Derivatives of Tris(2,2′-bipyridine)ruthenium(II) with Pendant Pyridyl or Phenol Ligands

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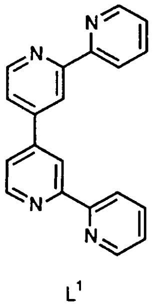
Reaction of 2,2′:4′,4″-terpyridine or 4-(4-pyridyl)-2,2′:4′,4″-terpyridine with [Ru(bipy)$_2$Cl$_2$] (bipy = 2,2′-bipyridine), and of 4-(*p*-methoxyphenyl)-2,2′-bipyridine with [Ru(bipy)$_2$Cl$_2$] followed by demethylation of the anisole with BBr$_3$, yields derivatives of Ru(bipy)$_3$$^{2+}$ which contain externally directed pendant pyridyl or phenol groups capable of ligation to other metals. These complexes are proposed as 'building blocks' for photoactive polynuclear complexes containing the Ru(bipy)$_3$$^{2+}$ chromophore. Methylation of the pendant pyridyl rings with methyl iodide generates electron-accepting groups covalently attached to the Ru(bipy)$_3$$^{2+}$ core.

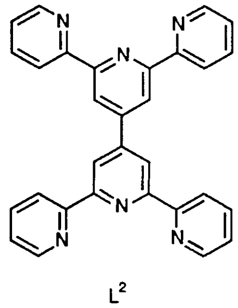
Now that the photochemical and photophysical properties of [Ru(bipy)$_3$]$^{2+}$ (bipy = 2,2′-bipyridine) and related species have been thoroughly examined,[1] attention has turned to incorporating this unit into polynuclear complexes with a view to constructing photochemical devices which can harness its excited-state energy. The [Ru(bipy)$_3$]$^{2+}$ fragment may act as a light-harvesting antenna, whose excited-state energy is captured by an adjacent reaction centre (either by energy transfer or electron transfer) across a bridging ligand or in a through-space process.[2,3] Crucial to this is the nature of the bridging ligand, which must confer the desirable photochemical properties on the ruthenium centre, contain one or more externally directed functional groups to allow attachment of the reaction centre, and permit electronic communication between the ruthenium 'antenna' and the reaction centre.

Numerous polynuclear complexes incorporating polypyridylruthenium chromophores have been synthesised and studied. Recent examples include homobinuclear complexes of the 'back-to-back' bis(bipyridine) (L^1)[4] and bis(terpyridine) (L^2),[5] 2,3-bis(2 pyridyl)pyrazine and its derivatives,[6] 3,4,3′,4′-tetraamino-1,1′-biphenyl[7] and 2,3,5,6-tetra(2-pyridyl)pyrazine.[8] Higher-nuclearity homonuclear complexes have also been reported: a trinuclear ruthenium(II) complex with 4,4′-bipyridine bridges,[9] tri- and tetra-nuclear complexes with 2,3- and 2,5-bis(2-pyridyl)pyrazine bridges[10] and a heptanuclear ruthenium(II) complex with 2,3-bis(2-pyridyl)pyrazine bridges.[11]

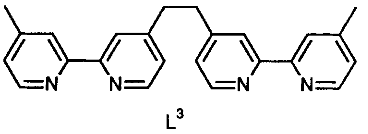
However, the construction of photochemical devices in which the reaction centre is a metal complex will require the *stepwise* syntheses of *heteronuclear* species using a 'complexes as ligands' approach.[10,11] Examples of these are much rarer, since they require isolation of a mononuclear intermediate in which the second binding site of the bridging ligand is not co-ordinated. For example [(terpy)(bipy)Os^{III}(4,4′-bipy)Ru^{II}(bipy)$_2$(H$_2$O)]$^{5+}$ (terpy = 2,2′:6′,2″-terpyridine) was prepared from reaction of [Os(bipy)(4,4′-bipy)(terpy)]$^{3+}$, which has a pendant 4-pyridyl group, with [Ru(bipy)$_2$(H$_2$O)$_2$]$^{2+}$.[12] There have been only five other examples of heterobinuclear complexes containing ruthenium with a 4,4′-bipyridine bridge reported in the last 20 years.[13] A recent report describes the synthesis of a ligand consisting of a bipyridyl group appended to a tetraaza macrocycle; stepwise attachment of Ru^{II} to the bipyridyl fragment and Ni^{II} to the macrocycle results in a heterobinuclear complex which shows efficient internal quenching of the [Ru(bipy)$_3$]$^{2+}$ chromophore by the Ni^{II}.[14] Stepwise attachment of Ru(bipy)$_2$ and Re(CO)$_3$(pyridyl) fragments to the binding sites of L^3 affords a heterobinuclear complex with two chromophores which shows multiple emission.[15]



