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GRAPHICAL ABSTRACT



Osmium-hydride-carbonyl complex with thioether containing Schiff base ligand: Synthesis, crystal structure, electrochemistry and catalytic transfer hydrogenation

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Abstract

A new osmium(II) carbonyl complex, $[Os(H)(CO)(PPh_3)_2(L)]$ (1) with thioether containg NNS donor ligand (where L = 2-(ethylthio)-N-((pyridine-2-yl)methylene))benzenamine) is synthesized and characterized by various spectroscopic techniques. The distorted octahedral environment around osmium in the complex is confirmed by single crystal X-ray structure. Cyclic voltammogram in acetonitrile exhibits Os(II)/Os(III) oxidation and ligand based reduction. The complex effectively catalyzed the transfer hydrogenation reaction of ketones in high yields in *i*-PrOH. The electronic structure and redox properties are interpreted by DFT studies.

Keywords: Osmium carbonyl complex; X-ray structure; Electrochemistry; DFT calculation; Transfer hydrogenation.

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1. Introduction

The search for highly efficient transition metal homogeneous catalysts is a current issue of industrial relevance for the synthesis of valuable organic compounds. In this context, ruthenium and more recently osmium complexes are among the preferred metals because of their high performance and versatility in a variety of processes [1]. Transfer hydrogenation is one of the most important methods for the reduction of carbonyl compounds to their corresponding alcohols [2-4] without the use of hazardous hydrogen gas or moisture-sensitive hydride reagents [5, 6]. Moreover, the transfer hydrogenation is widely accepted in industry as a cost-effective way for the production of a number of hydroxylated organic products [7]. The catalytic hydrogenation of carbonyl compounds are an elementary process for generated varieties of alcohols including chiral compounds, which are ultimate worthy products and precursors for the agrochemical, pharmaceutical, flavor, materials, and fine chemical industries [8-10].

The studies to develop the new catalysts for the transfer hydrogenation is still of considerable interest for the finding of more efficient catalyst. The most efficient and selective catalyst for transfer hydrogenation reactions are ruthenium, iridium and rhodium complexes [11-15], while the osmium complexes are rarely used [16,17]. As a part of our ongoing research on the synthesis, characterization and catalytic applications of transition metal complexes [18-22] and to explore the chemistry of osmium carbonyls, herein we have synthesized a osmium(II) carbonyl complex, $[Os(H)(CO)(PPh_3)_2(L)]Cl$ (1) bearing triphenylphosphine with thioether containing Schiff base ligand, 2-(ethylthio)-N-((pyridine-2-yl)methylene)benzenamine (L). An array of tools including X-ray diffractometry, electrochemistry, and electronic absorption and emission spectroscopy abetted with DFT calculations were used to characterize the complex.

Further, the catalytic activity of the complex towards transfer hydrogenation of ketones was investigated.

2. Experimental

2.1. Materials

2-(Ethylthio)-N-((pyridine-2-yl)methylene)benzenamine (L) was synthesized following the reported procedure [23]. 2-Aminothiophenol, ethyl iodide, 2-formylpyridine and $K_2OsCl_6.6H_2O$ were purchased from Sigma Aldrich. [Os(H)(Cl)(CO)(PPh₃)₃] was synthesized by reported method [24]. All other chemicals and solvents were reagent grade and used as received.

2.2. Physical measurements

Microanalyses (C, H, N) data were obtained using a PerkinElmer Series-II CHN-2400 CHNS/O elemental analyzer. Electronic spectra were measured on a Lambda 750 PerkinElmer spectrophotometer in methanol. IR spectra were recorded on a RX-1 PerkinElmer spectrometer in the range of 4000-400 cm⁻¹ with the samples in the form of KBr pellets. Fluorescence spectra were taken on a Shimadzu RF-6000 Spectrofluorophotometer. HRMS mass spectra were obtained on a Waters (Xevo G2 Q-TOF) mass spectrometer. NMR spectra were recorded in CDCl₃ 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. [Bu₄N]PF₆ was used as the supporting electrolyte in acetonitrile and the scan rate used was 50 mV s⁻¹ under nitrogen atmosphere.

