



Half-sandwich Ruthenium(II) Schiff base complexes: Synthesis, characterization and effective catalysts for one-pot conversion of aldehydes to amides

Muniyappan Premkumar^a, Paranthaman Vijayan^b, Galmari Venkatachalam^{a,*}

^a PG & Research Department of Chemistry, Government Arts College, Dharmapuri, 636 705, Tamilnadu, India

^b School of Chemistry & Physics, University of KwaZulu-Natal, Pietermaritzburg Campus, Scottsville, 3209, South Africa

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ABSTRACT

Five new Schiff base ligands and conformationally rigid half-sandwich organo ruthenium(II) Schiff base complexes (**1–5**) with the general formula $[\text{Ru}(\eta^6\text{-}p\text{-cymene})(\text{Cl})(\text{L}_{1-5})]$ (where, L = mono anionic Schiff base ligands) have been synthesized from the reaction of $[\{(\eta^6\text{-}p\text{-cymene})\text{RuCl}\}_2(\mu\text{-Cl})_2]$ with a bidentate Schiff bases ligands. These ruthenium(II) Schiff base complexes were fully characterized by elemental analysis, FT-IR, UV-Vis, ¹H & ¹³C NMR and mass spectroscopy studies. In chloroform solution, all the metal complexes exhibit characteristic metal to ligand charge transfer bands (MLCT) and emission bands in the visible region. The crystal structure of the complexes $[\text{Ru}(\eta^6\text{-}p\text{-cymene})(\text{Cl})(\text{L}_1)]$ (**1**) and $[\text{Ru}(\eta^6\text{-}p\text{-cymene})(\text{Cl})(\text{L}_3)]$ (**3**) were determined by single crystal X-ray crystallography. The complexes exhibited good catalytic activity for aldehydes to amides by one-pot conversion process in the presence of $\text{NaHCO}_3/\text{NH}_2\text{OH}\cdot\text{HCl}$.

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1. Introduction

The amide bond is one of the most fundamental groups in organic chemistry, and it plays a major role in the elaboration and composition of biological and chemical systems [1–6]. The amides are an important class of chemicals that have been widely used as chemical intermediates in organic synthesis and prolific functional groups, with a great importance in both research and industrial chemistry owing to their prevalence in detergents, engineering plastics, lubricants, biologically active compounds and pharmaceuticals [7]. The common preparation of amides from the reaction of amines with acid anhydrides or acylchlorides [8] involves highly toxic wastes. Hence the development of new catalytic processes with more atom economy and less toxic wastes getting importance. The Beckmann rearrangement is commonly used to transform oximes into the conversion of corresponding amides [9], and this rearrangement is commonly used to transform ketoximes into the corresponding N-substituted amides requiring the use of strong acids [10].

Further, the synthesis of primary amides from aldoximes is very

difficult and reactive reagents have to be used in stoichiometric amounts for the transformation to occur. In addition, the selectivities for the desired amides are often very low with reactive stoichiometric reagents because undesired carboxylic acids, aldehydes and nitriles are formed in some cases. While the migrating group can be aryl or alkyl, it is rarely hydrogen atom that migrates, and so the Beckmann rearrangement is not a general process for the conversion of aldoximes into corresponding primary amides [11–13]. The rearrangement of aldoximes into amides has been reported using transition metal catalysts containing iridium [14,15], copper [16], nickel [17], palladium [18], rhodium [19] and zinc [20].

Among the transition metal catalysts, ruthenium complexes have been extensively studied due to their catalytic significances in variety of organic conversions, such as the hydrogenation of esters to alcohols [21], synthesis of imines from amines and alcohols [22], the synthesis of amides from amines and esters [23], and the direct synthesis of polyamides from diamines and diols [24].

In the Schiff base metal complexes, the environment at coordination center can be modified by attaching different substituents to the ligand, which provides a useful range of electronic properties and steric essential for the fine-tuning of structure and reactivity [25]. Furthermore, transition metal complexes of ruthenium have attracted much interest mainly because of their vital applications in

* Corresponding author.

E-mail address: gvchem@gmail.com (G. Venkatachalam).

several organic syntheses [7,26]. The Schiff base ligands are among the most fundamental chelating systems particularly for transition metals [27]. The Schiff base ligands proved to be very attractive for creating new active and selective sites in ruthenium catalytic species [28,29]. As a special, N, O-bidentate Schiff base ligands allow the fine tuning of the steric and electronic environment at the ruthenium atom through an appropriate selection of bulky and/or electron -withdrawing or -donating substituents. The two donor atoms (N and O) of the chelated Schiff base exhibit opposite features: the phenolate oxygen atom is a hard donor and will stabilize a higher oxidation state of ruthenium whereas the imine nitrogen is a softer one and, accordingly, will rather stabilize the lower oxidation state of ruthenium. They have been used as catalyst precursors for a variety of purposes, including hydrogenation, carbon-carbon bond formation, polymerization, oxidation and aldehyde to amide conversion [30]. To the best of our knowledge, there are no reports available on catalytic aldehyde to amide conversion by η^6 -*p*-cymene ruthenium(II) Schiff base complexes incorporating N, O-donors in presence of NaHCO_3 .

In the present study, the synthesis of the half-sandwich η^6 -*p*-cymene ruthenium(II) complexes containing bidentate Schiff base ligands were performed. All the synthesized complexes have been characterized by elemental analysis, IR, UV-Vis, NMR and Mass spectroscopic techniques. The molecular structure of complexes **1** and **3** were confirmed through single crystal X-ray diffraction. The catalytic activity of the ruthenium(II) Schiff base complexes are investigated in the case of aldehyde to amide in the presence of NaHCO_3 (Fig. 1).

