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Electronic structure and catalytic aspects of $[(trpy)(Cl)Ru(L)]^n$ incorporating potential non-innocent ligands, L⁻: 9-Oxidophenalenone and trpy: 2,2':6',2"-terpyridine

Amit Das, Tamal Kanti Ghosh, Abhishek Dutta Chowdhury, Shaikh M. Mobin, Goutam Kumar Lahiri*

Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 400076, India

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ABSTRACT

The title complex [(trpy)(Cl)Ru^{II}(L)] (1) incorporating potential redox non-innocent ligands, L⁻ = 9-oxidophenalenone and trpy = 2,2':6',2"-terpyridine has been structurally characterized. The crystal structure of 1 establishes the distorted octahedral arrangement, meridional coordinating mode of trpy and delocalized C-O bond distances of coordinated L⁻. Compound 1 displays two one-electron oxidations at E_{298}^0 , 0.12 V (Ox1) and 1.32 V (Ox2) and one reduction, -1.58 V versus SCE. Predominantly ruthenium based first oxidation (Ox1) and L based second oxidation (Ox2) lead to the valence configurations of [(trpy)(Cl)Ru^{III}(L⁻)]⁺ (1⁺) and [(trpy)(Cl)Ru^{III}(L⁻)]²⁺ (1²⁺), respectively. The antiferromagnetic coupling of spins on Ru(III) (low-spin, t_{2g}^{5}) and L⁻ develops a singlet (*S* = 0) ground state in 1²⁺. The reduction, however, occurs at the trpy site. The electronic transitions in 1 and 1⁺ could be assigned based on the TD-DFT calculations. Interestingly, 1 has been established to be an efficient pre-catalyst for the oxidative cleavage of alkenes to carbonyl derivatives.

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1. Introduction

The mostly redox innocent 2,4-pentanedionate (= acetylacetonate) derivatives have been utilized since long as chelating ligands with most of the metal ions from the broader perspectives of coordination chemistry [1]. Furthermore, metal complexes of β -diketonates have been established to exhibit applications for MOCVD and related processes [2]. However, it has recently been demonstrated that unlike 2,4-pentanedionate derivatives, the analogous 1,9substituted β -diketonate form, 9-oxidophenalenone (L⁻) can undergo stepwise two-step reductions, L⁻ \rightarrow L²⁻ \rightarrow L³⁻ in



combination with Lewis-acids: B^{III}, Al^{III}, Si^{IV} and Ge^{IV} [3], as well as one-step oxidation to its radical state (L[·]) in selective ruthenium framework of $[(bpy)Ru(L)_2]^n$ (bpy = 2,2'-bipyridine) [4] due to the presence of underlying π orbitals.

Hence, as a part of our ongoing program of establishing electronic structural aspects of ruthenium complexes of redox active non-innocent ligands [5], the present report is directed towards the probing of non-innocent tendencies of L^- in the newer ruthenium molecular form of $[(trpy)(Cl)Ru(L^-)]^n$ (1) (trpy = 2,2': 6',2"-terpyridine).



Herein we describe the synthesis, characterization and single crystal X-ray structure of **1**. The electronic structural aspects of **1** in native and accessible redox states are investigated by experimental and DFT calculations. In addition, the catalytic potential of **1** towards the selective oxidative cleavage of alkenes to the corresponding carbonyl compounds has been explored as this sort of metal complex frameworks have recently been reported as

^{*} Corresponding author. *E-mail address:* lahiri@chem.iitb.ac.in (G.K. Lahiri).

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efficient pre-catalysts for oxidation of alkenes and single-site wateroxidation process [6,7].

It should be noted that the metal complexes of L have been primarily restricted to main group elements such as B^{III} , AI^{III} , Si^{IV} and Ge^{IV} [3], where B, Si and Al complexes show radical-based molecular conducting and catalytic properties, respectively. However, only one article involving the transition metal complexes of L: $[(bpy)_2R$ $u(L)]^n$, $[(bpy)Ru(L)_2]^n$, $[Ru(L)_3]^n$ has been appeared just recently [4].

