

Synthesis and electrochemical properties of bis(bipyridine)ruthenium(II) complexes bearing pyridinyl- and pyridinylidene ligands induced by cyclometalation of *N'*-methylated bipyridinium analogs

Take-aki Koizumi, Takashi Tomon, Koji Tanaka *

Institute for Molecular Science and CREST, Coordination Chemistry Laboratories, Japan Science and Technology Agency (JST), 5-1 Higashiyama, Myodaiji, Okazaki, Aichi 444-8787, Japan

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Abstract

Ruthenium complexes with bipyridine-analogous quaternized (N,C) bidentate ligands [RuL(bpy)₂](PF₆)₂ (bpy = 2,2'-bipyridine, (**1**), L = L¹ = *N'*-methyl-2,4'-bipyridinium; (**2**), L = L² = *N'*-methyl-2,3'-bipyridinium) were synthesized and characterized. The structure of complex **2** was determined by the X-ray structure analysis. The ¹³C{¹H} NMR spectroscopic and cyclic voltammetric studies indicate that the coordination modes of these ligands are quite different, that is, the C-coordinated rings of (N,C)-ligands in **1** and **2** are linked to ruthenium(II) with a pyridinium manner and a pyridinylidene one, respectively. The ligand-localized redox potentials of **1** and **2** also revealed the substantial difference in the electron donating ability of both ligands.

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1. Introduction

In recent years, ruthenium(II) complexes bearing 2,2'-bipyridine analogous (N,C) bidentate ligands such as 2-phenylpyridine (PhPy), 2-phenylquinoline (PhQn), and so on, have been reported and their photo- and electro-chemical properties have been investigated from the viewpoints of the comparison of analogous ruthenium(II) polypyridyl complexes [1–14]. The Ru–C bond-containing ruthenium complexes are thermally stable, and show significant differences in both the ground and excited state redox reactions compared to those of Ru-polypyridyl analogs. The ligand-localized

redox potentials of the complexes bearing (N,C) ligands appear at potentials more negative than those of (N,N) donors, because these (N,C) donors coordinate to metal centers as anion ligands. Several Pd and Pt complexes having quaternized (N,C) bidentate ligands derived from 2,2'- and 2,4'-bipyridine have been prepared [15–17]. The ligand-based redox potentials of those complexes with quaternized (N,C) ligands are similar or more positive as compared with those of bpy complexes. Despite a tremendous number of studies on ruthenium complexes with (N,N) ligands so far, analogous complexes having these quaternized (N,C) ligands have not been synthesized. Furthermore, there has been no example of transition metal complexes bearing quaternized 2,3'-bipyridine-derived (N,C) bidentate ligands. In this paper, we report the synthesis, structure and electronic

* Corresponding author. Tel.: +81564595580; fax: +81564595582.
E-mail address: ktanaka@ims.ac.jp (K. Tanaka).

properties of cyclometalated ruthenium(II) complexes with quaternized bipyridine-analogous (N,C) ligands.

2. Experimental

2.1. Materials and physical measurements

N'-methyl-2,4'-bipyridinium hexafluorophosphate ((**L**¹H)(PF₆)) and *N*-methyl-2,2'-bipyridinium hexafluorophosphate ((**L**³H)(PF₆)) were prepared by the anion exchange reaction of corresponding iodide ((**L**¹H)I [15d] and (**L**³H)I [17]) with NH₄PF₆ in water. 2,3'-bipyridine was synthesized by the Stille coupling reaction of 2-tri-(*n*-butyl)stannylpyridine with 3-bromopyridine, and [Ru(bpy)₂Cl₂] [18] were prepared according to the literature method. All other commercially available reagents were used as purchased. ¹H, ¹³C{¹H}, and ¹H-¹H COSY NMR spectra were recorded on a JEOL GX-500 spectrometer. ESI-MS spectra were obtained on a Shimadzu LCMS-2010 spectrometer. Electrochemical measurements were performed with ALS/chi Electrochemical Analyzer 660A. A conventional three-electrode configuration was used, with glassy carbon working (BAS PFCE carbon electrode) and platinum wire auxiliary electrode (BAS special order) and Ag|Ag⁺ reference (BAS RE-5). Cyclic Voltammogram were recorded at a scan rate of 100 mV s⁻¹. Elemental analyses were carried out by the Molecular Scale Nano-Science Center of IMS.