2. Results and discussion

2.1. Synthesis and characterization

The half-sandwich *p*-cymene ruthenium(II) Schiff base complexes **1–5** were readily prepared in high yield by reacting the dimeric [(*p*-cymene) RuCl_2]₂ precursor with the appropriate Schiff base ligands (L₁H–L₅H) in CH_2Cl_2 at room temperature in 1:2 M ratio as shown in Scheme 1. The complexes **1–5** were stable in air both solid and in solution state; they are highly soluble in polar solvents such as CH_3COCH_3 , CH_3CN , $\text{HCON}(\text{CH}_3)_2$, $(\text{CH}_3)_2\text{SO}$, CH_2Cl_2 and CHCl_3 solvents and partially soluble in methanol, ethanol and insoluble in non-polar solvents such as hexane and pentane. These ruthenium(II) Schiff base complexes were obtained as reddish-brown solids in yields up to 90%. The analytical data of all the ruthenium(II) Schiff base complexes are in good agreement with the molecular formula proposed.

The infrared spectra of the metal-free ligands (L₁H–L₅H) show absorption bands in the region 1261–1298 cm^{-1} can be assigned to phenolic C–O stretching. This bands shifted to 1300–1321 cm^{-1} in ruthenium(II) complexes, showing that the coordination through

the phenolic oxygen via deprotonation [31,32]. This is supported by the disappearance of the phenolic $\nu_{(\text{O}-\text{H})}$ and $\nu_{(\text{S}-\text{H})}$ absorption bands in all the complexes which observed in free Schiff base ligands around 3050–3367 cm^{-1} . The band around 1615–1662 cm^{-1} in the spectra of ligands can be attributed to $\nu_{(\text{C}=\text{N})}$ which is shifted to 1571–1604 cm^{-1} in ruthenium(II) complexes (**1–5**) indicating the coordination of azomethine nitrogen (C=N) with ruthenium(II) metal ion [33,34]. Coordination of the ligand to the ruthenium(II) ion through an azomethine nitrogen is expected to reduce the electron density in the azomethine link and thus lower the absorption frequency upon complexation. The band corresponding to $\nu_{(\text{S}-\text{H})}$ also disappears in the complex containing L₅H ligand. Moreover the absorption due to C–S of L₅H at 1252 cm^{-1} is shifted to 1276 cm^{-1} in the complex **5**, indicating that the second coordination site is a thiophenolic sulfur atom [35]. The IR spectra of all the complexes therefore confirm the mode of coordination of the Schiff base ligand to the ruthenium(II) metal ion via the azomethine nitrogen and phenolic oxygen and sulfur atom of thiol group [36–38].

The electronic transition spectra for all the new complexes have been recorded in CHCl_3 solvent in the region 800–200 nm. These (η^6 -*p*-cymene) ruthenium(II) Schiff base complexes show three to four bands in the visible and ultraviolet region 460–208 nm. The absorption spectra of ruthenium(II) Schiff base complexes in the high-intensity bands in the region 208–260 nm that are very similar and are attributable to the ligand-centered transitions ($\pi-\pi^*$, $n-\pi^*$) taking place in the aromatic group of Schiff base ligands. The lowest energy absorption bands in the electronic spectra of the complexes in the visible region 375–460 nm are ascribed to metal to ligand charge transfer transitions (MLCT). The representative spectra of complex **1–5** were shown in Fig. 2. Based on the pattern of the electronic spectra of all the complexes indicated the presence of an octahedral environment around the ruthenium(II) ion has been proposed similar to that of other ruthenium(II) Schiff base octahedral complexes [39,40].

The ¹H NMR spectra of ruthenium(II) complexes **1–5** were recorded in CDCl_3 which confirms the bonding of the Schiff base ligand to the ruthenium(II) metal ion. Multiplets observed in the region δ 6.3–8.1 ppm in the complexes have been assigned to the aromatic protons of Schiff base ligands. The signal due to the azomethine proton (CH=N) appears at δ 8.4–9.8 ppm. The position of azomethine signal in the complexes is slightly downfield in comparison with that of the free ligands, suggesting deshielding of azomethine proton due to its coordination to ruthenium(II) ion. A sharp singlet due to the –OH and –SH proton of the free Schiff base ligands in the region δ 11.8–13.15 ppm was disappeared in all the complexes, further supporting coordination of the phenolic oxygen and thiol oxygen to the ruthenium(II) ion [41–44]. Therefore, the ¹H NMR spectra of the all complexes confirm the bidentate coordination mode of the schiff base ligands to ruthenium(II) ions. In all the complexes, the cymene protons appear in the region of δ 4.0–5.6 ppm [45–47]. The isopropyl methyl protons of the *p*-cymene appeared as two doublets in the region of δ 0.8–1.62 ppm and the isopropyl methine (CH) protons appear as a septet in the region of δ 2.0–3.1 ppm. Further, the methyl proton of the *p*-cymene appears as a singlet around the range of δ 1.5–2.3 ppm. Additionally, methyl (CH₃) protons appeared as singlet for complex **2** at δ 2.45 ppm. The above observations made it clear that the Schiff base ligands have coordinated to the ruthenium(II) ion (see supporting information S1–S10).

2.2. X-ray structural studies

The crystal structure of the complexes **1** and **3** consist of neutral arene ring bonded to the ruthenium metal along with chloride and

