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Ruthenium(III) bis-bidentate Schiff base complexes mediated transfer hydrogenation of imines

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Abstract

The mono anionic bidentate Schiff base ligands of N, O bonding system has been employed to synthesize a series of new stable ruthenium(III) complexes of general composition $[RuX(EPh_3)(L)_2]$ (where, E = P or As, X = Cl or Br and L = O, N donor of Schiff bases). All the complexes have been fully characterized by elemental analyses, magnetic susceptibility measurements, FT-IR, UV–Vis, EPR and cyclic voltammetric techniques. The catalytic reactivity explored proving these complexes to be efficient in the transfer hydrogenation of imines to amine with moderate to high conversions.

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Keywords: N, O donors; Ru(III) bis-bidentate Schiff base complexes; Spectral studies; Transfer hydrogenation of imines

Ligands containing oxygen and nitrogen donors have been of research interest for many years [1-3], because of the versatility of their steric and electronic properties, which can be modified by choosing the appropriate amine precursors and ring substituents [4]. Bidentate ligands containing imine groups have also been used as the modulators of structural and electronic properties of transition metal centers [5]. Transition metal complexes are powerful catalysts for organic transformations when the suitable ligands are associated with the metal center, they can offer chemio, regio or stereo selectivity under mild conditions [6]. In fact, Schiff bases are able to stabilize many different metals in various oxidation states, controlling the performance of metals in a large variety of useful transformations. However, the appropriate choice of metal precursors and the reaction conditions are crucial for catalytic properties. Further, the transition metal catalyzed transfer hydrogenation of ketones and imines using isopropanol as hydrogen source has shown to be an effective method for forming alcohols and amines in organic synthesis [7-12]. Though

most of the catalysts used for this purpose are mainly based on Rh and Ir systems [10-12], ruthenium based catalytic systems are found to be effective in the transfer hydrogenation of ketones [7b–9] and imines [7a,13,14]. Particularly, ruthenium Schiff base complexes provides better catalyst performance for the transfer hydrogenation reactions [15,16] in terms of the reactivity and selectivity than those attained with the catalyst bearing the amine/diamines or oxazoline ligands [8,17]. Even though there have been several developments in the field of transfer hydrogenation of ketones by ruthenium complexes, there are relatively few reports available on transfer hydrogenation of imines [7a,13,14]. Owing to the synthetic interest in these reactions, it was decided to extend the methodology using the ruthenium system for the transfer hydrogenation of imines. As part of ongoing efforts to study the catalytic efficiency of ruthenium complexes in hydrogenation reactions [18], herein we describes the synthesis and characterization of a series of ruthenium(III) bis-bidentate Schiff base complexes along with the catalytic activity in transfer hydrogenation of imines.

The O, N donors of bidentate Schiff base ligands were prepared (Scheme 1) and characterized [19]. The reaction

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Scheme 1. Preparation of Schiff base ligands (where $R = C_6H_5$ (HL1), $p-ClC_6H_4$ (HL2), $p-CH_3C_6H_4$ (HL3), $p-NO_2C_6H_4$ (HL4)).

of bidentate Schiff bases (HL1-HL4) with ruthenium(III) precursors viz. [RuCl₃(PPh₃)₃], [RuCl₃(AsPh₃)₃], [RuBr₃-(AsPh₃)₃] and [RuBr₃(PPh₃)₂(CH₃OH)] in 2:1 molar ratio, respectively, in benzene under reflux for 5 h. The resulting solution of the complexes was reduced to 3 ml and the solid product was separated by addition of pet. ether (60–80 °C). Then the complexes were purified with CH₂Cl₂/pet. ether (60–80 °C) and a series of new ruthenium(III) bis-bidentate Schiff base complexes of the type [RuX(EPh₃)(L)₂] (X = Cl or Br, E = P or As; L = bidentate Schiff base ligands) (Fig. 1) was obtained. Characterization of these complexes was performed by elemental analysis, magnetic susceptibil-



Fig. 1. Structure of ruthenium(III) bis-bidentate Schiff base complexes (where, E = P or As; X = Cl or Br; $R = C_6H_5$, *p*-ClC₆H₄, *p*-CH₃C₆H₄, *p*-NO₂C₆H₄).

ity measurements, FT-IR, UV–Vis, EPR and cyclic vol-tammetric techniques.