Luminescence quantum yield was determined using carbazole as reference with a known ϕ_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:

 $\phi_{S}/\phi_{R} = [A_{S} / A_{R}] x [(Abs)_{R} / (Abs)_{S}] x [\eta_{S}^{2}/\eta_{R}^{2}]$

Here, ϕ_S and ϕ_R are the luminescence quantum yield of the sample and reference, respectively. A_S and A_R are the area under the emission spectra of the sample and the reference respectively, (Abs)_S and (Abs)_R are the respective optical densities of the sample and the reference solution at the wavelength of excitation, and η_S and η_R are the values of refractive index for the respective solvent used for the sample and reference.

Fluorescence lifetime was measured using a time-resolved spectrofluorometer from IBH, UK. The instrument uses a picoseconds diode laser (NanoLed-03, 370 nm) as the excitation source and works on the principle of time-correlated single photon counting [25]. The goodness of fit was evaluated by χ^2 criterion and visual inspection of the residuals of the fitted function to the data.

2.3. Synthesis of [Os(H)(CO)(PPh₃)₂(L)]Cl (1)

To a suspension of $[Os(H)(Cl)(CO)(PPh_3)_3]$ (0.223 g, 0.2 mmol) in dry toluene (20 mL), 2-(ethylthio)-N-((pyridine-2-yl)methylene))benzenamine (L) (0.048 g, 0.2 mmol) was added and the reaction mixture was refluxed for 10 h under N₂ atmosphere to yield a dark brown solution. The solvent was then removed under reduced pressure and the solid product of complex **1** was washed with *n*-hexane several times to remove the PPh₃. The product was air dried and collected. Yield, 0.161 g (77%).

Anal. Calc. for C₅₁H₄₆ClN₂OOsP₂S (1): Calculated C, 55.90; H, 4.53; N, 2.74; S, 3.14. Found: C, 55.6; H, 4.4; N, 2.6; S, 2.9. FT–IR *v*(KBr, cm⁻¹): 2060 (Os-H), 1926(CO), 1582(C=N). ¹H NMR (CDCl₃, ppm): -9.85 ppm of Os-H peak (${}^{2}J_{P-H}$, t, *J* = 20.3 Hz), 1.60 (3H, quartet , *J* = 7.6 Hz), 3.40 (2H, t, *J* = 8.2 Hz), 7.21 - 7.43 ppm (34H, m), 8.12 (1H, t, *J*=7.2 Hz), 8.41 (1H, d, *J*=4.4 Hz), 8.51 (1H, d, *J*=4.8 Hz), 8.70 (1H, s). ${}^{13}C$ { ^{1}H } NMR (CDCl₃, ppm): 204.5 (C=O), 155.2 (-HC=N), 117.2-141.6 (Ar C), 27.1 (-S-CH₂-CH₃), 15.2 (-S-CH₂-CH₃). ${}^{31}P$ { ^{1}H } NMR (CDCl₃, ppm): 18.2 (s). UV-Vis in acetonitrile (λ (nm); ε , M⁻¹cm⁻¹): 471 (3424), 375 (6308), 315 (16433). ESI-MS *m/z*: 987.4106. E_{1/2} (Os^{II}/Os^{III}): 1.15 V (ΔE = 90 mV); E_{pc}: -1.11 V.

2.4. Crystal structure determination and refinement

Single crystals of **1** were obtained by slow diffusion of *n*-hexane into dichloromethane solution of the complex. X-ray data were collected using an automated Bruker AXS Kappa smart Apex-II diffractometer equipped with an Apex-II CCD area detector using a fine focus sealed tube as the radiation source of graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Details of crystal analyses, data collection and structure refinement are summarized in Table 1. Reflection data were recorded using the ω scan technique. The structure was solved and refined by full-matrix least-squares techniques on F^2 using the SHELX-97 [26]. The absorption corrections were done by multi-scan (SHELXTL program package) and all the data were corrected for Lorentz, polarization effect. Hydrogen atoms were included in the refinement process as per the riding model.

