New Ruthenium(II) Complexes with Pyridylpyrazole Ligands. Photosubstitution and ¹H, ¹³C, and ⁹⁹Ru NMR Structural Studies

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The preparations and properties of ruthenium(II) complexes containing the bidentate ligand 1-(2-pyridyl)-3,5-dimethylpyrazole, L, are described. The tris complex RuL_3^{2+} is shown to readily undergo photosubstitution in acetonitrile solution to produce $RuL_2(CH_3CN)_2^{2+}$, which in the presence of other bidentate ligands undergoes thermal substitution of the coordinated acetonitrile. ¹H, ¹³C, and ⁹⁹Ru NMR spectra are reported for all the complexes. Proton and carbon-13 NMR reveal the presence of geometrical isomerism, where it exists; proton and ruthenium-99 NMR allow the evaluation of the percentage of these isomers. Ruthenium-99 NMR proves to be an excellent probe of electron density at the metal and is possibly useful to evaluate the amount of π-back-bonding depending on the ligands. Electronic spectral data and oxidation potential measurements are given for comparison with those of the well-known $Ru(bpy)_3^{2+}$ complex but do not lead to consistent results.

Introduction

The ground- and excited-state properties[2-13] of tris(2,2'-bipyridine)ruthenium(II), $Ru(bpy)_3^{2+}$, and its substituted-bipyridine and benzopyridyl analogues,[5,6,10,11] have been the subject of intense interest in recent years, particularly due to the utilization of such complexes as photosensitizers in the photoreduction of water.[2,14-19]

The majority of such studies have involved complexes containing symmetrical, π-deficient, bipyridine-type ligands such as substituted bipyridines, biquinolines, phenanthrolines,[2,5,6,10,11] and polyazabipyridines.[20-22] It is only relatively recently that such work has been extended to the preparation of complexes containing bidentate ligands, L, that are substantially different from bipyridine. Such complexes might be expected to possess properties different from those of Ru-

(bpy)₃²⁺, which in turn might lead to a better understanding of $Ru(bpy)_3^{2+}$ itself. However few RuL_3^{2+} complexes of this type have been reported, examples being tris(2,2'-bi-2-thiazoline)ruthenium(II), which exhibits[23] absorption and emission properties similar to those of $Ru(bpy)_3^{2+}$, and tris(2-*p*-tolyl-pyridinecarboxaldimine)ruthenium(II), which does not exhibit dπ* emission bands.[21] On the other hand, several reports describe studies of the influence of L on the properties of complexes of the type $[Ru(bpy)_2L]^{2+}$, examples of L being 1,2-diamines,[24] 1,2-diimines,[24] olefins,[25] biimidazole,[21] diphosphines,[26] 2-(arylazo)pyridine,[27] and *o*-quinodiimine.[28]

Our own work has been directed toward the preparation of ruthenium complexes containing aromatic biheterocyclic ligands with π-acceptor abilities that are substantially different from those of bipyridines. The only previously reported ruthenium(II) complex containing such a ligand is bis(2,2'-bipyridine)(2,2'-biimidazole)ruthenium(II);[21] but when we have prepared this same complex (along with its N-dimethylated analogue) and made sure of its structure, we have found[29] it to show properties different from those previously reported. Furthermore, our results are in agreement with the known weak π-acceptor nature of imidazole[30] compared to that of pyridine.

The present work describes the properties of the complexes **1–3**, which possess one or several dissymmetric pyridylpyrazole ligands; pyrazole itself has been previously shown[31] to have π-acceptor capabilities weaker than those of pyridine but stronger than those of imidazole.

Experimental Section

Physical Measurements. Proton NMR spectra were recorded with either Varian T60 or Varian HA100 spectrometers using Me₄Si as internal reference.

Carbon-13 NMR spectra were recorded with a Bruker WP80DS spectrometer operating at 20.115 MHz (standard resolution 0.9 Hz).