2. Experimental

2.1. Materials and instrumentation

The precursor complexes $Ru(trpy)Cl_3$ [8] (trpy = 2,2':6',2"-terpyridine) and the ligand (HL = 9-hydroxy-1*H*-phenalen-1-one) [9] were prepared according to the literature procedures. Other reagents and chemicals were obtained from Aldrich and used as received. Solvents were dried by following the standard procedures [10], distilled under nitrogen, and used immediately. For spectroscopic and electrochemical studies, HPLC-grade solvents were used. ¹H NMR spectrum was recorded on a Bruker Avance III 400 spectrometer. IR and UV-Vis spectra were recorded using Thermo Nicolet 320 and Perkin-Elmer Lambda 950 spectrophotometers, respectively. ESI-mass spectrum was recorded using a micromass Q-TOF mass spectrometer. The EPR measurement was made in a two-electrode capillary tube with an X-band Bruker system ESP300, equipped with a Bruker ER035M gaussmeter and a HP 5350B microwave counter [11]. Cyclic voltammetric studies were carried out using a PAR model 273A electrochemistry system. Platinum wire working and auxiliary electrodes and an aqueous saturated calomel electrode (SCE) were used in a three-electrode configuration. The supporting electrolyte was 0.1 M [NEt₄][ClO₄] and the solute concentration was $\sim 10^{-3}$ M. The half-wave potential E_{298}^0 was set equal to $0.5(E_{pa} + E_{pc})$, where E_{pa} and E_{pc} are the anodic and cathodic cyclic voltammetric peak potentials, respectively. Elemental analyses were carried out on a Perkin-Elmer 240C elemental analyzer.

2.2. Preparation of [(trpy)(Cl)Ru(L)] (1)

A mixture of 100 mg (0.23 mmol) Ru(trpy)Cl₃, 45 mg (0.23 mmol) HL and 23 mg (0.23 mmol) NEt₃ were taken in 30 mL of ethanol and the mixture was refluxed under N₂ atmosphere for 8 h. The initial reddish brown solution was gradually changed to blue. This mixture was evaporated to dryness and purified by using a neutral alumina column. The product was eluted by 20:1 dichloromethane-methanol. On evaporation of the solvent under reduced pressure yielded the pure complex **1** in the solid form. Yield: 80 mg (63%). Anal. Calc. for C₂₈H₁₈ClN₃O₂Ru: C, 59.47; H, 3.21; N, 7.44. Found: C, 59.42; H, 3.25; N, 7.39%. ESI MS (in dichloromethane): m/z = 564.94 corresponding to **1**⁺ (Calc. **1**⁺: 565.01) and m/z*z* = 528.97 corresponding to [**1**-Cl]⁺ (Calc. [**1**-Cl]⁺: 529.54. ¹H NMR in (CD₃)₂SO [δ /ppm(J/Hz)]: 8.69 (d, 5, 2H), 8.62 (d, 8.1, 2H), 8.52 (d, 8, 2H), 8.15 (d, 9.4, 1H), 8.08 (d, 6.68, 1H), 7.99 (d, 8.1, 2H), 7.89 (d, 7.6, 1H), 7.69 (t, 8, 1H), 7.61-7.53 (m, 4H), 7.33 (t, 7.6, 1H), 6.10 (d, 9.3, 1H). IR KBr disk: v_{CO}: 1624 cm⁻¹. UV–Vis in CH₃CN: $(\lambda [nm] (\epsilon [M^{-1} cm^{-1}]))$ **1**: 600 (23750); 510 (sh, 11900); 400 (23640); 375 (sh, 17150); 325 (53580); 310 (sh, 50100); 280 (58880). 1⁺: 720 (3900); 440 (23600); 400 (sh, 21100); 350 (sh, 26000); 320 (33400); 275 (sh, 39400).

2.3. Crystal structure determination

Single crystals of **1** were grown by slow evaporation of its 1:1 dichloromethane-hexane solution. X-ray data were collected using

Table 1

Selected crystallographic parameters for 1.

