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Remote 'Imidazole' Based Ruthenium(II) Para-Cymene Precatalyst for Selective Oxidative cleavage of C-C multiple bond

Manali Dutta,[a] Kusum Kumar Bania, and Sanjay Pratihar*[a]

Dedication ((optional))

Abstract: The dual role of remote 'imidazole' attached with the precatalyst [(*para*-cymene)Ru^{II}(L)Y]$^{+}$ (L = 2-(4-substituted-phenyl)-1H-imidazo[4,5-f][1,10] phenanthroline, Y = chloride/solvent) was explored for the selective oxidative cleavage of C-C multiple bonds to acetals/aldehydes. The presence of 'imidazole' in the precatalysts was found to be useful for the activation of oxidant and release of *para*-cymene from the precatalysts, which in turn was not effective without the 'imidazole' moiety. The mechanistic aspects of the precatalyst were evaluated from spectroscopic, kinetic, and few other controlled experiments. The loss of *para*-cymene is the key step for the reaction and found to be faster in solvated precatalyst, [(*para*-cymene)Ru^{II}(L)(MeOH)]$^{++}$ and thus showed 3-4 fold more effective as compared to [(*para*-cymene)Ru^{II}(L)Cl]$^{+}$.

Introduction

Transition metal catalyzed selective oxidation of alkenes and alkynes to their valuable building blocks is one of the most challenging reactions both on the laboratory and industry scale.[1] The development of active catalysts that are inexpensive, easily accessible and could overcome the dangerous and inconvenient ozonolysis method or the less selective, low-yielding Lemieux−Johnson protocol for the selective and controlled oxidation of olefins[2] continues to be an exacting challenge. Thus, to achieve this important oxidative transformation, various oxidizing systems such as; RuO_4, transition-metal complexes along with a sacrificial oxidant (such as tBuOOH, $(NH_4)_2Ce(NO_3)_6$, $NaIO_4$) has been adopted by several research groups. [3] Simultaneously, heterogeneous nano catalysts containing ruthenium or osmium have been developed for such type of oxidative transformation.[4] In most of these systems, high-valent ruthenium-oxo/dioxo complexes are believed to be the potential oxidizing intermediates[5], wherein a well defined ligand system have been employed not only to stabilize these high-valent intermediates but also to tune its reactivity and selectivity through ligand modification. [6] Such type of oxidative transformation mediated by these ruthenium-oxo/dioxo intermediates are known to occur *via* H atom abstraction, hydride transfer, electron transfer, proton coupled electron transfer (PCET), or oxygen atom transfer (OAT) mechanisms. The detailed mechanistic aspects of various ligand-bound well-defined high valent ruthenium-oxo/dioxo intermediates and their utility as oxidant for variety of organic substrate have been done by the group of Mayer, [7] Nam, [8] Saik, [9] Che, [10] Kojima, [11] Fukuzumi,[12] and others.[13] Although substantial efforts have been put forward to understand the nature of active species and its catalytic mechanism, but choice of ligand is of utmost importance in this research. [14] Thus, the control of the properties of active metal centers by a well defined ligand system is an ultimate goal for the selection of a catalyst for the activation of a particular substrate. [15] In order to get superior activity in a catalyst one has to understand the mode of activation of precatalyst and important step of the catalytic cycle.[16] In this regard, previous studies showed that the initial labilization/dissociation of the arene in [M(η^6-arene)] [17] or Cp* from [Ir(Cp*)L] [18] and oxidative loss of arenes from the precatalyst[19] is mainly responsible for the generation of active catalysts from their precatalysts (Figure 1). Herein, we presented [(*para*-cymene)Ru^{II}(L)Y] as precatalysts, where L and Y are imidazole based 1,10 phenathroline and chloride/solvent, for the selective oxidative cleavage of C-C multiple bonds to their corresponding products (Figure 1).

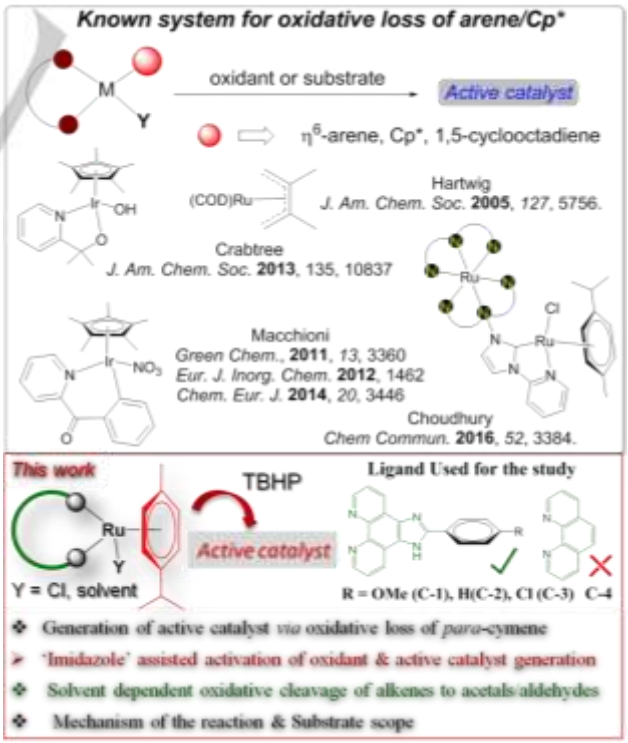

Figure 1. Known system for oxidative loss of arene/Cp*.

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The remote 'imidazole' moieties present in the precatalysts assisted both the activation of oxidant and release of *para*-cymene from the precatalyst to generate the active catalyst for selective oxidative cleavage of C-C multiple bonds to the corresponding acetals/aldehydes, which in turn was not observed without the 'imidazole' moiety.

Results and Discussion

Synthesis and Characterizations

The precatalysts [(*para*-cymene)$Ru^{II}(Cl)Y]^+$, (L = 2-(4-substituted-phenyl)-1H-imidazo[4,5-f][1,10] phenanthroline, **C-1** to **C-3**) have been synthesized from the reaction between [(*para*-cymene)$Ru^{II}Cl_2]_2$ and corresponding ligand followed by exchange of anion (chloride with KPF_6) under refluxing methanol in good to moderate yields (75-85%). For the synthesis of complex **C-5**, **C-3** was reacted with $AgPF_6$ (1 equiv.) in methanol at 50 °C for 2 h and reaction mixture was filtered to remove the precipitate of AgCl. After that, diethyl ether was added to the filtrate to get the precipitate of **C-5** in 75% yield (Figure 2).

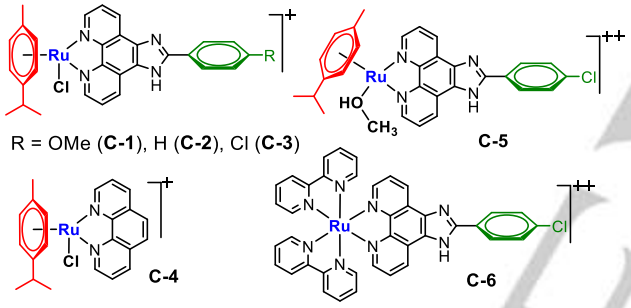


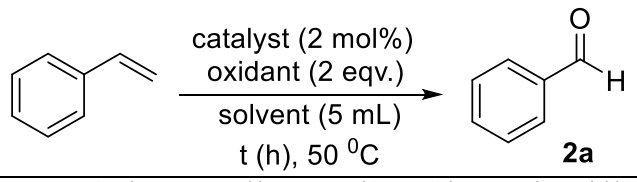
Figure 2. Precatalysts used for the study.