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(2) Balzani, V.; Boletta, F.; Gandolfi, M.-T.; Maestri, M. *Top. Curr. Chem.* **1968**, *75*, 1.
(3) Rillema, D. P.; Jones, D. S.; Levy, H. A. *J. Chem. Soc., Chem. Commun.* **1979**, 849.
(4) Ferguson, J.; Mau, A. W.-H.; Sasse, W. H. F. *Chem. Phys. Lett.* **1979**, *68*, 21.
(5) Anderson, S.; Seddon, K. R.; Wright, R. D. Cocks, A. T. *Chem. Phys. Lett.* **1980**, *71*, 220.
(6) Creutz, C.; Chou, M.; Netzel, T. L.; Okumura, M.; Sutin, N. *J. Am. Chem. Soc.* **1980**, *102*, 1309.
(7) Felix, F.; Ferguson, J.; Güdel, H. U.; Ludi, A. *J. Am. Chem. Soc.* **1980**, *102*, 4096.
(8) Weiner, M. A.; Basu, A. *Inorg. Chem.* **1980**, *19*, 2797.
(9) Delaive, P. J.; Foreman, T. K.; Giannotti, C.; Whitten, D. G. *J. Am. Chem. Soc.* **1980**, *102*, 5627.
(10) Elfring, W. H.; Crosby, G. A. *J. Am. Chem. Soc.* **1981**, *103*, 2683.
(11) Fabian, R. H.; Klassen, D. M.; Sonntag, R. W. *Inorg. Chem.* **1980**, *19*, 1977.
(12) Schmehl, R. H.; Whitten, D. G. *J. Am. Chem. Soc.* **1980**, *102*, 1938.
(13) Lee, P. C.; Meisel, D. *J. Am. Chem. Soc.* **1980**, *102*, 5477.
(14) Valenty, S. J. *J. Am. Chem. Soc.* **1979**, *101*, 1.
(15) Valenty, S. J.; Behnken, D. E.; Gaines, G. L. *Inorg. Chem.* **1979**, *18*, 2160.
(16) Johansen, O.; Kowala, C.; Mau, A. W.-H.; Sasse, W. H. F. *Aust. J. Chem.* **1979**, *32*, 1453.
(17) Kirch, M.; Lehn, J.-M.; Sauvage, J.-P. *Helv. Chim. Acta* **1979**, *62*, 1345.
(18) Kiwi, J.; Grätzel, M. *J. Am. Chem. Soc.* **1979**, *101*, 7214.
(19) Chan, S.-F.; Chou, M.; Creutz, C.; Matsubara, T.; Sutin, N. *J. Am. Chem. Soc.* **1981**, *103*, 369.
(20) Hunziker, M.; Ludi, A. *J. Am. Chem. Soc.* **1977**, *99*, 7370.
(21) Dose, E.; Wilson, L. J. *Inorg. Chem.* **1978**, *17*, 2660.
(22) Crutchley, R. J.; Lever, A. B. P. *J. Am. Chem. Soc.* **1980**, *102*, 7129.
(23) Krug, W. P.; Demas, J. N. *J. Am. Chem. Soc.* **1979**, *101*, 4394.
(24) Brown, G. M.; Weaver, T. R.; Keene, F. R.; Meyer, T. J. *Inorg. Chem.* **1976**, *15*, 190.
(25) Sullivan, B. P.; Baumann, J. A.; Meyer, T. J.; Salmon, D. J.; Lehmann, H.; Ludi, A. *J. Am. Chem. Soc.* **1977**, *99*, 7368.
(26) Sullivan, B. P.; Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 3334.
(27) Goswami, S.; Chakravarty, A. R.; Chakravorty, A. *Inorg. Chem.* **1981**, *20*, 2246.
(28) Belser, P.; von Zelewsky, A. Zehnder, M. *Inorg. Chem.* **1981**, *20*, 3098.
(29) Unpublished results.
(30) Sundberg, R. J.; Bryan, R. F.; Taylor, I. F.; Taube, H. *J. Am. Chem. Soc.* **1974**, *96*, 381.
(31) Sullivan, P.; Salmon, D. J.; Meyer, T. J.; Peedin, J. *Inorg. Chem.* **1979**, *18*, 3369.

$RuL_3(PF_6)_2$ (1)

$Ru(bpy)L_2(PF_6)_2$ (2)

$Ru(bpy)_2L(PF_6)_2$ (3)

Scheme I
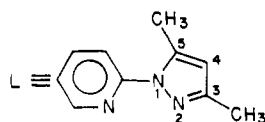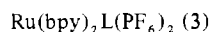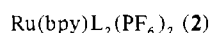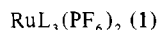
Ruthenium-99 NMR spectra were recorded with a Bruker WM250 spectrometer equipped with a multinuclear accessory, operating at 11.541 MHz and using 10-mm tubes.[32]

UV–visible absorption spectra were recorded on a Varian Superscan III spectrophotometer using 10-mm-path quartz cells. The cell compartment temperature was maintained at 21 ± 1 °C.

Luminescence spectra were recorded on a spectrofluorimeter built in the laboratory. It consists of a 150-W xenon lamp powered by a CUNOW stabilized power supply and two Instrument S.A. John Yvon M25 monochromators fitted with continuously variable slits and a grating of 1200 lines/mm (blazed at 350 nm in excitation and 500 nm in emission) having a linear dispersion of 3 nm/mm. An RCA 1P21 low-noise photomultiplier is used as a detector. The exciting light is chopped by means of a Brockdeal 9728 chopper, and lock-in detection is carried out with a PAR 5024 to enhance the S/N ratio. A beam splitter, in front of the square cell, reflects part of the exciting light toward a rhodamine B quantum counter followed by a Model 150 Si detector connected to a Model 88 XL radiometer from Photodyne Corp. The output signal of the PAR 5024 is divided by the latter signal to give corrected excitation spectra. Relative quantum yields are computed by the optically dilute method ($A < 0.02$), with $Ru(bpy)_3Cl_2$ in H_2O at 20 °C as a reference. Data are for air-equilibrated samples and are not corrected for instrument response, with the result that actual emission maxima should be red shifted by 5–10 nm. Slit and band widths were respectively 2 and 1 mm.
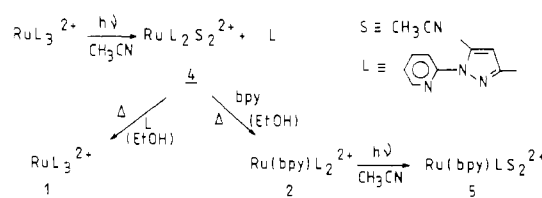
Electrochemical measurements were obtained on a PRT40 potentiostat driven by a Serwovit pilot from Tacussel. A standard three-electron circuit was used, with platinum rotating and auxiliary electrodes. The saturated calomel reference electrode was isolated from the sample by a solvent bridge. The solvent was dried Spectrograde acetonitrile from Merck, which was made 0.1 M in tetraethylammonium perchlorate. Oxidation curves were recorded on an EPL 2B recorder fritted with a TI 20G amplifier from Tacussel. A 60 mV/mm scan speed was used.

Materials and Syntheses. $RuCl_3 \cdot 3H_2O$ and $Ru(bpy)_2Cl_2 \cdot 2H_2O$ were purchased from Ega Chemie and Strem Chemicals. $Ru(bpy)Cl_3 \cdot H_2O$ was prepared according to the method of Krause.[33] The ligand 1-(2-pyridyl)-3,5-dimethylpyrazole was prepared by refluxing a solution of 2-hydrazinopyridine hydrochloride and acetylacetone in ethanol for 4 h instead of isopropyl alcohol as previously described.[34] After concentration the residue was dissolved in water, neutralized with sodium bicarbonate, and twice extracted with ether. The combined extracts were washed, dried, and concentrated to give an oil, which was purified by bulb-to-bulb distillation; bp(18 mm) 150 °C (bath temperature) (lit.[34] bp(18 mm) 130 °C). 1-(2-Pyridyl)pyrazole was obtained by an analogous procedure with tetraethoxypropane in place of acetylacetone; mp 37–38 °C (lit.[35] mp 38–40 °C).