The elemental analyses (C, H, N) are in good agreement with the molecular formula proposed for all the complexes. The IR spectra of all the complexes show that, the Schiff

Table 2

Electrochemical, EPR and magnetic moment data of ruthenium(III) bisbidentate Schiff base complexes

Complexes	Ru ^{IV} /Ru ^{III}	Ru ^{III} /Ru ^{II}	g_{\perp}	g_{\parallel}	$\langle g \rangle^*$	$\mu_{\rm eff}({ m BM})$
	$E_{1/2}$ (V)	$E_{1/2}$ (V)				
1	0.66	-0.25	2.68	1.66	2.34	1.81
2	0.62	-0.25	_	_	_	-
3	_	_	2.76	1.73	2.46	1.85
4	0.68	-0.21	2.81	1.82	2.44	-
5	0.66	-0.25	2.76	1.62	2.43	-
6	0.67	-0.45	_	_	_	-
7	_	_	2.80	1.74	2.44	1.91
8	0.87	-0.16	_	_	_	_
9	0.66	-0.21	2.95	1.56	2.57	-
10	0.65	-0.25	_	_	_	_
11	_	_	2.65	1.73	2.38	1.97
12	0.68	-0.23	2.28	1.76	2.12	_
13	_	_	2.76	1.63	2.44	-
14	0.80	-0.16	2.65	1.62	2.35	1.89
15	0.91	-0.13	2.95	1.63	2.58	_
16	0.83	-0.15	_	_	_	1.91

Supporting electrolyte: [(NBu₄)ClO₄] (0.005 M); Complexes: 0.001 M; $E_{1/2} = 0.5(E_{pa} + E_{pc}) : \langle g \rangle^* = [1/3g_x^2 + 1/3g_y^2 + 1/3g_z^2]^{1/2}.$

Table 1 Analytical, IR and UV–Vis spectral data of ruthenium(III) bis-bidentate Schiff base complexes

Complexes	Found (calcd.)%			$v_{C=N} (cm^{-1})$	$v_{C-O} (cm^{-1})$	$\lambda_{\rm max}$ (nm) (ϵ) (dm ³ /mol/cm)	
	С	Н	Ν				
(1) [RuCl(PPh ₃)(L1) ₂]	67.08 (66.78)	4.33 (3.99)	2.69 (2.34)	1606	1308	815 (645) ^a 427 (6808) ^b 290 (19,340) ^d	
(2) $[RuCl(AsPh_3)(L1)_2]$	64.36 (64.01)	4.16 (3.85)	2.58 (2.12)	1602	1306	$824 (209)^{a} 432 (3202)^{b} 288 (22,300)^{d}$	
(3) [RuBr(AsPh ₃)(L1) ₂]	61.82 (61.54)	3.99 (3.66)	2.48 (2.14)	1605	1310	$680 (520)^{a} 435 (14,035)^{b} 318 (29,620)^{c} 282 (37,530)^{d}$	
(4) $[RuBr(PPh_3)(L1)_2]$	64.33 (64.17)	4.15 (4.09)	2.58 (3.49)	1599	1307	$615 (533)^{a} 447 (6953)^{b} 312 (19780)^{c} 280 (25,540)^{d}$	
$(5) [RuCl(PPh_3)(L2)_2]$	62.79 (62.38)	3.87 (3.57)	2.52 (2.24)	1598	1314	811 (728) ^a 428 (15,888) ^b 312 (28,112) ^c 288 (48,068) ^d	
(6) $[RuCl(AsPh_3)(L2)_2]$	60.40 (60.05)	3.73 (3.31)	2.43 (2.10)	1601	1321	$827 (152)^{a} 431 (15,310)^{b} 249 (25,184)^{c}$	
(7) $[RuBr(AsPh_3)(L2)_2]$	58.16 (57.78)	3.59 (3.17)	2.33 (1.98)	1607	1310	677 (876) ^a 453 (12,553) ^b 246 (22,136) ^c	
(8) $[RuBr(PPh_3)(L2)_2]$	60.37 (59.99)	3.73 (3.39)	2.42 (2.02)	1602	1295	$616 (840)^{a} 425 (18,040)^{b} 264 (42,816)^{d}$	
(9) $[RuCl(PPh_3)(L3)_2]$	67.45 (67.32)	4.59 (4.26)	2.62 (2.34)	1601	1312	826 (593) ^a 434 (7065) ^b 325 (33,760) ^c 261 (38,065) ^d	
$(10) [RuCl(AsPh_3)(L3)_2]$	64.78 (63.55)	4.40 (4.12)	2.51 (2.16)	1602	1306	$827 (724)^{a} 438 (2169)^{b} 295 (49,792)^{d}$	
(11) $[RuBr(AsPh_3)(L3)_2]$	62.29 (61.86)	4.23 (3.88)	2.42 (2.10)	1609	1307	$671 (147)^{a} 460 (4676)^{b} 317 (18,640)^{c} 294 (27,315)^{d}$	
$(12) [RuBr(PPh_3)(L3)_2]$	64.75 (64.45)	4.40 (4.03)	2.51 (2.18)	1599	1318	$611 (313)^{a} 422 (8900)^{b} 281 (21,075)^{d}$	
$(13) [RuCl(PPh_3)(L4)_2]$	61.62 (61.48)	3.80 (3.64)	4.95 (4.58)	1598	1310	$803 (137)^{a} 441 (5988)^{b} 337 (26,432)^{c} 294 (31,552)^{d}$	
$(14) [RuCl(AsPh_3)(L4)_2]$	59.31 (58.97)	3.66 (3.26)	4.77 (4.32)	1598	1311	798 (160) ^a 430 (10,788) ^b 348 (39,536) ^c 283 (53,472) ^d	
$(15) [RuBr(AsPh_3)(L4)_2]$	57.15 (57.65)	3.53 (2.87)	4.55 (4.95)	1598	1310	$745 (395)^{a} 428 (8645)^{b} 318 (19,780)^{c} 288 (27,640)^{d}$	
(16) $[RuBr(PPh_3)(L4)_2]$	59.29 (59.86)	3.66 (3.65)	4.77 (4.09)	1599	1310	661 $(363)^a$ 423 $(8720)^b$ 315 $(11,276)^c$ 296 $(14,528)^d$	
(14) $[RuCl(AsPh_3)(L4)_2]$ (15) $[RuBr(AsPh_3)(L4)_2]$ (16) $[RuBr(PPh_3)(L4)_2]$	59.31 (58.97) 57.15 (57.65) 59.29 (59.86)	3.66 (3.26) 3.53 (2.87) 3.66 (3.65)	4.77 (4.32) 4.55 (4.95) 4.77 (4.09)	1598 1598 1599	1311 1310 1310	$\begin{array}{c} 786\ (160)^{-4}\ 430\ (10,788)^{-3}\ 548\ (39,536)^{-2}\ 283\ (53,472)\\ 745\ (395)^{a}\ 428\ (8645)^{b}\ 318\ (19,780)^{c}\ 288\ (27,640)^{d}\\ 661\ (363)^{a}\ 423\ (8720)^{b}\ 315\ (11,276)^{c}\ 296\ (14,528)^{d} \end{array}$	

