Conventional and Cyclometallated Complexes of Ruthenium(II) with Ambidentate Terdentate Ligands Displaying N_3 or N_2C Binding Modes[†]

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The potentially terdentate N-donor ligands 6-(2-dimethylaminophenyl)-2,2'-bipyridine (L1) and 2-(2dimethylaminophenyl)-1,10-phenanthroline (L²), which comprise a dimethylaminophenyl group attached to 2,2'-bipyridine or 1,10-phenanthroline fragments respectively, have been prepared. The ruthenium(II) complexes $[RuL_2][PF_6]_2$ (L = L¹ 1 or L² 2) and $[RuL(L - H)][PF_6](L = L^1 3 \text{ or } L^2 4)$ have been prepared and characterised by conventional spectroscopic, electrochemical and X-ray diffraction methods. In complexes 1 and 2 the ligands both co-ordinate in the expected N_a-donor mode to give RuN_s centres. The Ru-N(amine) bonds (2.22 and 2.24 Å respectively) are considerably longer than the Ru-N(pyridine) bonds (2.0-2.1 Å). In complexes 3 and 4 one ligand is bound as a conventional N₃ donor, but in the second the phenyl ring is turned around such that it co-ordinates in a cyclometallated fashion via C⁶ with the NMe₂ substitutent directed outwards. The Ru-C bonds (ca. 2.03 Å) are similar in length to typical Ru-N(pyridine) bonds, and their strongly electron-donating capability results in a lengthening of the trans Ru-N bonds. Detailed comparison of the structures of 1 with 3, and 2 with 4, allows the structural effects of cyclometallation to be clarified. The Ru[#]-Ru[#] couples for 1 and 2 are cathodically shifted by ca. 0.1 V with respect to the RuN_6 centre of [Ru(terpy)₂]²⁺ (terpy = 2,2':6',2''-terpyridine) which is consistent with the greater σ -donating and poorer π -accepting characteristics of tertiary amine ligands compared to pyridines; for 3 and 4, where the formally anionic carbon donor is a much stronger o donor, the Ru"-Ru" couple is shifted cathodically by a further 0.84 V in each case. The electronic spectra of 1-4 are also discussed.

The interesting electrochemical and photochemical characteristics of polypyridyl ruthenium(II) complexes have spurred the synthesis of a host of analogues and derivatives in which different ligand substitutents and different donor atoms have been used to try and 'fine-tune' these properties.¹ For example, recently many terdentate N-donor ligands have been prepared as analogues of 2,2':6',2"-terpyridine (terpy), in which one or more pyridyl donors are replaced by other ligating groups such as pyrazole.² Continuing our recent studies³ on the coordination chemistry of new mixed-donor polydentate ligands, we describe in this paper the synthesis and co-ordination behaviour of the new terdentate N-donor ligands 6-(2dimethylaminophenyl)-2,2'-bipyridine (L^1) and 2 - (2 dimethylaminophenyl)-1,10-phenanthroline (L^2) which comprise a tertiary amine (dimethylaminophenyl) donor group attached to bipyridine and phenanthroline fragments, respectively. Aliphatic tertiary amines are poor ligands, primarily for steric reasons, and there are relatively few examples of complexes containing simple monodentate tertiary amines such as NMe₃ or NEt₃;⁴ co-ordinated tertiary amines are far more common as components of polydentate chelates (such as openchain ligands,⁵ macrocycles⁶ or cryptands⁷), or if the steric interference of the alkyl groups is reduced due to incorporation of the N atom in a rigid polycyclic framework as in quinuclidine⁸ or 1,4-diazabicyclo[2.2.2]octane.⁹ The ligands \tilde{L}^1 and L^2 were therefore designed to permit the preparation and study of ruthenium(II) complexes based on a largely polypyridyl donor set but also incorporating tertiary amine ligands in the co-ordination sphere. We also found that under certain conditions L^1 and L^2 are also capable of behaving as N₂C-cyclometallating ligands, with the dimethylaminophenyl



ring co-ordinating in a 'turned-around' manner and the NMe₂ group directed outwards. Accordingly, the syntheses, crystal structures, electrochemical, spectroscopic and luminescence properties of $[RuL_2][PF_6]_2$ (L = L¹ 1 or L² 2) and $[Ru-L(L-H)][PF_6]$ (L = L¹ 3 or L² 4; L - H represents a deprotonated, cyclometallated ligand L) are described.

Experimental

Details of the equipment used for NMR and UV/VIS spectroscopic studies and electrochemical studies have been described before.³ Electron-impact (EI) and fast-atom bombardment (FAB) mass spectra were recorded with a VG-Autospec instrument. Luminescence spectra were recorded with a Perkin-Elmer LS50-B spectrometer. 2,2'-Bipyridine, 1,10-phenanthroline, N,N-dimethylaniline and n-butyllithium were purchased from Aldrich, and RuCl₃•xH₂O was purchased from Johnson Matthey: all starting materials were used as received, apart from N,N-dimethylaniline which was distilled under reduced pressure from sodium-benzophenone.

Preparation of 6-(2-Dimethylaminophenyl)-2,2'-bipyridine (L^1) .—A mixture of N,N-dimethylaniline $(14 \text{ cm}^3, 0.11 \text{ mol})$ and n-butyllithium $(1.6 \text{ mol } \text{dm}^{-3} \text{ solution in hexanes; } 35 \text{ cm}^3, 0.056 \text{ mol})$ under N₂ was heated to 90 °C with stirring for 60 h, during which time a white precipitate developed.¹⁰ After

[†] Supplementary data available: see Instructions for Authors, J. Chem. Soc., Dalton Trans., 1995, Issue 1, pp. xxv-xxx.

cooling to room temperature, solid 2,2'-bipyridine (8.7 g, 0.056 mol) was added in one portion through a powder funnel; a dark colour appeared immediately. The resulting mixture was stirred at room temperature overnight. After quenching with water, the yellow organic phase was separated off and dried (MgSO₄); the solvent was removed in vacuo to leave a yellow-brown oil. This was dissolved in acetone, excess powdered KMnO₄ added, and the suspension vigorously agitated in an ultrasound cleaning bath for 20 min. The suspension was then filtered through Celite and the filtrate evaporated to dryness. Analysis by TLC (alumina, 2:1 CH₂Cl₂-hexane) showed the presence of one major product eluting ahead of a trace of unreacted 2,2'bipyridine. Column chromatography with alumina (Brockmann activity III) and CH_2Cl_2 -hexane (2:1) afforded pure L¹ as a yellow oil in 30% yield; EI mass spectrum: m/z 275 (M^+), 260 $(M^+ - CH_3)$, 244 $(M^+ - 2CH_3)$, 231 $(M^+ - NMe_2)$; ¹H NMR (270 MHz, CDCl₃): δ 8.69 (1 H, ddd, J = 4.8, 1.8, 0.9,pyridyl H⁶'), 8.56 (1 H, d, J = 7.9, pyridyl H³'), 8.30 (1 H, dd, J = 7.7, 1.1, pyridyl H³ or H⁵), 7.98 (1 H, dd, J = 7.9, 1.1 Hz, phenyl H³), 7.73-7.84 (3 H, m, pyridyl H⁴, H⁴ and H⁵ or H³), 7.27-7.37 (2 H, m, pyridyl H⁵' and phenyl H⁵), 7.06-7.13 (2 H, m, phenyl H⁴ and H⁶), 2.63 (6 H, s, NMe₂) (Found: C, 78.7; H, 6.4; N, 15.3. Calc. for C₁₈H₁₇N₃: C, 78.6; H, 6.2; N, 15.3%).

