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PII: S0022-328X(16)30516-2

DOI: 10.1016/j.jorganchem.2016.11.012

Reference: JOM 19697

To appear in: Journal of Organometallic Chemistry

Received Date: 8 August 2016

Revised Date: 1 November 2016

Accepted Date: 4 November 2016

Please cite this article as: P. Roy, A.S. Mondal, A.K. Pramanik, T.K. Mondal, Ruthenium carbonyl complex of a redox non-innocent ONS donor azophenol ligand: Electrochemistry, photophysical property, electronic structure and catalytic activity towards oxidation of alcohols, *Journal of Organometallic Chemistry* (2016), doi: 10.1016/j.jorganchem.2016.11.012.

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## **GRAPHICAL ABSTRACT**

Ruthenium carbonyl complex of a redox non-innocent ONS donor azophenol ligand: Electrochemistry, photophysical property, electronic structure and catalytic activity towards oxidation of alcohols

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A ruthenium carbonyl complex,  $[Ru(CO)_2(L)(Cl)_2]$  (1) of a redox non-innocent thioethercontaining azo-phenol ligand has been synthesized and characterized. Cyclic voltammogram of 1 exhibits Ru(II)/Ru(III) quasireversible oxidation (E<sub>1/2</sub> = 1.22 V) along with ligand based reductions. DFT calculations have been used to interpret the electronic structure of the complex. Catalytic activities towards oxidation of alcohols have been studied.



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ligand: Electrochemistry, photophysical property, electronic structure and
catalytic activity towards oxidation of alcohols
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## 8 Abstract

9 A ruthenium carbonyl complex,  $[Ru(CO)_2(L)(Cl)_2]$  (1) with a redox non-innocent thioether-10 containing azo-phenol ligand has been synthesized and characterized by various spectroscopic 11 techniques, along with X-ray structure determination. Cyclic voltammogram of 1 exhibits 12 Ru(II)/Ru(III) quasireversible oxidation (E<sub>1/2</sub> = 1.22 V) along with ligand based two successive 13 reductions. Theoretical calculations using DFT/B3LYP method have been used to interpret the 14 electronic structure of the complex. Synthesized ruthenium(II) complex efficiently catalyzed the 15 oxidation of alcohols in presence of N-methylmorpholine-N-oxide.

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*Key words*: Ruthenium carbonyl complex; ONS donor azophenol ligand; X-ray structure;
Electronic structure; Electrochemistry; Catalytic activity.

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#### 23 **1. Introduction**

Chelating behavior of ONS donor ligands with transition metals has been studied with the aim of 24 gaining more information about their nature of coordination, structural and spectral features [1-25 5]. They can stabilize metal ion in uncommon oxidation states [6, 7], to generate uncommon 26 coordination numbers in the resultant complexes [6-8] and to participate in a variety of 27 interesting redox reactions. The chemistry of azo-ligands has been widely explored due to their 28 interesting physical, chemical, photophysical and photochemical, catalytic properties especially 29 in the low valent transition metal coordination and organometallic compounds [9-16]. Besides, 30 the study of compounds containing S and N atoms is interesting due to their significant 31 antifungal, antibacterial and anticancer activities [17-24]. 32

There has been considerable interest in transition metal ions catalyzed biological 33 oxidation events including hydroxylation, epoxidation, dehalogenation, sulfoxidation, 34 dehydrogenation, alcohol and aldehyde oxidation reactions [25-29]. The oxidation of alcohols 35 plays an important role in organic synthesis and the efforts are continuing for the development of 36 new oxidative processes to avoid the traditional methods for oxidation using stoichiometric 37 amount of inorganic oxidants [30-32]. Inspite of several proposed mechanism, the formation of 38 metal oxo moieties ( $M^{n+}$ =O) have been well accepted for late transition metal complexes as 39 40 active intermediates in most of the oxidation reactions [27-29, 33]. Ruthenium carbonyl complexes have been widely used as catalysts for oxidation of organic compounds [34-36]. In 41 the past few decades there has been a growing interest in transition metal-catalyzed oxidation of 42 alcohols, which take place at milder conditions using oxidants such as molecular oxygen, 43 hydrogen peroxide, *tert*-butyl hydroperoxide and N-methylmorpholine-N-oxide (NMO) [37-42]. 44

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Herein, we have synthesized a new ONS donor thioether containing azophenol ligand, 4chloro-2-((2-(ethylthio)phenyl)diazenyl)phenol (HL) and its ruthenium carbonyl complex, [Ru(CO)<sub>2</sub>(L)(Cl)<sub>2</sub>] (1). An array of tools including X-ray diffractometry, electrochemistry, and electronic absorption and emission spectroscopy abetted with DFT calculations were used to characterize the compounds. The catalytic activity of the ruthenium(II) complex for the oxidation of primary and secondary alcohols to the respective aldehyde and ketones were studied using Nmethylmorpholine-N-oxide (NMO) as oxidizing agent.

### 52 2. Experimental

#### 53 2.1. Materials and methods

RuCl<sub>3</sub>.3H<sub>2</sub>O was purchased from Arrora Matthey, Kolkata, India. [Ru(CO)<sub>2</sub>(Cl)<sub>2</sub>]<sub>n</sub> was prepared
following the reported method [43]. 2-(Ethylthio)benzenamine was synthesized by published
procedure [44]. All other chemicals and solvents were of reagent grade and were used without
further purification.

