

Synthesis, Structures and Fluxional Behavior of Ruthenium(II) Complexes Bearing a Bidentate 1,8-Naphthyridine Ligand

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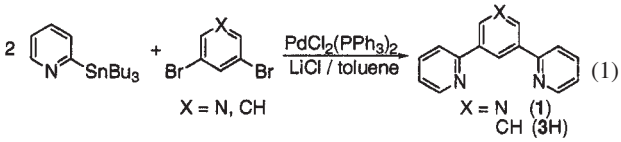
The ruthenium complexes bearing 1,8-naphthyridine (napy) and terpyridine analogous (N,C,N)-tridentate ligands were synthesized and characterized. The reaction of $[RuCl_2(napy\text{-}\kappa^2N,N')(dmso)_2]$ with 2 equiv of $AgPF_6$ and subsequent addition of LH and CO gave $[RuL(napy\text{-}\kappa^2N,N')(CO)](PF_6)_n$ (**6a**: L = *N*-methyl-3,5-di(2-pyridyl)-4-pyridyl, $n = 2$; **6b**: L = 2,6-di(2-pyridyl)phenyl, $n = 1$) via $[RuL(napy\text{-}\kappa^2N,N')(dmso)](PF_6)_n$ (**5a**: L = *N*-methyl-3,5-di(2-pyridyl)-4-pyridyl, $n = 2$; **5b**: L = 2,6-di(2-pyridyl)phenyl, $n = 1$). The crystal structures of **5a** and **6a** show distorted octahedral coordination with the tridentate (N,C,N)-ligand as *mer*-fashion, two nitrogens of bidentate napy and the sulfur of DMSO (**5a**) or the carbon of the CO ligand (**6a**). Detailed experiments for irradiation and variable-temperature ^{1}H NMR studies reveal a fluxional process of the chelated napy ligand in solution.

1,8-Naphthyridine (napy), which has two condensed pyridine rings, binds to metals with monodentate,[1,3] bidentate,[2,3] and bridging modes.[4] Among these various coordination patterns, napy and analogous 1,3-diazines linked to a metal center in monodentate fashion often show fluxional behavior such as metal site exchange (1,3-haptotoropic shift),[3b,5] Berry pseudorotation on square-planar[6] and octahedral complexes,[7] or equilibration between mononuclear and polynuclear complexes.[8] In addition, napy ligated on metals is often found in the ligand-localized redox reactions.[3b] As a result, one electron reduction of napy of *cis*-$[Ru(bpy)_2(napy\text{-}\kappa N)(CO)]^{2+}$ causes an intra-molecular attack of free nitrogen of monodentate napy on the carbon atom of the Ru–CO bond to form a metallacycle ring.[1] Thus, metal complexes often are endowed with entirely new physicochemical properties by ligand localized redox reactions. Ruthenium complexes with terpyridine-analogous (N,C,N)-tridentate ligands such as 2,6-di(2-pyridyl)phenyl have been also of interest from their characteristic photochemical and electrochemical properties such as photoinduced long range electron and energy transfer and luminescence in polynuclear systems.[9–12] Comparison of ruthenium complexes bearing (N,C,N)-tridentate ligands with a central phenyl group and a pyridinium one may give fundamental information about those (N,C,N)-tridentate ligands, since there has been no report of ruthenium complexes bearing a (N,C,N)-tridentate ligand containing a quaternized framework. This paper reports the synthesis and characterization of ruthenium(II) complexes bearing chelated napy and terpyridine-analogous (N,C,N) ligands, and the dynamic behavior of napy in the complexes in solutions.

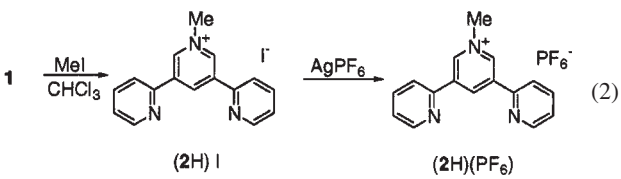
Results and Discussion

The (N,C,N)-tridentate ligand precursor, 2,3′:5′,2″-terpyridine (**1**), was prepared by a Pd-catalyzed cross coupling reaction of 2-(tri-*n*-butylstannyl)pyridine with 3,5-dibromopyridine in 71% yield as shown in Eq. 1;



(1)

the method was similar to a previously reported method for 1,3-di(2-pyridyl)benzene (**3**H) preparation.[13] Treatment of compound **1** with CH_3I in $CHCl_3$ gave *N*-methyl-3,5-di(2-pyridyl)pyridinium iodide ((**2**H)·I) in 90% yield. The ^{1}H NMR spectrum and ESI-MS measurement revealed that N-methylation occurred selectively at the central pyridine ring. Anion exchange by treatment of $AgPF_6$ afforded (**2**H)(PF_6) as off-white powder in 90% yield (Eq. 2).



(2)

Compound (**2**H)(PF_6) was recrystallized from an acetone solution into which diethyl ether vapor was allowed to diffuse slowly. Figure 1 shows the molecular structure of (**2**H)(PF_6) determined by X-ray crystallographic study.

Ruthenium complexes bearing the (N,C,N)-tridentate ligands were synthesized as shown in Eq. 3.