Formula	C28H18CIN3O2Ru
Formula weight	564.97
Crystal system	orthorhombic
Space group	Pbca
a (Å)	9.7270(12)
b (Å)	16.191(3)
<i>c</i> (Å)	29.494(3)
α (°)	90
β (°)	90
γ (°)	90
$V(Å^3)$	4645.2(11)
Ζ	8
$\mu ({\rm mm^{-1}})$	0.822
<i>T</i> (K)	293(2)
$D_{\text{calc}} (\text{mg m}^{-3})$	1.616
F(000)	2272
θ range (°)	3.26-25.00
Data/restraints/parameters	4080/0/316
R_1 , wR_2 $[I > 2\sigma(I)]$	0.0475, 0.0602
R_1 , wR_2 (all data)	0.1692, 0.0726
Goodness-of-fit (GOF)on F ²	0.651
Largest difference in peakand hole (e $Å^{-3}$)	0.631 and -0.430

an X-CALIBUR-S CCD diffractometer at 293 K. All data were corrected for Lorentz polarization and absorption effects. The structure was solved and refined using full matrix least-squares techniques on F^2 using the SHELX-97 program [12]. Hydrogen atoms were included in the refinement process as per the riding model. Selected crystallographic parameters are given in Table 1.

2.4. UV-Vis spectro-electrochemical measurements

UV–Vis spectra were recorded using a Perkin–Elmer Lambda 950 spectrophotometer at room temperature in acetonitrile. The cerium ammonium nitrate (CAN) titration experiments were done as follows: to a 1×10^{-4} M acetonitrile solution of complex **1** in a cuvette with a 1 cm light path length was gradually added $\sim 2 \times 10^{-3}$ M solution of CAN in acetonitrile. The absorption spectral changes were monitored after each addition. Each absorption spectrum was plotted with consideration of the volume change when the CAN solution was added.

2.5. Computational details

Full geometry optimizations were carried out using the density functional theory method at the (R)B3LYP level for **1**, 1^{2+} and (U)B3LYP for 1^+ [13]. All elements except ruthenium were assigned the 6-31G* basis set. The LANL2DZ basis set with effective core potential was employed for the ruthenium atoms [14]. All calculations were performed with GAUSSIANO3 program package [15]. No symmetry constraints were imposed during structural optimizations. The calculated structures were visualized with ChemCraft [16]. Chemissian 1.7 was used to calculate the fractional contributions of various groups to each molecular orbital [17].

2.6. General methods for catalytic reaction

In a typical reaction, the catalyst (0.01 mmol) and 2 equivalent of $PhI(OAc)_2$ in 3 mL of dichloromethane were placed in a 25 mL Schlenk tube and the mixture was stirred for 10 min. The solution immediately turned to reddish brown. The corresponding alkenes and dodecane (1.5 mmol each) were then added in additional 1 mL of solvent and then stirred at room temperature for 16 h at 298 K (353 K for aliphatic substrates). Then the reaction mixture was filtered through a short silica gel column using dichloromethane as eluent prior to GC analysis. The percent conversion and percent selectivity were determined either by GC against authenticated sample with respect to dodecane as an internal standard or by ¹H NMR.

3. Results and discussion

3.1. Synthesis and characterization

The complex [(trpy)(Cl)Ru(L⁻)] (1) (trpy = 2,2':6',2"-terpyridine, L⁻ = 9-oxidophenalenone) has been prepared via the reaction of the protonated free ligand, HL and the metal precursor Ru(trpy)Cl₃, under dinitrogen atmosphere and in presence of triethylamine as a base. The crude product has been purified by using a neutral alumina column and CH₂Cl₂-CH₃OH mixture as eluent (see Section 2). The ESI mass spectrometry shows peaks at 564.94 and 528.97, corresponding to 1⁺ (Calc. mass: 565.01) and [1-Cl]⁺ (Calc. mass: 529.54), respectively, with appropriate isotopic distributions (Fig. S1). The electrically neutral complex 1 gives satisfactory microanalytical data (see Section 2).

¹H NMR spectrum of the diamagnetic complex **1** exhibits partially overlapping calculated 18 aromatic proton resonances within the chemical shift range of 6–9 ppm (Fig. 1, see Section 2). It is rather difficult to make individual assignments of all the protons due to overlapping of signals with similar chemical shift values.