^a d–d transition.

^b Charge transfer transition.

 $^{c}_{d}$ *n*- π^{*} .

base ligands behave as bidentate chelating agents coordinating to the metal ions through azomethine nitrogen ($v_{C=N}$: 1609–1598 cm⁻¹) and phenolic oxygen (v_{C-O} : 1321–1295 cm⁻¹) atoms [20] (Table 1). Bands in the 550–500 and 450–400 cm⁻¹ regions are probably due to formation of M–O and M–N bond, respectively [21]. In addition, the other bands observed near 685, 740 and 1550 cm⁻¹ are due to triphenylphosphine or arsine fragments. The elec-

$$\begin{array}{c} \overset{\mathbf{N}-\mathbf{R}^{"}}{\underset{\mathbf{R}^{'}}{\overset{\mathbf{[RuCl(PPh_{3})(L1)_{2}]}}{\underset{\mathbf{i}^{'}-\mathrm{PrOH, 80^{\circ}C}}{\overset{\mathbf{N}}{\underset{\mathbf{R}^{'}}{\overset{\mathbf{R}^{'}}}{\overset{\mathbf{R}^{'}}{\overset{\mathbf{R}^{'}}{\overset{\mathbf{R}^{'}}{\overset{\mathbf{R}^{'}}{\overset{\mathbf{R}^{'}}{\overset{\mathbf{R}^{'}}{\overset{\mathbf{R}^{'}}{\overset{\mathbf{R}^{'}}{\overset{\mathbf{R}^{'}}{\overset{\mathbf{R}^{'}}}{\overset{\mathbf{R}^{'}}{\overset{\mathbf{R}^{'}}{\overset{\mathbf{R}^{'}}}{\overset{\mathbf{R}^{'}}}{\overset{\mathbf{R}^{'}}}{\overset{\mathbf{R}^{'}}}{\overset{\mathbf{R}^{'}}{\overset{\mathbf{R}^{'}}}{\overset{\mathbf{R}^{'}}{\overset{\mathbf{R}^{'}}{\overset{\mathbf{R}^{'}}{\overset{\mathbf{R}^{'}}}{\overset{\mathbf{R}^{'}}{\overset{\mathbf{R}^{'}}{\overset{\mathbf{R}}}}{\overset{\mathbf{R}^{'}}}{\overset{\mathbf{R}^{'}}{\overset{\mathbf{$$

Scheme 2. Catalytic transfer hydrogenation of imines (R, R', R'' = alkyl (or) aryl).