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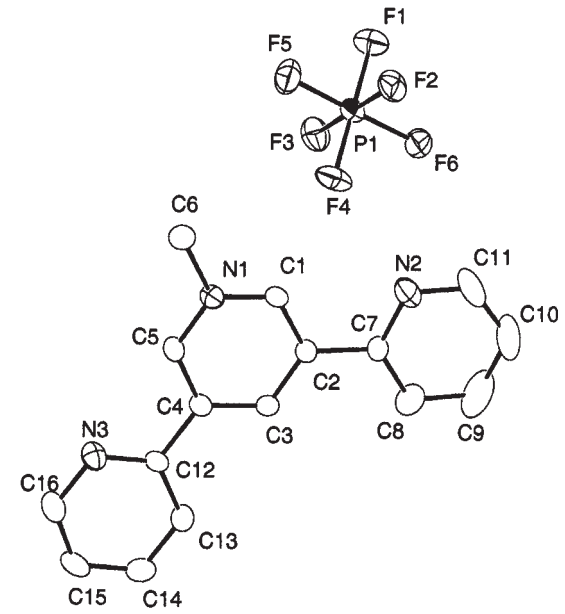
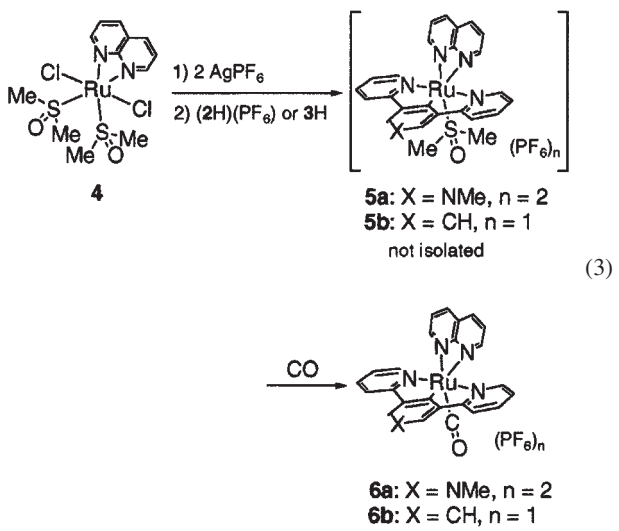


Fig. 1. ORTEP drawing of (**2**H)(PF_6) with 50% thermal ellipsoids. Hydrogen atoms are omitted for simplicity. Selected bond distances (Å) and angles (deg): N1–C1, 1.343(3); N1–C5, 1.357(3); N1–C6, 1.485(3); C1–C2, 1.386(3); C2–C3, 1.387(3); C3–C4, 1.396(3); C4–C5, 1.383(3); C1–N1–C6, 119.2(2); C5–N1–C6, 119.2(2).



(3)

Treatment of $[RuCl_2(napy\text{-}\kappa^2N,N')(dmso)_2]$ (**4**), which was prepared by the reaction of $[RuCl_2(dmso)_4]$ with 1 equiv of napy, with 2 equiv of $AgPF_6$ resulted in the formation of an orange solution with AgCl precipitation. The Ag salt was removed by filtration, and then (**2**H)(PF_6) was added to the filtrate to give a dark brown solution. The ESI-MS spectrum of the solution showed the formation of [Ru(**2**)(napy-κ^2N,N')(dmso)]$(PF_6)_2$ (**5a**) as the main product. However, some other products, $[Ru(\mathbf{2})(napy)_2]^{2+}$, $[RuCl(\mathbf{2})(napy)]^+$, and small amounts of unidentified species were also observed. Recrystallization of the crude products gave mixtures of several species, but the molecular structure of **5a** was determined by X-ray crystallographic study (see below). A 2-methoxyethanol solution containing crude **5a** was treated with CO and yellow-orange powder was obtained. After recrystallization, [Ru(**2**)(napy-κ^2N,N')(CO)]$(PF_6)_2$ (**6a**) was isolated as yellow crystals in 37% yield. Similarly, when **3**H was reacted instead of (**2**H)(PF_6), [Ru(**3**)(napy-κ^2N,N')(CO)]$(PF_6)_2$ (**6b**) was given as yellow powder. After recrystallization from THF–hexane, **6b** was obtained as yellow crystals (21% yield).

Figure 2 depicts the molecular structures of **5a** and **6a** determined by X-ray crystallography; selected bond distances and angles are collected in Table 1. Complex **5a** adopts a monomeric, distorted octahedral coordination around the Ru(II) center with one dimethylsulfoxide, one chelating napy and the (N,C,N)-tridentate ligand. DMSO is linked to Ru through the S atom. In **6a**, a CO ligand is coordinated to ruthenium instead of DMSO. Ru1–C8 bond distances, 1.905(5) Å (**5a**) and 1.928(6) Å (**6a**), are slightly shorter than those of $[Ru(tterpy)_2(tpbp)]^{2+}$ (Ru–C, 1.96(2) and 1.96(1) Å; tterpy = 4′-*p*-tolyl-2,2′,6′,2″-terpyridine, tpbp = 3,3′:5,5′-tetra(2-pyridyl)biphenyl).[9a,c] The narrow bite angle of chelating napy is ascribed to the four-membered ring (N4–Ru1–N5, 60.9(1)° (**5a**) and 61.0(2)° (**6a**)). In addition, angles of N4–C24–N5 (**5a**, 110.3(4)°; **6a**, 110.5(5)°) are somewhat smaller than those of non-chelated napy ligands such as $[Ru(bpy)_2(napy\text{-}\kappa N)(CH_3CN)]^{2+}$ (116.1(7)°),[3b] $[Mn(napy\text{-}\kappa N)(phen)(CO)_3]^+$ (114.5(7)°, phen = 1,10-phenanthroline),[5c] $[Mn(napy\text{-}\kappa N)(napy\text{-}\kappa^2N,N')(CO)_3]^+$ (115.2(6)°),[7] [*cis*-PtCl(napy)$(PEt_3)_2$]$^+$ (115(2)°),[6b] and $[Au(napy)(PPh_3)]^+$ (116.6(14)°),[5e] due to the chelation. Ru1–N5 bond distances of the complexes (**5a**, 2.330(4) Å; **6a**, 2.264(5) Å) are longer than Ru1–N4 bonds (**5a**, 2.099(4) Å; **6a**, 2.136(4) Å) due to a large trans influence of the aryl ligand. Although the Ru1–N4 bond distance of **5a**