3.2. Structural aspects

Crystal structure of [(trpy)(Cl)Ru(L⁻)] (1) is shown in Fig. 2 and selective crystallographic data and bond distances, bond angles are listed in Tables 1 and 2, respectively. The central ruthenium atom forms two five-membered chelate rings with the tridentate trpy ligand. The bidentate L⁻ is bonded to the Ru(II) atom via the oxygen donors forming a six-membered chelate ring. The *trans* angles involving trpy, L⁻ and Cl ligands, N(2)–Ru(1)–O(2), O(1)–Ru(1)–Cl(1) and N(1)–Ru(1)–N(3) are 178.7(2)°, 175.26(14)° and 161.1(3)°, respectively, indicating a distorted octahedral environment around the Ru atom. The geometrical constraints due to the meridional mode of trpy has been reflected in the appreciably smaller *trans* angle involving the trpy ligand, N(1)–Ru(1)–N(3) at 161.1(3)° as has been reported for the analogous ruthenium-terpyridine complexes [6a]. The central Ru^{II}–N2(trpy) bond length of 1.923(5) Å is significantly shorter than the corresponding

distances involving the terminal pyridine rings of trpy, Ru^{II}-N1(trpy), 2.050(5) Å and Ru^{II}–N3(trpy), 2.059(5) Å. The Ru^{II}–O(L) bond distances of 2.046(4) and 2.047(4) Å in 1 are close to the Ru^{II}–O(L) distances reported in [(bpy)₂Ru^{II}(L)]ClO₄ (Ru–O distances: 2.0337(16) and 2.0373(16) Å) but appreciably longer with respect to the Ru^{III} -O(L) distances in [(bpy) $Ru^{III}(L)_2$]ClO₄ (average Ru–O distance = 1.994(2) Å) [4]. The C–O bond distances of coordinated L⁻ of C1-O1, 1.248(7) Å and C11-O2, 1.268(7) Å in **1** exist in between the standard C–O single bond (1.34 Å) and C=O double bond (1.22 Å) distances. This in turn implies a delocalized situation as generally observed in β-diketonato complexes (average C-O(acac) distances: Ru(acac)₃: 1.282 Å [18], Co(acac)₂: 1.270 Å [19], Cu(acac)₂: 1.273 Å [20]. The average C–O distances of coordinated L in other two structurally characterized ruthenium complexes, $[(bpy)_2Ru^{II}(L)]ClO_4$ and $[(bpy)Ru^{III}(L)_2]ClO_4$ are 1.287(3)Å and 1.288(4) Å, respectively [4]. The other bond parameters involving coordinated L are similar to those reported for the structurally characterized Ge^{IV}, Si^{IV}, Al^{III}, Ru^{II} and Ru^{III} complexes of L [3b,c,4].

The bond parameters of DFT (B3LYP/LANL2DZ/6-31G*) optimized **1** (Fig. S2) are in fairly good agreement with the experimentally obtained values (Table 2).

3.3. Electrochemistry, EPR and DFT calculations

Complex 1 exhibits two one-electron oxidations and one oneelectron reduction in CH₃CN within the experimental potential range of ±2.0 V versus SCE (Fig. 3). The first oxidation (Ox1) at E_{298}^0 , V(ΔE_p , mV), 0.12 (80) may occur either at the metal or at the potentially redox active ligand (L) site to yield the valence formulation of $[(trpy)(Cl)Ru^{III}(L^-)]^+$ or $[(trpy)(Cl)Ru^{II}(L^-)]^+$, respectively, for $\mathbf{1}^+$. DFT calculations on the optimized structure (singlet (S = 0) state) of **1** (Fig. S2) reveal that the HOMO is primarily composed of ruthenium based orbitals with appreciable contributions from L and Cl (Ru, 54%; L, 22%; Cl, 17%; trpy, 7%, Table S1). This essentially suggests that the valence form of 1⁺ can be best described as a mixed situation of: [(trpy)(Cl)Ru^{III}(L⁻)]⁺ (major component)/[(trpy)(Cl)Ru^{II}(L[·])]⁺ (minor component) as has been frequently considered for the ruthenium-quinonoid moieties [5h–o]. However, the spin density plot of $\mathbf{1}^+$ shows that ruthenium is the primary spin-bearing center with minor contributions from other constituents (Mulliken spin distribution: Ru, 0.727; Cl, 0.112; trpy, 0.069; L, 0.05) (Fig. 4). This has further been experimentally authenticated by the observed Ru(III)-based broad



Fig. 1. ¹H NMR spectrum of 1 in (CD₃)₂SO.



