

Osmium and cobalt complexes incorporating facially coordinated N,N,O donor azo-imine ligands: Redox and catalytic properties

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MS received 25 July 2011; revised 29 August 2011; accepted 7 October 2012

Abstract. Reactions of 1-[[2-(aryloxy)phenyl]iminomethyl]-2-phenol, HL [where H represents the dissociable phenolic protons of ligands and aryl groups of HL are C₆H₅ (HL¹), *p*-CH₃C₆H₅ (HL²), *p*-ClC₆H₅ (HL³)] with Os(H)(CO)(Br)(PPh₃)₃ in toluene and with Co(ClO₄)₃·6H₂O in methanol afforded new facially coordinated complexes of composition [(L)Os(CO)(Br)(PPh₃)] and [(L)₂Co]ClO₄. The anionic ligand (L)[−], binds the metal in tridentate (N, N, O) manner in [(L)Os(CO)(Br)(PPh₃)] and [(L)₂Co]ClO₄ complexes. All the Os(II) and Co(III) complexes are diamagnetic and show characteristic ¹H NMR signals and intense MLCT transitions in the visible region. The cyclic voltammograms exhibited one quasi reversible oxidative response near 0.10 V vs SCE for [(L)Os(CO)(Br)(PPh₃)] and [(L)₂Co]ClO₄ complexes displayed serial reductive responses within −0.06 to −1.61 V vs SCE. Single point DFT calculation was carried out to examine the nature of redox orbitals. Conversion of ketones to corresponding alcohols has been studied using [(L)Os(CO)(Br)(PPh₃)] as catalyst.

Keywords. 2-(Aryloxy)-1-N-salicylidene phenylamine; face capped Os(II); Co(III); DFT; redox; hydrogen transfer reaction.

1. Introduction

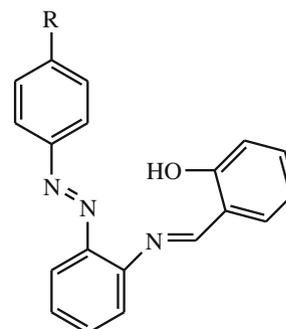
The ligands which bind the transition metal ion in a predictable way play important role in modern coordination chemistry since they may determine the reactive sites available at a metal centre and can modulate their reactivity.

Fascinating chemistry of transition metal complexes incorporating ligands that are capable of binding the metal centre in facial manner, enhanced the interest on the synthesis of new tridentate ligands that are suitable for obtaining facially coordinated complexes.^{1–7}

Facially capped piano-stool type of platinum metal complexes have received attention due to their interesting catalytic and biological activity. Conversion of dimethyl oxalate to ethylene glycol and hydrogenation of esters to yield alcohols in homogeneous media using such metal complexes as catalyst are notable examples.^{8–21}

Although several tridentate facially coordinating ligands, such as 1,4,7 tri aza cyclononane, 1,4,7 trithia cyclononane, *tris* pyrazolyl borate, a few scorpionate and tripod ligands, are known to form facially capped

platinum metal complexes,^{22–34} but only a few of the above mentioned ligands have been utilized for the preparation of Os(II) complexes.^{35,36} As a consequence, chemistry of Os(II) complexes with facially coordinating ligands have not been explored considerably. Coordination chemistry of osmium incorporating azo ligands has been studied with a few bidentate (N, N and N, O donors) and tridentate (C, N, O and N, N, N donors) ligands.^{37–41} Whereas the coordination chemistry of osmium with tridentate N, N, O donor ligands has not been reported so far. These background information prompted us to study the coordination chemistry of osmium incorporating the N, N, O donor azo-imine ligand system, **1**.



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In this paper, we have described the reactions of appropriate osmium and cobalt substrates with **1** to obtain Os(II) and Co(III) complexes where the tridentate (N,N,O) ligand is facially coordinated. Spectroscopic and redox properties of new complexes have been described. Catalytic transfer of hydrogen reactions using newly synthesized Os(II) complexes as catalyst have been reported. A plausible description of redox orbitals have been ascribed on the basis of single point DFT calculations.

2. Experimental

2.1 Materials

The solvents used in the reactions were of reagent grade (obtained this from E Marck, Kolkata, India) and were purified and dried by reported procedure.⁴² Os(H)(CO)(Br)(PPh₃)₃ was prepared according a reported procedure.⁴³ Cobalt (III) perchlorate was prepared by oxidation of Co (II) perchlorate with H₂O₂.⁴⁴ 1-[[2-(Arylazo)phenyl]iminomethyl]-2-phenol, HL [where H represents the dissociable protons upon complexation and aryl groups of HL are phenyl for HL¹; *p*-methyl phenyl for HL²; *p*-chloro phenyl for HL³], were prepared according to a reported procedure.⁴⁵

2.2 Syntheses of complexes

2.2a [(L)Os(CO)(Br)(PPh₃)]: The [(L)Os(CO)(Br)(PPh₃)] complexes were obtained by following a general procedure. Specific details are given below for a particular complex.

2.2b [(L¹)Os(CO)(Br)(PPh₃)] (**2a**): 2-(Phelazo)-1-N-salicylidene phenylamine, HL¹, (0.03 g, 0.102 mmol) was dissolved in 40 ml toluene, and to it Os(H)(CO)(Br)(PPh₃)₃ (0.10 g, 0.102 mmol) was added. The mixture was then heated to reflux for 8 h till the solution turned to dark brown. Evaporation of the solvent gave a dark brown residue, which was purified by thin-layer chromatography on silica gel. A green band separated in toluene–acetonitrile (95:5,V/V) mixed solvent. From the second band [(L¹)Os(CO)(Br)(PPh₃)] was isolated in pure form upon extracting with dichloromethane and methanol. Yield: 70%. *Anal. calc.* for 2a. C 52.97, H 3.36, N 4.87. Found: C 53.00, H 3.34, N 4.90%. Electronic spectrum (λ_{\max}/nm ($\epsilon/\text{dm}^2 \text{ mol}^{-1}$), dichloromethane):

650 (4570), 470 (4570), 350 (19380), 255 (29850), 240 (40790). IR (KBr pellets, cm^{-1}): $\nu_{\text{C}=\text{N}}$ 1605, $\nu_{\text{N}=\text{N}}$ 1434, ν_{CO} 1920. ¹H NMR (CDCl₃ ppm): δ 8.27 (d, 2H), 7.94–7.92 (d, 1H), 7.62 (t, 6H), 7.53–7.42 (m, 6H), 7.42–7.39 (m, 3H), 7.32–7.25 (m, 9H), 7.17–7.15 (t, 1H), 7.04 (s, 1H), 6.83 (d, 1H), 6.62 (d, 1H), 6.46 (d, 1H), 6.28 (t, 1H) ppm. $E_{1/2}$ [V] ($\Delta E_p/\text{mV}$): 1.1.