Table 1. Selected Bond Distances (Å) and Angles (deg) of **5a** and **6a**

	5a	**6a**
Ru1–N1	2.113(4)	2.089(5)
Ru1–N3	2.111(4)	2.106(5)
Ru1–N4	2.099(4)	2.136(4)
Ru1–N5	2.330(4)	2.264(5)
Ru1–C8	1.905(5)	1.928(6)
Ru1–S1	2.247(1)	
Ru1–C25		1.865(6)
N2–C11	1.475(7)	1.483(8)
O1–C25		
N2–C6	1.379(7)	1.343(8)
N2–C10	1.343(7)	1.353(8)
C6–C7	1.372(7)	1.364(9)
C7–C8	1.407(7)	1.395(8)
C8–C9	1.423(6)	1.394(8)
C9–C10	1.364(7)	1.365(8)
N1–Ru1–N3	158.4(2)	158.4(2)
N1–Ru1–C8	79.7(2)	79.3(2)
N3–Ru1–C8	79.7(2)	79.4(2)
N4–Ru1–N5	60.9(1)	61.0(2)
N4–Ru1–S1	169.1(1)	
N4–Ru1–C25		169.3(2)
N5–Ru1–C8	157.9(2)	157.0(2)
N5–Ru1–S1	108.3(1)	
N5–Ru1–C25		108.3(2)
N4–C24–N5	110.3(4)	110.5(5)

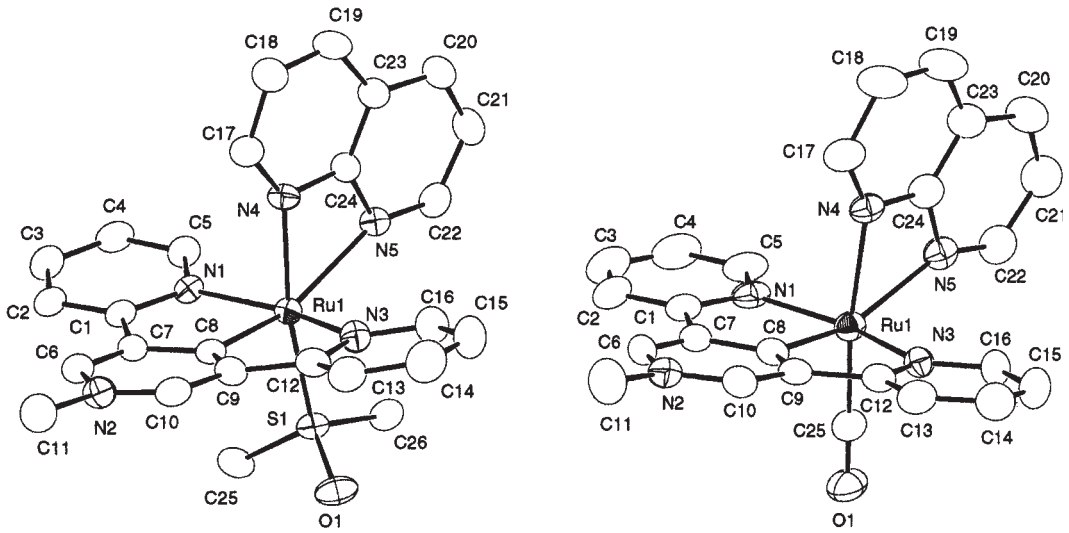


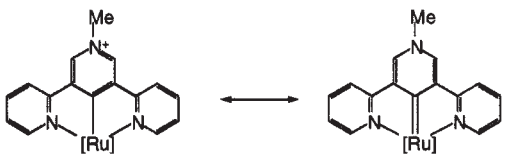
Fig. 2. ORTEP drawings of the cationic part of **5a** and **6a** with 50% thermal ellipsoids. Hydrogen atoms are omitted for simplicity.

is shorter than that found in **6a**, the distance of Ru1–N5 in **5a** is longer than that of **6a**. These results indicate that the trans influence of CO ligand is larger than that of DMSO ligand. The average of Ru–N bond distances, 2.215 Å (**5a**) and 2.200 Å (**6a**) are ca. 0.1 Å longer than the Ru–N(napy) bond distances found in $[Ru(bpy)_2(napy\text{-}\kappa^2N,N')](PF_6)_2$ (2.11(1) Å),[3b] suggesting that the bond strength between Ru and napy ligand in **5a** and **6a** is weakening due to the large trans influence.

The infrared spectrum of **6a** and **6b** showed a strong ν(C≡O) band at 1980 and 1942 cm^{-1}, respectively. The CO stretching frequency shifted to lower wavenumber compared with $[Ru(bpy)_2(napy\text{-}\kappa N)(CO)]^{2+}$ (ν(C≡O) = 2003 cm^{-1})[1a] and $[Ru(terpy)(bpy)(CO)]^{2+}$ (ν(C≡O) = 2004 cm^{-1}),[1a] indicating that the (N,C,N) ligand has a stronger donor character compared with that of terpy. In addition, the large lower shift of ν(C≡O) band of **6b** is also based on the *anionic* (N,C,N)-tridentate ligand.

The $^{13}C\{^1H\}$ NMR spectrum of **6a** shows a Ru–C resonance at δ 220.8, shifting to lower field than that of **6b** (δ 187.8); the value is similar to that found with Ru–pyridinylidene complex, $[Ru(L)(terpy)]^{2+}$ (L = *N*″-methyl-4′-methylthio-2,2′:6′:3″-terpyryridinium-κ^3N,N',C'') (δ 225.6),[14] suggesting the contribution of the Ru–pyridinylidene structure in **6a** (Scheme 1).

