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# Synthesis and characterization of chromium(III) complexes derived from tridentate ligands: Generation of phenoxyl radical and catalytic oxidation of olefins

## Kaushik Ghosh \*, Pramod Kumar, Isha Goyal

Department of Chemistry, Indian Institute of Technology, Roorkee, Roorkee-247667, Uttarakhand, India

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### ABSTRACT

The mononuclear chromium complexes  $[Cr(Phimp)_2](ClO_4)$  (1),  $[Cr(N-Phimp)_2](ClO_4)$  (2), and  $[Cr(Me-Phimp)_2](ClO_4)$  (3) (where PhimpH = (2-((2-phenyl-2-(pyridin-2-yl)hydrazono)methyl)phenol), N–PhimpH = (2-((2-phenyl-2-(pyridin-2-yl)hydrazono)methyl)phenol) where H stands for dissociable proton) were synthesized and characterized spectro-scopically. Electrochemical studies were investigated for the stabilization of Cr(III) complexes and electrochemically generation of phenoxyl radical complexes. Phenoxyl radical complexes were ealso generated by ceric ammonium nitrate (CAN) and characterized by UV–visible spectra. The complexes were evaluated for their activity as catalysts for the epoxidation of olefins. The chromium complexes catalyzed epoxidation of olefins, viz. styrene, *cis*-cyclooctene and *trans*-stilbene with hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) as terminal oxidant, to give corresponding epoxides and oxidative products at ambient temperature.

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Catalysis is known to play a key role in modern chemical technologies. Nowadays it is generally agreed that the key role in catalytic reactions is played by intermediate chemical interaction of reactive molecules with definite functional groups (active sites) of homogeneous, heterogeneous or biological catalysts (enzymes) [1]. Asymmetric oxidation of hydrocarbons under mild and environmental friendly conditions is an important research field, since industrial processes, especially in the pharmaceutical industry, for synthesizing synthons from readily available olefins [2]. However, selective oxidation of alkenes under mild conditions is a difficult task due to their chemical inertness. In this regard, use of coordination complexes of transition metals as catalysts is of abiding importance as it offers an effective possibility for synthesis of pure compounds [3.4]. Although transition metal Schiff base complexes of bear resemblance to enzymatic catalysts and are eye-catching since they provide advantages due to their relatively easy synthesis and versatile coordination structures [5–9]. In this regard, first row transition metals namely vanadium, chromium, iron and copper complexes are preferred because of their versatile coordination chemistry in different oxidation states [10]. Moreover, these transition metal-catalyzed oxidation reactions are chemical models for the monooxygenase, cytochrome P-450 enzymes [11,12].

Hence chromium is an important metal for catalytic studies because chromium exhibited variable oxidation states, spin states, coordination numbers and redox properties in different chromium complexes [13]. However, chromium(III) is an essential nutrient that is involved in the glucose tolerance factor (GTF) in maintenance of normal carbohydrate

E-mail address: ghoshfcy@iitr.ernet.in (K. Ghosh).

and lipid metabolism [14,15]. Schiff base complexes of chromium(III) such as N,N'-ethylene bis(salicylidene-iminate)diaquochromium(III) chloride, [Cr(salen)(H<sub>2</sub>O<sub>)2</sub>]Cl were used as a new model of GTF [16,17]. Chromium–salen complexes are well-known catalysts, both in heterogeneous and homogeneous systems. Other applications of theses complexes are reported, such as, the stereoselective alkene epoxidations [18,19] and alcohol oxidations [20]. There is a wide range of chromium complexes that are known to be capable of catalyzing asymmetric oxidation of unfunctionalized olefins as well as other organic molecules in presence of terminal oxidants, reports on the use of chromium complexes are sparse in the literature [3,4,21-24].

Herein we report the synthesis and characterization of chromium complexes  $[Cr(Phimp)_2](ClO_4)$  (1),  $[Cr(N-Phimp)_2](ClO_4)$  (2), and  $[Cr(Me-Phimp)_2](ClO_4)$  (3) derived from tridentate ligands PhimpH, N-PhimpH and Me-PhimpH respectively having NNO donors (Scheme 1). Electrochemical studies were also investigated for the stabilization of



Scheme 1. Schematic drawing of tridentate Schiff's base ligands and their abbreviations.

<sup>\*</sup> Corresponding author. Fax: +91 1332 273560.