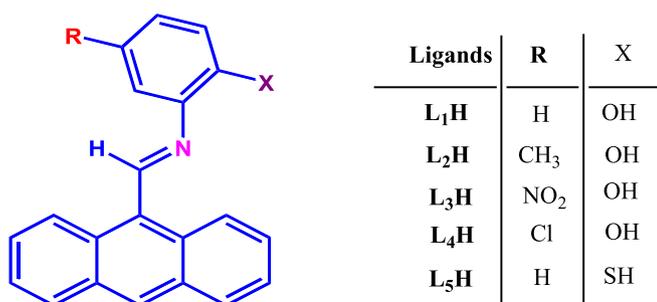
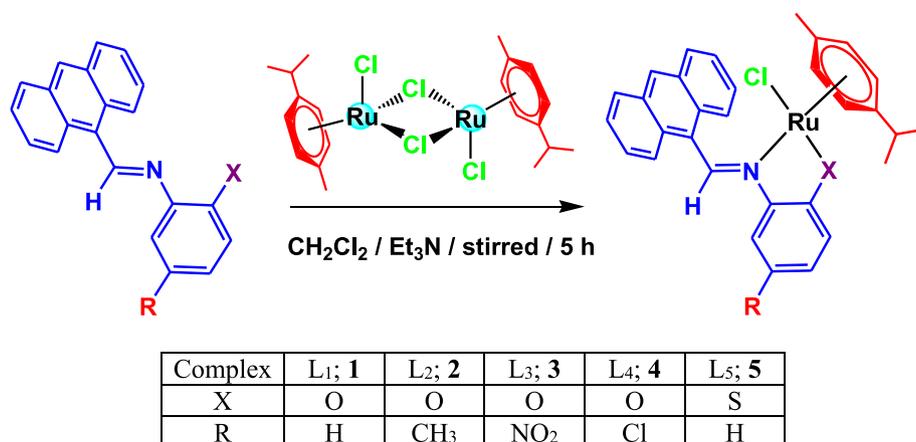


Fig. 1. General structure of the Schiff base ligands (L₁H–L₅H).



Scheme 1. Synthesis of new η^6 -*p*-cymene Ru(II) Schiff base complexes (**1–5**).

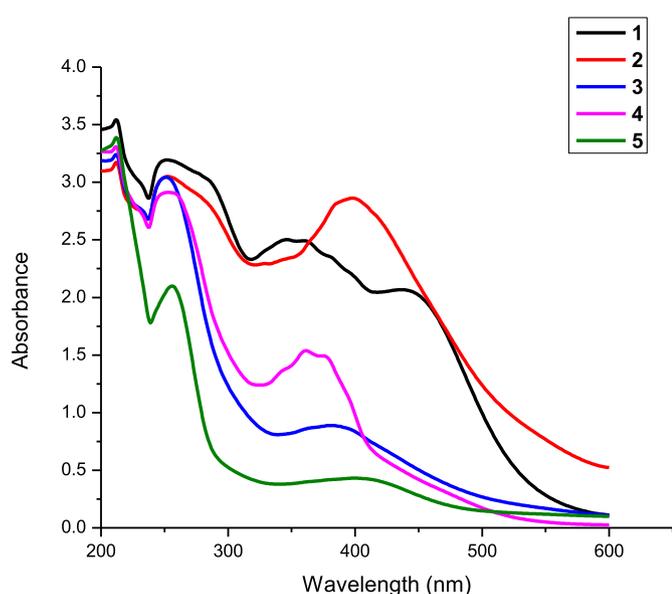


Fig. 2. UV-Vis spectra of $[\text{Ru}(\eta^6\text{-}p\text{-cymene})(\text{Cl})(\text{L}_{1-5})]$ (**1–5**).

NO-donors of Schiff base ligands. The Schiff base ligands acts in NO bidentate fashion, around the metal center at forming a five membered ring with bond angles of 78.7(1) Å (O(1)–Ru(1)–N(1)) for complex **1** and 78.4(3) Å (O(1)–Ru(1)–N(1)) for complex **3**. Crystallographic refinement data are summarized in Table 1 and the selected bond distances and angles are presented in Table 2. ORTEP diagram of the molecules **1** and **3** are shown in Fig. 3 and Fig. 4. The compounds **1** and **3** crystallized in the monoclinic crystal system with the C2/c space group and triclinic with the P1 space group respectively. The molecular structures of complexes **1** and **3** shows clearly that the Schiff base ligands coordinate in a bidentate manner to ruthenium ions via the Schiff base nitrogen atom and phenolate oxygen atom in addition to one arene group and one chlorine atom. The complexes adopt as commonly observed three-legged piano stool geometry with O, N and Cl atoms as the legs.

The Schiff base ligands bind to the ruthenium metal center at O and N forming the five membered chelate ring with bite angles Cl(1)–Ru(1)–O(1) 86.08(7)°, O(1)–Ru(1)–N(1) 78.73(9)° for complex **1** and Cl(1)–Ru(1)–O(1) 85.2(2)°, O(1)–Ru(1)–N(1) 78.9(3)° for complex **3**. The bond distances of Ru(1)–O(1) 2.052(2) Å, Ru(1)–N(1) 2.142(2) Å for the complex **1** and Ru(1)–O(1) 2.068(6) Å,

Ru(1)–N(1) 2.151(7) Å for complex **3** are 2.052(2) Å, 2.142(2) Å, 2.069(7) Å and 2.153(7) Å respectively. The Ru–Cl bond distance is found to be 2.419(8) Å and 2.399(3) Å. As all the compounds display similar spectral properties, the other three complexes are assumed to have similar structure to that of complexes **1** and **3**.

2.3. Catalytic conversion of aldehydes to amides

The catalytic organic conversion of aldehydes to amides by the synthesized η^6 -*p*-cymene ruthenium(II) Schiff base complexes have been studied in toluene in the presence of $\text{NaHCO}_3/\text{NH}_2\text{OH}\cdot\text{HCl}$. Our catalytic system is suitable for aromatic, conjugated and heterocyclic aromatic aldehydes. The ruthenium(II) Schiff base complexes efficiently catalyzes the conversion of aldehydes to their corresponding amides in good yield at one pot process. The effects of base, solvents and catalyst/substrate ratios were investigated using benzaldehyde which was selected as a test-substrate (Tables 3 and 4). No considerable reaction was observed in the absence of base or catalyst. The conversion of benzaldehyde to benzamide was performed in different solvent media such as benzene, dichloromethane, acetonitrile, chloroform, toluene. Among these, toluene was found to be best, with high conversion. To optimize, and study the effects of different bases in our catalytic system, we have chosen the reaction between benzaldehyde in the presence of various bases KHCO_3 , NaHCO_3 , Et_3N and CH_3COONa . Among the different bases, NaHCO_3 was selected as base with given maximum yield [48].