2.2c and 2.2.d [(L²)Os(CO)(Br)(PPh₃)] (**2b**) and [(L³)Os(CO)(Br)(PPh₃)] (**2c**): The complexes [(L²)Os(CO)(Br)(PPh₃)] was prepared following the same procedure as in the case of [(L¹)Os(CO)(Br)(PPh₃)] using HL² and HL³ in place of HL¹. The solvent used for thin-layer chromatographic separation is toluene–acetonitrile (95:5 V/V) mixed solvent.

Yield: 75% for HL² complex [(L²)Os(CO)(Br)(PPh₃)]. *Anal. calc.* for 2b. C 53.49, H 3.54, N 4.80. Found C 53.53, H 3.50, N 4.83%. Electronic spectrum (λ_{\max}/nm ($\epsilon/\text{dm}^2 \text{ mol}^{-1}$), dichloromethane): 650 (1300), 470 (4450), 357 (18940), 260 (27370), 232 (45400). IR (KBr pellets, cm^{-1}): $\nu_{\text{C}=\text{N}}$ 1604, $\nu_{\text{N}=\text{N}}$ 1436, ν_{CO} 1920. ¹H NMR (CDCl₃ ppm): δ 8.23 (d, 2H), 7.91 (d, 1H), 7.62 (t, 6H), 7.52–7.28 (m, 8H), 7.15–7.10 (m, 2H), 7.11 (d, 1H), 6.81 (d, 1H), 6.63(d, 1H), 6.28 (t, 1H), 2.41 (s, 3H) ppm. $E_{1/2}$ [V] ($\Delta E_p/\text{mV}$): 1.12.

Yield: 70% for HL³ complex [(L³)Os(CO)(Br)(PPh₃)]. *Anal. calc.* for 2c. C 50.93, H 3.12, N 4.69. Found C 51.00, H 3.15, N 4.67%. Electronic spectrum (λ_{\max}/nm ($\epsilon/\text{dm}^2 \text{ mol}^{-1}$), dichloromethane): 650 (1290), 468 (4440), 360 (20331), 256 (29940), 230 (49920). IR (KBr pellets, cm^{-1}): $\nu_{\text{C}=\text{N}}$ 1604, $\nu_{\text{N}=\text{N}}$ 1436, ν_{CO} 1927. ¹H NMR (CDCl₃ ppm): δ 8.30 (d, 2H), 7.92–7.91 (m, 1H), 7.78 (t, 6H), 7.61 (t, 1H), 7.53 (d, 2H), 7.41 (t, 2H), 7.34–7.28 (m, 8H), 7.15 (t, 1H), 7.04 (s, 1H), 6.81 (d, 1H), 6.64 (d, 1H), 6.46 (d, 1H), 6.29 (t, 1H). $E_{1/2}$ [V] ($\Delta E_p/\text{mV}$): 1.19.

2.2e [(L)₂Co]ClO₄: The [(L)₂Co]ClO₄ complexes were obtained by following a general procedure. Specific details are given below for a particular complex.

2.2f [(L¹)₂Co]ClO₄ (**7a**): To a solution of Co(ClO₄)₂·6H₂O (0.2 g, 0.429 mmol), in 40 mL methanol ligand HL¹ (0.5 g, 0.428 mmol) was added. The mixture was heated to reflux for 1 h. During this time greenish brown solid was precipitated. The solid product was then filtered and washed with water and a little methanol. It was recrystallized from

dichloromethane-petroleum ether to obtain pure product. Yield: 80%. *Anal. calc.* for **7a**. C 60.07, H 3.68, N 11.06. Found C 60.00, H 3.70, N 11.10%. Electronic spectrum (λ_{\max}/nm ($\epsilon/\text{dm}^2 \text{ mol}^{-1}$), dichloromethane): 370 (19700), 285 (48200), 230 (41100). IR (KBr pellets, cm^{-1}): $\nu_{\text{C}=\text{N}}$ 1604, $\nu_{\text{N}=\text{N}}$ 1436, $\nu_{\text{Cl}-\text{O}}$ 1083. ^1H NMR (CDCl_3 ppm): δ 8.02 (t, 1H), 7.90 (d, 1H), 7.82–7.79 (m, 3H), 7.49–7.44 (m, 2H), 7.37 (d, 2H), 7.24–7.18 (m, 2H), 6.71 (t, 1H), 6.09 (d, 1H) ppm. $E_{1/2}$ [V] ($\Delta E_p/\text{mV}$): -0.071 (116.4), E ($\Delta E_p/\text{mV}$): -1.60 , -0.85 .

2.2g and 2.2h $[(\text{L}^2)_2\text{Co}]\text{ClO}_4$ (**7b**) and $[(\text{L}^3_{\text{sal}})_2\text{Co}]\text{ClO}_4$ (**7c**): Complexes $[(\text{L}^2)_2\text{Co}]\text{ClO}_4$ and $[(\text{L}^3)_2\text{Co}]\text{ClO}_4$ were prepared by a similar procedure as described for $[(\text{L}^1)_2\text{Co}]\text{ClO}_4$ using ligand HL^2 and HL^3 in place of HL^1 .