Table 3

tronic spectra of all the complexes in CH₂Cl₂ showed moderately intense bands in the visible region at 827–611 nm ($\varepsilon = 137-876 \text{ dm}^3/\text{mol/cm}$) due to d–d transitions and an absorption at 460–422 nm ($\varepsilon = 2169-18040 \text{ dm}^3/\text{mol/cm}$) probably due to LMCT transitions in addition to $\pi-\pi^*$ and $n-\pi^*$ ligand centered transitions (λ_{max} : <400 nm) (Table 1). The pattern of the electronic spectra of all the complexes indicates the presence of an octahedral geometry around ruthenium(III) ion [22]. The room temperature magnetic moments show that the ruthenium(III) complexes are one electron paramagnetic, in the range 1.81–1.97 BM, which corresponds to the +3 state of ruthenium (low spin d⁵, S = 1/2) in the complexes. The solid state EPR spectra of the complexes exhibit an anisotropic spectra with axial distortion and the 'g' values measured are in the range of

Catalytic transfer hydrogenation of imines by [RuCl(PPh₃)(L1)₂] in the presence of *i*-PrOH/KOH^a

Entry	Substrate	Product	Time (h)	Conversion ^b (%)
1	N H ₃ CO	NH- H ₃ CO	3 (10)	78.5 (92.6)
2		NH-O H	3	56
3		NH	3	59.4
4		NH Cl	3	39
5	H ₃ CO H	NH H ₃ CO	3	79.1
6		NH	3	33.2
7	N - CH ₃ H ₃ CO	NH— CH ₃	3 (10)	12 (74)

^a Reaction conditions: reactions were carried out at 80 °C using substrate (1.25 mmol), catalyst (0.0125 mmol) in 5 ml of isopropanol, KOH (0.0625 mmol); catalyst/imine/KOH ratio 1:100:5.

^b Conversion of the product after adequate time was determined with authentic samples using HP 6890 series GC-FID with a DP-5 column of 30 m length, 0.32 mm diameter and 0.25 µm film thickness.

 $g_{\perp} = 2.95 - 2.28$ and $g_{\parallel} = 1.85 - 1.54$ with $g_{av} = 2.44 - 2.12$ (Table 2) which is derived from $\langle g \rangle * = [1/3 g_r^2 + 1/3 g_v^2 +$ $1/3 g_z^2$ ^{1/2}. In the solution spectra of the complexes at LNT, the resolution was improved and a three line spectrum showing in the range $g_x = 2.91-2.82$; $g_y = 2.62-2.36$; $g_z = 1.85 - 1.54$ is exhibited. The presence of three different 'g' values indicates rhombic distortion in the complexes. The rhombicity of the spectra reflects the asymmetry of the electronic environment around ruthenium in the complexes. Cyclic voltammogram of these complexes exhibit one reversible oxidation ($\Delta E_{\rm P} = 70-80 \,\mathrm{mV}$) and one quasi-reversible reduction ($\Delta E_{\rm P} = 90-110 \, {\rm mV}$) couples and the $E_{1/2}$ lies in the range +0.62 to +0.91 V (Ru^{IV}/Ru^{III}) and -0.45 to -0.13 V (Ru^{III}/Ru^{II}), respectively, versus Ag/ AgCl (Table 2). Both reversible oxidation and quasi-reversible reduction processes are readily assigned as successive metal centered couples only.

The catalytic transfer hydrogenation of imines to amines by one of the synthesized ruthenium(III) bis-bidentate Schiff base complexes $[RuCl(PPh_3)(L1)_2]$ was performed in the presence of isopropanol/KOH (Scheme 2) and the results of this study are listed in Table 3.