The optimized reaction conditions were 18 h and the different catalyst: substrate ratio (1:100, 1:200, 1:300, 1:500, 1:1000) was tested and the results are summarized in Table 4. We started the catalyst/substrate ratios of 1:100, 1:200, 1:300, 1:500 and 1:1000, the reaction proceeds with good conversion. When increasing the catalyst/substrate ratio from 1:500 and 1:1000 in toluene, the reaction still proceeds by a downfall in yield of amide. When decreasing the catalyst/substrate ratio 1:300 and 1:200, the reaction proceeds by a moderate yield. Then, it was concluded that catalyst/substrate ratio of 1:100 is the best compromise between optimal reaction rates in toluene and we obtained 89% yield of amide.

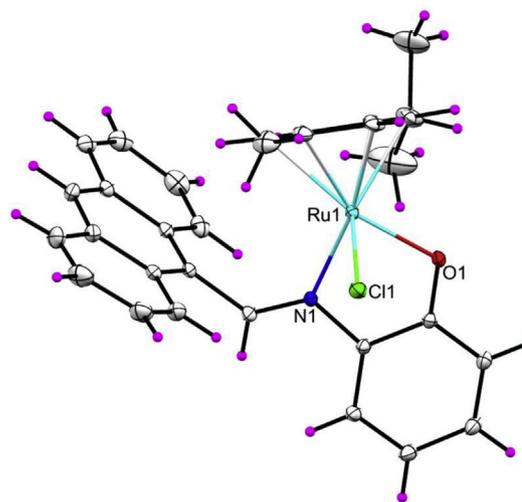
The above optimized conditions, the catalytic transformation of aldehydes to corresponding amides in the presence of NaHCO_3 and $\text{NH}_2\text{OH}\cdot\text{HCl}$, using all the synthesized ruthenium(II) Schiff base complexes as catalysts were tested and the results are summarized in Table 5. A proposed mechanism is given in Scheme 2 oxidative addition of the aldoxime N–OH bond to Ru(II), followed by

Table 1
Selected crystal data and structure refinement summary of complexes **1** and **3**.

	1		3
Empirical formula	C ₃₁ H ₂₈ ClNORu		C ₃₁ H ₂₇ ClN ₂ O ₃ Ru
Formula weight	567.06		612.06
Temperature	296(2) K		293(2) K
Wavelength	0.71073 Å		0.71073 Å
Crystal system	Monoclinic		Triclinic
Space group	C2/c		Pt
Unit cell dimensions	a = 16.5797(6) Å b = 18.8979(6) Å c = 16.3631(5) Å	α = 90° β = 95.2540(10)° γ = 90°	a = 11.086(5) Å α = 95.454(13)° b = 11.138(5) Å β = 99.165(9)° c = 13.250(6) Å γ = 93.586(11)°
Volume(Å ³)	5105.4(3)		1602.8(13)
Z	8		2
Density (calculated) (Mg/m ³)	1.475		1.268
Absorption coefficient (mm ⁻¹)	0.743		0.602
F(000)	2320		624
Crystal size (mm ³)	0.24 × 0.17 × 0.07		0.240 × 0.180 × 0.110
Theta range for data collection	1.638–29.050°		1.842–24.998°
Index ranges	−14 ≤ h ≤ 22, −25 ≤ k ≤ 25, −22 ≤ l ≤ 22		−13 ≤ h ≤ 13, −13 ≤ k ≤ 12, −15 ≤ l ≤ 15
Reflections collected	21404		7854
Independent reflections	6831 [R(int) = 0.0302]		5497 [R(int) = 0.0683]
Completeness to theta = 25.242°	99.6%		97.4%
Absorption correction	None		None
Refinement method	Full-matrix least-squares on F ²		Full-matrix least-squares on F ²
Data/restraints/parameters	6781/0/316		5497/0/323
Goodness-of-fit on F ²	1.061		1.017
Final R indices [I > 2σ(I)]	R1 = 0.0387, wR2 = 0.1052		R1 = 0.0966, wR2 = 0.2528
R indices (all data)	R1 = 0.0620, wR2 = 0.1284		R1 = 0.1319, wR2 = 0.2917
Largest diff. peak and hole	0.647 and −0.631 e.Å ⁻³		1.972 and −1.814 e.Å ⁻³

Table 2
Selected bond distances (Å) and bond angles (°) of complexes **1** and **3**.

Bond distances/angles	1	Bond distances/angles	3
Ru(1)–Cl(1)	2.419(8)	Ru(1)–Cl(1)	2.399(3)
Ru(1)–O(1)	2.052(2)	Ru(1)–O(1)	2.068(7)
Ru(1)–N(1)	2.142(2)	Ru(1)–N(1)	2.152(7)
N(1)–C(6)	1.281(4)	N(1)–C(7)	1.281(12)
Ru(1)–C(23)	2.222(4)	Ru(1)–C(23)	2.216(10)
N(1)–C(5)	1.435(4)	N(1)–C(6)	1.442(12)
O(1)–C(1)	1.314(3)	O(1)–C(1)	1.290(12)
C(5)–C(1)	1.403(4)	O(2)–N(2)	1.226(14)
Ru(1)–C(28)	2.175(3)	O(3)–N(2)	1.161(12)
O(1)–Ru(1)–N(1)	78.73(9)	O(1)–Ru(1)–N(1)	78.9(3)
N(1)–Ru(1)–Cl(1)	83.05(7)	N(1)–Ru(1)–Cl(1)	84.4(2)
Cl(1)–Ru(1)–O(1)	86.08(7)	Cl(1)–Ru(1)–O(1)	85.2(2)
N(1)–C(6)–C(7)	126.1(3)	O(2)–N(2)–O(3)	120.2(11)
C(6)–N(1)–Ru(1)	130.8(2)	C(7)–N(1)–Ru(1)	129.6(7)
C(1)–O(1)–Ru(1)	114.92(1)	C(1)–O(1)–Ru(1)	114.7(5)
C(5)–N(1)–Ru(1)	109.85(1)	C(6)–N(1)–Ru(1)	109.4(5)
N(1)–C(5)–C(1)	114.4(2)	O(2)–N(2)–C(4)	117.1(11)

