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A remote coordination booster enhances the catalytic efficiency by accelerating the generation of an active catalyst†

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A remote $Ru^{II}(terpy)_2$ unit incorporated in conjugation with the [NHC-Ru^{II}(*para*-cymene)] catalytic site, acts as a "coordination booster" for enhancing the catalytic efficiency to achieve excellent performance in selective oxidative scission of various carbon–carbon multiple bonds to the corresponding aldehydes, ketones and diketones. Generation of an active catalyst *via* oxidative loss of *para*-cymene from the precatalyst was found to be accelerated by the "coordination booster" through the electronic effect.

Enzymes modulate their catalytic activity through the allosteric effect wherein a remote activator triggers necessary changes enabling the active site with modified reactivity.[1] Learning this concept from Nature, chemists have shown tremendous efforts for remote modification of the activity of man-made catalytic systems *via* a stimuli-triggered strategy.[2] One important prerequisite for the exercise of modifying the activity of a synthetic catalyst is the knowledge of the mode of activation of the pre-catalyst and subsequently the key steps of the catalytic reaction. For example, the activation mode of many [M(η^6-arene)][3] and [Ir^{III}Cp*]-based[4] pre-catalysts involved the initial labilization/dissociation of the arene and oxidative loss of the Cp* ligand, respectively, to generate active catalysts; and therefore an oxidative stress was utilized to enhance the catalytic activity. A very similar class of complexes, [Ru^{II}(*para*-cymene)]-based one, was well studied as a catalyst precursor in many reactions including C–H functionalisation,[5] C-heteroatom coupling[6] and transfer hydrogenation;[7] however, it is believed that the *para*-cymene ligand remained coordinated during the catalytic cycle. To the best of our knowledge, there is no report on the generation of active catalysts under oxidizing conditions *via* loss of *para*-cymene from [Ru^{II}(*para*-cymene)]-based catalyst precursors. Herein, we show that dissociative loss of *para*-cymene from [(NHC)Ru^{II}(*para*-cymene)Cl]$^+$ complexes (NHC = N-heterocyclic carbene) to generate active catalysts is the key step in the catalytic selective oxidation of olefins and alkynes to carbonyl compounds[8] and a [$Ru^{II}(terpy)_2$] unit (terpy = 2,2′:6′,2″-terpyridine) placed remotely from the catalytically active (NHC)Ru center acts as a "coordination booster" which triggers and accelerates the loss of *para*-cymene efficiently to enhance the catalytic activity. Although a remote [$Ru^{II}(terpy)_2$] unit within a catalyst backbone was previously utilized as a photo-trigger,[9] its use as an electronic-trigger is not known. Few examples are known involving the use of $B(C_6F_5)_3$ or $Al(C_6F5)_3$ as an electronic trigger through Lewis-acid binding to a metal-coordinated ligand, for accelerating polymerization and reductive elimination reactions.[10,11]

The assembled pre-catalyst, [$Ru(terpy)_2$–(NHC)Ru^{II}(*para*-cymene)Cl]$^{3+}$, **2** was designed by attaching the remote activator $Ru(terpy)_2$ through the NHC-backbone, and synthesized from its precursor complex, **1** *via* a simple procedure (for details, see ESI†) for demonstrating the proposed boosting effect. A model complex, free of any remote modification, [(NHC)Ru^{II}(*para*-cymene)Cl]$^+$, **3**[12] was utilized to compare with the activity of **2** (Fig. 1).