The complex **C-6** was synthesized from the reaction between $Ru(BPy)Cl_2$ and the corresponding ligand in refluxing methanol followed by exchange of anion (chloride with PF_6^-). Similar procedure was followed for the synthesis of complex **C-4** from the reaction between [(*para*-cymene)$Ru^{II}Cl_2]_2$ and 1,10-phenanthroline. All the complexes were fully characterized by ^1H, $^{13}C\{^1H\}$ NMR and mass spectrometric methods (details supplied in supporting information). Initially, to check the effect of remote "imidazole", **C-3** was chosen as model complex and its ^1H NMR was recorded in DMSO-d_6 under variety of reaction conditions. The ^1H NMR spectrum of **C-3** showed the presence of two doublet peaks with the integration of one proton each in the range of 5.9 to 6.3 ppm, one septet peak at 2.6 ppm with the integration of one proton, and two singlet peaks with the integration of three protons each in the range of 1.0 ppm suggested the ruthenium coordinated *para*-cymene. The addition of base (triethyl amine, Et_3N) to **C-3** resulted up-field shift of *para*-cymene and ligand peaks. In contrast, the addition of acid (trifluoro acetic acid, TFA) did not show any shift of *para*-cymene peaks (Figure 4a). The complex **C-3** showed an intense absorption MLCT band centred at 410 nm in acetonitrile (Figure S14-15, SI†). Upon addition of Et_3N, a new low energy band centered at 465 nm was observed. However, addition of TFA to **C-3** in acetonitrile produced a decrease in the absorbance of existing band at 410 nm. The change in the absorbance pattern of **C-3** after the sequential addition of base-acid or acid-base was found to be reversible in acetonitrile. Next, **C-3** was reacted with $AgPF_6$ in methanol to generate [(*para*-cymene)Ru^{II}(L)(MeOH)]$^{2+}2PF_6^-$, **C-5** (Figure S13, SI†). The spectroscopic behavior of **C-5** was found to be similar with **C-3**.

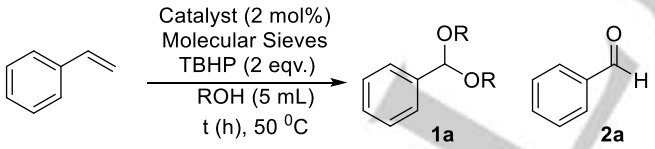
Optimization of the reaction conditions

In order to check the reactivity of the synthesized Ru(II)-complexes (**C-1** to **C-6**), initially oxidative transformation of styrene to benzaldehyde was chosen as model reaction. After the optimization of reaction conditions from the screening of solvents (Table 1, entry 1-5), catalyst loading (Table 1, entry 6-7), oxidant (Table 1, entry 8-11), our study began with **C-3**/**C-5** as catalyst. The superiority of **C-3**/**C-5** over other tested transition metal complexes (Table 1, entry 23-24) and metal salts (Table 1, entry 17-22) suggest the need of **C-3**/**C-5** as precatalyst to achieve higher yield, selectivity, and turn over frequency (TOF) for the selective transformation of styrene to benzaldehyde. It is noteworthy to mention that **C-4** promoted reaction afforded benzaldehyde in 32% yield (Table 1, entry 15). While, complex **C-6**, with a stable octahedral geometry, is failed to produce any benzaldehyde under optimized reaction condition and suggested the need of unsaturated coordination number at ruthenium for C-C bond cleavage reaction (Table 1, entry 16). During the optimization, we noticed the formation of dimethyl acetal in the model reaction using methanol as solvent. Thus, the progress of **C-5** promoted reaction of styrene to dimethyl acetal was monitored in gas chromatography (GC) and their products were characterized in GC-MS. Initially, styrene was converted into dimethyl acetal, which was slowly transformed into benzaldehyde through hydrolysis (Table 2).[20] Next, to check the effect of water, the model reaction was conducted under variety of reaction conditions. When the same reaction was performed in dry methanol in presence of activated molecular sieves (4Å), amount of aldehyde was found to be less over the time (Figure 3).[21] On the other hand, the addition of little amount of water with methanol, methanol/water (3.0 /0.1 or 0.2 mL) for the model reaction showed very little amount of dimethyl acetal (**1a**) at early stage and gradually converted to benzaldehyde with time. However, we failed to detect any **1a** for the mixture of methanol/water (3.0 /0.3 mL). Interestingly, in all the cases, 25-40 % of benzaldehyde was detected after 3 h, which clearly indicate that the amount of water present with methanol mainly drives the hydrolysis of dimethyl acetal to benzaldehyde (Table 2). Notably, the reaction of styrene with other alcohols such as ethanol, *n*-pronal, *n*-butanol, and *iso*-propanol failed to produce any acetal derivatives (Table 1). However, in all the cases, minor amount of benzaldehyde was formed (Table 1, entry 31-33). Under optimized reaction condition, selectivity of the products (acetal *vs.* aldehyde) upon changing the solvent (MeOH *vs*. MeCN) of the reaction for various alkenes (Table 4) were found to be consistent with both the precatalyst (**C-3** and **C-5**).

Table 1. Optimization of the reaction conditions for oxidative transformation of styrene to dimethyl acetal/benzaldehyde.



#	Catalyst	oxidant	mol %	Solvent	t, h	Yield % (**2a**)
1	**C-3**	TBHP	2	MeCN	6	78
2	**C-3**	TBHP	2	DCE	6	45
3	**C-3**	TBHP	2	DCM	6	48
4	**C-3**	TBHP	2	THF	6	52
5	**C-3**	TBHP	2	H_2O	6	0
6	**C-3**	TBHP	2	DMF	6	10
7	**C-3**	TBHP	1	MeCN	6	68
8	**C-3**	H_2O_2	2	MeCN	6	41
9	**C-3**	CAN	2	MeCN	6	32
10	**C-3**	O_2	2	MeCN	12	<10
11	**C-3**	$NaIO_4$	2	MeCN	3	42
12	**C-5**	TBHP	2	MeCN	3	87
13	**C-1**	TBHP	2	MeCN	6	68
14	**C-2**	TBHP	2	MeCN	6	71
15	**C-4**	TBHP	2	MeCN	6	32
16	**C-6**	TBHP	5	MeCN	6	0
17	$AgPF_6$	TBHP	5	MeCN	6	21
18	$Cu(OAc)_2$	TBHP	5	MeCN	5	19
19	$CuCl_2$	TBHP	5	MeCN	5	19
20	$FeCl_3$	TBHP	5	MeCN	6	29
21	$PdCl_2$	TBHP	5	MeCN	6	28
22	$RuCl_3.3H_2O$	TBHP	5	MeCN	6	21
23	$[RuCl_2(para\text{-}cymene)]_2$	TBHP	5	MeCN	6	40
24	$Ru(BPy)_2Cl_2$	TBHP	5	MeCN	6	32



#	Catalyst	mol %	Solvent	t, h	Yield % (**1a**)	Yield % (**2a**)
25	**C-3**	2	MeOH	6	73	7
26	**C-1**	2	MeOH	6	70	8
27	**C-2**	2	MeOH	6	65	6
28	**C-4**	2	MeOH	6	32	10
29	**C-5**	2	MeOH	2	87	<5
30	**C-6**	5	MeOH	4	0	0
31	**C-3**	2	EtOH	6	0	25
32	**C-3**	2	^{i}Pr-OH	6	0	32
33	**C-3**	2	^{n}Bu-OH	6	0	28
34	$[RuCl_2(para\text{-}cymene)]_2$	5	MeOH	6	35	15

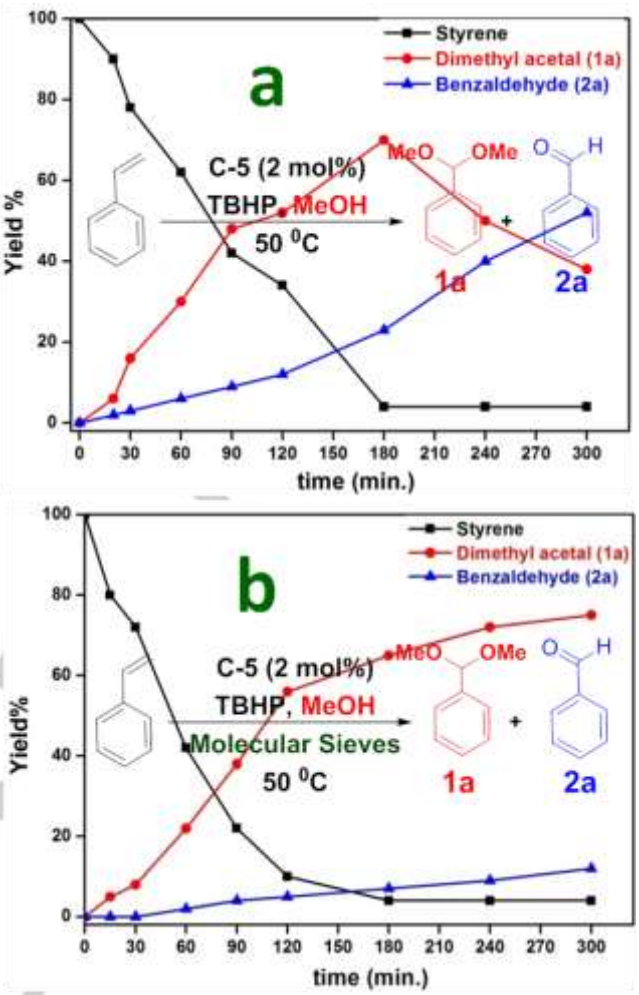
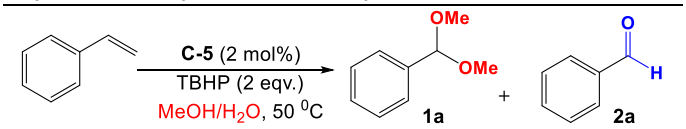


Figure 3. Effect of water on **C-5** promoted oxidative transformation of styrene to dimethyl acetal/benzaldehyde without molecular sieves (a) and with molecular sieves (b).

