Inorganica Chimica Acta 363 (2010) 2865–2873

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Studies on the reactions of ruthenium(II) substrates with tridentate (N,N,O) azo ligands

Poulami Pattanayak [a], Debprasad Patra [a], Jahar Lal Pratihar [a], Andrew Burrows [b], Mary F. Mahon [b], Surajit Chattopadhyay [a,*]

[a] Department of Chemistry, University of Kalyani, Kalyani 741235, India
[b] Department of Inorganic Chemistry, University of Bath, Claverton Down, Bath BA27AY, UK

ARTICLE INFO

Article history:
Received 29 January 2010
Received in revised form 5 April 2010
Accepted 8 April 2010
Available online 18 April 2010

Dedicated to Animesh Chakravorty

Keywords:
Facial
Meridional
Azo ligands
(N,N,O) donor
Oxygenation

ABSTRACT

Reactions of 1-{[2-(arylazo)phenyl]iminomethyl}-2-phenol, HL_{sal}, **1**, [where H represents the dissociable protons upon complexation and aryl groups of HL_{sal} are phenyl for HL^1_{sal}, *p*-methylphenyl for HL^2_{sal}, and *p*-chlorophenyl for HL^3_{sal}], ligands with $Ru(H)(CO)(Cl)(PPh_3)_3$ afforded complexes of composition $[(L_{sal})Ru(CO)(Cl)(PPh_3)]$ and $(L_{sal})_2Ru$ where the N,N,O donor tridentate $(L_{sal})^-$ ligands coordinated the metal centre facially and meridionally, respectively. Stepwise formation of $[(L_{sal})_2Ru]$ has been ascertained. Reaction of 1-{[2-(arylazo)phenyl]iminomethyl}-2-napthol, HL_{nap}, **2**, [where H represents the dissociable protons upon complexation and aryl groups of HL_{nap} are phenyl for HL^1_{nap}, *p*-methylphenyl for HL^2_{nap}, and *p*-chlorophenyl for HL^3_{nap}], ligands with $Ru(H)(CO)(Cl)(PPh_3)_3$ afforded exclusively the complexes of composition $[(L_{nap})Ru(CO)(Cl)(PPh_3)]$, where N,N,O donor tridentate $(L_{nap})^-$ was facially coordinated. The ligand 1-{[2-(phenylazo)phenyl]aminomethyl}-2-phenol, HL, **3**, was prepared by reducing the aldimine function of HL^1_{sal}. Reaction of HL with $Ru(PPh_3)_3Cl_2$ afforded new *azosalen* complex of Ru(III) in concert with regiospecific oxygenation of phenyl ring of HL. All the new ligands were characterized by analytical and spectroscopic techniques. The complexes were characterized by analytical and spectroscopic techniques and subsequently confirmed by the determination of X-ray structures of selected complexes.

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 modulate their reactivity. Although several kinds of azo ligands have been utilized to explore the coordination chemistry of transition metal ions but (N,N,O) donor azo ligands are scarce [1]. Therefore we paid attention to design and synthesis new (N,N,O) donor azo ligands as given in Chart 1.

Moreover, coordination chemistry of ruthenium incorporating (N,N,O) donor azo ligands have received only marginal attention [2]. Tridentate ligands may bind the transition metal ion either meridionally or facially in octahedral complexes. 1,4,7 tri aza cyclononane; 1,4,7 trithia cyclononane; tris pyrazolyl borate and a few scorpionate and tripodal ligands are good examples of facially coordinating ligands [3–6]. Fascinating chemistry of such metal complexes have enhanced the interest on the synthesis of new tridentate ligands that have potential to bind the metal centre facially. Facially capped complexes have received attention due to their catalytic and biological activity [7]. Ruthenium complexes based upon a tripodal phosphine ligand are used as catalysts for conversion of dimethyl oxalate to ethylene glycol [8]. Homogeneously-catalysed hydrogenation of esters to yield alcohols is also known to occur using the facially capped ruthenium complexes as catalyst [9–11].

Herein, we have described the reactions of appropriate ruthenium substrates with HL_{sal} and HL_{nap}. The conditions to obtain Ru(II) complexes incorporating facially and meridionally coordinated tridentate (N,N,O) donor azo ligands have been described. Reaction of new HL ligands with Ru(II) substrate resulting regiospecific oxygenation of phenyl ring of HL, with concomitant formation of new *azosalen* complex of Ru(III) have been delineated in this paper.

2. Results and discussion

2.1. Syntheses

The 1-{[2-(arylazo)phenyl]iminomethyl}-2-phenol ligands were prepared by the condensation of salicylaldehyde with 2-(arylazo) aniline as reported earlier [12]. These ligands are abbreviated as HL_{sal} [where aryl groups of HL_{sal} are phenyl for HL^1_{sal}, *p*-methyl

* Corresponding author. Tel.: +91 33 25828750; fax: +91 33 25828282.
E-mail address: scha8@rediffmail.com (S. Chattopadhyay).

0020-1693/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2010.04.016

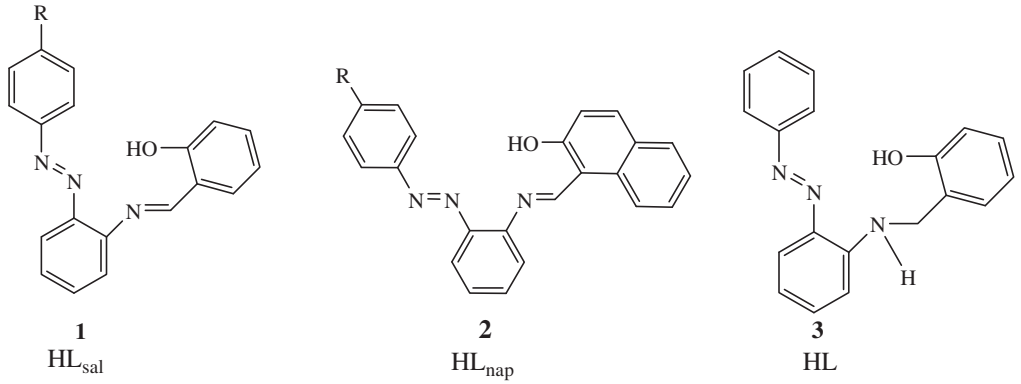
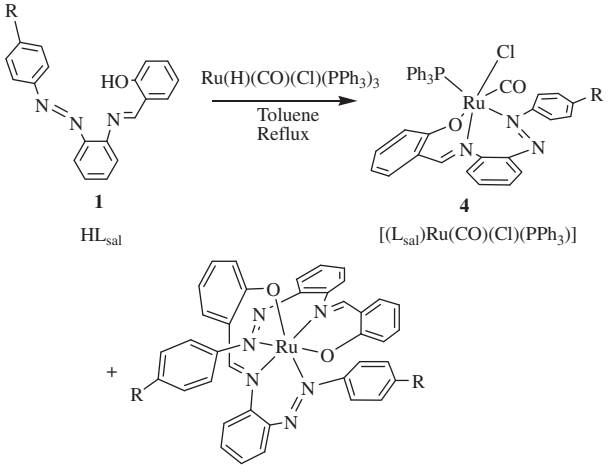


Chart 1.

phenyl for HL$^2_{sal}$ and *p*-chloro phenyl for HL$^3_{sal}$, H represents the dissociable phenolic proton] in this paper.

Reaction of one equivalent Ru(H)(CO)(Cl)(PPh$_3$)$_3$ with two equivalent HL$_{sal}$ in refluxing toluene afforded [(L$_{sal}$)Ru(CO)(PPh$_3$)(Cl)], **4**, and [(L$_{sal}$)$_2$Ru], **5**, in ~60% and ~20% yields, respectively after 8 h as shown in Eq. (1).



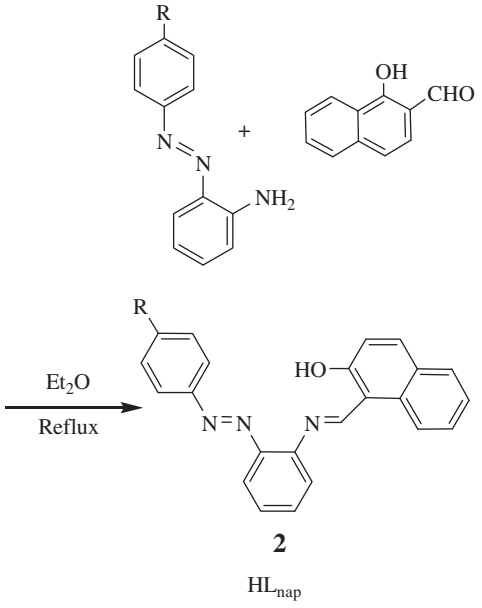
(1)

Compound		R
1a	HL$^1_{sal}$	H
1b	HL$^2_{sal}$	CH_3
1c	HL$^3_{sal}$	Cl
4a	[(L$^1_{sal}$)Ru(CO)(Cl)(PPh$_3$)]	H
4b	[(L$^2_{sal}$)Ru(CO)(Cl)(PPh$_3$)]	CH_3
4c	[(L$^3_{sal}$)Ru(CO)(Cl)(PPh$_3$)]	Cl
5a	[(L$^1_{sal}$)$_2$Ru]	H
5b	[(L$^2_{sal}$)$_2$Ru]	CH_3
5c	[(L$^3_{sal}$)$_2$Ru]	Cl