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Scheme 2. Schematic synthetic procedure of complexes 1-3.

Cr(III) oxidation states. Phenoxyl radical complexes are important intermediates in the catalytic oxidation of primary alcohol to aldehyde and aldehyde to carboxylic acid by galactose oxidase (GO) [25,26] and glyoxal oxidase [27] enzymes respectively. Due to the presence of phenolato function in the ligand frame we have explored the generation of phenoxyl radical complexes. The catalytic oxidation chemistry of olefins by the chromium complexes was examined.

The tridentate ligands PhimpH, N-PhimpH and Me-PhimpH were synthesized by the reported procedure [28]. Complexes were synthesized by the stirring of ligands with chromium(III) salt  $CrCl_3 \cdot 6H_2O$  in ethanol for 6 h. Bis complexes were obtained even though reaction was started by 1:1 ratio of ligand and salts or 2:1 ratio. Details of the syntheses are summarized in Scheme 2.

The characteristic band of azomethine ( $\nu_{-HC=N}$ ) group in IR spectra of the ligands were observed near 1607–1611 cm<sup>-1</sup> [29]. Coordination of the nitrogen to the metal center reduced the electron density in the azomethine moiety and thus lowered the  $(\nu_{-HC=N})$  frequency. Decrease in stretching frequencies for  $(v_{-HC=N})$  in complexes **1**, **2** and **3** clearly indicated the ligation of azomethine nitrogen (-HC==N-) to metal center [30,31]. The bands near 1090  $\text{cm}^{-1}$  together with a band at 623  $\text{cm}^{-1}$ were found in all chromium(III) complexes 1-3 which showed the presence of perchlorate ion. The lack of splitting of these two bands suggested the presence of non-coordinated perchlorate ion to the metal center [30,31]. A high intensity band near 1300 cm<sup>-1</sup> in the Schiff's bases can be assigned as phenol C–O ( $\nu_{\text{C-OPh}}$ ) stretching frequency. Shift of  $\nu_{\text{C-O}}$ to higher frequency supported the deprotonation of phenolate function and the formation of metal oxygen bond [32]. It was further supported by disappearance of the broad  $v_{O-H}$  band in IR spectra of all metal complexes. The absorption spectra of complexes were recorded in acetonitrile at room temperature (Fig. S1). The transition band near 235-245 nm was designated as  $\pi$ - $\pi$ <sup>\*</sup> transition in ligand (Table 1). The band near 420 nm for complexes 1, 2 and 3 was assigned as ligand-to-metal charge transfer

#### Table 1

Electronic spectra and cyclic voltammetric redox potentials of complexes 1–3 and their phenoxyl radical species.

Complex <sup>a</sup>	$\lambda_{max}/nm~(\epsilon/M^{-1}~cm^{-1})]^b$	$\begin{array}{l} [Cr(III)/Cr(II)]^{c}E_{1/2}{}^{d}\!/\!V\\ (\Delta E^{e}\!/\!V) \end{array}$
1	427(8700), 338 (18,200), 302 (21,400), 244 (37,900)	0.123(0.064)
[1] <sup>•+</sup>	601(420), 551(720), 422(8800), 336(18,280), 300(22,600), 246(36,800)	-
2	484 (4300), 445 (7900), 426 (7400), 350 (16,600), 257 (32,400), 244 (34,600)	0.92(0.112)
[2] <b>•</b> +	805(600), 672(360), 444(12,020), 424(11,940), 349(24,040)	1.20(0.093)
3	409 (7300), 354 (10,300), 308 (15,800), 235 (42,300)	-
[3] <b>•</b> +	740(100), 560(420), 399(6,100), 311(14,140), 268(23,960)	-

<sup>a</sup> All complexes in parentheses are radical species.

<sup>c</sup> Conditions: solvent dichloromethane; supporting electrolyte, TBAP (0.1 M); working electrode glassy carbon; reference electrode, Ag/AgCl; scan rate 0.1 V/s, concentration ~ $10^{-3}$ M at 298 K.

<sup>d</sup>  $E_{1/2} = 0.5(E_{pa} + E_{pc}).$ 

<sup>e</sup>  $\Delta E = (E_{pa} - E_{pc})$  where  $E_{pa}$ ,  $E_{pc}$  are anodic and cathodic peak potential.