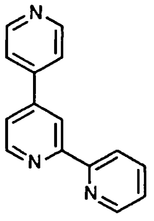
L^1



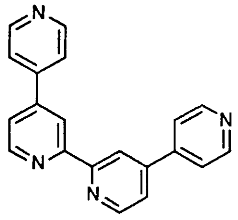
L^2



L^3



L^4



L^5

In this paper we report the syntheses of the potentially bridging ligands 2,2′:4′,4″-terpyridine (L^4), 4-(4-pyridyl)-2,2′:4′,4″-terpyridine (L^5) and 4-(*p*-hydroxyphenyl)-2,2′-bipyridine (L^6) and the syntheses and properties of the complexes [Ru(bipy)$_2$L][PF$_6$]$_2$ (L = L^4 **1**, L^5 **2** or L^6 **4**). These complexes contain the Ru(bipy)$_3$$^{2+}$ core with an externally directed pendant ligating group (pyridyl or phenol), and will thus be suitable 'building blocks' for the stepwise synthesis of photoactive heteropolynuclear complexes. In addition we report the synthesis and properties of the *N*-methylated derivatives of **1** and **2**, [Ru(bipy)$_2$L$^{4'}$][PF$_6$]$_3$ (**1′**) and [Ru(bipy)$_2$L$^{5'}$][PF$_6$]$_4$ (**2′**), which contain electron-accepting *N*-methylpyridinium substituents attached to the Ru(bipy)$_3$$^{2+}$ core.

Table 1 Elemental analyses, FAB mass and UV/VIS spectral data for the new complexes

	Analysis (%)[a]			FAB mass spectral peaks		UV/VIS spectral peaks[c]
Complex	C	H	N	m/z[b] and assignment		λ_{max}/nm ($10^{-3}\varepsilon$/dm^3 mol^{-1} cm^{-1})
1·Me_2CO[d]	45.9 (45.5)	3.3 (3.4)	9.9 (9.7)	792 647	$[Ru(bipy)_2L^4(PF_6)]^+$ $[Ru(bipy)_2L^4]^+$	454 (13), 425 (sh), 288 (65), 246 (37)
2	47.4 (47.2)	3.0 (2.8)	11.1 (11.0)	869 724	$[Ru(bipy)_2L^5(PF_6)]^+$ $[Ru(bipy)_2L^5]^+$	462 (15), 432 (sh), 358 (12), 288 (68), 246 (55)
3	45.7 (46.0)	3.2 (3.1)	8.5 (8.7)	821 676	$[Ru(bipy)_2L^7(PF_6)]^+$ $[Ru(bipy)_2L^7]^+$	456 (10), 424 (sh), 324 (15), 288 (46), 244 (17)
4	45.1 (45.4)	2.9 (2.9)	8.5 (8.8)	661	$[Ru(bipy)_2(L^6 - H)]^+$	456 (13), 424 (sh), 325 (18), 288 (58), 244 (22)
1′·$2H_2O$[e]	38.1 (38.2)	2.8 (3.0)	8.4 (8.7)	952 807 662	$[Ru(bipy)_2L^{4'}(PF_6)_2]^+$ $[Ru(bipy)_2L^{4'}(PF_6)]^+$ $[Ru(bipy)_2L^{4'}]^+$	478 (11), 434 (10), 286 (52), 246 (33)
2′·$2H_2O$[e]	37.1 (36.8)	3.1 (2.9)	8.2 (8.2)	1189 1044 899	$[Ru(bipy)_2L^{5'}(PF_6)_3]^+$ $[Ru(bipy)_2L^{5'}(PF_6)_2]^+$ $[Ru(bipy)_2L^{5'}(PF_6)]^+$	500 (14), 428 (17), 326 (20), 284 (59), 254 (51)

[a] Calculated values are in parentheses. [b] All m/z values based on ^{102}Ru, the most abundant isotope. All peaks have the appropriate isotopic pattern. [c] sh = Shoulder. [d] Recrystallised from acetone–diethyl ether. [e] Chromatographed in acetonitrile–water–KPF_6.

