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Ligand Modification of Cyclometalated Ruthenium Complexes in the Aerobic Oxidative Dehydrogenation of Imidazolines

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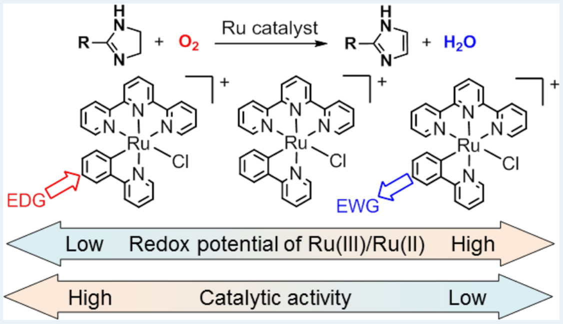
Supporting Information

ABSTRACT: New cyclometalated ruthenium(III) complexes bearing 2-phenylpyridine derivatives were synthesized and characterized. Chemical modification of the cyclometalating ligand affected its σ-donor character and resulted in regulation of the redox potential of the ruthenium metal center, which was elucidated by X-ray crystallography and cyclic voltammetry. The increase in the electron-donating ability of the cyclometalating ligand improved the catalytic activity of the ruthenium complexes in the aerobic oxidative dehydrogenation of 2-phenylimidazoline, and enabled the catalytic dehydrogenation of 2-phenylimidazoline in air at room temperature. The effect of the ligand structure on the catalytic activity was also elucidated by density functional theory (DFT) calculations and titration experiments.



KEYWORDS: *cyclometalated complex, ruthenium, homogeneous catalyst, dehydrogenation, aerobic oxidation*

INTRODUCTION

Imidazole derivatives have garnered significant attention because of their chemical, biological, and pharmaceutical properties. The oxidative dehydrogenation of 2-imidazolines to 2-substituted imidazoles provides a general and reliable method for their preparation because 2-imidazolines can be easily prepared from nitriles and ethylenediamine.[1] However, the use of oxidation reagents sometimes suffers from limitations such as toxicity, explosiveness, and the requirement for large amounts of the reagents.[2] Therefore, the aerobic oxidative dehydrogenation of imidazolines to imidazoles under mild conditions would be a promising method with great utility in terms of atom efficiency and environmental aspects.[2,3]

We previously reported a cyclometalated ruthenium complex, [RuCl(ppy)(tpy)][PF$_6$] (**1a**) (ppy = 2-phenylpyridine, tpy = 2,2′:6′,2″-terpyridine), that served as an efficient catalyst for the aerobic oxidative dehydrogenation of 2-imidazoline derivatives.[4] The key features of the complex **1a** were the presence of a ppy ligand and a Cl ligand; the σ-donor character of the cyclometalating ligand lowered the redox potential of the metal center, which allowed aerobic oxidation of the metal center. The trans effect of the ppy ligand also assisted in the dissociation of the Cl ligand, which was followed by coordination of a substrate. These features of **1a** allowed us to propose a catalytic reaction pathway for aerobic dehydrogenation different from the extensively investigated ruthenium-catalyzed aerobic oxidation of amines and alcohols, including ruthenium hydride species[5] (a plausible reaction pathway[4] is shown in the Supporting Information, Scheme S1). The catalytic reaction has also been utilized in the aerobic oxidation of other coordinative substrates such as benzylamines and benzyl alcohols.[6] These observations prompted our interest in the molecular design of efficient catalysts; we envisioned that the introduction of electron-donating substituent(s) would improve the σ-donor character of the cyclometalating ppy ligand and result in an acceleration of the catalytic activity in the aerobic oxidation of 2-imidazolines. To prove the concept, a series of the ruthenium complexes (**1b**−**d**) bearing ppy derivatives as the cyclometalating ligand (Scheme 1) were prepared. We herein report the preparation and characterization of **1b**−**d**, and examine the catalytic activity of **1a**−**d** in the aerobic oxidative dehydrogenation of 2-phenylimidazoline. Density functional theory (DFT) calculations and titration experiments of the complexes were also conducted to elucidate their catalytic activity.