Preparation of 2-(2-Dimethylaminophenyl)-1,10-phenanthroline (L^2) .—This was prepared by reaction of equimolar amounts of 1,10-phenanthroline and $Li(C_6H_4NMe_2-o)$, followed by rearomatisation with KMnO₄, as described above for L¹. The crude material was purified by column chromatography on alumina (Brockmann activity III) with CH₂Cl₂ as eluent to give L² as a yellow solid in 30% yield; EI mass spectrum: $m/z = 299 (M^+)$, 284 $(M^+ - CH_3)$, 268 $(M^+ - 2CH_3)$, 255 $(M^+ - NMe_2)$; ¹H NMR (270 MHz, CDCL) $\stackrel{\circ}{\sim} \stackrel{\circ}{\circ} \stackrel{\circ}{\circ$ CDCl₃): δ 9.21 (1 H, dd, J = 4.4, 1.8, phenanthroline H⁹), 8.29 (1 H, d, J = 8.4, phenanthroline H³ or H⁴), 8.25 (1 H, dd, J = 8.2, 1.8, phenanthroline H⁷), 8.20 (1 H, d, J = 8.4, phenanthroline H⁴ or H³), 7.94 (1 H, dd, J = 7.8, 1.8, phenyl H³), 7.79 (2 H, m, phenanthroline H⁵ and H⁶), 7.61 (1 H, dd, J = 8.1, 4.4 phenanthroline H⁸), 7.37 (1 H, td, J = 7.6, 1.8 Hz, phenyl H⁵), 7.15 (2 H, m, phenyl H⁴ and H⁶), 2.65 (6 H, s, NMe₂) (Found: C, 79.9; H, 6.0; N, 14.2. Calc. for C₂₀H₁₇N₃: C, 80.3; H, 5.7; N, 14.0%).

Preparations of $[Ru(L^1)_2][PF_6]_2$ 1 and $[Ru(L^2)_2][PF_6]_2$ 2.—A stirred mixture of $RuCl_3 \cdot xH_2O(0.5 \text{ mmol})$ and L^1 (for 1) or L^2 (for 2) (1.2 mmol) in ethylene glycol was heated to 150 °C for 1 h to give a dark orange solution. After cooling the complexes were precipitated by addition of aqueous KPF_6 , filtered off, washed with water and dried. The crude complexes were purified by chromatography on preparative-scale (1.5 mm View Article Online

thick) alumina TLC plates (Merck, article 5726) with MeCNtoluene (1:1) or CH₂Cl₂ as eluent. In each case the orange band was scraped off and the product dissolved out of the alumina with MeCN. The resulting solutions were evaporated to dryness. For both complexes most impurities could be removed using the former solvent system, but traces of dark brown and purple by-products did not separate completely from the desired orange band on the plate. Use of CH₂Cl₂ as eluent for a second plate using the partially purified material was successful at removing the last traces of these impurities, since they appear to be relatively non-polar and move rapidly up the plate whereas 1 and 2 remain near the baseline. Final purification was by crystallisation from CH₂Cl₂-hexane (for 1) or MeCNdiethyl ether (for 2). Yields for 1 and 2: 20-60%.

Preparations of $[RuL^{1}(L^{1} - H)][PF_{6}]$ 3 and $[RuL^{2}(L^{2} - H)][PF_{6}]$ H)][PF₆] 4.—A stirred mixture of RuCl₃·xH₂O (0.33 mmol), L^{1} (for 3) or L^{2} (for 4) (0.67 mmol) and N-methylmorpholine (0.5 cm^3) in ethylene glycol (20 cm^3) was heated to reflux for 1 h to give a dark purple solution. After cooling the mixtures and precipitation with aqueous KPF_6 as above, the crude solids were purified by chromatography on preparative-scale (1.5 mm thick) alumina TLC plates (Merck, article 5726) with MeCN-toluene (1:1) as eluent. The main purple product running at the front of the plate was isolated in each case. Yields: 3, 55%; 4, 38%. Final purification was by crystallisation from CH₂Cl₂-hexane.

Analytical and mass spectroscopic data for the new complexes are in Table 1.

Crystal-structure Determinations .--- Crystals were grown from the following solvents: 1, CH₂Cl₂-hexane (red needles); 2, MeCN-diethyl ether (red blocks); 3 and 4, CH₂Cl₂-hexane (purple blocks). The crystals selected were sealed in glass capillary tubes with some of the mother-liquor present, as a precaution against solvent loss. Data were collected using a Siemens R3m/V four-circle diffractometer (293 K, Mo-Ka X-radiation, graphite monochromator, $\overline{\lambda} = 0.71073$ Å). The data were corrected for Lorentz and polarisation effects, and for absorption using an empirical method based on azimuthal scan data.¹¹ Details of the crystal data and intensity collection are summarised in Table 2.

All structures were solved by conventional heavy-atom methods. Successive Fourier-difference syntheses were used to locate all non-hydrogen atoms; hydrogen atoms were included in calculated positions. For 1 the data were poorly resolved along the long b axis (ca. 37 Å) and an acceptable data set was only achieved using Wyckoff ω-scans and a narrow detector aperture. For 2 the asymmetric unit has a severely disordered molecule of Et_2O which could not be meaningfully modelled.

	Analysis ^a (%)			FAB mass spectrum
Complex	C	Н	N	m/z Assignment
1-CH ₂ Cl ₂	43.2 (43.3)	3.5 (3.5)	8.2 (8.2)	797 { $Ru(L^1)_2(PF_6)$ } 652 { $Ru(L^1)_2$ } 333 ^b
2	48.1 (48.5)	3.7 (3.4)	8.1 (8.5)	845 { $Ru(L^2)_2(PF_6)$ } 700 { $Ru(L^2)_2$ } 357 ^b
3-CH ₂ Cl ₂	50.3 (50.5)	4.1 (4.0)	9.5 (9.4)	796 {Ru(L ¹)(L ¹ - H)(PF ₆)} 651 {Ru(L ¹)(L ¹ - H)} 332 ^b
4-CH ₂ Cl ₂	53.3 (53.0)	4.0 (3.8)	9.0 (9.1)	844 {Ru(L ²)(L ² – H)(PF ₆)} 699 {Ru(L ²)(L ² – H)} 356 ^b

^a Calculated values in parentheses. ^b See text for assignment.

