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Four-Electron Oxidative Dehydrogenation Induced by Proton-Coupled Electron Transfer in Ruthenium(III) Complex with 2-(1,4,5,6-Tetrahydropyrimidin-2-yl)phenolate

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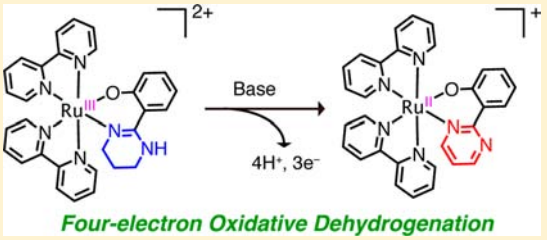
Supporting Information

ABSTRACT: New ruthenium(II or III) complexes with general formula $[Ru(O\text{-}N)(bpy)_2]^{n+}$ (O-N = unsymmetrical bidentate phenolate ligand; bpy = 2,2′-bipyridine) were synthesized, and their crystal structures and electrochemical properties were characterized. Ru^{II} complexes with 2-(2-imidazolinyl)phenolate ($Himn^-$) or 2-(1,4,5,6-tetrahydropyrimidin-2-yl)phenolate ($Hthp^-$) could be deprotonated by addition of excess KO^{t}Bu, although the deprotonated species were easily reprotonated by exposure to air. Unlike these Ru^{II} complexes, their Ru^{III} analogs showed interesting ligand oxidation reactions upon addition of bases. With $[Ru^{III}(Himn)(bpy)_2]^{2+}$, two-electron oxidation of $Himn^-$ and reduction of the Ru^{III} center resulted in conversion of the 2-imidazolinyl group to a 2-imidazolyl group. On the other hand, the corresponding $Hthp^-$ complex exhibited four-electron oxidation of the ligand to form 2-(2-pyrimidyl)phenolate (pym^-). These aromatization reactions of imidazolinyl and 1,4,5,6-tetrahydropyrimidyl groups were also achieved by the electrochemically generated Ru^{III} complexes.

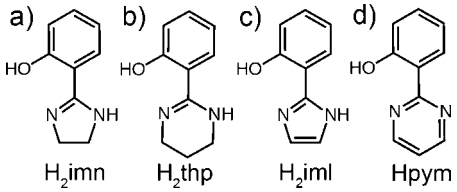


INTRODUCTION

Proton-coupled electron transfer (PCET) is a process in which electron transfer is accompanied by a change in protonation state (or vice versa). This process is currently one of the most fascinating research topics because this is a fundamental process in chemistry and biology.[1,2] For instance, in water oxidation catalysis, stepwise deprotonation of a coordinating water molecule leads to a higher oxidation state of the metal centers of the catalyst to achieve water oxidation.[3] PCET processes thus play crucial roles in catalytic reactions.[4,5] To achieve this pathway, a N−H or O−H moiety that is either directly coordinating or conjugating with a coordinating atom to a redox-active metal center is required. Maeda et al. reported an oxidation of 2-substituted imidazoline via a PCET process to afford the corresponding imidazole in $[Ru(dib)(tpy)]PF_6$ (Hdib = 1,3-di(imidazoline-2-yl)benzene; tpy = 2,2′:6′,2″-terpyridine).[5a] In this reaction, it was suggested that an intermediate Ru^{IV} species was produced by a PCET process induced by deprotonation of the imidazolinyl group. This active intermediate induces a two-electron oxidation of the imidazolinyl group to an imidazolyl group. In the ligand dib^-, an anionic phenyl-C donor with strong σ donicity presumably contributed to the low redox potential of the Ru center to achieve the high oxidation state.

We are interested in the phenolate-O donor because it is not only a strong σ donor but also a moderate π donor, while the phenyl-C donor is a π acceptor.[6] Although PCET studies on such phenolate-type ligands have not been conducted much so far, the difference in the π donicity compared with a phenyl-C donor would stabilize the high oxidation state of the metal center and lead the complex to have stronger oxidation ability. Thus, we designed phenolate-based ligand precursors with nonaromatic heterocycles, 2-imidazolinyl-2′-phenol (H_2imn) and 2-(1,4,5,6-tetrahydropyrimidin-2-yl)phenol (H_2thp) (Scheme 1), to investigate the redox behaviors of their Ru complexes upon deprotonation. Here, we report two oxidation reactions upon base addition: (1) two-electron oxidation of $Himn^-$ in $[Ru^{III}(Himn)(bpy)_2]^{2+}$ to form an imidazolate-type complex, $[Ru^{II}(iml)(bpy)_2]$ ($Himl^-$ = 2-(2-imidazolyl)-phenolate) and (2) an unprecedented four-electron oxidation of $Hthp^-$ in $[Ru^{III}(Hthp)(bpy)_2]^{2+}$ to form a pyrimidine-type complex, $[Ru^{II}(pym)(bpy)_2]^+$ (pym^- = 2-(2-pyrimidyl)-phenolate). We suggest that these reactions were induced by deprotonation of the coordinating ligand.

Scheme 1. Chemical Structures of Ligand Precursors of (a) H_2imn, (b) H_2thp, (c) H_2iml, and (d) Hpym



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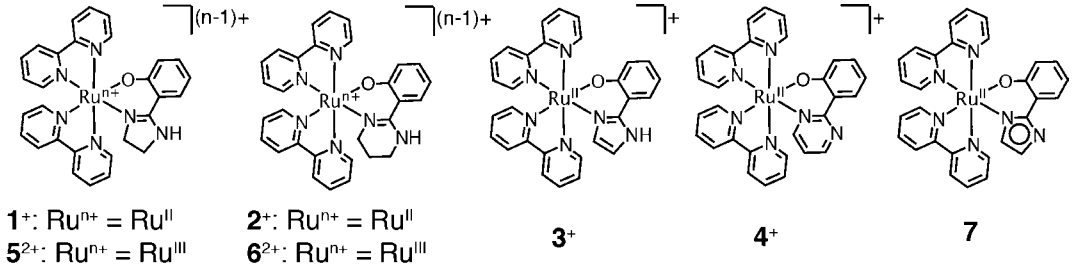
Scheme 2. Chemical Structures of the Ru Complexes