Table 2. Effect of water on **C-5** promoted oxidative transformation of styrene to dimethyl acetal/benzaldehyde.



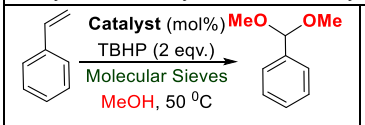
	MeOH/H_2O (3.0 / 0.1 mL)		MeOH/H_2O (3.0 / 0.2 mL)		MeOH/H_2O (3.0 / 0.3 mL)	
Time (min.)	**1a**	**2a**	**1a**	**2a**	**1a**	**2a**
60	12	8	10	15	0	12
120	14	10	0	28	0	25
180	16	24	0	40	0	34

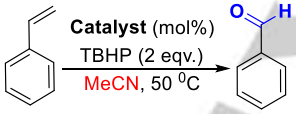
Comparative reactivity of the Precatalysts for oxidative transformation of styrene to dimethyl acetal/benzaldehyde

Next, to check the comparative reactivity between the precatalysts, oxidative transformation of styrene to dimethyl acetal was chosen as model reaction. The initial rate kinetics was monitored for four different precatalysts. In terms of initial rate constant, **C-5** showed 2-fold higher reactivity as compared to **C-3** (Table 3, entry 2-3). The higher reactivity of **C-5** as compared to **C-3** was found to be consistent for the oxidative transformation of other substartes such as 1-nitro-4-vinylbenzene, 1-chloro-4-vinylbenzene, and 1-methoxy-4-vinylbenzene to their corresponding dimethyl acetal (Table 3, entry 7-10). On the other hand, the initial rate constant of **C-5** was found to be 8 and 16-fold higher as compared to **C-4** and [Ru(para-cymene)Cl_2], respectively. The relative reactivity between the complexes was also checked for the oxidative transformation of styrene to benzaldehyde under optimized reaction condition. In this case, **C-5** was found to be 2-fold more reactive than **C-3**. The superiority of **C-5** as compared to **C-4** and [Ru(*para*-cymene)Cl_2] was also found to be consistent and showed 6 and 14-fold more reactive.

Table 3. Comparative reactivity of the precatalysts under variety of reaction conditions.

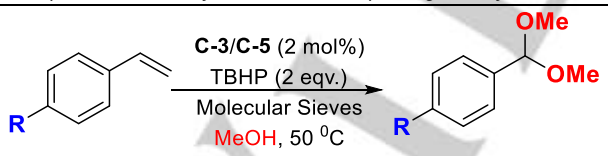
Initial rate kinetics of five different precatalysts for the oxidative transformation of styrene to dimethyl acetal/ benzaldehyde.





1	Catalyst (mol%)	k [a]×10 min^{-1}	Catalyst (mol%)	k [b]×10 min^{-1}
2	**C-5** (2)	9.8	**C-5** (2)	6.9
3	**C-3** (2)	4.5	**C-3** (2)	3.1
4	**C-4** (2)	1.2	**C-4** (2)	1.2
5	[Ru(*P-Cy*)Cl_2]$_2$ (2)	0.6	[Ru(P-Cy)Cl_2]$_2$ (2)	0.5
6	**C-6** (5)	NR	**C-6** (5)	NR
	Reaction Condition: precatalysts (mol%), styrenes (1 mmol), *tert*-butyl hydroperoxide (TBHP, 2.1 mmol), 300 mg activated molecular sieves (4Å, fine powder), methanol (5 mL), 50 °C.		**Reaction Condition**: precatalysts (mol%), styrenes (1 mmol), *tert*-butyl hydroperoxide (TBHP, 2.1 mmol), 300 mg activated molecular sieves (4Å, fine powder), acetonitrile (5 mL), 50 °C.	

Initial rate kinetics of C-3 and C-5 promoted oxidative transformation of four different para substituted styrene to their corresponding dimethyl acetal.



	#	k × 10 min^{-1}(**C-3**) [a]	k × 10 min^{-1}(**C-5**) [a]	k (**C-5**/**C-3**)
7	R = NO_2	8.9	17.4	1.9
8	R = Cl	7.0	14.4	2.1
9	R = H	4.5	9.8	2.2
10	R = OMe	3.3	8.6	2.6

Reaction Condition: **C-3**/**C-5** (2 mol%), styrenes (1 mmol), *tert*-butyl hydroperoxide (TBHP, 2.1 mmol), 300 mg activated molecular sieves (4Å, fine powder), methanol (5 mL), 50 °C. [a]The conversion of corresponding dimethyl acetal in each case was monitored in gas chromatography (GC) using *ortho*-xylene as external standard. [b]The conversion of benzaldehyde in each case was monitored in ^{1}H NMR analysis using diphenyl methane as external standard.

Mechanistic studies for C-3/C-5 promoted oxidative transformation of styrene to dimethyl acetal/benzaldehyde

Initially, to check the effect of oxidizing agent on both the complexes (**C-5** and **C-3**), the reaction was performed in methanol in presence of various reagents such as; hydrogen peroxide (H_2O_2), sodium metaperiodate ($NaIO_4$), *tert*-butyl hydroperoxide (TBHP), and ceric ammonium nitrate (CAN).[22] Amongst all, TBHP was found to be effective in methanol at 50 °C for the release of *para*-cymene from precatalysts **C-3**/**C-5** (evident from *in-situ* monitoring of ^{1}H NMR spectra) and subsequent generation of active species. However, the release of *para*-cymene is found to be faster in complex **C-5** as compared to **C-3** (Figure 4). Further to know the release of *para*-cymene in **C-4** under oxidizing environment, ^{1}H NMR spectra were monitored with time in presence of TBHP in CD_3OD at 50 °C. The analysis suggested a slow release of *para*-cymene in this case through the coordination of TBHP with Ru(II) (Figure S42, ESI). Thus, the catalytic activity of **C-5** for the transformation of styrene to dimethyl acetal is expected to be higher. In fact the activity of **C-5** was found to be 2 and 8-fold higher as compared to **C-3** and **C-4** (Table 3).

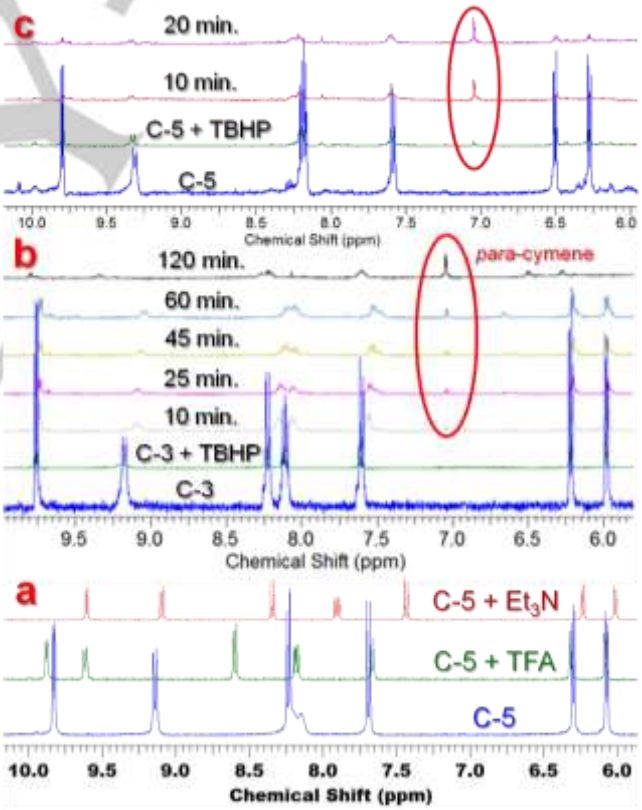


Figure 4. ^{1}H NMR monitoring of **C-5** in Et_3N and TFA in DMSO-d_6 (a), **C-3** in presence of TBHP at 50 °C in CD_3OD (b) and **C-5** in presence of TBHP at 50 °C in CD_3OD (c).