Microanalyses (C, H, N and S) were performed using a PerkinElmer 2400 CHNS/O 58 elemental analyzer. HRMS mass spectra were obtained on a Waters (Xevo G2 Q-TOF) mass 59 spectrometer. The electronic spectra were taken on a Lambda 750 PerkinElmer 60 spectrophotometer. IR spectra were recorded on RX-1 PerkinElmer spectrophotometer in the 61 spectral range 4000-400 cm<sup>-1</sup> with the samples in the form of KBr pellets. Luminescence 62 property was measured using LS-55 PerkinElmer fluorescence spectrophotometer at room 63 temperature (298 K) in acetonitrile by 1 cm path length quartz cell. Fluorescence lifetimes were 64 measured using a time-resolved spectrofluorometer from IBH, UK. The instrument uses a 65 picoseconds diode laser (NanoLed-03, 370 nm) as the excitation source and works on the 66 principle of time-correlated single photon counting [45]. The goodness of fit was evaluated by  $\chi^2$ 67

criterion and visual inspection of the residuals of the fitted function to the data. NMR spectra were recorded in CDCl<sub>3</sub> on a Bruker (AC) 300 MHz FT-NMR spectrometer in the presence of TMS as internal standard. Cyclic voltammetric measurements were carried out using a CHI Electrochemical workstation. A platinum wire working electrode, a platinum wire auxiliary electrode and Ag/AgCl reference electrode were used in a standard three-electrode configuration. Bu<sub>4</sub>NPF<sub>6</sub> was used as the supporting electrolyte in acetonitrile and the scan rate used was 50 mV

74  $s^{-1}$  under nitrogen atmosphere.

Luminescence quantum yield was determined using carbazole as reference with a known  $\phi_R$  of 0.42 in MeCN. The complex and the reference dye were excited at the same wavelength, maintaining nearly equal absorbance (~0.1), and the emission spectra were recorded. The area of the emission spectrum was integrated using the software available in the instrument and the quantum yield is calculated according to the following equation:

80  $\phi_S/\phi_R = [A_S / A_R] \times [(Abs)_R / (Abs)_S] \times [\eta_S^2 / \eta_R^2]$ 

Here,  $\phi_S$  and  $\phi_R$  are the luminescence quantum yield of the sample and reference, respectively. A<sub>S</sub> and A<sub>R</sub> are the area under the emission spectra of the sample and the reference respectively, (Abs)<sub>S</sub> and (Abs)<sub>R</sub> are the respective optical densities of the sample and the reference solution at the wavelength of excitation, and  $\eta_S$  and  $\eta_R$  are the values of refractive index for the respective solvent used for the sample and reference.

86 2.2. Synthesis

## 87 2.2.1. Synthesis of 4-chloro-2-((2-(ethylthio)phenyl)diazenyl)phenol (HL)

A solution of 2-(ethylthio)benzenamine (3.06 g, 0.02 mol) in 1:1 HCl (10 mL) was cooled in an
ice bath and an ice cold solution of NaNO<sub>2</sub> (2.0 g in 10 mL water) was added to it under stirring.
Then it was added to an ice cold solution of Na<sub>2</sub>CO<sub>3</sub> (6 g in 25 mL) and 4-chlorophenol (2.56 g,

0.02 mol) with vigorous stirring and an orange-red precipitate was obtained. The precipitate was
filtered and washed with cold water, then dried over CaCl<sub>2</sub>. The product was purified by using a
silica gel (mesh 60-120) column. An orange-red band of HL was eluted by 30% (v/v) ethyl
acetate-petroleum ether mixture. Evaporation of solvent under reduced pressure yielded the pure
HL. Yield, 3.7 g (72%).

Anal. Calc.C<sub>14</sub>H<sub>13</sub>ClN<sub>2</sub>OS (HL): C, 57.43; H, 4.48; N, 9.57; S, 10.95%. Found: C, 57.24; 96 H, 4.43; N, 9.48; S, 10.83%. IR data (KBr, cm<sup>-1</sup>): 3434 v(O-H), 1421 v(N=N). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 97 300 MHz):  $\delta$  (ppm): 12.67 (1H, s), 7.95 (1H, s), 7.85 (1H, d, J = 8.0 Hz), 7.28-7.45 (4H, m), 98 7.02 (1H, d, J = 8.8 Hz), 3.04 (2H, q, J = 7.2 Hz), 1.40 (3H, t, J = 7.3). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 99 MHz): δ (ppm): 14.02 (-S-CH<sub>2</sub>-CH<sub>3</sub>), 26.79 (-S-CH<sub>2</sub>-CH<sub>3</sub>), 116.49 (Ar-C), 119.75 (Ar-C), 100 124.36 (Ar-C), 125.97 (Ar-C), 127.95 (Ar-C), 131.99 (Ar-C), 132.09 (Ar-C), 132.87 (Ar-C), 101 137.72 (Ar-C), 138.62 (Ar-C), 147.75 (Ar-C), 150.98 (Ar-C). HRMS m/z, 293.6234 (calculated 102 for  $[C_{14}H_{13}CIN_2OS + H]^+$ : 293.8053). 103

#### 104 2.2.2. Synthesis of ruthenium complex (1)

To a suspension of  $[Ru(CO)_2Cl_2]_n$  (0.228 g, 1.0 mmol) in acetonitrile (30 mL), HL (0.257 g, 1.0 mmol) was added and the reaction mixture was refluxed for 8 h under N<sub>2</sub> atmosphere to yield a dark red solution. The solvent was then removed under reduced pressure. The dried crude product was purified by using a silica gel (mesh 60-120) column. The red band of **1** was eluted by 50% (v/v) ethyl acetate-petroleum ether mixture. On removal of the solvent under reduced pressure the pure complex **1** was obtained as a red solid which was further dried under vacuum. Yield, 0.305 g (63%).