	$[Ru(L^{1})_{2}][PF_{6}]_{2}\cdot CH_{2}Cl_{2}$ 1	[Ru(L ²) ₂][PF ₆] ₂ ·Et ₂ O 2	$[RuL1(L1 - H)][PF_6] \cdot CH_2Cl_2 3$	$[RuL^{2}(L^{2} - H)][PF_{6}]\cdot CH_{2}CI_{2}$
Formula M	C ₃₇ H ₃₆ Cl ₂ F ₁₂ N ₆ P ₂ Ru 1026.63	C44H44F12N60P2Ru	C ₃₇ H ₃₅ Cl ₂ F ₆ N ₆ PRu	C ₄₁ H ₃₅ Cl ₂ F ₆ N ₆ PRu
Crystal system	Monoclinic	Triclinic	Monoclinic	928.09 Manaclinic
Space group	$P2_1/n$	$P\bar{1}$	P2./n	P). (n
a/Å	8.894(2)	9.284(4)	(1).901(7)	14 689(8)
\hat{V}/q	37.067(9)	12.199(5)	13.565(10)	16 699(8)
c/A ~/0	12.359(3)	20.767(8)	23.608(13)	16.602(8)
a/ 0.0		97.94(3)		
þ/2 /9	95.70(2)	101.34(3)	90.82(5)	107.62(4)
-//_		92.63(3)		
$\overline{U}/\mathbf{A}^{3}$	4054(2)	2278(2)	3811(4)	3881(3)
	4	2	4	4
$D_{\rm c}/{\rm g~cm^{-3}}$	1.682	1.551	1.535	1 589
$\mu(Mo-K\alpha)/mm^{-1}$	0.691	0.506	0.659	0.657
F(000)	2064	1080	1784	1880
Crystal dimensions/mm	$0.5 \times 0.23 \times 0.25$	$0.55 \times 0.45 \times 0.1$	04 × 05 × 07	03 × 03 × 06
Unique reflections measured	5303	7987	6714	620
20 Range/°	5.0-45.0	5.0 - 50.0	40-500	0 20 0 1 0 20 0
Index ranges	$0 \leq h \leq 9$; $0 \leq k \leq 39$;	$0 \le h \le 11$; $-14 \le k \le 14$;	$0 \le h \le 14 \cdot 0 \le k \le 16$	0 < h < 17.0 < h < 10.0
	$-13 \leqslant l \leqslant 13$	$-24 \leq l \leq 24$	-28 < 1 < 28	
Final residuals	•			01 1 1 1 1
wR_2^a	0.129	0.136	0.162	0 166
$R_1^{\ b}$	0.047	0.048	0.056	0.056
Weighting factors: a, b	0.0623, 8.34	0.0799, 1.3607	0.0855. 5.5355	0.025
Largest difference peak, hole/e Å ³	0.70, -0.48	0.50, -0.35	0.71, -0.84	1.180.83
Details in common: collection method, V using all data: $wR_2 = \{\Sigma[w(F_o^2 - F_o^2)^2]$ with a typical threshold of $F \ge 4\sigma(F)$.	Vyckoff ω -scan; refinement method, fu $ \Sigma w(F_{\circ}^{2})^{2} ^{4}$ where $w^{-1} = [\sigma^{2}(F_{\circ}^{2}) +$	ull-matrix least squares on all F^2 data; R_i $(aP)^2 + bP$] and $P = [\max(F_o^2, 0) + 1]$	$ Y_1 = \Sigma F_0 - F_0 \Sigma F_0 $ and $w^{-1} = [\sigma^2(F_0) + 2F_c^2]/3$. ^b The R_1 value is given for comparison	$(gF_o{}^2]$. ^a Structure was refined on $F_o{}^2$ son with older refinements based on $F_o{}$

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Ru-N(121)	2.031(4)	Ru-N(221)	2.035(4)	Ru-N(111)	2.059(4)
Ru–N(231)	2.217(4)	Ru-N(131)	2.231(4)	Ru–N(211)	2.064(4)
N(121)-Ru-N(221)	175.5(2)	N(121)-Ru-N(111)	79.7(2)	N(221)-Ru-N(111)	97.2(2)
N(121)-Ru-N(211)	96.8(2)	N(221)-Ru-N(211)	79.5(2)	N(111)-Ru-N(211)	80.2(2)
N(121)-Ru-N(231)	95.3(2)	N(221)-Ru-N(231)	87.8(2)	N(111) - Ru - N(231)	90.3(2)
N(211)-Ru-N(231)	163.0(2)	N(121)-Ru-N(131)	88.0(2)	N(221)-Ru-N(131)	94.5(2)
N(111)-Ru-N(131)	163.5(2)	N(211)-Ru-N(131)	90.6(2)	N(231) - Ru - N(131)	101.8(2)
C(112)-N(111)-C(116)	118.2(5)	C(112)-N(111)-Ru	127.0(4)	C(116)-N(111)-Ru	113.4(4)
C(126)-N(121)-C(122)	119.2(5)	C(126)-N(121)-Ru	125.7(4)	C(122)–N(121)–Ru	115.0(4)
C(131)-N(131)-C(12)	113.4(5)	C(131) - N(131) - C(11)	106.0(4)	C(12)-N(131)-C(11)	104.0(4)
C(131)-N(131)-Ru	109.4(3)	C(12)-N(131)-Ru	113.3(3)	C(11)–N(131)–Ru	110.4(3)
C(212)-N(211)-C(216)	117.7(5)	C(212) - N(211) - Ru	127.5(4)	C(216)-N(211)-Ru	113.0(3)
C(222)-N(221)-C(226)	119.6(4)	C(222)-N(221)-Ru	115.1(3)	C(226) - N(221) - Ru	125.2(3)
C(231)-N(231)-C(22)	113.3(5)	C(231) - N(231) - C(21)	107.0(4)	C(22)-N(231)-C(21)	104.7(4)
C(231)-N(231)-Ru	107.7(3)	C(22)–N(231)–Ru	113.0(3)	C(21)-N(231)-Ru	111.0(3)

Table 3 Selected internuclear distances (Å) and angles (°) for 1.CH₂Cl₂



Fig. 1 Structure of the cation of complex 1

Electron density in this region was therefore best approximated by nine carbon atoms with refined fractional site occupancies. The asymmetric units of 3 and 4 both contain a disordered molecule of CH_2Cl_2 . These were most adequately refined with restraints to keep the C-Cl bonds within the expected range.

All initial calculations were performed with a DEC micro-Vax II computer with the SHELXTL PLUS system of programs.¹¹ The final least-squares refinements on F^2 were carried out on a Silicon Graphics Indigo R4000 computer using SHELX 93.¹¹ Scattering factors with corrections for anomalous dispersion were taken from ref. 12.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Ligand Syntheses.—2,2'-Bipyridine and 1,10-phenanthroline are electrophilic and susceptible to attack by lithium reagents at the C-terminus of the C=N bonds to afford dihydrobipyridines or dihydrophenanthrolines respectively, which may be rearomatised by a variety of oxidising agents. This is a well established method for the preparation of ortho-substituted polypyridine-based ligands.¹³ The yields of L¹ and L² are moderate but the procedure is simple and uses readily available starting materials, and several grams of each ligand may be prepared at a time. The EI mass spectra and ¹H NMR spectra of the ligands are fully in accord with the proposed structures;



Fig. 2 Structure of the cation of complex 2

the ¹H NMR spectra were assigned with the aid of twodimensional ¹H $^{-1}$ H correlation (COSY) spectra.

Preparation, Characterisation and Crystal Structures of Complexes 1 and 2.—The homoleptic ruthenium(II) complexes $[RuL_2][PF_6]_2$ (L = L¹ 1 or L² 2) were prepared by reaction of the ligand with RuCl₃·xH₂O in ethylene glycol at 150 °C followed by precipitation with KPF₆. Unlike the reaction with terpy under the same conditions, this is not a clean reaction and TLC analysis in each case showed the presence of numerous by-products in addition to the expected orange product. Formation of these by-products was lessened by performing the reaction at 150 °C rather than at reflux, however the yields still varied unpredictably between preparations; the best yields were 60%, but yields as low as 20% were also obtained on occasion. The complexes were purified by preparative-scale TLC followed by recrystallisation. The FAB mass spectra of complexes 1 and 2 showed, in addition to the expected peaks for RuL_2 fragments (Table 1), intense peaks at m/z = 333 and 357 respectively. These correspond to the formation of the cyclometallated species $[Ru(pbipy)]^+$ (Hpbipy = 6-phenyl-2,2'-bipyridine) and $[Ru(pphen)]^+$ (Hpphen = 2-phenyl-1,10phenanthroline) by loss of NMe₂ groups from the $\{RuL^1\}$ and {RuL²} fragments, a process which may be encouraged under the mass spectroscopic conditions by the fact that cyclometallated ruthenium(11) complexes with ligands such as Hpbipy are very stable.¹⁴ The formulations of complexes 1 and 2 were also

