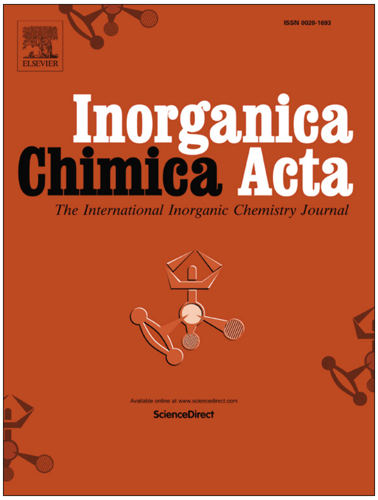

Research paper

Ancillary Ligands Switch the Activity of Ru–NHC-based Oxidation Precatalysts

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Ancillary Ligands Switch the Activity of Ru–NHC-based Oxidation Precatalysts

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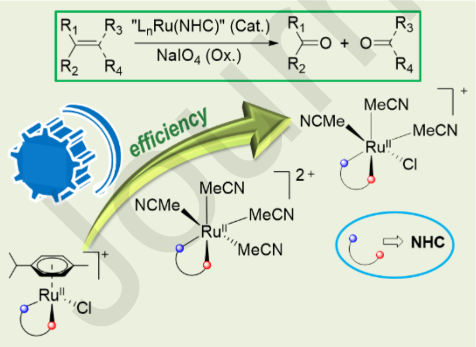
Dedication: This work is dedicated to Professor Goutam Kumar Lahiri on the occasion of his 60th birthday.

Abstract

Herein we demonstrate how the inner-sphere coordinating ligands switch the activity of Ru–NHC-based oxidation precatalysts in the oxidative conversion of olefins to carbonyl compounds, with the help of a series of systematically varied imidazolydene-NHC (**Im-NHC**) and triazolydene-NHC (**Tz-NHC**)-based ruthenium(II)-complexes. It is shown that the catalytic activity of the *para*-cymene-containing precatalysts varies in the order of [(**Tz-NHC**)Ru(*para*-cymene)Cl]$^+$ > [(**Im-NHC**)Ru(*para*-cymene)Cl]$^+$, while the order of activity of the MeCN-containing precatalysts is found to be reversed, i.e., [(**Im-NHC**)Ru(MeCN)$_4$]$^{2+}$ > [(**Tz-NHC**)Ru(MeCN)$_4$]$^{2+}$. Along with the electronic influence of the NHC ligands, the effect of the lability of the *para*-cymene and MeCN ligands, and the overall charge of the complexes might be attributed toward such a switching of catalytic activity. This finding led to develop a new precatalyst with improved activity which was further utilized in selective oxidation of a series of styrene substrates containing other oxidation-sensitive functionalities.

Graphical Abstract



Keywords

N-Heterocyclic carbene (NHC) / Ruthenium / Oxidation / Alkenes / Sodium Periodate

Highlights

- A series of imidazolydene-NHC (**Im-NHC**) and triazolydene-NHC (**Tz-NHC**)-based ruthenium(II)-complexes are utilized as precatalysts for oxidation of alkenes and alkynes
- Catalytic activity of the *para*-cymene-containing precatalysts varies in the order of [(**Tz-NHC**)Ru(*para*-cymene)Cl]$^+$ > [(**Im-NHC**)Ru(*para*-cymene)Cl]$^+$, while the order of activity of the MeCN-containing [(**NHC**)Ru(MeCN)$_4$]$^{2+}$-type precatalysts is found to be reversed
- Variable electronic effect of the NHC ligands plays a crucial role in controlling the activity order

1. Introduction

Designing an organometallic catalyst for selective and efficient oxidative conversion of unsaturated hydrocarbons to the valuable oxygenated derivatives is an important research area in organometallic chemistry and catalysis [1]. In case of oxidation of olefins to aldehydes, traditional strong oxidants are used in (over)stoichiometric amount [2]. Additionally, there are a few alternative catalytic systems based on OsO_4–Oxone/H_2O_2/$NaIO_4$/^{t}BuOOH and $RuCl_3$/$NaIO_4$ for this transformation although activity, selectivity and other issues are compromised to a great extent [3]. Along this line, effective and selective catalysts based on well-defined Ru-complexes are increasingly becoming popular during recent time [4]. In general, the advantage of using metal-complexes lies in the fact that the knowledge of the effect of coordinated ligands on the catalytic steps helps to improve the catalytic efficiency, selectivity and robustness by modifying their electronic and/or steric properties [5]. Our group has been actively involved in the development of metal–NHC-based robust catalytic systems for efficient oxidative functionalization of not only aliphatic and aromatic C–H bonds, but also of carbon-carbon multiple bonds [6]. We rationalized that the NHC ligands would provide the required stability to the reactive high-valent metal complex intermediates and also impart the resistance toward decomposition under strongly oxidizing and acidic conditions [6f]. Recently, we disclosed that the rate of (NHC)Ru^{II}(*para*-cymene)-catalyzed oxidative cleavage of carbon-carbon multiple bond to the corresponding carbonyl functionality can be accelerated through electronic modulation from a remote spectator Ru^{II}(terpy)$_2$ unit installed within the catalyst backbone [6e]. We also demonstrated that the efficiency of this oxidative catalysis can be tuned by modifying the ancillary NHC ligand backbone of the (NHC)Ru^{II}(*para*-cymene) precatalysts (Fig. 1a,b) [6d]. Controlled mechanistic studies on the proposed catalytic steps (Fig. 1c) revealed that the reversible dissociation of the *para*-cymene ligand from the precatalysts was slow and responsible for controlling the rate of the reaction. It was observed that the triazolydene-NHC (**Tz-NHC**) based ruthenium complex, [(**Tz-NHC**)Ru(*para*-cymene)Cl]$^+$ (**2-Cym**), being electron deficient system, releases *para*-cymene relatively faster as compared to imidazolydene NHC (**Im-NHC**) based ruthenium complex [(**Im-NHC**)Ru(*para*-cymene)Cl]$^+$ (**1-Cym**) and hence was more active than the later (Fig. 1d). These results motivated us to investigate the [(NHC)Ru(MeCN)$_4$]$^{2+}$-type precatalysts (**1-MeCN** when NHC = **Im–NHC**, and **2-MeCN** when NHC = **Tz–NHC**), wherein both the *para*-cymene and Cl ligands are removed from the Ru coordination-sphere and replaced with loosely-bound acetonitrile ligands. The aim was to probe the effect of eliminating the ligand dissociation barrier (which would have been created by bound *para*-cymene as well as Cl) on the catalytic activity. In the present study, we report the above-mentioned investigation and reveal an interesting behavior of the ancillary NHC ligands (**Im–NHC** and **Tz–NHC**) leading to a switching catalytic activity (Fig. 1d). To this end, we also show that how this finding led to develop a new precatalyst with improved catalytic efficiency which was further utilized in selective oxidation of a series of styrene substrates containing other oxidation-sensitive functionalities.