112 Anal. Calc. for  $C_{16}H_{12}Cl_2N_2O_3RuS$ : C, 39.68; H, 2.50; N, 5.78; S, 6.62%. Found: C, 113 39.36; H, 2.42; N, 5.70; S, 6.52%. IR data (KBr, cm<sup>-1</sup>): 2061, 1997  $\nu$ (CO); 1387  $\nu$ (N=N).<sup>1</sup>H 114 NMR data (CDCl<sub>3</sub>, ppm): 8.51 (1H, d, J = 7.2), 7.95 (1H, s), 7.46-7.57 (4H, m), 7.05 (1H, d, J = 115 8.4 Hz), 3.32 (2H, q, J = 7.3 Hz), 1.45 (3H, t, J = 7.4). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ (ppm): 116 14.37 (-S-CH<sub>2</sub>-CH<sub>3</sub>), 26.59 (-S-CH<sub>2</sub>-CH<sub>3</sub>), 115.27 (Ar-C), 122.72 (Ar-C), 126.41 (Ar-C), 128.36 117 (Ar-C), 129.63 (Ar-C), 132.53 (Ar-C), 134.65 (Ar-C), 137.22 (Ar-C), 138.62 (Ar-C), 143.13 118 (Ar-C), 146.65 (Ar-C), 150.67 (Ar-C), 197.45 (CO), 203.21 (CO). HRMS *m*/*z*, 507.4636 (M-119 Na<sup>+</sup>: 507.3360).  $E_{1/2}$  (Ru<sup>II</sup>/Ru<sup>III</sup>): 1.22 V (ΔE = 110 mV);  $E_{1/2}$ (L/L<sup>•-</sup>): -0.47 V (ΔE = 50 mV) and 120  $E_{1/2}$ (L<sup>•-</sup>/L<sup>2-</sup>): -1.18 V (ΔE = 120 mV).

### 121 2.3. Crystal structure determination and refinement

Single crystals of 1 were obtained by slow diffusion of *n*-hexane into dichloromethane solution 122 of the complex. X-ray data were collected using an automated Bruker AXS Kappa smart Apex-II 123 diffractometer equipped with an Apex-II CCD area detector using a fine focus sealed tube as the 124 radiation source of graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Details of crystal 125 analyses, data collection and structure refinement are summarized in Table 1. Reflection data 126 were recorded using the  $\omega$  scan technique. The structure was solved and refined by full-matrix 127 least-squares techniques on  $F^2$  using the SHELX-97 [46]. The absorption corrections were done 128 by multi-scan (SHELXTL program package) and all the data were corrected for Lorentz, 129 polarization effect. Hydrogen atoms were included in the refinement process as per the riding 130 model. 131

#### 132 2.4. Computational method

Full geometry optimization was carried out by density functional theory (DFT) method using B3LYP hybrid exchange correlation functional for the complex [47, 48]. All elements except ruthenium were assigned the 6-31G(d) basis set, whilst the LanL2DZ basis set with effective core potential was employed for ruthenium atom [49-51]. Vibrational frequency calculations

were performed to ensure that the optimized geometries were local minima on the potential 137 energy surface and only positive Eigen values were obtained. All calculations were performed 138 with Gaussian09 program package [52] with the aid of the GaussView, Version 5 visualization 139 program [53]. Natural bond orbital analyses were performed using the NBO 3.1 module of 140 Gaussian09 [54, 55]. Vertical electronic excitations based on B3LYP optimized geometry were 141 computed using the time-dependent density functional theory (TDDFT) formalism [56-58] using 142 conductor-like polarizable continuum model (CPCM) [59-61] in acetonitrile to simulate the 143 solvent. GaussSum [62] was used to calculate the fractional contributions of various groups to 144 each molecular orbital. 145

#### 146 2.5. Procedure for catalytic oxidation of alcohols

Catalytic oxidation of primary alcohols to corresponding aldehydes and secondary alcohols to 147 ketones by ruthenium(II) complexes were studied in the presence of NMO as oxidant. A typical 148 149 reaction using the complex as a catalyst and primary or secondary alcohol, as substrate at 1:100 molar ratio was described as follows. A solution of complex 1 (0.01 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (25 mL) 150 was added to the mixture containing PhCH<sub>2</sub>OH (1 mmol), NMO (3 mmol) and molecular sieves. 151 The reaction mixture was refluxed and conversion of PhCH<sub>2</sub>OH to PhCHO was monitored 152 taking the reaction mixture at 10 minutes time interval. The solvent of the reaction mixture was 153 evaporated under reduced pressure. The residue was then extracted with diethyl ether, 154 concentrated to  $\approx 1$  mL. Conversions were determined by GC instrument equipped with a flame 155 ionization detector (FID) using a HP-5 column of 30 m length, 0.53 mm diameter and 5.00 µm 156 film thickness. The column, injector and detector temperatures were 200, 250 and  $250^{\circ}$ C 157 respectively. The carrier gas was N<sub>2</sub> (UHP grade) at a flow rate of 30 mL/min. The injection 158 volume of sample was 2 µL. The oxidation products were identified by GC co-injection with 159

authentic samples. No significant conversion was observed after 50 minutes. All other alcohols
were oxidized by refluxing the reaction mixture for 1 h and conversions were monitored
following the identical protocol.

