Terpyridine-Analogous (N,N,C)-Tridentate Ligands: Synthesis, Structures, and Electrochemical Properties of Ruthenium(II) Complexes Bearing Tridentate Pyridinium and Pyridinylidene Ligands

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The cyclometalated complexes [RuL(terpy)][PF_6]$_2$ (**3**, L = *N*″-methyl-4′-methylthio-2,2′:6′,4″-terpyridinium; **4**, L = *N*″-methyl-4′-methylthio-2,2′:6′,3″-terpyridinium) with a (N,N,N)-(N,N,C)-coordination mode were synthesized in good yields and fully characterized by X-ray crystallographic, spectroscopic, and electrochemical measurements. $^{13}C\{^1H\}$ NMR and electronic spectra revealed that the Ru−C bond of complex **4**, which has a quaternized N-Me unit at the *para*-position of the carbon atom bonding to the metal center in the terminal ring of the tridentate ligand, involves carbenic (Ru=C) character in solution.

Introduction

Much attention has been paid to ruthenium complexes bearing cyclometalated tridentate ligands such as 2,2′:6′,2″-terpyridine (terpy) analogues because of their characteristic photochemical and electrochemical properties such as photoinduced long-range electron and energy transfer and luminescence in polynuclear systems.[1−7] Comparison of redox behavior of metal complexes with a cyclometalated (N,N,C)- or (N,C,N)-donor set and with a polypyridyl (N,N,N)-donor one will give fundamental information about the metal−carbon and metal−nitrogen bonds. Recently, quaternized 2,2′- and 2,4′-bipyridines have proven to work as (N,C)-bidentate ligands.[8−10] The reactivity of those cyclometalated metal complexes is essentially different from that of 2,2′-bipyridine ones. Accordingly, quaternization of one of three pyridyl rings of a terpyridine moiety will smoothly give cyclometalated metal complexes due to the assistance of a strong chelate effect of the remaining two pyridyl groups. In this paper, we wish to report preparation of terpyridine derivatives with a quaternized pyridyl moiety and selective formation of cyclometalated Ru(II) complexes with the (N,N,C)-tridentate ligand in good yields.

Results and Discussion

4′-Methylthio-2,2′:6′,4″-terpyridine (**1**) as a (N,N,C)-tridentate ligand precursor was prepared according to a previously reported procedure.[2b] 4′-Methylthio-

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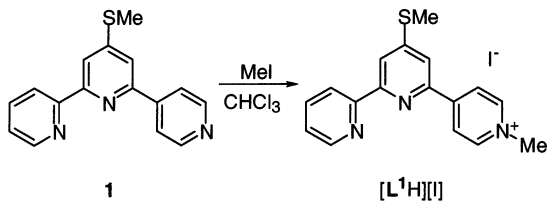
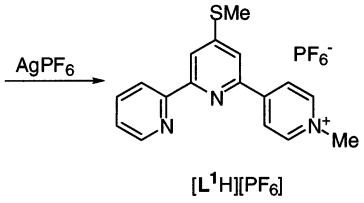
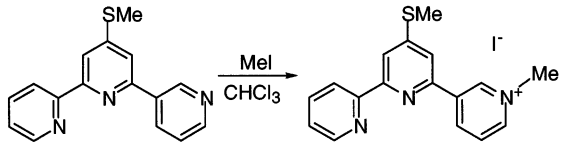
2,2′:6′,3″-terpyridine (**2**) was prepared similarly to **1** using 3-acetylpyridine instead of 4-acetylpyridine. Treatments of **1** and **2** with CH_3I in $CHCl_3$ gave the quaternized [$\mathbf{L^1}$H]·I and [$\mathbf{L^2}$H]·I in 91 and 98% yields, respectively (eqs 1 and 2). Anion exchanges of [$\mathbf{L^1}$H]·I and



(1)