**Fig. 3.** ORTEP diagram of the complex [Ru(η⁶-*p*-cymene)(Cl)(L₁)] (**1**).

nucleophilic attack on the co-ordinated imine in **2**, then b-elimination of cyclometallated **3**, and finally reductive elimination to give the amide. It has been observed that the aromatic aldehydes bearing an electron-withdrawing substance exhibit slightly higher reactivities (higher yields) as compared to that of benzaldehyde. Electron donating moiety on benzaldehyde gave slightly lower yields compared with benzaldehyde [49]. The presence of electron donating groups like –OH and –OCH₃ in the substrates alters the reactions and corresponding amides were obtained in good yields (87–79%) respectively. On the other hand, electron withdrawing groups, such as the –Cl and –NO₂ substituents offering better yields (98–82%) when compared to substrate containing electron donating group. The representative ¹H NMR spectra are showed in supporting information S16–S19.

If Ru(II) acted merely as Lewis acid we would expect to see product from the classical Beckmann rearrangement, such as secondary amides from ketoximes. If Ru(II)/(IV) conversion is possible

in this system, an alternative mechanism (Scheme 2) can be proposed.

3. Conclusion

In conclusion, we report here the synthesis of five new Schiff base ligands and η⁶-*p*-cymene ruthenium(II) Schiff base complexes containing bidentate O and N chelating 9-anthraldehyde phenolate ligands. All the complexes have been fully characterized by spectral methods (IR, UV–vis, ¹H & ¹³C NMR and Mass). The X-ray crystallographic molecular structures **1** and **3** by a X-ray diffraction study which reveals that the Schiff base ligand coordinates to ruthenium(II) ion via azomethine nitrogen and phenolic oxygen and Cl atoms as the legs, witnessed a typical three-legged “piano-stool” geometry. The catalytic ability of all the

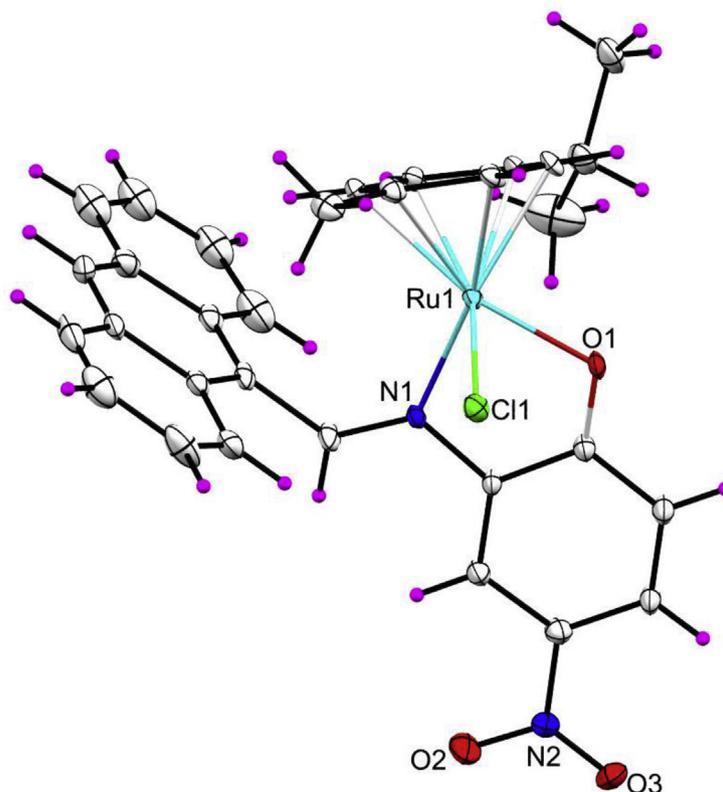


Fig. 4. ORTEP diagram of the complex $[\text{Ru}(\eta^6\text{-p-cymene})(\text{Cl})(\text{L}_3)]$ (3).

Table 3

Effect of base and solvent in the conversion of benzaldehyde to benzamide using catalyst complex $[\text{Ru}(\eta^6\text{-p-cymene})(\text{Cl})(\text{L}_1)]$ (**1**)^a.



Entry	Base	Solvent	Yield (%) ^b
1	NaHCO ₃	Benzene	55
2	NaHCO ₃	Dichloromethane	37
3	NaHCO ₃	Acetonitrile	72
4	NaHCO ₃	Chloroform	45
5	NaHCO ₃	Toluene	89
6	KHCO ₃	Toluene	85
7	Et ₃ N	Toluene	70
8	CH ₃ COONa	Toluene	81

^a Benzaldehyde (1 mmol), NH₂OH·HCl (1 mmol), base (1 mmol), catalyst **1** (1 mol %) and 3 mL solvent, reflux 18 h.

^b Isolated yield after column chromatography.

complexes were screened for aldehyde to amide conversion reaction presence of NaHCO₃ and NH₂OH·HCl and the conversion are found to be good.

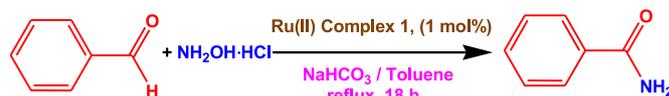
4. Experimental procedures

4.1. Materials

The synthetic work was performed in air and room temperature. All the chemicals in the current study were purchased from commercial sources and utilized without further purifications. Solvents were purified and dried according to standard procedures [50].