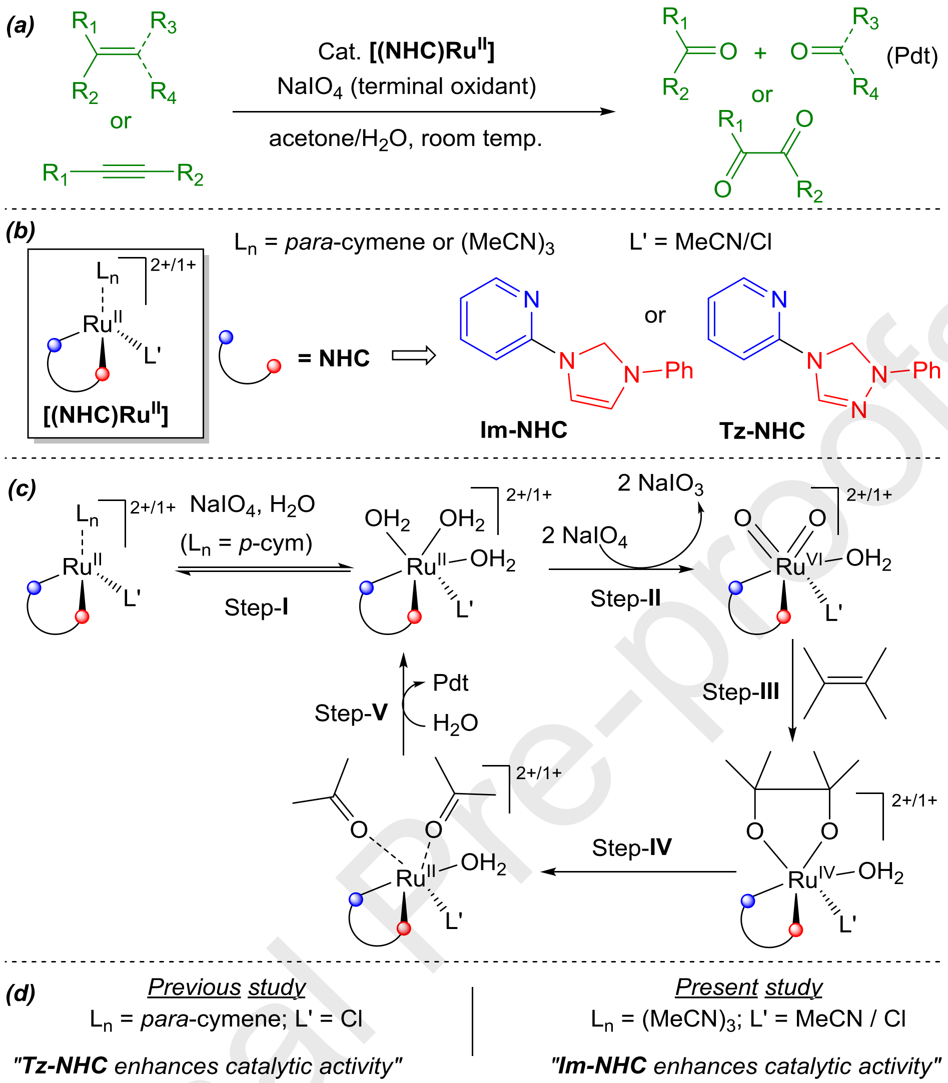


Fig. 1. (a) A general scheme for “(NHC)Ru”-catalyzed oxidation of alkenes and alkynes to carbonyl compounds; (b) design of the precatalysts used in this study; (c) suggestive catalytic steps; (d) key finding of the present study.

2. Experimental

2.1. General methods and materials

^{1}H and $^{13}C\{^{1}H\}$ 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 ($CHCl_3$: δ = 7.26 ppm for ^{1}H spectra, 77.2 ppm for $^{13}C\{^{1}H\}$ spectra; CH_3CN: δ = 1.94 ppm for ^{1}H spectra, 118.3 ppm and 1.3 ppm for $^{13}C\{^{1}H\}$ spectra). All coupling constants (*J*) are expressed in hertz (Hz) and only given for ^{1}H-^{1}H couplings unless mentioned otherwise. The following abbreviations were used to indicate multiplicity: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), dt (doublet of triplet), m (multiplet). ESI mass spectroscopy was performed on a Bruker microTOF QII spectrometer. GCMS analysis was performed on Agilent 7890A GC/5975C MS system. 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. Deuterated solvents were purchased from Aldrich. All the alkenes and alkynes are purchased from Aldrich. The products were previously reported and the identity of the products was verified by GC and GCMS with known samples. ^{1}H NMR spectroscopy was also used to match the products with the known samples. **1-Cym** and **2-Cym** were previously reported by our group and synthesized via the reported procedure [6d].