#### 163 **3. Results and discussion**

#### 164 3.1. Synthesis and formulation

The thioether-containing ONS donor azo-phenol ligand (HL) was synthesized by diazo-coupling 165 reaction between 2-(ethylthio)benzenamine and 4-chlorophenol. It was characterized by 166 elemental analysis along with various spectroscopic techniques. <sup>1</sup>H NMR spectrum of HL in 167 CDCl<sub>3</sub> showed a singlet peak at 12.67 ppm corresponding to the phenolic-OH proton. The 168 aromatic protons are appeared at 7.02-7.95 ppm. The S-CH<sub>2</sub>CH<sub>3</sub> protons are observed as triplet 169 and quartet at 1.40 and 3.04 ppm (Fig. S1). IR spectrum of HL exhibits characteristic v(N=N) 170 peaks at 1421 cm<sup>-1</sup> along with broad v(O-H) peak at 3434 cm<sup>-1</sup> (Fig. S3). The ruthenium 171 carbonyl complex,  $[Ru(CO)_2(L)(Cl)_2]$  (1) was synthesized by the reaction of HL and 172  $[Ru(CO)_2Cl_2]_n$  in acetonitrile under reflux (Scheme 1). Both HL and complex 1 exhibit 173 satisfactory microanalytical and mass spectral data in CH<sub>3</sub>CN (see the Experimental Section). 174 The IR spectrum of 1 exhibits stretching at 1387 cm<sup>-1</sup> correspond to v(N=N). It is appeared at 175 lower frequency region compared to free ligand, which is supported the coordination of azo-N. 176 In addition, two sharp peaks are observed at 1997 and 2061 cm<sup>-1</sup> correspond to v(CO) with *cis* 177 configuration in the complex (Fig. S5). <sup>1</sup>H NMR spectrum of **1** exhibits slight downfield shifting 178 of aromatic protons. A sharp downfield shift of the quartet signal is observed for S-CH<sub>2</sub>CH<sub>3</sub> 179 protons (3.32 ppm), which is indicated the coordination of S atom to ruthenium in the complex 180 (Fig. S6). 181



Scheme 1. Synthesis of ruthenium carbonyl complex, [Ru(CO)<sub>2</sub>(L)(Cl)<sub>2</sub>] (1)

#### 190 *3.2. Crystal structure*

The X-ray crystallographic data collection and refinement parameters of 1 are given in Table 1. 191 Selected bond lengths and bond angles are given in Table 2. ORTEP plot of the molecular 192 structure with the atomic numbering scheme for 1 is shown in Fig. 1. The ruthenium atom adopts 193 a distorted octahedral geometry and is coordinated by two carbonyl ligands in a *cis* arrangement, 194 along with the coordination of azo-N and O atoms of the ligand, while the trans positions are 195 occupied by thiether-S and chlorine atoms. The deviation of the ruthenium coordination sphere 196 from the ideal octahedron is because of the small bite angles of the chelate rings (Ru1-O1-C1-197 C6-N2-N1) [80.76(14)°] and (Ru1-N1-C7-C12-S1) (80.08(11)°). The Ru-C(CO) (Ru1-C13, 198 1.936(3) and Ru1-C14, 1.942(4) Å) and C-O (C13-O2, 1.145(5) and C14-O3, 1.161(6) Å) bond 199 distances are found as expected for similar ruthenium carbonyl complexes [63, 64]. The N1-N2 200 bond length, 1.315(4) Å is quite elongated as compared to the expected free ligand azo distance 201 [65], supporting the strong  $d\pi(Ru) \rightarrow \pi^*(N=N)$  back donation in the complex. 202

203 3.3. Absorption and emission spectra

The solution spectrum of HL in acetonitrile exhibits two sharp intense peaks at 413 ( $\epsilon = 22539$  M<sup>-1</sup> cm<sup>-1</sup>) and 321 nm ( $\epsilon = 35442$  M<sup>-1</sup> cm<sup>-1</sup>), along with a shoulder at 446 nm. In ruthenium complex, the high energy intense band appears at 370 nm ( $\epsilon = 24246$  M<sup>-1</sup> cm<sup>-1</sup>) along with a shoulder at 342 nm, while the low energy band is red shifted compared to free ligand and observed at 555 nm ( $\epsilon = 11535$  M<sup>-1</sup> cm<sup>-1</sup>) (Fig. 2).