2.5. Computational method

Full geometry optimization was carried out by density functional theory (DFT) method using B3LYP hybrid exchange correlation functional for the complex [27,28]. All elements except osmium were assigned the 6-31G(d) basis set, whilst the LanL2DZ basis set with effective core potential was employed for ruthenium atom [29-31]. Vibrational frequency calculations were performed to ensure that the optimized geometries were local minima on the potential energy

surface and only positive Eigen values were obtained. All calculations were performed with Gaussian09 program package [32] with the aid of the GaussView, Version 5 visualization program [33]. Vertical electronic excitations based on B3LYP optimized geometry were computed using the time-dependent density functional theory (TDDFT) formalism [34-36] using conductor-like polarizable continuum model (CPCM) [37-39] in acetonitrile to simulate the solvent. GaussSum [40] was used to calculate the fractional contributions of various groups to each molecular orbital.

2.6. Procedure for catalytic transfer hydrogenation

In a typical experiment the ketone (1 mmol), KOH (0.1 mmol), and osmium(II) complex (0.002 mmol) were added to 10 mL of 2-propanol, and the mixture was stirred at 80 °C in an inert atmosphere. The reaction was then monitored at various time intervals by the use of GC. After the reaction was complete, 2-propanol was removed on a rotary evaporator, and the resulting semisolid was extracted with diethyl ether (5 × 10 mL). The extract was passed through a short column of silica gel. The column was washed with ~100 mL of diethyl ether. All the eluates from the column were mixed, and the solvent from the mixture was evaporated off on a rotary evaporator. The resulting residue was dissolved in 2-3 mL of hexane. Conversions were determined by GC instrument equipped with a flame ionization detector (FID) using a HP-5 column of 30 m length, 0.53 mm diameter and 5.00 μ m film thickness. The column, injector and detector temperatures were 200, 250 and 250 °C respectively. The carrier gas was N₂ (UHP grade) at a flow rate of 30 mL/min. The injection volume of sample was 2 μ L. The alcohols were identified by GC co-injection with authentic samples.

3. Results and discussion

3.1. Synthesis and spectral characterization

The pseudo octahedral osmium(II) carbonyl complex, $[Os(H)(CO)(PPh_3)_2(L)]Cl(1)$ (where L = 2-(ethylthio)-N-((pyridine-2-yl)methylene))benzenamine) was synthesized and characterized by several spectroscopic techniques. The complex was synthesized by the reaction of [Os(H)(Cl)(CO)(PPh₃)₃] and L in dry toluene under refluxing condition for 10 h (Scheme 1). IR spectrum of the ligand shows a number of strong v(C-H) bands at 2800–3100 cm⁻¹. IR spectrum of the complex exhibits sharp signal at 1926 cm⁻¹ corresponds to v(CO) along with a close by weak peak at 2060 cm⁻¹ corresponding to ν (Os-H). The ν (C=N) is significantly shifted to lower frequency region compare to free ligand value suggesting the coordination of imine-N to osmium [23]. ¹H NMR spectrum of the complex was taken in CDCl₃. All the expected signals including aromatic protons are resolved. In the ¹H NMR spectrum, S-CH₂CH₃ protons appeared at 1.60 ppm and 3.40 ppm. The triplet signal at -9.85 ppm (${}^{2}J_{P-H}$, t, J=20 Hz) confirms the presence of Os-H proton in the complex. A series of overlapping multiplet signals appeared in the region 7.2 to 8.7 ppm correspond to the protons of coordinated triphenylphosphine in the complex. The UV-vis spectrum of the complex in acetonitrile exhibits a broad peak at 471 nm (ϵ , 3424 M⁻¹cm⁻ ¹) along with two ligand centered peaks at 375 (ϵ , 6308 M⁻¹cm⁻¹) and 315 (ϵ , 16433 M⁻¹cm⁻¹) in acetonitrile (Fig. 1).