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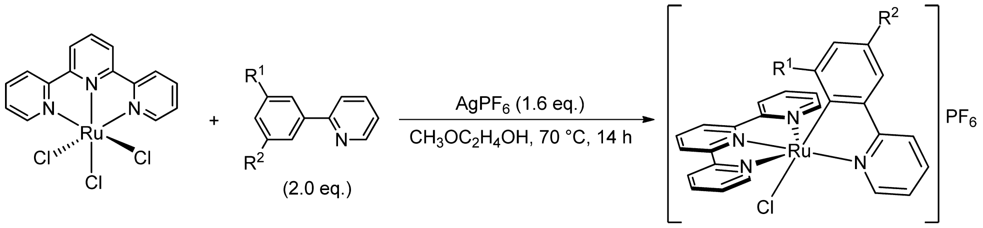
Scheme 1. Synthesis of Cyclometalated Ru(III) Complexes



2a: R^1 = H, R^2 = H
2b: R^1 = MeO, R^2 = H
2c: R^1 = MeO, R^2 = MeO
2d: R^1 = H, R^2 = CF_3

1a: R^1 = H, R^2 = H
1b: R^1 = MeO, R^2 = H
1c: R^1 = MeO, R^2 = MeO
1d: R^1 = H, R^2 = CF_3

RESULTS AND DISCUSSION

Synthesis and Characterization. Ppy derivatives (**2b−d**) were prepared according to literature procedures.[7] The cyclometalated ruthenium complexes, **1b−d**, were prepared by stirring [$RuCl_3$(tpy)] with **2b−d** in 2-methoxyethanol in the presence of $AgPF_6$ according to literature procedures (Scheme 1);[8] the products were characterized by electrospray ionization-mass spectrometry (ESI-MS) and elemental analysis. The structures of complexes **1b−d** were elucidated by X-ray crystallography. The ORTEP drawing of **1c** is shown in Figure 1. The detailed X-ray crystallographic results for the complexes are summarized in Supporting Information, Table S1, and the ORTEP drawings of **1b** and **1d** are shown in the Supporting Information, Figure S1. Complexes **1a−d** had distorted octahedral coordination geometries, in which the cyclometalating carbon (C(1)) of the ppy ligand was located at the trans position to the Cl ligand. The Ru−C(1) and Ru−Cl bond lengths are summarized in Table 1. Owing to the trans influence of the ppy ligand, the Ru−Cl bond length was increased with an increase in the electron-donating ability of the substituent on the ppy ligand in the order $(MeO\text{-})_2$ > MeO- ≥ H- > CF_3-. Meanwhile, the ORTEP drawing of **1b** shows that the methoxy substituent is located at the ortho position of the carbon attached to the metal center (Supporting Information, Figure S1). The steric hindrance of the methoxy group would depress the trans influence of the ppy ligand.

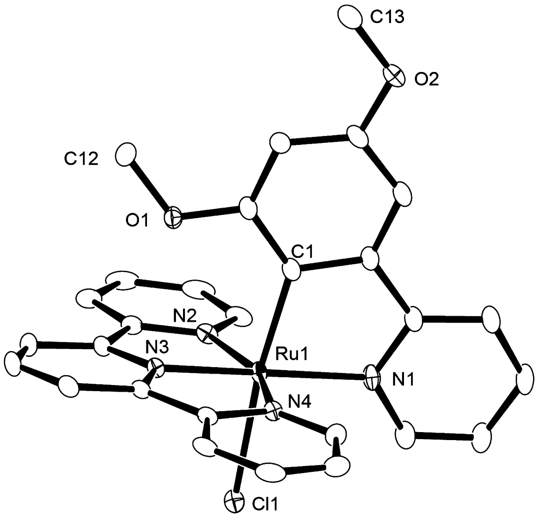


Figure 1. ORTEP drawing of Ru complex **1c** with thermal ellipsoids drawn at the 30% probability level. One of the two crystallographically independent molecules of **1c** is shown. Hydrogen atoms, a PF_6^- anion, and a solvated acetonitrile molecule are omitted for simplicity.

