ORGANOMETALLICS

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Dramatic Effect of Ancillary NHC Ligand in the Highly Selective Catalytic Oxidative Carbon−Carbon Multiple Bond Cleavage

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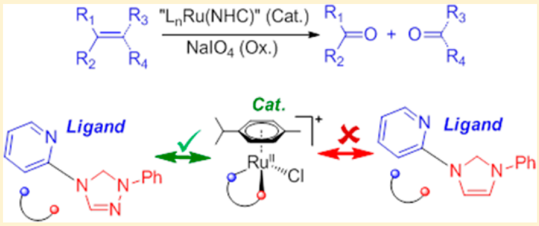
S *Supporting Information*



ABSTRACT: Selective and controlled oxidation of olefins to aldehydes is a commonly used important transformation in chemistry. However, chemists still use the dangerous and inconvenient ozonolysis method or the less selective, low-yielding Lemieux−Johnson protocol. In a program of developing effective catalysts for this important reaction, we disclose here that an ancillary ligand can play a dramatic role in the above catalytic phenomenon, depending on the design of the ligand precursor chosen. Proof-of-principle is demonstrated with the help of two newly designed [L_nRu^{II}-NHC] precatalysts (NHC = an imidazolydene-based NHC, **Im-NHC**, or a triazolydene-based NHC, **Trz-NHC**; L_n = *para*-cymene) for catalytic selective oxidation of olefins/alkynes to carbonyl compounds. With the electron-deficient **Trz-NHC** ligand, [(*para*-cymene)Ru^{II}(**Im-Trz**)]$^+$ precatalyst was found to be an order of magnitude more efficient than the [(*para*-cymene)Ru^{II}(**Im-NHC**)]$^+$ precatalyst.

INTRODUCTION

Modification of the electronic/steric properties of a catalyst can easily tune the catalytic performance by influencing the rate-limiting step, and undoubtedly ligands play a vital role in such controlled manipulation activity. Selective oxidation of alkenes to the corresponding carbonyl compounds, free from the subsequent overoxidation to carboxylic acids, is an indispensible reaction in synthetic chemistry.[1] It transforms hydrocarbons to more valuable oxygenated derivatives and is used in biomass processing[2] and for the synthesis of bioactive compounds,[3] thus rendering the process both industrially and academically relevant. Unfortunately, to achieve this, we are still seriously limited by the use of either the dangerous and inconvenient ozonolysis method with a reductive workup[2,3a,c,4,5] or the less selective and low-yielding Lemieux−Johnson oxidation protocol.[6] Strong oxidants[7] and OsO_4/oxidant[8] and $RuCl_3/NaIO_4$[9] systems are also known to carry out these transformations with major limitations. Although a few solitary moderately effective catalysts have been reported to date based on well-defined ruthenium complexes,[10−14] major problems related to efficient catalyst design remained unaddressed partly due to the lack of a systematic structure−activity study to evaluate the associated controlling and tuning factors of the catalytically relevant steps.

Ru^{II}**Im-NHC**-based (**Im-NHC** = an imidazolydene-based N-heterocyclic carbene) transition metal complexes have been extensively reported in the literature to carry out a series of transformations, which include cross-coupling (homo and hetero) reactions, C−H activation reactions, water oxidation, and transfer hydrogenation reactions. As an important application for the oxidative cleavage of carbon−carbon multiple bonds, recently we disclosed that a remote coordination site, $Ru^{II}(terpy)_2$, enhances the efficiency of a Ru^{II}**Im-NHC** catalytic center by accelerating the generation of active catalyst.[15] This enhancement was suggested due to electronic reasons, translated to the catalytic center from the remote tuner. Herein we show that the ancillary NHC ligand itself, when properly modified, can impose a dramatic electronic bias at the Ru(II) center, which ultimately leads to the development of a superior catalyst for the above reaction. It is noteworthy that only a few moderately active NHC-based ruthenium complexes are known to carry out this important catalysis.[12,14] In this report, the catalytic activity of "L_nRu^{II}(NHC)"-based precatalysts **1-Cym** and **2-Cym** as depicted in Figure 1 (L_n = *para*-cymene and NHC = an imidazolydene-based NHC, **Im-NHC**, or a triazolydene-based NHC, **Trz-NHC**) was explored to demonstrate the significant role of the **Trz-NHC** ligand for selective oxidation of alkenes and alkynes to the corresponding carbonyl compounds.