Experimental

The NMR spectra were recorded on JEOL GX270 or GX400 spectrometers, electron-impact (EI) mass spectra on a Kratos MS9 instrument, fast-atom bombardment (FAB) mass spectra on a VG-ZAB instrument using 3-nitrobenzyl alcohol as matrix and UV/VIS spectra on a Perkin-Elmer Lambda 2 spectrophotometer. Electrochemical experiments were performed using an EG&G PAR model 273A potentiostat. A standard three-electrode configuration was used, with platinum-bead working and auxiliary electrodes and a saturated calomel electrode (SCE) reference. Ferrocene was added at the end of each experiment as an internal standard; all potentials are quoted *vs.* the ferrocene-ferrocenium couple. The solvent was acetonitrile, purified by distillation twice from CaH_2. The base electrolyte was 0.1 mol dm^{-3} $[NBu_4][PF_6]$.

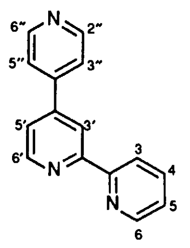
All solvents were dried by standard methods before use. 2,2′-Bipyridine, 4,4′-bipyridine, 2-bromopyridine, 4-methoxybenzaldehyde and 2-acetylpyridine were obtained from Aldrich and used as received.

Preparations.—*2,2′:4′,4″-Terpyridine* (L^4). To a solution of butyllithium (20 cm^3 of a 1.6 mol dm^{-3} solution, 32 mmol) in dry tetrahydrofuran (thf, 50 cm^3) at −78 °C under N_2 was added dropwise a solution of 2-bromopyridine (5.06 g, 32 mmol) in thf (20 cm^3) through a pressure-equalising funnel. The orange-brown colour of 2-pyridyllithium developed rapidly. The solution was stirred for 10 min, and then a solution of 4,4′-bipyridine (4.99 g, 32 mmol) in thf (50 cm^3) was added dropwise over 20 min whilst keeping the temperature below −70 °C. The deep brown solution was stirred for 1 h at −70 °C and allowed to warm slowly to room temperature, during which time a very intense purple colour developed. After 3 h of stirring at room temperature, water (50 cm^3) was added with vigorous stirring. Most of the thf was removed on a rotary evaporator, and the residue extracted with diethyl ether. The yellow ether extract was evaporated to dryness and redissolved in acetone (20 cm^3). A saturated solution of $KMnO_4$ in acetone was added dropwise until the purple colour persisted. The MnO_2 was removed by filtration through Celite, and the acetone removed on a rotary evaporator to give a brown oil. Column chromatography on alumina with $CHCl_3$–hexane (2:1) yielded 2,2′:4′,4″-terpyridine as a pale yellow oil (2.94 g, 30%) which crystallised on standing for several weeks. EI mass spectrum: m/z = 233 (M^+). The ^1H NMR spectrum was identical to that previously reported[16] (Found: C, 76.9; H, 5.1; N, 17.9. Calc. for $C_{15}H_{11}N_3$: C, 77.3; H, 4.7; N, 18.0%).

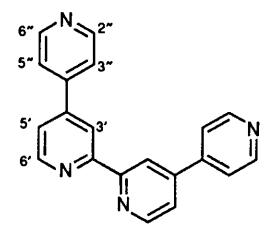
4-(4-pyridyl)-2,2′:4′,4″-Terpyridine (L^5). To a suspension of 4,4′-bipyridine (3.12 g, 20 mmol) in ether (100 cm^3) at −78 °C under N_2 was added in one portion a solution of lithium diisopropylamide (20 mmol) and hexamethylphosphoramide (7.17 g, 40 mmol) in ether (20 cm^3). A pale pink colour appeared. The solution was allowed to warm to room temperature, by which time a very intense purple colour had appeared, and stirred overnight (16 h). Water (50 cm^3) was added with vigorous stirring, and the grey precipitate of crude 4-(4-pyridyl)-2,2′:4′,4″-terpyridine was collected by filtration. The ether layer was separated from the residual solution and worked up with $KMnO_4$ as described above to yield a second batch of the crude product. After purification *via* isolation of the iron(II) complex and demetallation with alkaline H_2O_2,[17] followed by recrystallisation from aqueous ethanol, the yield was 0.8 g (26%). EI mass spectrum: m/z = 310 (M^+). The ^1H NMR spectrum was identical to that previously reported[18] (Found: C, 77.1; H, 4.7; N, 18.0. Calc. for $C_{20}H_{14}N_4$: C, 77.4; H, 4.5; N, 18.1%).