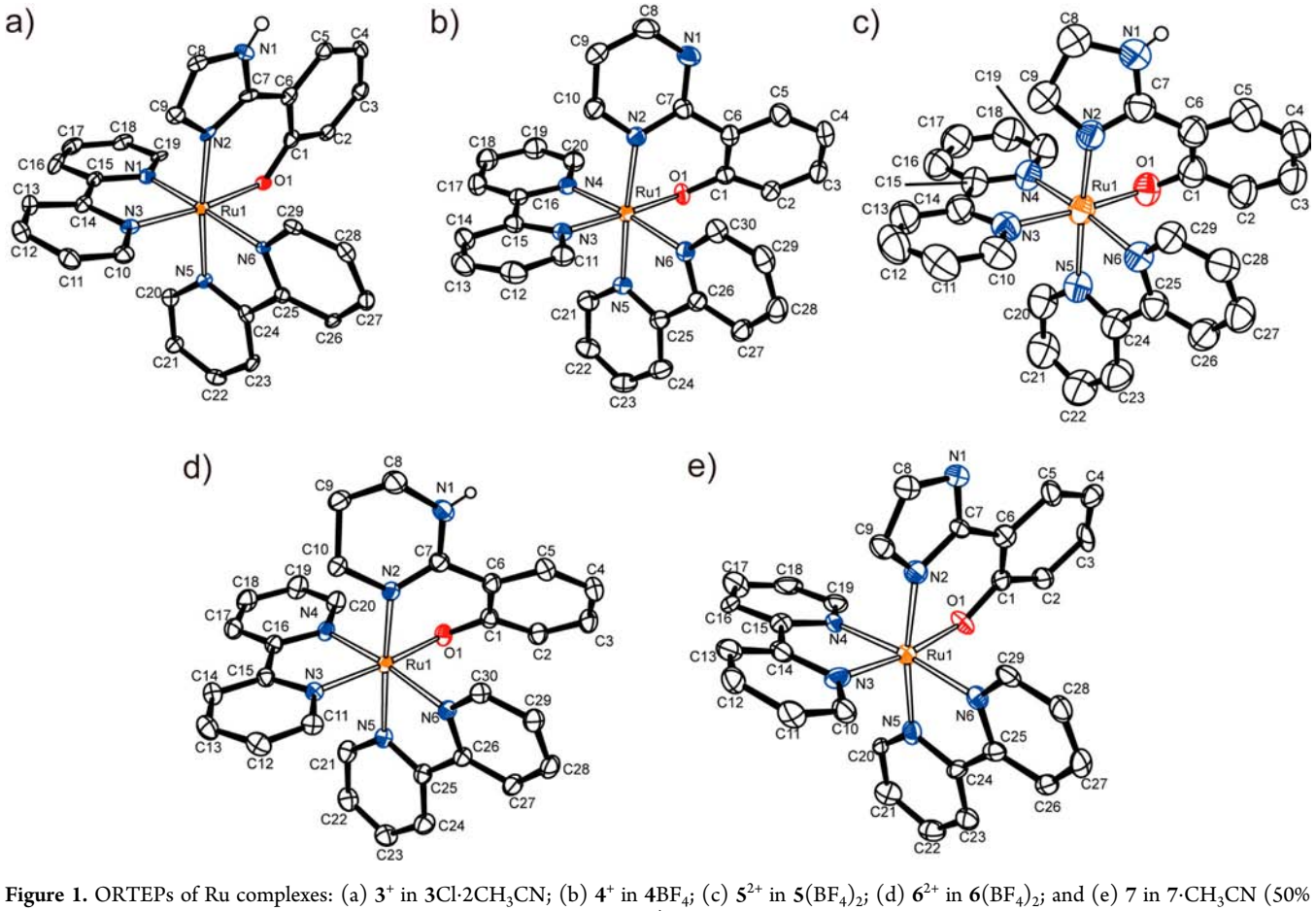


Figure 1. ORTEPs of Ru complexes: (a) 3^+ in $3Cl\cdot 2CH_3CN$; (b) 4^+ in $4BF_4$; (c) 5^{2+} in $5(BF_4)_2$; (d) 6^{2+} in $6(BF_4)_2$; and (e) 7 in $7\cdot CH_3CN$ (50% probability level, H atoms are omitted for clarity except for N−H atoms).

RESULTS AND DISCUSSION

Synthesis and Structures. The nonaromatic heterocyclic ligand precursors, H_2imn and H_2thp, were obtained by condensation of methyl salicylate and excess 1,2-diaminoethane or 1,3-diaminopropane at 130 °C. The aromatic heterocyclic ligand precursors, H_2iml and Hpym, were prepared by oxidation of the corresponding nonaromatic heterocycles using Pd/C and MnO_2, respectively.[7,8] Slow evaporation of methanol solutions of H_2imn, H_2thp, and Hpym afforded their colorless crystals, and X-ray crystallographic analyses of these crystals were carried out (see Supporting Information Figures S1−S3). In the crystals, H_2imn and H_2thp were found to exist in zwitterionic form; the phenol-O atom was deprotonated, and the imino-N atom was protonated. On the other hand, the O atom of Hpym has a proton in the crystal. These differences in their protonated forms are indicative of the stronger electron-donor ability of the N atom in nonaromatic heterocycles than that in aromatic heterocycles.

Stoichiometric reaction of the singly deprotonated ligand, $Himn^-$, $Hthp^-$, $Himl^-$, or pym^- with $[RuCl_2(bpy)_2]\cdot 2H_2O$ in refluxing methanol, followed by addition of $NaBF_4$, afforded the Ru^{II} complexes $[Ru(Himn)(bpy)_2]BF_4$ ($\mathbf{1}BF_4$), $[Ru(Hthp)(bpy)_2]BF_4$ ($\mathbf{2}BF_4$), $[Ru(Himl)(bpy)_2]BF_4$ ($\mathbf{3}BF_4$), and $[Ru(pym)(bpy)_2]BF_4$ ($\mathbf{4}BF_4$). The corresponding Ru^{III} complexes for $\mathbf{1}BF_4$ and $\mathbf{2}BF_4$ were readily obtained as $[Ru^{III}(Himn)(bpy)_2](BF_4)_2$ ($\mathbf{5}(BF_4)_2$) and $[Ru^{III}(Hthp)(bpy)_2](BF_4)_2$ ($\mathbf{6}(BF_4)_2$) by stoichiometric reaction of $\mathbf{1}BF_4$ or $\mathbf{2}BF_4$ with $AgBF_4$ in methanol.[9] Chemical structures of Ru complexes are shown in Scheme 2. Compositions of $\mathbf{5}(BF_4)_2$ and $\mathbf{6}(BF_4)_2$ were confirmed by elemental analyses. Oxidation of $\mathbf{3}BF_4$ using $[FeCp_2]PF_6$ was unsuccessful because of its decomposition. Moreover, $\mathbf{4}BF_4$ did not react with $[FeCp_2]PF_6$ because of its high oxidation potential. Single crystals of these complexes

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suitable for X-ray analysis were obtained by diffusion of diethyl ether vapor into a methanol solution of each complex, except for $3BF_4$. Single crystals of $3Cl{\cdot}2CH_3CN$ were obtained from a mixture of $3BF_4$, 1,8-diazabicyclo[5,4,6]undec-7-ene (DBU), and $NEt_3{\cdot}HCl$. Molecular structures of the complex cations in the crystals are shown in Figures 1 and S4, Supporting Information. All complexes except for $4BF_4$ possess a proton at the N1 position. All Ru^{II} complex cations showed similar bond distances, and their ^1H NMR spectra are consistent with the molecular structures obtained from X-ray analyses. In the complexes with nonaromatic heterocycles, the bond distances of N1−C7 and N2−C7 are different in the Ru^{II} complexes, whereas they are comparable in the Ru^{III} complexes. This indicates that the π conjugation between N1−C7−N2 is stronger in the Ru^{III} complexes and suggests that deprotonation of the coordinating ligand in Ru^{III} complexes is more probable.