2.2. Synthesis of complexes

*Synthesis of **1-MeCN**.* Bromide salt of **1–Cym** was converted to hexafluorophosphate salt by anion metathesis [7]. Hexafluorophosphate salt of **1–Cym** (96 mg, 0.15 mmol) and silver triflate (46 mg, 0.18 mmol) were taken together in a Schlenk tube. After addition of 5 mL of acetonitrile, reaction mixture was refluxed for 60 h under dark conditions. This reaction mixture was filtered through a Celite plug. The filtrate was reduced to a minimum volume of 0.5 mL. Addition of 10 mL of diethylether resulted into a solid product. Crystallization (MeCN/Et$_2$O) of this solid product resulted into the analytically pure product. Yield: = 100 mg (85%). ^{1}H NMR (500 MHz, CD$_3$CN, 300K): δ = 8.88 (d, *J* = 5.6 Hz, 1H), 8.18 (d, *J* = 2.3 Hz, 1H), 8.16 – 8.11 (m, 1H), 7.92 (d, *J* = 8.3 Hz, 1H), 7.70 – 7.60 (m, 5H), 7.53 (d, *J* = 2.2 Hz, 1H), 7.48 (t, *J* = 6.5 Hz, 1H), 2.15 (s, 6H), 1.96 (s, 3H), 1.90 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, CD$_3$CN, 300K): δ = 190.5, 156.2, 154.4, 142.1, 140.5, 131.6, 131.1, 128.9, 127.6, 126.3, 126.1, 125.1, 124.0, 113.3, 4.6, 4.5, 0.4 ppm. ^{19}F NMR (471 MHz, CD$_3$CN, 300K): δ = -79.30 (s, OTf), -72.88 (d, *J* = 706.5, PF$_6$) ppm. ^{31}P NMR (202 MHz, CD$_3$CN, 300K): δ = -144.62 ppm. Anal. Found: C, 34.88; H, 2.87; N, 12.54. Calcd for $C_{23}H_{23}N_7RuPSO_3F_9\cdot 0.5H2O$: C, 34.94; H, 3.04; N, 12.41.

*Synthesis of **2-MeCN**.* This complex was synthesized by following the same procedure as used for the synthesis of **1–MeCN**. Yield: = 88 mg (75%). ^{1}H NMR (500 MHz, CD$_3$CN, 300K): δ = 9.42 (s, 1H), 8.92 (d, *J* = 5.6 Hz, 1H), 8.25 – 8.18 (m, 1H), 8.09 (d, *J* = 8.3 Hz, 1H), 7.78 – 7.73 (m, 2H), 7.73 – 7.65 (m, 3H), 7.59 (t, *J* = 6.6 Hz, 1H), 2.15 (s, 6H), 1.96 (s, 3H), 1.96 (s, 3H) ppm. ^{13}C{^{1}H} NMR (125 MHz, CD$_3$CN, 300K): δ = 190.5, 154.3, 153.0, 142.0, 140.6, 139.8, 131.5, 130.5, 127.9, 126.5, 126.1, 125.2, 124.8, 123.5, 120.9, 113.9, 4.2, 4.0 ppm. ^{19}F NMR (471 MHz, CD$_3$CN, 300K): δ = -79.28 (s, OTf), -72.88 (d, *J* = 706.4, PF$_6$) ppm. ^{31}P NMR (202 MHz, CD$_3$CN, 300K): δ = -144.63 ppm. Anal. Found: C, 32.82; H, 2.88; N, 14.24. Calcd for $C_{22}H_{22}N_8RuPSO_3F_9\cdot H_2O$: C, 33.00; H, 3.00; N, 14.00.

*Synthesis of **1-Cl**.* **1-MeCN** (78.0 mg, 0.1 mmol and tetrabutylammonium chloride (139 mg, 0.5 mmol) were mixed in 5 mL of acetone-ether solvent mixture (2:1) in a round bottom flask and stirred for 30 minutes at room temperature, which resulted in a large amount of precipitate. This precipitate was filtered and the solid compound was washed with diethyl ether. The solid compound was recrystallized in acetonitrile/diethyl ether solvent mixture to get the desired product. Yield = 41 mg (80%). ^{1}H NMR (500 MHz, CD$_3$CN, 300 K) δ 9.67 (dd, *J* = 5.7, 0.9 Hz, 1H), 8.38 (d, *J* = 2.4 Hz, 1H), 8.06 (ddd, *J* = 18.6, 12.6, 4.8 Hz, 2H), 7.68 (tt, *J* = 6.0, 3.1 Hz, 4H), 7.64 – 7.60 (m, 1H), 7.51 (d, *J* = 2.4 Hz, 1H), 7.44 (ddd, *J* = 7.2, 5.8, 1.4 Hz, 1H). ^{13}C{^{1}H} NMR (126 MHz, CD$_3$CN, 300 K) δ 193.1, 156.2, 154.0, 140.5, 140.2, 130.6, 130.4, 128.4, 126.6, 124.8, 123.9, 111.9. HRMS (ESI, positive ion) *m/z* = 398.9957 (calculated for $[C_{16}H_{14}N_4ClRu]^+$ = 398.9946), 417.0043 (calculated for $[C_{16}H_{16}N_4OClRu]^+$ = 417.0051),. 440.0209 (calculated for $[C_{18}H_{17}N_5ClRu]^+$ = 440.0212).