RESULTS AND DISCUSSION

The [(*para*-cymene)Ru^{II}(NHC)Cl]$^+Br^-$ type of complexes **1-Cym** (NHC = **Im-NHC**) and **2-Cym** (NHC = **Trz-NHC**) were synthesized in 89% and 78% overall yields by first deprotonation of quaternized NHC-ligand precursors using Ag_2O as a mild base to provide "Ag-NHC" intermediate complexes[16] followed by transmetalation to [(*para*-cymene)-$Ru^{II}Cl_2]_2$. Both the complexes were fully characterized by ^1H, $^{13}C\{^1H\}$, and 2D NMR spectroscopic and mass spectrometric methods (details provided in the Supporting Information).

The proposed structures of **1-Cym** and **2-Cym** based on the above techniques were unambiguously confirmed by X-ray

Received: April 26, 2016

DOI: 10.1021/acs.organomet.6b00337
Organometallics XXXX, XXX, XXX−XXX

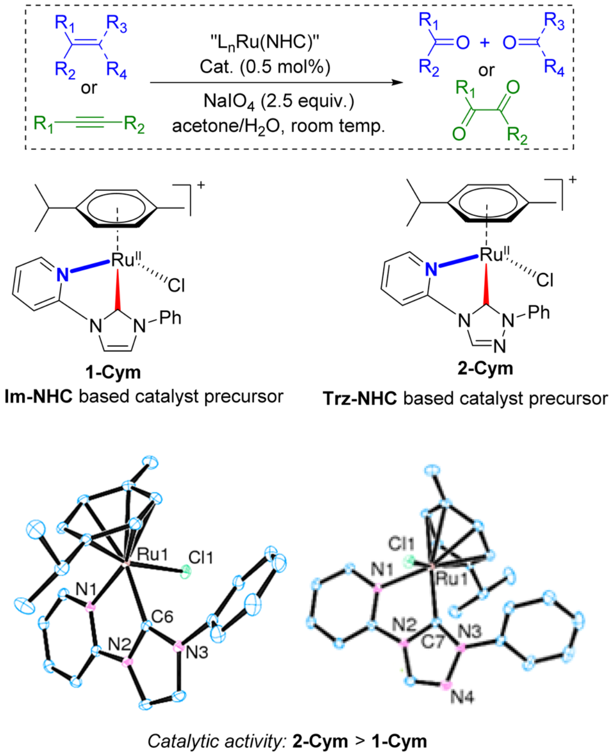


Figure 1. Molecular structures of the ruthenium(II) precatalysts used in oxidative cleavage of olefins/alkynes to carbonyl compounds. ORTEPs were drawn at the 30% ellipsoid probability level. Hydrogen atoms and counteranions are removed for clarity.

diffraction studies. **1-Cym** and **2-Cym** showed three-legged piano-stool geometries around the ruthenium center with $C_{NHC}-Ru^{II}-C_{pyridine}$ bite angles of 76.59(5)° and 76.61(6)° and $C_{NHC}-Ru^{II}$ bond lengths of 2.009(15) and 2.009(16) Å, respectively. Complexes **1-Cym** and **2-Cym** showed $Ru^{II/III}$ redox potential values of 1.392 and 1.484 V vs SCE, respectively (Figure 2). The potential for **2-Cym** was found