The ^{1}H NMR spectrum of **2** showed the absence of an NC*H*N proton in high chemical shift values (9.5–11.5 ppm) when compared with precursor **1**. The presence of four doublet peaks with the integration of one proton each in the range of 4.5–6.0 ppm, one septet peak at 2.21 ppm with the integration of one proton, and two doublet peaks with the integration of three protons each in the range of 0.84–0.98 ppm suggested the ruthenium-coordinated *para*-cymene backbone in **2**. In addition, the ^{1}H NMR spectrum of **2** also featured the NHC backbone protons with expected number and expected chemical shift values. Complex **2** showed an intense absorption band centered at 480 nm (Fig. S24, ESI†) which is the characteristic of the presence of a $Ru^{II}(terpy)_2$ unit (due to MLCT),[13] as confirmed by the presence of a similar absorption maximum at 480 nm in the case of precursor complex **1**. Similarly, the presence of the $Ru^{II}(terpy)_2$ unit in **2** was realized *via* electrochemical analysis. The reversible peak at 1.24 V *vs.* SCE

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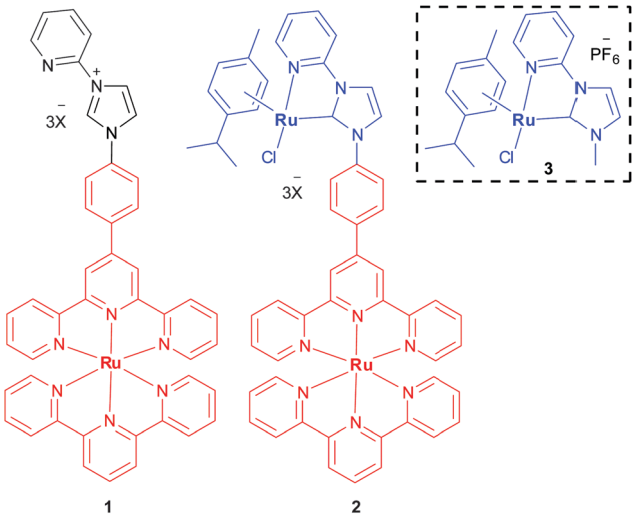


Fig. 1 Ruthenium complexes used in this study.

was confirmed to be due to the Ru^{II}/Ru^{III} couple of the $Ru(terpy)_2$ unit[13] which was present in both **2** and **1** (Fig. S25, ESI†). Most importantly, the proposed electronic effect of this remote $Ru(terpy)_2$ booster on the redox potential of the catalytic Ru center, [that is Ru^{II}(*para*-cymene) center in **2**], was evaluated by differential pulse voltammetry (Fig. 2). Interestingly, the redox potential of the Ru^{II}/Ru^{III} couple in the Ru^{II}(*para*-cymene) site in **2** was found to be shifted to more positive potential by 100 mV as compared to that in **3** [$E_{1/2}(Ru^{II}/Ru^{III})$ in **3** = 1.336 V *vs.* SCE and in **2** = 1.436 V *vs.* SCE]. This shift suggested a more electron-deficient Ru^{II}(*para*-cymene) center in the modified complex **2** than in the model unmodified complex **3**. Such electron-deficiency at the ruthenium center is supposed to promote the dissociation of *para*-cymene under oxidizing conditions due to a poor Ru→ *para*-cymene back-bonding effect.

The consequence of the above electronic effect on the oxidative activation of the Ru^{II}(*para*-cymene) pre-catalyst center was examined by ^{1}H NMR spectroscopy. Addition of 10 eq. of $NaIO_4$ to the solution containing complex **2** resulted in the complete decoordination of *para*-cymene in just 5 min (Fig. 3). Resonance peaks related to free *para*-cymene appeared at expected chemical shift values with an appropriate integration ratio (confirmed by comparing with the authentic sample). At the same time, the model unmodified complex **3** did not show

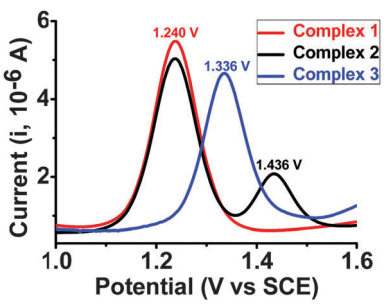


Fig. 2 Differential pulse voltammograms of complexes **1**, **2**, and **3** (for details see ESI†).