*Synthesis of **2-Cl***. This complex was synthesized by following the similar procedure as described for the synthesis of complex **1-Cl**. Yield = 47 mg (75%). ^{1}H NMR (500 MHz, CD_3CN, 300 K) δ 10.23 (s, 1H), 9.64 (d, *J* = 5.7 Hz, 1H), 8.54 (d, *J* = 8.3 Hz, 1H), 8.11 (t, *J* = 7.9 Hz, 1H), 7.79 (m, 2H), 7.70 – 7.61 (m, 3H), 7.53 – 7.46 (m, 1H). (ESI, positive ion) *m/z* = 399.9978 (calculated for $[C_{15}H_{13}N_5ClRu]^+$ = 399.9898), 418.0083 (calculated for $[C_{15}H_{15}N_5OClRu]^+$ = 418.0004), 441.0258 (calculated for $[C_{17}H_{16}N_6ClRu]^+$ = 441.0164).

2.3. Single crystal X-ray diffraction analyses

Single crystals of **1–MeCN**, **2–MeCN**, **1-Cl** and **2-Cl** suitable for X-ray diffraction studies were grown by diffusion of diethyl ether into the concentrated acetonitrile solution of the respected complexes. Data collection were carried out on a Bruker SMART APEX II CCD diffractometer with graphite monochromated Mo Kα (λ = 0.71073 Å) radiation at low temperature. The hydrogen atoms were placed in calculated positions and refined using a riding model with isotropic displacement parameters. The data quality of **2-Cl** was poor and the anion, PF_6, was found to be distorted. Attempts to grow better quality crystal of **2-Cl** resulted into a similar issue. Full crystallographic data (CIFs) of **1–MeCN** (*CCDC 1441845*), **2–MeCN** (*CCDC 1441847*), **1-Cl** (*CCDC 1875517*) and **2-Cl** (*CCDC 1875518*). can be obtained free of charge from The Cambridge Crystallographic data Center via www.ccdc.cam.ac.uk/data_request/cif.

2.4. Electrochemical studies

The electrochemical studies were carried out with three-electrode-configuration. Working electrode: Pt disk (1 mm diameter); counter electrode: a Pt wire; reference electrode: saturated calomel electrode, SCE. All the samples were prepared in dry deoxygenated acetonitrile. 0.1 M solution of $[NBu_4]PF_6$ solution was used as the supporting electrolyte. Ferrocene ($E_{1/2}$, Fc/Fc$^+$ = 0.37 volts *vs*. SCE) was used as an external calibration standard for all the experiments.

2.5. General procedure for the catalytic studies

Substrate (0.4 mmol) in 1 mL of acetone and catalyst (0.5 mol%) were taken in a round bottom flask. 2 mL 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 temperature for ~15 min–240 min. After this time, Na_2SO_3 (2.0 mmol) was added to the reaction mixture followed by addition of 2 mL of DCM and 3 mL of H_2O. The reaction mixture was further stirred for 10 min. A GC standard (ethylbenzene or mesitylene or 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 aqueous layer was again extracted with 5 mL of DCM (2 times). The combined organic layer was washed with 20 mL of brine solution. Products and unreacted substrates were analyzed by GCMS. The yields were calculated by GC analyses.

3. Results and discussion

The $[(NHC)Ru(MeCN)_4]^{2+}$-type complexes **1–MeCN** and **2–MeCN** were synthesized in good yields (85% and 75% respectively) by heating the corresponding precursors **1-Cym** and **2-Cym** respectively in MeCN solvent in the presence of AgOTf under dark (Fig. 2a, see Supplementary Information for details) [8]. These complexes were fully characterized by NMR spectroscopic and electron-spray ionization mass

(ESI-MS) spectrometric methods (details provided in Supplementary Information). The proposed structures of **1–MeCN** and **2–MeCN** based on the above characterization techniques were unambiguously confirmed by X–ray diffraction studies (Fig. 2b). Both **1–MeCN** and **2–MeCN** showed distorted octahedral geometries around the ruthenium centre with the C_{NHC}–Ru^{II}–$C_{pyridine}$ bite angle of 78.22(17)$^{\circ}$ and 79.20(2)$^{\circ}$ respectively, and C_{NHC}–Ru^{II} bond length of 1.994(4) and 2.004(7) Å respectively. The Ru–N_{MeCN} bond *trans* to the NHC ligand was found to be larger than the other Ru–N_{MeCN} bonds, due to strong *trans* influence of NHC ligand [8,9]. **1–MeCN** and **2–MeCN** showed $Ru^{II/III}$ redox potential values of 1.512 V and 1.692 V vs SCE respectively (Fig. 3). Notably these peaks were neither due to ligand oxidation nor solvent oxidation (see Supplementary Information for control analysis). The potential for **2–MeCN** was found to be anodically shifted by ~180 mV compared to that for **1–MeCN**. This shift may be attributed to the inherent poor σ–donor and better π–acceptor properties of **Tz–NHC** compared to **Im–NHC** [10]. However, the $Ru^{II/III}$ redox potential values of both **1–MeCN** and **2–MeCN** were found to be anodically shifted compared to their *para*–cymene counter-partners **1-Cym** (1.392 V vs SCE) and **2-Cym** (1.484 V vs SCE) respectively [6d]. This may be due to the fact that the former complexes are dicationic and the latter are monocationic. The extra positive charge may have caused the shifting of the oxidation potential toward more anodic.