Figure 3(A) shows the ^1H NMR spectrum of **6b** in acetone-d_6 showing six resonances assigned to chelated napy and six to the protons of symmetrical dipyridylphenyl ligand, respectively. In contrast, in the ^1H NMR spectrum of **6b** in a coordinatable solvent such as acetonitrile-d_3 (Fig. 3(B)) or DMSO-d_6, only three signals based on napy were observed. The chemical shifts assigned to the napy ligand are same as those of free napy. In addition, ESI-MS spectrum of **6b** in



Scheme 1.

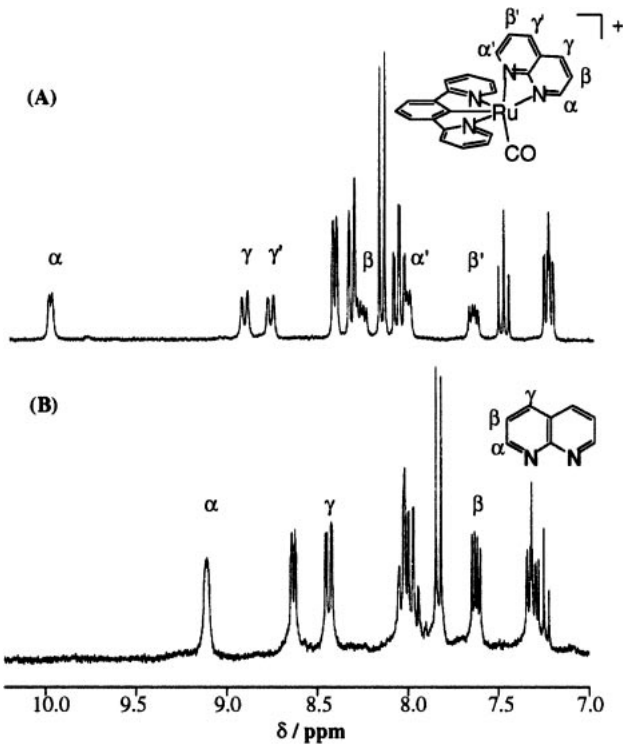
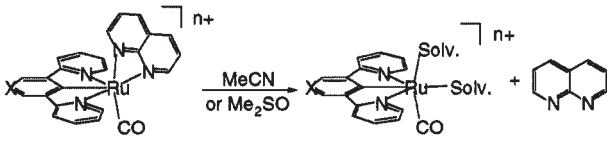


Fig. 3. ^1H NMR spectra (270 MHz) of **6b**. (A) In acetone-d_6; (B) in CD_3CN.

CH_3CN exhibited a parent peak at $m/z = 443$ assignable to $[Ru(\mathbf{3})(CH_3CN)_2(CO)]^+$; the peak at $m/z = 491$ of $[Ru(\mathbf{3})(napy\text{-}\kappa^2N,N')(CO)]^+$ vanished completely. These phenomena were also observed in the ESI-MS spectrum of **6a**. Thus, napy in **6a**,**b** dissociates in these coordinatable solvents (Scheme 2). On the other hand, no signal assigned to free napy was observed at all in the ^1H NMR spectra of **6a** and **6b** in acetone-d_6. Instead, the napy ligand of these complexes showed dynamic behavior in the variable temperature NMR spectra in the solvent. Figure 4 depicts the ^1H NMR spectra of **6b** in the aromatic hydrogen region at room temperature (a), at 30 °C (b), at 40 °C (c), at 50 °C (d) and at 54 °C (e) in acetone-d_6.



Scheme 2.

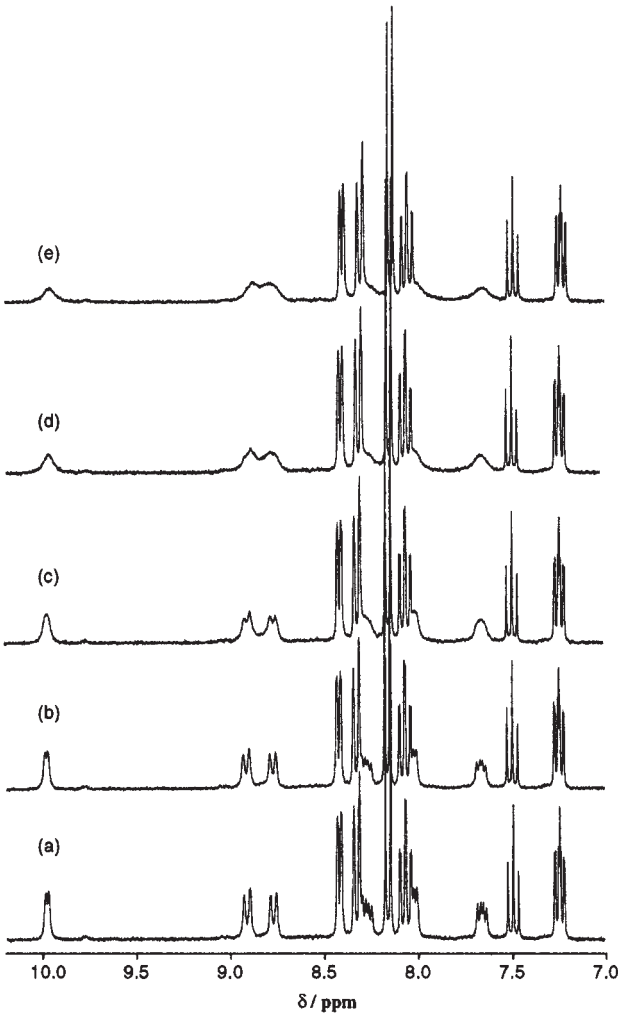


Fig. 4. Variable temperature ^{1}H NMR spectra (270 MHz) of **6b** in acetone-d_6. (a) Room temperature; (b) 30 °C; (c) 40 °C; (d) 50 °C; (e) 54 °C.