Yield: 85%. *Anal. calc.* for **7b**. C 60.53, H 3.88, N 10.86. Found C 60.60, H 3.90, N 10.94%. Electronic spectrum (λ_{\max}/nm ($\epsilon/\text{dm}^2 \text{ mol}^{-1}$), dichloromethane): 390 (21500), 290 (45600), 230 (38600). IR (KBr pellets, cm^{-1}): $\nu_{\text{C}=\text{N}}$ 1605, $\nu_{\text{N}=\text{N}}$ 1433, $\nu_{\text{Cl}-\text{O}}$ 1089. ^1H NMR (CDCl_3 ppm): δ 8.02 (t, 1H), 7.87 (d, 1H), 7.79 (d, 1H), 7.74 (t, 2H), 7.34 (d, 2H), 7.29–7.22 (m, 1H), 7.18 (d, 2H), 6.67 (t, 1H), 6.06 (d, 1H), 2.42 (s, 3H) ppm. $E_{1/2}$ [V] ($\Delta E_p/\text{mV}$): -0.081 (101.7). E ($\Delta E_p/\text{mV}$): -1.55 , -1.05 .

Yield: 75%. *Anal. calc.* for **7c**. C 57.45, H 3.40, N 10.58. Found C 7.50, H 3.35, N 10.60%. Electronic spectrum (λ_{\max}/nm ($\epsilon/\text{dm}^2 \text{ mol}^{-1}$), dichloromethane): 380 (24950), 285 (52575), 230 (43400). IR (KBr pellets, cm^{-1}): $\nu_{\text{C}=\text{N}}$ 1603, $\nu_{\text{N}=\text{N}}$ 1432, $\nu_{\text{Cl}-\text{O}}$ 1079. ^1H NMR (CDCl_3 ppm): δ 8.34 (d, 1H), 7.78 (d, 1H), 7.34 (t, 2H), 7.27–7.23 (m, 2H), 7.16–7.11 (m, 3H), 6.85–6.81 (m, 2H), 6.68 (d, 1H) ppm. $E_{1/2}$ [V] ($\Delta E_p/\text{mV}$): -0.063 (122.7), E ($\Delta E_p/\text{mV}$): -1.50 , -0.75 .

2.3 Physical measurements

Microanalysis (C, H, N) was performed using a Perkin-Elmer 2400 C, H, N, S / O series II elemental analyzer. Infrared spectra were recorded on a Parkin-Elmer L120-00A FT-IR spectrometer with the samples prepared as KBr pellets. Electronic spectra were recorded on a Shimadzu UV-1601 PC spectrophotometer. ^1H NMR spectra were obtained on Bruker DPX 400 and Bruker 500 RPX NMR spectrometers in CDCl_3 using TMS as the internal standard. Electrochemical measurements were made under dinitrogen atmosphere using a PAR model VARSASTAT-II potentiostat. A platinum disc working electrode, a platinum wire auxiliary electrode and an aqueous saturated

calomel reference electrode (SCE) were used in a three-electrode configuration. All electrochemical data were collected at 298 K and are uncorrected for junction potentials.

2.4 Transformation of ketones to 2° - alcohols via hydrogen transfer reactions

A mixture containing ketones (0.050 g, 2.8 mmol), the osmium complex (0.0009 g, 0.0013 mmol) and (0.0036 g, 0.0625 mmol) KOH was heated to reflux in 10 mL of *i*-PrOH for appropriate period of time as mentioned in table 3. The complex was removed as precipitate from the reaction mixture by the addition of diethyl ether followed by filtration. Subsequent neutralization with 5 mL of 1 (M) HCl the ether layer was separated and passed through a short path of silica gel. The product was purified by preparative thin-layer chromatography. The yields were calculated after isolation. The hydrogenated products were characterized by matching the UV-Vis, IR and ^1H NMR spectra of authentic samples.

2.5 DFT calculations

Using the X-ray coordinates of the complex $[(\text{L}^2)\text{Os}(\text{CO})(\text{Br})(\text{PPh}_3)]$ and $[(\text{L}^1)_2\text{Co}]\text{ClO}_4$ complex ground state electronic structure calculations have been carried out using DFT⁴⁶ methods with the Gaussian 03 program.⁴⁷ Becke's hybrid function⁴⁸ with the Lee–Yang–Parr (LYP) correlation function⁴⁹ was used throughout the study. We have employed a triple-z quality all-electron basis set (TZP)⁵⁰ for Os and Co. Double-all-electron basis set⁵¹ for C, N, and O, and a 6-31G basis set for H. LANL2DZ valence and effective core potential functions were used. All energy calculations were performed using the self-consistent field 'tight' option of the Gaussian 03 program to ensure sufficiently well-converged values for the state energies.

2.6 X-ray crystallographic study

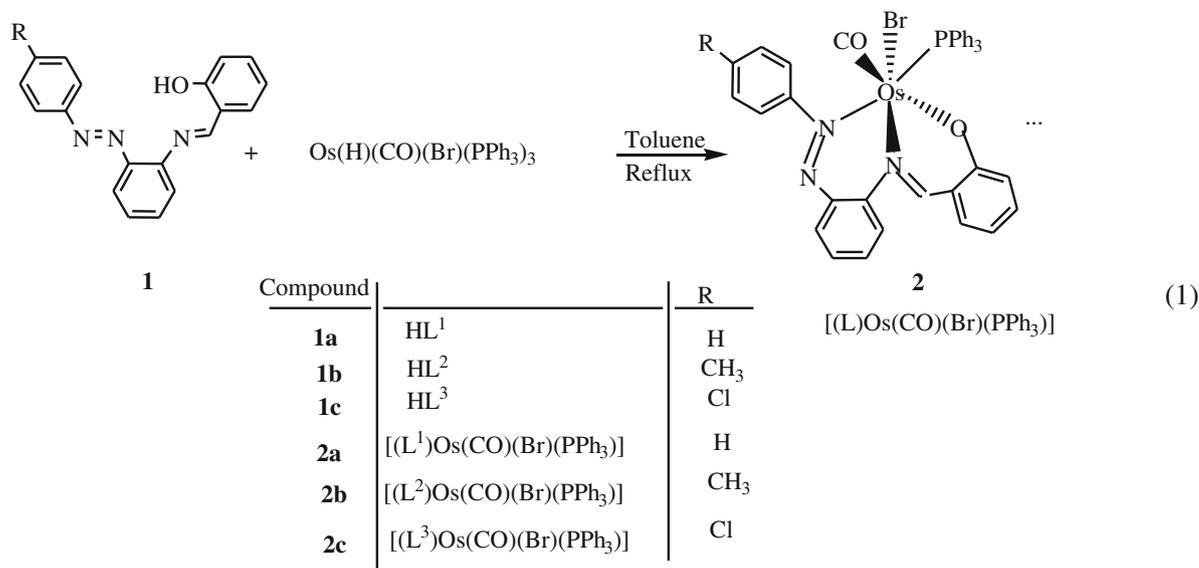
Single crystals of **2b** and **7a** were grown by slow evaporation of dichloromethane-acetonitrile mixed solution at 298 K. Data were collected on a Bruker SMART CCD diffractometer using Mo- $K\alpha$ monochromator ($\lambda = 0.71073$). Structure solutions were performed using Shelx 97 PC version program.⁵² Full matrix least square refinements on F2 were performed