RuL₃(PF₆)₂ (1) and Ru(bpy)₃(PF₆)₂ (7). These complexes were prepared from $RuCl_3 \cdot 3H_2O$ by a method analogous to that described by Lin et al.,[36] as recommended by Anderson and Seddon:[37] 1, dark yellow crystals, yield 60%. Anal. Calcd for $C_{30}H_{33}N_9RuP_2F_{12}$: C, 39.57; H, 3.65; N, 13.84. Found: C, 39.30; H, 3.65; N, 13.74.

Ru(bpy)L₂(PF₆)₂ (2). $Ru(bpy)Cl_3 \cdot H_2O$ (5×10^{-4} mol) and ligand L (2.2×10^{-3} mol) were refluxed in a 4:1 H_2O/EtOH solution for 24 h. After concentration to dryness the residue was carefully washed with ether to remove the excess ligand and the resulting solid dissolved in water (20 mL); the complex was precipitated as the hexafluoro-

phosphate by dropwise addition of a concentrated NH_4PF_6 solution. The precipitate was filtered, washed, and dried to give brown crystals, yield 60%. Anal. Calcd for $C_{30}H_{30}N_8RuP_2F_{12} \cdot H_2O$: C, 39.53; H, 3.54; N, 12.29. Found: C, 39.59; H, 3.32; N, 12.38.

The complex 2 was also obtained from $RuL_2(CD_3CN)_2(PF_6)_2$ (4) by overnight reflux in ethanol in the presence of excess bipyridine. The residue obtained after concentration to dryness was washed with ether and then dissolved in CH_3CN, and 2 was precipitated by addition of ether.

Ru(bpy)₂L(PF₆)₂ (3). *cis*-Dichlorobis(bipyridine)ruthenium(II) (2×10^{-4} mol) was dissolved in 3:1 $EtOH/H_2O$ (20 mL) and refluxed for 1 h. The ligand L was then added, and refluxing continued for a further 2–4 h until no further color change occurred. After filtration the solution was concentrated to dryness and the residue dissolved in water (20 mL). The complex was precipitated as the hexafluorophosphate by dropwise addition of a concentrated NH_4PF_6 solution. The product was filtered and recrystallized from $EtOH/H_2O$ to give pure 3 as red-brown crystals, yield 70%. Anal. Calcd for $C_{30}H_{27}N_7RuP_2F_{12}$: C, 41.11; H, 3.10; N, 11.19. Found: C, 41.26; H, 3.12; N, 11.14.

RuL₂(CD₃CN)₂(PF₆)₂ (4). The complex was obtained in quantitative yield by irradiation of 1 in CD_3CN with visible light for several days. The resulting solution was poured into ether to give a precipitate, which was filtered, washed with ether, and dried. Anal. Calcd for $C_{24}H_{22}D_6N_8RuP_2F_{12}$: C, 34.92; H, 3.50; N, 13.57. Found: C, 35.07; H, 3.51; N, 13.49.

Results and Discussion

Photochemistry of the Complex 1. The $Ru(bpy)_3^{2+}$ complex was for a long time thought to be photochemically inert.[38] However, this complex has been shown to be photochemically sensitive under acid conditions[39] and in chlorinated solvents[40] although in most cases the products of such photolyses were not identified, unlike those obtained by photoanation reactions.[41] Although acetonitrile has been reported to thermally substitute certain bidentate ligands[42] and photochemically substitute monodentate ligands such as azido groups[43] and amines,[44] no such photosubstitution of bidentate ligands has been reported to our knowledge.

Visible-light irradiation of the RuL_3^{2+} complex, 1, in acetonitrile produces a quantitative transformation that can be followed by absorption spectroscopy or proton NMR and that leads to formation of the complex 4 (Scheme I). That the reaction is indeed photochemical was verified by the fact that a solution of 1 in acetonitrile underwent no change in the absence of light, either at room temperature or under reflux for 6 days.

The presence of coordinated acetonitrile was demonstrated by proton NMR for a sample irradiated in CH_3CN and

(32) Brevard, C.; Granger, P. *Inorg. Chem.* **1983**, *22*, 532.

(33) Krause, R. A. *Inorg. Chim. Acta* **1977**, *22*, 209.

(34) Grandberg, I. I.; Krokhina, N. F.; Kondrat'ev, M. N. *Khim.-Farm. Zh.* **1968**, *2*, 24.

(35) Khan, M. A.; Polya, J. P. *J. Chem. Soc. C* **1970**, 85.

(36) Lin, C. T.; Bottcher, W.; Chou, M.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1976**, *98*, 6536.

(37) Anderson, S.; Seddon, K. R. *J. Chem. Res., Synop.* **1979**, 74.

(38) Malouf, G.; Ford, P. C. *J. Am. Chem. Soc.* **1974**, *96*, 601.

(39) Demas, J. N.; Adamson, A. W. *J. Am. Chem. Soc.* **1973**, *95*, 5159. Van Houten, J.; Watts, R. J. *Ibid.* **1976**, *98*, 4853. Van Houten, J.; Watts, R. J. *Inorg. Chem.* **1978**, *17*, 3381.

(40) Gleria, M.; Minto, F.; Beggiaro, G.; Bortolus, P. *J. Chem. Soc., Chem. Commun.* **1978**, 285.

(41) Hoggard, P. E.; Porter, G. B. *J. Am. Chem. Soc.* **1978**, *100*, 1457. Wallace, W.; Hoggard, P. *Inorg. Chem.* **1980**, *19*, 2141.