Fig. 2. ORTEP diagram of 1. Ellipsoids are drawn with 50% probability. Hydrogen atoms are omitted for clarity.

Table 2	
Selected bond distances and bond angles in 1 .	

Bond length (Å)	X-ray	DFT	Bond angle (°)	X-ray	DFT
Ru(1)-N(1)	2.050(5)	2.091	N(2)-Ru(1)-O(1)	91.3(2)	91.03
Ru(1)-N(2)	1.923(5)	1.950	N(2)-Ru(1)-O(2)	178.7(2)	177.70
Ru(1)-N(3)	2.059(5)	2.090	O(1)-Ru(1)-O(2)	88.81(18)	86.67
Ru(1)-O(1)	2.046(4)	2.082	N(2)-Ru(1)-N(1)	80.6(3)	79.87
Ru(1)-O(2)	2.047(4)	2.104	O(1)-Ru(1)-N(1)	88.61(18)	91.10
Ru(1)-Cl(1)	2.3761(19)	2.437	O(2)-Ru(1)-N(1)	100.7(3)	100.20
C(1)-C(2)	1.431(9)	1.449	N(2)-Ru(1)-N(3)	80.5(2)	79.88
C(1)-C(12)	1.440(9)	1.444	O(1)-Ru(1)-N(3)	92.4(2)	90.87
C(2)-C(3)	1.337(8)	1.358	O(2)-Ru(1)-N(3)	98.2(2)	100.09
C(3)-C(4)	1.385(10)	1.433	N(1)-Ru(1)-N(3)	161.1(3)	159.69
C(4)-C(5)	1.399(11)	1.405	N(2)-Ru(1)-Cl(1)	91.97(15)	91.92
C(4)-C(13)	1.409(10)	1.429	O(1)-Ru(1)-Cl(1)	175.26(14)	177.05
C(5)-C(6)	1.345(14)	1.392	O(2)-Ru(1)-Cl(1)	87.95(14)	90.38
C(6)-C(7)	1.439(11)	1.394	N(1)-Ru(1)-Cl(1)	88.59(14)	89.48
C(7)-C(8)	1.385(10)	1.403	N(3)-Ru(1)-Cl(1)	91.52(17)	89.59
C(8)-C(9)	1.404(10)	1.435			
C(8)-C(13)	1.414(9)	1.430			
C(9)-C(10)	1.343(9)	1.357			
C(11)-C(12)	1.441(9)	1.449			
C(12)-C(13)	1.454(9)	1.438			
O(1)-C(1)	1.248(7)	1.282			
O(2)-C(11)	1.268(7)	1.276			
C(10)-C(11)	1.455(8)	1.451			

anisotropic EPR signal of **1**⁺ in CH₃CN with ($g_1 = 2.379$, $g_2 = 2.118$, $g_3 = 1.989$, $\Delta g = 0.39$ ($\Delta g = g_{1-}g_3$) and $\langle g \rangle = 2.418$ ($\langle g \rangle = (1/3(g_1^2 + g_2^2 + g_3^2))^{1/2}$) [5a]. The highly rhombic EPR spectrum of **1**⁺ [5f] indeed corroborates the structurally characterized severely distorted octahedral geometry of **1** (Fig. 2 and Table 2).