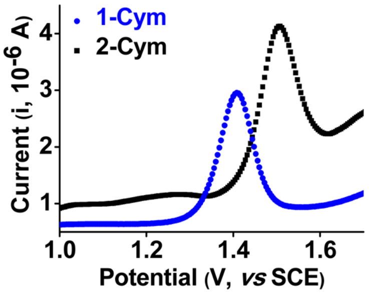
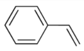
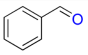
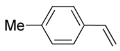
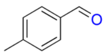
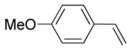
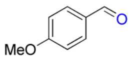
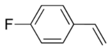
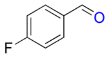
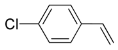
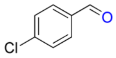
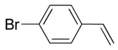
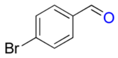
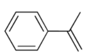
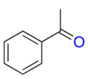
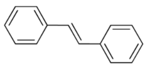
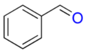
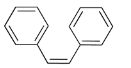
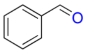
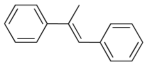
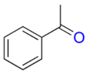
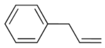
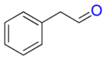
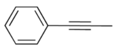
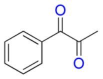
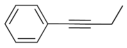
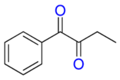
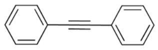
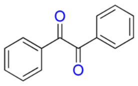
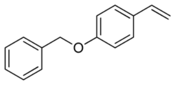
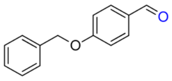
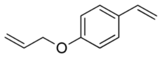
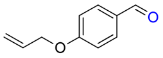
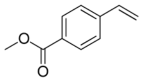
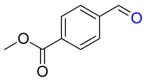
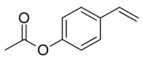
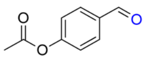


Figure 2. Differential pulse voltammetric plots of **1-Cym** and **2-Cym** in CH_3CN.

to be anodically shifted by ~92 mV compared to that for **1-Cym**. This shift may be attributed to the inherent poor σ-donor and better π-acceptor properties of **Trz-NHC** compared to **Im-NHC**.[17]

Both the complexes were utilized as precatalysts (0.5 mol % loading) for selective oxidation of various alkenes and alkynes to the corresponding aldehydes and ketones using $NaIO_4$ as a sacrificial mild oxidant in acetone/H_2O solvent mixture at ambient temperature. The results are shown in Table 1. With the best precatalyst, **2-Cym**, all the substrates were converted efficiently to the corresponding oxygen-inserted products in good to excellent yields. It is evident from Table 1 that **2-Cym** is a much more efficient catalyst than **1-Cym**. This trend was further verified and confirmed by more reliable kinetic profiles

Table 1. Comparative Study of 1-Cym- and 2-Cym-Catalyzed Oxidation of Olefins/Alkynes[a]

#	Substrate	Product	Yield (%) and TOF (min^{-1}) 1-Cym	2-Cym
1			8/0.27	82/2.73
2			5/0.17	79/3.95
3			13/0.11	55/0.56
4			3/0.10	84/4.20
5			8/0.18	78/2.60
6			2/0.07	75/2.50
7			5/0.04	52/0.43
8			17/0.57	90/3.00
9			13/0.65	80/4.00
10			22/2.93	92/12.27
11			5/0.04	55/0.46
12			6/0.13	68/1.51
13			5/0.11	70/1.56
14			58/1.93	60/2.00
15			10/0.11	65/0.67
16			8/0.40	70/3.5[b]
17			7/0.35	72/3.60
18			6/0.20	65/2.17

[a] Reaction conditions: substrate, 0.4 mmol; $NaIO_4$, 1.0 mmol; cat, 0.002 mmol; acetone/H_2O (1:1), 6 mL; room temp; time, 15−240 min. Yields were determined by GC. TOF = mmol (product)/{mmol (cat)·time (min)}. [b] 4-(2-Oxoethoxy)benzaldehyde also appeared in <5% yield.

of the reactions (Figure 3), which indeed supported the much higher reaction rate with **2-Cym** as compared to **1-Cym** for the oxidation of styrene to benzaldehyde. The difference in the rate of the reaction can be attributed to the change in the NHC backbone of the precatalysts and the contrasting electronic effects thereof, as evident from Figure 2.