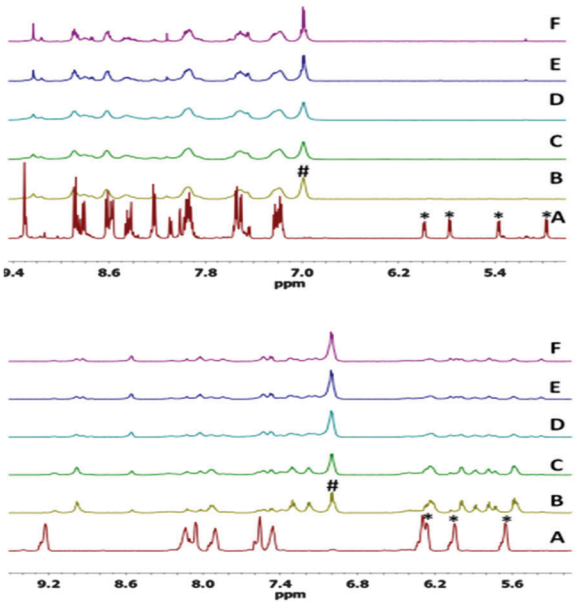
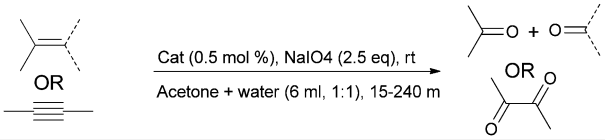


Fig. 3 ^{1}H NMR studies with complex **2** (top) and complex **3** (bottom) in the presence of 10 eq. of $NaIO_4$ (acetone-d_6 : D_2O; 3 : 2). A = only complex, B = 5 min (after addition of $NaIO_4$), C = 10 min, D = 15 min, E = 20 min, F = 30 min. * = resonance peaks related to ruthenium coordinated *para*-cymene. # = resonance peaks related to free *para*-cymene.

the complete loss of *para*-cymene under similar oxidizing conditions even after 30 min (Fig. 3).

The preliminary evidence that the bimetallic complex loses *para*-cymene extremely faster prompted us to utilize complex **2** for anticipated enhanced catalytic efficiency in the selective oxidation of alkenes and alkynes to the corresponding oxygen inserted products. The results of catalysis are summarized in Table 1, which indeed showed an augmented activity of **2** (Fig. 4). A similar activity of complex **2** observed under both normal and dark conditions suggested that the $Ru^{II}(terpy)_2$ unit did not act as a photo-trigger in our assembly (entry 2, Table 1). Complex **1** did not show any catalytic activity under similar conditions, as expected, since it did not possess any catalytic site. The unmodified complex **3** was found to be comparatively less active as compared to complex **2** when monitored in the model reactions with styrene and 4-methylstyrene as substrates under similar oxidative reaction conditions (entries 1 and 2, Table 1 and Fig. 4). The correlation between the loss of *para*-cymene and the observed catalytic activity at the Ru^{II}(*para*-cymene) center of **2** and **3**, as reflected from the above results, suggested the significance of the generation of an active catalyst to provide vacant sites for the substrate to be transformed during catalysis (vide Scheme 1). Sub-stoichiometric reactions of complex **2** with 4-methylstyrene in the presence of $NaIO_4$ (**2** : 4-methylstyrene : $NaIO_4$; 1 : 10 : 25) were carried out to get some information about the species present during the catalysis. GC analysis of the reaction mixture confirmed the formation of the product, 4-methylbenzaldehyde. At the same time, mass spectral analysis of the same reaction mixture showed a number of clusters in the mass spectrum (Fig. S38, ESI†). An intense peak at m/z = 601.5567 was assigned to the parent complex.