4-(p-Methoxyphenyl)-2,2′-bipyridine (L^7). To a mixture of *N*-[pyridincarbonylmethyl)pyridinium iodide[19] ('pyridacyl pyridinium iodide'; 5.22 g, 16 mmol) and ammonium acetate (12 g, a large excess) in glacial acetic acid (50 cm^3) at 100 °C was added 4-methoxycinnamaldehyde[20] (2.60 g, 16 mmol) in three equal portions at 1.5 h intervals. After leaving the reaction overnight most of the acetic acid was removed on a rotary evaporator. Water (50 cm^3) was added and the dark solution was adjusted to pH 8 with Na_2CO_3; it was then extracted with several portions of CH_2Cl_2. The combined organic extracts were dried ($MgSO_4$), evaporated to dryness, and treated with activated charcoal in refluxing ethanol. The suspension was filtered hot through Celite, evaporated to dryness, and purified by column chromatography on alumina with $CHCl_3$ to give 4-(*p*-methoxyphenyl)-2,2′-bipyridine as a pale yellow solid (1.59 g, 40%). EI mass spectrum: m/z = 262 (M^+) and 247 (M^+ − CH_3). ^1H NMR (270 MHz, $CDCl_3$): δ 7.00 (2 H, d, J = 8.8, phenyl $H^{3,5}$), 7.31 (1 H, m, $H^{5'}$), 7.48 (1 H, dd, J = 5.1, 1.8, H^5), 7.72 (2 H, d, J = 8.8, phenyl $H^{2,6}$), 7.82 (1 H, td, J = 7.7, 1.8, $H^{4'}$), 8.44 (1 H, d, J = 8.1, $H^{3'}$), 8.64 (1 H, d, J = 1.8, H^3), 8.67 (1 H, d, J = 5.1 Hz, H^6) and 8.70 (1 H, m, $H^{6'}$) (Found: C, 77.4; H,

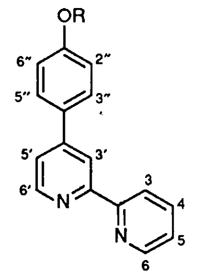
Table 2 400 MHz NMR spectral data for the new complexes in CD_3CN, J values in Hz*



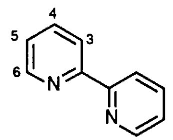
L^4



L^5

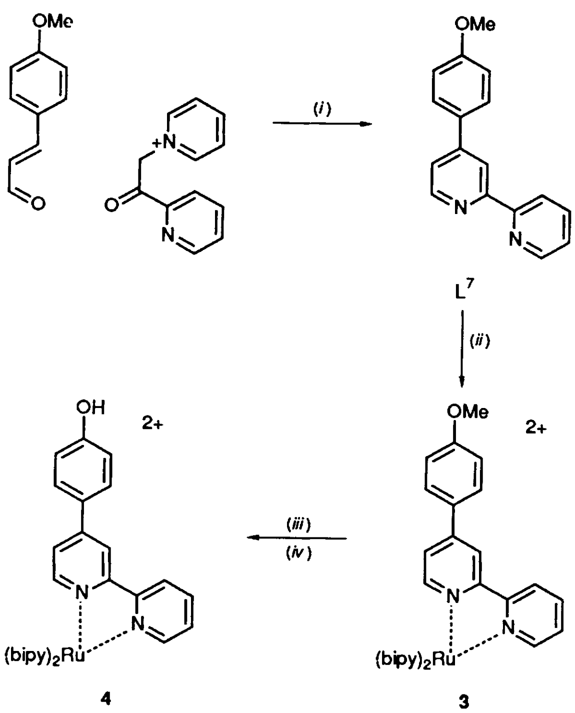


R = Me (L^6)
R = H (L^7)