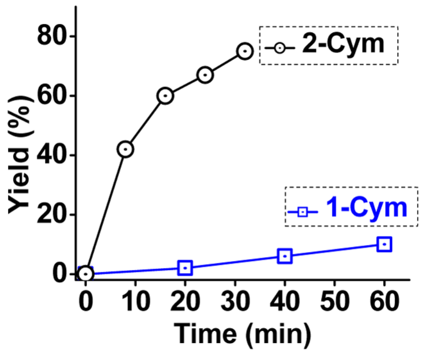
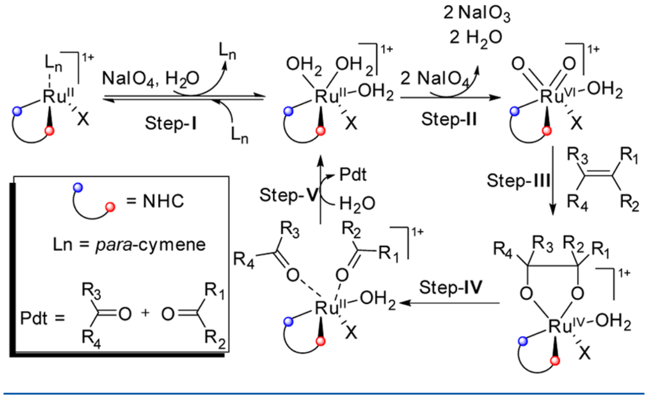


Figure 3. Reaction kinetics profile of the precatalysts for the oxidation of styrene to benzaldehyde.

To understand the effect of the NHC ligands **Im-NHC** vs **Trz-NHC**, the kinetic orders of dependency for the Ru(II) precatalysts, oxidant $NaIO_4$, and alkene were determined by the initial rate method for the oxidation of 4-methylstyrene to 4-methylbenzaldehyde. For both complexes, the kinetics data showed first-order rate dependency on precatalyst as well as $NaIO_4$ and zero-order rate dependency on the alkene substrate (Supporting Information). Nonetheless, in general, it is noteworthy that these results were found to be different from literature reports, where first-order rate dependency on precatalyst and substrate and zero-order rate dependency on $NaIO_4$ were reported, suggesting the alkene association as the rate-determining step.[13,14] Therefore, in the case of the present reactions, the rate-limiting step might not involve substrate, but it involved Ru(II) complex and $NaIO_4$. The possible steps in the plausible catalytic cycle are shown in Scheme 1. The proposed generation of ruthenium(VI)-dioxo species and its reaction with alkene to form a metallacycle followed by its cleavage to aldehyde was monitored by UV–vis spectroscopy along the line of Che's work, supporting a similar course of reaction (Figure 4; see Supporting Information for details).[13] Step I is proposed to be reversible loss of *para*-cymene for the precatalysts **1-Cym** and **2-Cym** in the presence of $NaIO_4/H_2O$. This step seems to be the key step for these complexes. To verify it, the catalytic oxidation of 4-methylstyrene with **2-Cym** was carried out in the presence of added *para*-cymene. The decrease in the yield of aldehyde was observed when excess *para*-cymene was added to the reaction mixture (Figure 5, left). Notably, *para*-cymene was found to remain unreacted in the catalytic conditions, which was confirmed by ^1H NMR studies (see the Supporting Information).

Scheme 1. Suggested Catalytic Steps



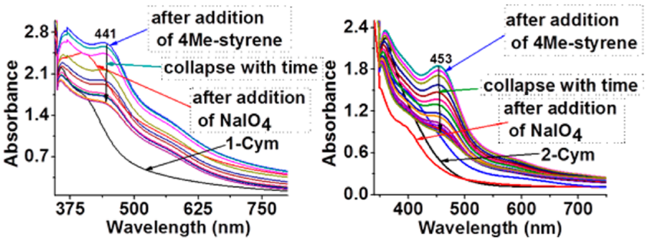


Figure 4. UV–vis study with **1-Cym** (left) and **2-Cym** (right).