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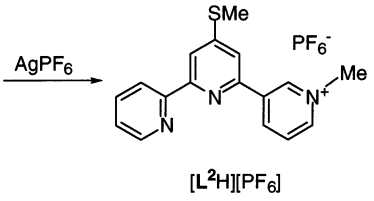
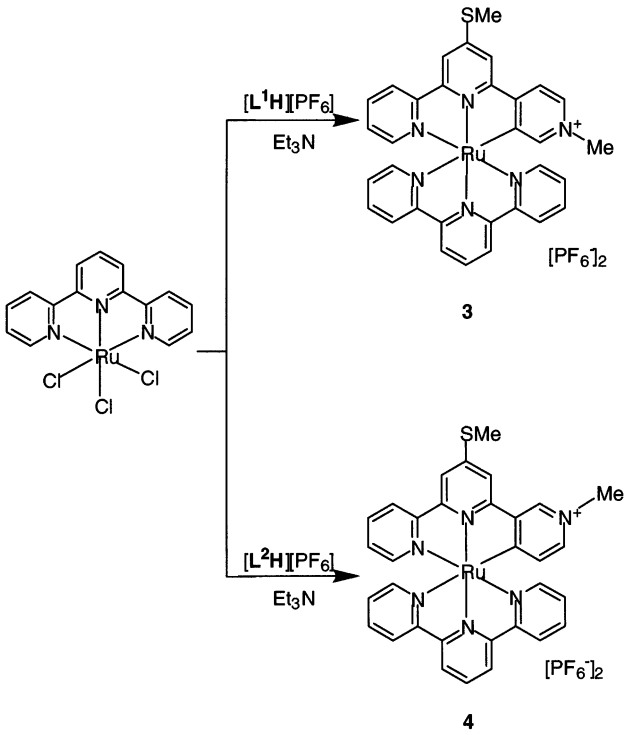


[$\mathbf{L^2}$H]·I with $AgPF_6$ afforded [$\mathbf{L^1}$H][PF_6] (94%) and [$\mathbf{L^2}$H][PF_6] (96%). ESI-MS spectra of [$\mathbf{L^1}$H][PF_6] and [$\mathbf{L^2}$H][PF_6] exhibited the parent ions at $m/z = 294$. The methyl groups of 4′-thiomethyl and quaternized *N*-methyl of [$\mathbf{L^1}$H][PF_6] were observed as two singlet signals at δ 2.78 and 4.67, respectively, in the ^{1}H NMR spectra, and [$\mathbf{L^2}$H][PF_6] showed those signals at δ 2.78 and 4.69. The appearance of 8 and 10 resonances for [$\mathbf{L^1}$H][PF_6] and [$\mathbf{L^2}$H][PF_6], respectively, in an aromatic region revealed that only one product was selectively formed under the reaction conditions. Indeed, further quaternization of [$\mathbf{L^1}$H] and [$\mathbf{L^2}$H][PF_6] in the presence of excess MeI did not take place under reflux conditions.[2g] Thus, *N*-methylation occurred selectively at the terminal outside-oriented *N*-position.

The heteroleptic ruthenium complex [Ru(terpy)($\mathbf{L^1}$)][PF_6]$_2$ (**3**) was obtained as a purple powder by refluxing Ru(terpy)Cl_3 and [$\mathbf{L^1}$H][PF_6] in EtOH in the presence of triethylamine, followed by anion exchange with NH_4PF_6 (85% yield) (Scheme 1). [Ru(terpy)($\mathbf{L^2}$)][PF_6]$_2$ (**4**) was obtained similarly to **3**, as a red-orange powder in 76% yield. In both reactions, cyclometalation progressed smoothly and cleanly. The ESI-MS spectra of **3** and **4** showed the parent peak of [Ru(terpy)**L**]$^{2+}$ (**L** = $\mathbf{L^1}$ or $\mathbf{L^2}$) at $m/z = 314$. Single crystals suitable for X-ray

Scheme 1



crystallography of **3** and **4** were grown from an acetone solution into which diethyl ether vapor was allowed to diffuse slowly. Figure 1 depicts the molecular structure of **3** and **4** determined by X-ray crystallography, and the selected bond distances and angles are summarized in Table 1. Each ruthenium center is coordinated by three nitrogen atoms of terpy and by three atoms of the (N,N,C)-ligands. The bond distances between Ru and the (N,N,C)-ligand for **3** (Ru(1)−C(13), 2.033(5); Ru(1)−N(2), 2.003(4); Ru(1)−N(1), 2.147(4) Å) are in good accordance with those of previously reported [Ru(mterpy-*N*,*N*′,*C*)(terpy)]$^{2+}$ (mterpyH = *N*-methyl-2,2′:6′,2″-terpyridinium).[2g] The structure of **4** is similar to **3**; however, the Ru(1)−C(14) (2.014(5) Å) and the Ru(1)−N(1) (2.171(5) Å) bond lengths of **4** are slightly shorter (0.019 Å) and longer (0.024 Å) than the Ru(1)−C(13) and the Ru(1)−N(1) bond distances of **3**. The C−C bond distances of *N*-methylated pyridinium rings in **3** and **4** are illustrated in Scheme 2.