Since Ru^{IV} state can also be accessible in **1** having electrondonating L⁻ and Cl⁻, as has been reported earlier for the analogous molecular framework [21], the second oxidation (Ox2, E_{298}^0 , V(ΔE_p , mV), 1.32(100)) may therefore be taken place either at the ruthenium center ($\text{Ru}^{\text{III}} \rightarrow \text{Ru}^{\text{IV}}$) or at the ligand-site (L⁻ \rightarrow L⁻). The DFT calculations on the optimized **1**⁺ in doublet (*S* = 1/2) ground state predict that the α -SOMO is dominated by the L based orbitals (66%) with reasonable contribution from Ru (22%) (Table S2). This indeed suggests that the second oxidation predominantly occurs at the ligand site to result in the valence configuration of **1**²⁺ as [(trpy)(Cl)Ru^{III}(L[·])]²⁺ where unpaired spins on Ru^{III} and (L[·]) are antiferromagnetically coupled leading to a singlet (*S* = 0) ground state [Δ*E*_{(*S*=1)-(*S*=0)} = 0.339 a.u]. However, sizable contribution of ruthenium based orbitals (22%) in the α-SOMO of **1**⁺ implies the minor contribution of the alternate valence configuration of [(trpy)(Cl)Ru^{IV}(L[−])]²⁺ for the doubly oxidized **1**²⁺. This has further been supported by the LUMO composition of the optimized **1**²⁺ in singlet (*S* = 0) ground state (LUMO of **1**²⁺: Ru, 52%; L, 30%; trpy, 6%; Cl, 12%) (Table S3). It should be noted that the oxidation of coordinated L[−] → L[·] has also been established recently in the molecular framework of [(bpy)Ru^{IV}(L[−])(L[·])]³⁺ [4].

On the other hand, LUMO and LUMO+1 of **1** is composed of trpy-based orbitals (82% and 89% trpy in LUMO and LUMO+1, respectively, Table S1) which suggests the involvement of trpy based redox orbitals for the observed reduction, E_{298}^0 , V(ΔE_p , mV),



Fig. 3. Cyclic voltammogram (–) and differential pulse (---) voltammograms of 1 in acetonitrile/0.1 M Et_4NCIO_4 (scan rate: 100 mV S^{-1}).



Fig. 4. Spin density plot of $\mathbf{1}^+$ in doublet (*S* = 1/2) ground state.

-1.58(70) [6a,21]. It should be noted that the reduction of the coordinated L⁻ (L⁻ \rightarrow L²⁻) has been reported in the tris-complexes of L⁻ with Si, Ge and Ru [3,4]. The LUMO+2 of **1** is however, mostly composed of L based orbitals (83% L and 12% trpy, Table S1) but no such second reduction has been detected within the experimental potential limit of -2.0 V versus SCE in CH₃CN.

3.4. Electronic spectra and TD-DFT calculations

In acetonitrile **1** exhibits two intense bands in the visible region at 600 nm (ε = 23750 M⁻¹ cm⁻¹) and 400 nm (ε = 23640 M⁻¹ cm⁻¹) (Fig. 5 and Table 3, see Section 2) which are assigned based

Table 3

TD-DFT	results	for 1^n	(<i>n</i> = +,	0).
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Fig. 5. UV–Vis-NIR spectro-electrochemical plots for the conversion of $1 \to 1^*$ in acetonitrile on addition of ${\sim}2 \times 10^{-3}\,M~(NH_4)_2 Ce(NO_3)_6~(CAN)$ solution in acetonitrile.

on the TD-DFT calculations as $\operatorname{Ru}^{II}(d\pi) \rightarrow \operatorname{trpy}(\pi^*)/L(\pi^*)$ and $\operatorname{Ru}^{II}(d\pi) \rightarrow \operatorname{trpy}(\pi^*)$ MLCT (metal-to-ligand charge-transfer) transitions, respectively [5g]. Multiple absorptions in the UV-region are originated from the intraligand $\pi \rightarrow \pi^*$ transitions involving coordinated trpy and L moieties [4,21].

On one-electron oxidation of **1** to **1**⁺ the charge-transfer bands at 600 and 400 nm are red shifted to 720 and 440 nm, respectively (Fig. 5 and Table 3). The TD-DFT calculations based on the optimized structure of **1**⁺ predict that the lowest energy band at 720 nm has been developed through the $L(\pi) \rightarrow \text{Ru}(d\pi)$ (ligand to metal charge-transfer (LMCT)) transition. The higher energy band at 440 nm has been originated via $\text{Ru}(d\pi)/\text{L}(\pi) \rightarrow \text{trpy}(\pi^*)$ (metal-ligand to ligand charge-transfer (MLLCT)) transition (Table 3, see Section 2).