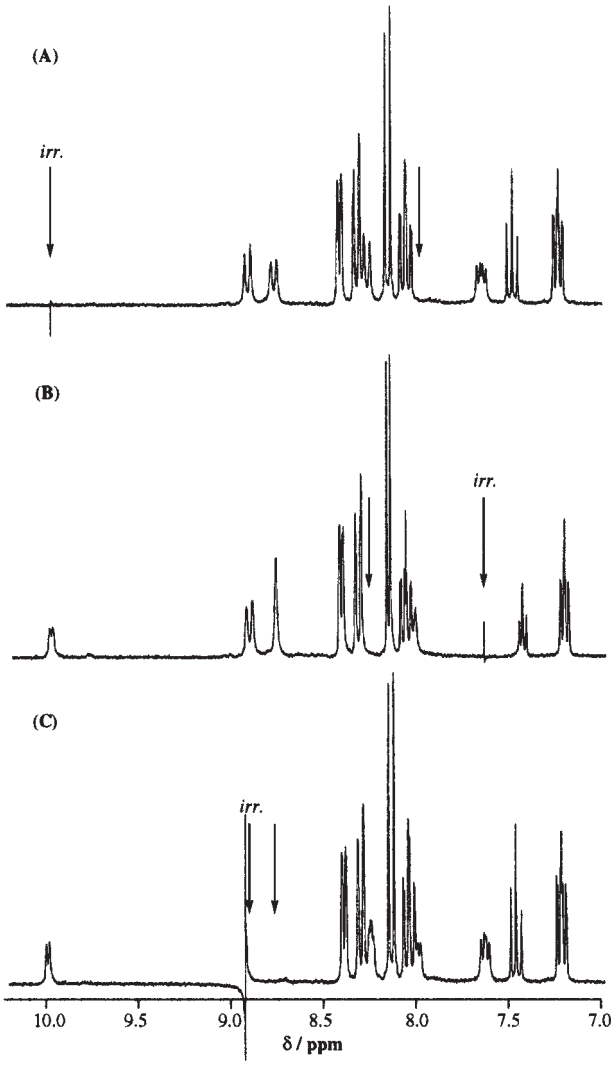


Fig. 5. Irradiation experimental ^{1}H NMR spectra (270 MHz) of **6b** in acetone-d_6. (A) Irradiation at the α resonance; (B) irradiation at the β' resonance; (C) irradiation at the γ resonance.

At room temperature, **6b** exhibited six well-resolved proton signals assigned to the two AMX spin systems $\alpha\beta\gamma$ and $\alpha'\beta'\gamma'$ as mentioned above. As the temperature is raised, only the resonances based on the napy ligand are broadening gradually, and the peaks of γ- and γ'-position almost coalesce at 54 °C. The detail of fluxional process of **5a**,**b** was determined by irradiation experiments. When the peak at δ 9.98 assigned to the proton at α-position of N atom of napy was irradiated, the doublet of doublet peak at δ 8.28 was decoupled, and simultaneously, the peak observed at δ 8.02 completely disappeared (Fig. 5(A)). Similarly, when the peaks at δ 7.62 (assigned to β'-position) and δ 8.92 (assigned to γ-position) were irradiated, the respective peaks at δ 8.28 and δ 8.78 vanished (Figs. 5(B) and 5(C)). These results indicate that these peak pairs (irradiated proton and proton that disappeared by irradiation) are exchanging each other in solution.

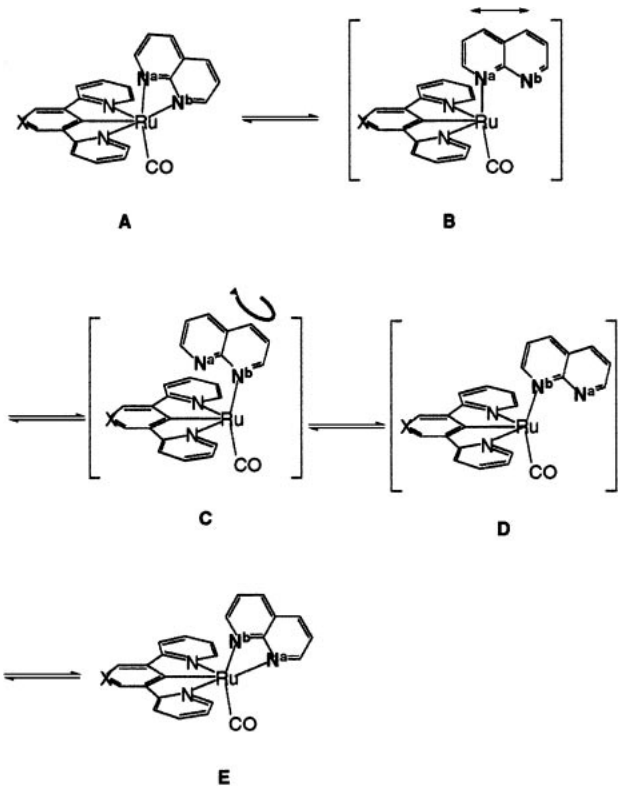
A plausible fluxional process of the chelating napy ligand is shown in Scheme 3. The chelated napy (**A**) is converted reversibly into the monodentate fashion (**B**). Since monodentate napy would give rise to the 1,3-haptotropic exchange, the coordination site changed from N^a to N^b (**B** and **C**). The napy ligand coordinated with N^b probably rotates (**C** and **D**) and recoordinates in chelating fashion; thus complex **E**, which has same structure as **A** has, would be generated.