Scheme 1. Synthesis of osmium carbonyl complex, [Os(H)(CO)(PPh₃)₂(L)]Cl (1)

Upon excitation at 375 nm, an emission band at 477 nm with emission quantum yield (ϕ) = 0.025 is observed for the complex in acetonitrile (Fig. 1). Lifetime data of the complex was taken at 298 K in acetonitrile when excited at 370 nm. The emission decay curve was deconvoluted with respect to the lamp profile. The observed florescence decay fits with biexponential nature (Fig. 2). We have used mean fluorescence lifetime ($\tau_f = a_1\tau_1 + a_2\tau_2$, where a_1 and a_2 are relative amplitude of decay process) to study the excited state stability of the complex. The luminescence lifetime of the complex is found to be 2.63 ns.

3.2. Molecular Structure

The molecular structure of the complex was confirmed by single X-ray crystal structure study. Selected bond distances and bond angles are summarized in Table 2. ORTEP plot with atomic numbering is shown in Fig. 3. The molecule consists of a central osmium surrounded by six donor centers, and the arrangement is distorted octahedral. The atomic arrangement involves two *trans*-PPh₃, chelating NN donors, hydrido (H) and CO *trans* to the pyridyl-N donor within the OsP₂N₂HC coordination sphere. The thioether containing NNS donor ligand coordinated through imine-N and pyridyl-N atoms to the osmium centre, while –SR remain free and away from the metal centre. The H⁻ is located *trans* to the imine-N. The deviation of osmium coordination sphere from ideal octahedron is because of the small bite angle of the five membered chelate ring (Os1-N1-C6-C7-N8) [74.5(2)°]. The Os-N(imine) (Os1-N8, 2.168(6) Å) is significantly longer than Os-N(pyridyl) (Os1-N1, 2.103(6) Å) distance. The *trans* phosphine angle P1-Os1-P2 of 168.23(6)° is found to be in the reported range [41].

3.3. DFT and TDDFT calculations

The geometry of complex **1** was optimized by DFT/B3LYP method to interpret the electronic structure. Optimized bond distances and angles are well correlated with the X-ray crystal

structure data (Table 2). The energy and compositions of selected molecular orbitals are summarized in Table 3. Contour plots of selected molecular orbitals are given in Fig. 4. HOMO, HOMO-2 and HOMO-3 of the complex are composed of $d\pi$ (Os) (49-55%) orbitals, the HOMO-1 is 94% π (L) character. The LUMO and LUMO+1 have 91-94% π^* (L) character, while LUMO+2 to LUMO+5 have π (PPh₃)character. The HOMO-LUMO energy gap is calculated to be 3.07 eV.

To go deep insight into the electronic transitions in the complex vertical electronic transitions were calculated using TDDFT/CPCM method in acetonitrile. The calculated vertical electronic transitions are summarized in Table 4. The experimental band at 471 nm corresponds to the admixture of HOMO \rightarrow LUMO (λ = 485 nm, f = 0.0622) and HOMO-1 \rightarrow LUMO (λ = 452 nm, f = 0.0904) transitions having mixed MLCT and ILCT character. The band at 375 and 315 nm corresponds to $\pi(L) \rightarrow \pi^*(L)$ transitions having ILCT character.

3.4. Electrochemistry

The electrochemical behavior of the complex was investigated by cyclic voltammetry (CV) in acetonitrile using tetrabutylammonium hexafluorophosphate [Bu₄N]PF₆ (0.1 M) as supporting electrolyte and a Ag/AgCl reference electrode. When scanned in the potential range of -2.0 to 2.0 V, the complex exhibits one irreversible cathodic reduction peak at -1.11 V along with a quasi-reversible oxidation couple with $E_{1/2}$, 1.11 V ($\Delta E = 90$ mV) (Fig. 5). The irreversible cathodic reduction peak corresponds to the ligand centered reduction as the LUMO of the complex has 91% $\pi^*(L)$ character. The oxidation process may be assigned as Os(II)/Os(III) oxidation couple as HOMO has 55% $d\pi$ (Os) character.