Table 4 Atomic positional parameters (fractional coordinates $\times 10^4$) for 1·CH₂Cl₂ with estimated standard deviations (e.s.d.s) in parentheses

Atom	x	у	Z	Atom	x	у	z
Ru	1461(1)	1209(1)	1729(1)	C(223)	2962(7)	2243(2)	2732(5)
NOID	1526(5)	1380(1)	149(4)	C(224)	4445(8)	2205(2)	3151(5)
C(112)	2267(7)	1667(2)	-192(5)	C(225)	5054(7)	1867(2)	3267(5)
C(113)	2029(9)	1795(2)	-1235(6)	C(226)	4194(6)	1564(2)	2960(4)
C(114)	1008(11)	1630(2)	- 1954(6)	N(231)	3559(5)	893(1)	1628(4)
C(115)	219(9)	1339(2)	- 1628(6)	C(231)	4350(6)	874(2)	2721(5)
C(116)	463(7)	1219(2)	- 566(5)	C(232)	4720(6)	1197(2)	3281(4)
N(121)	69(5)	841(1)	935(4)	C(233)	5555(6)	1169(2)	4308(5)
C(122)	-367(7)	920(2)	-129(5)	C(234)	5925(7)	841(2)	4772(6)
C(123)	-1521(8)	731(2)	- 720(6)	C(235)	5517(8)	535(2)	4222(7)
C(124)	-2203(8)	456(2)	-212(7)	C(236)	4749(7)	546(2)	3191(6)
C(125)	-1699(7)	357(2)	829(6)	C(21)	4604(7)	1081(2)	917(5)
C(126)	-516(6)	543(2)	1391(5)	C(22)	3276(7)	533(2)	1116(6)
N(131)	689(5)	1007(1)	3282(4)	C(9)	5784(16)	1582(3)	7051(8)
C(131)	830(6)	614(2)	3324(5)	Cl(2)	4098(3)	1772(1)	6290(2)
C(132)	197(6)	404(2)	2448(5)	Cl(1)	6229(4)	1774(1)	8241(2)
C(133)	284(8)	33(2)	2548(6)	P(1)	- 882(2)	2206(1)	-4916(2)
C(134)	957(9)	-134(2)	3462(7)	F(11)	-1321(9)	1802(2)	- 4835(10)
C(135)	1548(8)	72(2)	4314(7)	F(12)	- 1434(9)	2177(4)	- 6087(5)
C(136)	1489(7)	443(2)	4249(6)	F(13)	- 299(10)	2212(2)	- 3708(5)
C(11)	- 969(6)	1087(2)	3324(5)	F(14)	738(6)	2097(2)	- 5130(7)
C(12)	1442(7)	1191(2)	4267(5)	F(15)	-477(7)	2604(2)	- 4907(8)
N(211)	-87(5)	1625(1)	1689(4)	F(16)	-2512(6)	2305(2)	4689(6)
C(212)	- 1542(6)	1619(2)	1262(5)	P(2)	3881(2)	541(1)	-2364(1)
C(213)	-2364(7)	1925(2)	1033(5)	F(21)	5455(6)	476(2)	-2788(5)
C(214)	-1706(8)	2256(2)	1239(6)	F(22)	4347(5)	259(1)	- 1410(4)
C(215)	-215(7)	2269(2)	1669(5)	F(23)	3161(6)	224(1)	- 3067(4)
C(216)	568(6)	1953(1)	1898(4)	F(24)	2336(6)	598(1)	- 1884(5)
N(221)	2771(5)	1609(1)	2453(3)	F(25)	3460(6)	818(1)	- 3308(4)
C(222)	2154(6)	1944(1)	2373(4)	F(26)	4585(8)	850(1)	- 1611(4)
e 5 Selecto	ed internuclear dis	stances (Å) and	angles (°) for 2-Et ₂ O				
N(122)	2.040)(3)	Ru–N(222)	2.043(3)	Ru-1	N(211)	2.089(3)

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Ru = N(122) Ru = N(111)	2.040(3)	Ru = N(222) Ru = N(131)	2.043(3) 2 234(4)	Ru–N(211) Ru–N(231)	2.089(3) 2.243(4)
	2.072(3)	Ru ((151)	2.234(4)	Ru 1(251)	2.2.13(1)
N(122)-Ru-N(222)	174.20(13)	N(122)-Ru-N(211)	95.57(13)	N(222)-Ru-N(211)	79.83(13)
N(122)-Ru-N(111)	80.29(13)	N(222)-Ru-N(111)	95.34(13)	N(211)-Ru-N(111)	79.85(13)
N(122)-Ru-N(131)	86.51(13)	N(222)-Ru-N(131)	97.09(13)	N(211)-Ru-N(131)	91.60(13)
N(111)-Ru-N(131)	163.43(13)	N(122)-Ru-N(231)	97.39(13)	N(222)-Ru-N(231)	86.50(13)
N(211)-Ru-N(231)	163.09(12)	N(111)-Ru-N(231)	91.67(13)	N(131)-Ru-N(231)	99.97(13)
C(112)-N(111)-C(124)	116.7(4)	C(112)-N(111)-Ru	131.0(3)	C(124)-N(111)-Ru	111.2(3)
C(121) - N(122) - C(123)	118.4(3)	C(121)-N(122)-Ru	128.4(3)	C(123)-N(122)-Ru	113.1(3)
C(132)-N(131)-C(125)	113.4(4)	C(132) - N(131) - C(133)	105.4(3)	C(125)-N(131)-C(133)	106.0(3)
C(132)-N(131)-Ru	112.5(3)	C(125)-N(131)-Ru	108.6(2)	C(133)-N(131)-Ru	110.7(3)
C(212) - N(211) - C(224)	117.4(4)	C(212)N(211)Ru	129.8(3)	C(224)-N(211)-Ru	111.4(3)
C(221)-N(222)-C(223)	118.4(3)	C(221)-N(222)-Ru	128.2(3)	C(223)–N(222)–Ru	113.1(3)
C(232)-N(231)-C(225)	113.5(4)	C(232)-N(231)-C(233)	104.8(3)	C(225)-N(231)-C(233)	105.6(3)
C(232)-N(231)-Ru	112.6(3)	C(225)-N(231)-Ru	109.6(2)	C(233)-N(231)-Ru	110.4(3)

confirmed by elemental analyses (Table 1). The presence of one molecule of CH₂Cl₂ per complex molecule in the crystals of 1, which is apparent from the analytical data, was confirmed crystallographically.