2.2. Preparation of *N*'-methyl-2,3'-bipyridinium hexafluorophosphate ((**L**²H)(PF₆))

To a CHCl₃ solution (20 mL) of 2,3'-bipyridine (500 mg, 3.20 mmol) was added an excess amount of MeI (2 mL, 32.2 mmol, ca. 10 equiv) and the mixture was refluxed. A yellow solid was precipitated after 10 min. Refluxing was continued for 2 h, then the precipitated powder was collected by filtration and dried in vacuo. The resulting yellow powder was dissolved in water (30 mL) and addition of excess amount of NH₄PF₆ to the solution precipitated an off-white solid. The solid was collected by filtration and dried in vacuo (670 mg, 70%). ESI-MS: *m/z* 171 {M-PF₆}⁺. Anal. Calc. for C₁₁H₁₁F₆N₂P: C, 41.79; H, 3.51; N, 8.86. Found: C, 41.69; H, 3.48; N, 8.83. ¹H NMR (acetone-*d*₆, 500 MHz); δ 9.73 (s, 1H, H^{2'}), 9.29 (d, 1H, *J*(H-H) = 8.5 Hz, H^{6'}), 9.10 (d, 1H, *J*(H-H) = 6.0 Hz, H^{4'}), 8.81 (dd, 1H, *J*(H-H) = 5.0 and 2.0 Hz, H²), 8.34 (t, 1H, *J*(H-H) = 7.5 Hz, H^{5'}), 8.24 (d, 1H, *J*(H-H) = 8.0 Hz, H⁵), 8.07 (dt, 1H, *J*(H-H) = 7.5 and 2.0 Hz, H⁴), 7.58 (dt, 1H, *J*(H-H) = 5.0 and 2.0 Hz, H³), 4.73 (s, 3H, *N*-Me). ¹³C{¹H} NMR (acetone-*d*₆, 125.65 MHz); δ 150.9, 150.4, 145.5, 144.5, 142.6, 139.8, 138.5, 128.7, 125.7, 122.1, 49.4.

2.3. Preparation of [RuL¹(bpy)₂](PF₆)₂ (**1**)

[RuCl₂(bpy)₂] (100 mg, 0.206 mmol), [**L**¹H][PF₆] (65 mg, 0.206 mmol) and triethylamine (2 mL) were dissolved in CH₃CH₂OH and refluxed for 3 h. The purple solution turned immediately to crimson in color. The solution was concentrated to ca. 1 mL, and poured into aqueous NH₄PF₆ solution. The generated reddish-brown precipitate was collected by filtration and dried in vacuo. Recrystallization from an acetone-Et₂O mixture afforded **1** as reddish-brown crystals (75 mg, 42%). ESI-MS: *m/z* 292 {M-2PF₆}²⁺. Anal. Calc. for C₃₄H₃₂F₁₂N₆OP₂Ru (**1** · acetone): C, 43.83; H, 3.46; N, 9.02. Found: C, 43.83; H, 3.60; N, 8.92. ¹H NMR (acetone-*d*₆, 500 MHz); δ 8.76 (d, 1H, *J*(H-H) = 9.0 Hz), 8.69 (d, 1H, *J*(H-H) = 8.0 Hz), 8.64 (m, 3H), 8.45 (d, 1H, *J*(H-H) = 6.5 Hz), 8.36 (d, 1H, *J*(H-H) = 7.0 Hz), 8.23 (d, 1H, *J*(H-H) = 5.5 Hz), 8.18 (dt, 1H, *J*(H-H) = 8.0 and 1.0 Hz), 8.07–8.00 (m, 6H), 7.96 (d, 1H, *J*(H-H) = 5.5 Hz), 7.92 (d, 1H, *J*(H-H) = 5.5 Hz), 7.89 (s, 1H), 7.85 (d, 1H, *J*(H-H) = 5.5 Hz), 7.61 (t, 1H, *J*(H-H) = 9.0 Hz), 7.45–7.40 (m, 4H), 7.37 (dt, 1H, *J*(H-H) = 5.5 and 1.0 Hz), 4.13 (s, 3H, *N*-Me). ¹³C{¹H} NMR (acetone-*d*₆, 125.65 MHz); δ 190.1 (Ru-C), 161.9, 161.2, 156.5, 155.9, 155.8, 154.2, 154.1, 151.1, 149.9, 149.8, 148.3, 147.9, 136.8, 136.2, 136.1, 135.7, 135.2, 135.1, 126.9, 126.5, 126.4, 126.3, 126.2, 123.3, 123.1, 123.0, 123.0, 123.0, 119.1, 46.7 (N-Me).