Table 4

Effect of catalyst/substrate ratio (C/S) on the conversion of benzaldehyde to benzamide using complex $[\text{Ru}(\eta^6\text{-p-cymene})(\text{Cl})(\text{L}_1)]$ (**1**)^a.



Entry	Ratio (C:S)	Time (h)	Yield (%) ^b
1	1:1000	18	35
2	1:500	18	41
3	1:300	18	58
4	1:200	18	73
5	1:100	18	89
6	without catalyst	18	No product

^a Conditions: reaction were carried out with substrate (1–10 mmol), ruthenium catalyst (1 mol%), NH₂OH·HCl (1–10 mmol) and 3 mL of toluene were refluxed for 18 h.

^b Isolated yield after column chromatography.

Commercial RuCl₃·3H₂O was purchased from Himedia. 9-anthraldehyde, o-aminophenol, thiophenol, 2-amino-4-nitrophenol, 2-amino-4-methylphenol and 2-amino-4-chlorophenol were purchased from S.D. Fine Chem Limited, India. The ruthenium(II) precursor starting material $[\{\eta^6\text{-p-cymene}\}\text{RuCl}_2(\mu\text{-Cl})_2]$ was prepared according to literature method [51].

4.2. Physical measurements

The solid FT-IR spectra of the complexes and the free ligands were recorded in CARY 360, Agilent resolution pro spectrophotometer. UV-Vis spectra of the complexes were obtained on a JASCO-630 UV-Vis Varian spectrophotometer. ¹H NMR spectra of

Table 5
Catalytic aldehyde to amide conversion using ruthenium(II) arene Schiff base complexes $[\text{Ru}(\eta^6\text{-}p\text{-cymene})(\text{Cl})(\text{L}_{1-5})] \text{ (1–5)}$.



Complex	Aldehyde	Amide	Yield (%) ^b
1	Benzaldehyde	Benzamide	89
	4-nitrobenzaldehyde	4-nitrobenzamide	98
	2,4-dichlorobenzaldehyde	2,4-dichlorobenzamide	94
	4-methoxybenzaldehyde	4-methoxybenzamide	87
	4-hydroxybenzaldehyde	4-hydroxybenzamide	86
2	Benzaldehyde	Benzamide	85
	4-nitrobenzaldehyde	4-nitrobenzamide	93
	2,4-dichlorobenzaldehyde	2,4-dichlorobenzamide	90
	4-methoxybenzaldehyde	4-methoxybenzamide	81
	4-hydroxybenzaldehyde	4-hydroxybenzamide	84
3	Benzaldehyde	Benzamide	88
	4-nitrobenzaldehyde	4-nitrobenzamide	89
	2,4-dichlorobenzaldehyde	2,4-dichlorobenzamide	90
	4-methoxybenzaldehyde	4-methoxybenzamide	84
	4-hydroxybenzaldehyde	4-hydroxybenzamide	80
4	Benzaldehyde	Benzamide	83
	4-nitrobenzaldehyde	4-nitrobenzamide	85
	2,4-dichlorobenzaldehyde	2,4-dichlorobenzamide	82
	4-methoxybenzaldehyde	4-methoxybenzamide	79
	4-hydroxybenzaldehyde	4-hydroxybenzamide	81
5	Benzaldehyde	Benzamide	92
	4-nitrobenzaldehyde	4-nitrobenzamide	95
	2,4-dichlorobenzaldehyde	2,4-dichlorobenzamide	91
	4-methoxybenzaldehyde	4-methoxybenzamide	83
	4-hydroxybenzaldehyde	4-hydroxybenzamide	87

^a Aldehyde 1 mmol, NaHCO₃ (1 mmol), NH₂OH·HCl (1 mmol), catalyst (1 mol%) and toluene 3 mL were refluxed for 18 h.

^b Isolated yield after column chromatography.

the complexes were recorded on a Bruker 400 MHz instrument using TMS as an internal reference. Melting points were recorded with a Boetius micro-heating table and are uncorrected.

4.3. Preparation of the Schiff base ligands (L1H – L5H)

A mixture of substituted various amines (1 mmol; 0.1091–0.1541 mg) and 9-anthraldehyde (1 mmol; 0.2062 mg) in ethanol (10 mL) containing a drop of glacial acetic acid was refluxed for 1 h. The separated precipitated was filtered and dried in air. Ligands were further purified by recrystallization from methanol. Yield: 75–90%.

L₁H: m.p. 110 °C. Yield: 80%. Selected IR bands (cm⁻¹): 1655 (HC=N), 3277 (OH), ¹H NMR (CDCl₃) δ (ppm): 6.6–7.8 (m, Ar), 8.7 (1H, s, HC=N), 12.8 (1H, s, OH).

L₂H: m.p. 102 °C. Yield: 90%. Selected IR bands (cm⁻¹): 1618 (HC=N), 3339 (OH), ¹H NMR (CDCl₃) δ (ppm): 6.9–7.8 (m, Ar), 8.7 (1H, s, HC=N), 2.1 (s, 3H), 12.3 (1H, s, OH).

L₃H: m.p. 168 °C. Yield: 85%. Selected IR bands (cm⁻¹): 1662 (HC=N), 3367 (OH), ¹H NMR (CDCl₃) δ (ppm): 6.6–8.2 (m, Ar), 9.6 (1H, s, HC=N), 14.2 (1H, s, OH).

L₄H: m.p. 146 °C. Yield: 75%. Selected IR bands (cm⁻¹): 1638 (HC=N), 3050 (OH), ¹H NMR (CDCl₃) δ (ppm): 6.8–8.0 (m, Ar), 9.3 (1H, s, HC=N), 12.7 (1H, s, OH).

L₅H: m.p. 130 °C. Yield: 90%. Selected IR bands (cm⁻¹): 1615 (HC=N), 3339 (SH), ¹H NMR (CDCl₃) δ (ppm): 6.8–7.9 (m, Ar), 9.0

(1H, s, HC=N), 11.7 (1H, s, SH).

