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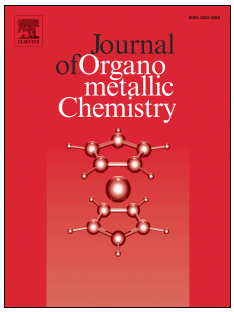

Half-sandwich ruthenium(II) complexes containing O, N bidentate azo ligands: Synthesis, structure and their catalytic activity towards one-pot conversion of aldehydes to primary amides and transfer hydrogenation of ketones

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Half-Sandwich ruthenium(II) complexes containing O, N bidentate azo ligands: Synthesis, Structure and their catalytic activity towards one-pot conversion of aldehydes to primary amides and Transfer hydrogenation of ketones

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Abstract

The ruthenium(II) complexes of the general formula [Ru(η^6–*p*–cymene)(Cl)($L_{1–5}$)] (L = O, N-donors of biphenylazo derivatives), formed by reacting 2–(biphenylazo)phenol (**HL_1 – HL_4**) and 1–(biphenylazo)naphthol ligands (**HL_5**) with [{η^6–*p*–cymene)RuCl}$_2$(μ–Cl)$_2$] have been synthesized. The compositions of the complexes have been established by IR, UV–Vis, ^{1}H–NMR spectral methods and X-ray crystallography. The synthesized complex could act as an efficient, reusable homogeneous catalyst for transformation of aldehydes to the corresponding primary amides in the presence of $NH_2OH{\cdot}HCl$, thus resulting an expansion of Beckmann rearrangement. The effect of solvent, base, temperature, time, catalyst loading and recyclability was also investigated. They also effectively catalyze the transfer hydrogenation reaction of various ketones with 2-propanol.

Keywords: Biphenylazo ligands, Ruthenium–*p*–cymene complexes, Structure, Amidation reaction, Beckmann rearrangement, Catalytic transfer hydrogenation.

1. Introduction

Half-sandwich η^6–*p*–cymene ruthenium complexes containg various ligands have played an important role in the development of modern organometallic chemistry. They have attracted an enormous interest due to their potential applications in catalytic activity in wide range of organic reactions [1, 2] and also display promising anti-cancer activity [3, 4]. Current interest in the organometallic chemistry of ruthenium(II) complexes lies in the development of the new catalytic system for different organic transformations such as oxidation [5–7], transfer hydrogenation reactions [8–11], amide conversion[12, 13], reduction of nitro compounds [14–16] etc.

The development of efficient methods for the synthesis of amides is very important because of their usefulness in a wide variety of applications in academia as well as in industry, especially as intermediates in organic synthesis, raw materials for engineering plastics, detergents, lubricants and pharmaceuticals. The conversion of carbonyl compounds, such as aldehydes, ketones, and oximes, is a good candidate for the synthesis of amides [17–20]. Beckmann rearrangement is commonly used to transform oximes into the corresponding amides [21]. This rearrangement is commonly used to transform ketoximes into the corresponding N-substituted amides requiring the use of strong acids [22]. 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. The one-pot synthesis of amide from aldehyde with amines can be a potentially elegant alternative pathway. It has attracted much attention because it (i) eliminates the isolation of unstable intermediates, (ii) reduces hazardous wastage, (iii) more efficient and selective and (iv) no by-product formation is observed [23]. Significant efforts have been developed in recent years to the development of one-pot process enabling the direct

formation of primary amides from aldehydes and hydroxylamine derivatives via rearrangement of the in situ formed aldoximes.