The σ-donor character of the cyclometalating ppy ligand was also estimated by cyclic voltammetry. Cyclic voltammetry of complexes **1b−d** was performed in a dimethylformamide (DMF) solution of 0.1 M [(n-Bu_4)N][PF_6] as a supporting electrolyte. Similar to **1a**, the complexes exhibited one oxidation wave and two reversible redox couples (Supporting Information, Figure S2), which were assigned to the metal-centered Ru(IV)/Ru(III) and Ru(III)/Ru(II) couples and a tpy ligand-localized redox couple, respectively.[4,8] Figure 2 shows the cyclic voltammograms of the metal-centered Ru(III)/Ru(II) redox couples of **1a−d**; the $E_{1/2}$ data are also included in Table 1. The metal-centered oxidation potential was also closely associated with the electron-donating ability of the substituent on the cyclometalating ppy ligand; the metal-centered oxidation potential shifted to lower oxidation potentials in the sequence CF_3- > H- > MeO- > $(MeO\text{-})_2$.

Aerobic Oxidation of 2-Phenylimidazoline. To examine the catalytic activity of **1a−d**, the oxidative dehydrogenation of 2-phenylimidazoline was carried out using the catalyst in

Table 1. Selected Bond Lengths, Redox Potential, HOMO Levels, Turnover Frequencies, and Association Constants of Ru Complexes 1a−d

complex	bond length/Å Ru−C(1)	bond length/Å Ru−Cl	$E_{1/2}$/V[a]	E_{HOMO}/eV[b]	$TOF_{50\%}$/h^{-1}[c]	K_a/M^{-2}[d]
1a	2.024(4)[e]	2.4431(13)[e]	−0.235	−4.5599	10	1.82×10^4
1b	1.998(11)	2.445(2)	−0.297	−4.4277	28	5.15×10^3
1c	2.008(2)[f] 2.010(2)	2.4488(5)[f] 2.4628(5)	−0.362	−4.3212	33	1.81×10^3
1d	2.024(4)	2.4249(10)	−0.131	−4.9102	(0.3)[g]	3.59×10^5

[a] $E_{1/2}$ of Ru(III)/Ru(II) vs Fc^+/Fc. [b] DFT calculation. [c] Turnover frequencies ((mol of product/mol of Ru)/time) was calculated at 50% conversion. [d] Titration experimental. [e] From ref 8a. [f] Crystallographically independent two molecules of **1c** were observed. [g] Extrapolation data.

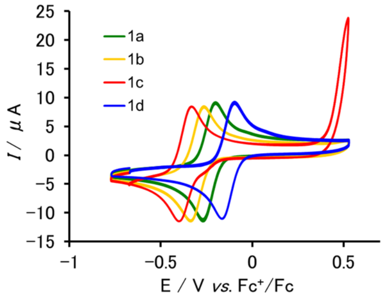


Figure 2. Cyclic voltammograms of Ru complexes **1a**−**d** (1.0 mM) in DMF containing 0.1 M $[(n\text{-Bu})_4N][PF_6]$ under N_2 at sweep rate of 100 mV.

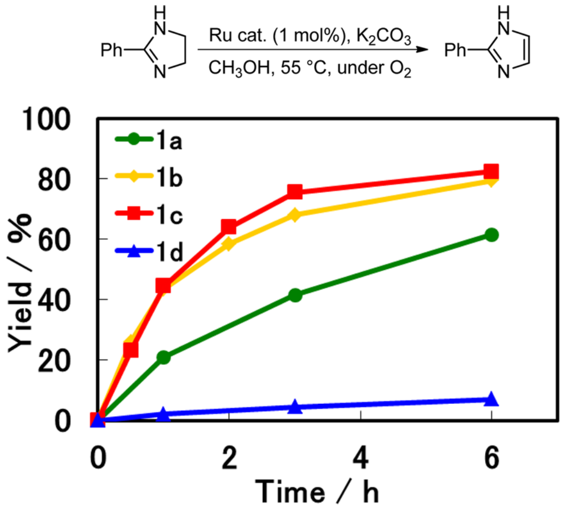
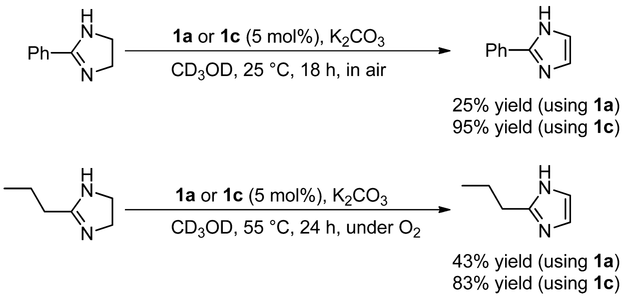