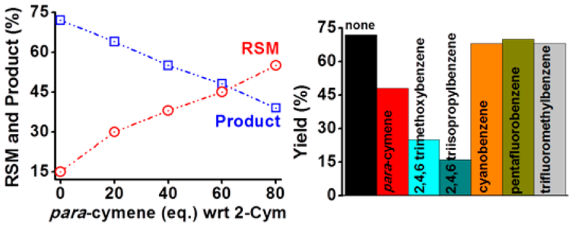


Figure 5. Effect of added *para*-cymene (left) and different arenes (right) on the catalytic oxidation of 4-methylstyrene with **2-Cym** (0.5 mol %) as the precatalyst (RSM = recovered starting material).

Interestingly, the decrease in the yield was also found in the presence of other electron-rich arenes (Figure 5, right). These studies suggested that in the case of **1-Cym** and **2-Cym** step I is a key step of the proposed catalytic cycle in the subsequent formation of the active catalyst. Since the **Trz-NHC**-based complex **2-Cym** is more electron-deficient than the **Im-NHC**-based complex **1-Cym** (confirmed from electrochemical studies), easy release of *para*-cymene is expected in the case of **2-Cym** under catalytic conditions (owing to strong Ru → **Trz-NHC** and poor Ru → *para*-cymene back-donation), making it a more active precatalyst. It is noteworthy to mention that "$LnRu^{II}NHC$"-type complexes have previously been reported for the oxidative cleavage of carbon–carbon double bonds by using $NaIO_4$ as a sacrificial oxidant, and it was shown that the NHC backbone is quite robust under these oxidizing conditions.[12,14] To check the integrity of the NHC-ligand backbone under the oxidizing catalytic conditions, a few control experiments were conducted. The reaction of 4-methylstyrene with **1-Cym** and with **2-Cym** (**1-Cym**:$NaIO_4$:4-methylstyrene; 1:25:10, and **2-Cym**:$NaIO_4$:4-methylstyrene; 2:125:50) was monitored by time-dependent ^1H NMR spectroscopic studies in a CD_3CN/D_2O solvent mixture. These studies showed that the NHC-ligand backbone remained intact for both the catalyst precursors with a ~15% and ~2% decrease of peak intensity after 15 min for **2-Cym** and **1-Cym**, respectively. 4-Methylstyrene was found to be converted to 4-methylbenzaldehyde gradually with time (Figures S42 and S43, Supporting Information). Next, for the more active catalyst precursor **2-Cym**, a 1:1 stoichiometric reaction of **2-Cym** and $NaIO_4$ was investigated in CD_3CN/D_2O. ^1H NMR studies indicated the existence of the (**Trz-NHC**)Ru(*para*-cymene) backbone along with only free *para*-cymene and no free/

transformed NHC ligand residues (Figure S44, Supporting Information). However, with excess $NaIO_4$ (20 equiv for 1 equiv of **2-Cym**) the ^1H NMR spectrum of the reaction mixture exhibited broadening of the peaks corresponding to bound **Trz-NHC** and *para*-cymene moieties (Figure S45, Supporting Information). No oxidized NHC derivatives could be detected by ^1H NMR spectroscopy when a reaction of **2-Cym** (0.03 mmol) and $NaIO_4$ (10 mmol) under the standard conditions but in the absence of substrate was analyzed (Figure S46, Supporting Information). Moreover, ESI-MS study of a reaction mixture of **2-Cym**/$NaIO_4$/4-methylstyrene (in 1:25:10 molar ratio) in acetone/water showed the presence of parent precursor cation ([(**Trz-NHC**)Ru(*para*-cymene)-Cl]$^+$) along with two (**Trz-NHC**)Ru-oxo species, [(**Trz-NHC**)Ru=O]$^+$ and [(**Trz-NHC**)Ru(OH_2)(=O)$_2$]$^+$ (Figure S47, Supporting Information). All of the above studies suggested the stability of the NHC-Ru backbone under catalytic conditions. It is notable that any paramagnetic oxo-Ru^{IV}(d^4)-NHC or oxo-Ru^{VI}(d^2)-NHC species would be invisible in ^1H NMR spectroscopy and hence might account for the partial loss of peak intensity. The variable catalytic activity and rate with **2-Cym** and **1-Cym** might be therefore related to the different electronic perturbation of **Trz-NHC** and **Im-NHC** ligands within the corresponding complexes.[18]