using SHELXL-97 program.⁵³ All the non-hydrogen atoms were refined anisotropically using full-matrix least squares method. Hydrogen atoms were included for structure factor calculations after placing them at calculated positions. The data collection parameters and relevant crystal data are collected in table 3. In table 3 only the cell parameters for $[(L^1)_2Co]ClO_4$, **7a**, are shown since it could not be refined well due to the poor quality of data.

3. Results and discussion

3.1 Syntheses

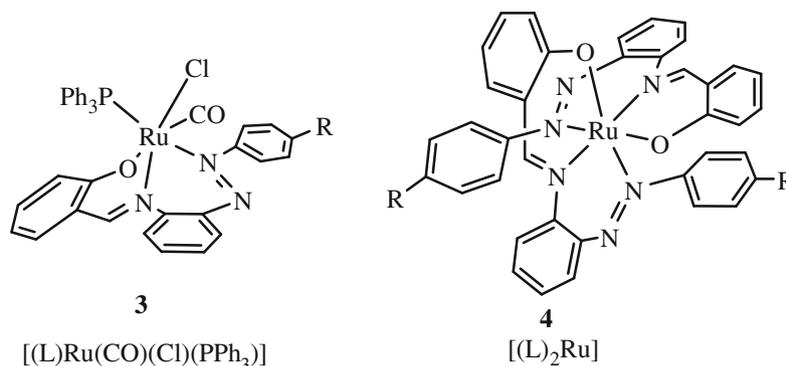
Reaction of one equivalent $[Os(H)(CO)(Br)(PPh_3)_3]$ with two equivalent 1- $\{[2-(arylazo)phenyl]iminomethyl\}$ -2-phenol, **1**, HL, in refluxing toluene afforded olive green $[(L)Os(CO)(Br)(PPh_3)]$, **2**, product in 70% yield after 8 h (Eq. 1).



Three complexes were prepared using HL¹, HL² and HL³ which are nonelectrolyte, diamagnetic and soluble in common organic solvents.

In $[(L)Os(CO)(Br)(PPh_3)]$ complexes deprotonated tridentate (N,N,O) donor L⁻ ligands are bound facially and the other three coordination sites are occupied by CO, Br and PPh₃ (*x-ray structure*).

Earlier we have reported that the reaction of HL with $Ru(H)(CO)(PPh_3)_3Cl$ substrate afforded both the complexes $[(L)Ru(PPh_3)(Cl)(CO)]$, **3**, and $[(L)_2Ru]$, **4**, where (L)⁻ ligands were bound to the Ru(II) centre

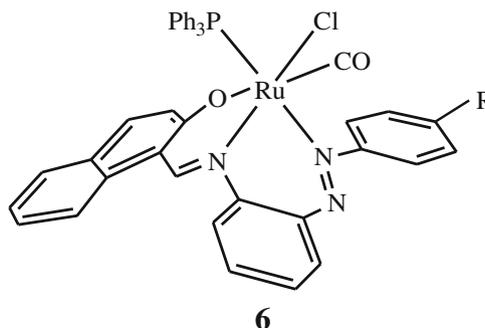
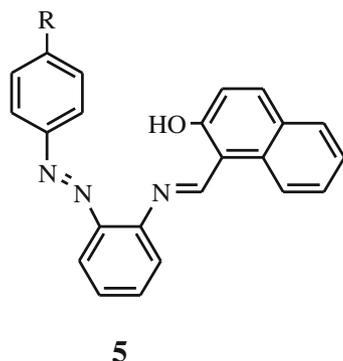


in facial and meridional fashion respectively.⁴¹ Further, the conversion of $[(L)Ru(PPh_3)(Cl)(CO)]$ to

$[(L)_2Ru]$, in the presence of excess free ligand, was also reported but the mechanism of facial to meridional

amendment of the ligand coordination could not be ascertained.⁴¹ Whereas, bulkier ligands, **5**, afforded

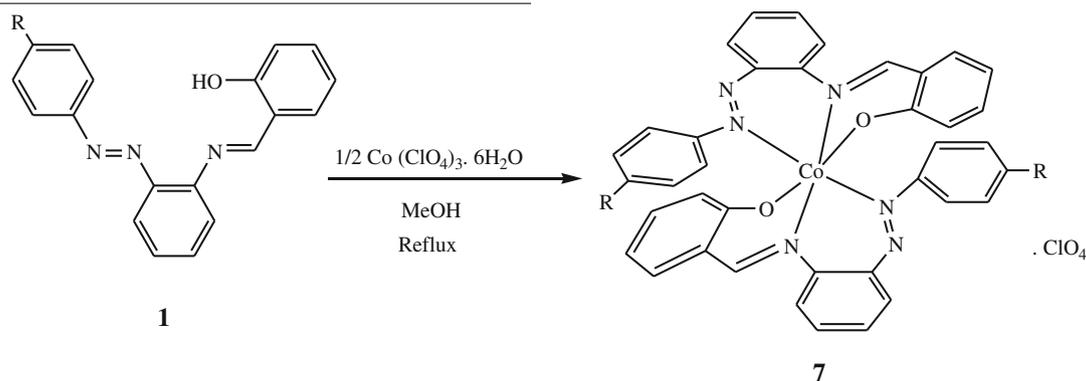
only the product **6** upon reaction with same ruthenium substrate.⁴¹



Thus, the fine tuning in the ligand backbone dictated the product in the case of ruthenium substrate. In this paper, we have described that subtle difference in the characteristics of metal ion is also an important factor and can be utilized to prepare the desired product. That is, on going from ruthenium substrates to the osmium substrate Os(H)(CO)(Br)(PPh₃)₃ afforded only [(L)Os(CO)(Br)(PPh₃)] was isolated without any analogue of (L)₂Ru for both the ligands, **5** and HL. We contemplated to examine the coordination mode of the same ligands in the *bis* complexes of metal ions that are smaller in size than Ru(II) and Os(II) with the academic interest to prepare *bis* complex with facially coordinated ligands. Since Co(III) is of smaller radii than Ru(II) and Os(II) in low spin octahedral geometry so it was chosen. The simple metal

substrate [Co(H₂O)₆].(ClO₄)₃ was used for reaction with HL to examine the proposition. Though Os(II) and Ru(II) are very close in size but Os(II) did not afford the *bis* complex possibly due to less lability of [(L)Os(CO)(Br)(PPh₃)] than the ruthenium analogue [(L)Ru(CO)(Cl)(PPh₃)].