The HL$_{sal}$ ligands coordinated Ru(II) centre dissociating the phenolic proton in both the complexes, [(L$_{sal}$)Ru(CO)(PPh$_3$)(Cl)] and [(L$_{sal}$)$_2$Ru]. Indeed the tridentate N,N,O donor anionic (L$_{sal}$)$^-$ species are held facially and meridionally in the coordination sphere of [(L$_{sal}$)Ru(CO)(Cl)(PPh$_3$)] and [(L$_{sal}$)$_2$Ru], respectively (X-ray structure, see below). The bis complexes, [(L$_{sal}$)$_2$Ru], were obtained as the major product in presence of excess ligand and upon extension of reaction time to ~24 h. On the other hand, the [(L$_{sal}$)Ru(CO)(Cl)(PPh$_3$)] products were major even after prolonged reflux when the ligand was taken in equivalent amount with respect to the ruthenium substrate. Subsequently, the conversion of [(L$_{sal}$)Ru(CO)(Cl)(PPh$_3$)] into [(L$_{sal}$)$_2$Ru] occurred upon reaction of HL$_{sal}$ with [(L$_{sal}$)Ru(CO)(Cl)(PPh$_3$)] in refluxing toluene signifying the stepwise formation of [(L$_{sal}$)$_2$Ru] according to the sequence as shown in Scheme 1.

Summarily, the HL$_{sal}$ ligands bind the metal centre facially as well as meridionally forming two types of complexes, [(L$_{sal}$)Ru(CO)(Cl)(PPh$_3$)] and [(L$_{sal}$)$_2$Ru]. Moreover, formation of [(L$_{sal}$)$_2$Ru] upon treatment of [(L$_{sal}$)Ru(CO)(Cl)(PPh$_3$)] with HL$_{sal}$ was significant in terms of the lability of [(L$_{sal}$)Ru(CO)(Cl)(PPh$_3$)] with respect to ligand substitution along with concomitant geometrical isomerisation. As a result attention was drawn to examine the reactions of Ru(H)(CO)(Cl)(PPh$_3$)$_3$ with the ligands that are bulkier than HL$_{sal}$. The bulkier ligands HL$_{nap}$, **2**, were designed and synthesized keeping the nature of coordinating sites similar to HL$_{sal}$.

The new ligand, 1-{[2-(arylazo)phenyl]iminomethyl}-2-napthol, HL$_{nap}$, **2**, [where aryl groups of HL$_{nap}$ are phenyl for HL$^1_{nap}$; *p*-methyl phenyl for HL$^2_{nap}$ and *p*-chloro phenyl for HL$^3_{nap}$] were prepared by refluxing appropriate 2-(arylazo)aniline with 2-hydroxy-1-naphthaldehyde in diethyl ether as shown in Eq. (2).

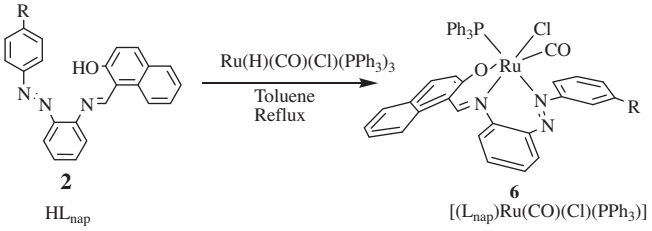


(2)

$$Ru(H)(CO)(Cl)(PPh_3)_3 + HL_{sal} \longrightarrow [(L_{sal})Ru(CO)(Cl)(PPh_3)]$$

$$[(L_{sal})Ru(CO)(Cl)(PPh_3)] + HL_{sal} \longrightarrow [(L_{sal})_2Ru]$$

Scheme 1.



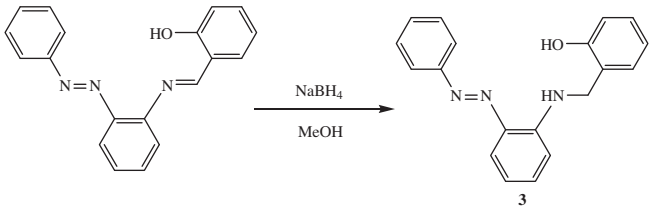
2
HL_{nap}

6
$[(L_{nap})Ru(CO)(Cl)(PPh_3)]$

Compound		R
2a	HL^1_{nap}	H
2b	HL^2_{nap}	CH_3
2c	HL^3_{nap}	Cl
6a	$[(L^1_{nap})Ru(CO)(Cl)(PPh_3)]$	H
6b	$[(L^2_{nap})Ru(CO)(Cl)(PPh_3)]$	CH_3
6c	$[(L^3_{nap})Ru(CO)(Cl)(PPh_3)]$	Cl

(3)

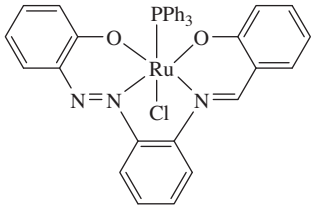
Reaction of $Ru(H)(CO)(Cl)(PPh_3)_3$ with the ligand system HL_{nap} in refluxing toluene yielded only one product of composition $[(L_{nap})Ru(CO)(Cl)(PPh_3)]$, **6**, as given in Eq. (3) where the anionic tridentate (N,N,O) ligands, $(L_{nap})^-$, bind the metal centre facially. It is important to note that the reaction of $[(L_{nap})Ru(CO)(Cl)(PPh_3)]$ with HL_{nap} or the reaction of $Ru(H)(CO(Cl)(PPh_3)_3$ with excess HL_{nap} in refluxing toluene did not afford the bis complex $[(L_{nap})_2Ru]$ justifying the exclusive formation of $[(L_{nap})Ru(CO)(Cl)(PPh_3)]$. It was anticipated that either the bulkier ligand system did not allow another HL_{nap} within the coordination sphere due to steric hindrance or the nature of HL_{nap} ligand itself was not suitable for further substitution. Thus, formation of Ru(II) complexes incorporating facially coordinated (N,N,O) donor azo ligands, HL_{sal} and HL_{nap}, depend on the ligand system, ligand to metal substrate stoichiometric ratio and reaction time. Since HL_{sal} and HL_{nap} ligands are conjugated and more rigid than the nonconjugated ligand systems so it was contemplated to introduce flexibility within such ligand backbones by reducing the aldimine functions into corresponding dihydro form. Therefore, new ligand system 1-{[2-(phenylazo)phenyl]aminomethyl}-2-phenol, HL, **3**, was prepared by reducing the HL^1_{sal} with sodium borohydride in methanol as shown in Eq. (4). The ligand HL was characterized unequivocally from its spectral data (see below).



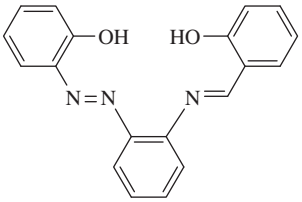
3

(4)

Reaction of HL with $Ru(H)(CO(Cl)(PPh_3)_3$ in refluxing toluene did not afford any isolable product. Therefore the metal substrate $Ru(PPh_3)_3Cl_2$ was chosen arbitrarily to carry out reaction with ligand HL**.** Upon refluxing $Ru(PPh_3)_3Cl_2$ with HL in toluene afforded new Ru(III) complex $[(OL)Ru(PPh_3)Cl]$, **7**, where H_2OL is shown in **8**.



7



8

During the reaction, the reduced aldimine form of HL was oxidized to the parent imine form with concomitant oxygenation at the *ortho* carbon of the phenyl ring of phenylazo fragment. It was believed that the two hard phenolic O donors of the oxygenated ligand stabilized the Ru(III).

2.2. Characterization

The UV–Vis spectra of The $[(L_{sal})Ru(CO)(Cl)(PPh_3)]$ and $[(L_{nap})Ru(CO)(Cl)(PPh_3)]$ complexes in dichloromethane solution exhibited characteristic absorptions near 440 and 340 nm. The bis complexes $[(L_{sal})_2Ru]$ exhibited absorption near 630 nm.

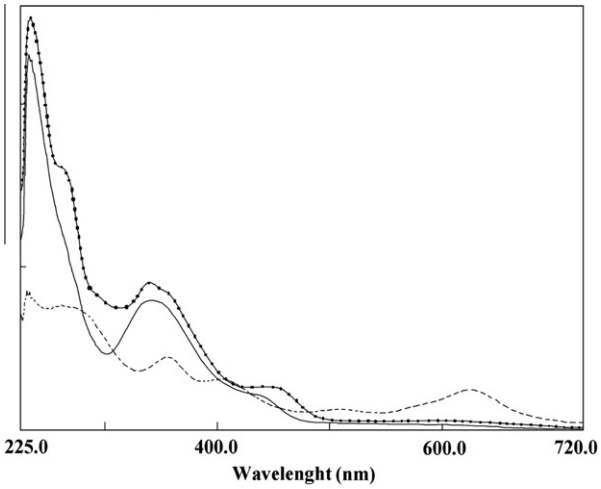


Fig. 1. UV–Vis spectra of $[(L^1_{sal})Ru(CO)(Cl)(PPh_3)$ (—), $[(L^1_{nap})Ru(CO)(Cl)(PPh_3)]$ (-●-●-) and $[(L^1_{sal})_2Ru]$ (- - -) in dichloromethane solution.