■ SUMMARY

In summary, with the help of two newly designed "L_nRu^{II}(NHC)"-type complexes, it was shown that just by introducing a nitrogen atom at the C4/C5 position of an imidazole-based ligand backbone, that is, modifying **Im-NHC** to 1,2,4-**Trz-NHC**, the catalytic efficiency for the oxidation of carbon−carbon multiple bonds was found to increase by an order of magnitude. Electrochemical and a few other controlled studies suggested that the **Trz-NHC**-based catalyst precursors are electron deficient, wherein the key step involving reversible loss of *para*-cymene controlled the observed enhanced reactivity. Detailed mechanistic investigations including DFT calculations are under way in our laboratory.

■ EXPERIMENTAL SECTION

General Information. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker AVANCE III 400 and 500 MHz NMR spectrometers at room temperature unless mentioned otherwise. Chemical shifts (δ) are expressed in ppm using the residual proton resonance of the solvent as an internal standard ($CHCl_3$: $\delta = 7.26$ ppm for ^1H spectra, 77.2 ppm for $^{13}C\{^1H\}$ spectra; CH_3COCH_3: $\delta = 2.05$ ppm for ^1H spectra, 29.8 ppm for $^{13}C\{^1H\}$ spectra; CH_3CN: $\delta = 1.94$ ppm for ^1H spectra, 118.3 and 1.3 ppm for $^{13}C\{^1H\}$ spectra). All coupling constants (J) are expressed in hertz (Hz) and only given for $^1H-^1H$ couplings unless mentioned otherwise. The following abbreviations were used to indicate multiplicity: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), dt (doublet of triplets), m (multiplet). ESI mass spectroscopy was performed on a Bruker microTOF QII spectrometer. GC-MS analysis was performed on a Agilent 7890A GC/5975C MS system. The UV−visible absorption and kinetic studies were carried out on a Cary 100 UV−vis spectrophotometer using 1.0 cm quartz cuvettes at room temperature. The electrochemical measurements (differential pulse voltammetry, DPV) were carried out using a CHI 620E electrochemical analyzer at room temperature. Dry solvents and reagents were obtained from commercial suppliers and used without further purification. $RuCl_3\cdot xH_2O$ and deuterated solvents were purchased from Aldrich. [Ru(para-cymene)Cl_2]$_2$[19] and 1-phenyl-3-(pyridin-2-yl)-1*H*-imidazol-3-ium bromide[20] were prepared by following a reported method. All the products were previously reported, and the identity of the products was verified by GC and GC-MS with known samples. In a few cases, ^1H NMR spectroscopy was also used to match the products with the known samples.