Reaction of two equivalent of HL, **1**, with one equivalent of cobalt (III) perchlorate, hexahydrate, Co(ClO₄)₃·6H₂O, in refluxing methanol precipitated the facially coordinated dark coloured crystalline complex [(L)₂Co]ClO₄, **7**, which was collected by filtration (Eq. 2). A little more crop of product was isolated upon concentrating the filtrate. In concurrence with our expectation the *bis* complex of Co(III), [(L)₂Co]ClO₄, **7**, is incorporated



Compound		R
7a	[(L ¹) ₂ Co]ClO ₄	H
7b	[(L ²) ₂ Co]ClO ₄	CH ₃
7c	[(L ³) ₂ Co]ClO ₄	Cl

with two facially coordinated tridentate (N,N,O) ligands, L⁻, (*X-ray structure*). The unipositive charge of

the complex cation, [(L)₂Co]⁺, **7**, was satisfied by one ClO₄⁻ ion. These complexes are soluble in common

organic solvent and the colour of the solution is greenish brown. The complex is 1:1 electrolyte in acetonitrile solution and diamagnetic signifying the low spin d^6 configuration in octahedral ligand field. The composition of diamagnetic $[(L)_2Co]ClO_4$ complexes matched well with the analytical data and total proton count in 1H NMR spectrum (*vide infra*).

3.2 Characterization

The green solutions of $[(L)Os(CO)(Br)(PPh_3)]$ complexes in dichloromethane display characteristic UV-Vis spectra where a low energy absorption near 655 nm is diagnostic of $d-d$ transition. Spectral data are collated in experimental section.

The UV-Vis spectra of the greenish brown solutions of $[(L)_2Co]ClO_4$ in CH_2Cl_2 feature a relatively weak absorption band near 670 nm for $d-d$ transition.^{45,54} The $[(L)_2Co]ClO_4$ complexes show a weak absorption band near 375 nm. A representative spectrum of $[(L^1)_2Co]ClO_4$ is shown in figure 1. The UV-Vis spectral data are given in the experimental section. All the UV-Vis spectra are given in supplementary material (figures S1–S6).

IR spectra of all the complexes were recorded in solid KBr support. The spectra displayed $\nu_{C=N}$ for $[(L)Os(CO)(Br)(PPh_3)]$ and $[(L)_2Co]ClO_4$ near 1604 and 1603 cm^{-1} , respectively. The $\nu_{N=N}$ ($[(L)Os(CO)(Br)(PPh_3)]$ and $[(L)_2Co]ClO_4$, appeared near 1434 and 1435 cm^{-1} , respectively. These stretching frequencies are of lower energy than the corresponding ligand characteristics ($\nu_{C=N}$, ~ 1615 cm^{-1}

and $\nu_{N=N}$ 1456 cm^{-1}) signifying the coordination of aldimino ($-CH=N-$) and azo ($-N=N-$) nitrogens.^{55–57} The ν_{CO} appeared near 1920 cm^{-1} for $[(L)Os(CO)(Br)(PPh_3)]$ complexes. A broad band appeared near 1080 cm^{-1} , which is the characteristic of uncoordinated ClO_4^- for $[(L)_2Co]ClO_4$. The IR data are collected in experimental section. The IR spectra of the complexes are shown in supplementary materials (figures S7–S12).

The 1H -NMR spectral pattern matched well with the composition of $[(L)Os(CO)(Br)(PPh_3)]$ and $[(L)_2Co]ClO_4$. The 1H -NMR spectra of $[(L)Os(CO)(Br)(PPh_3)]$ complexes were recorded in $CDCl_3$. The 1H -NMR data are collected in experimental section. Absence of phenolic OH signal indicated the coordination of phenoxide oxygen for all the complexes.^{41,56,57} The upfield shift of aldimine protons (appeared near $\sim \delta$ 7.10 as a singlet for $[(L)Os(CO)(Br)(PPh_3)]$) than the ligands ($\sim \delta$ 8.55) were observed for all the complexes consistent with the imine coordination.^{55–57} All other aromatic proton resonances appeared within $\sim \delta$ 8.51– δ 6.28 for $[(L)Os(CO)(Br)(PPh_3)]$. The fifteen protons of PPh_3 appear as two multiplets within the range δ 7.53– δ 7.44 for six protons and δ 7.32– δ 7.25 for nine protons. The aldimine and aromatic protons for $[(L)_2Co]ClO_4$ did not resolve well due to overlapping signals. The $-CH_3$ protons signal appears at δ 2.42 for $[(L^2)_2Co]ClO_4$. The 1H -NMR spectra of $[(L)Os(CO)(Br)(PPh_3)]$ and $[(L)_2Co]ClO_4$ complexes are given in supplementary materials (figures S13–S18).

3.3 X-ray structure

Single crystals of $[(L^2)Os(CO)(Br)(PPh_3)]$ was grown by slow evaporation of dichloromethane and acetonitrile mixed solvents. Suitable crystals were picked for X-ray studies. A perspective view of the molecule has been shown in figure 2 and selected bond distances and angles are collected in table 1.