	Bipy protons				Ligand L protons									
Complex	H^3	H^4	H^5	H^6	$H^{3'}$	$H^{5'}$	$H^{6'}$	$H^{3'',5''}$	$H^{2'',6''}$	H^3	H^4	H^5	H^6	Me
1	7.73–7.80 (part of 5 H, m)	8.05–8.14 (part of 5 H, m)	7.39–7.46 (part of 5 H, m)	8.50–8.55 (4 H, m)	8.78 (1 H, d, J 2.0)	7.68 (1 H, dd, 6.0, J 2.0)	7.84 (1 H, dd, J 6.1)	8.81 (2 H, d, J 5.6)	7.81 (2 H, d, J 5.6)	7.73–7.80 (part of 5 H, m)	8.05–8.14 (part of 5 H, m)	7.39–7.46 (part of 5 H, m)	8.70 (1 H, d, J 8.0)	—
1′	7.72–7.77 (part of 5 H, m)	8.06–8.16 (part of 5 H, m)	7.45–7.50 (part of 5 H, m)	8.54 (4 H, d, J 8.5)	8.88 (1 H, br s)	7.72–7.77 (part of 5 H, m)	7.99 (1 H, d, J 6.1)	8.80 (2 H, d, J 6.1)	8.41 (2 H, d, J 6.1)	7.80 (1 H, d, J 5.8)	8.06–8.16 (part of 5 H, m)	7.45–7.50 (part of 5 H, m)	8.73 (1 H, d, J 8.4)	4.41 (3 H, s)
2	7.77 and 7.83 (2 × 2 H, d, J 5.5)	8.10 and 8.11 (2 × 2 H, td, J 7.8, 1.7)	7.40–7.47 (4 H, m)	8.54 (4 H, d, J 8.5)	8.97 (2 H, d, J 1.7)	7.73 (2 H, dd, 5.9, J 1.7)	7.88 (2 H, d, J 5.9)	8.83 (4 H, d, J 5.5)	7.84 (4 H, d, J 5.5)	—	—	—	—	—
2′	7.75 and 7.79 (2 × 2 H, d, J 5.6)	8.11 and 8.12 (2 × 2 H, td, J 7.8, 1.7)	7.42–7.48 (4 H, m)	8.55 (4 H, d, J 8.4)	9.10 (2 H, d, J 1.7)	7.82 (2 H, dd, 6.0, J 1.7)	8.04 (2 H, d, J 6.0)	8.82 (4 H, d, J 6.3)	8.45 (4 H, d, J 6.3)	—	—	—	—	4.42 (6 H, s)
3	7.77–7.82 (4 H, m)	8.06–8.14 (part of 5 H, m)	7.42–7.47 (part of 5 H, m)	8.52–8.57 (4 H, m)	8.73 (1 H, d, J 1.7)	7.64 (1 H, dd, 6.1, J 1.7)	7.69 (1 H, d, J 6.1)	7.16 (2 H, d, J 9.0)	7.90 (2 H, d, J 9.0)	7.84 (1 H, d, J 5.2)	8.06–8.14 (part of 5 H, m)	7.42–7.47 (part of 5 H, m)	8.71 (1 H, d, J 8.3)	3.91 (3 H, s)
4	7.73–7.88 (part of 7 H, m)	8.04–8.14 (part of 5 H, m)	7.39–7.48 (part of 5 H, m)	8.50–8.56 (4 H, m)	8.67–8.71 (part of 2 H, m)	7.60 (1 H, dd, 6.1, J 2.2)	7.66 (1 H, d, J 6.1)	7.01 (2 H, d, J 8.8)	7.73–7.88 (part of 7 H, m)	7.73–7.88 (part of 7 H, m)	8.04–8.14 (part of 5 H, m)	7.39–7.48 (part of 5 H, m)	8.67–8.71 (part of 2 H, m)	—

* The numbering scheme for ligands L^5 and L^6 is not IUPAC standard but allows for direct comparison of protons in all the complexes.



Scheme 1 (*i*) $NH_4(O_2CMe)$, $MeCO_2H$, reflux; (*ii*) $[Ru(bipy)_2Cl_2]$, $HOCH_2CH_2OH$, reflux; (*iii*) BBr_3, CH_2Cl_2, room temperature; (*iv*) water

5.2; N, 10.5. Calc. for $C_{17}H_{14}N_2O$: C, 77.8; H, 5.4; N, 10.7%), m.p. 131–132.5 °C.

Complexes **1**–**3**. Equimolar amounts of $[Ru(bipy)_2Cl_2]\cdot 2H_2O$[21] and the appropriate ligand (L^4, L^5 or L^7 respectively) were heated to reflux in ethylene glycol for 1 h. Addition of aqueous KPF_6 to the cooled orange solutions precipitated the complexes, which were collected by filtration, washed with water, dried and purified by preparative-scale thin-layer chromatography on either 1.5 mm thick alumina plates (Merck, article 5726) eluting with acetonitrile–toluene or 2 mm thick silica plates (Merck, article 5717) eluting with acetonitrile–aqueous KPF_6. Yields were typically 80%.

Complex **4**. To a solution of $[Ru(bipy)_2L^7][PF_6]_2$ (0.2 g, 0.21 mmol) in dry CH_2Cl_2 (50 cm^3) under N_2 was added BBr_3 (0.21 g, four-fold excess). After stirring for 3 h, water (50 cm^3) was added and the two phases separated. Addition of KPF_6 to the aqueous phase precipitated the complex, which was collected by filtration, dissolved in acetonitrile and filtered to remove a small amount of an insoluble orange by-product. After chromatographic purification as described above the yield of complex **4** was 80%.

N-*Methylation of Complexes* **1** *and* **2**.—A mixture of the appropriate complex and a ten-fold molar excess of methyl iodide in acetonitrile was stirred at 50 °C for 8 h. The solvent was removed on a rotary evaporator. The brown-orange residue was redissolved in aqueous methanol (1 : 1) and KPF_6 added to precipitate the product, which was collected by filtration and dried. Yield: 80–90%.