3.5. Catalytic transfer hydrogenation reactions

The transfer hydrogenation is an important and efficient reaction in organic synthesis. The ruthenium(II) [41-43], rhodium [44-46] and iridium [47,48] complexes were used exclusively as effective catalysts for transfer hydrogenation reactions. In comparison the catalytic properties of osmium complexes is less explored [13]. That encourages us to synthesize new osmium-hydrido-carbonyl complex and explore its catalytic properties towards transfer hydrogenation of ketones. The results of the screening of the catalytic properties of complex **1** are described below.

In order to optimize the reaction conditions such as base, reaction time and catalyst:substrate (C:S) ratios, the transfer hydrogenation of acetophenone to 1-phenylethanol in presence of complex 1 as catalyst using *i*-PrOH as the solvent was carried out (Table 5). The conversion rates were varied significantly with the base employed and a variety of base was screened. The conversions were found to be very effective when KOH or NaOH was used as base. The reaction rates were significantly decreased when weak base like Na₂CO₃ and CH₃COONa were used. A moderate conversion was observed in presence of KO^tBu as base. The progress of the conversion was also monitored with time to time and it was found that the formation of 1-phenylethanol initially increased with the progress of the reaction and after 5 h no appreciable change in conversion rate was observed. Again, to understand the catalytic efficiency of the complex 1, different catalyst:substrate (C:S) ratios were tested. It is found that the conversion is excellent in C:S ratio of 1:300 and with the variation of C:S ratio to 1:500, 1:700, 1:1000 or 1:1500, the reaction still proceeds but a sharp decrease in rate of conversion is observed for C:S ratio 1:700 to 1:1500. The conversion (96%) is excellent with appreciable turnover number (TON) when the C:S ratio is 1:500 and thus from this study it may be concluded that this C:S ratio is the best choice for catalytic transfer hydrogenation reactions for complex 1. A series of ketones were screened in transfer hydrogenation reaction using the

optimum condition, C:S ratio of 1:500 and KOH as base. The results are summarized in Table 6. The maximum conversion was observed for *p*-methoxycetophenone (98.2%). The conversions of other acetophenones are found to be in the range 88-98%.

4. Conclusion

Herein, a new osmium(II) carbonyl complex, $[Os(H)(CO)(PPh_3)_2(L)]$ (1) with thioether containg NNS donor ligand (where L = 2-(ethylthio)-N-((pyridine-2-yl)methylene))benzenamine) is synthesized and characterized by various spectroscopic techniques. X-ray structure confirms the distorted octahedral environment around osmium. Cyclic voltammogram exhibits Os(II)/Os(III) oxidation and ligand based reduction. The redox properties are well interpreted by theoretical studies. Vertical electronic transitions calculated by TDDFT/CPCM method are used to interpret the UV-Vis spectrum of the complex and a good correlation between experimental bands with calculated transitions are observed. Moreover, the complex effectively catalyzed the transfer hydrogenation reaction of ketones with high yields in *i*-PrOH.

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Supplementary materials

Crystallographic data for the structure **1** has been deposited with the Cambridge Crystallographic Data center, CCDC No. 804954. 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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Empirical formula	$C_{52}H_{47}Cl_3N_2OSP_2Os$
Formula weight	1106.51
Crystal system	Triclinic
Space group	Pī
<i>a</i> / Å	13.7098(3)
b / Å	14.3084(3)
<i>c</i> / Å	15.1566(5)
α (°)	104.4660(10)
β(°)	107.1100(10)
γ(°)	107.5110(10)
V / Å ³	2516.31(11)
Ζ	2
$ ho_{ m calcd}$ / g cm ⁻³	1.460
μ / mm ⁻¹	2.836
<i>T</i> / K	293(2)
<i>hkl</i> range	-17 to 17, -18 to 18, -19 to 19
<i>F</i> (000)	1108
θ range (°)	1.70 to 27.32
Reflns collected	38855
Unique reflns (<i>R</i> _{int})	11338
Observed data ($I > 2\sigma(I)$)	10250
Data/restraints/parameters	11338 / 0 / 542
R1 ^a , wR2 ^b ($I > 2\sigma(I)$)	0.0661, 0.1855
R1, wR2 (all data)	0.0714, 0.1914
GOF ^c	1.071
Largest diff. peak/hole / e $Å^{-3}$	1.632 / -0.959