Electrochemical potentials for **6a**, **6b**, and ligand (**2**H)(PF_6) are collected in Table 2. Complex **6a** exhibited two irreversible ligand-based redox processes in acetone. The reduction of napy is observed at $E_{pc} = -1.33$ V, and that of (N,C,N)-tridentate ligand is at -1.63 V. **6b** showed only one quasi-reversible reduction wave at $E_{pc} = -1.45$ V due to the napy localized reduction,[15] indicating that (N,C,N)-ligands containing 2,6-phenylene unit as the central ring do not undergo electrochemical reduction up to -2.0 V. The fact that **6a** and **6b** ex-

Table 2. Electrochemical Data for **6a**, **6b** and (**2**H)(PF_6)

Species	Solvent	E_{pc}/V		
		Ru(Ⅲ)/Ru(Ⅱ)	$[Ru]^{n+}/[Ru]^{(n-1)+}$	$[Ru]^{(n-1)+}/[Ru]^{(n-2)+}$
6a ($n = 2$)	acetone[a)]	n.d.	−1.33 (E_{pc}, irr)	−1.63 (E_{pc}, irr)
	DMSO[b)]	n.d.	−1.60 (E_{pc}, irr)	
6b ($n = 1$)	acetone[a)]	0.93 ($E_{1/2}$)	−1.45 (E_{pc}, quasi)	
	DMSO[b)]	0.57 ($E_{1/2}$)	−1.90 (E_{pc}, irr)	
(**2**H)(PF_6)	DMSO[b)]		(**2**H)$^+$/(**2**H)^0 −1.49 (E_{pc}, irr)	

a) Electrolyte, 0.1 M Bu_4NBF_4. b) Electrolyte, 0.1 M Me_4NBF_4. These potentials are based on $[RuL(CO)(dmso)_2]^{n+}$.



Scheme 3.

hibited only one irreversible wave at −1.60 and −1.90 V, respectively, in DMSO apparently results from the dissociation of napy in the solvent.

Conclusion

We have demonstrated the synthesis, structure and properties of ruthenium complexes having chelated napy and (N,C,N)-tridentate ligands. The X-ray diffraction study of **5a** and **6a** shows that the napy ligand is coordinated in bidentate fashion, and these complexes are in a distorted octahedral coordination structure. In ^{1}H NMR spectra, the appearance of the six resonances of the napy in acetone-d_6 indicates that the napy binds to Ru with the chelated coordination mode. However, napy in **6a** and **6b** dissociates in coordinatable solvents such as DMSO and CH_3CN. Variable-temperature and irradiation ^{1}H NMR in acetone revealed the dynamic process of the chelating napy ligand, probably due to strong trans effect of the (N,C,N)-ligand.

Experimental

Measurements and Materials. ^{1}H, ^{13}C{^{1}H}, and ^{1}H–^{1}H COSY NMR spectra were recorded on JEOL EX 270 or GX 500 FT NMR spectrometers. IR spectra were recorded on a Shimadzu-FTIR 8100 spectrophotometer. 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 voltammograms were recorded at a scan rate of 100 mV s^{-1}. Elemental analyses were conducted at the Molecular Scale Nano-Science Center of IMS. 2,6-di(2-pyridyl)benzene[13] and $[RuCl_2(dmso)_4]$[16] were prepared according to the literature methods.

2,3′:5′,2″-Terpyridine (1). A mixture of 2-pyridyltri(*n*-butyl)stannane (5.88 g, 16.0 mmol), 3,5-dibromopyridine (1.26 g, 5.31 mmol), $[PdCl_2(PPh_3)_2]$ (297 mg, 0.423 mmol), and LiCl (2.25 g, 53.1 mmol) in toluene (50 mL) was refluxed for 72 h. The resulting black suspension was allowed to stand at room temperature for 1 h. An aqueous solution saturated with KF (15 mL) was added to the suspension, and the mixture was stirred for 30 min. The solid residue that formed was filtered off. Then CH_2Cl_2 (200 mL) and a 5% $NaHCO_3$ solution (150 mL) were added to the filtrate, and the organic phase was separated, and dried over Na_2SO_4; finally the solvent was evaporated. The crude product was chromatographed (Silica gel; AcOEt) to give colorless powder (886 mg, 72%). ^{1}H NMR (270 MHz in $CDCl_3$): δ 9.26 (d, 2H, $J = 2.0$ Hz, H^2), 8.95 (t, 1H, $J = 2.0$ Hz, H^4), 8.26 (d, 2H, $J = 5.0$ Hz, H$^{6'}$), 7.85 (m, 4H, H$^{3'}$ and H$^{4'}$), 7.32 (d, 2H, $J = 5.6$ Hz, H$^{5'}$). Found C, 77.30; H, 4.72; N, 17.98%. Calcd for $C_{15}H_{11}N_3$: C, 77.23; H, 4.75; N, 18.01%.

***N*-Methyl-3,5-di(2-pyridyl)pyridinium Iodide ((2H)I).** To a $CHCl_3$ solution (10 mL) of 2,3′:5′,2″-terpyridine (300 mg, 1.29 mmol) was added an excess amount of MeI (3.42 g, 24.1 mmol) and this mixture was refluxed. White solid was generated after 5 min. Reflux was continued for 1 h; then the precipitated powder was collected by filtration and dried in vacuo to obtain [**2**H]I (440 mg, 90% yield). ^{1}H NMR (270 MHz in CD_3OD): δ 9.76 (s, 1H, H^4), 9.66 (s, 2H, H^2), 8.83 (d, 2H, $J = 4.3$ Hz, H$^{6'}$), 8.28 (d, 2H, $J = 7.9$ Hz, H$^{3'}$), 8.07 (dt, 2H, $J = 6.6$ and 1.0 Hz, H$^{4'}$), 7.58 (dt, 2H, $J = 6.9$ and 5.0 Hz, H$^{5'}$), 4.60 (s, 3H, *N-Me*). MS[ESI(acetone)]: m/z 248 $[M - I]^+$. Found C, 50.78; H, 3.70; N, 11.06%. Calcd for $C_{16}H_{14}IN_3$: C, 51.22; H, 3.76; N, 11.20%.