The ^{1}H NMR spectra (acetone-d_6 solution) of **3** and **4** showed two singlet methyl signals of the S-Me and N-Me groups and six and nine resonances for 20 protons of the terpy and the (N,N,C)-ligands, respectively, in aromatic region. These spectra were fully assigned by use of a ^{1}H−^{1}H COSY experiment. A remarkable difference in the ^{13}C{^{1}H} NMR spectra of **3** and **4** was found. The resonance of Ru−C_{ipso} of **3** was observed at 183.7 ppm in accordance with that of previously reported Ru-aryl complexes (150−195 ppm)[11,12] and *C*-coordinated pyridinium rhodium complexes (158−190 ppm).[13]

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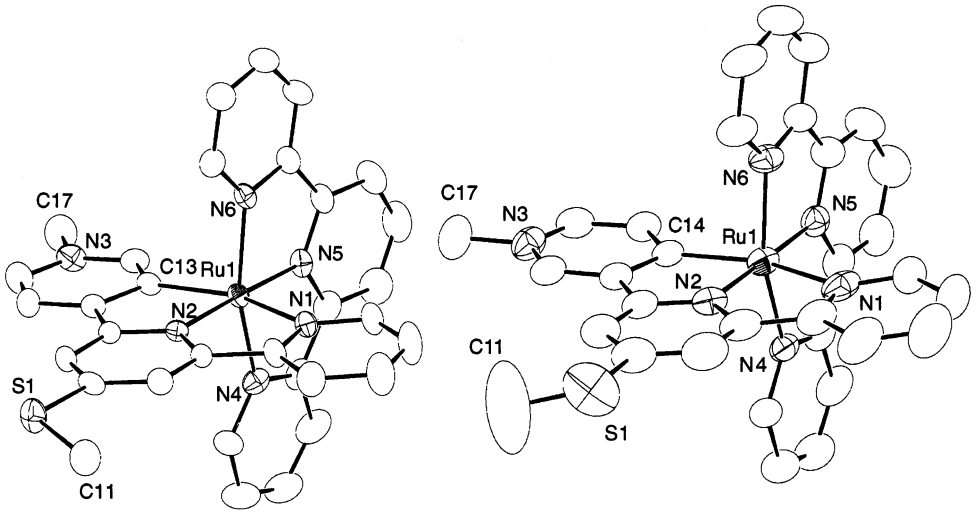


3 **4**

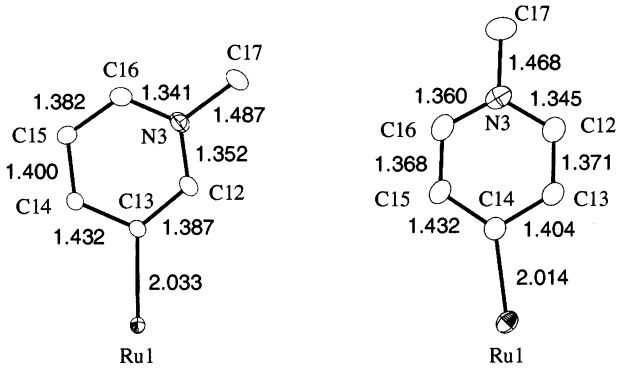
Figure 1. ORTEP drawings of the cationic part of **3** and **4** with 50% thermal ellipsoids. Hydrogen atoms are omitted for simplicity.

Table 1. Selected Bond Distances (Å) and Angles (deg) of 3 and 4

	3	4
Ru1−N1	2.147(4)	2.171(5)
Ru1−N2	2.003(4)	2.000(5)
Ru1−N4	2.059(5)	2.087(4)
Ru1−N5	1.968(4)	1.971(5)
Ru1−N6	2.070(4)	2.072(4)
Ru1−C13	2.033(5)	
Ru1−C14		2.014(5)
N3−C17	1.487(7)	1.468(8)
N1−Ru1−N2	77.4(2)	76.4(2)
N1−Ru1−C13	156.8(2)	
N1−Ru1−C14		156.5(2)
N2−Ru1−C13	79.4(2)	
N2−Ru1−C14		80.1(2)
N4−Ru1−N5	79.1(2)	78.4(2)
N4−Ru1−N6	157.9(2)	156.9(2)
N5−Ru1−N6	78.8(2)	78.5(2)
N4−Ru1−C13	90.8(2)	
N4−Ru1−C14		92.5(2)
N5−Ru1−C13	102.2(2)	
N5−Ru1−C14		99.6(2)
N6−Ru1−C13	92.9(2)	
N6−Ru1−C14		92.6(2)