4.4. Procedure for the synthesis of ruthenium(II) Schiff base complexes (1–5)

A mixture containing the ruthenium(II) precursor material $[(\eta^6\text{-}p\text{-cymene})\text{RuCl}_2]_2$ (1 mmol; 0.06 mg), Schiff base ligands (L₁H – L₅H) (0.2 mmol; 0.594–0.684 mg) and triethylamine (0.3 mL) in dichloromethane (20 mL) was taken in a clean 100 mL round bottom flask. This mixture was allowed to react under stirring at room temperature for 5 h. A color change of the solution from dark red to red brown was observed. The solution was concentrated to 1 mL, and hexane was added to initiate the precipitation of the complexes. The reaction progress was monitored through TLC.

$[\text{Ru}(\eta^6\text{-}p\text{-cymene})(\text{Cl})(\text{L}_1)]$ (1). Brown solid. Yield = 88%; m.p. 196 °C; Elemental Anal. Calc: C, 65.66; H, 4.94; N, 2.47; Found: C, 65.72; H, 4.91; N, 2.53 (%). IR (cm⁻¹): 1582 $\nu_{(\text{C}=\text{N})}$, 1320 $\nu_{(\text{C}-\text{O})}$. UV–Vis (CHCl₃, $\lambda_{\text{max}}/\text{nm}$): 460, 390, 250. ¹H NMR (400 MHz, CDCl₃) (δ ppm): 6.6–7.8 (m, 13H, aromatic), 8.4 (s, 1H, HC=N), 4.0–5.4 (4H, *p*-*cym*-H), 2.2 (s, 3H, CCH₃), 2.7–2.8 (m, 1H, *p*-*cym* CH(CH₃)₂), 1.1–1.2 (d, 3H, *p*-*cym* CH(CH₃)₂). ¹³C NMR (CDCl₃) δ (ppm): 163 (HC=N), 117–137 (m, Ar). ESI mass m/z = 566.

$[\text{Ru}(\eta^6\text{-}p\text{-cymene})(\text{Cl})(\text{L}_2)]$ (2). Brown solid. Yield = 85%; m.p. 283 °C; Elemental Anal. Calc: C, 66.20; H, 5.17; N, 2.41; Found: C, 66.88; H, 5.09; N, 2.37 (%). IR (cm⁻¹): 1594 $\nu_{(\text{C}=\text{N})}$, 1321 $\nu_{(\text{C}-\text{O})}$. UV–Vis (CHCl₃, $\lambda_{\text{max}}/\text{nm}$): 410, 260, 215. ¹H NMR (400 MHz, CDCl₃) (δ ppm): 6.9–7.8 (m, 12H, aromatic), 8.7 (s, 1H, HC=N), 4.1–5.4 (d, 4H, *p*-*cym*-H), 3.1 (s, 3H, CCH₃), 1.1–1.2 (m, 1H, *p*-*cym* CH(CH₃)₂), 2.1 (d, 3H, *p*-*cym* CH(CH₃)₂). ¹³C NMR (CDCl₃) δ (ppm): 158 (HC=N), 114–130 (m, Ar), 46 (CH₃).

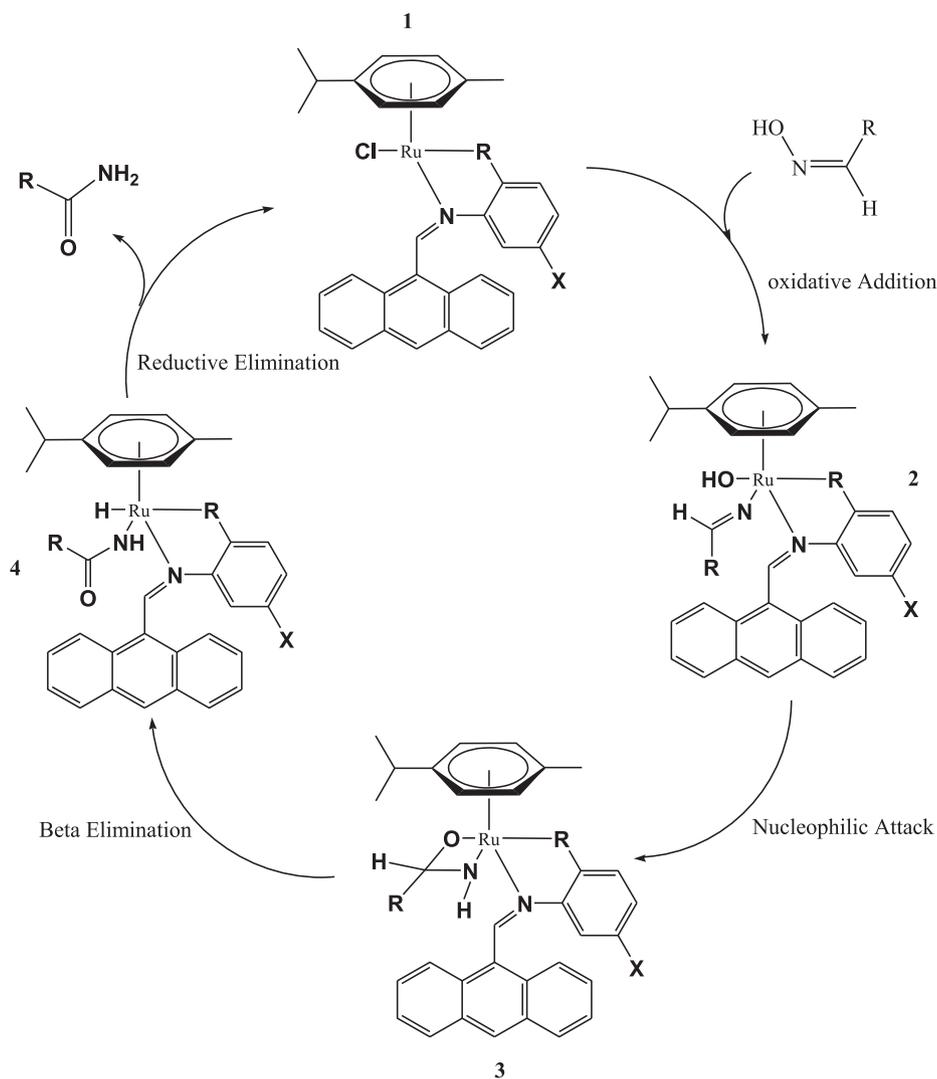
$[\text{Ru}(\eta^6\text{-}p\text{-cymene})(\text{Cl})(\text{L}_3)]$ (3). Brown solid. Yield = 71%; m.p. 238 °C; Elemental Anal. Calc: C, 60.83; H, 4.41; N, 4.57; Found: C, 60.85; H, 4.40; N, 4.53 (%). IR (cm⁻¹): 1604 $\nu_{(\text{C}=\text{N})}$, 1304 $\nu_{(\text{C}-\text{O})}$. UV–Vis (CHCl₃, $\lambda_{\text{max}}/\text{nm}$): 390, 265, 210. ¹H NMR (400 MHz, CDCl₃) (δ ppm): 6.8–7.9 (m, 12H, aromatic), 8.5 (s, 1H, HC=N), 3.8–5.4 (d, 4H, *p*-*cym*-H), 2.2 (s, 3H, CCH₃), 1.1–1.3 (m, 1H, *p*-*cym* CH(CH₃)₂), 0.8–0.9 (d, 3H, *p*-*cym* CH(CH₃)₂). ESI mass m/z = 610.7.