2.4. Preparation of [RuL²(bpy)₂](PF₆)₂ (**2**)

[RuCl₂(bpy)₂] (100 mg, 0.206 mmol) and [**L**²H][PF₆] (65.0 mg, 0.206 mmol) were dissolved in CH₃CH₂OH and stirred at 80 °C for 10 min. A CH₃OH solution of AgPF₆ (105 mg, 0.413 mmol) was added and the solution was refluxed. The purple solution turned immediately to orange in color, and a off-white precipitate (AgCl) appeared soon. After 1 h, the Ag salt was filtered off, and the solution was concentrated to ca. 1 mL, and poured into an aqueous NH₄PF₆ solution. The generated orange-brown precipitate was collected by filtration and dried in vacuo. Recrystallization from an MeCN-Et₂O mixture afforded **2** as dark orange crystals (74 mg, 41%). ESI-MS: *m/z* 292 {M-2PF₆}²⁺. Anal. Calc. for C₃₄H₃₂F₁₂N₆OP₂Ru (**2** · acetone): C, 43.83; H, 3.46; N, 9.02. Found: C, 43.47; H, 3.47; N, 9.03. ¹H NMR (acetone-*d*₆, 500 MHz); δ 9.00 (s, 1H), 8.81 (d, 1H, *J*(H-H) = 7.5 Hz), 8.71 (d, 1H, *J*(H-H) = 9.5 Hz), 8.69 (d, 1H, *J*(H-H) = 8.0 Hz), 8.44 (d, 2H, *J*(H-H) = 8.5 Hz), 8.22 (t, 1H, *J*(H-H) = 8.0 Hz), 8.13 (t, 1H, *J*(H-H) = 6.0 Hz), 8.11 (t, 1H, *J*(H-H) = 7.5 Hz), 8.05 (t, 1H, *J*(H-H) = 7.5 Hz), 8.05 (d, 1H, *J*(H-H) = 3.5 Hz), 8.04 (t, 1H, *J*(H-H) = 7.5 Hz), 8.02 (d, 1H, *J*(H-H) = 5.0 Hz), 8.01 (d, 1H, *J*(H-H) = 7.5 Hz), 7.98 (d, 1H, *J*(H-H) = 4.5 Hz), 7.92 (d, 1H, *J*(H-H) = 5.5 Hz), 7.87 (d, 1H, *J*(H-H) = 5.5 Hz), 7.75 (d,

^1H , $J(\text{H-H}) = 6.5$ Hz), 7.65 (t, 1H, $J(\text{H-H}) = 7.0$ Hz), 7.52 (t, 1H, $J(\text{H-H}) = 7.0$ Hz), 7.48 (t, 1H, $J(\text{H-H}) = 7.5$ Hz), 7.36 (t, 1H, $J(\text{H-H}) = 5.5$ Hz), 7.34 (t, 1H, $J(\text{H-H}) = 7.5$ Hz), 7.30 (d, 1H, $J(\text{H-H}) = 7.0$ Hz), 4.18 (s, 3H, N-Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (acetone- d_6 , 125.65 MHz); δ 232.1 (Ru-C), 161.2, 156.1, 155.8, 155.7, 153.3, 153.2, 150.3, 150.0, 149.9, 148.0, 147.1, 137.3, 136.4, 136.3, 136.2, 135.6, 134.5, 133.6, 132.4, 126.9, 126.7, 126.6, 126.5, 126.0, 124.8, 123.4, 123.1, 123.1, 123.0, 119.9, 45.7 (N-Me).