In contrast, the Ru−C_{ipso} resonance of **4** appeared at 225.6 ppm. The shift of the Ru−C_{ipso} resonance to lower field by 42 ppm compared with that of **3** indicates that quaternization of the nitrogen atom at the *para*-position of the Ru−C bond of **4** induces a carbene (4(1*H*)-pyridinylidene) structure (Scheme 3). Commonly, ruthenium-carbene complexes show their C_{ipso} resonances at 280−320 ppm.[12,14] In the case of metallaquinone, a ruthenium complex bearing a phenolic PCP ligand exhibits the Ru=C carbon resonance at 303.08 ppm.[12] On the other hand, the chemical shifts of M=C_{ipso} in M-pyridinylidene complexes are in the range 211−260 ppm (M = Cr),[15] 212−219 ppm (M = W),[15,16] 241−242 ppm (M = Mn),[17] and 252 ppm (M = Rh).[18] The Ru−C_{ipso} resonance at 225.6 ppm of **4**, therefore, indicates that **4** contains the Ru−pyridinylidene bond rather than the Ru−pyridinium one. There has been only one example of Ru−(*N*-methyl)-pyridinylidene based on the IR spectra,[19] but neither

Scheme 2



3 **4**

Scheme 3

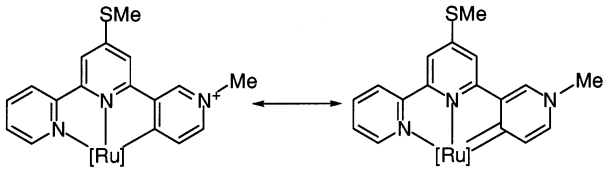


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Table 2. UV−Vis Spectral Data for Complexes 3 and 4 in CH_3CN

species	λ_{max} (nm) (ϵ (L mol^{-1}cm^{-1}))				
3	496.5 (15260)	350.0 (sh)	295.0 (59920)	258.5 (55070)	215.5 (48030)
4	481.0 (16200)	344.5 (10390)	293.5 (53820)	257.0 (48850)	215.0 (46690)

Table 3. Cyclic Voltammetry Potentials for Complexes[a]

species	$E_{1/2}$, V		
	Ru(II)/Ru(III)	$[RuL_2]^{2+}/[RuL_2]^+$	$[RuL_2]^+/[RuL_2]^0$
3	+0.560	−1.407	−1.875
4	+0.612	−1.708 (E_{pc}, irrev)	−1.970 (E_{pc}, irrev)
$[Ru(terpy)_2][PF_6]_2$ (**5**)	+0.965	−1.478	−1.732
$[Ru(mtterpy)(terpy)][PF_6]_2$ (**6**)	+0.955	−1.522	−1.731
$[Ru(mtterpy)_2][PF_6]_2$ (**7**)	+0.937	−1.533	−1.721

[a] In dimethyl sulfoxide−0.1 mol dm^{-3} Me_4NBF_4. Potentials in V vs Fc/Fc^+ (= Ag/Ag^+ + 0.06 V).

structural nor NMR data of the complex have been reported so far.

The electronic spectra of **3** and **4** in CH_3CN are summarized in Table 2. The lowest energy band at λ_{max} = 496 nm (ϵ = 15 260 dm^3 mol^{-1} cm^{-1}) of **3** was assigned to a metal-to-ligand charge transfer (MLCT) transition. The second MLCT process was observed as a shoulder ($\lambda \approx$ 350 nm) of the ligand-centered (LC) transitions at λ_{max} = 295 (ϵ = 59 920), 258.5 (ϵ = 55 070), and 215.5 nm (ϵ = 48 030). Complex **4** also showed two MLCT transitions at λ_{max} = 481 nm (ϵ = 16 200) and λ_{max} = 344.5 nm (ϵ = 10 390). The blue-shift of the first MLCT band of **4** probably results from a wide Ru(dπ)−L(π*) gap compared with that of **3**. The second MLCT one has been correlated with the π* orbital of cyclometalating ligands.[2a,c,g]