However, model reaction was found to be extremely slow with **C-3** or **C-5** in presence of base. The precatalysts **C-1** and **C-2** also showed similar type of reactivity as we observed in **C-3**

(Table 1). However, the presence of acid either with **C-3** or **C-5** does not show any significant enhancement to their catalytic activity. The P^H of the reaction medium is found to be slightly acidic (5.8 to 6.4) during the entire course of the reaction. Further, to understand the mechanism, kinetic orders of dependency for precatalyst, oxidant (TBHP), and styrene were determined with model reaction by using initial rate methods.[23] The rate kinetics data showed first order rate dependency on precatalyst and TBHP. While, zero order rate dependency was observed with substrate, which indicate that the substrate does not involve in the rate determining step (page no. S-33 to S-35 SI†). Interestingly, the reaction rate was found to be independent in presence of acid or base. However, when we conducted the model reaction in presence of different arenes or added *para*-cymene, change in the conversion of product was observed, suggested that the release of *para*-cymene from the precatalyst involve in the rate determining step (Figure 9b). Next, the precatalysts promoted transformation of styrene to dimethyl acetal under optimized reaction condition was monitored at the initial stage to know the involvement of *para*-cymene in the rate determining step.

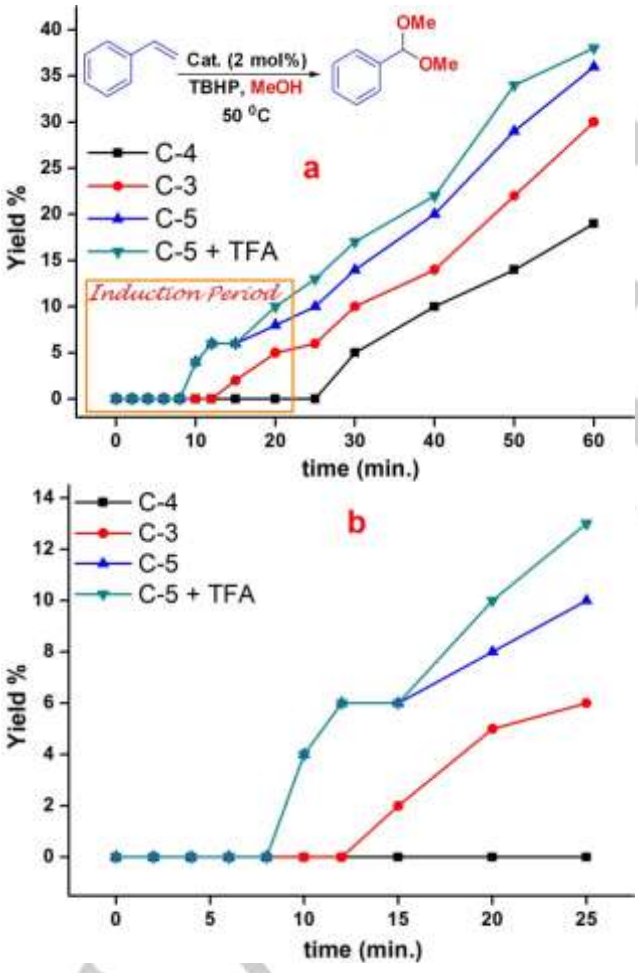


Figure 5 Comparative reactivity of the complexes for the oxidative transformation of styrene to dimethyl acetal. (a) % of conversion at different time interval. (a) % of conversion versus time plot at the initial stage of the reaction.

The yield *versus* time plot in all the cases showed an induction period, which further justify that the release of *para*-cymene from the precatalysts is the rate determining step (Figure 5). Further, temperature dependence of the rate constants for the generation of active catalyst from precatalyst (**C-3** and **C-5**, *vide* UV-vis monitoring) allowed us to determine the activation parameters to shed some lights on the transition state of active species from Eyring plots (Figure 6). Interestingly, more positive entropy of activation in complex **C-5** ($\Delta S^{\#}$ = 63 ± 6.0 $JK^{-1}mol^{-1}$) implied faster release of *para*-cymene and subsequent generation of active catalyst in comparison to **C-3** ($\Delta S^{\#}$ = -24 ± 3.5 $JK^{-1}mol^{-1}$). Moreover, the generation of active catalyst from precatalyst is entropy driven process.

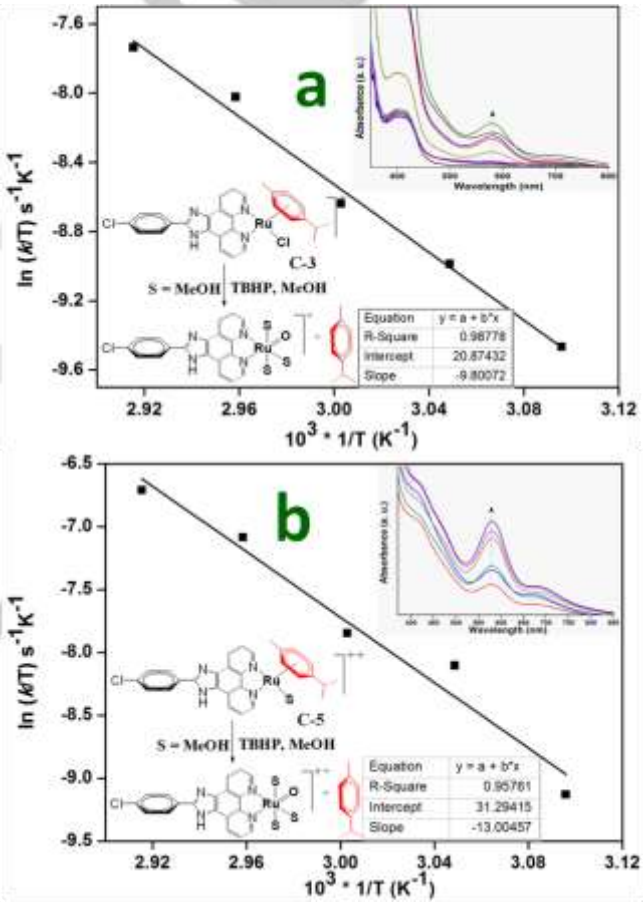


Figure 6. Temperature dependence of the rate constants for the generation of active catalyst from precatalysts (**C-3**, a and **C-5**, b) *via* oxidative loss of *para*-cymene from precatalysts.

The precatalysts (**C-3** or **C-5**) to active species generation proceeded smoothly in solvents such as MeOH, EtOH, and MeCN (Figure S17 & 18, SI†). However, its generation was not observed in non coordinating solvents like DCM, DCE, $CHCl_3$ and toluene. The studies suggest that solvent coordinated to Ru(II) not only facilitate the release of *para*-cymene but also helps to stabilize the active species. Thus, ESI-MS study with a

reaction mixture of **C-3**/TBHP (1:3 molar ratios) in methanol was done to know the different intermediate species (Figure 7-8). The ESI-MS spectra showed the presence of parent [*para*-cymene(L)Ru(Cl)]$^+$ along with other species such as [*para*-cymene(L)Ru-H]$^+$, [*para*-cymene(L)RuCl(MeOH)$_n$]$^+$, [(L)Ru-Na]$^+$ and [(L)Ru(H_2O)(MeOH)-H]$^+$. Gratifyingly, we could observe the presence of TBHP coordinated species such as [*para*-cymene(L)Ru(TBHP)(MeOH)-Na]$^+$. During the course of the reaction, these intermediates finally transformed into active species such as [(L)Ru(MeOH)$_2$(=O)]$^+$ and [(L)Ru(MeOH)$_3$(=O)]$^+$, which suggest the involvement of Ru=O as the active catalyst (Figure S22 to S31, SI†).[24] The FT-IR spectra of the reaction mixture suggest an intense band at 855 cm^{-1} assigned to the corresponding ν_{asy} Ru=O strectch (Figure S19, SI†). Next to check the stability of the complexes under oxidizing condition *in-situ* ^{1}H NMR spectra was monitored with time for both **C-3** (**C-3**:styrene:TBHP; 1:50:100) and **C-5** (**C-5**:styrene:TBHP; 1:50:100) in CD_3CN for the oxidation of styrene to benzaldehyde. In both the cases styrene was gradually converted into benzaldehyde with time (Figure S42, SI†). We could not able to monitor the peak intensity of the ligand because of the broadness of peaks due to presence of paramagnetic (L)Ru=O species. Thus, **C-3** was reacted with TBHP (C-3: TBHP; 1:50) in methanol and its analysis in ESI-MS spectroscopy showed the presence of active species [(L)Ru(MeOH)$_2$(=O)]$^+$ and [(L)Ru(MeOH)$_2$(H_2O)(=O)]$^+$ apart from its parent complex, which is evident for its stability under oxidizing environment. To obtain further support, rate kinetics was monitored with four different *para*-substituted styrenes (p-Y-$C_6H_4CH=CH_2$; Y = OMe, H, Cl, NO_2) to their corresponding dimethyl acetal with both the intermediate. The relative reactivity of these *para*-substituted styrenes are in the order Y = NO_2 > Cl > H > OMe (Table 3). The Hammett analysis led to a small positive ρ-value in both the cases (reaction constant, ρ = 0.41 for **C-3** and 0.30 for **C-5** (Figure S38, ESI†), which indicates the generation of a negligible negative charge at the α-carbon of styrene and further support [2+1] cycloaddition adduct between intermediate and substrate (Figure 9a). A tentative mechanistic route has been shown in Figure 9a.[25,26] Further, initial rate kinetics for **C-3** promoted oxidative transformation of four different *para*-substituted styrenes (p-Y-$C_6H_4CH=CH_2$; Y = OMe, H, Cl, NO_2) to their corresponding benzaldehyde was monitored and showed the order as Y = NO_2 > Cl > H > OMe. The small positive Hammett reaction constant (ρ = 0.69) for **C-3** further suggested (Figure S38, ESI†) the generation of a small negative charge at the α-carbon of styrene and further support [2+1] cycloaddition adduct between intermediate and substrate during its oxidative transformation to its corresponding benzaldehyde.[26]