The asymmetric unit of $[(L^2)Os(CO)(Br)(PPh_3)]$ contains two molecules. The geometry and bond parameters are similar for both the molecules. The molecular structure of each monomer molecule exhibit octahedral coordination with facial geometry about Os, where the monoanionic ligand, $(L^2)^-$, binds the metal in tridentate (N,N,O) fashion. The other three ligands, Br, CO and PPh_3 complete the hexacoordination about Os. The Os-N(azo) length [2.179(4)Å] *trans* to Os1-P1 [2.33387(15)Å] is longer than the Os1-N3(aldimine) length [2.037(16) Å] which is *trans* to Os1-Br1 [2.5620(6) Å]. The N(1)-N(2) length [1.273(6) Å] in

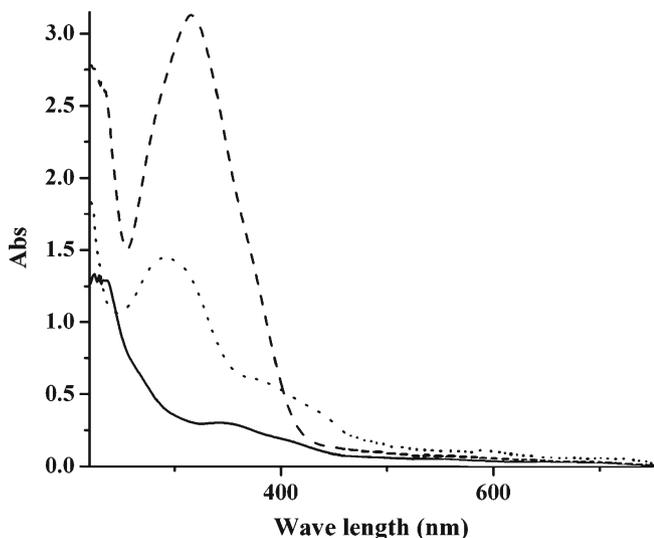


Figure 1. UV-Vis spectra of **1a** (---), **2a**(—) and **7a** (.....).

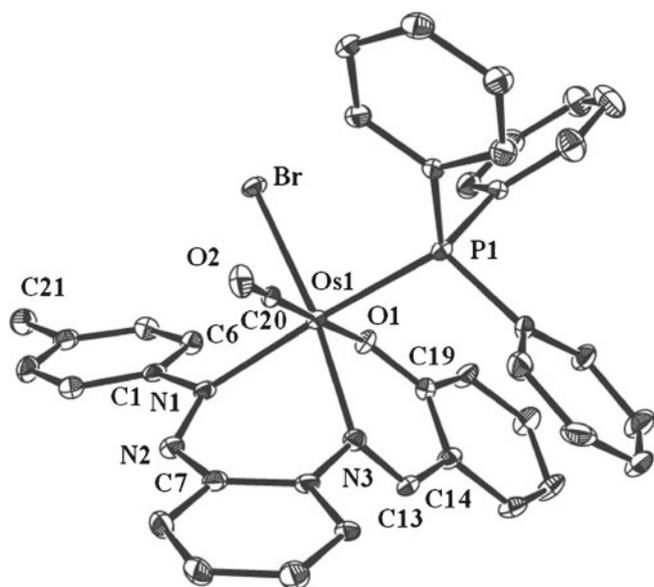


Figure 2. Perspective view (30% probability ellipsoids) of **2b**, with atom numbering scheme. The hydrogen atoms have been omitted for clarity.

the coordinated azo function is shorter than other Os(II) azo complexes.^{37–41} The Os1-P1 distance is longer than other reported Os-P distances.^{40,41}

Crystals of $[(L^1)_2Co]ClO_4$, **7a**, were grown by slow diffusion of dichloromethane solution into petroleum ether. A perspective (ball stick) view of the molecule has been shown in figure 3. The asymmetric unit of $[(L^1)_2Co]ClO_4$ contains two molecules.

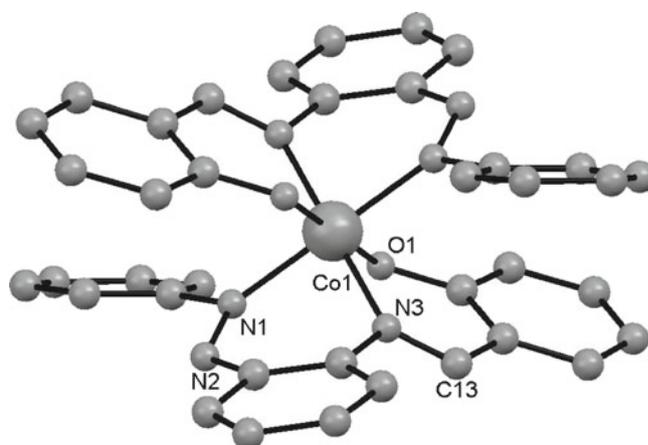


Figure 3. Perspective (ball stick) view of **7a**, (except ClO_4^-) with atom numbering scheme. The hydrogen atoms have been omitted for clarity.

The molecular structure exhibits octahedral coordination about Co(III), where the two anionic ligand, $(L^1)^-$, coordinated facially as tridentate N,N,O donor through phenoxide-O, azo nitrogen and aldimino nitrogen. Each ligand binds the metal forming two six-membered chelate ring. A perchlorate $(ClO_4)^-$ ion satisfied the unipositive charge of the complex cation, $[(L^1)_2Co]^+$. The relative orientations of donor atoms (azo N, imine N, and phenoxide O) of two ligands are *trans*, *trans* and *trans*, respectively. The X-ray structure of $[(L^1)_2Co]ClO_4$ could not be refined well due to poor quality of data. Although the refinement was poor but the facial coordination modes of the ligands could be recognized.

Table 1. Selected bond distances (Å) and angles (°) for compound **2b**.