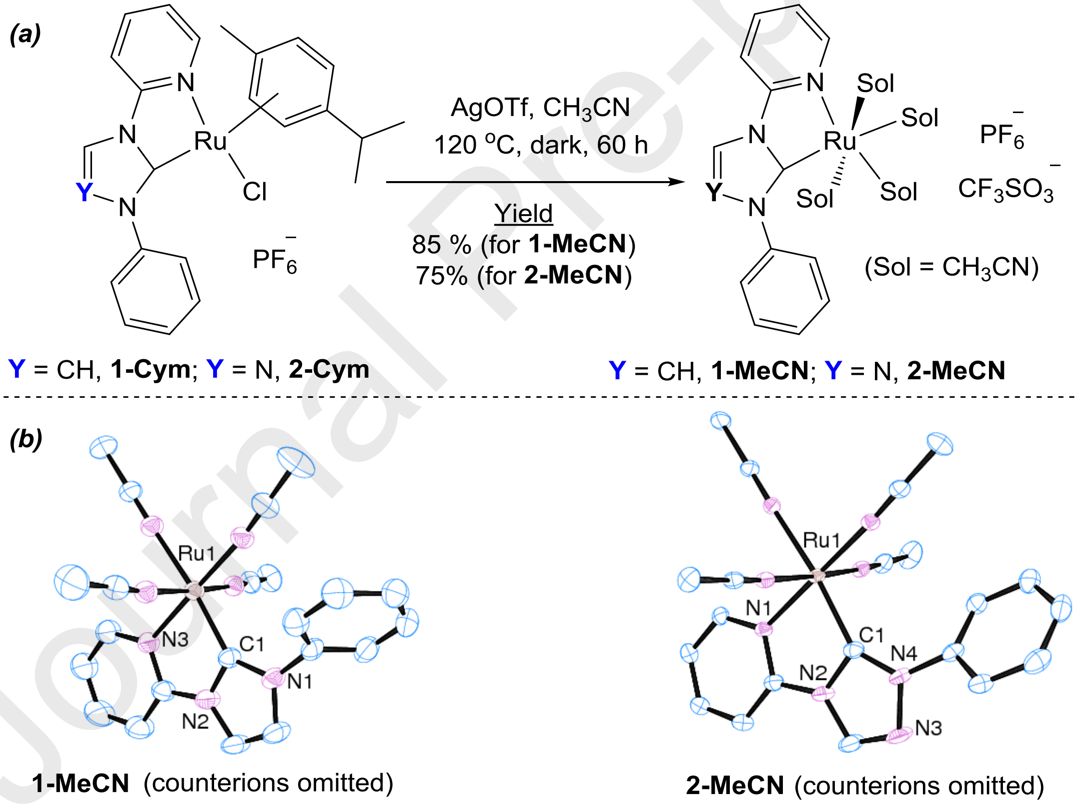


Fig. 2. (a) Synthesis of the precatalysts **1-MeCN** and **2-MeCN**; (b) molecular structures of **1-MeCN** and **2-MeCN** (H atoms and counterions have been omitted for clarity). Selected bond lengths (Å) and bond angles (°): **1-MeCN**: Ru(1)-C(1) = 1.994(4), Ru(1)-N(3) = 2.068(4), Ru(1)-N(4) = 2.027(4), Ru(1)-N(5) = 2.116(4), Ru(1)-N(6) = 2.036(4), Ru(1)-N(7) = 2.030(4), C(1)-Ru(1)-N(3) = 78.22(17), N(2)-C(1)-N(1) = 104.2(4). **2-MeCN**: Ru(1)-C(1) = 2.004(7), Ru(1)-N(1) = 2.068(5), N(3)-N(4) = 1.391(8), Ru(1)-N(5) =

2.026(5), Ru(1)-N(6) = 2.027(6), Ru(1)-N(7) = 2.113(5), Ru(1)N-N(8) = 2.026(5), C(1)-Ru(1)-N(1) = 79.2(2), N(4)-C(1)-N(2) = 102.2(6).

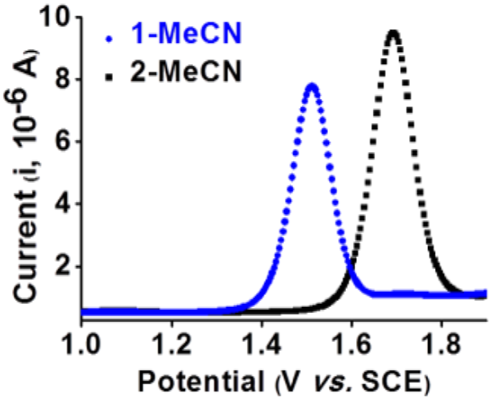


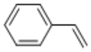
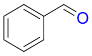
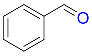
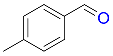
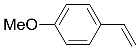
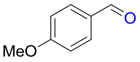
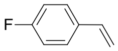
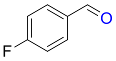
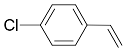
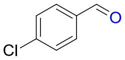
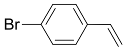
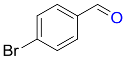
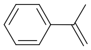
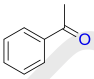
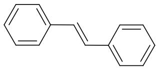
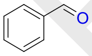
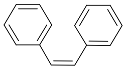
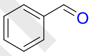
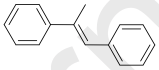
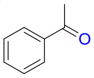
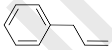
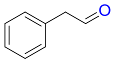
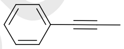
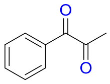
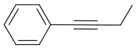
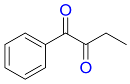
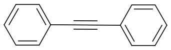
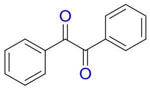
Fig. 3. Differential pulse voltammetric (DPV) plots of **1-MeCN** and **2-MeCN** recorded in CH_3CN.