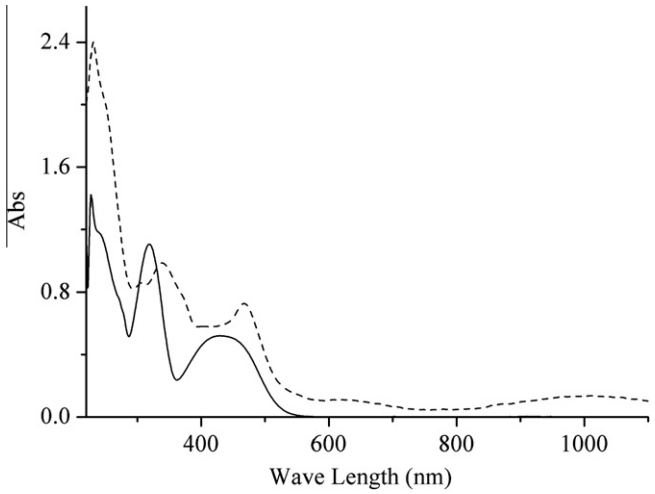


Fig. 2. UV–Vis spectra of **3** (—), and **7** (- - -) in dichloromethane solution.

Representative UV–Vis spectra of $[(L^1_{sal})Ru(CO)(Cl)(PPh_3)]$, $[(L^1_{sal})_2Ru]$ and $[(L^1_{nap})Ru(CO)(Cl)(PPh_3)]$ have been given in Fig. 1.

Complex $[(OL)Ru(PPh_3)Cl]$ displayed low energy absorption at 1040 nm. The spectra of ligand HL and Complex $[(OL)Ru(PPh_3)Cl]$ are shown in Fig. 2.

Relevant UV–Vis spectral data are collected in experimental section and the spectra of other the new compounds are given in Figs. S1–S14 as Supplementary materials.

IR spectra of all the complexes were recorded in solid KBr support. The $[(L_{sal})Ru(CO)(Cl)(PPh_3)]$, $[(L_{nap})Ru(CO)(Cl)(PPh_3)]$ and $[(L_{sal})_2Ru]$ complexes exhibited $\nu_{C=N}$ absorptions (~1607, 1615 and 1603 cm^{-1}, respectively) at slightly lower frequency than that of the corresponding ligands HL_{sal} and HL_{nap} (~1615 and ~1624 cm^{-1}, respectively) indicating coordination of aldimine (–N=CH–) nitrogen [12]. The ν_{NH} of ligand HL appeared at 3401 cm^{-1} and $\nu_{C=N}$ is absent indicating reduction of C=N to the dihydro species. Whereas, the IR band at 1600 cm^{-1} and no trace of ν_{NH} for $[(OL)Ru(PPh_3)Cl]$ signified the conversion of reduced imine of HL into imine form during the complexation. The $\nu_{N=N}$ of $[(L_{sal})Ru(CO)(Cl)(PPh_3)]$, $[(L_{nap})Ru(CO)(Cl)(PPh_3)]$, $[(L_{sal})_2Ru]$ and $[(OL)Ru(PPh_3)Cl]$ appeared at slightly lower frequency range (1425–1435 cm^{-1}) than those of the ligands (1450–1483 cm^{-1}) indicating coordination of azo (–N=N–) nitrogen [13]. A sharp singlet near 1940 cm^{-1} has been assigned to $\nu_{C=O}$ for $[(L_{sal})Ru(CO)(Cl)(PPh_3)]$ and $[(L_{nap})Ru(CO)(Cl)(PPh_3)]$ [13]. Relevant IR spectral data are collected in experimental section and the spectra of all the new compounds are given in Figs. S15–S28 in Supplementary material.

The composition of $[(L_{sal})Ru(CO)(Cl)(PPh_3)]$, $[(L_{sal})_2Ru]$ and $[(L_{nap})Ru(CO)(Cl)(PPh_3)]$ matched well with the C, H, N analytical data and ^1H NMR spectral data. The ^1H NMR spectra of the complexes

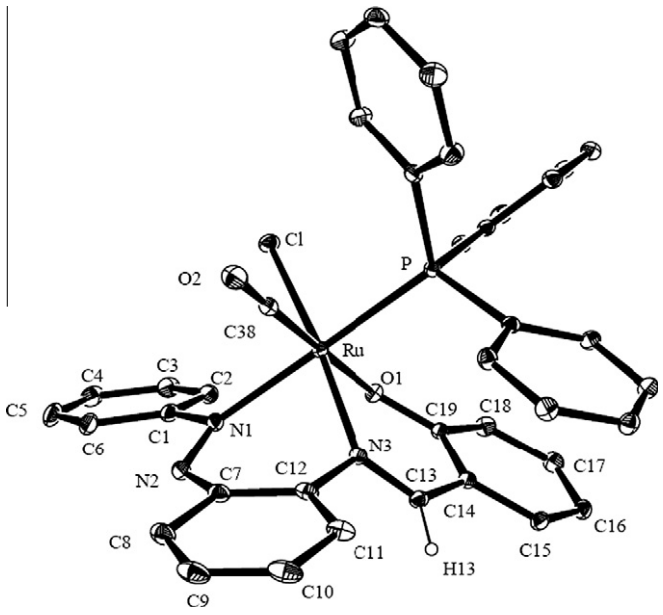


Fig. 3. Molecular structure of $[(L^1_{sal})Ru(CO)(Cl)(PPh_3)]$ with atom numbering scheme. The hydrogen atoms excepting on –N=C–H (13) of the imine group has been omitted for clarity.

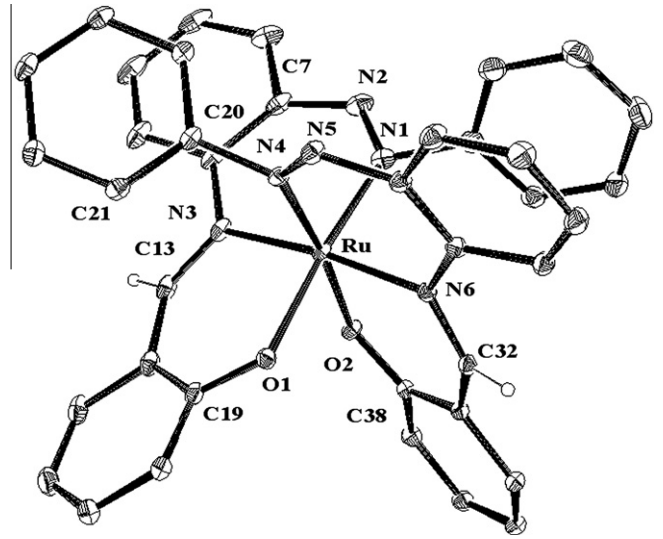


Fig. 4. Molecular structure of $[(L^1_{sal})_2Ru]$ with atom numbering scheme. The hydrogen atoms excepting on –N=C–H (13, 32) of the imine groups have been omitted for clarity.

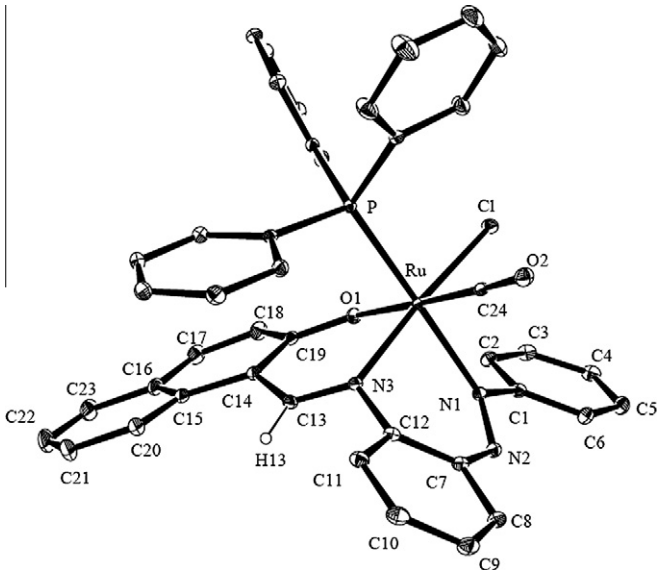


Fig. 5. Molecular structure of $[(L^1_{nap})Ru(CO)(Cl)(PPh_3)]$ with atom numbering scheme. The hydrogen atoms excepting on –N=C–H (13) of the imine group has been omitted for clarity.