Cyclic voltammograms of **3**, **4**, and reference complexes such as $[Ru(terpy)_2][PF_6]_2$ (**5**), [Ru(terpy)(mtterpy)][PF_6]$_2$ (**6**), and $[Ru(mtterpy)_2][PF_6]_2$ (**7**) (mtterpy = 4′-methylthio-2,2′:6′,2″-terpyridine) were measured in DMSO, and the results are collected in Table 3. Complex **3** exhibited one reversible (Ru(II)/Ru(III)) redox couple at $E_{1/2}$ = +0.56 V (vs Fc/Fc^+) and two reversible ligand-based redox processes at $E_{1/2}$ = 1.41 and −1.88 V. The Ru(II)/Ru(III) redox potential of **3** was more negative than that of **5**−**7** approximately by 400 mV. The (N,N,C) and terpy localized redox potentials shifted anodically by 70−120 mV and cathodically by 140−150 mV, respectively, based on those of **5**−**7**. This tendency is consistent with that of [Ru(mterpy-*N*,*N*′,*C*)(terpy)][PF_6]$_2$.[2g] The negative shift of the Ru(II)/Ru(III) redox potential apparently results from strong σ-donation due to the change of an N donor by a C^- donor. The positive shift of the (N,N,C)-ligand-localized redox potential is ascribed to the electron withdrawing by the quaternized moiety. In contrast to **3**, **4** showed one reversible Ru(II)/Ru(III) redox couple ($E_{1/2}$ = 0.61 V) and two irreversible ligand-localized reduction waves at E_{pc} = −1.71 and −1.97 V, which are 0.31 and 0.04 V more negative than those of **3** (E_{pc} = −1.40 and −1.93 V). The difference of the redox behavior of **3** and **4** is correlated with the quaternized position in a pyridine ring. As mentioned above, quaternization of the N atom at the *para*-position to the Ru−C bond induces carbenic character. The ligand would become more electron withdrawing since the Ru=C bond in the pyridinylidene form is formed through electron donation by Ru (Scheme 3). The (N,N,C)-ligand-localized redox potential of **4**, therefore, shifts to a more negative value than that of **3**.

Conclusion

We have demonstrated the synthesis, structure, and electrochemical behavior of Ru(terpy) complexes bearing quaternized (N,N,C)-tridentate ligands. The tridentate ligands [$\mathbf{L^1}$H]$^+$ and [$\mathbf{L^2}$H]$^+$ smoothly afford metallacycles in high yields. Few ruthenium complexes having a terpy-type (N,N,C)-ligand containing a quaternized moiety have been obtained in low yields.[2c,g] Quaternized (N,N,C)-ligands have both strong σ-donor and π-electron-withdrawing character. The $^{13}C\{^1H\}$ NMR spectra and cyclic voltammograms revealed that **4** has a ruthenium-carbene (4(1*H*)-pyridinylidene) structure in solutions, though the solid-state structures of **3** and **4** are not so different from each other. This is the first example of a structurally and spectrometrically well-defined ruthenium-pyridinylidene complex.

Experimental Section

General Procedures. ^1H, $^{13}C\{^1H\}$, and $^1H-^1H$ COSY NMR spectra were recorded on a JEOL EX 270 spectrometer. IR spectra were recorded on a Shimadzu-FTIR 8100 spectrophotometer. Electronic spectra were revealed on a Shimadzu UV-3100PC UV−vis−NIR scanning spectrometer. ESI-MS spectra were obtained on a Shimadzu LCMS-2010 spectrometer. Electrochemical measurements were performed with an ALS/chi 660A electrochemical analyzer. A conventional three-electrode configuration was used, with glassy carbon working (BAS PFCE carbon electrode) and platinum wire auxiliary electrodes (BAS special order) and Ag/Ag^+ reference (BAS RE-5). Purified dimethyl sulfoxide was used as a solvent and 0.1 M [Me_4N][BF_4] as a supporting electrolyte. Elemental analyses were carried out by the Molecular Scale Nano-Science Center of IMS. $RuCl_3$(terpy),[20] 4′-methylthio-2,2′:6′,4″-terpyridine,[2c] and 4′-methylthio-2,2′:6′,3″-terpyridine[21] were prepared according to the literature method. [Ru(terpy)(mtterpy)][PF_6]$_2$ (**6**) and $[Ru(mtterpy)_2][PF_6]_2$ (**7**) were prepared by the reaction of $RuCl_3$(mtterpy)[22] with 1 equiv of terpy or mtterpy in refluxing

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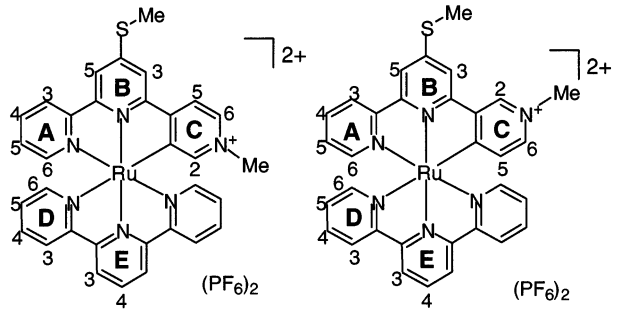
Scheme 4



3 **4**

EtOH in the presence of Et_3N, followed by anion exchange with NH_4PF_6, respectively. The numbering of aromatic protons of **3** and **4** is shown in Scheme 4.