Synthesis of 1-Phenyl-4-(pyridin-2-yl)-1*H*-1,2,4-triazol-4-ium Bromide. 1-Phenyl-1*H*-1,2,4-triazole (350.4 mg, 2.0 mmol) and 2-bromopyridine (314 mg, 2.0 mmol) were mixed in a pressure tube and stirred under neat conditions at 140 °C for 48 h. After this, the reaction mixture was allowed to cool to room temprature. After cooling to room temprature, the formed solid was washed with THF and dried under high vacuum for 1 h to afford the desired product. Yield: 392 mg (65%). ^1H NMR (500 MHz, $CDCl_3$, 300 K): δ 13.61 (s, 1H), 9.51 (s, 1H), 9.29 (d, $J = 8.2$ Hz, 1H), 8.56 (dd, $J = 4.7$, 1.1 Hz, 1H), 8.45 (dd, $J = 7.7$, 1.6 Hz, 2H), 8.11 (td, $J = 8.1$, 1.7 Hz, 1H), 7.63 (m, 2H), 7.56 (m, 2H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 300 K): δ 149.2, 144.4, 141.4, 140.3, 138.9, 134.8, 131.5, 130.5, 126.4, 120.9, 117.1 ppm. HRMS (ESI, positive ion): $m/z = 223.09$ (calcd for $[C_{13}H_{11}N_4]^+ = 223.0978$).

Synthesis of 1-Cym. Silver(I) oxide (26 mg, 0.11 mmol) and ligand precursor (62 mg, 0.2 mmol) were mixed in degassed acetonitrile (8 mL) in a Schlenk tube. The reaction mixture was stirred for 6 h at room temperature under dark conditions. [Ru(*para*-cym)Cl_2]$_2$ (62 mg, 0.1 mmol) was added to the reaction mixture. This reaction mixture was again stirred overnight under dark conditions. The resulting yellow solution was filtered through a Celite plug. The yellow filtrate was reduced to 0.5 mL under vacuum. Addition of diethyl ether to this concentrated solution resulted in a large amount of precipitate. This precipitate was filtered and washed with diethyl ether to afford the desired product (Scheme S1). Yield: 102 mg (89%). ^1H NMR (500 MHz, $CDCl_3$, 300 K): δ 9.46 (d, $J = 5.5$ Hz, 1H), 9.16 (s {br}, 1H), 8.73 (d, $J = 8.2$ Hz, 1H), 8.05 (t, $J = 7.7$ Hz, 1H), 7.85−7.79 (m, 2H), 7.65 (dd, $J = 6.9$, 3.4 Hz, 3H), 7.48 (d, $J = 1.9$ Hz, 1H), 7.47−7.42 (m, 1H), 5.97 (d, $J = 6.1$ Hz, 1H), 5.66 (d, $J = 6.2$ Hz, 1H), 5.13 (d, $J = 6.0$ Hz, 1H), 4.63 (d, $J = 6.0$ Hz, 1H), 2.29 (dt, $J = 13.8$, 6.9 Hz, 1H), 2.11 (s, 3H), 0.87 (d, $J = 6.9$ Hz, 3H), 0.84 (d, $J = 6.9$ Hz, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 300 K): δ 184.0, 156.1, 151.7, 141.8, 139.3, 130.4, 130.1, 126.5, 125.5, 124.0, 119.5, 114.5, 109.0, 106.7, 92.3, 89.1, 86.9, 82.9, 31.3, 22.9, 22.1, 19.3. HRMS (ESI, positive ion): $m/z = 492.0771$ (calcd for $[C_{24}H_{25}N_3ClRu]^+ = 492.0778$). Anal. Found: C, 42.75; H, 3.90; N, 6.23. Calcd for $C_{24}H_{25}N_3ClRuBr\cdot 1.5CH_2Cl_2\cdot H2O$: C, 42.79; H, 4.19; N, 5.87.