Table	1	Crystallogra	nhic da	ata and	refinement	narameters f	for com	nlex 1	
I able	1.	Crystanogra	ipine u <i>c</i>	ita anu	rennement	parameters		DICX I	

 ${}^{a}R_{1} = \sum |(|F_{o}| - |F_{c}|)| / \sum |F_{o}|$

^b $wR_2 = \{\sum [w (F_o^2 - F_c^2)^2] / \sum [w (F_o^2)^2] \}^{1/2}, w = 1/[\sigma^2 (F_o^2) + (0.1305P)^2 + 9.6342P], where P = (F_o^2 + 2F_c^2)/3$

^c GOF = { $\sum [w(F_0^2 - F_c^2)^2] / (n-p)$ }^{1/2}, where n = number of measured data and p = number of parameters.

Bonds (Å)	X-ray	Calc.
Os1-H1	1.63(2)	1.626
Os1-Cl7	1.851(8)	1.871
Os1-N1	2.103(6)	2.178
Os1-N8	2.168(6)	2.256
Os1-P1	2.3685(18)	2.461
Os1-P2	2.3609(18)	2.433
O1-Cl7	1.152(10)	1.167
Angles (°)		
N1-Os1-H1	88.7(7)	90.534
N1-Os1- C17	179.2(3)	178.376
N1-Os1-N8	74.5(2)	74.522
N1-Os1-P1	91.17(17)	90.884
N1-Os1-P2	91.22(17)	91.589
N8-Os1-H1	162.4(7)	164.913
N8-Os1- C17	106.3(3)	103.870
N8-Os1-P1	99.26(17)	98.575
N8-Os1-P2	92.48(17)	96.462
C17-Os1-H1	90.6(7)	91.062
C17-Os1-P1	88.8(2)	89.583
C17-Os1-P2	88.7(2)	88.359
P1-Os1-H1	85.8(7)	83.443
P1-Os1-P2	168.23(6)	164.877
P2-Os1-H1	82.8(7)	81.618

Table 2. Some Selected bond distances (Å) and angles (°) of complex $\mathbf{1}$

МО	Energy (eV)	% of composition			
	-	Os	L	СО	PPh ₃
LUMO+5	-2.82	05	02	02	92
LUMO+4	-2.91	08	13	01	79
LUMO+3	-2.93	07	04	01	89
LUMO+2	-3.21	13	03	01	83
LUMO+1	-3.71	02	94	02	03
LUMO	-4.95	05	91	01	03
НОМО	-8.02	55	15	0	30
HOMO-1	-8.14	03	94	01	03
HOMO-2	-8.56	54	22	13	10
HOMO-3	-8.71	49	04	06	41
HOMO-4	-8.77	06	72	01	21
HOMO-5	-8.83	14	02	02	82
HOMO-6	-8.90	03	01	0	96
HOMO-7	-8.89	11	05	02	82
HOMO-8	-9.02	10	50	02	38
HOMO-9	-9.05	04	09	01	86
HOMO-10	-9.08	03	55	0	42
	R CR				

Table 3. Energy and compositions of some selected molecular orbitals of $\boldsymbol{1}$