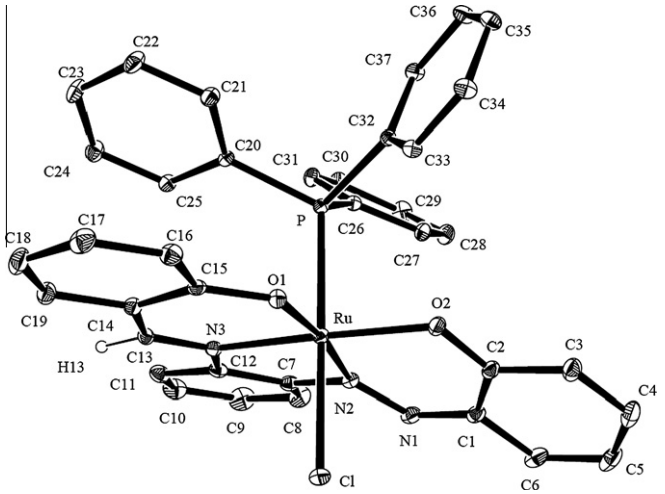


Fig. 6. Molecular structure of $[(OL)Ru(PPh_3)Cl]$ with atom numbering scheme. The hydrogen atoms excepting on –N=C–H (13) of the imine group has been omitted for clarity.

Table 1
Selected bond distances (Å) and angles (°) for [(L^1_{sal})Ru(CO)(PPh_3)(Cl)], [(L^1_{sal})$_2$Ru], [(L^1_{nap})Ru(CO)(Cl)(PPh_3)] and [(OL)Ru(PPh_3)Cl].

[(L^1_{sal})Ru(CO)(PPh_3)(Cl)]			
Ru–Cl	2.414 (2)	Ru–N3	2.055 (2)
Ru–P	2.345 (1)	N3–C13	1.298(3)
Ru–O1	2.103 (4)	N1–N2	1.266(2)
Ru–N1	2.162 (1)	O1–C19	1.310(2)
Ru–C38	1.838(2)		
O1–Ru–N1	91.63(6)	P–Ru–N3	97.74(5)
Cl–Ru–O1	89.12(4)	N1–C1–C2	118.43(18)
O1–Ru–N3	84.57(6)	Ru–N3–C13	126.73(14)
Ru–O1–C19	123.42(12)	Ru–N1–N2	124.53(14)
N1–Ru–N3	80.87(7)	N1–N2–C7	120.69(17)
Ru–N3–C12	116.19(12)		
[(L^1_{sal})$_2$Ru]			
Ru–O1	2.039 (1)	Ru–N5	1.979 (1)
Ru–O2	2.036 (1)	Ru–N6	2.049 (1)
Ru–N1	1.977 (2)	N4–N5	1.280(2)
Ru–N3	2.045 (2)	N2–N1	1.269(2)
Ru–N4	1.979 (1)	N6–C32	1.318(2)
N3–C13	1.313(1)	O1–C19	1.301(2)
O1–Ru–O2	86.80(5)	O1–Ru–N6	81.50(6)
O1–Ru–N1	175.38(6)	O2–Ru–N1	92.29(6)
O1–Ru–N3	93.40(6)	O2–Ru–N3	82.23(6)
O1–Ru–N4	89.88(6)	O2–Ru–N4	174.01(6)
Ru–N1–N2	132.05(15)	O2–Ru–N6	93.36(6)
N1–Ru–N3	90.96(7)	N1–Ru–N4	91.41(7)
N1–Ru–N6	94.04(7)	N3–Ru–N4	93.01(6)
Ru–O1–C19	125.21(12)	N4–Ru–N6	91.07(6)
[(L^1_{nap})Ru(CO)(Cl)(PPh_3)]			
Ru–Cl	2.406 (1)	O1–C19	1.298 (9)
Ru–P	2.338 (1)	N3–C13	1.311(2)
Ru–O1	2.096 (1)	N1–N2	1.266 (1)
Ru–N1	2.160 (1)	Ru–C24	1.835 (1)
Ru–N3	2.048 (2)		
O1–Ru–N1	91.63(6)	O1–Ru–N3	84.57(6)
P–Ru–N3	96.02(3)	Ru–N3–C13	126.73(14)
Cl–Ru–O1	89.29(3)	Ru–N3–C12	116.19(12)
Ru–O1–C19	127.56(9)	N1–Ru–N3	80.87(7)
Cl–Ru–N1	91.50(3)	Ru–N1–N2	125.12(9)
Cl–Ru–N3	170.86(3)		
[(OL)Ru(PPh_3)Cl]			
Ru–Cl	2.434 (2)	O1–C15	1.312(2)
Ru–P	2.361 (1)	O2–C2	1.311(2)
Ru–O1	2.032 (1)	N1–N2	1.291(2)
Ru–O2	1.998 (1)	Ru–N3	2.000 (1)
Ru–N2	1.957 (2)	N3–C13	1.300(2)
O2–Ru–N3	173.80(5)	N2–Ru–N3	82.59(6)
Cl–Ru–P	179.07(2)	Ru–N2–N1	129.48(12)
Cl–Ru–N2	85.03(4)	Ru–N2–C7	113.67(11)
Cl–Ru–N3	90.68(4)	Ru–N3–C12	112.43(10)
P–Ru–O1	90.42(4)	Ru–O2–C2	121.47(11)
P–Ru–O2	90.48(4)	Ru–O1–C15	124.55(11)
O1–Ru–O2	93.29(5)	O1–Ru–N2	172.18(5)

were recorded in $CDCl_3$. The Phenolic OH signal of HL_{sal} (~δ 13.60) and HL_{nap} (~δ 13.15) ligands were absent in the spectra of these complexes indicating the coordination of phenoxide O. The aldimine (–CH=N–) proton resonance of [(L_{sal})Ru(CO)(Cl)(PPh_3)] (~δ 8.5), and [(L_{sal})$_2$Ru] (~δ 8.67) shifted marginally compared to the HL_{sal} ligand (~δ 8.63). The aldimine (–CH=N–) proton resonance of HL_{nap} appeared as doublet near δ 9.20 due to the protonation of imine nitrogen by the phenolic proton via intramolecular hydrogen bonding. The ligand HL displayed well resolved spectrum where methylene proton resonances appeared at δ 4.29. OH and NH proton resonances appeared at δ 8.11 and δ 6.72, respectively. The aromatic protons of all the compounds appeared in the range δ 6.87–δ 7.95. Relevant NMR spectral data are collected in experimental section and the spectra are given in Figs. S29–S41 as Supplementary material.

2.3. X-ray structure

Crystal structures of [(L^1_{sal})Ru(CO)(Cl)(PPh_3)], [(L^1_{sal})$_2$Ru], [(L^1_{nap})Ru(CO)(Cl)(PPh_3)] and [(OL)Ru(PPh_3)Cl] were determined by single crystal X-ray crystallography. The perspective views of the molecular structures of [(L^1_{sal})Ru(CO)(Cl)(PPh_3)], [(L^1_{sal})$_2$Ru], [(L^1_{nap})Ru(CO)(Cl)(PPh_3)] and [(OL)Ru(PPh_3)Cl] are given in Figs. 3–6, respectively with atom numbering scheme. Selected bond distances and angles are given in Table 1.

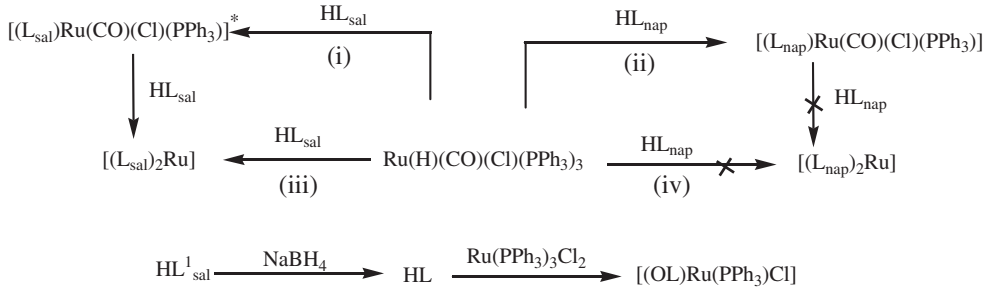
Tridentate N,N,O donor L_{sal}^- and L_{nap}^- are bound facially to the Ru(II) centre in [(L^1_{sal})Ru(CO)(Cl)(PPh_3)] and [(L^1_{nap})Ru(CO)(Cl)(PPh_3)] along with three monodentate ligands Cl^-, CO and PPh_3 in a distorted octahedral geometry. Two N,N,O donor L_{sal}^- ligands are coordinated meridionally in [(L^1_{sal})$_2$Ru] complex and the geometry about Ru(II) is distorted octahedral. Octahedral ruthenium centre of [(OL)Ru(PPh_3)Cl] is equatorially coordinated by tetradentate (O,N,N,O) dianionic $(OL)^{2-}$ ligand. Chloride (Cl^-) and phosphine (PPh_3) ligands are held at axial *trans* positions. The Ru–N(azo), Ru–N(imine) and Ru–O distances in [(L^1_{sal})$_2$Ru] (av. 1.978, 2.047 and 2.037 Å, respectively) are shorter than those of [(L^1_{sal})Ru(CO)(Cl)(PPh_3)] (2.162(1), 2.055(2) and 2.103(1) Å). The Ru–N(azo), Ru–N(imine) and Ru–O lengths of [(L^1_{nap})Ru(CO)(Cl)(PPh_3)] are marginally shorter than [(L^1_{sal})Ru(CO)(Cl)(PPh_3)] which is attributed to enhanced conjugation due to the napthyl ring. In general, Ru–N and Ru–O distances are shorter in [(OL)Ru(PPh_3)Cl] than the other three complexes in concurrence with higher oxidation state of Ru (i.e. Ru(III)) in [(OL)Ru(PPh_3)Cl]. The molecular structure of [(OL)Ru(PPh_3)Cl] confirmed the oxygenation of the phenyl ring (C14–C19). The N3–C13 distances in all the complexes are within the range 1.298(3)–1.318(2) Å which is similar to N-coordinated aldimine C–N distances [12,14,15]. Azo (N=N) distances in all the complexes are within the normal range (1.266(3)–1.291(2) Å) [14]. The azo (N=N) distances in facially coordinated L_{sal}^- and L_{nap}^- ligands (av. 1.266 Å) are shorter than meridionally bound L_{sal}^- and coordinated $(OL)^{2-}$ ligands (av. 1.280 Å) signifying superior metal to azo (N=N) π back bonding in [(L^1_{sal})$_2$Ru] and [(OL)Ru(PPh_3)Cl].