The free ligand (HL) does not exhibit any emission upon excitation in both the absorption 209 bands at 413 nm and 321 nm. However, upon excitation at 370 nm for complex 1, emission is 210 observed with emission maxima at 480 nm along with a shoulder at 440 nm (Fig. 3). The 211 emission quantum yields ( $\phi$ ) of the complex is 0.018. Lifetime data of the emission decay curve 212 was deconvoluted with respect to the lamp profile. The observed emission decay fits with bi-213 exponential profile with  $\chi^2 = 1.123$  (Fig. 4). We have used mean fluorescence lifetime ( $\tau_f = a_1 \tau +$ 214  $a_2\tau_2$ , where  $a_1$  and  $a_2$  are relative amplitude of decay process) to study the excited state stability 215 of the complex. The emission lifetime of the complex is found to be 3.66 ns. 216

#### 217 3.4. DFT computation and electronic structure

The geometry of HL and complex **1** were optimized by DFT method in singlet ground state using the B3LYP correlation functional. The optimized bond parameters for complex **1** are given in Table 2. The calculated bond distances and angles are well correlated with the X-ray crystal structure data.

The contour plots of selected molecular orbitals of HL are given in Fig. 5. The HOMO is concentrated on phenol moiety and is  $\pi$  character; the HOMO-1 and HOMO-2 are non-bonding in character and concentrated on S atom and azo moiety respectively. The LUMO has  $\pi^*(L)$ character with major contribution of  $\pi^*(N=N)$  orbital. The energy and compositions of some selected molecular orbitals of complex 1 are summarized in Table 3. Contour plots of some

selected molecular orbitals of 1 are given in Fig. 6. The HOMO is 85%  $\pi$ (L) character along with 227 reduced contribution of  $d\pi(Ru)$  in the complex. The HOMO-1 and HOMO-2 are mixed  $d\pi(Ru)$ 228 (22-26%) and  $p\pi$ (Cl) (62-67%) character. Other high energy occupied molecular orbitals 229 (HOMO-3 to HOMO-10) have mixed  $d\pi(Ru)$  and  $\pi(L)$  character. The low energy unoccupied 230 molecular orbital (LUMO) has 97%  $\pi^*(L)$  character with major contribution of  $\pi^*(N=N)$  orbital. 231 The significant contribution of  $d\pi(Ru)$  orbitals along with  $\pi^*(L)$  and  $\pi^*(CO)$  in LUMO+1 to 232 LUMO+5, indicative of the mixing of metal *d*-orbitals with ligand group of orbitals in the 233 complex. 234

To understand the nature of Ru-CO bonding, natural bond orbitals (NBOs) calculations 235 were performed on the optimized geometry of the complex. The occupancies and hybridizations 236 of the calculated Ru-C and C-O natural bond orbitals (NBOs) are summarized in Table 4. For 237 each carbonyl group three natural bond orbitals are detected for the C-O bond, and one orbital 238 for the Ru-C bond. The NBOs of Ru-C bonds have ~31% Ru and ~69% C character (bond order 239 Ru1-C13, 1.1990 and Ru1-C14, 1.0115). The  $sp^2$  hybridized NBOs of C–O bonds have ~30% C 240 and ~70% O character, while the NBOs, mostly having *p*-character, have reduced contribution 241 (~25%) of C and 75% character of O in the complex (bond order C13-O2, 2.1683 and C14-O3, 242 2.2056). 243

244

The bonding between CO ligands and Ru atom is supported by the resonance structure

M—C=O: from the calculated atomic charges (Table 4). The calculated natural charges on the carbon atoms of the carbonyl ligands are positive, whereas the oxygen atoms are negatively charged. The calculated charge on the ruthenium atom (-0.726 a.u.) is considerably lower than the formal charge (+2). The populations of the  $4d_{xy}$ ,  $4d_{xz}$ ,  $4d_{yz}$ ,  $4d_{x}^{2}$ ,  $y^{2}$  and  $4d_{z}^{2}$  of the ruthenium atom are 1.7273, 1.8137, 1.7497, 1.1309 and 1.0913.

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#### 250 3.4. TDDFT calculation and electronic spectra

To interpret the electronic spectra singlet-singlet vertical electronic excitations were carried out 251 by TDDFT/CPCM method in acetonitrile. The sharp intense peaks of HL at 413 and 321 nm 252 correspond to HOMO  $\rightarrow$  LUMO and HOMO-3  $\rightarrow$  LUMO transitions and have  $\pi \rightarrow \pi^*$  character. 253 The HOMO-3  $\rightarrow$  LUMO transition (n  $\rightarrow \pi^*$ ) corresponds to the shoulder peak at 446 nm (Table 254 5). In complex 1, the low energy band at 555 nm corresponds to HOMO  $\rightarrow$  LUMO transition 255 having intra-ligand charge transfer (ILCT) character along with minor contribution of metal to 256 ligand charge transfer (MLCT) transition. The band at 370 nm has mixed halogen to ligand 257 charge transfer (XLCT) and MLCT character. In addition, ligand centered transition (HOMO-3 258  $\rightarrow$  LUMO) is observed at 344 nm. 259