After successful synthesis and characterization, the solvato complexes **1–MeCN** and **2–MeCN** were utilized as precatalysts (0.5 mol% loading) for selective oxidation of various alkenes and alkynes to the corresponding aldehydes and ketones (Table 1). The catalytic activity of **1–MeCN** containing the **Im-NHC** ligand was found to be an order of magnitude higher than that of **2–MeCN** containing the **Tz-NHC** ligand. This activity order is in stark contrast to our previous findings with the corresponding *para*-cymene-containing precatalysts **1-Cym** and **2-Cym**, wherein the order was **2–Cym**>**1–Cym** [6d]. This contrasting order of activity (**2–Cym**>**1–Cym** but **1–MeCN**>**2–MeCN**) was further verified by the kinetic profiles of a model reaction for the oxidation of 4-methystyrene to 4-methylbenzaldehyde as shown in Fig. 4. Apparently, the change in reactivity seemed to be related to a probable contrasting influence of the two NHC ligands imparted to the structurally different two sets of precatalysts. However, the precatalysts under consideration are different in terms of the lability of the *para*-cymene and MeCN ligands, charge and solubility. The effect of such factors on the change in reactivity could not be ruled out at this stage.

Nevertheless, to derive additional kinetic information for the present MeCN-based precatalysts, the initial rate studies were carried out for the **1-MeCN** and **2-MeCN**-catalyzed reactions, by varying the concentration of the precatalyst, substrate and oxidant one by one. The kinetic data showed that for both cases, the rate of reaction is dependent on the concentration of the Ru^{II}–precatalysts (first order), oxidant $NaIO_4$ (first order), whereas it is independent of the concentration of the alkene substrate (zero order) (see Supplementary Information for details). This fact implied that the interaction of the $[(NHC)Ru(MeCN)_4]^{2+}$- precatalysts and $NaIO_4$ might be involved as the major rate-influencing factor. In such a scenario, the formation of the high-valent Ru-oxo species (probably *cis*-dioxo) from the reaction of $[(NHC)Ru(MeCN)_4]^{2+}$ species and $NaIO_4$, would be favored by electron-donating **Im-NHC** ligand in **1-MeCN** *via* electronic stabilization of the high-valent Ru (e.g., Ru^{VI}). This effect should have favored the observed activity order of **1-MeCN**>**2-MeCN**.

Table 1

Oxidation of carbon–carbon multiple bonded substrates to carbonyl compounds.[a]

#	Substrate	Product	Yield (%)/Time(min)	
			1-MeCN	2-MeCN
1			75/80	15/80
2			81/90	18/90
3			70/40	15/40
4			78/90	17/90
5			78/60	13/60
6			73/90	16/90
7			75/120	52/120
8			81/15	56/15
9			95/15	65/15
10			96/15	86/15
11			65/120	14/120
12			68/40	38/40
13			78/90	35/90
14			70/90	40/90

[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. Yields were determined by GC.

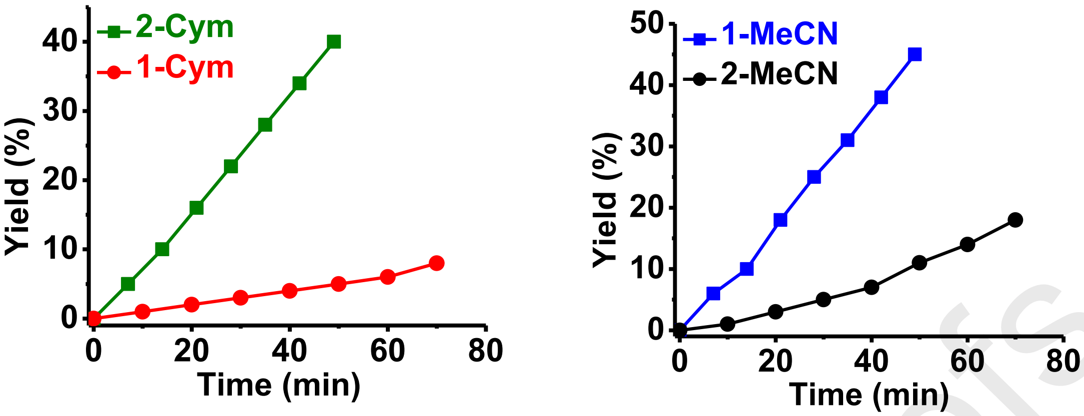


Fig. 4. Reaction kinetics profile of (left) **1-Cym/2-Cym** and (right) **1-MeCN/2-MeCN** precatalysts for the oxidation of 4-methylstyrene to 4-methylbenzaldehyde. Reaction conditions: 4-methylstyrene, 0.4 mmol; $NaIO_4$, 1.0 mmol; mesitylene, 0.2 mmol, internal standard; cat, 0.002 mmol; acetone:H_2O (1:1), 6 mL; room temp. Yields were determined by GC.

To further verify the hypothesis that the increase in the electron density at the ruthenium center of the solvato complexes $[(NHC)Ru(MeCN)_4]^{2+}$, can increase the activity, two new solvato complexes, **1-Cl** and **2-Cl** of the type $[(NHC)Ru(MeCN)_3Cl]^+$ were prepared where one of the four MeCN ligands was replaced with a chloride ligand (Fig. 5a). Molecular structures of both the complexes were confirmed by single crystal X-ray diffraction (Fig. 5b) along with other spectroscopic characterization (see Supplementary Information). The anionic π-donor Cl ligand and the less positive charge on the complex should make Ru center relatively more electron-rich in complexes **1-Cl** and **2-Cl** as compared to **1-MeCN** and **2-MeCN** respectively. The time vs yield profile for the catalytic oxidation of 4-methylstyrene was derived with these new **1-Cl** and **2-Cl** precatalysts. Indeed, both **1-Cl** and **2-Cl** showed higher activity relative to their MeCN analogs (Fig. 6). Notably, in this case also, the effect of overall charge of the complexes might play additional role as well for the enhancement of the activity. Kinetic studies with **1-Cl** and **2-Cl** showed similar rate-dependency profile as observed with **1-MeCN** and **2-MeCN**, that is, the rate of the reaction is dependent on the concentration of the Ru^{II}–precatalysts (first order), oxidant $NaIO_4$ (first order), and it is independent of the concentration of alkene (zero order) (see Supplementary Information for details), thus indicating similar nature of the rate-influencing step with these complexes as well.