Table 1 Catalytic oxidation of carbon–carbon multiple bonds to carbonyl compounds[a]



#	Substrate	Product	Yield (%)/TOF (min^{-1}) 2	3	4
1	Styrene	Benzaldehyde	80/2.67, 58/1.93[b]	30/1.00	68/2.27
2	4-Methylstyrene	4-Methylbenzaldehyde	78/3.90, 55/1.83,[b] 73/3.65[c]	25/0.83	51/2.04
3	4-Chlorostyrene	4-Chlorobenzaldehyde	81/2.70	18/0.60	75/2.50
4	4-Fluorostyrene	4-Fluorobenzaldehyde	78/3.90	14/0.70	70/2.80
5	α-Methyl styrene	Acetophenone	88/0.73	42/0.35	46/0.76
6	4-Vinylanisole	4-Methoxybenzaldehyde	60/0.50	35/0.29	60/3.00
7	4-Bromostyrene	4-Bromobenzaldehyde	79/2.63	20/0.66	82/1.82
8	*trans*-Stilbene	Benzaldehyde	85/2.83	61/2.03	82/10.93
9	*cis*-Stilbene	Benzaldehyde	92/4.60	65/3.25	84/11.20
10	Allylbenzene	2-Phenylacetaldehyde	60/1.0	18/0.30	70/1.17
11	*trans*-α-Methyl stilbene	Acetophenone, benzaldehyde	91/12.13	68/9.06	85/11.33
12	Diphenylacetylene	Benzil	74/2.47	42/1.40	78/3.90
13	1-Phenyl-1-butyne	1-Phenylbutane-1,2-dione	78/3.90	40/2.00	68/3.40
14	1-Phenyl-1-propyne	1-Phenylpropane-1,2-dione	80/4.00	35/1.75	65/3.25

[a] Reaction conditions: Halide ($2Cl^-$ and Br^-) salt of **2** (0.5 mol%), starting material (0.4 mmol), acetone + water (1 : 1, 6 mL), $NaIO_4$ (1.0 mmol), room temperature. [b] PF_6 salt of **2**. [c] Under dark conditions. The yields of the products were calculated by GC analyses. TOF = mmol (product)/{mmol (cat) × time (min)}.

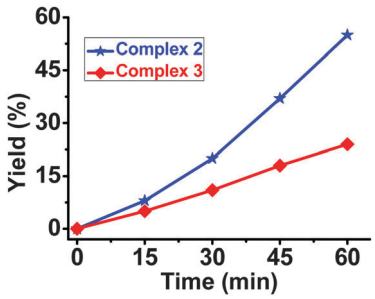
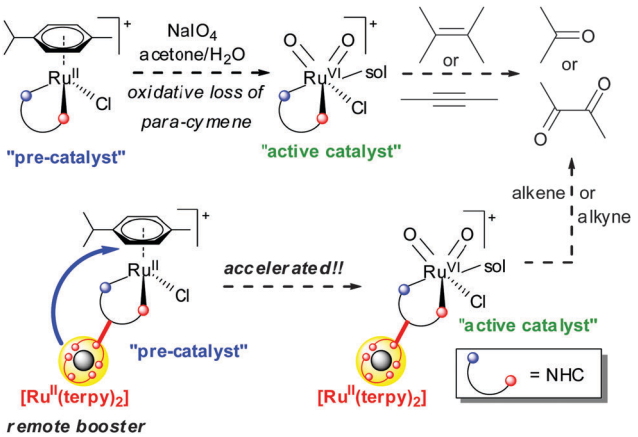


Fig. 4 Comparison of the catalytic activity of **2** and **3**.



Scheme 1 Proposed "boosting" effect of a remote $[Ru(terpy)_2]$ unit on the catalytic activity of the Ru(NHC) center.

Along with this peak, the mass spectrum also showed peaks at m/z = 296.0180 for $[C_{44}H_{31}N_9Ru^{II}Ru^{II}–H]^{3+}$, m/z = 306.6811 for $[C_{44}H_{31}N_9Ru^{II}Ru^{VI}–H + (O)_2]^{3+}$ and m/z = 339.3787 for $[C_{44}H_{31}N_9Ru^{II}Ru^{II}(CH_3COCH_3)(H_2O)_2Cl]^{3+}$ fragments. The presence of all these fragments showed that the removal of *para*-cymene and the formation of *cis*-dioxo ruthenium(VI) species are the necessary steps for this kind of transformation as depicted in Scheme 1. To check whether *para*-cymene dissociation is a key step, oxidation of 4-methylstyrene was carried out in the presence of added *para*-cymene. A decrease in the yield in the oxidation of 4-methylstyrene to the corresponding aldehyde was observed (Fig. 5). A decrease in the yield was also observed with the addition of other electron rich arenes (Fig. 5), due to the expected strong coordination of these molecules to the high-valent metal center. Electron-deficient arenes, being poor donors and efficient acceptors, were ineffective to decrease the yield; instead a slight enhancement was observed as expected. We also confirmed that *para*-cymene did not undergo any transformation under similar catalytic conditions (Scheme S4 ESI†). These studies suggested that the removal of *para*-cymene is a necessary step for the activation of