(42) Staniewica, R. J.; Sumpson, R. F.; Hendricker, D. G. *Inorg. Chem.* **1977**, *16*, 2166. Staniewicz, R. J.; Hendricker, D. G. *J. Am. Chem. Soc.* **1977**, *99*, 6581.

(43) Brown, G. M.; Callahan, R. W.; Meyer, T. J. *Inorg. Chem.* **1975**, *14*, 1915.

(44) Keene, F. R.; Salmon, D. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1976**, *98*, 1884.
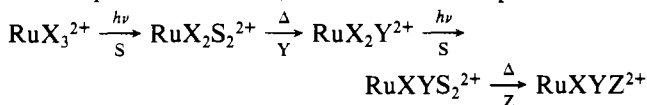
Table I. ^{1}H Chemical Shifts (ppm) of the L and Bipyridine Ligands Free and Complexed[a] with Ruthenium in Deuterated Acetonitrile[b]

compd		3-CH$_3$	5-CH$_3$	H4	H3'	H4'	H5'	H6'	bpy
							L		
L		2.22	2.58	6.00	~7.7	~7.7	7.16	8.30	
bpy									8.49 (H3), 7.80 (H4), 7.28 (H5), 8.70 (H6)
RuL$_3$$^{2+}$	1A	1.65 (−0.57)	2.84 (+0.26)	6.37 (+0.37)	8.00 (+0.3)	~7.7	7.22 (+0.06)	8.00 (−0.30)	
	1B	1.52 (−0.70), 1.55 (−0.67), 1.63 (−0.59)	2.84 (+0.26)	6.37 (+0.37)	8.00 (+0.3)	~7.7	7.22 (+0.06)	8.00 (−0.30)	
Ru(bpy)L$_2$$^{2+}$	2C	1.44 (−0.78)	2.84 (+0.26)	6.31 (+0.31)			7.1–8.0		8.44 (H3)
	2D	1.57 (−0.65)	2.84 (+0.26)	6.42 (+0.42)					
	2E	1.47 (−0.75), 1.68 (−0.54)	2.84 (+0.26)	6.28 (+0.28), 6.37 (+0.37)					
Ru(bpy)$_2$L^{2+}	3	1.50 (−0.72)	2.84 (+0.26)	6.35 (+0.35)			7.2–8.2		8.44 (H3)
Ru(bpy)$_3$$^{2+}$									8.50 (H3), 8.05 (H4), 7.39 (H5), 7.73 (H6)
Ru(CH$_3$CN)$_2$L$_2$$^{2+}$ ^{c}	4C	2.62 (+0.40)	2.86 (+0.28)	6.59 (+0.59)	7.5–8.00	~7.1	7.5–8.00		
	4D	1.50 (−0.72)	2.86 (+0.28)	6.21 (+0.21)	7.5–8.00	~7.1	7.5–8.00		
	4E	1.62 (−0.60), 2.66 (+0.44)	2.86 (+0.28)	6.21 (+0.21), 6.59 (+0.59)	7.5–8.00	~7.1	7.5–8.00		

^{a} In all cases the anion is PF$_6$$^-$. ^{b} Values in parentheses are the chemical shift differences between the complexed and noncomplexed ligand. ^{c} δ(CH$_3$CN) = 2.26, 2.30.

concentrated to dryness, and its spectrum was recorded in CD$_3$CN. Elemental analysis of the complex 4 excluded the possibility of a photoaddition leading to a 7- or 8-coordinate system or a partial photodisplacement in which, for example, only the pyridine part of the ligand remained coordinated. Photorearrangement of the ligand was also discounted since the displaced ligand could be recovered unchanged. The proposed photosubstitution of one ligand, L, by two acetonitrile molecules is further supported by the oxidation potential and absorption spectrum of compound 4 (see below).

The coordinated CH$_3$CN molecules were observed, by proton NMR, to slowly exchange with CD$_3$CN at room temperature. Such exchange has previously[45] been observed, as have thermal substitutions of acetonitrile molecules by bidentate ligands in ruthenium(II) complexes containing π-allyl and dienyl ligands. This thermal lability, along with the photochemical substitution reaction, were incorporated into a new method for the syntheses of mixed-ligand ruthenium(II) complexes of the type RuX$_2$Y^{2+} and RuXYZ^{2+} such as 2 and 5. Care must be taken with the order of introduction of the ligands, X, Y, and Z, according to their stabilities toward further photosubstitution, for the reaction sequence

$$RuX_3{}^{2+} \xrightarrow[S]{h\nu} RuX_2S_2{}^{2+} \xrightarrow{\Delta}_{Y} RuX_2Y^{2+} \xrightarrow[S]{h\nu}$$

$$RuXYS_2{}^{2+} \xrightarrow{\Delta}_{Z} RuXYZ^{2+}$$

Nuclear Magnetic Resonance. Proton NMR. The proton chemical shifts for complexes 1–4 are listed in Table I. Signals have been attributed by the use of H–H coupling constants and also, for the bipyridine moiety, by comparison with the signals of bipyridine complexes already described.[48,52] The proton NMR spectra allow the observation and identification of the geometrical isomers[46a] present in the octahedral complexes RuX$_3$$^{2+}$, RuX$_2(bpy)^{2+}$, and RuX$_2$(CH$_3$CN)$_2$$^{2+}$, where X is a nonsymmetrical bidentate ligand. While such