3.5. Catalytic activity of 1 towards the oxidative cleavage of alkenes

Oxidation of olefins is an important process for the production of fine chemicals. The oxidation of olefin can be divided into three categories: (i) the cleavage of C=C bond of alkenes to form carbonyl compounds [22], (ii) the ozonolysis of olefins to ozonides and the subsequent conversion to aldehydes or ketones in reductive workup conditions [22a,23] and (iii) oxidation of olefins by hydrogen peroxide or other oxidizing agents [24] to yield carbonyl compounds or epoxides or diols. Furthermore, such oxidative cleavage of alkene is a frequently utilized method in synthetic organic chemistry for the introduction of oxygen functionalities, selective splitting of large molecules and specifically for removal of protecting groups. In this regard reductive ozonolysis is considered to be the "cleanest"

Energy (eV)	λ (nm) (DFT)	λ (nm) (expt.)	osc. strength (f)	$\epsilon (M^{-1} cm^{-1})$	Key transitions	Character
[(trpy)(Cl)Ru ^{III} (I	$[L]^{+}(1^{+})(S = 1/2)$					
1.7195	721	720	0.0975	3900	$HOMO-2(\beta) \rightarrow LUMO(\beta) (0.72)$	$L(\pi) \rightarrow Ru(d\pi)$
3.0531	406	440	0.1010	23600	HOMO−1(β) → LUMO+1(β) (0.39) HOMO−1(α) → LUMO+1(α) (0.46)	$L(\pi) \rightarrow trpy(\pi^*)$ $Ru(d\pi) \rightarrow trpy(\pi^*)$
3.6424	340	345	0.0444	sh	$\begin{array}{l} HOMO-3(\alpha) \rightarrow LUMO(\alpha) \ (0.56) \\ HOMO-10(\beta) \rightarrow LUMO(\beta) \ (0.37) \end{array}$	$L(\pi) \rightarrow trpy(\pi^*)/Ru(d\pi)$ $Cl(p\pi) \rightarrow trpy(\pi^*)$
[(trpy)(Cl)Ru ^{II} (L)] (1) ($S = 0$)					
2.1867	567	600	0.0252	23 750	HOMO → LUMO+3 (0.48) HOMO → LUMO (0.38) HOMO-1 → LUMO+1 (0.34)	$\operatorname{Ru}(d\pi) \to \operatorname{trpy}(\pi^*)/L(\pi^*)$
3.1987	388	400	0.047	23 640	HOMO \rightarrow LUMO+3 (0.70)	$\operatorname{Ru}(d\pi) \to \operatorname{trpy}(\pi^*)$
3.7858	327	325	0.1129	53 580	$HOMO-4 \rightarrow LUMO (0.60)$	$L(\pi) \rightarrow trpy(\pi^*)$
4.5624	271	280	0.2997	58 880	HOMO-3 → LUMO+2 (0.41) HOMO-1 → LUMO+5 (0.20)	$\operatorname{Ru}(d\pi)/\operatorname{Cl}(p\pi) \to \operatorname{L}(\pi^*)$

$$R \xrightarrow{\text{catalyst 1}} R \xrightarrow{\text{catalyst 2}} R \xrightarrow{\text{catalyst 1}} R$$

Scheme 1. General catalytic reaction.

Table -	4
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Optimization of solvent for the catalytic reaction in Scheme 1.^a

Solvent	Conversion (%)	Selectivity (%) ^b
CH_2Cl_2	98	86
CHCl ₃	96	88
Toluene	76	74
Xylene	68	78
EtOH	12	83

^a Detailed reaction conditions are given in Section 2 with styrene as a model substrate. Products are characterized by GC with respect to dodecane as an external standard.

^b Selectivity in terms of benzaldehyde formation.