The crystal structures of complexes 1 and 2 are shown in Figs. 1 and 2; bond lengths and angles are in Tables 3 and 5 respectively, and atomic coordinates are in Tables 4 and 6 respectively. In each case the geometry, as expected, is approximately octahedral, with the ligands crystallographically inequivalent but similar. The Ru-N(sp²) bond lengths are typical,¹⁵ with the bonds to the central heterocyclic ligands [for 1, Ru-N(121) and Ru-N(221) ca. 2.03 Å; for 2, Ru-N(122) and Ru-N(222), ca. 2.04 Å] being slightly shorter than those to the terminal ones [for 1, Ru-N(111) and Ru-N(211) ca. 2.06 Å; for 2, Ru-N(111) and Ru-N(211), ca. 2.09 Å] which is similar to the variation generally observed in the structures of terpyridine complexes.¹⁶ The Ru-N(sp²) bonds trans to the NMe₂ donors are not unusually long, which is perhaps surprising. The Ru-N(amine) bonds are in contrast much longer, at ca. 2.22 Å for 1

and ca. 2.24 Å for 2. There are two obvious reasons for this. First, there can be no metal-to-ligand back bonding. Secondly, the amine N atoms are sp³ hybridised whereas the pyridyl N atoms are sp² hybridised; this is confirmed by the bond angles at the amine N atom [Me-N-Me ca. 104° in each ligand for 1 and ca. 105° in each ligand for 2: Ru-N-C(phenyl) 107.7 and 109.4° in the two independent ligands of 1, and 108.6 and 109.6° in the two independent ligands of 2]. The methyl groups of each ligand are directed away from the metal and from the other ligand and do not appear to cause significant steric hindrance. A search of the Cambridge Crystallographic Database showed that no other ruthenium(II) complexes of open-chain tertiary amines have been structurally characterised, so comparison of these bond lengths with others is not possible. The C₆H₄NMe₂ fragments of the ligands are substantially twisted with respect to the diimine fragments (Table 7), since the amine lone pair, at a tetrahedrally hybridised centre, will not lie in the same plane as those of the diimine fragment. This is a common feature of ligands of this type.³

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Table 6 Atomic positional parameters (fractional coordinates $\times 10^4$) for 2-Et₂O with e.s.d.s in parentheses

					-		
Atom	x	у	Z	Atom	x	у	z
Ru	2 366(1)	2 611(1)	2 778(1)	N(222)	4 032(3)	3 512(3)	3 464(2)
N(111)	3 518(4)	2 469(3)	2 004(2)	C(223)	4 363(4)	4 530(3)	3 308(2)
C(112)	4 896(5)	2 807(4)	1 993(3)	C(224)	3 335(4)	4 894(3)	2 784(2)
C(113)	5 397(6)	2 828(4)	1 408(3)	C(225)	3 542(4)	1 241(4)	3 880(2)
C(114)	4 497(7)	2 488(5)	812(3)	C(226)	4 370(4)	2 193(4)	4 259(2)
C(115)	3 018(6)	2 136(4)	788(2)	C(227)	4 651(6)	2 275(4)	4 960(2)
C(116)	1 952(8)	1 773(5)	189(2)	C(228)	4 121(7)	1 450(5)	5 266(3)
C(117)	560(8)	1 456(5)	198(3)	C(229)	3 319(7)	519(5)	4 895(3)
C(118)	71(6)	1 441(4)	816(2)	C(230)	3 024(5)	421(4)	4 195(3)
C(119)	-1 355(6)	1 083(4)	870(3)	N(231)	3 318(4)	1 100(3)	3 146(2)
C(120)	-1662(5)	1 031(4)	1 477(3)	C(232)	2 452(5)	65(4)	2 813(2)
C(121)	- 576(4)	1 355(3)	2 062(2)	C(233)	4 836(5)	975(4)	2 991(2)
N(122)	756(3)	1 805(3)	2 026(2)	P(1)	703(1)	7 032(1)	4 047(1)
C(123)	1 097(5)	1 790(3)	1 409(2)	$\mathbf{F}(1)$	- 704(4)	7 665(4)	4 172(3)
C(124)	2 580(5)	2 147(3)	1 398(2)	F(2)	1 028(7)	7 864(4)	3 578(2)
C(125)	-197(4)	1 741(4)	3 342(2)	F(3)	2 082(4)	6 361(4)	3 963(2)
C(126)	-824(4)	1 113(3)	2 716(2)	F(4)	363(5)	6 200(3)	4 531(2)
C(127)	-1611(5)	103(4)	2 709(3)	F(5)	1 652(4)	7 811(3)	4 672(2)
C(128)	-1 732(6)	-285(5)	3 300(4)	F(6)	-255(6)	6 245(3)	3 448(2)
C(129)	-1.081(7)	320(6)	3 886(4)	P(2)	4381(2)	8 759(1)	1 120(1)
C(130)	-339(6)	1 342(5)	3 920(3)	F(7)	2 782(5)	8 804(7)	1 211(3)
N(131)	606(4)	2 844(3)	3 369(2)	F(8)	4 262(8)	7 475(4)	933(4)
C(132)	1 184(6)	3 420(5)	4 055(2)	F(9)	6 055(4)	8 712(4)	1 066(2)
C(133)	-532(5)	3 571(4)	3 060(3)	F(10)	3 994(7)	8 907(8)	396(2)
N(211)	2 134(4)	4 179(3)	2 491(2)	F(11)	4 687(6)	10 026(3)	1 386(2)
C(212)	1 169(5)	4 499(4)	1 993(2)	F(12)	4 784(6)	8 571(4)	1 867(2)
C(213)	1 350(6)	5 525(4)	1 785(3)	C(1)*	-1.361(92)	4 685(63)	124(14)
C(214)	2 524(6)	6 243(4)	2 078(3)	C(2)	-2072(63)	4 354(53)	332(33)
C(215)	3 578(5)	5 931(4)	2 599(2)	C(3)	-3109(95)	4 942(32)	-128(37)
C(216)	4 872(6)	6 618(4)	2 935(3)	C(4)	-2944(41)	5 856(30)	1 208(28)
C(217)	5 855(6)	6 277(4)	3 424(3)	C(5)	-2.138(15)	5 004(15)	1 037(10)
C(218)	5 615(5)	5 225(4)	3 635(2)	C(6)	-2376(19)	5 841(24)	1 974(9)
C(219)	6 572(5)	4 813(5)	4 148(3)	C(7)	-4 414(161)	4 383(111)	2 435(49)
C(220)	6 195(5)	3 831(5)	4 330(2)	C(8)	-2491(24)	4 943(33)	2 039(14)
C(221)	4 889(4)	3 184(4)	4 001(2)	C(9)	- 1 943(19)	6 950(19)	1 982(8)
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* Complex contains a severely disordered molecule of Et_2O which could not be satisfactorily modelled and was best approximated by nine C atoms [C(1)–C(9)] with the following refined fractional site occupations: C(1), 0.93; C(2), 1; C(3), 0.83; C(4), 0.58; C(5), 0.67; C(6), 0.72; C(7), 0.16; C(8) 0.54; C(9), 1.

Table 7 Torsion angles (to the nearest °) within the ligands in the crystal structures of $1\!-\!4$

	Torsie	on/°	
Complex	1	2*	3
1	1	37	
	5	34	-
2	1	36	
	0	35	
3	6	39	
	5		10
4	0	35	
	1		8

Torsion 1: angle between the two aromatic rings of the bipyridine or phenanthroline fragments; torsion 2: angle between the central aromatic ring and the $C_6H_4NMe_2$ ring in the N₃-bound ligands; torsion 3: angle between the central aromatic ring and the $C_6H_3NMe_2$ ring in the cyclometallated ligands.

* The error associated with torsion 2 is large $(\pm 3^\circ)$ since the two aromatic rings concerned are not exactly coaxial with the inter-ring bond; the calculated torsion angle is therefore dependent on which four atoms are used to define it.

Preparation, Characterisation and Crystal Structures of Complexes 3 and 4.—As mentioned above, TLC analysis of crude 1 and 2 revealed the presence of (amongst others) a deep purple by-product in each case, which is characteristic of cyclometallated ruthenium(II) species with an N_5C donor set.^{14,17} Together with the observation that fragments of 1 and 2 undergo cyclometallation under FAB mass spectroscopic conditions, this prompted us to see if any cyclometallated species could be isolated.