Analytical and FAB mass spectroscopic data for the complexes are presented in Table 1; the NMR data are summarised in Table 2.

Results and Discussion

2,2′:4′,4″-Terpyridine (L^4) was prepared in 30% yield by addition of 2-pyridyllithium to 4,4′-bipyridine, followed by oxidation of the intermediate dihydroterpyridine with $KMnO_4$ in acetone. This method is considerably simpler and more efficient than the only other literature preparation of this compound,[16] which involves preparation of 6-carboxy-2,2′:4′,4″-terpyridine (from pyridine-4-carbaldehyde, 2-acetylpyridine and pyruvic acid followed by treatment with ammonium acetate) and then thermal decarboxylation in an overall yield of 14%. The addition of alkyllithium and aryllithium reagents at the 6 position of 2,2′-bipyridine[22] and 2,2′:6′,2″-terpyridine[23] is well known, but this is the first example of functionalisation of 4,4′-bipyridine by this method.

A synthesis of 4-(4-pyridyl)-2,2′:4′,4″-terpyridine (L^5) has also been accomplished recently by coupling of 4,4′-bipyridine with Pd on charcoal.[18] The alternative method presented here uses $LiNPr^i_2$ as the coupling reagent. The latter is known to react with pyridine to give a radical anion, which undergoes coupling to give 4,4′-bipyridine, 2,4′-bipyridine or 2,2′-bipyridine in varying amounts depending on the reaction conditions.[24] With 3,3′-bipyridine it gives 3,3′:4′,4″:3″,3‴-quaterpyridine *via* coupling at the 4-position,[25] whereas upon reaction with 2,2′-bipyridine it gives predominantly 2,2′:6′,4″:2″,2‴-quaterpyridine *via* a 2,4 coupling.[26] We reasoned that the radical anion of 4,4′-bipyridine could only undergo coupling at the 2 position and this proved to be the case.

4-(*p*-Methoxyphenyl)-2,2′-bipyridine (L^7) has been synthesised for the first time, according to the method outlined in Scheme 1. This is a standard Kröhnke-type synthesis,[27] in which the central pyridyl ring is generated by condensation of a 1,5-dicarbonyl intermediate (from the Michael reaction of 'pyridacyl pyridinium iodide' with *p*-methoxycinnamaldehyde). Demethylation of this to give L^6 was performed on the ruthenium complex rather than on the free ligand (see below).

The complexes **1** and **2** were prepared by reaction of equimolar amounts of $[Ru(bipy)_2Cl_2]\cdot 2H_2O$ and L^4 or L^5 respectively in ethylene glycol at reflux. Whilst reaction of $[Ru(bipy)_2Cl_2]$ with other derivatives of 2,2′-bipyridine proceeds smoothly under much milder conditions, it was found that lower temperatures (aqueous ethanol as solvent)[21] resulted in very low yields of **1** and **2** and in each case a significant amount of a less polar, dark brown material. The latter has not been fully characterised, but is believed to be the kinetic product arising from initial attack of a 4-pyridyl group (rather than a chelating 2,2′-bipyridyl group) on the ruthenium, giving RuN_5Cl^+ species. Consistent with this is the observation that both L^4 and L^5 are selectively alkylated at the less-hindered 4-pyridyl positions with methyl iodide.[16,18] With ethylene glycol as solvent there is no trace of these materials in the reaction mixtures, and **1** and **2** are produced in high yields. This problem was obviously not encountered with L^7, but use of ethylene glycol rather than aqueous ethanol as solvent still gave somewhat cleaner reaction mixtures. Demethylation of complex **3** to give **4** was accomplished with BBr_3 in CH_2Cl_2 at room temperature.[28] It is a quick, easy and high-yield procedure, and takes advantage of the very high stability of the $Ru(bipy)_3{}^{2+}$ core, which is unaffected by the HBr liberated in the work-up. Whilst demethylation of the free ligand (*e.g.* with pyridinium chloride[29]) followed by complexation would be equally feasible, the chosen route is easier and avoids the problem of competing attack of the phenol group during complex formation. Conversion of **1** into **1′** and of **2** into **2′** was readily achieved by methylation of their pendant pyridyl groups with methyl iodide in warm acetonitrile.