(45) Schrock, R. R.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1974**, 951.
(46) (a) Hawkins, C. J. "Absolute Configuration of Metal Complexes"; Wiley-Interscience: New York, 1971. (b) Holm, R. H. "Dynamic Nuclear Magnetic Resonance Spectroscopy"; Jackman, L. M., Cotton, F. A., Eds., Academic Press: New York, 1975, p 340.
(47) Wilson, L. J.; Bertini, I. *J. Coord. Chem.* **1971**, *1*, 237.
(48) Belser, P.; von Zelewsky, A. *Helv. Chim. Acta* **1980**, *63*, 1675.
(49) Cook, M. J.; Lewis, A. P.; Mcauliffe, G. S. G.; Thomson, A. J. *Inorg. Chim. Acta* **1982**, *64*, 125.
(50) Walsh, J. L.; Durham, B. *Inorg. Chem.* **1982**, *21*, 329.
(51) Spotswood, T. M.; Tanzer, C. I. *Aust. J. Chem.* **1967**, *20*, 1227.
(52) Bryant, G. M.; Fergusson, J. E. *Aust. J. Chem.* **1971**, *24*, 441. Lytle, F. E.; Petrosky, M.; Carlson, L. R. *Anal. Chim. Acta* **1971**, *57*, 239.

Figure 1. Geometric isomers of the complex RuL$_3$(PF$_6$)$_2$ (1).

Figure 2. Geometric isomers of the complexes Ru(bpy)L$_2$ (PF$_6$)$_2$ (2) and Ru(CH$_3$CN)$_2$L$_2$(PF$_6$)$_2$ (4) (S = CH$_3$CN).

isomerism has been detected by proton NMR for complexes of various other transition metals,[46a,b] particularly cobalt,[47] it has not been reported for ruthenium complexes of nonsymmetrical ligands[21,48] until very recently.[49]

In the complexes reported here the methyl group in position 3 of the ligand, L, acts as an excellent probe for this isomerism due to its spatial relationship to the pyridine and pyrazole rings of the other ligands in the complex. Thus, in the NMR spectrum of the RuL$_3$(PF$_6$)$_2$ complex, 1, the methyl group in position 3 gives four signals due to the presence of the two isomers 1A and 1B (Figure 1) even at 60 MHz whereas anisochrony of bipyridyl protons becomes observable only at 400 MHz.[49] In isomer 1A, which possesses a C$_3$ axis of symmetry, the three ligands are equivalent while in isomer 1B, which possesses no internal symmetry, all three ligands are nonequivalent.

Similarly the methyl group in position 3 gives rise to four signals in complexes 2 and 4 due to the presence of the three isomers C, D, and E (Figure 2). In the case of complex 4 the possibility of additional trans isomers is excluded by steric interactions, as has been shown to be the case for the Ru-(bpy)$_2$(CH$_3$CN)$_2$$^{2+}$ complex.[43,50] Isomers C and D each possess a C$_2$ axis of symmetry, which renders the two ligands equivalent, while isomer E possesses no internal symmetry. Examination of molecular models of the complexes explains the observed chemical shifts and leads to full spectral assignment. The signals due to the methyl in position 3 can be

classified into four groups according to the spatial relationship of the methyl to the other ligands in the complex:

(i) Signals displaced approximately 0.75 ppm upfield relative to those of the uncomplexed ligand, L, correspond to methyl groups that lie above the plane of a pyridine ring of a bipyridine ligand. These upfield shifts are very similar to those reported[49] for the methyls of the Ru(bpy)$_2$(2,9-dimethyl-phenanthroline)(PF$_6$)$_2$ complex, which are shielded by 0.73 ppm relative to those of the uncomplexed ligand.

(ii) Signals shifted by 0.65–0.70 ppm to high field are assigned to methyl groups that lie above a pyridine ring of the ligand, L.

(iii) Signals shifted approximately 0.55 ppm upfield correspond to methyl groups lying above the plane of a pyrazole ring.

(iv) Signals shifted approximately 0.40 ppm downfield represent methyl groups that are deshielded by an acetonitrile molecule.

Although the signals due to the other protons of the ligands in complexes **1**, **2**, and **4** either are broadened or show a multiplicity greater than that of the uncomplexed ligand, as is the case for the proton in position 4, they do not allow an identification of the isomers present. These signals are shifted relative to those of the uncomplexed ligand but to a smaller extent than the methyls in position 3 since the anisotropic effect of neighboring ligands is no longer predominant and several other factors must be considered such as electronic perturbation due to complexation and a variation in conformation between the uncomplexed ligand, which exists preferentially in the transoid form,[51] and the complexed ligand, which is obligatorily cisoid.[52] The shifts observed, on complexation, of the pyridine protons of L are the same type, but smaller, as those observed for Ru(bpy)$_3$$^{2+}$.[48,52]

The 1:4 isomeric ratio observed for **1A:1B** indicates a slightly greater stability of the trans isomer, which is consistent with the steric interaction between the three methyls of the cis isomer **1A**. In the case of complex **2** the relative percentages of the three isomers formed in the two methods of preparation described in the Experimental Section were not the same.

Carbon-13 NMR. The carbon-13 chemical shifts and coupling constants are listed in Table II; signals have been assigned to specific carbon atoms by using direct and long-distance C–H coupling constant ($^1J_{CH}$, $^2J_{CCH}$, $^3J_{CCCH}$) values mainly for the pyridinic moieties as they depend on C and H positions toward the nitrogen atom.[53] The complexity of the carbon-13 NMR spectra of complexes **1** and **2** is such that it was not possible to assign specific resonances to individual isomers, with the effect of different spatial environments being felt by all the carbons present. The asymmetry introduced by the ligand, L, in complex **3**, Ru(bpy)$_2$L^{2+}, makes all four pyridine rings nonequivalent, with the result that up to four peaks are observed for each bipyridine carbon. Very recently such a complexity has been reported for Ru(II) tris complexes of unsymmetrical 2,2'-bipyridyls.[49]