Whereas reaction of RuCl₃ with L^1 or L^2 (in a 1:2 ratio) in ethylene glycol resulted in formation of 1 or 2 respectively as the major product, with the supposed cyclometallated by-products being formed only in minor amounts, addition of Nmethylmorpholine to the reaction mixture reversed this behaviour. Analysis by TLC [alumina, MeCN-toluene (1:1)] showed that the purple materials (3 and 4 respectively) were the major products, with 1 and 2 (and other by-products) being formed only in trace amounts. It has been noted before that Nmethylmorpholine promotes formation of cyclometallated species,¹⁷ although its precise role is unclear. The relative mobility of 3 and 4 on TLC plates compared to 1 and 2 suggests that they are monocationic. Elemental analyses and FAB mass spectra were consistent with the formulations [RuL(L – H)][PF₆] (L = L¹ 3 or L² 4) in which one ligand is deprotonated and therefore co-ordinated in a cyclometallated mode. (Repeatable elemental analytical data for both 3 and 4 indicated the presence of one molecule of CH₂Cl₂ per complex molecule; this was subsequently confirmed crystallographically.) The ¹H NMR spectra of complexes 3 and 4 confirmed that cyclometallation had occurred, showing 21 inequivalent aromatic signals. The spectra were not assigned fully, but a doublet at low chemical shift in each case (δ 5.65 and 5.52 for 3 and 4 respectively) is characteristic of a phenyl proton adjacent to the site of metallation,^{14,17} and COSY spectra (Fig. 3 shows that of complex 4) confirm that the phenyl rings bearing these protons only have three attached protons in total. The

Table 8 Selected internuclear distances (Å) and angles (°) for 3-CH₂Cl₂

Ru-N(51)	1.995(4)	Ru–N(31)	2.019(4)	Ru-N(61)	2.168(5)
Ru-N(21)	2.007(4)	Ru-C(43)	2.031(5)	Ru-N(10)	2.216(4)
N(51)-Ru-N(21)	173.2(2)	N(31)-Ru-C(43)	86.6(2)	N(51)-Ru-N(10)	97.4(2)
N(51) - Ru - N(31)	94.9(2)	N(51)-Ru-N(61)	77.6(2)	N(21)-Ru-N(10)	88.5(2)
N(21) - Ru - N(31)	79.0(2)	N(21) - Ru - N(61)	105.5(2)	N(31)-Ru-N(10)	167.0(2)
N(51)-Ru-C(43)	80.1(2)	N(31) - Ru - N(61)	94.4(2)	C(43)-Ru-N(10)	91.3(2)
N(21) - Ru - C(43)	96.6(2)	C(43) - Ru - N(61)	157.7(2)	N(61)-Ru-N(10)	92.4(2)
C(11) - N(10) - C(10B)	114.3(4)	C(11)-N(10)-C(10A)	107.8(4)	C(10B)-N(10)-C(10A)	106.6(4)
C(11) - N(10) - Ru	105.2(3)	C(26)-N(21)-C(22)	118.7(5)	C(26)-N(21)-Ru	126.1(4)
C(22)-N(21)-Ru	115.1(3)	C(32) - N(31) - C(36)	117.9(5)	C(32)-N(31)-Ru	127.7(4)
C(36)-N(31)-Ru	114.1(3)	C(44)-C(43)-C(42)	117.2(5)	C(44)C(43)Ru	128.8(4)
C(42) - C(43) - Ru	113.9(4)	C(52)-N(51)-C(56)	121.4(5)	C(52)–N(51)–Ru	119.4(4)
C(56)-N(51)-Ru	118.8(4)	C(62)-N(61)-C(66)	117.9(5)	C(62)-N(61)-Ru	129.4(4)
C(66)–N(61)–Ru	112.7(3)				

Table 9 Atomic positional parameters (fractional coordinates × 10⁴) for 3-CH₂Cl₂ with e.s.d.s in parentheses

Atom	x	у	z	Atom	x	у	2
Ru	637(1)	2004(1)	1224(1)	C(43)	-219(4)	745(4)	1391(2)
N(10)	- 338(4)	2228(3)	428(2)	C(44)	44(5)	-224(4)	1242(2)
C(10Å)	-683(5)	1289(4)	148(2)	C(45)	-634(5)	- 1003(5)	1398(3)
C(10B)	-1383(5)	2773(5)	548(2)	C(46)	-1620(5)	-843(5)	1680(3)
C(11)	425(5)	2742(4)	50(2)	N(51)	-508(3)	2528(3)	1755(2)
C(12)	1473(5)	2333(4)	-77(2)	C(52)	-421(5)	3472(4)	1943(2)
C(13)	2160(6)	2859(5)	-444(3)	C(53)	-1097(5)	3817(5)	2373(3)
C(14)	1862(8)	3757(6)	-674(3)	C(54)	-1874(6)	3188(5)	2591(3)
C(15)	854(8)	4136(6)	-552(3)	C(55)	- 1982(5)	2235(5)	2395(3)
C(16)	119(6)	3642(5)	-198(2)	C(56)	-1293(4)	1893(4)	1968(2)
N(21)	1852(3)	1376(3)	766(2)	N(61)	1079(4)	3552(3)	1279(2)
C(22)	2557(4)	769(4)	1062(2)	C(62)	1873(5)	4053(4)	1005(2)
C(23)	3287(5)	134(5)	789(3)	C(63)	2086(6)	5030(5)	1096(3)
C(24)	3326(5)	142(5)	209(3)	C(64)	1487(6)	5522(5)	1488(3)
C(25)	2692(5)	819(5)	-84(3)	C(65)	673(6)	5038(4)	1778(3)
C(26)	1980(4)	1459(4)	196(2)	C(66)	460(5)	4048(4)	1666(2)
N(31)	1727(3)	1584(3)	1841(2)	Р	5537(2)	2288(2)	3859(1)
C(32)	1714(5)	1832(4)	2394(2)	F(1)	5196(5)	3028(4)	4329(3)
C(33)	2448(6)	1465(5)	2783(3)	F(2)	4317(4)	2150(6)	3684(3)
C(34)	3228(6)	778(5)	2615(3)	F(3)	5696(6)	3173(5)	3452(3)
C(35)	3261(5)	489(5)	2062(3)	F(4)	5904(5)	1529(5)	3402(3)
C(36)	2509(4)	912(4)	1671(2)	F(5)	5413(10)	1446(6)	4288(4)
N(40)	-2947(4)	279(4)	2131(2)	F(6)	6800(6)	2427(7)	4030(4)
C(40A)	- 3467(6)	-535(6)	2419(4)	Cl(1)	-3664(4)	3881(3)	1225(2)
C(40B)	- 3750(6)	843(7)	1797(4)	C1(2)	- 5471(4)	2675(4)	965(3)
C(41)	-1924(5)	107(5)	1848(2)	C(1)	-4782(9)	3721(8)	778(5)
C(42)	-1195(4)	890(4)	1732(2)				