Deprotonation of the Complexes. Since X-ray crystallography indicated that all complexes except for $4BF_4$ have a noncoordinating N−H group, deprotonation of the complexes was examined. Ru^{II} complexes with nonaromatic heterocycles, $1BF_4$ and $2BF_4$, were not easily deprotonated by common bases such as triethylamine, DBU, or sodium hydroxide in acetonitrile. However, the colors of acetonitrile solutions changed from violet to green when excess KO^tBu was added under an N_2 atmosphere (Figures 2 and S5, Supporting Information). When a drop of deaerated water was added to the resulting green solution or it was exposed to air, the solutions immediately (within 10 s) returned to violet. ^1H NMR spectra of $2BF_4$ in CD_3CN, a mixture of $2BF_4$ and KO^tBu in a dry N_2 atmosphere, and the same mixture after air exposure are shown in Figure 3. Since the spectra showed only a slight shift and broadening of the resonances upon adding KO^tBu, it is suggested that deprotonated species were produced. The spectra also indicated that the deprotonated green complex returned to its original species upon air exposure. With $1BF_4$, decomposition of 1^+ was observed after air exposure, as shown in Figure S5, Supporting Information. These results indicate that the deprotonated ligands, imn^{2-} and thp^{2-}, in the complex were highly reactive and easily reprotonated by the moisture in the air, showing the strong basicity of these ligands.

In contrast to $1BF_4$ and $2BF_4$, $3BF_4$, with an aromatic imidazole ring, was readily deprotonated by adding an excess amount of DBU in acetonitrile in air, and the deprotonated species, $[Ru^{II}(iml)(bpy)_2]$ (7), was observed by ^1H NMR spectroscopy. Single crystals of $7{\cdot}CH_3CN$ suitable for X-ray analysis were obtained by standing $3BF_4$ with 10 equiv of DBU in acetonitrile. The crystal structure of 7 in $7{\cdot}CH_3CN$ is shown in Figure 1e. The UV−vis spectral change for $3BF_4$ upon DBU titration is shown in Figure 4. The spectral change for $3BF_4$

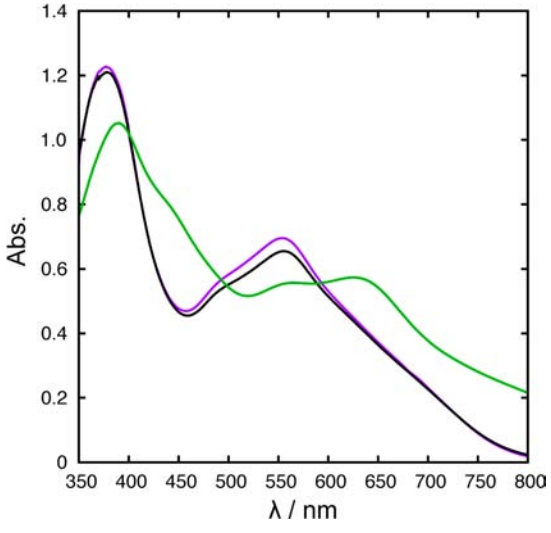

Figure 2. Absorption spectra of $2BF_4$ (violet), with excess KO^tBu (green) and after air exposure (black) in acetonitrile. $2BF_4$ solution was 1.0×10^{-4} M. Other solutions have the same concentration, although exact values are uncertain.

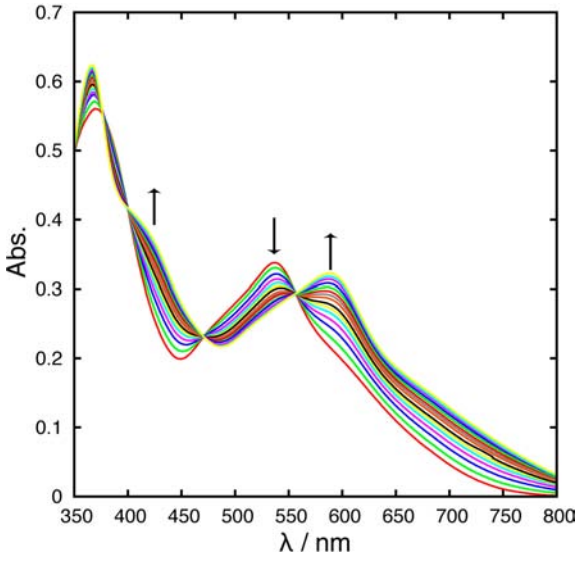

Figure 4. UV−vis spectra of $3BF_4$ upon addition of DBU in acetonitrile (0−15 equiv).

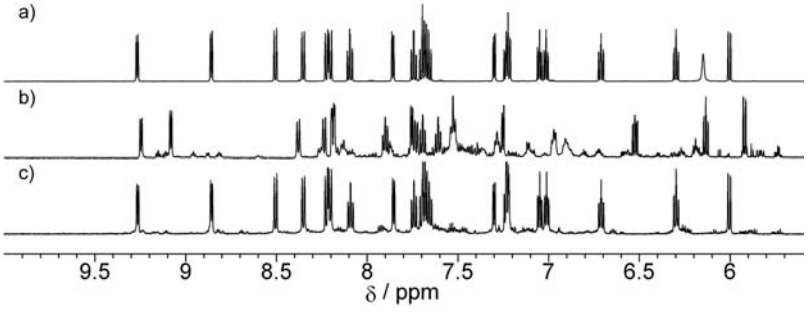

Figure 3. (a) ^1H NMR spectra of $2BF_4$, (b) $2BF_4$ with KO^tBu under N_2, and (c) $2BF_4$ with KO^tBu after air exposure in CD_3CN.

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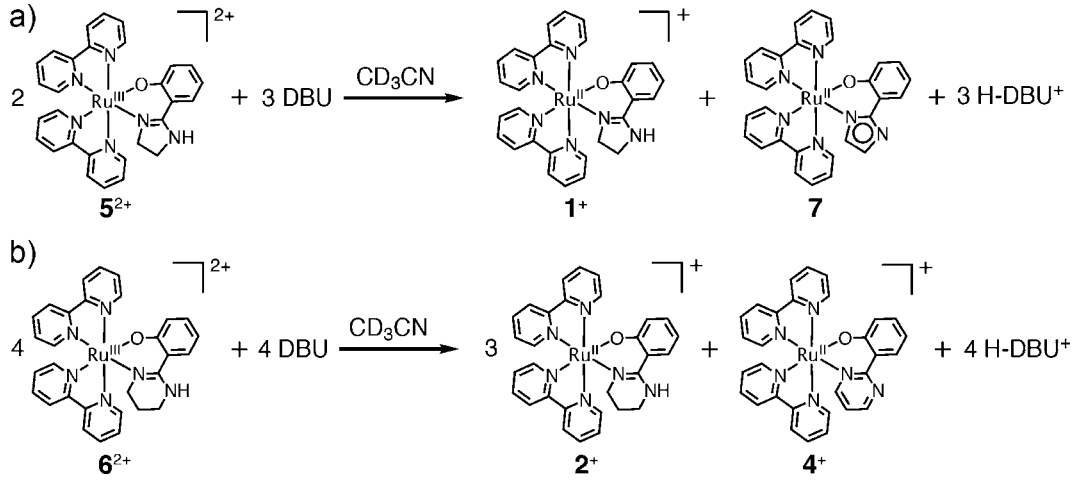
Scheme 3. (a) Two-Electron Oxidation of $Himn^-$ in 5^{2+} to iml^{2-}, and (b) Four-Electron Oxidation of $Hthp^-$ in 6^{2+} to pym^-