3. Conclusions

Reactions of several tridentate (N,N,O) donor azo ligands with Ru(II) substrates have been carried out to prepare new Ru(II) and Ru(III) complex. The results have been summarised and shown schematically in Scheme 2 with the reaction conditions.

The Ru(II) substrate, Ru(H)(CO)(Cl)(PPh_3)$_3$, underwent ligand substitution with one L_{sal}^- or L_{nap}^- to form [(L_{sal})Ru(CO)(Cl)(PPh_3)] or [(L_{nap})Ru(CO)(Cl)(PPh_3)], respectively. In both the complexes tridentate (N,N,O) donor ligands coordinated the metal centre facially.

In the case of [(L_{sal})Ru(CO)(Cl)(PPh_3)], further substitution occurred in presence of excess HL_{sal} ligand to form (L_{sal})$_2$Ru where the ligands are meridionally coordinated. Preparation of [(L_{sal})$_2$Ru] upon treatment of [(L_{sal})Ru(CO)(Cl)(PPh_3)] with HL_{sal} indicated stepwise formation of [(L_{sal})$_2$Ru] in conjunction with geometrical isomerisation of the ligand coordination. On contrary to this, [(L_{nap})$_2$Ru] complex was not obtained in presence of excess ligand or upon treatment of [(L_{nap})Ru(CO)(Cl)(PPh_3)] with HL_{nap}. Therefore, HL_{nap} dictated the formation of [(L_{nap})Ru(CO)(Cl)(PPh_3)] exclusively. The new ligand HL was synthesized by reducing the aldimine function of HL^1_{sal} with the expectation to obtain more flexible ligand. Reaction of HL with Ru(PPh_3)$_3$Cl$_2$ in aerobic condition produced the new complex [(OL)Ru(PPh_3)Cl] after oxygenation at the *ortho* position of pendent phenyl ring. Oxidation of dihydro aldimine to aldimine and Ru(II) to Ru(III) were occurred during the reaction. Mechanism of this aromatic oxygenation is unclear at present and it is supposed that metal and ligand oxidations prior to oxygenation produced reactive oxygen species (ROS) by



(i) 1:1 stoichiometric ratio with respect to HL_{sal} and $Ru(H)(CO)(Cl)(PPh_3)_3$, 8h refluxin toluene
(ii) 1:1 stoichiometric ratio with respect to HL_{nap} and $Ru(H)(CO)(Cl)(PPh_3)_3$, 8h refluxin toluene
(iii) Excess $HL_{sal}$with respect to $Ru(H)(CO)(Cl)(PPh_3)_3$, ~ 24h reflux in toluene
(iv) Excess $HL_{nap}$with respect to $Ru(H)(CO)(Cl)(PPh_3)_3$, ~ 24h reflux in toluene

*This is major product with a minor amount of $[(L_{sal})_2Ru]$

Scheme 2.

reducing the dioxygen. The ROS, thus produced, oxygenated the phenyl ring via metal mediated pathway.

4. Experimental

4.1. Materials

All commercially available chemicals and solvents utilized during the present work were of analytical grade and in most of the cases these were used as obtained. The chemicals and there sources were as follows: Salicylaldehyde, benzene, dichloromethane, acetonitrile, petroleum ether, sodium hydroxide, diethyl ether, formaldehyde, triphenylphosphene, methylcellosolve, Sodium borohydride from E. Merck (India). Ruthenium chloride was purchased from Johnson Mathey. 2-Hydroxy-1-naphthaldehyde was prepared according to a reported procedure [16]. $Ru(H)(CO)(Cl)(PPh_3)_3$, $Ru(PPh_3)_3Cl_2$ were prepared following a procedure reported earlier [17]. All the solvents were purified and distilled after receiving from E. Merck India. Silical gel G with binder was used for thin layer chromatography.

4.2. Syntheses of compounds

4.2.1. Preparation of ligands

The 1-{[2-(arylazo)phenyl]iminomethyl}-2-phenol ligands, HL_{sal}, were synthesized by the reported procedure [12]. 1-{[2-(arylazo)phenyl]iminomethyl}-2-napthol, HL_{nap} ligands were prepared by the following procedure as described below for $HL^1{}_{nap}$.

4.2.1.1. $HL^1{}_{nap}$ ***2a***. 2-(Phenylazo) aniline (0.1 g, 0.50 mmol) was dissolved in dry diethyl ether (40 mL), and to it 2-hydroxy-1-naphthaldehyde (0.087 g, 0.50 mmol) was added. The mixture was then refluxed for 9 h and solvent was evaporated in vaccuo for 2 h to obtain the solid product. It was further kept in a vacuum desiccator for 24 h before use and characterization. Yield: 0.16 g (90%). *Anal.* Calc. for $HL^1{}_{nap}$: C, 78.61; H, 4.87; N, 11.95. Found: C, 78.63; H, 4.90; N, 11.97%. Electronic spectrum (λ_{max}/nm (ε/dm^2 mol^{-1}), dichloromethane): 334 (12 096), 311 (14 073), 235 (39 384). IR (KBr pellets, cm^{-1}): ν(N=N) 1481; ν(C=N) 1624. ^{1}H NMR ($CDCl_3$, ppm): δ 13.17 (s, 1H, OH); 10.82 (s, 1H, –CH=N); 9.22 (d, 1H, Ph); 9.21 (d, 1H, Ph); 8.18–8.15 (m, 2H, Ph); 7.98 (d, 1H, v); 7.90 (d, 1H, Ph); 7.74 (d, 1H, Ph); 7.62 (d, 2H, Ph); 7.58–7.54 (m, 3H, Ph); 7.51–7.44 (m, 2H, Ph); 7.36–7.25 (m, 2H, Ph).

4.2.1.2. $HL^2{}_{nap}$ ***2b***. Yield: 0.14 g (85%). *Anal.* Calc. for $HL^2{}_{nap}$: C, 78.88; H, 5.24; N, 11.49. Found: C, 78.85; H, 5.26; N, 11.52%. Electronic spectrum (λ_{max}/nm (ε/dm^2 mol^{-1}), dichloromethane): 358 (8662); 319 (12 039); 231 (30 318). IR (KBr pellets, cm^{-1}): ν(N=N) 1483; ν(C=N) 1620. ^{1}H NMR ($CDCl_3$, ppm): δ 13.15 (s, 1H, OH); 10.81 (s,1H, –CH=N); 9.17 (d, 1H, Ph); 9.18 (d, 1H, Ph); 8.05 (d, 1H, Ph); 7.95 (d, 1H, Ph); 7.85 (d, 1H, Ph); 7.70 (d, 1H, Ph); 7.58 (t, 2H, Ph); 7.51 (t, 1H, Ph); 7.44 (t, 1H, Ph); 7.35 (d, 2H, Ph); 7.29–7.26 (m, 2H, Ph); 6.95 (d, 1H, Ph); 2.43 (s, 3H).

4.2.1.3. $HL^3{}_{nap}$ ***2c***. Yield: 0.13 g (80%). *Anal.* Calc. for $HL^3{}_{nap}$: C, 71.59; H, 4.17; N, 10.89. Found: C, 71.62; H, 4.20; N, 10.92%. Electronic spectrum (λ_{max}/nm (ε/dm^2 mol^{-1}), dichloromethane): 335 (15 860); 314 (18 215); 235 (42 439). IR (KBr pellets, cm^{-1}): ν(N=N) 1482; ν(C=N) 1615. ^{1}H NMR ($CDCl_3$, ppm): δ 13.15 (s,1H, OH); 10.83 (s,1H, –CH=N); 9.20 (d, 1H, Ph); 9.19 (d,1H, Ph); 8.12 (d, 1H, Ph); 7.99 (d, 2H, Ph); 7.89 (d, 1H, Ph); 7.81–7.76 (m, 1H, Ph); 7.73(d, 1H, Ph); 7.62 (d, 1H, Ph); 7.60–7.56 (m, 1H, Ph); 7.54 (d, 1H, Ph); 7.49–7.42 (m, 1H, Ph); 7.32–7.28 (m, 1H, Ph); 7.20 (t, 1H, Ph); 6.96 (d, 1H, Ph).