2.5. Crystal structure determination

Crystals for X-ray analyses were obtained as described in the preparations. Suitable crystals were mounted on glass fibers or sealed in thin-walled glass capillaries. Data collection for $[\text{L}^2\text{H}](\text{PF}_6)$ and **2** were performed at -100 °C on a Rigaku/MSC Mercury CCD diffractometer with graphite monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.7107$ Å). The structure was solved by using the TEXSAN software package. Atomic scattering factors were obtained from the literature [19]. Refinements were performed anisotropically for all non-hydrogen atoms by the full-matrix least-squares method. Hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. The residual electron densities were of no chemical significance. Crystal data and processing parameters are summarized in Table 4.

3. Results and discussion

The (N,C) ligand precursors, *N'*-methyl-2,4'-bipyridinium hexafluorophosphate ($(\text{L}^1\text{H})(\text{PF}_6)$) and *N'*-methyl-2,3'-bipyridinium hexafluorophosphate ($(\text{L}^2\text{H})(\text{PF}_6)$) were prepared by the reaction of corresponding 2,4'- or 2,3'-bipyridine with MeI, followed by the anion exchange by using NH_4PF_6 (Eq. (1)). Single crystals of $(\text{L}^2\text{H})(\text{PF}_6)$ suitable for X-ray diffraction were grown from acetone- Et_2O .

The molecular structure of $(\text{L}^2\text{H})(\text{PF}_6)$ is shown in Fig. 1. The Ru(II) complex $[\text{RuL}^1(\text{bpy})_2](\text{PF}_6)_2$ (**1**) was synthesized by the reaction of $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$ with $(\text{L}^1\text{H})(\text{PF}_6)$ in ethanol in the presence of NEt_3 under reflux conditions (Scheme 1). The cyclometalation reaction took place smoothly, and **1** was obtained in 42% yield after recrystallization. Complex **2** was also prepared by the reaction of $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$ with $(\text{L}^2\text{H})(\text{PF}_6)$, similarly to complex **1**. However, the product was mixtures of several species, and separation of **2** was not succeeded. Therefore, **2** was synthesized by the reaction of $(\text{L}^2\text{H})(\text{PF}_6)$ with AgPF_6 -treated $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$ in ethanol (41% yield). The ESI-MS spectra of **1** and **2** showed the parent peak at $m/z = 292$. Inter-

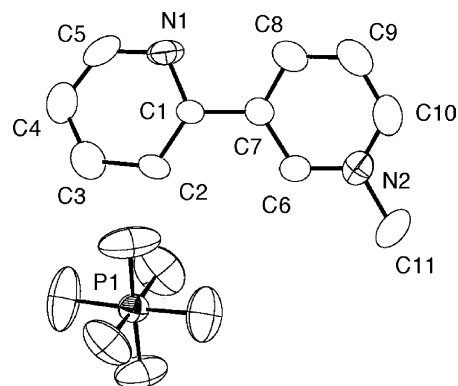
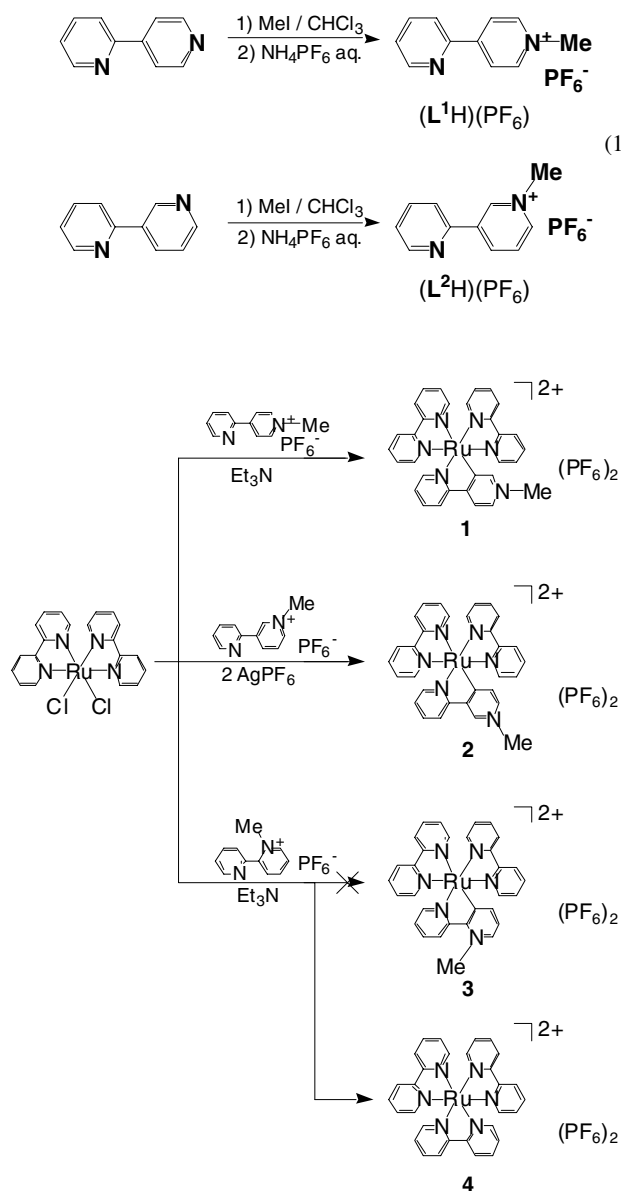