All of the complexes were characterised by elemental analyses (Table 1), FAB mass spectra (Table 1) and 400 MHz ^1H NMR spectra (Table 2). The NMR spectra are complicated due to the low symmetry of the complexes; full assignments were made on the basis of correlation spectroscopy (COSY) in all cases. Because of the low symmetry the pyridyl rings of the two bipy ligands are not all equivalent; in **1**, **1′**, **3** and **4** all four rings are inequivalent, and in **2** and **2′** the bipy pyridyl rings split into two pairs. As a result their protons generally give rise to complex multiplets of overlapping signals. However in **2** and **2′** the two types of bipy H^3 proton are different enough to give well separated signals. Similarly, the two td signals for the two bipy

Table 3 Electrochemical data for the new complexes[a]

Complex	$E_{\frac{1}{2}}$/V (ΔE_p/mV)				
	2^+–3^+	Methylpyridinium	Ligand reductions		
1	+0.92 (90)	—	−1.64 (70)	−1.88 (90)	−2.12 (90)
1′	+0.94 (90)	−1.11 (60)	−1.60 (90)	−1.91 (60)	−2.16 (90)
2	+0.91 (70)	—	−1.57 (60)	−1.88 (70)	−2.09 (70)
2′	+0.95 (60)	−1.10 to −1.23	−1.66 (70)	−1.88 (80)	−2.10 (80)
$[Ru(bipy)_2(4,4'\text{-mbipy})_2]^{4+}$[b]	+0.94 (70)	−1.16 (75)	−1.68 (75)		
3	+0.85 (80)	—	−1.73 (80)	−1.92 (90)	
4	+0.89 (90)[c]	—	−1.77 (80)		
$[Ru(bipy)_3]^{2+}$[d]	+0.89 (70)	—	−1.72 (60)	−1.92 (80)	−2.16 (80)

[a] All cyclic voltammograms recorded at 100 mV s^{-1}. Potentials quoted *vs.* ferrocene–ferrocenium. [b] Ref. 30. [c] Not fully reversible, see text. [d] Recorded under identical conditions for comparison.

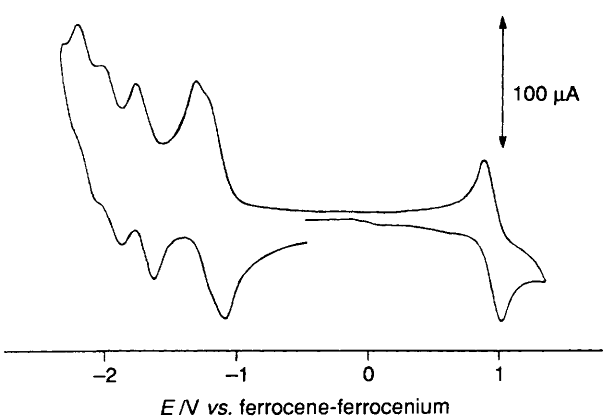


Fig. 1 Cyclic voltammogram of complex **2′** at 0.5 V s^{-1} in MeCN

H^4 environments in **2** and **2′** overlap closely enough to give the appearance of a single tdd. *N*-Methylation of complexes **1** and **2** results most noticeably in a downfield shift of the adjacent $H^{2''}$ and $H^{6''}$ protons by 0.6 ppm in each case, and of the $H^{6'}$ proton on the adjacent pyridyl ring by 0.16 ppm in each case.

The cyclic voltammetric results are summarised in Table 3, with the results for $[Ru(bipy)_3]^{2+}$ measured under identical conditions included for comparison. All of the waves are reversible or near-reversible ($i_{p,a} = i_{p,c}$, ΔE_p = 60–90 mV at a scan rate of 100 mV s^{-1}; under the same conditions the ferrocene–ferrocenium wave gave ΔE_p values of 60–80 mV between experiments) except where stated otherwise. Complexes **1**–**4** show the typical behaviour of these types of complex,[1] with a Ru^{II}–Ru^{III} oxidation and up to three ligand-based reductions. For **4** the oxidation is not fully reversible, with the return wave being rather smaller than the outward wave at low scan rates. At a scan rate of 20 mV s^{-1} the return wave is only just apparent, whereas at 500 mV s^{-1} the wave is nearly symmetric. The ΔE_p value only varies from 80 to 110 mV between these extremes.

