl	92.81(12)	N(61)–Ru–Cl	86.90(12)
N(21)–Ru–Cl	166.45(13)		

Table 4 Torsion angles (°) between adjacent rings in the complex cations

	Ring numbers	Torsion angle		Ring numbers	Torsion angle
1a	1,2	7	**2**	1,2	94
	2,3	9		2,3	19
	4,5	3		4,5	12
	5,6	3		5,6	6
	7,8	1			
	8,9	1			
	10,11	1			
	11,12	10			

two halves of the terpy ligand are equivalent and only 16 resonances are observed for the 21 aromatic protons (Fig. 3). The presence of only 21 and not 22 protons in the aromatic region confirms that the complex is indeed cyclometallated. Most aromatic resonances were assigned by comparison with the spectra of the similar *N*-protonated cyclometallated complex [Ru(terpy)(Hterpy*-*N*,*N*′,*C*)][PF_6]$_2$.[6] The resonances of the cyclometallated ring C were assigned by studying the coupling interactions; for a pyridine ring with positions numbered in this way, expected *ortho*-coupling interactions are $^3J(H^{4C}H^{5C})$ 5.5–6.0 and $^3J(H^{5C}H^{6C})$ ≈ 7.5–8.0 Hz. A singlet resonance integrating to 3 H at δ 4.61 is ascribed to the methyl group of the quaternised pyridine ring.

The ^{1}H NMR spectrum of complex **2** was assigned with the aid of a 400 MHz ^{1}H–^{1}H correlation (COSY) spectrum. The symmetry of the cation in solution is lower than for **1**, and all six pyridine rings are non-equivalent. In addition, the π stacking of the pendant, methylated pyridine ring C with the co-ordinated terpy ligand (Fig. 2) prevents it from rotating freely in solution.

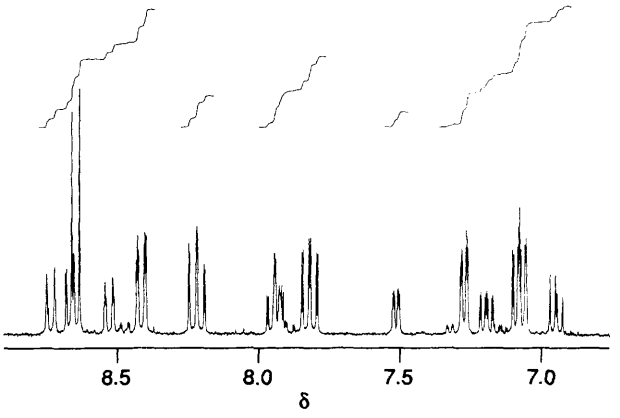

Fig. 3 Aromatic region of the 300 MHz ^{1}H NMR spectrum of complex **1** (CD_3CN solution)

This means that the plane containing Cl, N(31) and N(21) is not a plane of symmetry, as it would be if the pendant ring were rotating rapidly on the NMR time-scale, and consequently all of the protons of the terpy ligand are inequivalent. This behaviour contrasts with that of [Ru(terpy)(Hpbipy)Cl][PF_6] and [Ru(terpy)(Hterpy*-*N*,*N*′)Cl][PF_6] in which the non-co-ordinated aromatic rings are symmetrical. The aromatic resonances integrate to 22 protons, consistent with the non-metallated structure. One notable feature of the spectrum is the high chemical shift of H^{6A} (δ 10.17) as a result of the close proximity of this proton to the deshielding co-ordinated chloride. This is a normal feature of complexes of this type containing N_5Cl donor sets.[5,6,18] Also of interest is the observation that the singlet resonance of the methyl group protons of the non-co-ordinated pyridine ring occurs at δ 2.87 (compared to δ 4.61 for **1** above) as these protons are shielded by the ring current of the adjacent pyridine ring with which it stacks.