Figure 3. Time courses for the oxidative dehydrogenation of 2-phenylimidazoline with complexes **1a**−**d** as a catalyst. Reaction conditions: 2-phenylimidazoline (0.15 mmol), catalyst (1.5×10^{-3} mmol), K_2CO_3 (0.15 mmol), methanol (1 mL), 55 °C, O_2 atmosphere.

methanol at 55 °C under a balloon pressure of molecular oxygen. The appropriate reaction conditions, except for the catalyst loading (1 mol%), were previously determined using **1a**.[4] The production of 2-phenylimidazole and the consumption of 2-phenylimidazoline were monitored by ^1H NMR spectroscopy using mesitylene as an internal standard. The oxidative dehydrogenation of 2-phenylimidazoline with the catalysts **1a**−**c** proceeded smoothly to give 2-phenylimidazole. Figure 3 compares the time-course curves of the catalytic reactions obtained with the catalysts **1a**−**d**; the estimated turnover frequencies at 50% conversion ($TOF_{50\%}$) are included in Table 1. Catalytic activity was improved by the introduction of electron-donating substituent(s) in the cyclometalating ppy ligand in the sequence $(MeO\text{-})_2 \geq$ MeO- > H- > CF_3-, however, the activity appeared to approach saturation for **1b** and **1c**. These results were associated with effect that increasing the σ-donor character of the cyclometalating ppy ligand lowered the oxidation potential of the metal center. The resulting acceleration of the aerobic oxidation of the metal center was followed by the smooth metal-promoted oxidative dehydrogenation of the coordinated substrate.

Because complex **1c** exhibited the highest catalytic activity, the aerobic oxidation reactions of 2-phenylimidazoline in air at room temperature as well as the oxidation of 2-*n*-propylimidazoline under O_2 were conducted. Previous reactions using these substrates and **1a** were found to proceed slowly and result in hydrolysis of the starting material.[4] As shown in Scheme 2, the high catalytic activity of **1c** allowed progress of the oxidative dehydrogenation reactions and gave the corresponding 2-substituted imidazoles in good yields.

Scheme 2. Oxidative Dehydrogenation of 2-Phenylimidazoline and 2-*n*-Propylimidazoline Using 1a and 1c



Elucidation of the Catalysts. Since the metal-centered Ru(III)/Ru(II) redox potential strongly affects the catalytic activity of complexes **1a**−**d**, density functional theory (DFT) calculations were conducted at the B3LYP level for **1a**−**d** with the LANL2DZ basis set implemented in the Gaussian 09 program suite.[9,10] The molecular orbitals (MO) for **1c** are depicted in Figure 4. The highest occupied MO (HOMO) was located on the metal center with the phenyl group of the cyclometalating ppy ligand. Complexes **1a**, **1b**, and **1d** also showed similar localizations of the HOMO and the lowest unoccupied MO (LUMO) (the HOMO levels data are included in Table 1). The introduction of electron-donating substituent(s) in the ppy ligand shifted the HOMO level to higher energy in the sequence **1c** > **1b** > **1a** > **1d**. The calculated data correlated well with both the electrochemical data and the catalytic activity of complexes **1a**−**d**. Since the aerobic oxidation of the metal center is associated with the oxidation potential of the metal center,[4,6] a higher HOMO energy level is anticipated to be favorable for effective catalytic reactions.