[[L ² Os(CO)(Br)(PPh ₃)]			
Distances (Å)			
Os1-Br	2.5620(6)	Os1-C20	1.834(6)
Os1-P1	2.3387(15)	N1-N2	1.273(6)
Os1-O1	2.091(4)	N1-C1	1.440(7)
Os1-N1	2.179(4)	N2-C7	1.423(7)
Os1-N3	2.037(5)	N3-C12	1.431(7)
N3-C13	1.309(7)	O1-C19	1.315(7)
Angles (°)			
Br-Os1-P1	92.77(4)	N3-Os1-C20	94.5(2)
Br-Os1-O1	88.34(10)	Os1-O1-C19	126.4(3)
Br-Os1-N1	91.78(12)	N2-N1-C1	111.5(4)
Br-Os1-N3	168.79(14)	Os1-N1-N2	122.5(4)
Br-Os1-C20	91.54(17)	Os1-N1-C1	125.5(4)
N1-Os1-N3	78.88(17)	N1-N2-C7	121.2(5)
N1-Os1-C20	89.3(2)	Os1-N3-C12	114.5(3)
Os1-N3-C13	128.7(4)	C12-N3-C13	116.4(5)

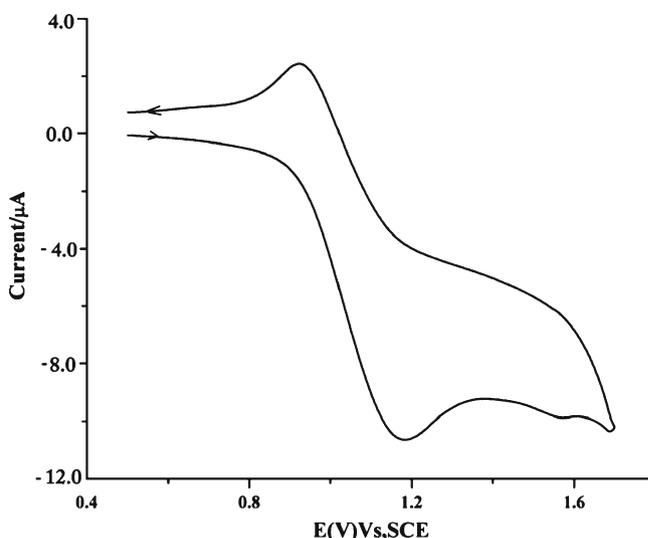


Figure 4. Cyclic voltammogram of the **2b** complex in dichloromethane solution (0.1 M TBAP) at scan rate of 50 mV s^{-1} .

3.4 Electrochemistry

$[(L)Os(CO)(Br)(PPh_3)]$ complexes exhibit an one electron reversible oxidative cyclic voltammetric response



Representative cyclic voltammograms of $[(L^2)Os(CO)(Br)(PPh_3)]$ has been shown in figure 4 and all other cyclic voltammograms were given in supplementary material (figures S19–S21).

To gain insight into the redox orbitals, single point DFT calculations were performed using the crystallographic coordinates of $[(L^2)Os(CO)(Br)(PPh_3)]$. Two frontier orbitals HOMO and LUMO are shown in figure 5a and b. From the DFT results, it appears that the HOMO has considerable metal character, whereas the LUMO is essentially ligand centred. Therefore, on the basis of DFT result, the oxidative couple may be

near 1.0 V in dichloromethane solution. The oxidation has been assigned according to the couple of Eq. (3), where $[(L)Os(CO)(Br)(PPh_3)]^+$ is the Os(III) analogue of $[(L)Os(CO)(Br)(PPh_3)]$.

inferred to be due to the metal centred Os(II)/Os(III) redox couple signifying accessibility to variable redox levels of metal.

The $[(L)_2Co]ClO_4$ Complexes exhibit a one electron reversible reductive cyclic voltammetric response in the range of -0.06 to -0.12 V vs SCE and two irreversible reductive responses within -0.75 V to -1.62 V vs SCE in dichloromethane solution. A representative cyclic voltammogram of $[(L^1)_2Co]ClO_4$ is shown in figure 6 and other data are given in experimental section. To gain insight into the redox orbitals of the cobalt complexes, DFT restricted single point

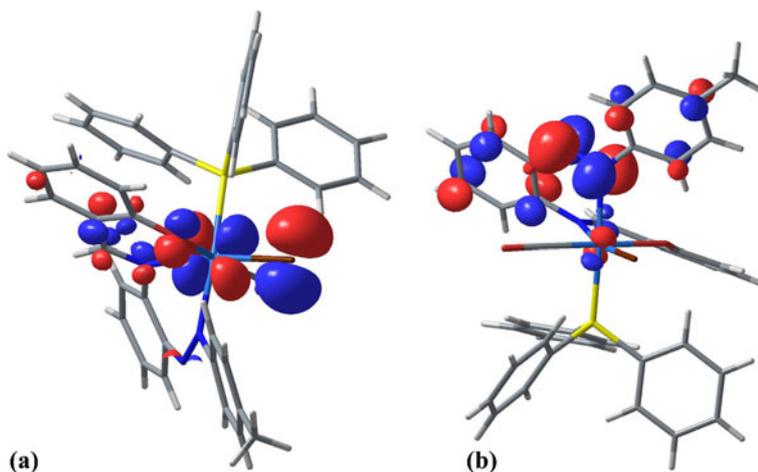


Figure 5. (a) HOMO of **2b** and (b) LUMO of **2b**.

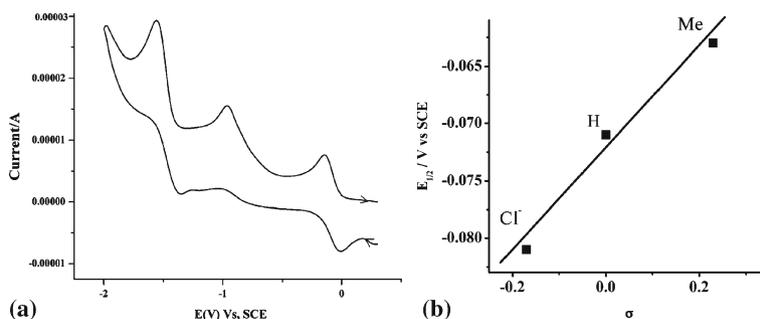


Figure 6. (a) Cyclic voltammogram of the **7a** complex in dichloromethane solution (0.1 M TBAP) at scan rate of 50 mV s^{-1} . (b) A least-squares plot of $E_{1/2}$ values of **7a** complexes vs. σ (Hammett substituent constant).