$[\text{Ru}(\eta^6\text{-}p\text{-cymene})(\text{Cl})(\text{L}_4)]$ (4). Brown solid. Yield = 83%; m.p. 182 °C; Elemental Anal. Calc: C, 61.89; H, 4.49; N, 2.32; Found: C, 61.95; H, 4.60; N, 2.30 (%). IR (cm⁻¹): 1571 $\nu_{(\text{C}=\text{N})}$, 1300 $\nu_{(\text{C}-\text{O})}$. UV–Vis (CHCl₃, $\lambda_{\text{max}}/\text{nm}$): 375, 260, 208. ¹H NMR (400 MHz, CDCl₃) (δ ppm): 6.9–7.8 (m, 12H, aromatic), 8.8 (s, 1H, HC=N), 4.0–5.5 (4H, *p*-*cym*-H), 1.5 (s, 3H, CCH₃), 2.0–2.2 (m, 1H, *p*-*cym* CH(CH₃)₂), 0.8–1.0 (d, 3H, *p*-*cym* CH(CH₃)₂). ESI mass m/z = 600.6.

$[\text{Ru}(\eta^6\text{-}p\text{-cymene})(\text{Cl})(\text{L}_5)]$ (5). Brown solid. Yield = 87%; m.p. 260 °C; Elemental Anal. Calc: C, 63.85; H, 4.80; N, 2.40; Found: C, 63.92; H, 4.99; N, 2.46 (%). IR (cm⁻¹): 1577 $\nu_{(\text{C}=\text{N})}$, 1276 $\nu_{(\text{C}-\text{S})}$. UV–Vis (CHCl₃, $\lambda_{\text{max}}/\text{nm}$): 405, 263, 210. ¹H NMR (400 MHz, CDCl₃) (δ ppm): 6.9–7.9 (m, 13H, aromatic), 8.7 (s, 1H, HC=N), 3.8–5.6 (4H, *p*-*cym*-H), 2.1 (s, 3H, CCH₃), 2.7–3.0 (m, 1H, *p*-*cym* CH(CH₃)₂), 0.8–1.4 (d, 3H, *p*-*cym* CH(CH₃)₂).

4.5. General procedure for the conversion of aldehyde to amide

Under a nitrogen atmosphere, the reaction vessel was charged with aldehyde (1 mmol), NaHCO₃ (1 mmol), NH₂OH·HCl (1 mmol) and ruthenium catalyst (0.01 mmol) and the mixture was refluxed in toluene for 18 h. The reaction mixture was cooled to room temperature. On completion of the reaction, 2 mL of methanol was added to the mixture, followed by filtration through celite to remove the NaHCO₃ and ruthenium catalyst. The crude product was then purified by column chromatography (CH₂Cl₂/MeOH, 1:1



Scheme 2. Proposed mechanism for the Ru(II) catalyzed rearrangement of aldoximes.

ratio) over silica gel using as solid phase, providing the amide in good yield. The identity of the resulting amides was assessed by comparison of their ^1H NMR spectroscopic data with those reported in the literature [52].

4.6. X-ray crystallographic studies

The single crystals of $[\text{Ru}(\eta^6\text{-}p\text{-cymene})(\text{Cl})(\text{L}_1)]$ (**1**) and $[\text{Ru}(\eta^6\text{-}p\text{-cymene})(\text{Cl})(\text{L}_3)]$ (**3**) were grown from mixture of chloroform–hexane solution at room temperature. A single crystal of suitable size was covered with Paratone oil, mounted on the top of a glass fiber, and transferred to a Bruker APEX-II CCD single crystal X-ray diffractometer using graphite monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073$). Data were collected at 120 K. The structure was solved by direct methods using SIR-97 and the final refinement of the structure was carried out using full matrix least-squares method on F^2 with SHELXL-2018 [53]. All non-hydrogen atoms were refined with anisotropy thermal parameters. All the hydrogen atoms were geometrically fixed and collected to refine using a riding model. Cell parameters were retrieved using Bruker SMART [54–56] software and refined using Bruker SAINT Plus (Version 7.06a) on all the observed reflections. In addition, some disordered

electron density in complex **3** could not be modelled accurately and thus was corrected by using the SQUEEZE command of PLATON.30. The electrons recovered corresponded to CHCl_3 solvent molecule.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jorganchem.2019.120964>.

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