Electrochemical properties

Both complexes were studied by cyclic and square-wave voltammetry in acetonitrile solution. Cyclometallated complex **1** exhibits a reversible Ru^{II}–Ru^{III} couple at +0.49 V *vs.* internal ferrocene–ferrocenium. This is comparable to the couple at 0.52 V observed for the protonated cyclometallated complex [Ru(terpy)(Hterpy*-*N*,*N*′,*C*)][PF_6]$_2$.[6] The low redox potential compared to those of ruthenium complexes with six pyridyl donors is due to the presence of the electron-rich (anionic) carbon ligand in the donor set, but it should be noted that the electron-withdrawing effect of the quaternised cyclometallated pyridine ring shifts this process anodically by *ca.* 400 mV compared to those of other ruthenium(II) complexes with N_5C donor sets such as [Ru(terpy)(pbipy)][PF_6] (0.12 V).[5] Two one-electron ligand-based reversible reductions are observed at −1.48 and −1.98 V. A third process lying near the edge of the solvent window was found by square-wave voltammetry to occur at −2.27 V. The process at −1.48 V occurs at a considerably less negative potential than the first process observed for [Ru(terpy)(pbipy)][PF_6] (−2.04 V),[5] and is therefore ascribed to the reduction of the quaternised cyclometallated mterpy ligand.

The cyclic voltammogram of non-metallated complex **2** shows a reversible ruthenium(II)–ruthenium(III) process at 0.61 V. This compares with values of 0.43 V for non-quaternised [Ru(terpy)(Hterpy*-*N*,*N*′)Cl][PF_6][6] and 0.45 V for [Ru(terpy)(Hpbipy-*N*,*N*′)Cl][PF_6].[5] The change in the Ru^{II}–Ru^{III} potential on quaternisation is less marked than for the cyclometallated complexes, since the quaternised pyridine ring is now remote from, rather than co-ordinated to, the ruthenium centre. The reduction processes of **2** are complex and non-reversible, an observation which is in accord with data for other non-metallated complexes.[5]

Table 5 Electronic spectral data for complexes **1** and **2** in MeCN

Complex	λ_{max}/nm ($10^{-3}\varepsilon$/dm^3 mol^{-1} cm^{-1})						
1	505 (12.9)	440 (5.8)*	357 (8.5)*	313 (53)		272 (41)	233 (40)
2	505 (9.9)			315 (31)	301 (36)	277 (27)	242 (32)

* Shoulder.

Electronic spectra

Electronic spectroscopic data for the two complexes in acetonitrile solution are presented in Table 5. In each case the most notable feature is the broad, intense, low-energy metal-to-ligand charge transfer (m.l.c.t.) transition [5–7,25] which is largely responsible for the colouration of the complex. Complex **1** exhibits its lowest-energy m.l.c.t. transition at 505 nm (ε 12 900 dm^3 mol^{-1} cm^{-1}). This transition is broad and asymmetric, and incorporates a shoulder on its high-energy side. This transition is slightly blue-shifted compared to that for [Ru(terpy)(pbipy)][PF_6] (λ_{max} 512 nm, ε 13 800 dm^3 mol^{-1} cm^{-1}),[5] as is that for the more comparable complex [Ru(terpy)(Hterpy*-*N*,*N*′,*C*]][PF_6]$_2$ (λ_{max} 500 nm, ε 10 800 dm^3 mol^{-1} cm^{-1}).[6] A shoulder at 357 nm is ascribed to a second, higher-energy m.l.c.t. process associated with the π^* level of the cyclometallating ligand, rather than the terpy ligand. Similar transitions have been reported for [Ru(terpy)(Hterpy*-*N*,*N*′,*C*)][PF_6]$_2$ (λ_{max} 354, ε 6 000)[6] and [Ru(terpy)(pbipy)][PF_6] (λ_{max} 380 nm, ε 10 600 dm^3 mol^{-1} cm^{-1}).[5]

The low-energy m.l.c.t. transition of complex **2** has λ_{max} 505 nm. This compares with 502 nm for [Ru(terpy)(Hpbipy)Cl][PF_6][5] and 503 nm for [Ru(terpy)(Hterpy*-*N*,*N*′)Cl][PF_6].[6] As is expected given that the non-co-ordinated aromatic ring is approximately perpendicular to the co-ordinated 2,2′-bipyridine moiety of the potentially trinucleating ligand, the exact nature of the non-co-ordinated aromatic ring is observed to have little effect on the energy of the m.l.c.t. transition of the complex. Indeed, the m.l.c.t. transition of [Ru(terpy)(bipy)Cl][PF_6] which has no pendant aromatic ring occurs at λ_{max} 502 nm.[5] In addition, each complex exhibits an assortment of intense ligand-centred (l.c.) transitions at higher energy.

Conclusion

Terpyridine, which usually acts as a terdentate ligand, can be forced to adopt unusual *N*,*N*′-didentate and *N*,*N*′,*C*-terdentate cyclometallating bonding modes if one of the terminal pyridine ring N atoms is protected by quaternisation.

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