A mixture containing imines (1.25 mmol), the ruthenium catalyst (0.0125 mmol) and KOH (0.0625 mmol) were heated to reflux for 3 h in 5 ml of *i*-PrOH under inert atmosphere. The reactions were monitored by TLC. Then the catalyst was removed from the reaction mixture by the addition of diethyl ether. The ether layer was filtered through a short path of silica gel by column chromatography. The filtrate was subjected to GC or GC-MS analysis and the product conversion was determined with authentic samples. The complexes catalyzed both ketimines and aldimines to corresponding amines with moderate to high conversion. The conversion of aromatic aldimine containing p-methoxy group is 78.5% after 3 h and 92.6% was achieved after 10 h (entry 1). Aldimines are efficiently converted into amines than ketimines by this ruthenium complex. The reduction of aromatic ketimine i.e., $Ph(Me)C=N-CH_2Ph$ resulted 59.4% conversion (entry 3) whereas the electron withdrawing group -Cl on the aromatic ring of the imines results 39% (entry 4) conversion after 3 h. Only 12% conversion was obtained in the case of Ph(OMe)CH₃C= N-CH₃ in 3 h and 74% conversion (entry 7) was observed when the reaction time was increased to 10 h. The reaction rate of imines is much lower when compared to ruthenium-catalyzed transfer hydrogenation of ketones. This is due to the fact that both steric and electronic effects may lead to a slower hydrogen transfer from isopropanol to imines when compared to ketones. Moreover, this complex showed good activity of 79.1% for the reduction of *p*-methoxy benzylidine benzylamine (entry 5). This complex also catalyzed the reduction of cyclic imines i.e., cyclohexyl benzylamine, but the conversion is low (33%). The presence of a catalytic amount of a base is necessary for the transfer hydrogenation of imines. The transfer hydrogenation using isopropanol as the hydrogen source would proceed via reactive intermediate, which is

an active species. All the reactions are believed to proceed via metal hydrides as intermediate proposed in the literature [7a,11,13,23]. The catalytic activity of present complexes is comparatively lower than that of the ruthenium(III) Schiff base complexes of [ONNO]-type mediated transfer hydrogenation of ketones reported by us [18a].

In conclusion, we have synthesized and characterized a series of ruthenium(III) bis-bidentate Schiff base complexes and one of the complexes was utilized and gained as a catalyst for the transfer hydrogenation of imines to amines.

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 [19] General procedure for preparing ligands: The 5-chloro-4-methyl-2hydroxy benzophenone was prepared from the benzoylation of 4chloro-3-methyl phenol followed by fries rearrangement reaction (Scheme 1). The equivalent amount of 5-chloro-4-methyl-2hydroxy benzophenone (1 mmol) with primary amines (1 mmol) such as aniline, *p*-chloroaniline, *p*-toluidine and *p*-nitroaniline was

refluxed in methanol for 1 h. The resulting crude product was recrystallized from hot ethanol gave a crystalline solids. Spectral data for the ligands: HL1 (1): yield: 100 mg, 62.15%. m.p.: 162-164 °C. IR (KBr, cm⁻¹): 3439 (OH), 1615 (C=N), 1284 (C-O). ¹H NMR (200 MHz, CDCl₃): δ 11.94 (s, 1H, OH), δ 6.98–7.79 (m, 12H, Ar–H), δ 2.41 (s, 3H, CH₃). UV–Vis (CH₂Cl₂): λ_{max} (nm) = 256, 318. HL2 (2): yield: 92 mg, 54.93%. m.p.: 145-146 °C. IR (KBr, cm⁻¹): 3439 (OH), 1614 (C=N), 1280 (C-O). ¹H NMR (200 MHz, CDCl₃): δ 11.92 (s, 1H, OH), δ 6.97-7.58 (m, 11H, Ar-H), δ 2.50 (s, 3 H, CH₃). UV-Vis (CH₂Cl₂): λ_{max} (nm) = 248, 316. HL3 (3): yield: 80 mg, 43.40%. m.p.: 129-131 °C. IR (KBr, cm⁻¹): 3361 (OH), 1621 (C=N), 1292 (C-O). ¹H NMR (200 MHz, CDCl₃): δ 11.94 (s, 1H, OH), δ 6.97-8.09 (m, 11H, Ar-H), δ 2.40 (s, 6H, CH₃). UV-Vis (CH₂Cl₂): λ_{max} (nm) = 256, 318. HL4 (4): yield: 110 mg, 65.31%. m.p.: 144-145 °C. IR (KBr, cm⁻¹): 3424 (OH), 1618 (C=N), 1288 (C-O). ¹H NMR (200 MHz, CDCl₃): δ 11.91 (s, 1H, OH), δ 6.97–7.68 (m, 11H, Ar–H), δ 2.40 (s, 3H, CH₃). UV–Vis (CH₂Cl₂): λ_{max} (nm) = 254, 315.

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