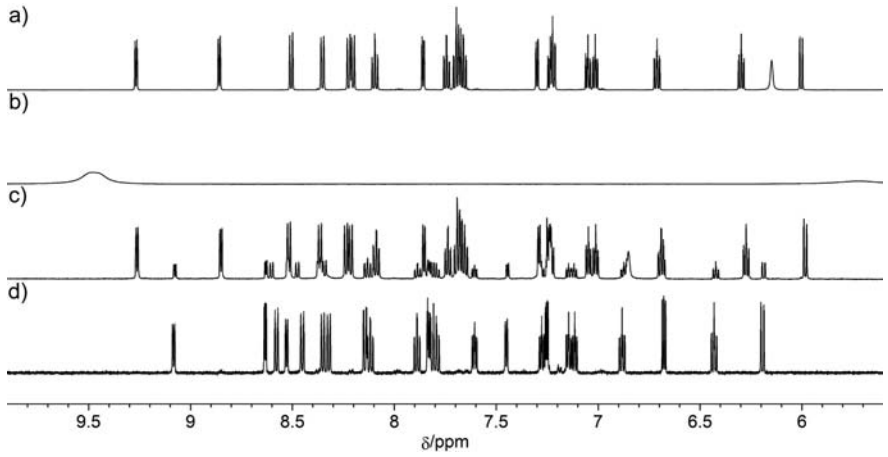


Figure 5. ^1H NMR spectra of (a) $2BF_4$, (b) $6(BF_4)_2$, (c) $6(BF_4)_2$ with excess DBU, and (d) $4BF_4$ in CD_3CN. Resonance corresponding to the N–H atom was shifted from 6.15 ppm in $2BF_4$ to 6.85 ppm in $6(BF_4)_2$ with excess DBU because of the hydrogen bond with DBU.

solution is quite similar to that for $1BF_4$ and $2BF_4$. This is further evidence that $1BF_4$ and $2BF_4$ were deprotonated by KO^tBu in acetonitrile under an N_2 atmosphere. The pK_a value for $3BF_4$ was determined to be 24.1 from the change in the absorbance (see Supporting Information for detail). This value is slightly higher than those for the analogous complexes, $[Ru^{II}(py\text{-}imH)(acac)_2]$ and $[Ru^{II}(py\text{-}imH)(hfac)_2]$ (pK_a = 22.1 and 19.3, respectively; py-imH = 2-(2′-pyridyl)imidazole, $acac^-$ = acetylacetonate, $hfac^-$ = hexafluoroacetylacetonate),[10] suggesting the low acidity of the phenol-type ligand.

Since a higher oxidation state of the metal center generally gives a stronger acidity of the coordinating ligand,[10,11] we supposed that deprotonation of the corresponding Ru^{III} complexes, $5(BF_4)_2$ and $6(BF_4)_2$, was accessible. When a brown acetonitrile solution of $5(BF_4)_2$ was reacted with DBU, the reaction solution turned violet. This reaction was followed by ^1H NMR measurements (Figure S6, Supporting Information). The spectrum of the reaction mixture in CD_3CN showed diamagnetic features, while $5(BF_4)_2$ showed paramagnetically shifted resonances (Figure S6c, Supporting Information). In this spectrum, two sets of resonances were observed and no unreacted 5^{2+} was detected. Since two-electron oxidative conversion of the coordinating imidazoline-type ligand to an imidazole-type ligand was reported by Maeda et al.,[5] we postulated that the Ru^{III} center was reduced by a similar oxidation process of the imidazoline group in this reaction (Scheme 3a). From comparison of the ^1H NMR spectra, it is clear that 1^+ and **7** exist in the reaction mixture, indicating that the ligand, $Himn^-$, in 5^{2+} underwent two-electron oxidation and deprotonation of the imidazole group. In general, such a conversion of imidazoline to an imidazole group without a strong oxidant such as MnO_2 or $NaIO_4$ and high temperature is limited.[12] However, in the present Ru^{III} complex, conversion of the imidazolinyl group to the imidazolyl group proceeded readily. This was presumably because of formation of a Ru^{IV} active species, which oxidizes the imidazolinyl group, by the PCET process.[5]

Similar to $5(BF_4)_2$, the reaction solution of $6(BF_4)_2$ and excess DBU in acetonitrile showed a color change from brown to violet. The ^1H NMR spectrum of the reaction mixture showed two sets of resonances without those of unreacted 6^{2+} (Figure 5c). Since one of the products was consistent with a Ru^{II} complex with $Hthp^-$, 2^+, and the other product also showed diamagnetic features, it is suggested that the Ru^{III} ion in $6(BF_4)_2$ was reduced to Ru^{II}. In addition, the formation ratio of 2^+ and the other product was found to be 3:1. From these results, we assumed that the coordinating ligand $Hthp^-$ was oxidized by a four-electron process to give a pyrimidine-type complex, 4^+, accompanied by the reduction of the Ru^{III} center and regeneration of three 2^+ cations (Scheme 3b). The ^1H

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NMR spectrum of pure $4BF_4$ was identical to that of one of the products other than 2^+ in the reaction. Thus, 2^+ and 4^+ were formed in a 3:1 ratio as a consequence of the four-electron oxidation of $Hthp^-$ in 6^{2+} by deprotonation with DBU. It is worth noting that four-electron oxidation of the 1,3,4,5-tetrahydropyrimidyl group was readily achieved under mild conditions, although such a reaction generally requires a strong oxidant and high reaction temperature.[8]

The possibility of utilizing NH_3, NEt_3, KO^tBu, or NMe_4OH as bases was examined for this unusual four-electron oxidation reaction induced by deprotonation. KO^tBu and NMe_4OH showed similar reactions. However, when 6^{2+} was treated with NEt_3, 2^+ was obtained without formation of 4^+. This suggests that oxidation of NEt_3 is more favorable than oxidation of ligand $Hthp^-$ because of the low oxidation potential of NEt_3.[13] Furthermore, bubbling NH_3 gas into an acetonitrile solution of $6(BF_4)_2$ for 15 min produced no change in the ^1H NMR spectrum, indicating that NH_3 is not basic enough to deprotonate 6^{2+}. These results suggest that deprotonation of 6^{2+} is necessary for this interesting reaction as well as the stability of the base against oxidation.