Fig. 6. Conversion (%) and benzaldehyde formation (%) as a function of time with complex 1 as a pre-catalyst under experimental catalytic conditions taking styrene as a model substrate.

option. However, there are several practical limitations of this process such as the requirement of specially designed equipment (ozonizer), low reaction temperature (generally -78 °C), use of additional stoichiometric reducing reagent for reductive workup (e.g. dimethyl sulfide, zinc, hydrogen, phosphines) and accidental issues. Due to these inherent problems of ozonolysis, metal catalyzed chemoselective oxidative cleavage of alkene functionalities has been considered to be an attractive approach. Metal complex derived pre-catalysts such as Fe^{III}(Salen)Cl (Salen = 2,2'-(1E,1' E)-(ethane-1,2-diylbis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene)diphenolate) and $[cis-Ru^{II}(dmp)_2(H_2O)_2]^{2+}(dmp =$ 2,9-dimethylphenanthroline) have been effectively utilized for the transformation of olefins to carbonyl compounds via the selective cleavage of C=C bond [25]. Alternatively, He and co-workers have employed PdCl₂ as a catalyst for the oxidation of styrene in scCO₂/ PEG biphasic catalytic system which however shows moderate selectivity towards the formation of benzaldehyde [26]. It should also be noted that such oxidative alkene cleavage has been reported to take place as a minor or undesired side product catalyzed by peroxidases [27].



(continued on next page)

Table 5 (continued)



^a Detailed reaction conditions are given in Section 2. Products are characterized by GC with respect to dodecane as an external standard and ¹H NMR.

^b Selectivity in terms of aldehyde formation.

^c NMR yield.

In this regard complex **1** has been explored towards the oxidation of a wide variety of alkenes and it shows selective oxidative cleavage of the C=C bond to yield the carbonyl compounds in presence of suitable oxidizing agent, iodobenzene diacetate in dichloromethane solution (Scheme 1).

Initial optimization for the appropriate catalytic conditions with styrene as a model substrate establishes that the combination of 0.75 mol % of the catalyst and 2 equivalent of oxidant (iodobenzene diacetate) yields the best results. Among the various oxidants tested, iodobenzene diacetate has been found to be the most effective one. Unfortunately, the present catalytic protocol failed

to activate the desired hydrogen peroxide or molecular oxygen. In general the chlorinated solvents, CH₂Cl₂ and CHCl₃ have shown the maximum impact on the desired chemoselectivity of the catalytic process (Table 4). Effectivity of the chlorinated solvents could be attributed to their non-coordinating nature as well as their inherent tendency to stabilize the intermediates during the oxidation process [28]. Thus, dichloromethane has been selectively chosen for rest of the catalytic processes (Table 4). Furthermore, most of these catalytic reactions proceed well at room temperature except for aliphatic substrates where heating of about 80 °C is necessary to maximize the conversion. The time monitored reaction profile shows that chemoselectivity enhances with the increase in conversion up to 12 h and then it levels off with slight increase in conversion (Fig. 6). As stated above the present catalytic protocol is effective to oxidize the terminal alkene functionalities to the corresponding carbonyl compounds via the oxidative C=C bond cleavage (Table 5). Better conversion and selectivity have been achieved with the substrates comprising of electron donating group whereas poor conversion is obtained for the substrates having electron withdrawing group. Interestingly, the observed very poor conversion for the electron rich 2-methoxystyrene could be attributed to the catalytic site inhibition via possible co-ordination of the o-methoxy group to the active ruthenium center. The advantage of using the preformed catalyst (1) for the said process is clearly evident from the formation of only 8% benzaldehyde by the in situ generated catalyst (RuCl₃ + L + trpy + oxidant) with styrene as a model substrate [6a]. In essence, 1 can function as an effective pre-catalyst for the oxidation of terminal alkene functionalities to the corresponding carbonyl compounds under mild optimized reaction conditions.

4. Conclusion

Monomeric ruthenium-terpyridine complex, $[(trpy)(Cl)Ru^{ll}(L^{-})]$ (1) incorporating potential non-innocent ligand L⁻ [4] has been synthesized and structurally characterized. Considerable mixing of Ru and L based frontier orbitals in the MOs (HOMO/SOMO) have led to the complex valence situations at the oxidized states, 1⁺ and 1²⁺. Compound 1 has been established to be an efficient catalyst for the oxidative cleavage of alkenes to the corresponding carbonyl compounds under mild reaction conditions.

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Appendix A. Supplementary data

CCDC 878994 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge via http:// www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2012.06.057.

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