In the Ru(bpy)$_3$(PF$_6$)$_2$ complex, **7**, all carbons are shifted downfield as a result of complexation with the ruthenium. The Hexakis(pyridine)ruthenium(II) complex Ru(py)$_6$(PF$_6$)$_2$ shows[54] similar behavior although the magnitudes of the shifts are quite different (C2, +5.3 ppm; C3, +0.6 ppm; C4, +0.7 ppm), particularly for carbons β to the complexing nitrogen. The only other related complexes studied by carbon-13 NMR are a series of the type Ru(NH$_3$)$_5$py^{2+}, where the pyridine is variously substituted.[55] The study suggested that the chemical shift of the carbon para to the complexed nitrogen reflects the
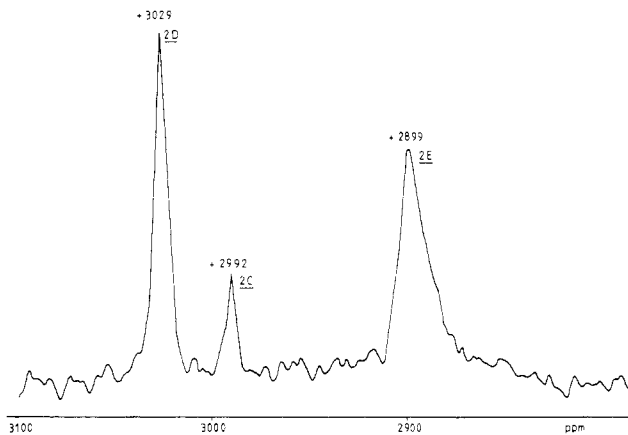

Figure 3. ^{99}Ru NMR spectrum of the complex Ru(bpy)L$_2$(PF$_6$)$_2$ (**2**) in acetonitrile.

degree of π-back-bonding present; in these compounds the para carbon was shifted upfield. This result has recently[56] been contested on the basis of π-electron density calculations. In the case of our complexes the pyridine carbon atoms para to the coordinated nitrogen atom, C4 or C4', experience similar shifts (+2.0 to +2.3 ppm for C4 and +2.6 ppm for C4') regardless of the other ligands present (L or bipyridine). In fact comparison of the spectra of comploexes **2**, **3**, and **7** shows that the effect of complexation on the chemical shifts of all the bipyridine carbons is independent of the number (2, 1, or 0) of ligands L present.

For comparison Table II also lists the effects of monoprotonation (as has previously been done for pyridine[55]) as well as complexation with iron(II)[57] on the chemical shifts of bipyridine. Complexes of Ru(II) and Fe(II) have often been compared,[58] and it has been shown that the iron complexes are less sensitive to π-back-bonding; it is interesting to note that the carbon-13 shifts are of the same magnitude in both cases, even for the para carbon. These results support the suggestion[56] that the carbon-13 chemical shifts are more related to other factors than to the degree of π-back-bonding present.

It is also noteworthy that the effect of complexation is quite different for the pyridine ring carbons of the ligand L (except C4') compared to those of the bipyridine, and particularly so for C3', which is systematically shifted upfield. This carbon is probably very much affected by the change in conformation between the free and complexed ligand and may experience an upfield shift due to steric compression from the methyl group in position 5 of the pyrazole.

Complexation with ruthenium leads to an increase in all ^{13}C–H coupling constants, $^1J_{CH}$, $^2J_{ortho}$, $^3J_{meta}$, of the pyridine carbons, and these variations are of the same magnitude as those observed for protonated bipyridine.

Ruthenium-99 NMR. The NMR spectroscopy of this nucleus has only recently been developed,[32,59,60] and it has been shown[32] that it is a sensitive probe to the electron density about the metal. The ^{99}Ru NMR chemical shifts of our complexes show a strong dependence on the nature of the ligands present (see Table III). For example, successive replacement of a bipyridine ligand by a ligand L (complexes **7**, **3**, **2**, and **1**) leads

(53) Hansen, M.; Jakobsen, H. J. *J. Magn. Reson.* **1973**, *10*, 74.
(54) Templeton, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 4906.
(55) Lavallee, D. K.; Baughman, M. D.; Phillips, M. P. *J. Am. Chem. Soc.* **1977**, *99*, 718.

(56) Van Dam, H.; Booxhoorn, G.; Stufkens, D. J.; Oskam, A. *Inorg. Chim. Acta* **1981**, *53*, L235.
(57) Tanzer, C.; Price, R.; Breitmaier, E.; Jung, G.; Voelter, W. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 963.
(58) Bryant, G. M.; Fergusson, J. E.; Powell, H. K. J. *Aust. J. Chem.* **1971**, *24*, 257. Creutz, C.; Chou, M.; Netzel, T. L.; Okumara, M.; Sutin, N. *J. Am. Chem. Soc.* **1980**, *102*, 1309. Weiner, M. A.; Basu, A. *Inorg. Chem.* **1980**, *19*, 2797.
(59) Brevard, C.; Granger, P. *J. Chem. Phys.* **1981**, *75*, 4175.
(60) Dykstra, R. W.; Harrison, A. M. *J. Magn. Reson.* **1981**, *45*, 108.