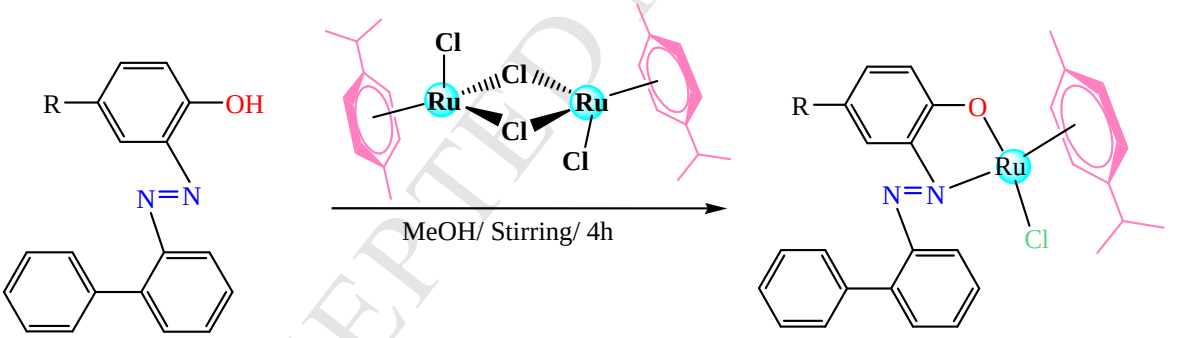
The powerful of ruthenium metal compounds to dehydrogenate alcohol and delivered the hydride to a ketone [24, 25] or an α, β-unsaturated ketone has make them useful as transfer hydrogenation catalysts [26–30]. The reaction conditions for transfer hydrogenations are economic, relatively mild and environmentally friendly. Experimental and theoretical studies to improve the new catalysts for transfer hydrogenation is still of substantiate importance, in order to find most efficient catalysts.

Ruthenium(II) *p*-cymene complexes showed a piano-stool three legged structure in the ruthenium metal center have a similar octahedral geometry and this structural feature opens the possibility to introducing in the molecules of two type of stereogenic center: (i) the ligand and (ii) the metal. It has been found in the reported literature that the azo phenol ligand is well known to coordinate center metal ions usually with O, N bidentate ligands forming a five and six membered rings. The arylazo groups due to its more acidic nature stabilizes ruthenium metal in lowest oxidation state while phenolate oxygen atom being a hard base stabilized the higher oxidation states of the ruthenium metal ion [31].

We describe here, the synthesis and characterization of new mononuclear ruthenium(II) complexes containing 2–(biphenylazo)phenol and 1–(biphenylazo)naphthol ligands. The molecular structure of the complexes is investigated with the help of the single crystal XRD structure in combination with spectral studies. Further, the catalytic study of the (η^6–*p*–cyemene) ruthenium(II) complexes for both aldehyde to amide conversion and transfer hydrogenation of ketones have been carried out. Density Functional Theory calculations (DFT) also performed to support the experimental findings.

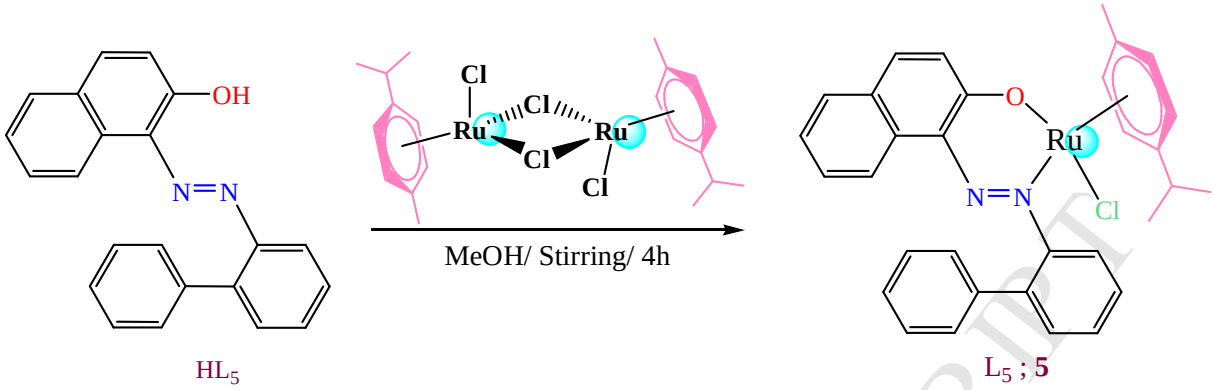
2. Results and Discussion

The reaction of 2–(biphenylazo)phenol and 1–(biphenylazo)naphthol ligands with chloro–bridged (η^6–*p*–cymene) ruthenium precursor complex [{η^6–*p*–cymene)$RuCl_2$}(μ–Cl)$_2$] in methanol at room temperature in 1:2 molar ratio resulted in the formation of conformationally rigid new monomeric ruthenium(II) complexes (Scheme 1). The complexes were found to be air stable and are soluble in polar solvents such as dichloromethane and acetone, but insoluble in non-polar solvents such as pentane and hexane. The data obtained from elemental analysis are in good agreement with the compositions proposed for the structure of complexes. It is noted that the present ligand system binds the metal center as five membered chelate rings in complexes **1-4** and six membered chelate rings in complex **5**.