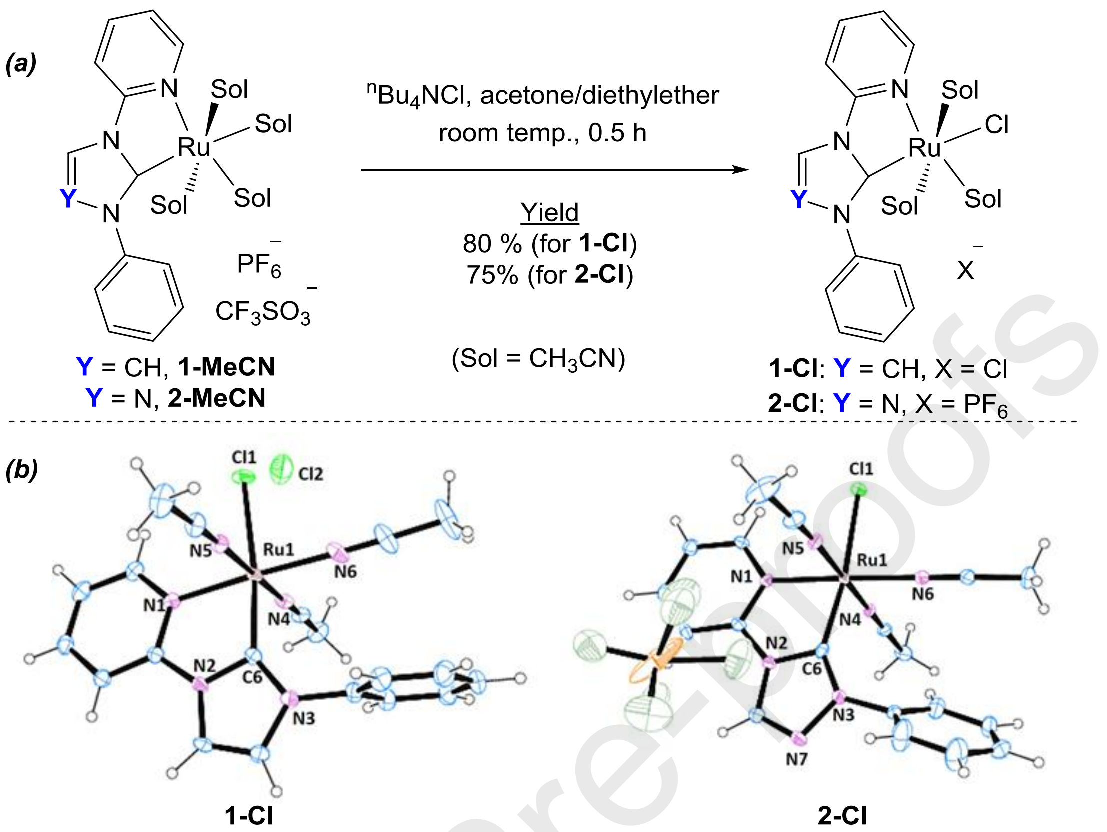


Fig 5. (a) Synthesis of the precatalysts **1-Cl** and **2-Cl**; (b) molecular structures of **1-Cl** and **2-Cl**. Selected bond lengths (Å) and bond angles (°): **1-Cl**: Ru(1)-C(6) = 1.962(4), Ru(1)-N(1) = 2.083(3), Ru(1)-N(4) = 2.050(5), Ru(1)-N(5) = 1.995(5), Ru(1)-N(6) = 2.027(4), Ru(1)-Cl(1) = 2.4997(12), C(6)-Ru(1)-N(1) = 78.03(16), C(6)-Ru(1)-Cl(1) = 172.68(13), N(6)-Ru(1)-N(1) = 177.14(16), N(5)-Ru(1)-N(4) = 178.50(2). **2-Cl**: Ru(1)-C(6) = 1.968(7), Ru(1)-N(1) = 2.069(5), Ru(1)-N(4) = 2.018(6), Ru(1)-N(5) = 2.032(6), Ru(1)-N(6) = 2.023(6), Ru(1)-Cl(1) = 2.4798(17), C(6)-Ru(1)-N(1) = 79.0(2), C(6)-Ru(1)-Cl(1) = 171.75(19), N(6)-Ru(1)-N(1) = 178.4(2), N(5)-Ru(1)-N(4) = 178.1(2).

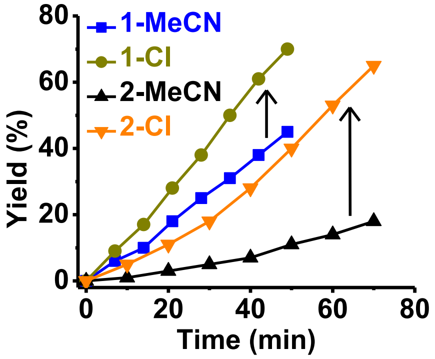


Fig. 6. Comparison of the reaction kinetics profile of **1-MeCN**/**2-MeCN** versus **1-Cl**/**2-Cl** for the oxidation of 4-methylstyrene to 4-methylbenzaldehyde. Reaction conditions: 4-methylstyrene, 0.4 mmol; $NaIO_4$, 1.0 mmol; mesitylene, 0.2 mmol, internal standard; cat, 0.002 mmol; acetone:H_2O (1:1), 6 mL; room temp. Yields were determined by GC.