Electrochemistry. Oxidation of the coordinating ligand was also carried out via an electrochemical $1^+/5^{2+}$ or $2^+/6^{2+}$ oxidation process in the presence of a base. Cyclic voltammograms (CVs) of the Ru complexes are shown in Figures 6 and

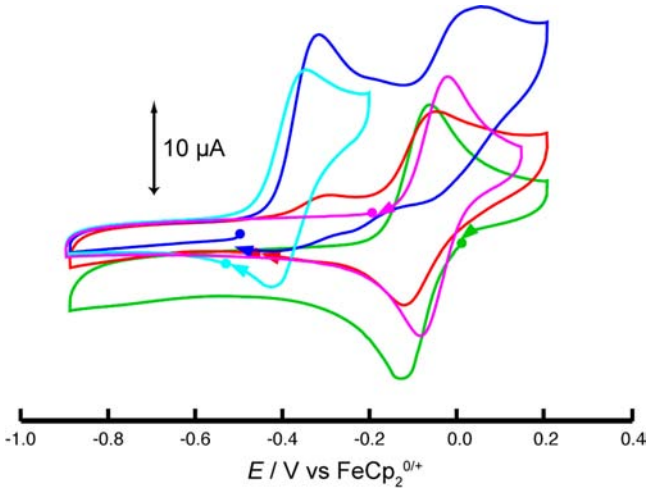

Figure 6. Cyclic voltammograms of $5(BF_4)_2$ (green), $5(BF_4)_2$ with 1 equiv of DBU (red), $5(BF_4)_2$ with 3 equiv of DBU (blue), and $3BF_4$ (magenta) and $3BF_4$ with 1 equiv of DBU, i.e., 7 (cyan). All scans were started from the rest potential.

7, and electrochemical data are summarized in Table 1. The $Ru^{II/III}$ redox couple was observed at −0.095 V vs $FeCp_2^{0/+}$ (ΔE = 64 mV) for $5(BF_4)_2$ and −0.162 V (ΔE = 64 mV) for $6(BF_4)_2$. The CVs of $1BF_4$ and $2BF_4$ were identical to those of $5(BF_4)_2$ and $6(BF_4)_2$, respectively. The redox couples of 2-phenylpyridinate and 2-benzoimidazolyl-phenolate analogs in the literature were reported as $E_{1/2}$ = 0.06 and 0.07 V, respectively.[14] The lower redox potentials of $1^+/5^{2+}$ and $2^+/6^{2+}$ compared with these analogs are indicative of the stronger donor ability of the phenolate group and nonaromatic heterocycle. When DBU (1 equiv) was added to the solution of $5(BF_4)_2$, the rest potential was cathodically shifted (from 0.02 to −0.45 V), which indicates reduction of the Ru^{III} center. On addition of 3 equiv of DBU, two redox couples were observed, which correspond to $3^{+/2+}$ and $7^{0/+}$ ($E_{1/2}$ = −0.052

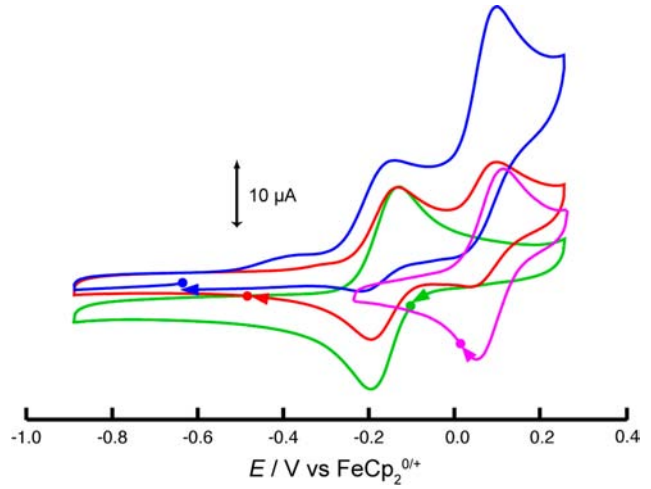

Figure 7. Cyclic voltammograms of $6(BF_4)_2$ (green), $6(BF_4)_2$ with 1 equiv of DBU (red), $6(BF_4)_2$ with 3 equiv of DBU (blue), and $4BF_4$ (magenta). All scans were started from the rest potential.

Table 1. Electrochemical Data for $5(BF_4)_2$, $6(BF_4)_2$, $3BF_4$, and $4BF_4$ upon Addition of DBU (vs $FeCp_2^{0/+}$)

	E_a/V	E_c/V	$E_{1/2}$/V	ΔE/mV
$5(BF_4)_2$	−0.063	−0.127	−0.095	64
$5(BF_4)_2$ + 3DBU	−0.317			
	0.054			
$6(BF_4)_2$	−0.130	−0.194	−0.162	64
$6(BF_4)_2$ + DBU	−0.142	−0.214	−0.178	72
	0.099	0.042	0.070	57
$3BF_4$	−0.021	−0.083	−0.052	62
$3BF_4$ + DBU	−0.360	−0.431	−0.395	71
$4BF_4$	0.114	0.051	0.082	62

and −0.395 V, respectively), while the original $1^+/5^{2+}$ couple almost disappeared (see Figure 6). In these CVs, the $7^{0/+}$ redox couple appears to be irreversible, presumably because of the deposition of 7 on the surface of the electrode during the reduction process. With $6(BF_4)_2$, the rest potential was cathodically shifted by addition of 1 equiv of DBU in the same manner (Figure 7). The $6^{2+}/2^+$ reduction current decreased significantly without any shift in the $2^+/6^{2+}$ redox potential. In addition, a new reversible redox couple at $E_{1/2}$ = 0.070 V was observed. After addition of 3 equiv of DBU, the $6^{2+}/2^+$ reduction process nearly disappeared and the oxidation current of the new redox couple became larger. The i_{pc}/i_{pa} ratio (i_{pc} = cathodic current, i_{pa} = anodic current) got closer to 1 in high scan rate (Figure S8, Supporting Information). The decrease of the $6^{2+}/2^+$ reduction current and scan rate dependence of the i_{pc}/i_{pa} ratio indicate the existence of a subsequent chemical reaction. Since the new redox couple was consistent with that of $4^{+/2+}$ ($E_{1/2}$ = 0.082 V), it is suggested that 4^+ was formed by electrochemical reaction. Thus, conversion of 1,4,5,6-tetrahydropyrimidyl to the pyrimidyl group was also readily accessible by electrochemical reaction in the presence of a base under mild conditions.

CONCLUSION

We succeeded in synthesizing and characterizing seven $[Ru(O-N)(bpy)_2]^{n+}$-type complexes with ligands $Himn^-$, $Hthp^-$, $Himl^-$, iml^{2-}, and pym^-. Ru^{II} complexes of $1BF_4$ and $2BF_4$ were hardly deprotonated, because of the weak acidity of the

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nonaromatic heterocyclic ligands, although deprotonated Ru^{II} derivatives were spectroscopically observed. On the other hand, $\mathbf{3}BF_4$ with $Himl^-$ was deprotonated by addition of DBU and the pK_a value for $\mathbf{3}^+$ was determined by a UV−vis titration experiment. Ru^{III} complexes, $\mathbf{5}(BF_4)_2$ and $\mathbf{6}(BF_4)_2$, showed aromatization reactions upon addition of a base. Complex $\mathbf{5}(BF_4)_2$ showed two-electron oxidation of the coordinating $Himn^-$ ligand to afford an imidazolate-type complex, **7**. Furthermore, $\mathbf{6}(BF_4)_2$ showed unprecedented four-electron oxidation of the coordinating $Hthp^-$ ligand to form a pyrimidine-type complex, $\mathbf{4}^+$. These fascinating aromatization reactions were also achieved by electrochemical oxidation of $\mathbf{1}BF_4$ or $\mathbf{2}BF_4$. In general, such four-electron transfer reactions using one metal center without a strong oxidant are difficult because the metal center can accommodate only a limited number of electrons. Therefore, this new reaction, in which only one metal center mediates a four-electron process without a strong oxidant, will provide new insights for various multielectron reactions.