4′-Methylthio-*N*′′-methyl-2,2′:6′,4′′-terpyridinium Iodide ([L¹H][I]). To a $CHCl_3$ solution (10 mL) of 4′-methylthio-2,2′:6′,4′′-terpyridine (500 mg, 1.79 mmol) was added an excess amount of MeI (1 mL, 16.1 mmol), and the mixture was refluxed. A pale yellow solid was precipitated after 5 min. Reflux was continued for 1 h, then the precipitated powder was collected by filtration and dried in vacuo (660 mg, 91%). ESI-MS: *m*/*z* 294 $\{M - I\}^+$. Anal. Calcd for $C_{17}H_{16}IN_3S$: C, 48.47; H, 3.83; N, 9.97. Found: C, 48.06; H, 3.74; N, 9.92.

4′-Methylthio-*N*′′-methyl-2,2′:6′,4′′-terpyridinium Hexafluorophosphate ([L¹H][PF₆]). To a $CH_3OCH_2CH_2OH$ solution (20 mL) of [**L¹H**][I] (167 mg, 0.411 mmol) was added a $CH_3OCH_2CH_2OH$ solution (5 mL) of $AgPF_6$ (110 mg, 0.435 mmol), and the mixture was stirred at 60 °C. A white precipitate (AgI) appeared soon. 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 (164 mg, 94%). ESI-MS: *m*/*z* 294 $\{M - PF_6\}^+$. Anal. Calcd for $C_{17}H_{16}F_6N_3PS$: C, 46.47; H, 3.67; N, 9.56. Found: C, 46.18; H, 3.58; N, 9.53. ^{1}H NMR (acetone-d_6, 270 MHz): δ 9.20 (d, 2H, H$^{2''}$ and H$^{6''}$, J(H−H) = 6.9 Hz), 9.09 (d, 2H, H$^{3''}$ and H$^{5''}$, J(H−H) = 6.9 Hz), 8.78 (d, 1H, H,[6] J(H−H) = 5.0 Hz), 8.70 (d, 1H, H^3, J(H−H) = 8.3 Hz), 8.53 (d, 1H, H$^{5'}$, J(H−H) = 1.7 Hz), 8.28 (d, 1H, H$^{3'}$, J(H−H) = 1.7 Hz), 8.06 (dt, 1H, H,[4] J(H−H) = 7.6 and 1.7 Hz), 7.57 (ddd, 1H, H,[5] J(H−H) = 7.6, 4.6, and 1.0 Hz), 4.69 (s, 3H, N-*Me*), 2.78 (s, 3H, S-*Me*). ^{13}C{^{1}H} NMR (acetone-d_6, 67.8 MHz): 155.5, 154.8, 153.6, 149.9, 149.8, 145.8, 144.6, 144.5, 143.1, 139.2, 139.1, 128.5, 125.9, 118.6, 118.2, 49.4, 13.9.

4′-Methylthio-*N*′′-methyl-2,2′:6′,3′′-terpyridinium Iodide ([L²H][I]). To a $CHCl_3$ solution (10 mL) of 4′-methylthio-2,2′:6′,3′′-terpyridine (582 mg, 2.08 mmol) was added an excess amount of MeI (1 mL, 16.1 mmol), and the mixture was refluxed. A pale yellow solid was precipitated after 5 min. Reflux was continued for 1 h, then the precipitated powder was collected by filtration and dried in vacuo (830 mg, 98%). ESI-MS: *m*/*z* 294 $\{M - I\}^+$. Anal. Calcd for $C_{17}H_{16}IN_3S$: C, 48.47; H, 3.83; N, 9.97. Found: C, 48.33; H, 3.77; N, 9.80.

4′-Methylthio-*N*′′-methyl-2,2′:6′,3′′-terpyridinium Hexafluorophosphate ([L¹H][PF₆]). To a $CH_3OCH_2CH_2OH$ solution (50 mL) of [**L²H**][I] (400 mg, 0.985 mmol) was added a $CH_3OCH_2CH_2OH$ solution (5 mL) of $AgPF_6$ (250 mg, 0.989 mmol), and the mixture was stirred at 60 °C. A white precipitate (AgI) was generated soon. 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 (400 mg, 96%). ESI-MS: *m*/*z* 294 $\{M - PF_6\}^+$. Anal. Calcd for $C_{17}H_{16}F_6N_3PS$: C, 46.47; H, 3.67; N, 9.56. Found: C, 46.36; H, 3.54; N, 9.49. ^{1}H NMR (acetone-d_6, 270 MHz): δ 9.90 (s, 1H, H$^{2''}$), 9.42 (d, 1H, H$^{6''}$, J(H−H) = 8.3 Hz), 9.11 (d, 1H, H$^{4''}$, J(H−H) = 5.9 Hz), 8.87 (d, 1H, H,[6] J(H−H) = 3.3 Hz), 8.69 (d, 1H, H^3, J(H−H) = 7.9 Hz), 8.40 (d, 1H, H$^{5'}$, J(H−H) = 1.7 Hz), 8.30 (dd, 1H, H$^{5''}$, J(H−H) = 8.2 and 5.9 Hz), 8.14 (dt, 1H, H,[4] J(H−H) = 7.9 and 1.7 Hz), 8.11 (d, 1H, H$^{3'}$, J(H−H) = 1.7 Hz), 7.66 (dd, 1H, H,[5] J(H−H) = 6.6 and 5.0 Hz), 4.67 (s, 3H, N-*Me*), 2.78 (s, 3H, S-*Me*). ^{13}C{^{1}H} NMR (acetone-d_6, 67.8 MHz): 156.0, 155.0, 154.4, 153.9, 153.8, 149.8, 146.4, 138.2, 125.6, 125.5, 122.2, 119.6, 119.1, 48.6, 14.0.