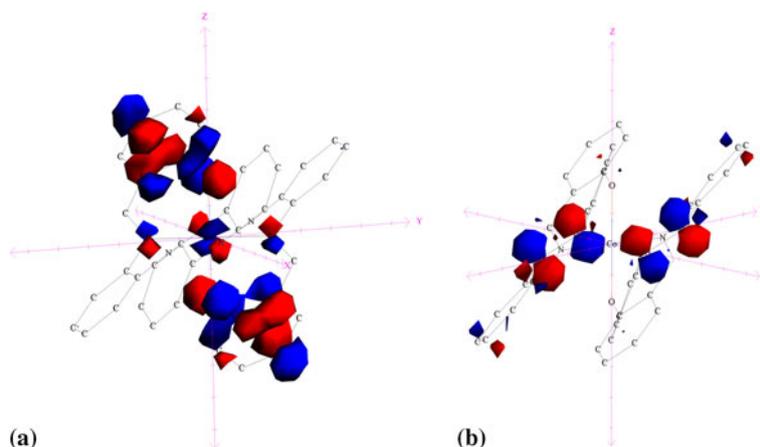


Figure 7. (a) HOMO of **7a** and (b) LUMO of **7b**.

calculations were performed were carried out on $[(L^1)_2Co]^+$ moiety using the crystallographic coordinates. Plot of HOMO and LUMO are shown in figure 7a and b. Although HOMO has considerable metal character but LUMO is ligand centred. As a result, reductive responses of $[(L)_2Co]ClO_4$ are attributed to ligand centred reductions. Plot of $E_{1/2}$ values of $[(L)_2Co]ClO_4$, within -0.06 – 0.12 V Vs SCE, against Hamett constants of $-CH_3$, $-Cl$ and $-H$ is linear indicating the ligand contribution in redox orbital.

3.5 Transformation of ketones to 2^0 - alcohols via hydrogen transfer reactions

Hydrogenation of organic molecules in homogeneous media by means of catalytic transfer hydrogen

process has received attention in recent years.^{57–59} Several platinum metal complexes have been used as catalyst for the reductive conversion of ketones to 2^0 - alcohols.^{60–63} To the best of our knowledge, use of Os(II) complexes as transfer hydrogen catalyst have not been studied considerably.^{64–66} Therefore, we were encouraged to examine the catalytic activity of $[(L^1)Os(CO)(Br)(PPh_3)]$, toward transfer hydrogenation of representative aliphatic and aromatic ketones. The conversion of ketones to corresponding alcohols were studied in 2-propanol adding catalytic amount of $[(L^1)Os(CO)(Br)(PPh_3)]$ and KOH in the reaction mixture as given in Eq. (4). The results of transformations are listed in table 2.

After the catalytic reactions neither the original complex, $[(L^1)Os(CO)(Br)(PPh_3)]$, nor the transformed

Table 2. Transformation of ketones to 2^0 - alcohols via hydrogen transfer reactions for **2a**.

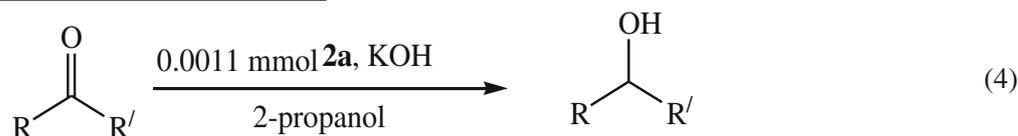
Entry	Substrate	Product	Time (h)	Isolated yield (%)
1			1	80
2			1	75
3			1.5	50
4			1.5	50

Table 3. Crystallographic data for **2b** and **7a**.

	2b	7a
Chemical formula	C ₃₉ H ₃₁ BrN ₃ O ₂ OsP	C ₃₈ H ₂₈ CoN ₆ O ₂ , ClO ₄
Formula weight	874.77	759.11
Crystal system	Monoclinic	Triclinic
Space group	P21	P-1
A [Å]	9.10100(10)	10.6348(5)
B [Å]	18.0120(2)	13.7687(6)
C [Å]	20.8460(2)	14.5032(5)
α [°]	90	86.013(2)
β [°]	89.8550(10)	69.330(2)
γ [°]	90	78.255(2)
λ [Å]	0.71073	0.71073
V [Å ³]	3417.22(6)	1945.36(14)
F(000)	1712	864
Z	4	2
T/K	150	273
D/g/cm ³	1.700	–
μ/mm ⁻¹	4.987	–
R1 (all data)	0.0396	–
wR2[I > 2σ(I)]	0.0773	–
GOF	1.00	–

complex could be isolated and identified indicating the fact that the possibility of [(L¹)Os(CO)(Br)(PPh₃)] complex to be a precatalyst can not be ruled out.

Notably, similar Ru complexes, reported earlier,⁴¹ did not exhibit the catalytic activity for such transfer hydrogen reactions.



All the reactions were carried out in ambient condition. A series of blank reactions were carried out in the absence of complex [(L¹)Os(CO)(Br)(PPh₃)]. This has ascertained the necessity of the complex during the reaction. The yields of the alcohols obtained from all the ketones were determined after isolation (table 3).

4. Concluding remarks

Reaction of tridentate N,N,O donor ligand HL with Os(H)(CO)(Br)(PPh₃)₃ afforded new face capped complexes of Os(II). The new face capped [(L)Os(CO)(Br)(PPh₃)] complexes exhibit an one electron reversible oxidative cyclic voltammetric response near 1.0 V in dichloromethane solution. The new Os(II) complexes are catalytically active toward transfer hydrogen catalysis. Reaction of HL with Co(H₂O)₆·(ClO₄)₃ afforded *bis* complex where both the ligands are facially coordinated unlike the *bis* complex of Ru(II), where both the ligands are meridionally

bound. Reversible accessibility to the different redox states for [(L)₂Co]ClO₄ have been attributed to ligand centred electron transfer processes according to the DFT calculations.

Supplementary data

Figures S1–S6 shows the UV-Vis spectra, figures S7–S12 show the IR spectra, figures S13–S18 the ¹H NMR spectra and figures S19–S24 show the cyclic voltammogram of all the complexes (these supplementary figures S1–S6 can be seen in www.ias.ac.in/chemsci.website). CCDC-764971 for **2b** and CCDC-808866 for **7a** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgements

Authors thank the Department of Science and Technology (DST) (New Delhi) for funding under DST-SERC (SR/S1/IC-0026/2007) project. The necessary laboratory and infrastructural facility are provided by the Department of Chemistry, University of Kalyani. The support of DST under FIST and the University Grants Communication (UGC) SAP program to the Department of Chemistry, University of Kalyani is also acknowledged.

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