Fig. 1. ORTEP drawing of $(\text{L}^2\text{H})(\text{PF}_6)$. Only one of the two molecules constituting the asymmetric unit is depicted. Hydrogen atoms are omitted for clarity.



Scheme 1.

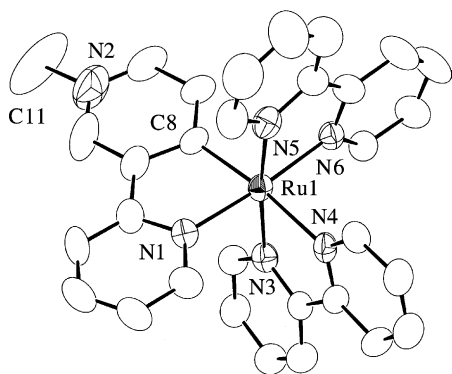


Fig. 2. ORTEP drawing of the cationic part of **2**. Hydrogen atoms are omitted for clarity.

estingly, when *N*-methyl-2,2'-bipyridinium hexafluorophosphate ($(L^3H)(PF_6)$) was reacted with $[RuCl_2(bpy)_2]$, corresponding (N,C) complex **3** was not obtained but $[Ru(bpy)_3]^{2+}$ (**4**) was only generated.

Fig. 2 shows the molecular structure of **2** determined by X-ray diffraction study, and selected bond lengths and angles are summarized in Table 1. The dication of the complex is hexacoordinated and the structure is quite similar to those of $[Ru(bpy)_3]^{2+}$ [20] and $[Ru(bpy)_2(PhPy)]^+$ [3b]. The Ru–C bond length of **2** (2.011(6) Å) is shorter than those of Ru–N bonds (2.058(4)–2.120(5) Å) and other Ru–C distances in ruthenium complexes involving cyclometallated bipyridine analogs (2.017(3)–2.133(5) Å) [1b,11b,12b,14,21], indicating that the Ru–C bond of **2** contains carbenic character. Because of the trans influence, the Ru–N4 bond, which is located at trans position of Ru–C8 bond, is longer than other Ru–N bonds.

The symmetry of these complexes are lower, hence, every aromatic protons in these complexes are inequivalent chemically and magnetically. In the 1H NMR spectra, both complexes showed 23 resonances for two bpy and the (N,C) ligands in the aromatic region, and one singlet methyl signal of the N–Me group at δ 4.13 (**1**) and 4.18 (**2**), respectively. Resonances of the proton in the quaternized moiety-containing ring were observed

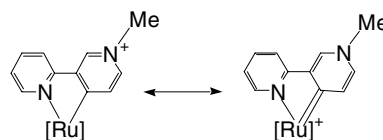
at δ 7.89 (singlet), 8.36 (doublet), and 8.45 (doublet) in **1**, and δ 7.30 (doublet), 7.75 (doublet), and 9.00 (singlet) in **2**, respectively.