(LMCT) transition of phenolato oxygen to chromium(III) [33]. However, in addition **2** possesses one absorption band ~450 nm which was also of charge transfer type. The molar conductivity measurements in dimethylformamide at *ca*.10<sup>-3</sup> M determined at 298 K for complexes were found to be 48–59  $\Omega^{-1}$ cm<sup>2</sup>mol<sup>-1</sup>. These values confirmed the uni-univalent (1:1) electrolyte behavior in solution [34]. For complexes, magnetic moments were measured at room temperature (300 K) (Table S1). Complexes were paramagnetic in nature and stabilized the 3d<sup>3</sup> system [35].

Electrospray ionization of methanolic solution of  $[Cr(Phimp)_2](ClO_4)$ (1),  $[Cr(N-Phimp)_2](ClO_4)$  (2) showed intense signals corresponding to  $[Cr(Phimp)_2]^+$  (m/z = 628) and  $Cr(N-Phimp)_2]^+$ (m/z = 728) respectively after losing the  $ClO_4^-$  appeared as the leading cationic species. Representative ESI-MS spectra for  $[Cr(Phimp)_2](ClO_4)$  (1),  $[Cr(N-Phimp)_2](ClO_4)$  (2) are presented in Figs. S2 and S3.

The redox potentials of complexes **1–3** are described in Table 1 and representative voltammograms are shown in Fig. 1 and Figs. S4–S5. The neutral uncomplexed ligands did not show any cyclic voltammogram over the range from 0.0 to 1.1 V; hence all the curves were attributed to the redox activity of our complexes. Complexes **1** and **2** showed quasi-reversible peaks and from the Table 1, it has been shown that one electron is involved in this redox process. The wave detected at 0.12–0.92 V vs. Ag<sup>+</sup>/AgCl has been considered as one-electron-redox process attributed to the reduction of  $[Cr^{III}L_2]^+$  to  $[Cr^{II}L_2]$  (where L= Phimp<sup>-</sup>, N-Phimp<sup>-</sup>) indicating Cr(III)/Cr(II) redox couple. On the other hand, complex **3** showed irreversible peak at -1.3 V (Fig. S5). We want to mention here that for complex **2**, we found small peaks at ~–0.75 V and +0.5 V during our scan from -1.4 V to +1.4 V vs. Ag/AgCl. If we



**Fig. 1.** Cyclic voltammograms of a  $10^{-3}$  M solution of complex **2**: using working electrode: glassy-carbon, reference electrode: Ag<sup>+</sup>/AgCl; auxiliary electrode: platinum wire, scan rate 0.1 V/s. Inset: Cyclic voltammograms at100–500 mV/s scan rates.

<sup>&</sup>lt;sup>b</sup> Solvent: acetonitrile.



**Fig. 2.** UV–visible spectra of generated phenoxyl radical complex of **2** (50  $\mu$ M) in acetonitrile by CAN (50–400  $\mu$ M) at 0 °C. Inset: decomposition of generated phenoxyl radical complex of **2** monitored by 805 nm at 0 °C.

measure the cyclic voltammogram in the range of -1.3 to 0 V and 0 to -1.35 V, we did not get those peaks (Fig. S6). So these small peaks are not due to impurities. These may be due to some species generated during the scan from -1.4 V to +1.4 V vs. Ag/AgCl. Interestingly, cyclic voltammogram of 2 afforded a reversible peak at ~1.2 V due to ligand centered oxidation (Fig. 1). We measured the cyclic voltammograms for generation of phenoxyl radical with different scan rates of 100-500 mV/s (Inset of Fig. 1). Repeated scans as well as different scan rates clearly expressed the stability and generation of a phenoxyl radical complex of **2** [36,37]. The  $E_{1/2}$  and  $\Delta E$ values were found to be + 1.20 V and 0.093 V respectively vs. Ag<sup>+</sup>/ AgCl and was also described as phenoxyl radical redox couple [36]. Recently, we have reported copper complex [Cu(<sup>t</sup>BuPhimp)(Cl)] derived from tridentate ligand <sup>t</sup>BuPhimpH, showed a guasi-reversible redox couple near + 1.0 V, which clearly indicated ligand-centered oxidation, i.e., the generation of a phenoxyl radical [37].