#### 260 3.5. Electrochemistry

The electrochemical behavior of the complex was investigated by cyclic voltammetry (CV) in 261 presence of Bu<sub>4</sub>NPF<sub>6</sub> in MeCN at scan rate 50 mV S<sup>-1</sup>. Complex 1 exhibits one quasireversible 262 oxidation couple at 1.22 V ( $\Delta E = 110 \text{ mV}$ ) along with one reversible reduction couple at -0.47 V 263  $(\Delta E = 50 \text{ mV})$  and a quasireversible reduction with  $E_{1/2}$ , -1.18 V ( $\Delta E = 120 \text{ mV}$ ), positive and 264 negative to reference electrode respectively (Ag/AgCl) in the potential range 2.0 to -2.0 V (Fig. 265 7). The oxidation is assigned as Ru(II) to Ru(III) oxidation, while the two successive reduction 266 couples correspond to the reduction of azo ligand with the formation of  $L^{\bullet-}$  and  $L^{2-}$  respectively. 267 3.6. Catalytic oxidation 268

The catalytic activities of our synthesized ruthenium complex (1) towards the oxidation of primary and secondary alcohols were tested in dichloromethane in the presence of NMO oxidant. In order to optimize the reaction conditions, different substrate:catalyst ratios in presence of NMO were carried out and the results are summarized in Table 6. For these initial experiments

benazyl alcohol was selected as a test-substrate and allowed it to react with catalytic quantities of 273 complex in dichloromethane in presence of NMO. In the C:S ratio 1:50 and 1:100 the conversion 274 of benzyl alcohol to benzaldehyde is almost same but with increasing the C:S ratio to 1:200 or 275 1:300, the reaction still proceeds smoothly accompanied by a moderate drop in conversions 276 while in C:S ratio 1:500 sharp drop in conversion is observed. Thus, it was concluded that 277 catalyst:substrate ratio is 1:100 in presence of NMO is the best compromise between optimal 278 conversion in dichloromethane. Other alcohols like, 2-butanol, 1-phenylethanol, cyclopentanol, 279 cyclohexanol, cycloheptanol and cycloctanol selectively converted into corresponding carbonyl 280 compounds with 1 mol% of catalyst in presence of NMO. A series of reactions were carried out 281 282 with either the ruthenium complex or NMO only under identical condition but there was no detectable oxidation in absence ruthenium complex or NMO. 283

Complex (1) oxidizes primary alcohols to corresponding aldehydes and secondary 284 285 alcohols to ketones with moderate to high conversion (77-88%) (Table 7). The isolated yield for the oxidation of 2-butanol to 2-butanone is reduced to 45% may be due to the loss of volatitle 2-286 butanone. Results of the investigations suggest that the ruthenium complex efficiently reacts with 287 NMO to yield a high valent ruthenium-oxo species [66, 67], which is capable of oxygen atom 288 transfer to alcohols. This is further supported by the appearance of a new stretching band at 858 289 cm<sup>-1</sup> (Fig. S9), characteristic of Ru(IV)=O species in the IR spectrum of the solid mass of the 290 reaction mixture obtained by evaporation of the resultant solution to dryness [68-70]. Further 291 support in favour of the formation such species identified by the appearance of a new peak at 398 292 nm corresponds to the formation of Ru(IV)=O [71] in the UV-Vis spectrum of a 293 dichloromethane solution of the complex in presence of NMO (Fig. 8). The appearance of a new 294 peak at 398 nm corresponds to the formation of Ru(IV)=O species [71]. The complex catalyzes 295

the oxidation of benzyl alcohol to benzaldehyde with 77% conversion. In case of cyclohexanol the oxidation product cyclohexanone is 88%. The catalytic efficiency of our synthesized complex is less when we compared to the catalytic efficiency of some reported ruthenium complexes reported earlier [72-74]. However, the present complex shows catalytic activity comparable to our previously reported ruthenium complexes [16, 27, 28] and even shows better catalytic activity than the other ruthenium(II) complexes reported earlier [75].

302

#### 303 **4. Conclusion**

We have synthesized and characterized a ruthenium carbonyl complex (1) of ONS donor thioether ligand (HL). X-ray structure of 1 confirmed the pseudo-octahedral geometry around ruthenium centre. The metal based oxidation and ligand based reduction processes were studied by cyclic voltammetric studies. The electronic structure of the complex was interpreted by DFT calculations. The ruthenium(II) catalyzed oxidation of alcohols was studied and showed moderate to high yield.

#### 310 Acknowledgement

Financial support received from the Department of Science and Technology, New Delhi, India is
gratefully acknowledged. P. Roy and A. Sau Mondal thankful to UGC, New Delhi, India for
fellowships.

314 Supplementary materials

Crystallographic data for the structure **1** was deposited with the Cambridge Crystallographic Data center with the CCDC No. 1478954. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (e-mail: <u>deposit@ccdc.cam.ac.uk</u> or www:htpp://www.ccdc.cam.ac.uk).