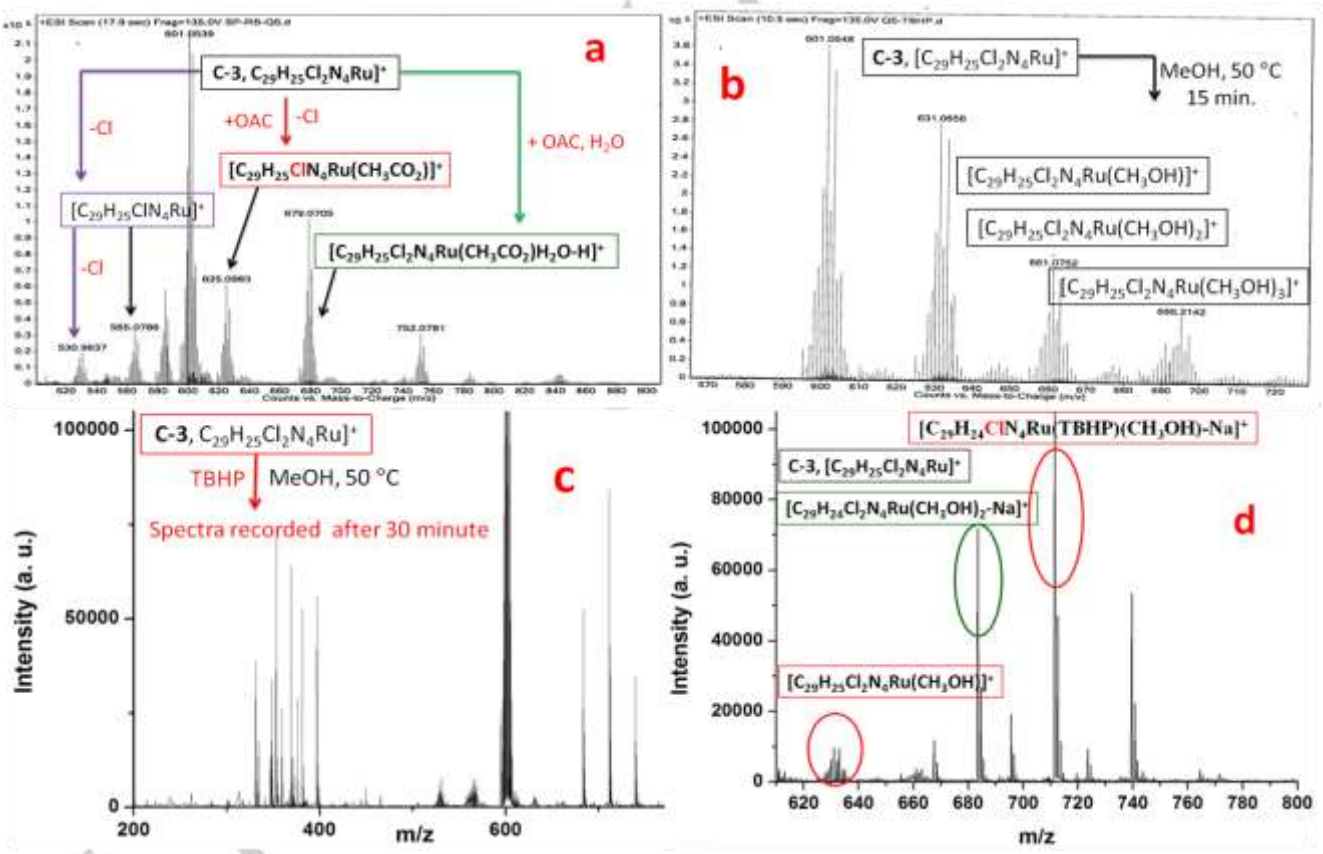


Figure 7. ESI-MS spectra recorded in methanol under variety of reaction conditions. **C-3** (a); reaction mixture of **C-3** in methanol after stirring at 50 °C for 15 minutes (b); reaction mixture of **C-3** in methanol after reaction w ith *tert*-butyl hydroperoxide (TBHP) at 50 °C for 30 minutes (c and d).