Generation of phenoxyl radical complexes through the ligand centered oxidation of phenolato chromium(III) complexes 1-3 by addition of two equivalents of the CAN afforded the corresponding phenoxyl radical complexes at 0 °C. The formation of the phenoxyl radical complexes of 1-3 showed dark reddish brown color and have been confirmed by the characteristic peaks in UV-visible spectra for phenoxyl radical complexes [36-39]. Upon addition of CAN, the LMCT band for the complex 2 near 484 nm readily disappeared together with the concomitant appearance of the new bands at 805(600) nm, 672(360) nm which indicated the formation of phenoxyl radical complex (Fig. 2). A similar absorption spectrum (601(420) nm, 551(720) nm, 422(8,800) nm) of 1 and 740(100) nm, 560(420) nm, 399(6,100) nm) of 3 were also obtained during the oxidation in the same procedure given as above (Figs. S7 and S8). Reddish brown color and characteristics peaks in UV-visible spectra (Fig. 2, Figs. S7 and S8 and Table 1) showed the generation of phenoxyl radical complexes of 1-3.

During our studies on the synthesis of phenoxyl radical complexes, we found that the radicals were unstable and gradually decomposed within a very short time (2-5 min) because of the participation of oxygen or solvent for the regeneration of the precursor complex [28,39,40]. The decomposition rate of radical complexes of 1-3 was monitored by a time dependent study at  $\lambda$  values of 601 nm (Fig. S9), 805 nm (inset of Fig. 2) and 740 nm (Fig. S10). It is reported in the literature that stability of the phenoxyl radical complexes increases with the increase in  $\lambda$  value of the lowest energy transition [39,40], hence, the stability order of the phenoxyl radical complexes was 2 > 3 > 1. The higher stability of phenoxyl radical complex of 2 may be due to engagement of ortho and para position of phenolato function in naphthol ring. We have generated and characterized the phenoxyl radical complexes, however the catalytic activity of these radical complexes (conversion of primary alcohol to aldehydes) are under progress.

In the present investigation, the heating rates were suitably controlled at 10 °C min<sup>-1</sup> under nitrogen atmosphere and the weight loss was measured from ambient temperature up to ~800 °C. The results of the thermogravimetric analysis of the complexes are not very conclusive in terms of the loss of specific group(s) on increasing the temperature under nitrogen atmosphere. However, it is clear from the thermogravimetric profiles that these complexes are stable up to 260 °C (Table S2). Complex **1** loses weight in three steps. A weight



Scheme 3. Various oxidation products of (A) styrene, (B) cis- cyclooctene and (C) trans-stilbene.



**Fig. 3.** Bar diagram showing total conversion of (A) styrene, (B) *cis*-cyclooctene and (C) *trans*-stilbene and selectivity of their various products in 6 h respectively.

loss of 31.5% was observed up to 310 °C in the first two overlapping steps followed by a weight loss of 68.3% in a sharp and narrow temperature range of 310–420 °C. The total weight loss of complex **1** is 99.8%. Similarly, complexes **2** and **3** loss the maximum weight of 63.6% and 45.7% in the third, a sharp narrow step (between 360 °C and 440 °C) and in the second step (between 257 and 267 °C) respectively. Finally, the remaining loss of 4.6% for **2** and 12.4% for **3** is in the range of 400–770 °C. The initial decomposition and inflection temperatures have been used as an indication on the thermal stability of complexes [41].

Table 2

Catalyst	Time (h)	Conversion%	Produ	Product selectivity%				
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			SO	BzAc	BzAc <sup>a</sup>	PhED <sup>e</sup>	PhAc	
1	1	34. 5	15.1	80.7	-	4.2	-	-
	2	38.1	3.1	91.9	-	5.0	-	-
	6	96. 5	2.7	47.3	28.6	4.4	16.5	192.5
2	1	29.4	1.7	95.0	-	3.2	-	-
	2	47.0	2.1	93.2	-	4.6	-	-
	6	86.0	3.6	57.8	25.4	3.6	9.6	170.0
3	1	39.6	1.2	90.5	2.6	-	5.7	-
	2	50.4	1.4	88.5	2.5	1.0	6.6	-
	3	92.7	2.2	41.5	36.7	9.7	10.0	192.3

<sup>a</sup>Reaction conditions: styrene (0.208 g, 2.0 mmol), catalyst (0.01 mmol), oxidant (0.453 g, 4.0 mmol), temperature (90 °C) and acetonitrile (2.0 mL).<sup>b</sup>Styrene oxide, <sup>c</sup>Benzaldehyde, <sup>d</sup>Benzoic acid, <sup>e</sup>1-Phenylethane-1,2-diol, <sup>f</sup>Phenylacetaldehyde.