Table II. ¹³C Chemical Shifts (ppm) and ¹³C–H Coupling Constants of Free and Complexed Ligands in Deuterated Acetonitrile

| compd	R3	R5	C3	C4	C5	C2'	C3'	C4'	C5'	C6'	C2	C3	C4	C5	C6
					L								bpy		
bpy[c]											156.3	121.1 (167, 6)	136.8 (164, 7)	123.7 (165, 7)	149.2 (178, 6, 4)
RuL₃²⁺ (1)	13.6 (128)	14.4 (130)	149.3	109.1 (174)	141.7	154.0	115.9	138.3	120.7	147.7					
Ru(bpy)L₂²⁺ (2)	12.4 (129) [−1.2]	15.6 (131) [+1.2]	152.3–153.2 [+3.0 to +3.9]	114.3–114.9 [+5.2 to +5.8]	146.6, 147.0 [+4.9, +5.3]	157.6, 157.8 [+3.6, +3.8]	114.3–114.9 [−1.0 to −1.6]	140.9 (+2.6)	124.3, 124.5 (~170) [+3.6, +3.8]	152.3–153.2 [+4.7 to +5.3]	158.5, 158.65, 158.8 [+2.2 to +2.5]	125.3, 125.4, 125.5 [−4.2 to +4.4]	138.7, 138.85, 139.0 [+1.9 to +2.2]	128.5–128.9 [+4.8 to +5.2]	151.8–154.0
Ru(bpy)₂L²⁺ (3)	12.4, 12.5 [−1.1, −1.2]	15.65 [+1.25]	151.8–154.0	114.4–114.9 [+5.3 to +5.8]	146.7, 146.9, 147.0 [+5.0 to +5.3]	157.6, 157.7 [+3.6, +3.7]	114.4–114.9 [−1.0 to −1.5]	140.8, 140.9 [+2.5, +2.6]	124.2, 124.3, 124.4 [+3.5 to +3.7]	151.8–154.0	158.1–158.7 [+1.8 to +2.4]	125.4 (169) [+4.3]	138.9, 139.1 (170) [+2.1, 2.3]	128.5–128.8 (170) [+4.8 to 5.1]	152.9–153.4 (182) [+3.7 to 4.2]
Ru(bpy)₃²⁺ (7)[c]	12.5 [−1.1]	15.7 [+1.3]	152.9–153.4	114.7 [+5.6]	147.0 [+5.3]	157.6 [+3.6]	114.9 [−1.0]	140.8 [+2.5]	124.3 [+3.6]	151.85 [+4.15]	158.2 [+1.9]	125.5 (169, 7) [+4.4]	139.0 (170, 7) [+2.2]	128.8 (172, 7, 7) [+5.1]	152.9 (185, 7, 4) [+3.7]
Fe(bpy)₃Cl₂[56]											[+3.1]	123.5	142.7	127.1	146.7
bpyH⁺ [d]											147.7 [−8.6]	123.5 (170, 6) [+2.4]	142.7 (170, 6) [+5.9]	127.1 (173, 6, 6) [+3.4]	146.7 (187, 6, 4) [−2.5]

[a] Values in parentheses are ¹J_CH coupling constants in Hz. [b] Values in brackets are the chemical shift differences between the complexed and noncomplexed ligands. [c] In CDCl₃. [d] BF₄⁻ in Me₂SO-d₆.

Table III. Electronic Spectra, Oxidation Potentials, and ⁹⁹Ru NMR Chemical Shifts in Acetonitrile

compd	absorption		emission			$E_{1/2}$, V	⁹⁹Ru NMR, ppm (relative to RuO₄)
	λ_{max}, nm	ϵ, M⁻¹ cm⁻¹	λ_{max}, nm	Q^a (±10%)			
RuL₃²⁺ (1)	382	15 200	...	0[b]		1.17	+2997 (1A) +3035 (1B)
Ru(bpy)L₂²⁺ (2)	435 (377) (272)	12 200	604	<1 × 10⁻³ [c]		1.21	+2992 (2C) +3029 (2D) +2899 (2E)
Ru(bpy)₂L²⁺ (3)	450 (413) (368) (350)	10 800	602	4 × 10⁻³		1.22	+2780
Ru(CD₃CN)₂L₂²⁺ (4)	360					1.36	
Ru(bpy)(CH₃CN)₂L²⁺ (5)	410 (350)	10 700		0[b]			
Ru(bpy)₂(CH₃CN)₂²⁺ (6)	425[50]					1.44	
Ru(bpy)₃²⁺ (7)	453 (430)	13 900	610	16 × 10⁻³		1.26	+2588

[a] Quantum yield of Ru(bpy)₃²⁺ undegassed in H₂O at 20 °C: 0.042.[39] [b] Even at 77 K. [c] See text.
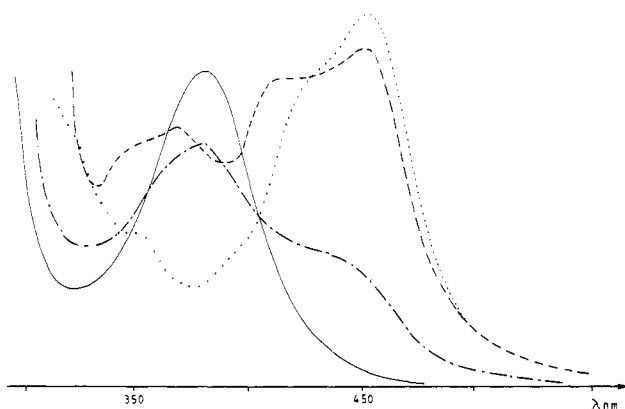
Figure 4. Absorption spectra of $RuL_3(PF_6)_2$ (1) (—), Ru(bpy)L$_2$-$(PF_6)_2$ (2) (—·—·), Ru(bpy)$_2$L$(PF_6)_2$ (3) (——), and Ru(bpy)$_3(PF_6)_2$ (7) (···) in CH_3CN.

to successive shifts to lower field, which seems consistent with decreased π-back-bonding since it is known that $Ru(NH_3)_6^{2+}$ resonates at +5800 ppm.[32]

Ruthenium-99 NMR was also found to be an excellent probe for the geometrical isomerism in complexes 1[32] and 2 (see Figure 3). Dissymmetric isomers can be distinguished by the distinct broadening of their signals as is the case in cobalt-59 NMR,[61] and isomer percentages can be straightforwardly measured, as is not always possible with proton NMR.

Electronic Spectra. The absorption and emission spectral parameters are listed in Table III. The $RuL_3(PF_6)_2$ complex, 1, shows an absorption maximum in acetonitrile at 378 nm which is of considerably higher energy than that of the Ru-(bpy)$_3(PF_6)_2$ complex (λ_{max} = 455 nm).