In $^{13}C\{^1H\}$ NMR, a remarkable difference between **1** and **2** was observed. Complex **1** exhibited a resonance at δ 190.1 which is assigned to the carbon which is bonding to ruthenium directly. This chemical shift is similar to those of the carbon directly coordinating to the Ru center in the PhPy ligand of $[Ru(bpy)_2(PhPy)]^+$ (δ 193.1) [12d], and that in the quaternized (N,N,C) tridentate ligand of $[RuL(terpy)]^{2+}$ (δ 183.7, L = *N*'-methyl-4'-methylthio-2,2':6',4''-terpyridine) [22], suggesting that this C₅N ring has aromaticity and coordinates to the Ru center as pyridinium. In contrast with **1**, the resonance of corresponding carbon in **2** was observed at δ 232.1, shifting to lower field by ca. 40 ppm. This lowfield shift indicates that the Ru–C bond in **2** contains a carbenic character, that is, the C₅N ring forms a pyridinylidene structure (Scheme 2). Such bidentate ligands coordinating by a pyridinylidene fashion have not been reported so far.

Cyclic voltammetry data for the complexes **1**, **2**, and reference complexes such as $[Ru(bpy)_3](PF_6)_2$ (**4**), $[Ru(bpy)_2(PhPy)](PF_6)$ (**5**), and $[Ru(bpy)_2(NPP)](PF_6)_2$ (**6**, NPP = 4'-nitro-2-(2-pyridyl)phenyl) are given in Table 2. Complex **1** showed one reversible Ru(III)/Ru(II) redox couple at $E_{1/2} = 0.51$ V (vs Fc/Fc⁺) and two reversible ligand-based redox processes at $E_{1/2} = -1.49$ and -1.88 V. Those redox potentials are much the same as those of **6**, suggesting that not only t_{2g} orbital energy of the central ruthenium atoms in **1** and **6** but also π^* -orbital levels of the quaternized (N,C) ligand and the NPP one in those complexes are quite close with each other. It is worthy of note that the Ru(III)/Ru(II) redox potentials of **1** and **2** are situated at more negative than that of **4** approximately by 450 mV, and at more positive than that of **5** by 400 mV. The difference in the redox potentials of the Ru(III)/Ru(II) couple between **4** and **5** apparently results from the strong electron donor ability of the C-coordinated phenyl ring compared with that of N-coordinated pyridyl one. The order of the redox potentials in Table 2, therefore, indicates that the electron donor ability of C-coordinated pyridinyl rings is substantially weakened by quaternization but still is stronger than that of N-coordinated pyridyl ring. The first and the second ligand-localized redox potentials in **1** and **2** are assigned to the reductions of the (N,C) ligand (-1.49 V (**1**) and -1.74 V (**2**)) and the bpy one

Table 1
Selected bond distances (Å) and angles (°) of **2**

Ru1–N1	2.071(5)	Ru1–N3	2.077(5)
Ru1–N4	2.120(5)	Ru1–N5	2.064(6)
Ru1–N6	2.058(4)	Ru1–C8	2.011(6)
N2–C11	1.50(1)		
N1–Ru1–N3	84.7(2)	N1–Ru1–N4	95.9(2)
N1–Ru1–N5	98.4(2)	N1–Ru1–N6	175.2(2)
N1–Ru1–C8	79.6(2)	N3–Ru1–N4	77.4(2)
N3–Ru1–N5	172.4(2)	N3–Ru1–N6	98.6(2)
N3–Ru1–C8	96.4(2)	N4–Ru1–N5	95.3(2)
N4–Ru1–N6	88.2(2)	N4–Ru1–C8	172.7(2)
N5–Ru1–N6	78.7(2)	N5–Ru1–C8	91.0(2)
N6–Ru1–C8	96.6(2)		



Scheme 2.