R = CH_3 (HL_1); OCH_3 (HL_2); $C(CH_3)_3$ (HL_3); Cl (HL_4)

R = CH_3 (L_1; **1**), OCH_3 (L_2; **2**), $C(CH_3)_3$ (L_3; **3**), Cl (L_4; **4**)



Scheme 1. Synthesis of *p-cymene* Ru(II) 2–(biphenylazo)phenolate (**1–4**) and 1–(biphenylazo)naphtholate complexes (**5**)

2.1. Characterization of the complexes

Infrared spectra of all the ligands displayed strong bands around 1403–1445 and 1257–1270 cm^{-1} corresponding to υ–N=N– and phenolic υC–O stretching, respectively. After complexation υ–N=N– appears at 1384–1389 cm^{-1} and the red shifting is corroborated with N (azo) coordination. FT–IR spectra of complexes **1**–**5** are given in Figs. S1–S5 (see supporting information). The coordination through phenolic oxygen is confirmed by the increase of C–O at higher frequencies in the region 1305–1323 cm^{-1} in all the complexes. This is further supported by the disappearance of υ–OH band in the range 3440–3457 cm^{-1} in all the complexes [32–34].

The UV–Vis spectra of all complexes in chloroform solutions exhibit characteristic absorptions in the region 200–800 nm. The representative UV-Vis spectra of complexes **1**–**5** are given in Figs. S6–S10 (see supporting information). The absorption at 445–460 nm is probably due to metal-to-ligand charge transfer transitions. The high intensity bands around 340–325 nm and 260–250 nm has been designated as n–π* and π–π* transitions respectively for the biphenylazo ligands in these complexes. The obtained electronic spectral pattern of all

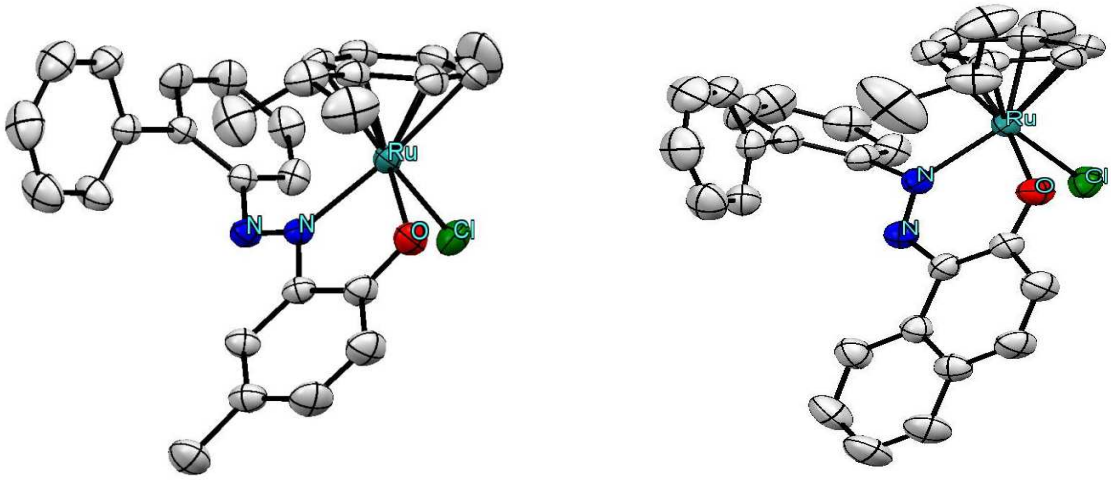
complexes clearly shows the presence of an octahedral environment around the ruthenium(II) ion which is consistent with other reported ruthenium octahedral complexes [35, 36, 50].

The ^{1}H–NMR spectra of the complexes **1–5** have been recorded in $CDCl_3$ and were in agreement with their molecular structures. Complexes **1–5** are given in the supporting information (S11–S15). All the complexes show multiplets at δ 6.4–7.9 ppm for the presence of biphenylazo phenol ligands. The methyl protons appear as singlet and isopropyl protons appear as two doublets of the *p*-cymene ligand in the range of δ 2.1–2.2 ppm and δ 0.8–1.4 ppm, respectively. The isopropyl CH protons appear as a septet in the range of δ 2.3–2.8 ppm and the *p*-cymene ring protons are observed in the ranges of δ 4.2–5.8 ppm as either four doublets (4H) or two doublets (2H) and one singlet (2H) for all the complexes. In additional, methyl signals are observed as singlet for complex **1** at δ 2.3 and methoxy signals are observed as singlet for complex **2** at δ 3.7 ppm. A sharp singlet appeared for OH protons of all the ligands (HL_1–HL_5) in the region δ 11.7 ppm was disappeared in all the complexes.