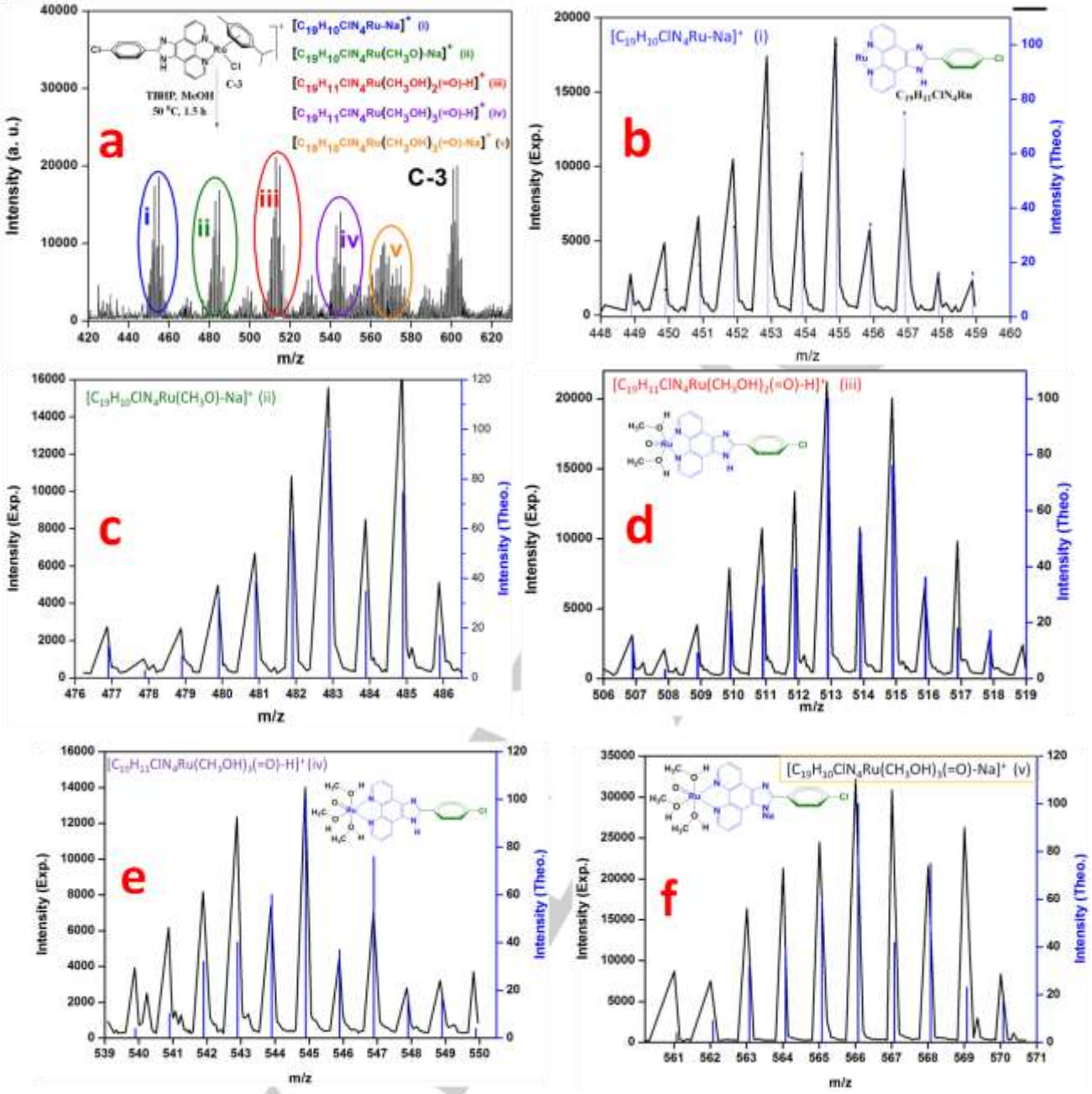


Figure 8. ESI-MS spectra of the reaction mixture of **C-3** in methanol after reaction with *tert*-butyl hydroperoxide (TBHP) at 50 °C for 90 minutes and the plausible active species (a); the isotropic distribution of each of the species and their simulated versus experimental plot (b-f).

Next, to check the stability of the metal-ligand backbone under oxidizing environment and probable formation of "ligand-free" RuO_4 the reactivity of **C-3** was compared with other reagent systems for the oxidative cleavage of styrene to benzaldehyde. The significantly higher catalytic activity of **C-3**/TBHP (87% yield of benzaldehyde) was achieved as compared with other systems (Table 1) such as; $RuCl_3/NaIO_4$ (known to generate RuO_4, 28% yield of benzaldehyde), [Ru(para-cymene)Cl_2]/TBHP (40% yield of benzaldehyde) and [$Ru(BPy)_2Cl_2$]/TBHP (32% yield of benzaldehyde). So, regarding the integrity of the metal-ligand backbone in the active catalysts and its involvement in the reaction, above mentioned comparative reactivity study suggested that complete degradation of ligand backbone in **C-3** to form "ligand-free" RuO_4 was unlikely in the present system. Under optimized reaction condition, **C-3** promoted oxidative transformation of styrene in presence of radical scavenger (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) afforded 25% benzaldehyde after 6 h and suggested the possible involvement of TBHP radical in the reaction. However, the model reaction produced benzaldehyde in 21% with $RuCl_3$/TBHP, 32% with

$RuCl_3$/TBHP, and 0% with **C-6**. These evidences further support the involvement of active catalyst of **C-3/C-5** in the model reaction to achieve higher yield and selectivity of the reaction.

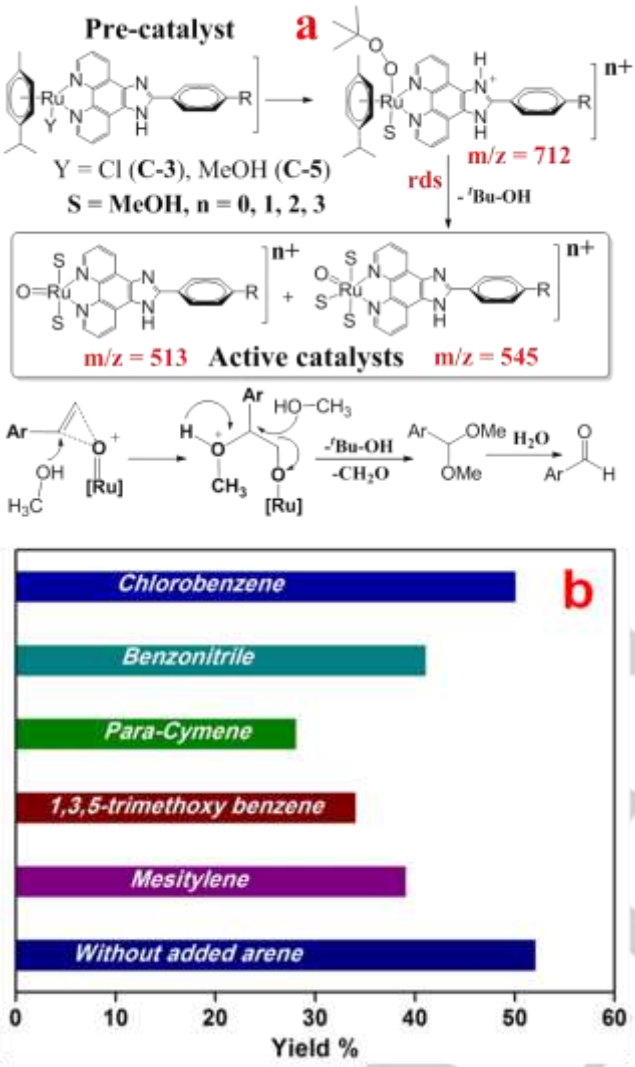


Figure 9. **C-3**/**C-5** promoted C-C multiple bond cleavage and its proposed Mechanism (a); C-3 promoted oxidative transformation of styrene in presence of different added arenes at 45 °C after 2 h (b).

Substrate scope for C-3/C-5 promoted oxidative cleavage of C-C multiple bonds

Next, to check the generality of **C-3/C-5** promoted oxidative transformation of styrenes to corresponding dimethyl acetal, four different *para*-substituted styrenes were attempeted for the reaction under optimized reaction condition (Table 4, entry 1-4). In all the cases, turn over frequency of **C-5** was found to be 2-3 folds higher as compared to **C-3**. On the other hand, upon changing the solvent from methanol (MeOH) to acetonitrile (MeCN) we observed selective oxidative transformation of styrenes to corresponding aldehydes with both the precatalyst (**C-3** and **C-5**) for variety of substrate. The **C-3/C-5** promoted transformation of styrenes substituted with both electron-withdrawing or -donating groups at para-/ortho/meta position were effective and produced their corresponding aldehydes selectively with very good to moderate yield (Table 4). In all the cases, 2-3 fold higher TOF was achieved with **C-5** as compared to **C-3**. The oxidative transformation of (Z)-1,2-diphenylethene with **C-3** and **C-5** also produced two equivalent of benzaldehyde with overall yield of 68% and 70%, respectively. Whereas, **C-3** or **C-5** promoted oxidative transformation of (Z)-1-methoxy-4-styrylbenzene under optimized reaction condition produced both benzaldehyde (**2a**) and 4-methoxy benzaldehyde (**2d**) in equal amount (1:0.95, **C-3** and 0.9 :1, **C-5**) with overall yield of 64% and 72%, respectively (entry 17, Table 4). The oxidative transformation of 2-vinylnaphthalene produced corresponding 2-naphthaldehyde (**2g**) with TOF of 10 and 24 with **C-3** and **C-5**, respectively (Table 4, entry 12). The substrate scope of the methodology was also extended for other substrates such as phenyl acetylene, diphenyl acetylene, and α-methyl styrene. In all the cases, both **C-3** and **C-5** was found to be effective to produce their corresponding oxygen inserted products in good to moderate yield (Table 4, entry 9-11).

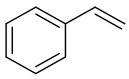
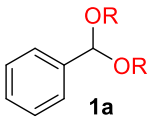
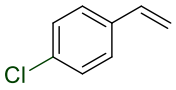
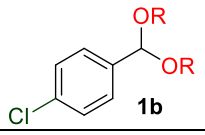
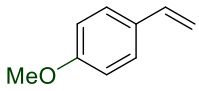
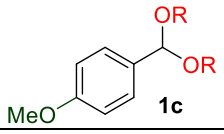
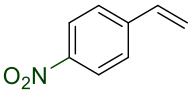
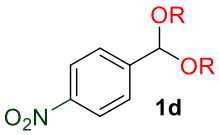
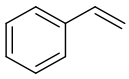
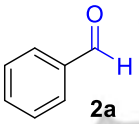
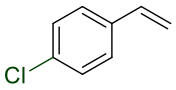
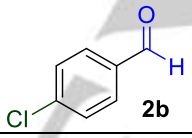
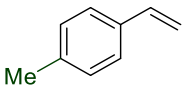
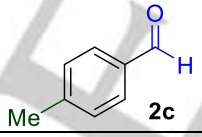
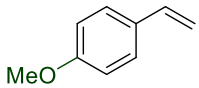
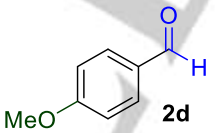
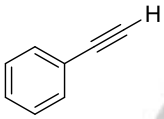
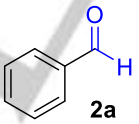
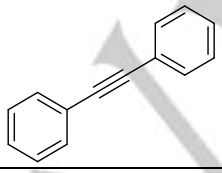
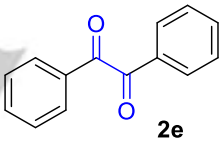
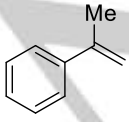
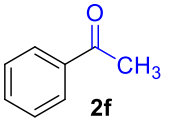
Conclusions

