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Synthesis, characterization and reactivity of a novel ruthenium(II) complex containing polypyridyl ligand

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Abstract

The $[Ru^{II}(trpy)(pic)(H_2O)]^+$ (**1**) was synthesized and characterized by analytical, spectral (UV–Vis and IR), molar conductivity, magnetic moment and electrochemical studies. Complex **1** catalyzes the epoxidation of styrene and stilbenes in presence of *tert*-butyl hydroperoxide (*t*-BuOOH) in dichloromethane at room temperature. No epoxide formation was observed in presence of the radical trapping agent (benzoquinone). A mechanism involving formation of [Ru–O(*t*-Bu)–O]˙ type of radicaloid intermediate as an active intermediate responsible for epoxide formation is proposed for the catalytic epoxidation process.

Keywords: Ruthenium(II)-complex; Ruthenium(IV)-complex; Terpyridine ligand; *t*-BuOOH; Alkene epoxidation

1. Introduction

Over the past two decades it has been shown that the polypyridyl complexes of ruthenium are of great significance as they are coordinatively stable both in higher and lower oxidation states, and a variety of polypyridyl complexes of ruthenium are reportedly known to be effective stoichiometric and/or catalytic reagents toward oxidation of a variety organic and inorganic substrates. In this regard ruthenium-oxo-polypyridyl complexes such as $[Ru(bipy)_2(py)(O)]^{2+}$ (biy = 2,2′-bipyridine) [1] and $[Ru^{IV}(trpy)(bipy)(O)]^{2+}$ (tpy = 2,2′,6′,2″-terpyridine) [2] are reportedly known to be a very powerful oxidants toward oxidation of various organic substrates. However, catalytic application of $[Ru^{II}(tpy)(XY)(H_2O)]$ type of complexes toward hydrocarbon oxidation using a terminal oxidant has not been reported till date. Recently, we have been engaged in developing [Ru(TDL)(XY)(H_2O)] type of ruthenium(III) catalyst complexes (where TDL = tridentate ligands; XY = bidentate ligands) that exhibit selectivity toward oxo-functionalization of saturated and unsaturated hydrocarbons [3]. The use of mixed-ligand complexes of ruthenium of the type $[Ru^{III}(TDL)(XY)(H_2O)]$ are particularly intriguing in view of exploiting a combined effects with regards to the metal redox chemistry and geometry. Incorporation of nearly 'flat' TDL in the metal complexes could afford a near planar geometry for the catalytic species for which side-on-approach for the organic substrate would be easier stereochemically. Moreover, TDL's provide sites that can undergo stereogenic as well as chiral substitution, thus rendering promising chiral controlling shapes for asymmetric catalysis [3c,3d]. Secondly, the electrophilicity of the ruthenium center could be tuned by changing the ancillary ligand (XY). The present investigation is undertaken to examine the catalytic properties of $[Ru^{II}(tpy)(XY)(H_2O)]$ type of complexes toward olefin epoxidation using a terminal oxidant. We wish to report herein, the synthesis and characterization of a new $[Ru^{II}(tpy)(pic)(H_2O)]^+$ ($pic^- =$ picolinate) complex and its catalytic application, first instance of any $[Ru^{II}(tpy)(XY)(H_2O)]$ complex, toward epoxidation of various alkenes (viz. styrene and substituted styrenes, stilbenes, cyclohexene, 1,2-dihydronaphthalene) in presence of *t*-BuOOH as a terminal

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oxidant under ambient conditions. The use of *t*-BuOOH is of significance in regard to its by-product, environmentally friendliness and price.

2. Experimental

2.1. Materials

The starting compound $[Ru(tpy)Cl_3]\cdot 2H_2O$ was prepared by following the literature procedure [4] and characterized by elemental analysis and spectral data which were in agreement with data reported in the literature [4]. $[Ru^{II}(trpy)(pic)H_2O]ClO_4$ (**1**) was synthesized by adopting the procedure reported for $[Ru^{II}(trpy)(bipy)H_2O]ClO_4$ [5]. All other chemicals used were of AR grade and doubly distilled H_2O was used to prepare all solutions.