Table 2
Electrochemical data for ruthenium(II) complexes

Species	$E_{1/2}$ V			Rest potential
	Ru(III)/Ru(II)	$[\text{Ru}]^{n+}/[\text{Ru}]^{(n-1)+}$	$[\text{Ru}]^{(n-1)+}/[\text{Ru}]^{(n-2)+}$	
1	+0.51	−1.49	−1.88	−0.47
2	+0.59	−1.74	−1.92	−0.45
[Ru(bpy) ₃ (PF ₆) ₂ (4)	+0.96	−1.59	−1.76	−0.55
[Ru(bpy) ₂ (PhPy)](PF ₆) (5)	+0.10	−1.80	−2.09	−0.31
[Ru(bpy) ₂ (NPP)](PF ₆) ₂ (6) ^a	+0.51	−1.50	− ^b	− ^b

Data taken from cyclic voltammetry at 50 mV s^{−1}, in DMSO, with 0.1 M Me₄NBF₄ as supporting electrolyte at room temperature. Potentials in V vs Fc/Fc⁺.

^a Reference [3b].

^b Not measured.

(−1.88 V (**1**) and −1.92 V (**2**)), respectively. The redox potentials of the Ru(III)/Ru(II) couple, the first ligand-centered process, and the second one of **2** appear at 80 mV more positive, 250 and 40 mV more negative, respectively, compared with those of **1**. Among the three redox couples, the significant cathodic shift of the first ligand-localized potential of **2** ($\Delta E_{1/2} = -250$ mV) based on that of **1** would be correlated with strong π back donation from ruthenium(II) to the pyridinylidene ligand in **1**, since such d– π interaction is not expected for the Ru–C bond in **1**.

Electronic spectra of **1** and **2**, and of reference complexes **4** and **5** in CH₃CN are shown in Fig. 3, and these data are summarized in Table 3. Complexes **1** and **2** show a strong absorption maximum at 490 nm (**1**) and 452 nm (**2**), respectively, which are attributed to metal-to-ligand charge transfer (MLCT). Metal–carbon bond formation results in an increase of the σ -donor character which apparently destabilizes the metal t_{2g} orbital. As a result, introduction of metal–carbon bond shifts the MLCT band maximum to longer wavelength [3]. The electron withdrawing group-substituted (N,C) ligand also causes a bathochromic shift of the MLCT band, since introduction of π -acceptor substituents to

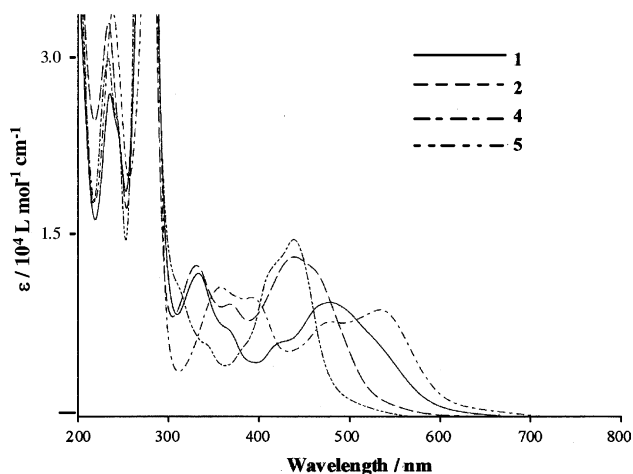


Fig. 3. UV–Vis absorption spectra of **1**, **2**, **4**, and **5** in CH₃CN solutions at room temperature.

ligands lowers the energy level of the π^* orbital. In the present study, the bathochromic shift of the MLCT band of **1** approximately by 40 nm compared with that of **4** is ascribed to the σ -donating pyridinium ligand. On the other hand, The MLCT absorption maximum of **2** is close to that of **4** ($\lambda_{\text{max}} = 451$ nm). Based on the comparison of the first ligand-localized reduction potentials between **1** and **2**, the carbenic character of **2** increases the electron density of the ligand probably due to the π -back donation. So, we propose that the π -bond character of **2**