4.2.1.4. HL ***3***. To a 40 mL methanolic solution of 1-{[2-(phenylazo)phenyl]iminomethyl}-2-phenol, $HL^1{}_{sal}$, (0.5 g, 1.66 mmol) little excess of $NaBH_4$ (0.065 g, 1.7 mmol) was added. The resulting mixture was then stirred for 1 h. The solvent was then evaporated. The resulting solid mass was washed with water and the mass was extracted with dichloromethane. After evaporation of the solvent the ligand was introduced for purification by thin layer chromatography on silica gel using pet ether: toluene (50:50 V/V). The lower band was collected as pure compound. Isolated yield: 0.478 g (95%). *Anal.* Calc. for $C_{19}H_{17}N_3O$: C, 75.24; H, 5.61; N, 13.86. Found: C, 75.27; H, 5.62; N, 13.88%. Electronic spectrum (λ_{max}/nm (ε/dm^2 mol^{-1}), dichloromethane): 435 (3240), 319 (7000), 239 (7440). IR (KBr pellets, ν, cm^{-1}): ν(–NH) 3182; ν(N=N) 1454. ^{1}H NMR ($CDCl_3$, ppm): δ 8.11 (s, NH); 7.83–7.85 (d, 1H, Ph); 7.76–7.79 (m, 2H, Ph); 7.45–7.49 (m, 2H, Ph); 7.39–7.42 (m, 1H, Ph); 7.20–7.26 (m, 2H, Ph); 6.87–6.96 (m, 3H, Ph); 4.29 (d, CH_2).

4.2.2. Synthesis of complexes

4.2.2.1. [(L^1_{sal})Ru(CO)(Cl)(PPh_3)] and [(L^1_{sal})$_2$Ru] ***4a*** *and* ***5a***. 1-{[2-(Phenylazo)phenyl]iminomethyl}-2-phenol, (0.063 g, 0.209 mmol) was dissolved in 40 mL toluene and to it Ru(H)(CO)(Cl)(PPh_3)$_3$ (0.1 g, 0.105 mmol) was added. The mixture was then heated to reflux for 8 h to afford greenish brown solution. Evaporation of the solvent gave a greenish brown residue, which was introduced for purification by thin layer chromatography on silica gel. Two green bands separated in toluene–acetonitrile (95:5, V/V) mixed solvent. From the first and second bands [(L^1_{sal})Ru(CO)(Cl)(PPh_3)] and [(L^1_{sal})$_2$Ru], respectively, were isolated in pure form upon extracting with dichloromethane and methanol.

[(L^1_{sal})Ru(CO)(Cl)(PPh_3)]: Yield: 0.045 g (60%). *Anal.* Calc. for [(L^1_{sal})Ru(CO)(Cl)(PPh_3)]: C, 62.71; H, 3.98; N, 5.77. Found: C, 62.68; H, 4.00; N, 5.80%. Electronic spectrum (λ_{max}/nm (ε/dm^2 mol^{-1}), dichloromethane): 437 (4500); 341 (17 968); 232 (52 395). IR (KBr pellets, cm^{-1}): ν(N=N) 1436; ν(C=N) 1607; ν(CO) 1941. ^{1}H NMR ($CDCl_3$, ppm): δ 8.51 (d,1H, Ph); 7.94–7.92 (m,1H, Ph); 7.67 (t, 6H, Ph); 7.51 (t, 2H, Ph); 7.47–7.45 (m, 3H, PPh_3); 7.34 (t, 3H, PPh_3); 7.29–7.25 (m, 9H, PPh_3); 7.05 (t, 2H, Ph); 6.85 (d, 1H, Ph); 6.62 (t, 1H, Ph); 6.38 (d,1H, Ph); 6.24 (t, 1H, Ph).

[(L^1_{sal})$_2$Ru]: Yield: 0.018 g (25%). *Anal.* Calc. for [(HL^1_{sal})$_2$Ru]: C, 53.99; H, 3.97; N, 11.97. Found: C, 60.01; H, 3.95; N, 11.95%. Electronic spectrum (λ_{max}/nm (ε/dm^2 mol^{-1}), dichloromethane): 625 (6500); 508 (3320); 403 (8340); 357 (11 960). IR (KBr pellets, cm^{-1}): ν(N=N) 1454, ν(C=N) 1604. ^{1}H NMR ($CDCl_3$, ppm): δ 8.67 (s, 1H, –CH=N); 7.96 (dd, 1H, Ph); 7.52 (d, 1H, Ph); 7.46 (t, 1H, Ph); 7.27–7.24 (m, 1H, Ph); 7.16–7.12 (m,1H, Ph); 6.94 (t, 1H, Ph); 6.79 (t, 2H, Ph); 6.72–6.66 (m, 2H, Ph); 6.48 (d, 1H, Ph); 6.31(d, 2H, Ph).

4.2.2.2. [(L^2_{sal})Ru(CO)(Cl)(PPh_3)] and [(L^2_{sal})$_2$Ru] ***4b*** *and* ***5b***. *[(L^2_{sal})-Ru(CO)(Cl)(PPh_3)]: Yield: 0.042 g (55%). Anal. Calc. for Complex [(L^2_{sal})Ru(CO)(Cl)(PPh_3)]: C, 63.14; H, 4.04; N, 5.66. Found: C, 63.10; H, 4.00; N, 5.70%. Electronic spectrum (λ_{max}/nm (ε/dm^2 mol^{-1}), dichloromethane): 441 (6250); 355 (15 524); 232 (59 531). IR (KBr pellets, cm^{-1}): ν(N=N) 1435, ν(C=N) 1605, ν(CO) 1949. ^{1}H NMR ($CDCl_3$, ppm): δ 8.45 (d, 1H, Ph); 7.91–7.89 (m, 1H, Ph); 7.69 (t, 6H, PPh_3); 7.46–7.43 (m, 2H, PPh_3); 7.34–7.25 (m, 7H, PPh_3); 7.06–7.03 (m, 1H, Ph); 6.82 (d, 1H, Ph); 6.62–6.60 (m, 1H, Ph); 6.38 (d, 1H, Ph); 6.23 (t, 1H, Ph).*

[(L^2_{sal})$_2$Ru]: Yield: 0.0087 g (12%). *Anal.* Calc. for [(L^2_{sal})$_2$Ru]: C, 65.77; H, 4.38; N, 11.51. Found: C, 65.74; H, 4.40; N, 11.49%. Electronic spectrum (λ_{max}/nm (ε/dm^2 mol^{-1}), dichloromethane): 626 (7336), 507 (4750), 404 (10 828), 354 (16 038). IR (KBr pellets, cm^{-1}): ν(N=N) 1454, ν(C=N) 1602. ^{1}H NMR ($CDCl_3$, ppm): δ 8.67 (s, 1H, –CH=N); 7.95 (dd, 1H, Ph); 7.52 (d, 1H, Ph); 7.45–7.42 (m, 1H, Ph); 7.27–7.24 (m, 1H, Ph); 7.14–7.11 (m, 1H, Ph); 6.71–6.67 (m, 2H, Ph); 6.56 (d, 2H, Ph); 6.47 (d, 1H, Ph); 6.21(d, 2H, Ph).

4.2.2.3. [(L^3_{sal})Ru(CO)(Cl)(PPh_3)] and[(L^3_{sal})$_2$Ru] ***4c*** *and* ***5c***. *[(L^3_{sal})-Ru(CO)(Cl)(PPh_3)]: Yield: 0.044 g (55%). Anal. Calc. for complex [(L^3_{sal})Ru(CO)(Cl)(PPh_{31}): C, 59.87; H, 3.67; N, 5.51. Found: C, 59.90; H, 3.65; N, 5.55%. Electronic spectrum (λ_{max}/nm (ε/dm^2 mol^{-1}), dichloromethane): 437 (4150); 351 (15 524); 232 (45 781). IR (KBr pellets, cm^{-1}): ν(N=N) 1434; ν(C=N) 1605; ν(CO) 1949. ^{1}H NMR ($CDCl_3$, ppm): δ 8.55 (d, 1H, Ph); 7.94–7.91 (m, 2H, Ph); 7.64 (t, 6H, PPh_3); 7.49 (t, 5H, PPh_3); 7.35–7.26 (m, 8H, PPh_3); 7.07 (t, 2H, Ph); 6.83 (d,1H, Ph); 6.64 (t, 1H, Ph); 6.38 (d, 1H, Ph); 6.26 (t,1H, Ph).*

[(L^3_{sal})$_2$Ru]: Yield: 0.011 g (14%). *Anal.* Calc. for complex [(L^3_{sal})$_2$-Ru]: C, 59.16; H, 3.37; N, 10.89%. Found: C, 59.20; H, 3.40; N, 10.85%. Electronic spectrum (λ_{max}/nm (ε/dm^2 mol^{-1}), dichloromethane): 632 (6918), 511 (5110), 401 (10 175), 358 (14 660). IR (KBr, cm^{-1}): ν(N=N) 1455, ν(C=N) 1603. ^{1}H NMR ($CDCl_3$, ppm): δ 8.68 (s, 1H, –CH=N); 7.96 (dd, 1H, Ph); 7.54–7.50 (m, 1H, Ph); 7.48 (m, 1H, Ph); 7.42–7.38 (m, 1H, Ph); 7.16 (t, 1H, Ph); 6.78–6.71 (m, 4H, Ph); 6.46 (d, 1H, Ph); 6.24 (d, 2H, Ph).