The most interesting electrochemical results are those for complexes **1′** and **2′**, in which one or two electron-accepting viologen groups are attached directly to the $Ru(bipy)_3{}^{2+}$ core. The positive charges result in a slight electrostatic destabilisation of the ruthenium(III) oxidation state (by 20 mV for **1′** and 40 mV for **2′**) compared to **1** and **2**. For **1′** the additional reduction at − 1.11 V is due to a one-electron transfer to the *N*-methylpyridinium group; for **2′** there is a two-electron reduction between −1.10 and −1.23 V which appears to consist of two closely spaced one-electron reductions of the two weakly interacting pyridinium groups (Fig. 1). Introduction of the *N*-methylpyridinium groups has therefore created chemically attached sites which are 0.6 V better as oxidants than is bipy in $[Ru(bipy)_3]^{2+}$. Since the photochemically excited state of $[Ru(bipy)_3]^{2+}$ is known to be quenched by pyridinium ions such as paraquat (1,1′-dimethyl-4,4′-bipyridinium),[1,31] the direct attachment of these sites to the $Ru(bipy)_3{}^{2+}$ core should result in an excited state in which the excited electron is localised on the *N*-methylpyridinium rather than the bipy acceptors. The closest analogue in the literature is $[Ru(bipy)_2(4,4'\text{-mbipy})_2]^{4+}$, in which the pendant pyridyl groups of two 4,4′-bipyridine ligands are *N*-methylated.[30] In this case the two *N*-methylpyridinium reductions are exactly coincident, which is not surprising as there is no direct link between them. The data for this complex are included in Table 3.

The UV/VIS spectral data are summarised in Table 1. For complexes **1**–**4** the spectra are unremarkable and may be assigned by comparison with that of $[Ru(bipy)_3]^{2+}$. Thus, the two maxima between 420 and 460 nm are from ^{1}m.l.c.t. (metal to ligand charge transfer) processes, the single peak between 320 and 360 nm (not visible for **1**) is due to a metal-centred (m.c.) d–d transition, the strong band at about 286 nm is from a ligand-centred (l.c.) π–π^* transition, and finally the band at around 250 nm is another m.l.c.t. process. For **1′** and **2′** the two m.l.c.t. bands between 400 and 500 nm appear as well separated, distinct peaks rather than one peak with a shoulder. Both are still in the region due to $\pi^*(bipy) \leftarrow d_\pi(Ru)$ transitions, with the lower-energy process probably involving the bipyridine to which the pendant pyridinium groups are attached. As with $[Ru(bipy)_2(4,4'\text{-mbipy})_2]^{4+}$ there are no distinct absorption bands arising from a charge transition between the Ru^{II} and the remote pyridinium acceptors. The difference in $E_{\frac{1}{2}}$ values between the reduction processes at bipy and the methylpyridinium groups means that these absorptions should occur at a much lower energy than those of the $\pi^*(bipy) \leftarrow d_\pi(Ru)$ transitions;[32] they should also be much weaker.[30] These transitions are probably responsible for the tailing of the absorption spectra of **1′** and **2′** much further into the visible region than those of **1** and **2**. The absorption of complex **1** is virtually zero by 550 nm, whereas **1′** has $\varepsilon > 1000$ dm^3 mol^{-1} cm^{-1} at 550 nm and its absorption does not reach zero until about 590 nm; similarly, the absorption of **2** has fallen to zero by 570 nm, whereas **2′** has $\varepsilon \approx 1500$ dm^3 mol^{-1} cm^{-1} at that wavelength and its absorption does not reach zero until about 630 nm. Some recent reports suggest that emission from the $\pi^*(bipy) \leftarrow d_\pi(Ru)$ excited states is unlikely to be detectable, since they will be quenched by internal electron transfer to the paraquat-like acceptor group on a picosecond time-scale, followed by non-radiative back transfer to regenerate the ground state;[33,†] in contrast, Meyer and co-workers[30] observed emissions from *both* $\pi^*(bipy) \leftarrow d_\pi(Ru)$ and methylpyridinium $\leftarrow d_\pi(Ru)$ excited states in $[Ru(bipy)_2(4,4'\text{-mbipy})_2]^{4+}$. Further photochemical studies on **1′** and **2′** are in progress.

[†] We wish to thank one of the referees for pointing out these references.

Complexes **1**, **2** and **4** should in principle be able to act as ligands to metal complexes which are co-ordinatively unsaturated or bear a labile ligand which is easily displaced. For example, numerous phthalocyanine and porphyrin complexes are known to form adducts with axial pyridine ligands,[34] and may therefore be expected to bind **1** in axial positions to give bi- and tri-nuclear complexes. Similarly, the seventeen-electron complex $[MoL(NO)Cl_2]$ [L = tris(3,5-dimethylpyrazolyl)borate] is known to react with phenol to give [MoL(NO)Cl(OPh)];[35] reaction with **4** under the same conditions may afford a Ru–Mo binuclear complex in which the $Ru(bipy)_3^{2+}$ chromophore is attached to an electron-deficient molybdenum centre. These and other possibilities are currently being examined.

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