Finally, the precatalyst **1-Cl** was further applied for selective oxidation of styryl double bond in presence of several oxidation-sensitive functional groups (Fig. 7). For this purpose, some specific substrates were tested as shown in Fig. 7. It is interesting to note that only styryl double bond was converted to the corresponding aldehyde functionality under the given reaction conditions. Other oxidation-sensitive functional groups such as aliphatic olefins – both internal and terminal, aliphatic primary alcohol, benzylic C–H bonds and aromatic alkynes remained intact. All the oxidized products were isolated in good yields as depicted in Fig. 7 (see Supplementary Information for details). Next, to examine the stability and attachment of the Ru-bound NHC ligand backbone under the catalytic conditions, a reaction of 4-methylstyrene with **1-MeCN** (**1-MeCN**:$NaIO_4$:4-methylstyrene = 1:42:17) was monitored by time-dependent ^1H NMR spectroscopy in CD_3CN/D_2O solvent mixture. The ^1H NMR peaks related to the bound NHC ligand of the complex remained intact with just ~20% decrease of peak intensity only after 80 min. 4-Methylstyrene was found to be converted to 4-methylbenzaldehyde gradually with time (Supplementary Information). Interestingly no diol or epoxide intermediates were detected in the ^1H NMR spectra, thus ruling out the alternate pathways to the carbon-carbon multiple bond cleavages for the present system.

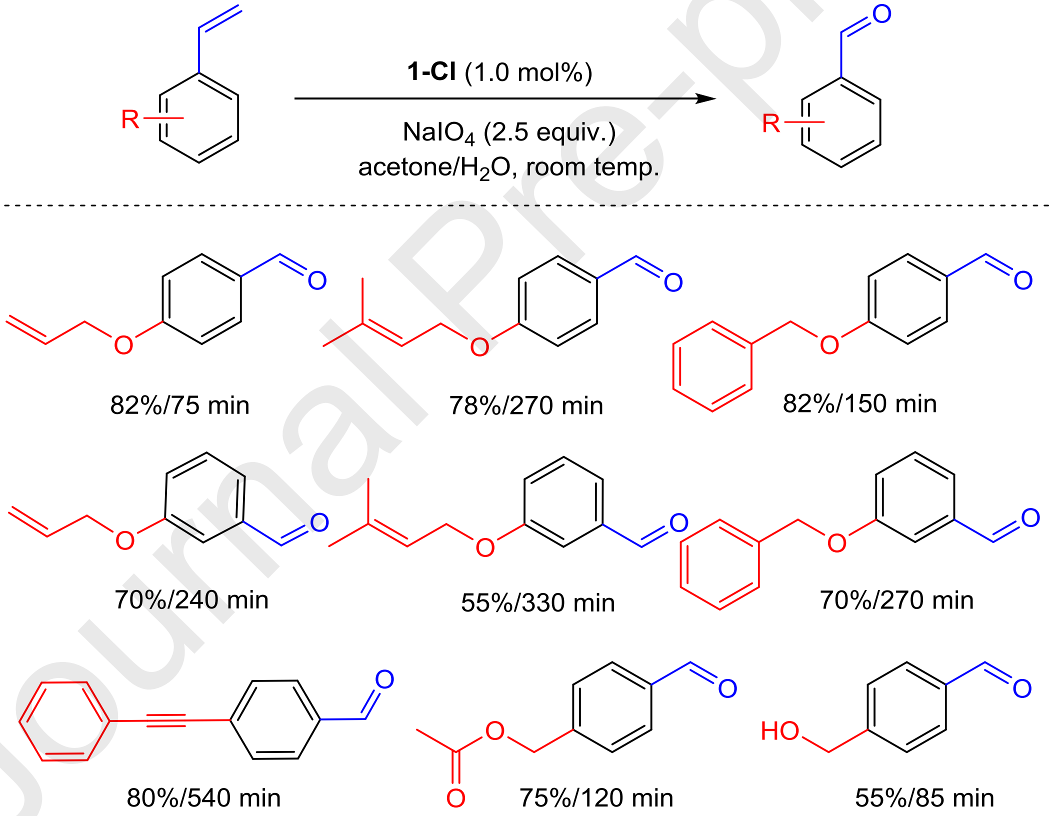


Fig. 7. **1-Cl** catalyzed selective oxidation of styryl bond in the presence of other oxidation-sensitive functionalities. Reaction conditions: substrate, 0.4 mmol; $NaIO_4$, 1.0 mmol; cat, 0.002 mmol; acetone:H_2O (1:1), 6 mL; room temp. Yields represent isolated yields..

4. Conclusion

In summary, this study demonstrated that the influence of two electronically-different NHC ligands was crucial to guide the choice of other labile co-ligands (*para*-cymene or MeCN) within the ruthenium coordination sphere of the precatalysts for oxidative conversion of olefins to carbonyl compounds under mild conditions. While the relatively less electron-donating triazolydene-NHC (**Tz-NHC**) ligand enhances catalytic activity of "Ru(*para*-cymene)"-type precatalysts, the more electron-donor imidazolydene (**Im-NHC**) ligand makes the "Ru(MeCN)$_3$"-type precatalysts more active for the same reaction. Along with the electronic influence of the NHC ligands, the effect of the lability of the *para*-cymene and MeCN ligands, and the overall charge of the complexes might also be attributed toward such interesting results. Finally, the [(**Tz-NHC**)Ru(MeCN)$_3$Cl]$^+$ precatalyst which was found to be best choice among these precatalysts, was further utilized for selective oxidation of a series of styryl substrates to the corresponding aldehydes without affecting the other oxidation-sensitive functionalities in the compounds.

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Appendix

Supplementary content

Supplementary information containing additional experimental details, characterization data, kinetics data and additional figures are available.

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