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- 437

		440
Formula	$C_{16}H_{12}Cl_2N_2O_3RuS$	4.4.1
Formula Weight	484.31	441
Crystal System	Triclinic	442
Space group	$P\overline{1}$	443
a, b, c [Å]	10.155(5), 10.431(5), 11.691(5)	444
α	85.132(5)	445
β	67.245(5)	146
γ	65.176(6)	440
V [ Å <sup>3</sup> ]	1003.6(8)	447
Z	2	448
D(calc) [g/cm <sup>3</sup> ]	1.603	449
Mu(MoKa) [ /mm]	1.167	450
F(000)	480	450
Absorption Correction	multi-scan	451
Temperature (K)	293(2)	452
Radiation [Å]	0.71073	453
θ(Min-Max) [°]	1.92-26.37	454
Dataset (h; k; l)	-12 to 12; -12 to 12; -14 to 14	455
Total, Unique Data, R(int)	14616, 4061, 0.0262	455
Observed data $[I > 2\sigma(I)]$	3815	456
Nref, Npar	4061, 217	457
$R, wR_2$	0.0707, 0.1791	458
$\Delta q(max)$ and $\Delta q(min) [e/Å^3]$	0.245 and -0.124	450
Goodness of fit(S)	1.088	4JJ
X		460

439	Table 1. Crystallographic data and refin	ement parameters of $[Ru(CO)_2(L)(Cl)_2]$ (1)
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	X7	C 1	465
Bonds(A)	X-ray	Calc.	466
Ru1-Cl2	2.3900(17)	2.422	
Ru1-S1	2.3965(17)	2.431	467
Ru1-O1	2.125(4)	2.112	468
Ru1-N1	2.081(2)	2.130	469
Ru1-C13	1.936(3)	1.927	470
Ru1-C14	1.942(4)	1.919	
O2-C13	1.145(5)	1.149	4/1
O3-C14	1.161(6)	1.152	472
N1- N2	1.315(4)	1.296	473
			474
Angles(°)	X-ray	Calc.	175
O1-Ru1-C13	94.51(12)	91.67	475
O1-Ru1-C14	172.55(11)	173.55	476
O1-Ru1-Cl2	91.36(11)	89.57	477
O1-Ru1-S1	92.92(11)	94.88	478
O1-Ru1-N1	80.76(14)	80.46	170
O2-C13-Ru1	178.6(4)	177.82	475
O3-C14-Ru1	175.7(4)	176.67	480
N1-Ru1-C13	171.77(18)	171.75	481
N1-Ru1-C14	92.24(16)	94.85	482
N1-Ru1-Cl2	94.95(10)	93.02	483
N1-Ru1-S1	80.08(11)	78.71	
S1-Ru1-C13	93.53(15)	96.63	484
S1-Ru1-C14	88.35(15)	90.30	485
S1-Ru1-Cl2	172.83(4)	169.85	486
Cl2-Ru1-C13	91.88(15)	90.12	487
Cl2-Ru1-C14	86.68(15)	86.66	100
C13-Ru1-C14	92.7(2)	91.21	4ŏŏ

# 464 Table 2. Selected X-ray and calculated bond distances and angles of $[Ru(CO)_2(L)(Cl)_2]$ (1)

МО	Energy		% Co	mposition	
		Ru	Cl	СО	L
LUMO+5	-0.44	17	0	59	24
LUMO+4	-0.77	25	03	37	35
LUMO+3	-0.90	24	01	70	05
LUMO+2	-1.16	18	0	08	74
LUMO+1	-1.41	53	07	10	20
LUMO	-2.59	02	0	01	97
НОМО	-5.47	11	03	01	85
HOMO-1	-6.31	26	62	03	09
HOMO-2	-6.37	22	67	03	08
HOMO-3	-6.60	04	05	01	90
HOMO-4	-6.84	30	04	06	60
HOMO-5	-7.31	09	04	03	84
HOMO-6	-7.63	36	20	05	39
HOMO-7	-7.70	22	06	03	69
HOMO-8	-7.70	19	39	08	34
HOMO-9	-7.89	19	16	05	60
HOMO-10	-8.27	50	10	12	28

489	Table 3.	Energy a	nd composit	ions of	some selected	molecular	orbitals of	f 1
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# 494 Table 4. Hybridization and Occupancy of M–C(CO), C–O(CO) and N=N(azo) bonds and NBO

## 495 atomic charges of **1** obtained from NBO analysis

		Bond			NBO cha	arges
Bonds	Occupancy	order	Contribution	Hybridization	atoms	charge
Ru1-C13	1.8929(0.0912)	1.1990	31.32%Ru + 68.68%C	$Ru(sp^{2.16}d^{1.48}) + C(sp^{0.53})$	Ru1	-0.7258
Ru1-C14	1.8905(0.0970)	1.0115	29.32%Ru + 70.68%C	$Ru(sp^{2.48}d^{1.44}) + C(sp^{0.52})$	C12	-0.3923
Ru1-N1	1.9052(0.1618)	0.5420	19.07%Ru + 80.93%N	$Ru(sp^{3.36}d^{2.58}) + N(sp^{1.80})$	S1	0.5824
C13-O2	1.9973(0.1364)	2.1683	25.54%C + 74.46%O	$C(sp^{52.26}) + O(sp^{39.95})$	N1	-0.1530
	1.9974(0.1497)		25.23%C + 74.77%O	$C(sp^{99.99}) + O(sp^{99.99})$	N2	-0.1417
	1.9955(0.0168)		30.42%C + 69.58%O	$C(sp^{1.99}) + O(sp^{1.27})$	C13	0.7913
C14-O3	1.9977(0.1183)	2.2056	25.24%C + 74.76%O	$C(sp^{99.99}) + O(sp^{99.99})$	C14	0.8096
	1.9970(0.1090)		25.59%C + 74.41%O	$C(sp^{42.71}) + O(sp^{30.52})$	O2	-0.4259
	1.9906(0.0153)		30.07%C + 69.93%O	$C(sp^{2.04}) + O(sp^{1.29})$	O3	-0.4177
N1-N2	1.9861(0.0162)	1.0975	51.48%N1 + 48.52%N2	$N1(sp^{2.24}) + N2(sp^{2.27})$		
	1.9045(0.4742)		59.54%N1 + 40.46%N2	$N1(sp^{99.99}) + N2(sp^{99.99})$		