EXPERIMENTAL SECTION

All chemicals were used as received without further purification. The starting material of the Ru complexes, $[Ru(bpy)_2Cl_2]\cdot 2H_2O$, was prepared according to the reported procedure.[15] UV−vis absorption spectra were recorded at room temperature on a Jasco V-550 spectrophotometer. Proton NMR measurements were carried out at 22 °C using Varian NMR system 600 and Varian Mercury 300 spectrometers. Chemical shifts were referenced to the solvent residual peak.[16]

2-(2-Imidazolinyl)phenol (H_2imn). A mixture of methyl salicylate (7.61 g, 50.0 mmol) and 1,2-diaminoethane (9.03 g, 150.0 mmol) was refluxed overnight. The unreacted 1,2-diaminoethane was evaporated off under ambient pressure. After cooling, the colorless residue was dissolved in methanol (60 mL). Colorless crystals were obtained by slow evaporation of methanol. Yield: 3.94 g (49%). ^{1}H NMR (CD_3OD, 22 °C): δ 3.91 (s, 4H, $-CH_2-$), 6.47 (ddd, J = 8.1, 7.0, and 1.1 Hz, 1H, aryl-H), 6.71 (dd, J = 8.6 and 0.8 Hz, 1H, aryl-H), 7.26 (ddd, J = 8.7, 6.9, and 1.8 Hz, 1H, aryl-H), 7.41 (dd, J = 8.1 and 1.1 Hz, 1H, aryl-H).

2-(1,4,5,6-Tetrahydropyrimidin-2-yl)phenol (H_2thp). This ligand precursor was prepared by a similar method to that for H_2imn using methyl salicylate (7.61 g, 50.0 mmol) and 1,3-diaminopropane (11.12 g, 150.0 mmol). Yield: 7.56 g (86%). ^{1}H NMR (CD_3OD, 22 °C): δ 2.01−2.06 (m, 2H, $-CH_2-$), 3.54 (t, J = 5.9 Hz, 4H, $-CH_2-$), 6.49 (ddd, J = 8.2, 7.0, and 1.2 Hz, 1H, aryl-H), 6.70 (dd, J = 8.6 and 1.2 Hz, 1H, aryl-H), 7.20 (ddd, J = 8.6, 6.8, and 1.7 Hz, 1H, aryl-H), 7.42 (dd, J = 8.1 and 1.7 Hz, 1H, aryl-H).

2-(2-Imidazolyl)phenol (H_2iml). This compound was prepared by a similar method to that reported in the literature.[7] H_2imn (1.77 g, 10.9 mmol) and 10% Pd/C (0.15 g) were added to diphenyl ether (12 mL). The mixture was refluxed for 5 h, followed by filtration through Celite while the solution was hot. The cooled filtrate was chromatographed on a silica gel column. H_2iml was eluted from the column with toluene, and the toluene was removed by evaporation. H_2iml was obtained as a colorless solid. Yield: 1.41 g (81%). ^{1}H NMR (CD_3OD, 22 °C): δ 6.89 (dd, 1H, J = 7.9 and 7.3 Hz, aryl-H), 6.93 (d, 1H, J = 8.2 Hz, aryl-H), 7.12 (s, 2H, aryl-H), 7.20 (dd, J = 8.2 and 7.3 Hz, 1H, aryl-H), 7.73 (d, J = 7.8, Hz, 1H, aryl-H).

2-(2-Pyrimidyl)phenol (Hpym). This compound was synthesized using a method modified from that reported in the literature.[8] A mixture of H_2thp (0.86 g, 4.90 mmol) and MnO_2 (3.20 g) in toluene (30 mL) was refluxed for 3 days, followed by filtration through Celite while hot. The cooled filtrate was chromatographed on a silica gel column. Hpym was eluted with toluene, and the toluene was removed by evaporation. Hpym was obtained as a colorless solid. Yield: 0.046 g (6%). ^{1}H NMR (CD_3OD, 22 °C): δ 6.93−6.96 (m, 2H, aryl-H), 7.36−7.39 (m, 2H, aryl-H), 8.46 (d, 1H, J = 8.4 Hz, aryl-H), 8.86 (d, 2H, J = 4.8 Hz, aryl-H).

[Ru(Himn)(bpy)$_2$]BF$_4$·CH$_3$OH ($\mathbf{1}BF_4\cdot CH_3OH$). H_2imn (0.090 g, 0.60 mmol), sodium methoxide (0.029 g, 0.60 mmol), and $[Ru(bpy)_2Cl_2]\cdot 2H_2O$ (0.258 g, 0.50 mmol) were added to methanol (20 mL). The mixture was refluxed under an N_2 atmosphere overnight. After cooling the solution to room temperature, a methanol (10 mL) solution of $NaBF_4$ (0.195 g, 1.8 mmol) was added and the mixture was stirred for 10 min. Solvent was removed by evaporation, and the resulting oily residue was dried in vacuo. The residue was extracted with CH_2Cl_2 (20 mL). The filtered extract was evaporated under reduced pressure, and the residue was dissolved again in methanol (15 mL). Diethyl ether vapor was diffused into the solution to give dark violet crystals. Yield: 0.271 g (78%). Anal. Calcd for $[Ru(Himn)(bpy)_2]BF_4\cdot CH_3OH = C_{30}H_{29}BF_4N_6O_2Ru$: C, 51.96; H, 4.22; N, 12.12. Found: C, 51.61; H, 4.01; N, 12.00. ^{1}H NMR (CD_3CN, 22 °C): δ 2.63 (m, 1H, $-CH_2-$), 3.19 (m, 1H, $-CH_2-$), 3.32 (m, 1H, $-CH_2-$), 3.45 (m, 1H, $-CH_2-$), 5.93 (s, 1H, N−H), 6.35 (m, 2H, aryl-H), 6.94 (ddd, J = 8.6, 6.9, and 1.8 Hz, 1H, aryl-H), 7.08 (ddd, J = 7.4, 5.8, and 1.5 Hz, 1H, aryl-H), 7.14 (ddd, J = 7.4, 5.8, and 1.3 Hz, 1H, aryl-H), 7.24 (dd, J = 8.1 and 1.8 Hz, 1H, aryl-H), 7.46 (ddd, J = 7.4, 5.8, and 1.3 Hz, 1H, aryl-H), 7.52 (dd, J = 5.7 and 1.5 Hz, 1H, aryl-H), 7.59 (ddd, J = 7.4, 5.8, and 1.3 Hz, 1H, aryl-H), 7.78 (m, 3H, aryl-H), 7.92 (dt, J = 7.9 and 1.5 Hz, 1H, aryl-H), 8.03 (dt, J = 7.9 and 1.5 Hz, 1H, aryl-H), 8.33 (m, 2H, aryl-H), 8.38 (d, J = 8.0 Hz, 1H, aryl-H), 8.44 (d, J = 8.1 Hz, 1H, aryl-H), 8.77 (d, J = 5.6 Hz, 1H, aryl-H), 8.87 (d, J = 5.6 Hz, 1H, aryl-H).