[RuL¹(terpy)][PF₆]₂ (3). $RuCl_3$(terpy) (100 mg, 0.227 mmol), [**L¹**H][PF_6] (100 mg, 0.227 mmol), and triethylamine (2 mL) were dissolved in CH_3CH_2OH and refluxed for 3 h. The brown solution turned immediately to purple in color. The solution was concentrated to ca. 1 mL and poured into an aqueous NH_4PF_6 solution. The generated purple precipitate was collected by filtration and dried in vacuo (178 mg, 85%). Recrystallization from an acetone−Et_2O mixture afforded **3** as purple crystals. ESI-MS: *m*/*z* 314 $\{M - 2\ PF_6\}^{2+}$. Anal. Calcd for $C_{32}H_{26}F_{12}N_6P_2RuS$: C, 41.88; H, 2.86; N, 9.16. Found: C, 41.53; H, 3.01; N, 9.09. ^{1}H NMR (acetone-d_6, 270 MHz): δ 8.93 (d, 2H, H^{3E}, J(H−H) = 7.9 Hz), 8.89 (d, 1H, H^{3A}, J(H−H) = 7.9 Hz), 8.81 (d, 1H, H^{3B}, J(H−H) = 1.3 Hz), 8.76 (d, 1H, H^{5B}, J(H−H) = 1.3 Hz), 8.72 (d, 2H, H^{3D}, J(H−H) = 7.9 Hz), 8.57 (d, 1H, H^{5C}, J(H−H) = 6.3 Hz), 8.36 (t, 1H, H^{4E}, J(H−H) = 7.9 Hz), 8.29 (d, 1H, H^{6C}, J(H−H) = 6.3 Hz), 8.07 (td, 1H, H^{4A}, J(H−H) = 7.9 and 1.7 Hz), 7.99 (td, 2H, H^{4D}, J(H−H) = 7.9

Table 4. Crystal Data and Details of the Structure Refinement of 3, 4, and [L²H][PF₆]

compound	**3**·2acetone	**4**·2acetone	[**L²H**][PF_6]
formula	$C_{38}H_{38}F_{12}N_6O_2P_2RuS$	$C_{38}H_{38}F_{12}N_6O_2P_2RuS$	$C_{17}H_{16}F_6N_3PS$
mol wt	1033.82	1033.82	439.36
cryst syst	triclinic	triclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
a (Å)	8.817(5)	8.784(5)	5.903(5)
b (Å)	14.085(8)	14.213(9)	31.00(3)
c (Å)	18.655(10)	17.36(1)	10.002(9)
α (deg)	106.570(5)	96.77(1)	
β (deg)	94.999(5)	93.450(8)	93.76(1)
γ (deg)	104.288(5)	97.979(9)	
V (Å^3)	2120(1)	2124(2)	1826(2)
Z	2	2	4
μ (cm^{-1})	5.90	5.89	3.32
F(000)	1044.00	1044.00	896.00
D_{calcd} (g cm^{-1})	1.619	1.616	1.598
no. unique reflns	9281	9276	4088
no. rflns measd	7529 ($I > 2\sigma(I)$)	7480 ($I > 2\sigma(I)$)	4088 ($I > 2\sigma(I)$)
no. variables	559	559	253
R_1[a]	0.088	0.087	0.106
R_w[a]	0.180	0.207	0.245