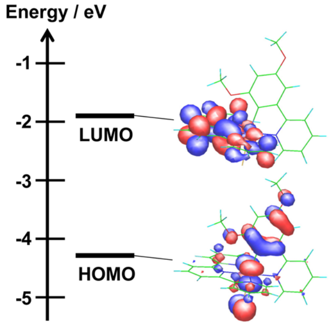


Figure 4. Molecular orbitals and their levels of **1c**.

We previously proposed a reaction pathway (Supporting Information, Scheme S1) in which oxidation of 2-imidazolines proceeds only if the coordination of the substrate to the ruthenium center takes place in situ.[4] Thus, to evaluate the association constants (K_a) of complexes **1a**−**d** with substrates, titration experiments with 2-methylimidazoline and 2-phenylimidazoline were performed using UV−vis absorption spectroscopy. In the UV−vis absorption spectrum of **1a**, the absorption bands at 390 and 511 nm increased upon the addition of 2-phenylimidazoline with isosbestic points at 439 and 464 nm (Figure 5). The Job's plot experiments (Supporting Information, Figure S3) gave a maximum at 0.6−0.7, indicative of a 1:2 stoichiometry as shown in Scheme 3; this is a tentative assumption to simplify the estimation of K_a. The K_a value was estimated by nonlinear least-squares curve-fitting.[11] Similar trends in the absorption spectra of **1b−d** were observed during titration with 2-phenylimidazoline (Supporting Information, Figures S4 and S5). The K_a data for **1a−d** with 2-phenylimidazoline are also included in Table 1. The K_a values decreased with the increasing σ-donor character of the cyclometalating ppy ligand, and correlated well with the coordination ability of the metal center; however, the trend may be unfavorable for the catalytic reaction. These contradictory results lead to our interpretation that the initial coordination of the substrate to the catalyst was unlikely to predominantly dictate the catalytic reaction, whereas the coordination ability of the complexes could account for the comparable catalytic activity of **1b** and **1c**.

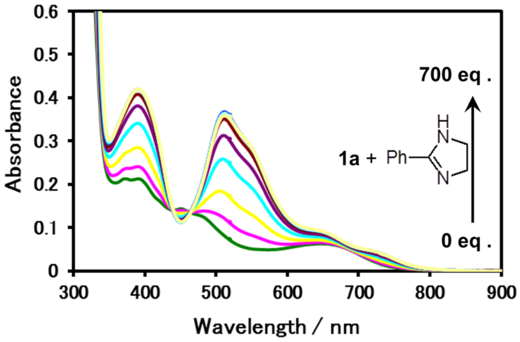
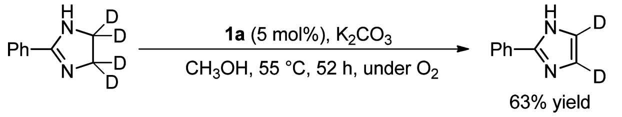


Figure 5. Changes in absorption spectrum of **1a** (5×10^{-5} M in acetonitrile at room temperature under N_2) upon the addition of 2-phenylimidazoline.

Another advantage of the aerobic oxidation should be the formation of H_2O as a byproduct.[2] To determine the byproduct of this catalytic reaction, the oxidative dehydrogenation of isotopically labeled 2-phenylimidazoline-4,4,5,5-d_4[12] was carried out under the catalytic conditions using **1a** (Scheme 4). In the deuterium NMR spectrum of the reaction mixture, signals assignable to 2-phenylimidazole-4,5-d_2 (δ 7.1) and D_2O (δ 4.9) were observed (Supporting Information, Figure S6). Thus, the oxidative dehydrogenation afforded D_2O as a byproduct. Alternatively, since the signal assignable to 2-phenylimidazoline-4,4,5,5-d_4 at δ 3.6 ppm remained even after 52 h, the aerobic oxidation of 2-phenylimidazoline underwent C−H dehydrogenation faster than that of the deuterated analogue (Supporting Information, Scheme S2),[4] indicative of a kinetic isotope effect. These results were consistent with the above-mentioned prediction that the initial coordination of 2-phenylimidazoline to the complex was unlikely to predominate the catalytic activity.