[Ru(Hthp)(bpy)$_2$]BF$_4$·CH$_3$OH ($\mathbf{2}BF_4\cdot CH_3OH$). This compound was prepared by analogy with $\mathbf{1}BF_4$ using H_2thp (0.211 g, 1.2 mmol), sodium methoxide (0.065 g, 1.2 mmol), $[Ru(bpy)_2Cl_2]\cdot 2H_2O$ (0.525 g, 1.0 mmol), and $NaBF_4$ (0.336 g, 3.1 mmol). Yield: 0.599 g (84%). Anal. Calcd for $[Ru(Hthp)(bpy)_2]BF_4\cdot CH_3OH = C_{31}H_{31}BF_4N_6O_2Ru$: C, 52.63; H, 4.42; N, 11.88. Found: C, 52.49; H, 4.00; N, 11.62. ^{1}H NMR (CD_3CN, 22 °C): δ 1.36 (m, 1H, $-CH_2-$), 1.66 (m, 1H, $-CH_2-$), 2.15 (m, 1H, $-CH_2-$), 2.50 (m, 1H, $-CH_2-$), 3.14 (m, 1H, $-CH_2-$), 3.31 (m, 1H, $-CH_2-$), 6.00 (dd, J = 8.3 and 1.2 Hz, 1H, aryl-H), 6.13 (s, 1H, N−H), 6.30 (ddd, J = 8.0, 6.9, and 1.2 Hz, 1H, aryl-H), 6.71 (ddd, J = 8.5, 6.8, and 1.6 Hz, 1H, aryl-H), 7.01 (ddd, J = 6.6, 5.0, and 1.5 Hz, 1H, aryl-H), 7.05 (ddd, J = 6.6, 4.9, and 1.4 Hz, 1H, aryl-H), 7.22 (dd, J = 7.6 and 1.8 Hz, 1H, aryl-H), 7.23 (ddd, J = 7.4, 5.8, and 1.4 Hz, 1H, aryl-H), 7.30 (ddd, J = 5.7, 1.5, and 0.8 Hz, 1H, aryl-H), 7.70 (m, 4H, aryl-H), 7.85 (ddd, J = 5.8, 1.4, and 0.8 Hz, 1H, aryl-H), 8.09 (ddd, J = 8.7, 7.1, and 1.1 Hz, 1H, aryl-H), 8.21 (m, 2H, aryl-H), 8.35 (ddd, J = 8.3, 1.3, and 0.8 Hz, 1H, aryl-H), 8.50 (ddd, J = 8.3, 1.2, and 0.9 Hz, 1H, aryl-H), 8.86 (ddd, J = 5.7, 1.5, and 0.8 Hz, 1H, aryl-H), 9.26 (ddd, J = 5.6, 1.6, and 0.8 Hz, 1H, aryl-H).

[Ru(Himl)(bpy)$_2$]BF$_4$ ($\mathbf{3}BF_4$). This compound was prepared by analogy with $\mathbf{1}BF_4$ using H_2iml (0.041 g, 0.26 mmol), sodium methoxide (0.014 g, 0.26 mmol), $[Ru(bpy)_2Cl_2]\cdot 2H_2O$ (0.101 g, 0.19 mmol), and $NaBF_4$ (0.102 g, 0.91 mmol). Yield: 0.115 g (0.17 mmol, 89%). Anal. Calcd for $[Ru(Himl)(bpy)_2]BF_4 = C_{29}H_{23}BF_4N_6ORu$: C, 52.82; H, 3.52; N, 12.74. Found: C, 52.97; H, 3.80; N, 12.70. ^{1}H NMR (CD_3CN, 22 °C): δ 5.67 (d, J = 1.6 Hz, 1H), 6.40 (ddd, J = 7.9, 6.9, and 1.1 Hz, 1H), 6.41 (dd, J = 8.4 and 0.9 Hz, 1H), 6.88 (ddd, J = 8.5, 6.9, and 1.7 Hz, 1H), 6.95 (d, J = 1.6 Hz, 1H), 7.14 (ddd, J = 7.4, 5.8, and 1.4 Hz, 1H), 7.16 (ddd, J = 7.4, 5.9, and 1.4 Hz, 1H), 7.33 (ddd, J = 6.4, 5.7, and 1.3 Hz, 1H), 7.34 (dd, J = 6.1 and 1.6 Hz, 1H), 7.52 (ddd, J = 7.4, 5.8, and 0.9 Hz, 1H), 7.63 (d, J = 5.1 Hz, 1H), 7.78 (dt, J = 7.8 and 1.4 Hz, 1H), 7.82 (ddd, J = 8.5, 7.1, and 1.0 Hz, 1H), 7.86 (d, J = 5.7 Hz, 1H), 7.89 (dt, J = 7.9 and 1.4 Hz, 1H), 7.98 (ddd, J = 8.6, 7.2, and 1.0 Hz, 1H), 8.23 (d, J = 5.6 Hz, 1H), 8.35 (m, 2H), 8.39 (d, J = 8.2 Hz, 1H), 8.43 (d, J = 8.1 Hz, 1H), 8.94 (d, J = 4.9 Hz, 1H), 10.60 (s, 1H, N−H). The single crystal for X-ray analysis was obtained as $\mathbf{3}Cl\cdot 2CH_3CN$ by standing the mixture of $\mathbf{3}BF_4$ (0.0067 g, 10.2 μmol), DBU (15.0 μL, 96.9 μmol), and $NEt_3\cdot HCl$ (0.0370 g, 268.8 μmol) in 5 mL of acetonitrile.