Oxidation of styrene has been investigated using homogeneous as well as heterogeneous catalysts and the major oxidation products generally obtained are styreneoxide, benzaldehyde, benzoic acid, phenyl acetaldehyde and 1-phenylethane-1,2-diol [12,18,42]. We have found that Cr(III) complexes 1, 2 and 3 satisfactorily catalyze the oxidation of styrene using H<sub>2</sub>O<sub>2</sub> as oxidant and gives styreneoxide, benzaldehyde, 1-phenylethane-1,2-diol and benzoic acid along with some unidentified products in homogeneous conditions (Scheme 3A) [12,43]. In order to get the maximum oxidation of styrene, effect of time on the oxidation of styrene reaction has been studied in detail. Carrying out this reaction in 2.0 mL acetonitrile at 90 °C with 30% aqueous H<sub>2</sub>O<sub>2</sub> under these reaction conditions (i.e. 1:2, substrate to oxidant ratio) gave 80-90% conversion after 6 h but the recovery of the catalyst from the reaction mixture became very difficult due to partial decomposition as well as blending of the complexes with solvent. Thus, under the above reaction conditions (i.e. styrene (0.208 g, 2.0 mmol), catalyst (0.01 mmol) and 30% aqueous H<sub>2</sub>O<sub>2</sub> (0.453 g, 4.0 mmol), acetonitrile (2.0 mL), temperature (90 °C) and time (6 h)), catalytic activity of all the three complexes 1, 2 and 3 was analyzed (Fig. 3A).

The percent conversion of styrene follows the order: 96. 5%  $[Cr(Phimp)_2](ClO_4) > 92.7\%$   $[Cr(Me-Phimp)_2](ClO_4) > 86.0\%$   $[Cr(N-Phimp)_2](ClO_4)$ , where formations of styreneoxide are 2.7, 2.2 and 3.6%, respectively. The oxidation of styrene after 6 h of the reaction time is illustrated in Table 2. Thus, turns over number (TON: moles of substrate converted per mole of metal in the solid catalyst) of the three catalysts are ~192.2 (for 1 and 3) and 170.0 (for 2). However, in all cases, the selectivity of various products follows the order: benzaldehyde > benzoic acid > Phenylacetaldehyde > 1-phenylethane- 1,2-diol > styreneoxide. The highest formation of benzaldehyde is probably due to a nucleophilic attack of  $H_2O_2$  to styreneoxide. Benzaldehyde formation may also be facilitated by direct oxidative cleavage of the styrene side chain double bond via radical mechanism. Other products, e.g. benzoic acid formation

Table 🕻	3
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Catalyst <sup>a</sup>	Time (h)	Conversion%	Product selectivity%		TON
			EC <sup>b</sup>	Others	
1	1	5.7	100	-	-
	2	56.8	92.7	7.3	-
	6	68.7	90.4	9.6	137.0
2	1	34.4	92.1	7.9	-
	2	74.5	86.9	13.1	-
	6	91.8	76.4	23.5	186.3
3	1	40.8	88.6	11.4	-
	2	58.0	85.4	14.6	-
	3	95.0	82.4	17.6	188.1

 <sup>a</sup> Reaction conditions: *cis*-cyclooctene (0.22 g, 2.0 mmol), catalyst (0.01 mmol), oxidant (0.453 g, 4.0 mmol), temperature (90 °C) and acetonitrile (2 mL).
<sup>b</sup> Epoxycyclooctane. through benzaldehyde is rather slow in all reactions. Water present in  $H_2O_2$  as well as formed during the reaction if any, is probably responsible for partial hydrolysis of styreneoxide to 1-phenylethane-1,2-diol.

Oxidation of *cis*-cyclooctene catalysed by complexes **1**, **2** and **3** gave epoxycyclooctane (Scheme 3B) [44] along with some unidentified products. Catalytic activity of all the three complexes **1**, **2** and **3** was analyzed at reaction conditions (i.e. *cis*-cyclooctene (0.220 g, 2.0 mmol), catalyst (0.01 mmol) and 30% aqueous  $H_2O_2$  (0.453 g, 4.0 mmol), acetonitrile (2.0 mL), temperature (90 °C) and time (6 h)), (Fig. 3B). As 90 °C was found an ideal temperature to run the homogeneous catalytic reaction, achieve the maximum oxidation of *cis*-cyclooctene using complexes **1**, **2** and **3** as a representative catalyst. The oxidation of *cis*-cyclooctene after 6 h of the reaction time is illustrated in Table 3.