Scheme 4. Oxidative Dehydrogenation of 2-Phenylimidazoline-4,4,5,5-d_4 Using 1a



CONCLUSION

We prepared new cyclometalated ruthenium complexes **1b−d**, and demonstrated their improved catalytic activity in the aerobic oxidative dehydrogenation of 2-imidazolines as a result of the introduction of electron-donating methoxy group(s) into the cyclometalating ppy ligand. The high catalytic activity of **1c** allowed the oxidative dehydrogenation of 2-phenylimidazoline in air at room temperature. These features supported the previously proposed catalytic reaction pathway and elucidated that the lowering Ru(III)/Ru(II) redox potential was a key factor in the catalytic reaction. Although kinetic measurements are essential for the elucidation of any catalytic mechanism, this work is expected to contribute to the design of efficient molecular catalysts for aerobic oxidation. Further studies expanding the range of aerobic oxidation reactions using the cyclometalated ruthenium complexes are in progress.

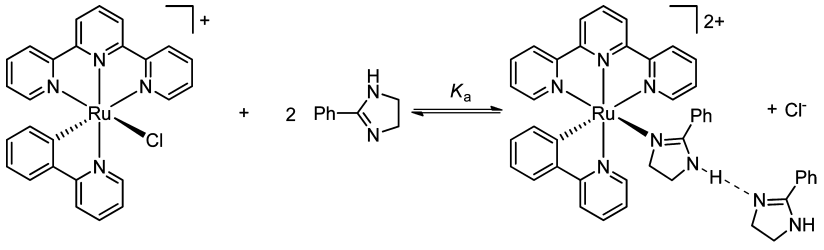
EXPERIMENTAL SECTION

Synthesis of Ru(III) Complexes 1b−d. $[RuCl_3(tpy)]$[13] (200 mg, 0.45 mmol), a phenylpyridine derivative (**2b−d**, 0.91 mmol), and $AgPF_6$ (184 mg, 0.73 mmol) were dissolved in 2-methoxyethanol (55 mL) and stirred at 70 °C for 14 h. The solution was cooled to −20 °C for 1 h and then filtered through Celite to remove the AgCl precipitate. The filtrate was concentrated to about 1 mL. An aqueous NH_4PF_6 solution was added to the concentrate. The resulting precipitate was filtered off and purified by column chromatography (grade III alumina, acidic, toluene/acetonitrile = 2/1). The green band was collected and concentrated to about 50 mL. The precipitate was collected by filtration to give the Ru complex.

1b: The compound was obtained as a green solid (95 mg, 30%). ESI-MS: m/z = 554{M-PF$_6$}$^+$. Anal. Calcd. for **1b** ($C_{27}H_{21}ClF_6N_4OPRu$): C, 46.40; H, 3.03; N, 8.02. Found C, 46.16; H, 3.35; N, 8.25.

1c: The compound was obtained as a green solid (147 mg, 44%). ESI-MS: m/z = 584{M-PF$_6$}$^+$. Anal. Calcd. for **1c**·H_2O

Scheme 3. Suggested Equilibrium Reaction of 1a and 2-Phenylimidazoline



($C_{28}H_{25}ClF_6N_4O_3PRu$): C, 45.02; H, 3.37; N, 7.50. Found C, 44.79; H, 3.41; N, 7.50.

1d: The compound was obtained as a green solid (92 mg, 27%). ESI-MS: m/z = 592{M-PF_6}$^+$. Anal. Calcd. for **1b** ($C_{27}H_{18}ClF_9N_4PRu$): C, 44.00; H, 2.46; N, 7.60. Found C, 43.82; H, 2.60; N, 7.60.

Oxidative Dehydrogenation of 2-Phenylimidazoline. A mixture of 2-phenylimidazoline (65.8 mg, 0.45 mmol), ruthenium complex (4.5×10^{-3} mmol), K_2CO_3 (62.2 mg, 0.45 mmol), and mesitylene (31.3 μL, 0.225 mmol) in methanol (3 mL) was stirred at 55 °C under a balloon pressure of O_2 (1 atm). The yield and conversion were determined by ^{1}H NMR spectroscopy using mesitylene as an internal standard.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

General experimental and characterization procedures, computational details, crystallographic data, and spectroscopic data. 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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