[Ru(pym)(bpy)$_2$]BF$_4$ ($\mathbf{4}BF_4$). This compound was prepared by analogy with $\mathbf{1}BF_4$ using Hpym (0.043 g, 0.25 mmol), sodium methoxide (0.016 g, 0.30 mmol), $[Ru(bpy)_2Cl_2]\cdot 2H_2O$ (0.110 g, 0.21

mmol), and $NaBF_4$ (0.103 g, 0.94 mmol). Yield = 0.117 g (0.17 mmol, 81%). Anal. Calcd for $[Ru(pym)(bpy)_2]BF_4$ = $C_{30}H_{23}BF_4N_6O_1Ru$: C, 53.67; H, 3.45; N, 12.52. Found: C, 53.30; H, 3.35; N, 12.61. ^1H NMR (CD_3CN, 22 °C): δ 6.19 (ddd, J = 8.4, 1.3, and 0.3 Hz, 1H), 6.43 (ddd, J = 8.2, 6.8, and 1.3 Hz, 1H), 6.68 (dd, J = 6.0 and 4.5 Hz, 1H), 6.88 (ddd, J = 8.5, 6.7, and 1.8 Hz, 1H), 7.11 (ddd, J = 7.4, 5.8, and 1.5 Hz, 1H), 7.14 (ddd, J = 7.4, 5.8, and 1.4 Hz, 1H), 7.25 (dd, J = 5.9 and 2.2 Hz, 1H), 7.28 (ddd, J = 7.5, 5.6, and 1.4 Hz, 1H), 7.45 (ddd, J = 5.6, 1.4, and 0.8 Hz, 1H), 7.61 (ddd, J = 7.6, 5.6, and 1.3 Hz, 1H), 7.78−7.84 (m, 3H), 7.89 (ddd, J = 8.1, 7.6, and 1.5 Hz, 1H), 8.12 (ddd, J = 8.2, 7.6, and 1.6 Hz, 1H), 8.14 (dd, J = 8.2 and 1.9 Hz, 1H), 8.32 (d, J = 8.0 Hz, 1H), 8.35 (d, J = 8.0 Hz, 1H), 8.45 (ddd, J = 8.2, 1.2, and 0.8 Hz, 1H), 8.53 (ddd, J = 5.64, 1.44, and 0.8 Hz, 1H), 8.58 (ddd, J = 8.3, 1.2, and 0.9 Hz, 1H), 8.63 (dd, J = 4.5 and 2.2 Hz, 1H), 9.08 (ddd, J = 5.6, 1.5, and 0.8 Hz, 1H).

[Ru(Himn)(bpy)$_2$](BF$_4$)$_2$ (5(BF$_4$)$_2$). $1BF_4$ (0.066 g, 0.10 mmol) was dissolved in methanol (10 mL), and a methanol solution (5 mL) of $AgBF_4$ (0.021 g, 0.11 mmol) was added dropwise. After stirring for 1 h in the dark, the resulting white precipitate was removed by filtration. The filtrate was concentrated to 5 mL under reduced pressure. Brown crystals were obtained by diffusing diethyl ether vapor into the solution. Yield: 0.055 g (74%). Anal. Calcd for $[Ru(Himn)(bpy)_2](BF_4)_2$ = $C_{29}H_{25}B_2F_8N_6ORu$: C, 46.55; H, 3.37; N, 11.23. Found: C, 46.52; H, 3.16; N, 11.13.

[Ru(Hthp)(bpy)$_2$](BF$_4$)$_2$ (6(BF$_4$)$_2$). This compound was prepared by analogy with $5(BF_4)_2$ using $2BF_4{\cdot}CH_3OH$ (0.142 g, 0.20 mmol) and $AgBF_4$ (0.043 g, 0.22 mmol). Yield: 0.125 g (82%). Anal. Calcd for $[Ru(Hthp)(bpy)_2](BF_4)_2$, $C_{30}H_{27}B_2F_8N_6ORu$: C, 47.27; H, 3.57; N, 11.03. Found: C, 47.41; H, 3.30; N, 10.90.

[Ru(iml)(bpy)$_2$] (7). This compound was obtained by reacting $3BF_4$ with excess DBU in acetonitrile. The mixture was stable even in air for a few hours. However, isolation of the deprotonated species was unsuccessful because of gradual reprotonation or decomposition in solution. Single crystals for X-ray analysis were obtained as $7{\cdot}CH_3CN$ by standing the mixture of $3BF_4$ (0.0031 g, 4.7 μmol) and DBU (7.5 μL, 50.1 μmol) in 5 mL of acetonitrile. ^1H NMR (CD_3CN, 22 °C): δ 5.48 (d, J = 0.5 Hz, 1H), 6.24 (ddd, J = 7.9, 6.8, and 1.1 Hz, 1H), 6.30 (dd, J = 8.2 and 1.3 Hz, 1H), 6.62 (ddd, J = 8.4, 6.8, and 1.8 Hz, 1H), 6.75 (d, J = 0.5 Hz, 1H), 7.06 (ddd, J = 7.4, 5.8, and 1.4 Hz, 1H), 7.13 (ddd, J = 7.3, 5.8, and 1.4 Hz, 1H), 7.28 (ddd, J = 7.3, 5.8, and 1.4 Hz, 1H), 7.44 (ddd, J = 7.4, 5.8, and 1.4 Hz, 1H), 7.63 (d, J = 5.0 Hz, 1H), 7.68 (dt, J = 7.8 and 1.5 Hz, 1H), 7.74−7.79 (m, 3H), 7.85 (dt, J = 7.9, 1.4 Hz, 1H), 7.94−7.95 (m, 2H), 8.29 (d, J = 8.2 Hz, 1H), 8.32 (d, J = 8.3 Hz, 1H), 8.36 (d, J = 8.0 Hz, 2H), 9.12 (d, J = 5.6 Hz, 1H).

Electrochemical Measurements. Electrochemical measurements were carried out using an ECstat-100 (EC Frontier, Inc.). A three-electrode system was utilized: a glassy carbon working electrode, a $Ag^{0/+}$ reference electrode ($Ag/AgNO_3$ in NEt_4BF_4/CH_3CN solution), and a Pt counter electrode. A 0.1 M NEt_4BF_4 solution in acetonitrile was employed as a supporting electrolyte. The measurement used a 1.0 mM solution of Ru complexes. Potentials were reported using the $FeCp_2^{0/+}$ couple as a reference redox system.

X-ray Crystallography. X-ray diffraction data were obtained at −80(2) or −170(2) °C using a Rigaku R-axis rapid diffractometer equipped with an imaging plate with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). For some crystals, VariMax with Saturn (Rigaku) was also utilized. A single crystal was mounted with a cryoloop and flash cooled using a cold nitrogen gas stream. Data were processed using the Process-Auto or CrystalClear software packages.[17] Absorption corrections were applied using either numerical or empirical methods.[18] Structures were solved using the direct method employing the SIR2008 or SIR2004 software packages[19ab] and refined on F^2 (with all independent reflections) using the SHELXL97 software package.[20] In the X-ray analysis of ligand precursors, all hydrogen atoms were located from the electron-density difference maps and refined isotropically. For the Ru complexes, H atoms were located using a riding model, except for the H atom at the N1 position, which was located from the electron-density difference maps. In the analysis of $2BF_4{\cdot}CH_3OH$, the C9 atom in $(Hthp)^-$ showed positional disorder over two possible positions. Therefore, C9 was separated into C9A and C9B, each with an occupancy of 0.5.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystal structures of H_2imn, H_2thp, Hpym, $1BF_4{\cdot}CH_3OH$, and $2BF_4{\cdot}CH_3OH$; absorption spectra of $1BF_4$ upon base addition; ^1H NMR spectra of $1BF_4$, $3BF_4$, and $5BF_4$ upon DBU addition; experimental details for pK_a determination; X-ray crystallographic information for all of the compounds analyzed in this study in PDF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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