Synthesis of 2-Cym. This complex was synthesized by following the same procedure as used for the synthesis of **1-Cym** but in CH_2Cl_2 solvent (Scheme S1). Yield: 90 mg (78%). ^1H NMR (500 MHz, $CDCl_3$, 300 K): δ 10.83 (s, 1H), 9.49 (d, $J = 4.5$ Hz, 1H), 9.13 (d, $J = 6.4$ Hz, 1H), 8.10 (s {br}, 1H), 7.94 (m, 2H), 7.65 (m, 3H), 7.53 (s {br}, 1H), 6.03 (d, $J = 4.4$ Hz, 1H), 5.74 (d, $J = 5.3$ Hz, 1H), 5.35 (d, $J = 5.7$ Hz, 1H), 4.93 (d, $J = 5.8$ Hz, 1H), 2.34−2.39 (m, 1H), 2.14 (s, 3H), 0.90 (dd, $J = 8.9$, 7.1 Hz, 6H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 300 K): δ 184.8, 156.8, 149.0, 142.4, 141.9, 138.7, 130.8, 129.9, 125.9, 125.4, 116.5, 109.0, 108.7, 92.6, 89.3, 87.7, 84.0, 31.4, 23.0, 22.0, 19.4 ppm. HRMS (ESI, positive ion): $m/z = 493.0744$ (calcd for $[C_{23}H_{24}N_4RuCl]^+ = 493.0730$). Anal. Found: C, 47.95; H, 4.48; N, 9.70. Calcd for $C_{23}H_{24}N_4ClRuBr$: C, 48.25; H, 4.19; N, 9.79.

Electrochemical Analysis of the Complexes. A three-electrode configuration was used to carry out the electrochemical studies (DPV). Working electrode: Pt disk (1 mm diameter); counter electrode: a Pt wire; reference electrode: saturated calomel electrode, SCE. Both samples were prepared in dry deoxygenated acetonitrile. Hexafluorophosphate salts of **1-Cym** and **2-Cym** were used for this study. A 0.1 M solution of $[NBu_4]PF_6$ solution was used as the supporting electrolyte. Ferrocene ($E_{1/2}$, Fc/Fc$^+$ = 0.37 V vs SCE) was used as an external calibration standard for all the experiments.

General Procedure for the Catalysis Studies. Substrate (0.4 mmol) in 1 mL of acetone and catalyst (0.5 mol %, bromide salts) were taken in a round-bottom flask. A 2 mL amount of acetone and 2 mL of H_2O were added to it. $NaIO_4$ (213 mg, 1.0 mmol) was dissolved in 1 mL of H_2O and transferred to the reaction mixture. The reaction mixture was stirred at room temprature for ∼15−240 min. After this time, Na_2SO_3 (2.0 mmol) was added to the reaction mixture followed by the addition of 2 mL of dichloromethane (DCM) and 3 mL of H_2O. The reaction mixture was further stirred for 10 min. Standard (ethylbenzene, mesitylene, stilbene, or acetophenone) was added as a reference, and the reaction mixture was again stirred for 5 min. It was then transferred to a separating funnel with the help of 3 mL of H_2O and 8 mL of DCM. The organic layer was separated, and the aqueous layer was again extracted with 5 mL of DCM (two times). The combined organic layer was washed with 20 mL of brine solution. Products and unreacted substrates were analyzed by GC-MS. The yields of the products were calculated by GC analyses.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00337.

> Additional experimental details and schemes, characterization data, kinetic data, and additional figures (PDF)
>
> Crystallographic data for **1-Cym** (CCDC 1441844) and **2-Cym** (CCDC 1441846) (CIF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

J.C. sincerely thanks DST and IISER Bhopal for generous financial support. S.K.G. is a recipient of a CSIR doctoral fellowship. S.K.S. thanks DST-INSPIRE for a BSMS fellowship. We thank Professor Robert H. Crabtree for helpful discussions.

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(18) We compared the catalytic activity of the **2-Cym**/$NaIO_4$ system with the $RuCl_3$/$NaIO_4$ system for 1-octene and cyclooctene oxidation (see the Supporting Information for details). The disparate results obtained thus far suggested that the active catalysts might be different in these two systems. However, the possibility of generation of a trace amount of RuO_4 via complete degradation of all organic ligands in the case of **2-Cym** and **1-Cym** could not be fully excluded at this level of experimental analyses. This point needs further rigorous investigation beyond the scope of this paper.

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