Table 3
UV–Vis spectral data for complexes in CH₃CN

Species	λ_{max} (nm) (ϵ (L mol ^{−1} cm ^{−1}))			
1	490 (5016)	431 (sh)	378 (sh)	344 (6368)
2	479 (sh)	452 (13610)	379 (9618)	341 (12,890)
4	451 (15,000)	423 (sh)	356 (sh)	323 (sh)
5	547 (8500)	492 (7570)	404 (9487)	368 (10,300)

Table 4
Crystal data and details of the structure refinement of **2** and (L²H)(PF₆)

	2 · MeCN	(L ² H)(PF ₆)
Formula	C ₃₃ H ₂₉ F ₁₂ N ₇ P ₂ Ru	C ₁₁ H ₁₀ F ₆ N ₂ P
Molecular weight	914.64	315.18
Crystal system	Monoclinic	Orthorhombic
Space group	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>P</i> na2 ₁ (No. 33)
<i>a</i> (Å)	9.032(1)	15.347(8)
<i>b</i> (Å)	32.565(4)	20.16(1)
<i>c</i> (Å)	12.872(2)	8.410(4)
β (°)	99.242(2)	
<i>V</i> (Å ³)	3737.1(9)	2602(2)
<i>Z</i>	4	8
μ (cm ^{−1})	6.01	2.74
<i>F</i> (000)	1832.00	1272.00
<i>D</i> _{calc} (g cm ^{−3})	1.626	1.609
No. unique reflns	8304	3058
No. reflns used	8304	3168
No. variables	514	362
<i>R</i> ₁	0.098	0.092
<i>R</i>	0.146	0.155
<i>R</i> _w	0.232	0.189

$R_1 = \sum |F_o| - |F_c| / \sum |F_o|$ for $I > 2.0\sigma(I)$ data, $R_w = \sum [\omega(F_o^2 - F_c^2)]^2 / \sum \omega(F_o^2)^2$. Weighting scheme $\{[\sum(F_o)]^2\}^{1/2}$.

causes the hypsochromic shift of the MLCT band compared with that of **1** because of a rise of the π^* level of the ligand [23]. Although emission spectra for **1** and **2** were measured in CH_3CN solutions, these intensities were very weak similar to that of **5** [3c].

4. Conclusion

We have synthesized two novel cyclometalated ruthenium(II) complexes and characterized their chemical and electrochemical properties. *N'*-methylated 2,4'- and 2,3'-bipyridinium smoothly coordinates to ruthenium by an (N,C) bidentate fashion via a cyclometalation process. The coordination forms of C-coordinated ring of **1** and **2** are different. The $^{13}\text{C}\{^1\text{H}\}$ NMR, electronic spectral and cyclic voltammetric data indicate that the C-coordinated ring in **1** is pyridinium, and that in **2** is pyridinylidene. There have been no reports on such a complex having pyridinylidene ligand forming chelated fashion, that is to say, **2** is the first example of the transition metal complex bearing a bidentate pyridinylidene ligand. The redox potentials of the complexes are greatly influenced by the electronic effect of C-coordinated rings. The Ru(III)/Ru(II) redox potentials of **1** and **2** show between those of $[\text{Ru}(\text{bpy})_3]^{2+}$ (N_6 complex) and $[\text{Ru}(\text{bpy})_2(\text{PhPy})]^+$ (N_5C complex). Electronic spectral data indicate competing σ -donor and π -acceptor effects from the quaternized unit. The MLCT transfers are facilitated by the added electron density on the metal, therefore, the transition of **1**, which has pyridinium as a σ -donor, occurs lower energy than **2**, which contains a pyridinylidene ligand. Both $[\text{L}^1\text{H}]^+$ and $[\text{L}^2\text{H}]^+$ have a pyridinium structure, however, when these molecules coordinate to ruthenium, ligated L^1 forms a pyridinium fashion, and that of L^2 exhibits a pyridinylidene structure.

5. Supplementary materials

Crystallographic data for the structural analysis of **2** and $[\text{L}^2\text{H}](\text{PF}_6)$ in CIF format have been deposited with the Cambridge Crystallographic Data Centre under CCDC Nos. 248968 and 248969. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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