***N*-Methyl-3,5-di(2-pyridyl)pyridinium Hexafluorophosphate ((2H)PF_6).** To a $CH_3OCH_2CH_2OH$ solution (50 mL) of *N*-Methyl-3,5-di(2-pyridyl)pyridinium iodide (300 mg, 0.80

mmol) was added a $CH_3OCH_2CH_2OH$ solution (5 mL) of $AgPF_6$ (202 mg, 0.80 mmol); this mixture was stirred at 60 °C. White precipitate (AgI) soon appeared. After 1 h, AgI was filtered off, and the solution was concentrated to ca. 1 mL and poured into an aqueous NH_4PF_6 solution. The generated off-white powder was collected by filtration and dried in vacuo (283 mg, 90%). ^{1}H NMR (270 MHz in CD_3OD): δ 9.76 (t, 1H, $J = 1.3$ Hz, H^4), 9.63 (d, 2H, $J = 1.3$ Hz, H^2), 8.82 (dt, 2H, $J = 5.0$ and 1.0 Hz, $H^{6'}$), 8.27 (d, 2H, $J = 7.9$ Hz, $H^{3'}$), 8.07 (dt, 2H, $J = 7.9$ and 1.7 Hz, $H^{4'}$), 7.58 (ddd, 2H, $J = 7.6$, 4.6 and 1.0 Hz, $H^{5'}$), 4.59 (s, 3H, *N-Me*). MS[ESI(acetone)]: m/z 248 $[M - PF_6]^+$. Found C, 48.79; H, 3.54; N, 10.57%. Calcd for $C_{16}H_{14}F_6N_3P$: C, 48.87; H, 3.59; N, 10.68%.

[RuCl$_2$(napy-κ^2*N*,*N*′)(dmso)$_2$] (4). To an EtOH–MeOH solution (4:1 v/v, 20 mL) of $[RuCl_2(dmso)_4]$ (500 mg, 1.03 mmol) was added an EtOH solution (5 mL) of 1,8-naphthyridine (135 mg, 1.03 mmol) at 60 °C. The mixture turned from yellow to red soon, and red precipitation appeared after 10 min. The resulting solid was collected by filtration, and dried in vacuo (440 mg, 93%). ^{1}H NMR (270 MHz in CD_2Cl_2): δ 9.23 (d, 2H, $J = 4.0$ Hz, H^α), 8.40 (d, 2H, $J = 8.3$ Hz, H^γ), 7.71 (dd, 2H, $J = 8.3$ and 4.6 Hz, H^β), 3.45 (s, 12H, *S-Me*). Found C, 31.26; H, 3.91; N, 6.15%. Calcd for $C_{12}H_{18}Cl_2N_2O_2RuS_2$: C, 31.44; H, 3.96; N, 6.11%.

[Ru(2)(napy-κ^2*N*,*N*′)(CO)](PF$_6$)$_2$ (6a). To a $CH_3OCH_2CH_2$-OH solution (20 mL) of $[RuCl_2(napy\text{-}\kappa^2N,N')(dmso)_2]$ (100 mg, 0.218 mmol) was added a $CH_3OCH_2CH_2OH$ solution (5 mL) of $AgPF_6$ (110 mg, 0.436 mmol); this mixture was stirred at 60 °C for 1 h. The resulting brown solid was eliminated by celite filtration, and then the orange filtrate was added to a $CH_3OCH_2CH_2OH$ solution (5 mL) of *N*-methyl-3,5-di(2-pyridyl)pyridinium hexafluorophosphate (86 mg, 0.218 mmol). The reaction mixture was stirred at 80 °C for 48 h, the color turned immediately from orange to dark brown. A rubber balloon (ca. 1 L) filled with carbon monoxide was connected to the flask through a glass stopcock; then the flask was cooled below −100 °C with liquid N_2. After evacuation of the system, CO was introduced to the flask through the stopcock. The reaction mixture was stirred at 60 °C. The color turned from dark brown to yellow-orange. After 2 days, the solution was concentrated to ca. 1 mL, and poured into an aqueous NH_4PF_6 solution; yellow solids then precipitated. The resulting solid was collected and dried in vacuo, and recrystallized from acetone-hexane to give **6a** as yellow crystals (65 mg, 37%). IR (KBr disk): 1980 cm^{-1} (C≡O). ^{1}H NMR (500 MHz in acetone-d_6) δ 10.03 (d, 1H, $J = 4.3$ Hz, H^α), 9.39 (s, 2H, H^2), 8.93 (d, 1H, $J = 8.6$ Hz, H^γ), 8.76 (d, 1H, $J = 7.9$ Hz, $H^{\gamma'}$), 8.58 (d, 4H, $J = 7.3$ Hz, $H^{3'}$ and $H^{6'}$), 8.29 (dd, 1H, $J = 8.6$ and 4.9 Hz, H^β), 8.25 (td, 2H, $J = 7.9$ and 1.2 Hz, $H^{4'}$), 8.17 (d, 1H, $J = 3.7$ Hz, $H^{\alpha'}$), 7.56 (dd, 1H, $J = 8.6$ and 4.9 Hz, $H^{\beta'}$), 7.49 (ddd, 2H, $J = 7.9$, 5.5, and 1.2 Hz, $H^{5'}$). ^{13}C{^{1}H} NMR (125 MHz in acetone-d_6) δ 220.8 (Ru–*C*), 193.2 (Ru–*C*O), 160.5, 157.0, 155.7, 153.9, 152.4, 143.5, 139.2, 139.1, 137.9, 134.9, 125.8, 124.6, 121.7, 121.2, 47.9 (*N*-*C*H$_3$). MS[ESI(acetone)]: m/z 246 $[M - 2\ PF_6]^{2+}$. Found C, 39.35; H, 2.97; N, 8.12%. Calcd for $C_{28}H_{25}F_{12}N_5O_2P_2Ru$ (**6a**·acetone): C, 39.35; H, 2.95; N, 8.20%.