2.2. Synthesis of $[Ru^{II}(trpy)(pic)H_2O]ClO_4$ (1)

To a solution of $[Ru(tpy)Cl_3]\cdot 2H_2O$ (442.5 mg, 1 mmol) in water–ethanol mixture (40 ml, 75:25) containing LiCl (0.25 g, 6 mmol) and triethylamine (0.25 ml) was added picolinic acid (123.1 mg, 1 mmol), and the resultant mixture was refluxed for 4 h and filtered hot. The filtrate was cooled and the volume was reduced in rotary evaporator. A dark brown precipitate so obtained was collected on a frit and washed with chilled 3 M HCl followed by washing with acetone and finally by ether. The product [Ru(trpy)-(pic)Cl] so obtained was treated with $AgClO_4$ to obtain the desired aquo-product, $[Ru(trpy)(pic)H_2O]ClO_4$. To a hot solution of $[Ru(trpy)(pic)Cl]\cdot 3H_2O$ (1 mmol, 550.5 mg) was added $AgClO_4$ (1 mmol, 225.3 mg) and the reaction mixture was heated for 15 min. AgCl produced was filtered off and the volume of the filtrate was reduced in rotary evaporator. A brown mass was obtained which was washed with a minimum amount of cold water and dried in air. Yield. (65%). *Anal.* Calc. for $C_{21}H_{17}N_4O_7RuCl$: Calc. C, 43.9; H, 2.96; N, 9.76. Found. C, 44.2; H, 3.1; N, 9.5%. Λ_M ($\Omega^{-1}\,M^{-1}\,cm^2$) in $H_2O = 86$. $m/z = 473.98$. UV–Vis in H_2O: λ_{max} (ε_{max}): 495 (5234), 361s (5800), 316 (20 746), 284 (18 000), 268 (20 200); UV–Vis in CH_3CN: λ_{max} (ε_{max}): 540 (3600), 380 (5250), 316 (12 700), 240 (16 000); IR: ν_{COO^-} 1626 cm^{-1}, $\nu_{C=N}$ 1595 cm^{-1}. ^1H NMR (in CD_3CN, δ ppm): 8.54 (t, 2H, $J = 7.3$, H3′), 8.29 (t, 3H, $J = 7.8$, H3 + a), 8.05 (t, 1H, $J = 8.0$, H4′), 7.92 (td, 2H, $J_1 = 7.7$, $J_2 = 1.3$, H4), 7.61 (d, $J = 6.7$, Hb), 7.26 (d, 2H, $J = 5.8$, Hc), 6.92 (d, $J = 5.7$, Hd).

2.3. Instrumentation

The UV–Vis electronic absorption spectra were obtained on a Perkin–Elmer (Model Lambda 35) spectrophotometer. IR spectra were collected on a Perkin–Elmer (Model 783) spectrometer using KBr pellets. NMR studies were performed on a Bruker 300AC NMR spectrometer. Cyclic voltammetric experiments were conducted in a glass cell equipped with a glassy carbon working electrode, platinum-wire auxiliary electrode and standard calomel electrode (SCE) as reference electrode. A CH Electrochemical Instruments (CHI-660B) was used for this purpose. Coulometric experiments were performed using a platinum gauge working electrode. A sample of **1** (5 mg) dissolved in 25 ml of an aqueous solution of $NaClO_4$ (0.2 M) was used for constant potential electrolysis. Electrolysis of the bulk solution was carried out at pH 6.7. The values of '*n*' estimated from the coulomb readings were found to lie in the range 0.95–0.98. The oxidized solution was suitably diluted for spectrophotometric measurements. Magnetic susceptibility was measured by using a PAR-155 vibrating sample magnetometer. A Perkin–Elmer 240C elemental analyzer was used to collect microanalytical (C,H,N) data.

2.4. Kinetic studies

The kinetics of the reaction of **1** with terminal oxidant *t*-BuOOH was studied spectrophotometrically under pseudo-first order condition of excess oxidant (10–40 times) at 500 nm where appreciable spectral changes exist. The solution temperature was maintained to within ±0.1 °C using a circulating water bath (JEIO TECH RW-1025G). The pH of the solutions was measured with a Mettler Delta 350 pH meter. Phosphate buffer was used to maintain the pH at 6.2 during the kinetic studies.

2.5. Procedure of catalytic studies

In a typical experiment 0.01 mmol of the catalyst complex (**1**), 1.0 mmol of 70% aqueous *t*-BuOOH oxidant and 1.0 mmol of substrate in 5 ml of CH_2Cl_2 were rapidly magnetically stirred at room temperature (25 °C). For radical trapping experiments 1.0 mmol of benzoquinone (used as radical trapping agent) was added to the above catalytic system. At the end of the reaction an internal standard (decane) was added and an aliquot was taken for GC analysis. GC analysis was performed with a Carlo Erba GC 8000^{Top} series on Tenax column fitted with FID. GC parameters were quantified with authentic samples of product prior to the analysis.

3. Results and discussion

3.1. Characterization of ruthenium complexes

Complex **1** together with the NMR numbering scheme is pictorially represented in Fig. 1. A strong band in the IR spectra of the **1** appeared in the region 1590–1600 cm^{-1} is assigned to ν(C=N) stretching, whereas, the strong band in the region 1630–1635 cm^{-1} is assigned to the coordinated carboxylate group. The absorption spectrum of **1** in H_2O exhibited a number of bands in the UV–Vis region. The bands appearing in the UV region are characterized by intra-ligand ($\pi \rightarrow \pi^*$) charge transition, whereas, spectral features in the visible region (Fig. 2a) are attributed to the metal to ligand, $d\pi(Ru) \rightarrow \pi^*$(polypyridyl) charge