Eexcitation	$\lambda_{excitation}$	Osc.	Key transitions	Character ^a
(eV)	(nm)	strength (f)		A
2.5541	485.44	0.0622	(94%) HOMO \rightarrow LUMO	$d\pi(\text{Os}) \rightarrow \pi^*(\text{L}), \text{MLCT}$
2.7414	452.27	0.0904	(87%)HOMO-1 \rightarrow LUMO	$\pi(L) \rightarrow \pi^*(L), ILCT$
3.1371	395.22	0.0193	(90%) HOMO-2 \rightarrow LUMO+1	$d\pi(\mathrm{Os})/\pi(\mathrm{L}) \to \pi^*(\mathrm{L}),$
				MLCT/ ILCT
3.5543	348.83	0.1449	(76%) HOMO-4 \rightarrow LUMO	$\pi(L) \rightarrow \pi^{*}(L), ILCT$
3.9821	311.36	0.0989	(82%)HOMO-8 \rightarrow LUMO	$\pi(L) \rightarrow \pi^*(L)$, ILCT
4.1779	296.76	0.0514	(63%)HOMO-10 \rightarrow LUMO	$\pi(L) \rightarrow \pi^*(L), ILCT$

Table 4. Vertical electronic excitations calculated by TDDFT/CPCM method of complex 1

^a MLCT: metal to ligand charge transfer transition and ILCT: intra-ligand charge transfer transition

CEP (E)

Table 5. Effect of S:C ratio, base and reaction time on the transfer hydrogenation of acetophenone^a

2

Q		ŎН
	Complex 1	
	<i>i</i> -PrOH, Base	

Entry	S:C ratio	<mark>Base</mark>	Time (h)	Conversion ^b (%)	TON ^c
1	1:300	KOH	<mark>3</mark>	72	216
2	1:300	KOH	<mark>4</mark>	85	255
3	1:300	KOH	<mark>5</mark>	97	291
4	1:300	KOH	<mark>7</mark>	97	291
5	1:300	KOH	10	97	291
6	1:300	NaOH	5	96	288
7	1:300	Na ₂ CO ₃	5	38	114
8	1:300	CH₃COONa	5	32	96
9	1:300	KO ^t Bu	<mark>5</mark>	63	189
10	1:500	KOH	<mark>5</mark>	96	480
11	1:700	KOH) <mark>5</mark>	83	581
12	1:1000	KOH	<mark>5</mark>	42	420
13	1:1500	KOH	<mark>5</mark>	25	375

^a Reaction condition: acetophenone (3 mmol), complex **1** (10-2 μ mol), catalyst:KOH 1:4 in *i*-PrOH (10 mL) at 80 °C; ^b Conversion was determined by GC analysis; ^c Turnover number (TON) = mole of product/mol of catalyst.

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Table 6. Transfer hydrogenation of ketones using complex 1^{a}



^a Experimental condition: reactions were carried out at 80 °C, ketone (3 mmol), Os (II) complex (0.2 mol%), KOH (0.1 mmol), *i*-PrOH (10 mL); ^b Conversion was determined by GC analysis; ^c Turnover number (TON) = mole of product/mol of catalyst

Figure captions

- Fig. 1. UV-vis (–) and emission (–) spectra of **1** in acetonitrile.
- Fig. 2. Life time decay profile of **1** in acetonitrile ($\lambda_{\text{excitation}} = 370 \text{ nm}$).
- Fig. 3. ORTEP plot with 35% ellipsoidal probability of 1.
- Fig. 4. Contour plots of some selected molecular orbitals of **1**. Isodensity value 0.04 e Bohr⁻³.
- Fig. 5. Cyclic voltammogram of complex 1 in acetonitrile.







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НОМО

HOMO-1

НОМО-2





LUMO+2

Fig. 4



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HIGHLIGHTS

- A new osmium(II) carbonyl complex with thioether containg NNS donor ligand is synthesized and characterized.
- Single crystal X-ray structure exhibits distorted octahedral environment around osmium in the complex.
- Cyclic voltammogram in acetonitrile exhibits Os(II)/Os(III) oxidation and ligand based reduction in the complex.
- The complex effectively catalyzed the transfer hydrogenation reaction of ketones with high yields in *i*-PrOH.
- The electronic structure and redox properties of the complex are interpreted by DFT studies.