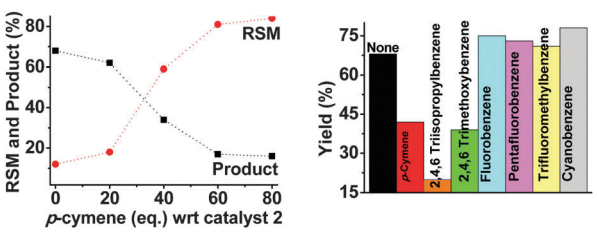
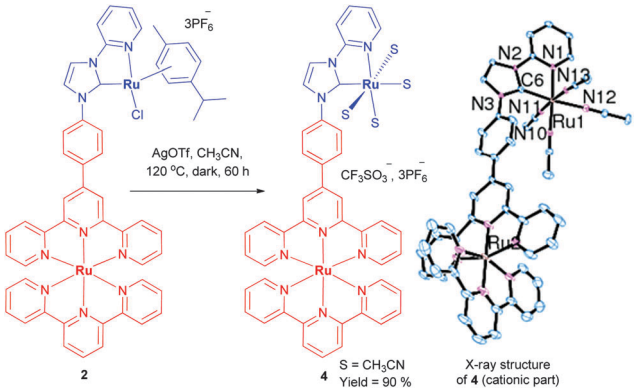


Fig. 5 Effect of added *para*-cymene (left) and other arenes (right).

the pre-catalyst and thereafter for the catalytic oxidation of carbon–carbon multiple bonds with complex **2** (or **3**).

These controlled studies encouraged us to synthesize a derivative of complex **2**, $[Ru^{II}(terpy)_2–(NHC)Ru^{II}(MeCN)_4]^{4+}$, **4**,



Scheme 2 Synthesis and the molecular structure of complex **4**.

which was devoid of *para*-cymene at the catalytic ruthenium(II) center. Complex **4** was synthesized by heating complex **2** with silver triflate (1.2 eq.) in acetonitrile under reflux conditions for 60 h (Scheme 2). Complex **4** was fully characterized by NMR spectroscopic methods and X-ray diffraction analysis. ^{1}H NMR showed the absence resonance peaks related to the *para*-cymene moiety whereas the resonance peaks related to the NHC backbone were found to be intact with the appropriate integration ratio at the expected chemical shift values (see ESI† for details). After successful synthesis of complex **4**, we checked its intermediacy in the catalytic oxidation reactions. Interestingly, complex **4** showed almost equal activity as compared to complex **2** (Table 1), which again suggested that activation of the pre-catalyst was a key step during catalytic reactions.

In conclusion, we demonstrated that the loss of *para*-cymene is a necessary step to generate the active catalyst, starting from [L_nRu^{II}(*para*-cymene)]-based catalyst precursors for the oxidative conversion of olefins and alkynes to oxygenated products. A simple coordination complex unit, such as Ru^{II}(terpy)$_2$, remotely attached by a phenyl linker of the ligand backbone to the [Ru^{II}(*para*-cymene)] catalytic site, was found to be highly effective in accelerating the loss of *para*-cymene to generate the active catalyst under oxidizing conditions, and thereby in boosting the overall catalytic activity. This strategy of using a "remote booster" to tune the catalytic activity seems to be general in other reactions as well. A detailed mechanistic study is underway in our laboratory to generalize the concept.

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