4.2.2.4. [(L^1_{nap})Ru(CO)(Cl)(PPh_3)] ***6a***. 1-{[2-(Phenylazo)phenyl]iminomethyl}-2-napthol, HL^1_{nap} (0.2 g, 0.57 mmol) was dissolved in 50 mL toluene and to it Ru(H)(CO)(Cl)(PPh_3)$_3$ (0.27 g, 0.28 mmol) was added. The mixture was then heated to reflux for 5 h to afford the greenish brown solution. Evaporation of the solvent gave a greenish brown residue which was introduced for purification by thin layer chromatography on silica gel. Green band separated in benzene–acetinitrile (95:5) mixed solvent and was isolated in pure form upon extracting with dichloromethane and methanol. Yield: 0.132 g (60%). *Anal.* Calc. for complex [(L^1_{nap})Ru(CO)(Cl)(PPh_3)]: C, 64.85; H, 3.98; N, 5.40. Found: C, 64.83; H, 4.00 N, 5.42%. Electronic spectrum (λ_{max}/nm (ε/dm^2 mol^{-1}), dichloromethane): 600 (1250), 450 (5600), 340 (19 600). IR (KBr pellets, cm^{-1}): ν(N=N) 1433, ν(C=N) 1613, ν(CO) 1945. ^{1}H NMR ($CDCl_3$, ppm): δ 8.43 (d, 2H, Ph); 7.93 (t, 1H, Ph); 7.77–7.64 (m, 6H, PPh_3); 7.52 (t, 2H, Ph); 7.46 (t, 3H, PPh_3); 7.28–7.24 (m, 3H, PPh_3); 7.19 (t, 4H, PPh_3); 7.12 (t, 1H, Ph); 7.06 (d, 1H, Ph); 7.00 (d, 1H, Ph); 6.49 (t, 1H, Ph).

4.2.2.5. [(L^2_{nap})Ru(CO)(Cl)(PPh_3)] ***6b***. The complexes [(L^2_{nap})Ru (CO)(Cl)(PPh_3)] was prepared following the same procedure as in the cases of [(L^1_{nap})Ru(CO)(Cl)(PPh_3)] using HL^2_{nap}, in place of HL^1_{nap}. The solvent used for thin layer chromatographic separation is toluene–acetonitrile (95:5 V/V) mixed solvent. Yield: 0.128 g (57%). *Anal.* Calc. for complex [(L^2_{nap})Ru (CO)(Cl)(PPh_3)]: C, 65.21; H, 4.58; N, 5.30. Found: C, 65.19; H, 4.60; N, 5.27%. Electronic spectrum (λ_{max}/nm (ε/dm^2 mol^{-1}), dichloromethane): 600 (940); 450 (5563); 360 (19 300). IR (KBr pellets, cm^{-1}): ν(N=N) 1435, ν(C=N) 1616, ν(CO) 1955. ^{1}H NMR ($CDCl_3$, ppm): δ 8.38 (d, 2H, Ph); 7.90 (t, 1H, Ph); 7.77–7.64 (m, 6H, PPh_3); 7.50–740 (m, 4H, PPh_3); 7.33–7.25 (m, 4H, PPh_3); 7.19 (t, 5H, PPh_3); 7.14 (t, 1H, Ph); 7.03 (d, 1H, Ph); 7.00 (d, 1H, Ph); 6.48 (d, 1H, Ph); 2.42 (s, CH_3).

4.2.2.6. [(L^3_{nap})Ru(CO)(Cl)(PPh_3)] ***6c***. The complexes [(L^3_{nap})Ru (CO)(Cl)(PPh_3)] was prepared following the same procedure as in the cases of [(L^1_{nap})Ru(CO)(Cl)(PPh_3)] using HL^3_{nap}, in place of HL^1_{nap}. The solvent used for thin layer chromatographic separation is toluene–acetonitrile (95:5 V/V) mixed solvent. Yield: 0.119 g (52%). *Anal.* Calc. for complex [(L^1_{nap})Ru(CO)(Cl)(PPh_3)]: C, 62.09; H, 3.69; N, 5.17. Found: C, 62.10; H, 3.67; N, 5.20%. Electronic spectrum (λ_{max}/nm (ε/dm^2 mol^{-1}), dichloromethane): 600 (690), 450 (5072), 350 (18 555). IR (KBr pellets, cm^{-1}): ν(N=N) 1435, ν(C=N) 1614, ν(CO) 1959. ^{1}H NMR ($CDCl_3$, ppm): δ 8.46 (d, 2H, Ph); 7.91 (t, 1H, Ph); 7.69–7.63 (m, 6H, PPh_3); 7.28–7.24 (m, 3H, PPh_3); 7.22–7.18 (m, 4H, PPh_3); 7.13 (t, 1H, Ph); 7.03 (d, 1H, Ph); 6.98 (d, 1H, Ph); 6.50 (t, 1H, Ph).

4.2.2.7. [(OL)Ru(PPh_3)Cl] ***7***. Ligand HL (63 mg, 0.209 mmol) was dissolved in 40 mL toluene and to it Ru (PPh_3)$_3$$Cl_2$ (100 mg, 0.105 mmol) was added. The mixture was then heated to reflux for 8 h to afford brown solution. Evaporation of the solvent afforded brown crystals of composition [(OL)Ru(PPh_3)Cl]. The [(OL)-Ru(PPh_3)Cl] was synthesized by the same procedure as described above using authentic ligand H_2OL in place of ligand HL. Yield: 0.037 g (50%). *Anal.* Calc. for [(OL)Ru(PPh_3)Cl]: C, 63.14; H, 4.04; N, 5.66. Found: C, 63.10; H, 4.00; N, 5.70%. Electronic spectrum (λ_{max}/nm (ε/dm^2 mol^{-1}), dichloromethane): 1043 (1823), 639 (1560), 464 (10 360), 339 (14 000), 303 (13 440). IR (KBr pellets, cm^{-1}): ν(NH) 3042, ν(C=N) 1600, ν(N=N) 1434, ν(Ru–Cl) 295.

4.3. 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

Table 2
Crystallographic data for $[(L^1_{sal})Ru(CO)(Cl)(PPh_3)]$, $[(L^1_{sal})_2Ru]$, $[(L^1_{nap})Ru(CO)(Cl)(PPh_3)]$ and $[(OL)Ru(PPh_3)Cl]$.

	$[(L^1_{sal})Ru(CO)(Cl)(PPh_3)]$	$[(L^1_{sal})_2Ru]$	$[(L^1_{nap})Ru(CO)(Cl)(PPh_3)]$	$[(OL)Ru(PPh_3)Cl]$
Chemical formula	$C_{38}H_{29}ClN_3O_2PRu$	$C_{38}H_{28}N_6O_2Ru$	$C_{42}H_{31}ClN_3O_2PRu$	$C_{37}H_{28}ClN_3O_2PRu$
Formula weight	727.13	701.73	777.19	714.11
Crystal system	monoclinic	triclinic	monoclinic	triclinic
Space group	$P21/n$	$P\bar{1}$	$P21/n$	$P\bar{1}$
a (Å)	11.1840(1)	9.7770(1)	9.3910(4)	10.2515(2)
b (Å)	20.0490(2)	10.8280(2)	20.7543(8)	11.0396(2)
c (Å)	14.5660(2)	15.8320(3)	17.8198(6)	15.0526(2)
α (°)	90	71.6890(10)	90	77.2190(10)
β (°)	100.6800	74.1380(10)	97.378(2)	77.6140(10)
γ (°)	90	84.4700(10)	90	70.5910(10)
λ (Å)	0.71073	0.71073	0.71073	0.71073
V (Å^3)	3209.53(6)	1530.50(4)	3444.4(2)	1548.40(5)
$F(0\,0\,0)$	1480	716	1584	726
Z	4	2	4	2
T (K)	150	150	293	293
D (g cm^{-3})	1.505	1.523	1.499	1.532
μ (mm^{-1})	0.661	0.559	0.622	0.684
R_1 (all data)	0.0324	0.0285	0.0220	0.0247
wR_2 [$I > 2\sigma(I)$]	0.0863	0.0680	0.0599	0.0635
GOF	1.01	1.07	0.99	1.08
θ minimum, maximum (°)	3.8, 30.0	3.8, 27.5	1.5, 28.7	1.4, 28.7
R_{int}	0.047	0.035	0.023	0.024
N_{ref}	9362	6979	8894	8008
N_{par}	415	425	451	406

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. ^{1}H NMR spectra were obtained on Brucker DPX 400 and Brucker 500 RPX NMR spectrometers in $CDCl_3$ using TMS as the internal standard.

4.4. Crystallography

Crystals of $[(L^1_{sal})Ru(CO)(Cl)(PPh_3)]$, $[(L^1_{sal})_2Ru]$, $[(L^1_{nap})Ru(CO)(Cl)(PPh_3)]$ and $[(OL)Ru(PPh_3)Cl]$ were grown by slow evaporation of dicholoromethane–acetonitrile mixed solution at 298 K. Data were collected on a Brucker SMART CCD diffractometer using Mo Kα monochromator ($\lambda = 0.71073$). Structure solutions were performed using SHELX-97 PC version program [18]. 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 2.