Table 10 Selected internuclear distances (Å) and angles (°) for 4-CH₂Cl₂

P. N(21)	1 097(4)	D ₁₁ N(51)	2 015(4)	$\mathbf{P}_{\mathbf{W}} = C(15)$	2 022(5)
Ru=IN(21)	1.967(4)	Ru = N(31)	2.013(4)	Ru = C(13)	2.055(5)
Ru–N(62)	2.042(4)	Ru–N(40)	2.200(5)	Ru–N(32)	2.205(5)
N(21)-Ru-N(51)	173.6(2)	C(15)-Ru-N(62)	83.7(2)	N(21)-Ru-N(32)	78.2(2)
N(21)-Ru-C(15)	79.0(2)	N(21)-Ru-N(40)	98.4(2)	N(51)-Ru-N(32)	104.4(2)
N(51)-Ru-C(15)	98.2(2)	N(51)-Ru-N(40)	87.4(2)	C(15)-Ru-N(32)	157.2(2)
N(21)-Ru-N(62)	93.4(2)	C(15) - Ru - N(40)	91.6(2)	N(62) - Ru - N(32)	97.0(2)
N(51)-Ru-N(62)	80.5(2)	N(62) - Ru - N(40)	166.2(2)	N(40) - Ru - N(32)	92.3(2)
C(14)-C(15)-C(16)	117.0(5)	C(14)-C(15)-Ru	128.3(4)	C(16)-C(15)-Ru	114.5(4)
C(34) - N(21) - C(22)	121.0(5)	C(34)-N(21)-Ru	118.4(4)	C(22)-N(21)-Ru	120.3(4)
C(31)-N(32)-C(33)	116.5(5)	C(31)-N(32)-Ru	132.9(4)	C(33)-N(32)-Ru	110.4(4)
C(41) - N(40) - C(40A)	113.7(5)	C(41) - N(40) - C(40B)	108.0(5)	C(40A) - N(40) - C(40B)	106.3(5)
C(41)-N(40)-Ru	107.2(3)	C(52)-N(51)-C(64)	118.3(5)	C(52)-N(51)-Ru	128.1(4)
C(64)-N(51)-Ru	113.6(3)	C(61)-N(62)-C(63)	117.1(5)	C(61)-N(62)-Ru	129.9(4)
C(63) - N(62) - Ru	112.2(3)				

analytical and spectroscopic data therefore confirm that in 3 and 4 one ligand is bound in the usual N₃-terdentate fashion, whereas the other presents an N₂C donor set to the metal with the phenyl ring turned around such that C^6 is bonded to the metal and the NMe₂ group at the C² position is directed away from the metal.

The crystal structures of complexes 3 and 4 are depicted in Figs. 4 and 5; bond lengths and angles are in Tables 8 and 10, and atomic coordinates in Tables 9 and 11. They confirm that one ligand is cyclometallated in each case, resulting in an N_5C donor set. Both complexes are approximately octahedral within the constraints imposed by the ligands: the N-Ru-C bite angles

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of the cyclometallated ligands are 157.7 and 157.2° for 3 and 4 respectively, which are comparable to those of terpyridine complexes. 16 The $\rm N_3$ -co-ordinated ligands have similar twisted conformations to those of 1 and 2, but as expected the cyclometallated ligands adopt a more nearly planar conformation with much smaller dihedral angles between the central heterocyclic and terminal phenyl rings (Table 7). Cyclometallation has significant effects on the metal-ligand bond lengths, and comparison of the structures of 1 with 3, and of 2 with 4, allows the effects of cyclometallation to be seen clearly. The Ru-C bonds (2.031 Å for 3 and 2.033 Å for 4) are comparable in length to the Ru-N bonds involving the pyridyl or phenanthroline fragments. There is a noticeable trans effect: the Ru-N(sp²) bond lengths *trans* to the site of cyclometallation are lengthened by over 0.1 Å [Ru-N(trans to C) 2.168 Å for 3



Fig. 4 Structure of the cation of complex 3

Table 11 Atomic positional parameters (fractional coordinates $\times 10^4$) for 4-CH₂Cl₂ with e.s.d.s in parentheses

Atom	x	у	z	Atom	x	у	Ζ
Ru	2386(1)	1335(1)	3225(1)	C(43)	-809(5)	2716(5)	1671(6)
N(10)	5609(4)	1208(3)	2353(4)	C(44)	-1323(5)	2096(5)	1841(5)
C(10A)	5346(6)	1858(5)	1738(5)	C(45)	- 887(4)	1366(4)	2082(5)
C(10B)	6421(6)	759(5)	2261(7)	C(46)	71(4)	1241(4)	2151(4)
C(11)	4832(4)	753(4)	2438(4)	N(51)	1372(3)	491(3)	3100(3)
C(12)	4715(5)	-43(4)	2192(4)	C(52)	479(4)	473(4)	2544(3)
C(13)	3931(5)	-473(4)	2245(4)	C(53)	- 50(4)	-243(4)	2434(4)
C(14)	3220(4)	-113(4)	2500(4)	C(54)	269(5)	- 894(4)	2941(4)
C(15)	3297(4)	695(3)	2766(3)	C(55)	1147(4)	- 847(4)	3601(4)
C(16)	4152(4)	1113(3)	2773(3)	C(56)	1523(5)	-1451(4)	4219(4)
N(21)	3484(3)	2086(3)	3439(3)	C(57)	2355(5)	-1344(4)	4841(4)
C(22)	4269(4)	1885(3)	3208(3)	C(58)	2895(4)	-626(4)	4897(4)
C(23)	5075(4)	2392(3)	3472(4)	C(59)	3747(5)	-474(4)	5534(4)
C(24)	5061(4)	3074(4)	3929(4)	C(60)	4197(5)	249(4)	5544(4)
C(25)	4240(4)	3289(3)	4149(4)	C(61)	3799(4)	821(4)	4919(4)
C(26)	4128(5)	3984(4)	4606(4)	N(62)	2992(3)	694(3)	4301(3)
C(27)	3325(5)	4131(4)	4800(4)	C(63)	2548(4)	-32(3)	4297(3)
C(28)	2533(4)	3587(4)	4565(4)	C(64)	1665(4)	-147(3)	3641(3)
C(29)	1666(5)	3710(4)	4748(4)	P	2078(1)	6335(1)	5992(2)
C(30)	959(5)	3169(5)	4469(4)	F(1)	2671(5)	5583(5)	6292(7)
C(31)	1075(4)	2494(4)	4016(4)	F(2)	1452(6)	7070(5)	5676(7)
N(32)	1889(3)	2351(3)	3829(3)	F(3)	2559(7)	6467(8)	5305(6)
C(33)	2603(4)	2907(3)	4106(4)	F(4)	2886(5)	6860(6)	6572(6)
C(34)	3469(4)	2762(3)	3891(3)	F(5)	1278(5)	5787(5)	5439(5)
N(40)	1579(3)	1748(3)	1950(3)	F(6)	1593(5)	6260(4)	6705(5)
C(40Á)	2033(5)	2478(4)	1737(5)	C(1)	-1799(22)	- 539(9)	3594(23)
C(40B)	1578(5)	1139(4)	1285(4)	Cl (1)	-1539(7)	-1325(5)	4263(6)
C(41)	582(4)	1870(4)	1943(4)	Cl(2)	- 1004(8)	152(6)	4150(7)
C(42)	135(5)	2600(4)	1709(4)	.,			





Fig. 3 Aromatic region of the ${}^{1}H{-}^{1}H$ COSY spectrum of complex 4 (400 MHz, CD₃CN, 295 K)

 Table 12.
 Electrochemical and electronic spectral data for complexes 1-4

	Redox potentials	s ($E_{\frac{1}{2}}/V vs.$ ferrocene-ferrocenium) ^{<i>a,b</i>}	Electronic spectral data ^b
Complex	Ru ^{II} -Ru ^{III}	Ligand based	$\lambda_{max}/nm (10^{-3} \epsilon/dm^3 mol^{-1} cm^{-1})$
1 2 3 4	+0.78 (80) +0.83 (100) -0.06 (70) -0.01 (60)	+1.15, -1.50, -1.67, -1.95 +1.14, -1.35, -1.63, -1.94 +0.75, -2.03 (60), -2.34 (90) +0.75, -2.01 (70), -2.30 (120)	480 (sh), 452 (5.8), 300 (32), 244 (27) 490 (sh), 435 (9.1), 340 (sh), 325 (sh), 286 (44), 242 (47) 550 (sh), 502 (8.0), 350 (sh), 312 (24), 243 (39) 532 (14), 388 (8.8), 330 (sh), 290 (39), 243 (57)

^a For chemically reversible processes (cathodic and anodic peak currents equal), the figure in parentheses is the peak-peak separation ΔE_p . For irreversible processes the peak potentials were taken from square-wave voltammograms. ^b Measurements made in MeCN.