The maximum percent conversion of *cis*-Cyclooctene is in the order of 95.0% for  $[Cr(Me-Phimp)_2](ClO_4) > 91.8\%$  for  $[Cr(N-Phimp)_2](ClO_4) > 68.7\%$  for  $[Cr(Phimp)_2](ClO_4)$  where formations of epoxycyclooctane are 82.4, 76.4 and 90.4\%, respectively. Thus, turns over number of the three catalysts are ~188.1 (for **2**and **3**) and 137.0 (for **1**). However, in all cases, the selectivity of epoxycyclooctane is appreciable.

Complexes were also tested for the oxidation of *trans*-stilbene where *trans*-stilbeneoxide, benzaldehyde, benzoic acid and 1,2-diphenylethanedione (benzil) were obtained as major oxidation products (Scheme 3C) [45]. All reactions were carried out by the above procedure which followed in the oxidation of styrene and cis-cyclooctene. Complex complexes **1**, **2** and **3** were used as a representative catalyst.

Results presented in Table 4 shows that time of reaction plays an important role in that increasing the oxidation of *trans*-stilbene. However, the selectivity of epoxide increases from ~0.4 to 23%. A considerably lower formation of *trans*-stilbeneoxide is probably due to further reaction of *trans*-stilbeneoxide with  $H_2O_2$  to give benzyl which in turn converted into benzaldehyde due to hydrolysis. The percentage conversion of all three catalysts along with the selectivity of oxidation products are presented as bar diagrams in Fig. 3C. Thus, turns over number of the three catalysts are ~127.0 (for **1** and **2**) and 142.0 (for **3**). However, unidentified products are further oxidation products of benzil as indicated by GCMS, but these are only in trace amounts and in the frame of the present study, no efforts were undertaken to separate them.

A new family of mononuclear chromium complexes derived from tridentate ligands have been synthesized and characterized. Investigations of UV–visible, IR spectral studies and magnetic moment data confirmed the formation of this family of complexes **1–3**. The ligands stabilized the Cr(III) complexes which were found to paramagnetic in nature. The complexes **1, 2** and **3** described in this report showed a good oxidation catalytic activity comparable to that of a large number

Table 4

Effect of time on the oxidation of trans-stilbene and the product selectivity.

Catalyst <sup>a</sup>	Time (h)	Conversion %	Product selectivity %				TON	
			TSO <sup>b</sup>	Bzlc	BzA <sup>d</sup>	BzAc <sup>e</sup>	Others	
1	1	14.6	0.4	12.8	83.7	-	3.1	-
	2	15.3	13.0	11.8	56.2	10.7	8.3	-
	6	64.0	22.9	3.9	33.3	36.2	3.8	127.6
2	1	19.5	2.6	8.9	78.7	-	9.8	-
	2	40.7	3.7	4.0	88.3	1.5	2.5	-
	6	62.9	19.0	3.4	48.7	26.8	2.1	124.0
3	1	16.2	2.7	9.5	81.0	1.6	5.3	-
	2	34.8	8.5	7.6	75.1	3.3	5.6	-
	3	71.3	17.0	3.3	58.3	18.2	3.2	141.8

<sup>a</sup> Reaction conditions: *trans*-stilbene (0.364 g, 2.0 mmol), catalyst (0.01 mmol), oxidant (0.453 g, 4.0 mmol), temperature (90 °C) and acetonitrile (2 ml).

<sup>b</sup> trans-stilbene oxide.

<sup>c</sup> Benzil.

<sup>d</sup> Benzaldehyde,

<sup>e</sup> Benzoic acid.

of Cr(III) complexes already reported in the literature. The results of the catalytic studies revealed that oxidation of various unfunctionalized alkenes is achievable in the presence of either **1**, **2** or **3** using with 30%  $H_2O_2$  as a precursor oxidant, though **2** is comparatively less efficient. We examined the ligand centered oxidation of complexes **1–3** in relevance with the active site modeling of GO and phenoxyl radical complexes were generated in solution at 0 °C.

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#### **Appendix A. Supplementary material**

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.inoche.2012.07.028.

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