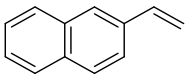
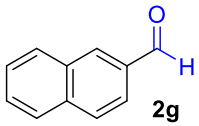
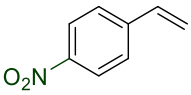
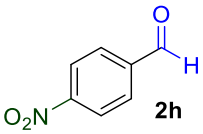
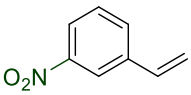
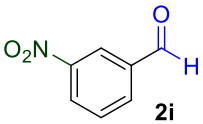
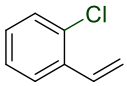
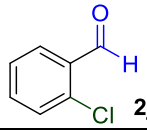
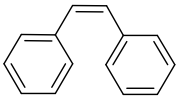
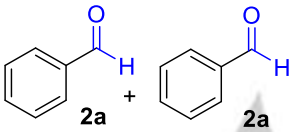
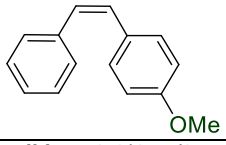
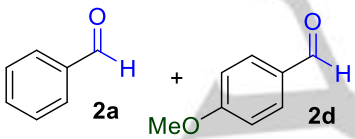
In summary, we demonstrated the remote 'imidazole' based precatalysts [(*para*-cymene)Ru^{II}(L)Cl]$^+$, **C-3** and [(*para*-cymene)Ru^{II}(L)(MeOH)]$^{++}$, **C-5**, where L = 2-(4-substituted-phenyl)-1H-imidazo[4,5-f][1,10] phenanthroline) for the selective oxidative cleavage of C-C multiple bond to aldehyde or acetals. The remote 'imidazole' moiety present in the complexes (**C-3**/**C-5**) was effective for the release of *para*-cymene from the pre-catalyst under oxidizing condition for the generation of active catalyst, which in turn was found to be slow in **C-4**. The mechanistic evidences based on spectroscopic, kinetic, and few other controlled experiments suggested that the release of *para*-cymene from precatalyst involve in the rate determining step (rds) and it is entropy driven process. Thus, the induction period for the reaction in solvated precatalyst, **C-5** was found to be less as compared to **C-3** and showed 3-4 fold more activity than **C-3** for the oxidative cleavage of C-C multiple bonds to acetals/aldehydes. The pre-catalysts (**C-3** and **C-5**) showed promising catalytic activity and good selectivity for a variety of substrates, which in turn was not effective without the 'imidazole' moiety.

Experimental Section

Experimental Details: For the synthesis of complexes, reactions were performed under a dry oxygen free argon atmosphere using standard vacuum lines and Schlenk techniques. The solvents used for the synthesis of complexes were dried and distilled by standard methods and previously deoxygenated in the vacuum line. 1H (400 MHz) and 13C NMR (100 MHz) spectra (chemical shifts referenced to signals for residual solvent) were recorded on 400 MHz spectrometers at 298 K. Electron spray Ionization mass spectra (ESI-MS) were recorded on ESI-Q-TOF mass spectrophotometer.

Table 4. Substrate scope of C-3/C-5 catalyzed reaction of various alkenes and alkynes.

#	Substrate	Product	Solvent	C-3[a]	C-5[a]
1		 **1a**	MeOH	73/12.1	87/29
2		 **1b**	MeOH	61/15.2	66/33
3		 **1c**	MeOH	73/14.6	79/23
4		 **1d**	MeOH	86/21.5	86/57.3
Reaction Condition: **C-3**/**C-5** (2 mol%), styrenes (1 mmol), *tert*-butyl hydroperoxide (TBHP, 2.1 mmol), 300 mg activated molecular sieves (4Å, fine powder), methanol (5 mL), 50 °C. The conversion of corresponding dimethyl acetal in each case was monitored in gas chromatography (GC) using *ortho*-xylene as external standard. [a]Yield % / TOF in h^{-1} (isolated yield %).					
5		 **2a**	MeCN	74/18.5(68)[a,b]	85/28.3[b]
6		 **2b**	MeCN	61/7.6	89/35.6(78)
7		 **2c**	MeCN	69/11.5[c,d]	52/22.5[c,d]
8		 **2d**	MeCN	74/12.3	65/21.6
9		 **2a**	MeCN	66/6.6	70/35(58)
10		 **2e**	MeCN	86/10.7(77)	85/42.5
11		 **2f**	MeCN	45/4.5[b]	80/40(70)

12		 **2g**	MeCN	86/10.7(73)	72/24
13		 **2h**	MeCN	89/14.8	87/21.7(79)
14		 **2i**	MeCN	86/14.3	88/22
15		 **2j**	MeCN	56/9.3	64/21(48)
16		 **2a** + **2a**	MeCN	68/11.3[e]	70/17.5[e]
17		 **2a** + **2d**	MeCN	64/8[e] (**2a** : **2d** = 1 : 0.95)	72/12[e] (**2a** : **2d** = 0.9 : 1)

Reaction Condition: **C-3**/**C-5** (2 mol%), styrenes (1 mmol), *tert*-butyl hydroperoxide (TBHP, 2.1 mmol), acetonitrile (5 mL), 50 °C. All the reactions were performed twice to check the reproducibility. The average yields of two reactions calculated from ^{1}H NMR analysis with diphenyl methane as an external standard. [a]Yield % / TOF in h^{-1} (isolated yield %), [b] the degraded product is formaldehyde for **C-3**/**C-5** promoted oxidative transformation of styrene derivatives to their corresponding benzaldehydes, [c]terephthalaldehyde was also detected as minor product (08%, **C-3** & 12%, **C-5**). [d] the formation of terephthalaldehyde was found to be higher when we used higher amount (21%, **C-3** & 24%, **C-5**) of TBHP (4 mmol) for the oxidation. [e]Isolated Yields.

Synthesis of 1, 10-phenanthroline [5, 6]-dione

In a 100 mL round bottom flask, 4 g of 1, 10-phenanthroline is mixed thoroughly with 4 g of Potassium bromide. To it, 40 mL concentrated H2SO4 is added drop wise and then 20 mL of concentrated HNO3 is added drop wise by maintaining the temperature at 0ºC-10ºC. After that, the reaction mixture was refluxed for 5 h to get the yellow solution. The obtained mixture is then neutralized with dilute NaOH solution. The product was collected through the extraction with dichloromethane (100 mL ×5). After that, the dichloromethane solution was washed with brine solution (200 mL × 2) and dried over sodium suplphate. Finally, the product was collected after the evaporation of dichloromethane and subsequent drying under vacuum. Yield = 3.8 g.

General procedure for the synthesis of ligands

A mixture of 1 mmol (210 mg) of 1, 10-phenanthroline [5, 6]-dione, 1 mmol of substituted benzaldehyde derivatives and 1 g of ammonium acetate were taken in 5 mL glacial acetic acid in a 25 mL round bottom flask attached with a reflux condenser. The reaction mixture was then refluxed at 100 °C for 12 h under nitrogen atmosphere. Upon neutralization of the reaction mixture with $NaHCO_3$ solution, the precipitation of the ligand was observed. The precipitate was subsequently filtered, washed with water (5 mL × 5), cold methanol (1 mL × 2), and diethyl ether (1 mL × 3) and then dried under vacuum. *2-phenyl-1H-imidazo[4,5-f][1,10]phenanthroline* (***L-1***): Yellow solid, Yield = 220 mg, 78%, δ_H (400MHz, DMSO-d_6): 8.85 (2H, d, *J* = 4Hz), 8.82 (2H, d, *J* = 8 Hz), 8.32 (2H, m), 7.66 (2H, m), 7.47 (2H, d, *J* = 12 Hz). *2-(4-methoxyphenyl)-1H-imidazo[4,5-f][1,10]phenanthroline* (***L-2***)*:* Yellow solid, Yield = 200 mg, 61%, δ_H (400MHz, DMSO-d_6):8.98 (2H, d, *J* = 4Hz), 8.87 (2H, d, *J* = 4Hz), 8.21 (2H, d, *J* = 12 Hz), 7.79 (2H, m) 7.16 (2H, d, *J* = 12 Hz) and 3.83 (3H, s). *2-(4-chlorophenyl)-1H-imidazo[4,5-f][1,10]phenanthroline* (***L-3***)*:* Orange solid, Yield = 250 mg, 76%, δ_H (400MHz, DMSO-d_6):8.95 (2H, d, *J* = 4 Hz), 8.89 (2H, d, *J* = 8 Hz), 8.31 (2H, d, *J* = 8 Hz), 7.75 (2H, m) 7.53 (2H, t, *J* = 8 Hz).