Acknowledgements

We are thankful to the DST (New Delhi) for funding under DST-SERC (SR/S1/IC-0026/2007) project. We are thankful to Prof. J. H. Huang of National Changhua University of Education, Changhua, Taiwan for X-ray studies. The necessary laboratory and infrastructural facility are provided by the Department of Chemistry, University of Kalyani. The support of DST under FIST and UGC SAP program to the Department of Chemistry, University of Kalyani is acknowledged.

Appendix A. Supplementary material

Supplementary material CCDC 763726, 763727, 763728 and 763729 contain the supplementary crystallographic data for complexes $[(L^1_{sal})Ru(CO)(Cl)(PPh_3)]$, $[(L^1_{sal})_2Ru]$ and $[(L^1_{nap})Ru(CO)(Cl)(PPh_3)]$ and $(OL)Ru(PPh_3)Cl$. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. UV–Vis, IR spectra and ^{1}H NMR spectra of all the new complexes are given in Figs. S1–S41. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.04.016.

References

[1] (a) H. Adams, R.M. Bucknal, D.E. Fenton, M. Graccia, J. Oakes, Polyhedron 17 (1998) 4169;
(b) S. Mukhopadhyay, D. Ray, Dalton Trans. (1995) 265.
[2] S. Basu, S. Halder, I. Pal, S. Samanta, P. Karmakar, M.G.B. Drew, S. Bhattacharya, Polyhedron 27 (2008) 2943.
[3] (a) P. Chaudhuri, K. Wieghardt, Prog. Inorg. Chem. 35 (1987) 329;
(b) A.J. Blake, M. Schröder, Adv. Inorg. Chem. 35 (1990) 1;
(c) B.R. Cameron, M.C. Darkes, I.R. Baird, R.T. Skerlj, Z.L. Santucci, S.P. Fricker, Inorg. Chem. 42 (2003) 13.
[4] (a) M.R.St.-J. Foreman, A.F. Hill, G.R. Owen, A.J.P. White, D.J. Williams, Organometallics 22 (2003) 4446;
(b) A.N.W. Cannadine, J.C. Clark, G.R. Hill, J. Chem. Soc., Dalton Trans. (1993) 1131;
(c) A. Hill, F. Alcock, N.W. Cannadine, J.C. Clark, G.R. Owen, J. Organomet. Chem. 426 (1992) C40;
(d) J.C. Cannadine, A.F. Hill, A.J.P. White, D.J. Williams, J.D.E.T. Wilton-Ely, Organometallics 15 (1996) 5409;
(e) X. Sala, I. Romero, M. Rodríguez, A. Llobet, Inorg. Chem. 43 (2004) 5403.
[5] (a) S. Trofimenko, Chem. Rev. 93 (1993) 943;
(b) S. Trofimenko, J. Am. Chem. Soc. 88 (1966) 1842;
(c) J.C. Calabrese, S. Trofimenko, J.S. Thompson, J. Chem. Soc., Chem. Commun. (1986) 1122;
(d) S. Trofimenko, Prog. Inorg. Chem. 34 (1986) 115;
(e) K. Niedenzu, S. Trofimenko, Top. Curr. Chem. 131 (1986) 1;
(f) M.D. Curtis, K.-B. Shiu, W.M. Butler, J. Am. Chem. Soc. 108 (1986) 1550;
(g) S. Trofimenko, J.C. Calabrese, J.S. Thompson, Inorg. Chem. (1987) 1508;
(h) I.B. Gorrell, G. Parkin, Inorg. Chem. 29 (1990) 2452;
(i) R. Han, A. Looney, G. Parkin, J. Am. Chem. Soc. 111 (1989) 7276;
(j) R. Han, G. Parkin, J. Am. Chem. Soc. 112 (1990) 3662.
[6] C.A. Dodds, M.-A. Lehmann, J.F. Ojo, J. Reglinski, M.D. Spicer, Inorg. Chem. 43 (2004) 4927.
[7] (a) L.A. Huxham, E.L.S. Cheu, B.O. Patrick, B.R. James, Inorg. Chim. Acta 352 (2003) 238;
(b) Y.K. Yan, M. Melchart, A. Habtemariam, P.J. Sadler, Chem. Commun. (2005) 4764;
(c) A.F.A. Peacock, A. Habtemariam, R. Fernandez, V. Walland, F.P.A. Fabbiani, S. Parsons, R.E. Aird, D.I. Jodrell, P.J. Sadler, J. Am. Chem. Soc. 128 (2006) 1739;
(d) R.E. Morris, R.E. Aird, P. Del Socorro Murdoch, H. Chen, J. Cummings, N.D. Hughes, S. Parsons, A. Parkin, G. Boyd, D.I. Jodrell, P.J. Sadler, J. Med. Chem. 44 (2001) 3616;
(e) O. Novakova, H. Chen, O. Vrana, A. Rodger, P.J. Sadler, V. Brabec, Biochemistry 42 (2003) 11544;
(f) H. Chen, J.A. Parkinson, R.E. Morris, P.J. Sadler, J. Am. Chem. Soc. 125 (2003) 173;
(g) R. Fernandez, M. Melchart, A. Abtemariam, S. Parsons, P.J. Sadler, Chem. Eur. J. 10 (2004) 5173;
(h) B. Boardman, M.J. Hanton, H.V. Rensburg, R.P. Tooze, Chem. Commun. (2006) 2289.

[8] (a) M.C. van Engelen, H.T. Teunissen, J.G. De Vries, C.J. Elsevier, J. Mol. Catal. A: Chem. 206 (2003) 185;
(b) H.T. Teunissen, C.J. Elsevier, Chem. Commun. (1997) 667.
[9] (a) R.A. Grey, G.P. Pez, A. Wallo, J. Am. Chem. Soc. 103 (1981) 7536;
(b) R.A. Grey, G.P. Pez, J. Corsi, A. Wallo, J. Chem. Soc., Chem. Commun. (1980) 783;
(c) R.A. Grey, G.P. Pez, Fundam. Res. Homogeneous Catal. 4 (1984) 97;
(d) R.A. Grey, G.P. Pez, Prepr. – Am. Chem. Soc., Div. Pet. Chem. 25 (1980) 399.
[10] (a) U. Matteoli, G. Menchi, M. Bianchi, F. Piacenti, P. Frediani, J. Mol. Catal. 22 (1984) 353;
(b) U. Matteoli, G. Menchi, M. Bianchi, P. Frediani, F. Piacenti, J. Mol. Catal. 29 (1985) 269;
(c) U. Matteoli, G. Menchi, M. Bianchi, F. Piacenti, J. Mol. Catal. 44 (1988) 347;
(d) U. Matteoli, G. Menchi, M. Bianchi, F. Piacenti, S. Ianelli, M. Nardelli, J. Organomet. Chem. 498 (1995) 177.
[11] (a) U. Matteoli, G. Menchi, M. Bianchi, F. Piacenti, J. Organomet. Chem. 299 (1986) 233;
(b) U. Matteoli, G. Menchi, M. Bianchi, F. Piacenti, J. Mol. Catal. 64 (1991) 257;
(c) K. Nomura, H. Ogura, Y. Imanishi, J. Mol. Catal. A: Chem. 166 (2001) 345;
(d) K. Nomura, H. Ogura, Y. Imanishi, J. Mol. Catal. A: Chem. 178 (2002) 105;
(e) Y. Hara, H. Inagaki, S. Nishimura, K. Wada, Chem. Lett. (1992) 1983.
[12] P. Pattanayak, J.L. Pratihar, D. Patra, A. Burrows, M. Mohan, S. Chattopadhyay, Eur. J. Inorg. Chem. (2007) 4263.
[13] J.L. Pratihar, S. Bhaduri, P. Pattanayak, D. Patra, S. Chattopadhyay, J. Organomet. Chem. 694 (2009) 3401.
[14] (a) S. Halder, R. Acharyya, S.-M. Peng, G.-H. Lee, M.G.B. Drew, S. Bhattacharya, Inorg. Chem. 45 (2006) 9654;
(b) S. Nag, P. Gupta, R.J. Butcher, S. Bhattacharya, Inorg. Chem. 43 (2004) 4814.
[15] P. Pattanayak, J.L. Pratihar, D. Patra, S. Mitra, A. Bhattacharyya, H.M. Lee, S. Chattopadhyay, Dalton Trans. (2009) 6220.
[16] A.I. Vogel, A.R. Tatchell, B.S. Furnis, A.J. Hannaford, Vogel's Textbook of Practical Organic Chemistry, Longman (ELBS), fifth ed., 1996, p. 993.
[17] (a) N. Ahmed, J.J. Levison, S.D. Robinson, M.F. Uttlky, E.R. Wonchoba, G.W. Parshall, Inorg. Synth. 15 (1974) 45;
(b) T.A. Stephenson, G. Wilkinson, J. Inorg. Nucl. Chem. 28 (1966) 945.
[18] G.M. Sheldrick, Acta Crystallogr. A64 (2008) 112.