Fig. 5 Structure of the cation of complex 4

and 2.205 Å for 4, compared to *ca*. 2.06 Å for 1 and *ca*. 2.09 Å for 2]. This may be ascribed to electronic repulsion between the ligating electron pairs of the *trans* C- and N-donor atoms in the cyclometallated ligands, which are directed approximately towards each other. In contrast no such obvious lengthening of Ru–N(sp²) bonds is observed for pyridyl ligands *trans* to other σ donors such as NMe₂ (this work) or phenolate, ¹⁸ which is an indication of how much more effective a σ donor the carbon anion is; in complexes 3 and 4 the effect may be further enhanced by the pendant electron-donating NMe₂ substituents on the cyclometallating phenyl rings. A similar lengthening of the bond *trans* to the cyclometallation site was observed in [Pt(pbipy)(NCMe)][PF₆].¹⁹

The other three Ru-N(sp²) bonds, which all lie approximately perpendicular to the axis of cyclometallation, are shortened on average by 0.04 Å in 3 and 4 compared to 1 and 2 (the average estimated standard deviation in the bond lengths is 0.005 Å). The shortest bond in each case is to the central donor atom of the cyclometallated ligand. It is difficult to separate the possible steric and electronic contributions to this. Since the Ru^{II} centre is rendered more electron rich by cyclometallation, it is possible that these ligands (which are not trans to the carbon donor and therefore not directly electrostatically repelled) will be able to participate in increased $d(\pi)-p(\pi)$ back-bonding, which would shorten the bonds. However since the ligands are fairly rigid terdentate chelates, a change in one bond distance must necessarily affect the others in the same ligand: the much closer approach of the terminal ring to the metal when cyclometallation occurs may also account for the accompanying decrease in the $Ru-N(sp^2)$ distance involving the neighbouring binding site. The removal of a bulky NMe₂ group from the immediate

co-ordination sphere of the metal centres does have a noticeable steric effect. We would expect that the high electron density on the metal centres would result in increased distances for the remaining Ru–N(amine) bonds in 3 and 4 on electronic grounds: however the remaining Ru–N(amine) bond in each case is slightly shortened (2.216 Å in 3, 2.200 Å in 4) which can only be ascribed to the less sterically hindered environment at the positions *cis* to them.

Electrochemical and Spectroscopic Properties of Complexes 1-4.—The electrochemical and UV/VIS spectroscopic properties of 1-4 are summarised in Table 12. The presence of two tertiary amine donors in the co-ordination sphere of complex 1 results in a decrease of the potential of the chemically reversible Ru^{II}-Ru^{III} couple by 110 mV compared to $[Ru(terpy)_2]^{2+}$ $(E_{\frac{1}{2}} =$ +0.89 V vs. ferrocene-ferrocenium). This reflects the fact that a tertiary amine ligand is a better electron donor and a poorer π acid than a pyridyl ligand, both of which factors will result in stabilisation of the Ru^{III} state. Complex 2 behaves similarly; the slight difference in the potentials of the Ru^{II}-Ru^{III} couples of 1 and 2 is due to the fact that the phenanthroline fragments of 2 stabilise the Ru^{II} state more effectively than the bipyridine fragments of 1 as they are stronger π acids. At higher potentials both 1 and 2 undergo a completely irreversible oxidation of the C₆H₄NMe₂ ligand fragments. Reductive cyclic and squarewave voltammetry of 1 and 2 revealed the presence of irreversible, poorly defined ligand-based reductions, in striking contrast to the well defined reversible reductions of $[Ru(terpy)_2]^{2^+,1}$ The peak potentials for these reductions in Table 12 are therefore taken from square-wave voltammograms.

Replacement of one tertiary amine group by a cyclometallated phenyl ligand results in a dramatic drop in the Ru^{II}-Ru^{III} couples, by 0.84 V in each case. This is comparable to, but slightly larger than, a decrease of 0.7–0.8 V in the Ru^{II}-Ru^{III} couples of [Ru(terpy)₂]²⁺ derivatives when a pyridyl ligand is similarly replaced by a cyclometallating phenyl ligand,¹⁴ and is due to the increased electron density at the metal provided by the strong σ donor: the additional effect of the electrondonating NMe₂ substituent on the cyclometallated rings is apparent. Both complexes also undergo an irreversible ligandbased oxidation, at +0.75 V vs. ferrocene–ferrocenium, and two reversible or quasi-reversible ligand-based reductions at extreme negative potentials.

Complexes 1 and 2 both undergo a metal-to-ligand chargetransfer (m.l.c.t.) transition in the visible region, with maxima at 452 and 435 nm respectively in acetonitrile, as compared to 474 nm for $[Ru(terpy)_2]^{2+.1}$ The blue-shift of the absorption maxima compared to that of $[Ru(terpy)_2]^{2+}$ means that the $Ru(d\pi)-L^1(\pi^*)$ gap is slightly higher. Since amines are weakerfield ligands than pyridines it cannot be the case that the $Ru(d\pi)$ levels are lowered due to a higher ligand field; the dominant effect must be that the lowest unoccupied molecular orbitals of L^1 and L^2 are higher in energy than that of terpy due to (*i*) loss of a stabilising heterocyclic N atom from the aromatic network, and (*ii*) the presence of an electron-donating NMe₂ group. The 834

presence of low-energy shoulders on these m.l.c.t. peaks is consistent with the low symmetry of the complexes; the $Ru(d\pi)$ levels are not degenerate and a range of m.l.c.t. energies is to be expected. Complexes 1 and 2 show no luminescence in acetonitrile solution at room temperature.

The characteristic ¹⁴ m.l.c.t. bands of complexes 3 and 4 are at 502 and 532 nm respectively in MeCN; there is a pronounced shoulder on the low-energy side of this transition in the spectrum of 3. The lower energy of the m.l.c.t. maximum of 4 relative to 3 is in contrast to the higher energy of the m.l.c.t. band of 2 relative to 1. Thus the m.l.c.t. band of 1 is red-shifted by 2200 cm⁻¹ on cyclometallation, whereas that of 2 shifts by 4200 cm^{-1} . The reason for this is not known.

Conclusion

Both L^1 and L^2 are ambidentate ligands which can bind to Ru^{II} either as 'conventional' meridional N₃ donors or cyclometallating meridional N₂C donors, in which the phenyl rings are turned around such that the deprotonated C⁶ binds to the metal and the NMe₂ substitutent at the C² position is directed away from the metal. Cyclometallation requires the presence of *N*-methylmorpholine in the reaction mixture. In complexes 1 and 2 both ligands bind to the metal in the 'conventional' mode, whereas 3 and 4 both contain one 'conventional' and one cyclometallated ligand. We found no evidence for complexes in which *both* ligands were cyclometallated. The electrochemical properties are consistent with the expected observations that (*i*) tertiary amines are weak σ donors and (*ii*) formally anionic carbon-donor ligands are strong σ donors.

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