Synthesis of Ru(II) complexes

A mixture of 0.1 mmol (56 mg) Ru_2(*para*-cymene)$_2Cl_4$ and the corresponding ligand (0.2 mmol) in 20 mL dry methanol was refluxed at 90 °C for 4 h. During the course of the reaction, the color of the solution changes from orange to brown. After that, potassium hexafluorophosphate, KPF_6 (0.2 mmol) was added and refluxed for another 1h. Then, the reaction mixture was filtered to remove the precipitate of KCl. To the filtrate, diethyl ether was added to get a precipitate of the complex. The precipitate of the complex was washed

with water (1 mL × 3), cold methanol (0.5 mL × 2), and diethyl ether (1 mL × 3) and then dried under vacuum.

C-1: Brown solid, Yield = 120 mg, 85%, δ_H (400MHz, DMSO-d_6): 9.79 (2H, d, *J* = 4Hz), 9.15 (2H, d, *J* = 8Hz) 8.19 (2H, d, *J* = 8Hz), 8.12 (2H, m), 7.64 (2H, d, *J* = 8 Hz), 6.24 (2H, d, *J* = 8 Hz), 6.04(2H, d, *J* = 8 Hz), 2.68 (1H, m), 2.29 (3H,s), 1.01 (6H, d, *J* = 8Hz). δ_C (100MHz, DMSO-d_6): 153.7, 143.4, 132.8, 130.4, 129.3, 127.0, 126.2, 86.6, 84.4, 79.3, 31.1, 22.1. ESI-MS calcd for **C-1**, $[C_{29}H_{26}ClN_4Ru]^+$ = 567.09 found 567.09

C-2: Brown solid, Yield = 115 mg, 78%, δ_H (400MHz, DMSO-d_6): 9.78 (2H, d, *J* = 4Hz), 9.26 (2H, d, *J* = 8Hz), 8.31 (2H, d, *J* = 4Hz), 8.14 (2H, m), 7.13 (2H, d, *J* = 8Hz), 6.28 (2H, d, *J* = 8Hz), 6.07 (2H, d, *J* = 4Hz), 2.56 (1H, s), 2.16(3H, s), 0.84 (6H, d, *J* = 8Hz). δ_C (100MHz, DMSO-d_6): 162.5, 154.3, 144.5, 134, 130, 127.8, 115.2, 104.3, 87.5, 84.2, 56.5, 32.3, 22.5, 19.2. ESI-MS calcd for **C-2,** $[C_{30}H_{28}ClN_4ORu]^+$ = 597.10 found 597.10.

C-3: Brown solid, Yield = 125 mg, 84%, δ_H (400MHz, DMSO-d_6): 9.79 (2H, d, *J* = 4Hz), 9.15 (2H, d, *J* = 8Hz) 8.19 (2H, d, *J* = 8Hz), 8.12 (2H, m), 7.64 (2H, d, *J* = 8 Hz), 6.24 (2H, d, *J* = 8 Hz), 6.04(2H, d, *J* = 8 Hz), 2.68 (1H, m), 1.01 (3H, s), 0.99 (3H, s); δ_C (100MHz, DMSO-d_6): 152.7, 141.4, 132.8, 131.4, 128, 127, 125.1, 85.6, 84.2, 78, 31.1, 22.1; ESI-MS calcd for **C-3,** $[C_{29}H_{25}Cl_2N_4Ru]^+$ = 601.05 found 601.05.

C-4: Orange solid, Yield = 100 mg, 84%, δ_H (400MHz, DMSO-d_6): 9.89 (2H, d, *J* = 4Hz), 8.87 (2H, d, *J* = 8Hz), 8.24 (2H, s), 8.11 (2H, m), 6.31 (2H, d, *J* = 8Hz), 6.08 (2H, d, *J* = 4Hz), 2.59 (1H, m) , 2.13 (3H, s), 0.83 (6H, d, *J* = 4 Hz). δ_C (100MHz, DMSO-d_6): 158.5, 146.7, 139.2, 132.4, 130, 128.8, 106.1, 104.3, 86.5, 84.3, 32, 22.1, 18. ESI-MS calcd for **C-4**, $[C_{22}H_{22}ClN_2Ru]^+$ = 451.05 found 451.38.

General procedure for C-3/C-5 promoted oxidation transformation of styrenes to dimethyl acetals

In a Schlenk tube, 300 mg activated molecular sieves (4Å, fine powder) were taken in 5 mL dry methanol. To it, styrene (1 mmol), catalyst (2 mol%) and TBHP (2.1 mmol) was added and the reaction mixture stirred at room temperature for 5 minutes. After that, reaction mixture was stirred at 50 ^oC for required time. The yellow/orange colour solution initially tuned into yellowish green and finally into deep green. After the completion of the reaction (*via* TLC monitoring), water was added to the reaction mixture and the product was extracted with ethylacetate (50 mL × 3), washed with brine solution (50 mL × 2) and dried over anhydrous Na_2SO_4. The yield of the reaction was calculated from gas chromatography (GC) analysis using ortho-xylene as external standard. The products of the reaction were characterized by gas chromatography mass spectroscopy (GC- MS) analysis.

General procedure for C-3/C-5 promoted oxidation transformation of C-C multiple bond to aldehydes

In a Schlenk tube, substrate (1 mmol), catalyst (2 mol%) and TBHP (2.1 mmol) was taken in 5 mL acetonitrile. The reaction mixture stirred at room temperature for 5 minutes. After that, it was stirred at 50 ^oC for required time. Initial yellow/orange colour of the solution turned yellowish green, which finally turned into deep green. After the completion of the reaction (*via* TLC monitoring), water was added to the reaction mixture and the product was extracted with ethylacetate (50 mL × 3), washed with brine solution (50 mL × 2) and dried over anhydrous Na_2SO_4. The yield of the reaction was calculated from gas chromatography (GC) analysis using ortho-xylene as external standard and ^1H NMR analysis using diphenyl methane as external standard. Some of the isolated products were characterized via $^1H/^{13}C$ NMR analysis.

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Keywords: Oxidation • Ruthenium • Dimethyl acetal • Imidazole • Release of Para-Cymene

Entry for the Table of Contents
FULL PAPER

The present work disclosed the dual role of remote 'imidazole' attached with the precatalyst [(*para*-cymene)Ru^{II}(L)Y]$^{+}$ (L = 2-(4-substituted-phenyl)-1H-imidazo[4,5-f][1,10] phenanthroline, Y = chloride/solvent) for the activation of oxidant (*tert*-butyl hydroperoxide, TBHP) and release of *para*-cymene from the precatalysts to generate active catalyst for solvent dependent selective oxidative cleavage of C-C multiple bonds to acetals/aldehydes.

*Manali Dutta, Kusum Kumar Bania, and Sanjay Pratihar**

Page No. – Page No.

Remote 'Imidazole' Based Ruthenium(II) Para-Cymene Precatalyst for Selective Oxidative cleavage of C-C multiple bond

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[21] **C-3**/**C-5** promoted oxidative transformation of styrene in dry MeOH in presence of molecular sieves must give almost negligible transformation of benzaldehyde. However, we could not able to protect the reaction from moisture under standard Schlenk line during the collection of reaction mixture at different time interval.

[22] Although the addition of $NaIO_4$ produced a color change from orange to green, but we failed to characterize the species.

[23] For initial rate kinetics, the conversion data considered for the plot was strictly maintained within the half-life of the reaction.

[24] Although, the experimental evidences suggest the presence of $(L)Ru^{IV}=O$. However, the presence of other active species such as; $(L)Ru^{III}=O$ or $(L)Ru^{V}=O$ or $(L)Ru^{VI}(O_2)$ cannot be ruled out from the reaction mixture. For such types of active species please see ref; 12 and references therein.

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[26] However, the involvement of other active species such as $(L)Ru^{VI}(O_2)$ in the reaction cannot be ruled out from these analysis. A detailed investigation would be further required to consider or nullify other possibilities.