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

and 1.0 Hz), 7.73 (d, 1H, H^{6A}, J(H−H) = 4.6 Hz), 7.69 (d, 2H, H^{6D}, J(H−H) = 4.9 Hz), 7.53 (s, 1H, H^{2C}), 7.33 (ddd, 1H, H^{5A}, J(H−H) = 7.9, 4.6, and 1.7 Hz), 7.27 (ddd, 2H, H^{5D}, J(H−H) = 7.3, 5.6, and 1.3 Hz), 3.95 (s, 3H, N-*Me*), 3.00 (s, 3H, S-*Me*). $^{13}C\{^1H\}$ NMR (acetone-d_6, 67.8 MHz): δ 183.7, 164.8, 159.9, 158.8, 157.3, 156.1, 155.6, 152.6, 152.3, 152.2, 150.4, 139.4, 139.1, 137.6, 133.3, 128.6, 128.2, 125.5, 124.9, 124.2, 121.2, 120.5, 120.4, 47.9, 15.1.

[RuL²(terpy)][PF₆]₂ (4). $RuCl_3$(terpy) (100 mg, 0.227 mmol), [**L²**H][PF_6] (100 mg, 0.227 mmol), and triethylamine (2 mL) were dissolved in CH_3CH_2OH and refluxed for 3 h. The color of the solution turned immediately from brown to reddish-purple. The solution was concentrated to ca. 1 mL and poured into an aqueous NH_4PF_6 solution. The generated reddish-purple precipitate was collected by filtration and dried in vacuo. The obtained reddish-purple solid was purified by column chromatography (Al_2O_3(basic); eluent, acetonitrile) to give **4** as a red powder (160 mg, 76%). Recrystallization from an acetone−Et_2O mixture afforded **4** as brownish-red crystals. ESI-MS: m/z 314 $\{M - 2\ PF_6\}^{2+}$. Anal. Calcd for $C_{32}H_{26}F_{12}N_6P_2RuS$: C, 41.88; H, 2.86; N, 9.16. Found: C, 41.50; H, 2.88; N, 9.22. ^1H NMR (acetone-d_6, 270 MHz): δ 9.06 (s, 1H, H^{2C}), 8.96 (d, 2H, H^{3E}, J(H−H) = 7.9 Hz), 8.91 (d, 1H, H^{3A}, J(H−H) = 8.2 Hz), 8.77 (d, 1H, H^{3B}, J(H−H) = 1.3 Hz), 8.76 (d, 2H, H^{3D}, J(H−H) = 7.9 Hz), 8.54 (d, 1H, H^{5B}, J(H−H) = 1.3 Hz), 8.39 (t, 1H, H^{4E}, J(H−H) = 8.3 Hz), 8.13 (dt, 1H, H^{4A}, J(H−H) = 8.3 and 1.7 Hz), 8.04 (td, 2H, H^{4D}, J(H−H) = 7.9 and 1.3 Hz), 7.94 (d, 1H, H^{6A}, J(H−H) = 4.6 Hz), 7.70 (d, 2H, H^{6D}, J(H−H) = 5.6 Hz), 7.57 (dd, 1H, H^{6C}, J(H−H) = 6.3 and 1.3 Hz), 7.37 (ddd, 1H, H^{5A}, J(H−H) = 9.1, 7.1, and 0.8 Hz), 7.32 (ddd, 2H, H^{5D}, J(H−H) = 8.9, 5.6, and 1.3 Hz), 6.79 (d, 1H, H^{5C}, J(H−H) = 6.3 Hz), 4.11 (s, 3H, N-*Me*), 2.97 (s, 3H, S-*Me*). $^{13}C\{^1H\}$ NMR (acetone-d_6, 67.8 MHz): δ 225.6, 159.9, 158.6, 157.2, 155.7, 153.3, 153.0, 152.6, 150.3, 140.1, 138.2, 137.9, 135.6, 134.3, 133.6, 128.9, 128.4, 125.5, 125.1, 124.5, 119.5, 117.3, 47.3, 15.1.

X-ray Crystallographic Studies. Crystals for X-ray analyses were obtained as described in the preparations. Suitable crystals were mounted on grass fibers or sealed in thin-walled glass capillaries. Data collections for [**L²**H][PF_6], **3**, and **4** were performed at −100 °C on a Rigaku/MSC Mercury CCD diffractometer, using graphite-monochromated Mo Kα radiation (λ = 0.71070 Å). All data were collected and processed using the Crystal Clear program (Rigaku). All structures were solved by using the teXsan software package. Atomic scattering factors were obtained from the literature.[23] 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.

Supporting Information Available: The aromatic region of $^1H-^1H$ COSY spectra of **3** and **4**, molecular structure of [**L²**H][PF_6], tables of atomic coordinates, thermal parameters, and bond distances and angles for **3**, **4**, and [**L²**H][PF_6]. This material is available free of charge via the Internet at http://pubs.acs.org.

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