Factors that may contribute to this energy difference are as follows: (i) the important electronic changes resulting from the presence of pyrazole rings, which are known[31] to be poorer π-acceptors than bipyridines; (ii) the change in nature of the interring bond (C–N rather than C–C); (iii) geometrical factors resulting from the different "bite" of a 6–5 biheterocycle and associated changes in metal–ligand orbital overlaps.

The mixed complexes $Ru(bpy)_2L^{2+}$ or $Ru(bpy)L_2^{2+}$ are interesting in that their absorption spectra are in the form of a weighted superposition of the tris complexes, RuL_3^{2+} and $Ru(bpy)_3^{2+}$ (see Figure 4).

Until now two different types of behavior have been observed for such complexes. In the case of $Ru(bpy)_n(phen)_{3-n}^{2+}$ [62,63] the authors consider that the coupling between the ligands is strong enough to observe a single charge-transfer band, the position of which is intermediate between those of $Ru(phen)_3^{2+}$ and $Ru(bpy)_3^{2+}$. Recently it has been shown[5] in the case of $Ru(bpy)_n[2-(2-pyridyl)quinoline]_{3-n}^{2+}$ complexes that the charge-transfer states populated by absorption of visible light are essentially localized on individual ligands, which corresponds to a weak coupling between ligands. This last behavior seems to be clearly demonstrated in the case of $Ru(bpy)_3^{2+}$ itself, in which, in the excited MLCT state, the electronic density is localized on one of the bipyridines[64] and corresponds to a state representation of the type $Ru^{III}(bpy)_2(bpy^-·*)^{2+}$.[65] For the complexes described in this report, distinct low-energy bands with molecular absorption coefficients close to 10^4 are

observed (see Table III); thus they seem to belong to charge-transfer transitions localized on individual ligands with a weak coupling between them. This conclusion is reinforced by the luminescence results: in the case of RuL_3^{2+} (1) there is no emission even at 77 K. When L is replaced by a bipyridine as in compound 2, luminescence appears with energetic properties close to those of $Ru(bpy)_3^{2+}$ ($\lambda_{max} \simeq 604$ nm) but with a smaller quantum yield ($Q \simeq 10^{-3}$); excitation spectra analysis showed that this weak emission could be a composite due to, at least, two species, one being 3 or 7; however, the amount of such an impurity, possible formed through a thermal process, must be small: we have observed that complex 1 refluxed in ethanol with a bipyridine excess does not incorporate any bipyridine ligand as shown by ^1H NMR spectroscopy or only traces as shown by fluorescence. With the second bipyridine substitution, compound 3, the energy remains constant (λ_{max} = 602 nm) but Q increases to 4×10^{-3}. In the present case, the excitation spectrum clearly shows that the luminescence is not due to traces of 7 or of other Ru(II) complexes. If coupling between the two types of ligands were strong, one would have expected no emission for compounds 2 and 3.

Oxidation Potentials. Oxidation potentials of all the complexes studied are listed in Table III. For the series of complexes 7, 3, 2, 1, successive substitution of a bipyridine ligand by a ligand L results in a regular decrease in the oxidation potential. The measured potential for the $Ru(bpy)_2L^{2+}$ complex, 3, corresponds to those reported for complexes of the type $Ru(bpy)_2(diimine)^{2+}$ (1.20–1.33 V) and $Ru(bpy)_2(imino$ pyridine)$^{2+}$ (1.27 V).[24] The increased potential of complex 4 is consistent with significant π-back-bonding due to the nitrile groups[44] as is also the case for 6.[50]

Concluding Remarks

The ligand L, 1-(2-pyridyl)-3,5-dimethylpyrazole, is shown to bind easily to ruthenium(II) to give complexes such as RuL_3^{2+}, $Ru(bpy)L_2^{2+}$, and $Ru(bpy)_2L^{2+}$, the properties of which are compared to those of the well-known $Ru(bpy)_3^{2+}$. The distinguishing feature of these new complexes is their ready substitution in acetonitrile, and this property may be used synthetically to obtain mixed complexes; further work is in progress in this little-studied area of photosubstitution reactions of bidentate ligands that are coordinated to Ru(II). ^1H and ^{13}C NMR spectroscopic investigations, a technique rarely employed until now for this type of complex, are shown to be useful methods to indicate the presence of geometrical isomers. The usual electrochemical and spectroscopic methods (UV, visible, fluorescence) give somewhat contradictory results for the complexes that are the subject of this report concerning the extent of π-back-bonding; this demonstrates the difficulty in obtaining such information from various methods that measure different phenomena. A direct probe of the effect of changing ligands at the metal site has been provided by ^{99}Ru NMR spectroscopic measurements; preliminary studies show ^{99}Ru chemical shifts to be very sensitive to electron density at the metal and thus to the ligand nature. A study of Ru(II) complexes with bidentate 5-ring or 6-ring biheterocycles is in progress, in which the properties are modified by changing the nature, number, and position of the heteroatoms.

(61) Kidd, R. G.; Goodfellow, R. J. "NMR and the Periodic Table"; Harris, R. K., Mann, B. E., Eds., Academic Press: New York, 1978, p 225.
(62) Bosnich, B. *Inorg. Chem.* **1968**, 7, 2379.
(63) Crosby, G. A.; Elfring, W. H., Jr. *J. Phys. Chem.* **1976**, 80, 2206.
(64) Dallinger, R. F.; Woodruff, W. H. *J. Am. Chem. Soc.* **1979**, 101, 1355.
(65) Bradley, P. G.; Kress, N.; Hornberger, B. A.; Dallinger, R. F.; Woodruff, W. H. *J. Am. Chem. Soc.* **1981**, 103, 7441.