Compd.	$\lambda$ (nm)	E (eV)	Osc.	Key excitations	Character	$\lambda_{expt.}(nm)$
			Strength (f)			$(\epsilon, M^{-1}cm^{-1})$
	486.63	2.5478	0.0030	(71%)HOMO-1→LUMO	$n \rightarrow \pi^*$	446 (sh.)
HL	424.93	2.9178	0.1656	(72%)HOMO→LUMO	$\pi \rightarrow \pi^*$	413 (22539)
	330.06	3.7564	0.4865	(69%)HOMO-3→LUMO	$\pi { ightarrow} \pi^*$	321 (35442)
	547.2	2.2658	0.1002	(95%)HOMO→LUMO	$\pi(L)/d\pi(Ru) \rightarrow \pi^*(L)$	555 (11535)
1	401.6	3.0873	0.0064	(84%)HOMO→LUMO+1	$\pi(\mathbf{L}) \rightarrow d\pi(\mathbf{R}\mathbf{u})$	
1	367.4	3.3744	0.2355	(49%)HOMO-2→LUMO	$d\pi(\mathrm{Ru})/p\pi(\mathrm{Cl}) \rightarrow \pi^*(\mathrm{L})$	370 (24246)
				(45%)HOMO-1→LUMO		
	343.7	3.6073	0.0863	(69%)HOMO-3→LUMO	$\pi(L) \rightarrow \pi^*(L)$	342 (sh.)
				$\overline{\mathbf{A}}'$		

507 Table 5. Vertical electronic transition calculated by TDDFT/CPCM method of HL and complex
508 1

Conversion (%)<sup>b</sup>

	1	1:50	77	
	2	1:100	77	
	3	1:200	73	
	4	1:300	65	
	5	1:500	52	
522				
523	<sup>a</sup> Substrate (1	mmol); NMO (3 mm	ol); complex (0.01 n	nmol); solvent dichloromethane; ten
524	40°C.			$ \rightarrow $
525	<sup>b</sup> Conversions	s determined by GC		
526				
527			A A A A A A A A A A A A A A A A A A A	
528				
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534				
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536				
537				

# **521** Table 6. Optimization of oxidation reaction by PhCH<sub>2</sub>OH with $\mathbf{1}^{a}$

C:S ratio

Entry

Substrate	Product	Conversion (%)	Isolated yield (%)
Benzyl alcohol	Benzaldehyde	77	71
2-Butanol	2-Butanone	79	45
1-Phenylethanol	Acetophenone	83	76
Cyclopentanol	Cyclopentanone	81	68
Cyclohexanol	Cyclohexanone	88	75
Cycloheptanol	Cycloheptanone	85	80
Cycloctanol	Cycloctanone	79	75

538 Table 7. Catalytic oxidation of alcohols by Ru(II) complex I using NMO as oxi
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<sup>a</sup> Substrate (1 mmol); NMO (3 mmol); complex (0.01 mmol); solvent dichloromethane;Temp.

 $40^{\circ}$ C; Conversions determined by GC instrument equipped with a flame ionization detector

542 (FID) using a HP-5 column of 30 m length, 0.53 mm diameter and 5.00  $\mu$ m film thickness.

# Fig. 2. UV-Vis spectra of HL (–) and 1 (–) in acetonitrile Fig. 3. Emission spectrum of 1 in acetonitrile ( $\lambda_{excitation} = 370$ nm) Fig. 4. Exponential decay profiles of prompt (**III**) and **1** (**•••**) in acetonitrile ( $\lambda_{\text{excitation}} = 370 \text{ nm}$ ) Fig. 5. Contour plots of selected molecular orbitals of HL Fig. 6. Contour plots of selected molecular orbitals of 1 Fig. 7. Cyclic voltammogram of 1 in acetonitrile Fig. 8. UV-Vis spectra of 1 (-) and [1 + NMO] (-) in dichloromethane

**Figure captions** 

Fig. 1. ORTEP plot of **1** with 35% ellipsoidal probability



















# HIGHLIGHTS

Ruthenium carbonyl complex of a redox non-innocent ONS donor azophenol ligand: Electrochemistry, photophysical property, electronic structure and catalytic activity towards oxidation of alcohols

Puspendu Roy, Apurba Sau Mondal, Ajoy Kumar Pramanik and Tapan Kumar Mondal<sup>\*</sup>

- A ruthenium carbonyl complex of a redox non-innocent thioether-containing azo-phenol ligand has been synthesized and characterized.
- Cyclic voltammetric study has been used to interpret the redox properties.
- Absorption and emission properties have been studied.
- Catalytic oxidation of alcohols has been studied in presence of NMO.
- DFT calculations have been used to interpret the electronic structure.