[Ru(3)(napy-κ^2*N*,*N*′)(CO)](PF$_6$) (6b). To a $CH_3OCH_2CH_2$-OH solution (20 mL) of $[RuCl_2(napy\text{-}\kappa^2N,N')(dmso)_2]$ (100 mg, 0.218 mmol) was added a $CH_3OCH_2CH_2OH$ solution (5 mL) of $AgPF_6$ (110 mg, 0.436 mmol); this mixture was stirred at 60 °C for 1 h. The resulting brown solid was eliminated by celite filtration, and then to the orange filtrate was added a $CH_3OCH_2CH_2OH$ solution (5 mL) of **3**H (51 mg, 0.218 mmol). The reaction mixture was stirred at 60 °C for 1 h, the color turned immediately from orange to dark brown. A rubber balloon (ca. 1 L) filled with carbon monoxide was connected to the flask through a glass stopcock. Then the flask was cooled below −100 °C with liquid N_2. After evacuation of the system, CO was introduced to the flask through the stopcock. The reaction mixture was stirred at 60 °C. The color turned from dark brown to yellow-orange. After

Table 3. Crystal Data and Details of the Structure Refinement of **5a**, **6a**, and (**2**H)(PF$_6$)

Compound	**5a**· 2acetone	**6a**	(**2**H)(PF$_6$)
Formula	$C_{32}H_{37}F_{12}N_5O_3P_2RuS$	$C_{25}H_{19}F_{12}N_5OP_2Ru$	$C_{16}H_{14}F_6N_3P$
Mol wt	962.73	796.46	393.27
Cryst syst	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/n$ (No. 14)	$C2/c$ (No. 15)	$P2_12_12_1$ (No. 19)
a/Å	14.423(8)	23.522(2)	11.464(1)
b/Å	11.032(6)	17.079(1)	20.920(2)
c/Å	24.65(1)	16.056(2)	6.6991(7)
β/deg	93.035(5)	105.833(4)	
V/Å^3	3917(3)	6205.4(10)	1606.6(7)
Z	4	8	4
μ/cm^{-1}	6.33	7.10	2.41
F(000)	1944.00	3152.00	800.00
D_{calcd}/g cm^{-1}	1.632	1.705	1.626
No. unique reflns	9329	7048	2033
No. rflnsured	7711	4881	1857
	($I > 2\sigma(I)$)	($I > 2\sigma(I)$)	($I > 2\sigma(I)$)
No. variables	505	415	236
R_{int}	0.059	0.049	0.078
R_1	0.073	0.063	0.053
R	0.086	0.088	0.058
R_w	0.103	0.088	0.081

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

2 days, the solution was concentrated ca. 1 mL, and poured into an aqueous NH_4PF_6 solution; yellow precipitate was produced. The resulting solid was collected and dried in vacuo, and recrystallized from THF–hexane to give **6b** as yellow crystals (30 mg, 21%). IR (KBr disk): 1942 cm^{-1} (C≡O). ^1H NMR (270 MHz in acetone-d_6) δ 9.98 (d, 1H, $J = 4.3$ Hz, H^{α}), 8.92 (d, 1H, $J = 8.9$ Hz, H^{γ}), 8.78 (d, 1H, $J = 8.3$ Hz, $H^{\gamma'}$), 8.43 (ddd, 2H, $J = 5.6$, 1.3 and 0.7 Hz, $H^{6'}$), 8.34 (d, 2H, $J = 8.3$ Hz, $H^{3'}$), 8.28 (dd, 1H, $J =$ 8.6 and 4.6 Hz, H^{β}), 8.17 (d, 2H, $J = 7.6$ Hz, H^{3}), 8.07 (dt, 2H, $J = 7.6$ and 1.3 Hz, $H^{4'}$), 8.02 (d, 1H, $J = 5.0$ Hz, $H^{\alpha'}$), 7.67 (dd, 1H, $J = 8.3$ and 4.6 Hz, $H^{\beta'}$), 7.50 (t, 1H, $J = 7.6$ Hz, H^{4}), 7.25 (ddd, 2H, $J = 7.3$, 5.6, and 1.7 Hz, $H^{5'}$). $^{13}C\{^1H\}$ NMR (125 MHz in acetone-d_6) δ 194.7 (Ru–*C*O), 187.8 (Ru–*C*), 165.5, 156.8, 155.3, 153.0, 151.5, 142.8, 138.7, 137.9, 137.2, 125.5, 124.5, 124.1, 122.8, 122.6, 121.0, 119.5. MS[ESI(acetone)]: m/z 491 $[M - PF_6]^+$. Found C, 47.96; H, 3.25; N, 8.20%. Calcd for $C_{26}H_{21}F_6N_4OPRu$: C, 47.93; H, 3.25; N, 8.60%.

X-ray Crystallographic Studies. 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 collections for **5a** and **6a** were performed at −100 °C on a Rigaku/MSC Mercury CCD diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.7107$ Å). All structures were solved by using the teXsan software package. Atomic scattering factors were obtained from the literature.[17] 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 3. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers: (**2**H)(PF_6), 204553; **5a**, 204551; **6a**, 204552.

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