2.2. X-ray crystallographic studies

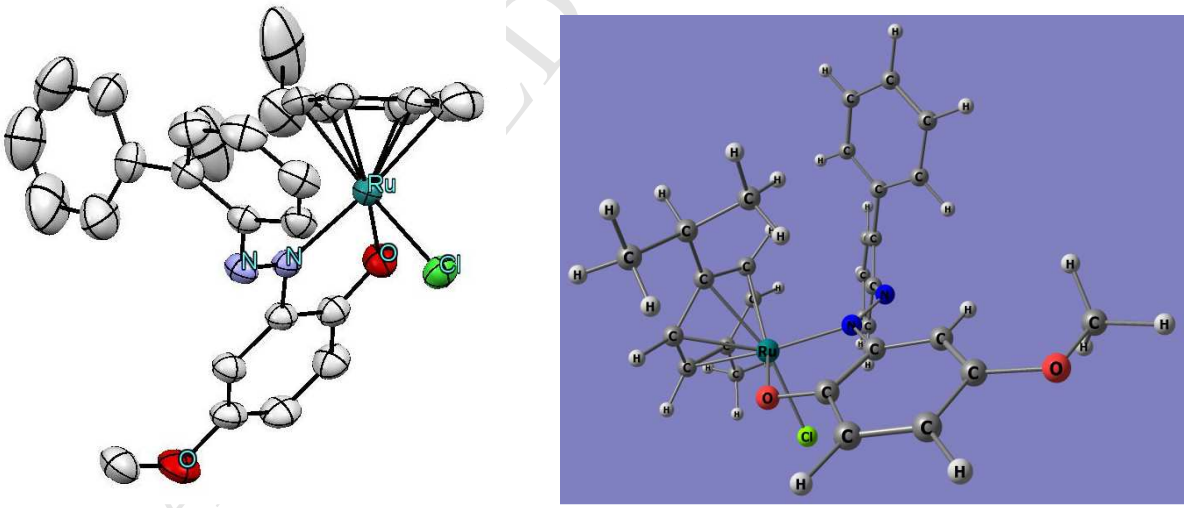
The structure of the compound (**1**), (**2**) and (**5**) consist of neutral arene ring bonded to the ruthenium along with chloride and O, N-donors of 2–(biphenylazo) phenol ligands. The molecular structure of complexes (**1**), (**2**) and (**5**) with atom labeling scheme is shown in **Fig 1 & 2**. The summary of single crystal X-ray structure refinement is given in the supporting information **S16**. The selected bond parameters are presented in **Table 1**. In the crystal structure of **1**, the complex crystallized in the triclinic with the P -1 space group whereas the complexes **2** and **5** are recrystallized in monoclinic with the P 21/c space group. The complexes **1, 2, 5** adopt a typical three-legged piano stool conformation with N, O and Cl atoms as the legs. More importantly the isopropyl group of the complex **2** is the successive refinements lead to the

permissible R factor values. The position and the bond parameters of the isopropyl group are supported and confirmed from the DFT calculations. Computational methods and experimental findings are being used together nowadays to complete the structural characterization [37].



1 **5**

Fig 1. ORTEP drawing of complexes **1** and **5** with hydrogen atoms being omitted for clarity.



2 (a) **(b)**

Fig 2. (a) ORTEP drawing of complex **2** (with hydrogen atoms being omitted for clarity) and (b) DFT (BP86/TZVP) optimized geometry with isopropyl group.

The 2–(biphenylazo) phenolate ligands bind the metal center at O and N forming the five membered chelate ring with bite angle O(1)–Ru(1)–N(1) 79.10(15), 79.34(9) and bond lengths of Ru(1)–O(1) and Ru(1)–N(1) are 2.059(4), 2.0520(1) and 2.052(2), 2.100(2) in **1** and **2**. The 1–(biphenylazo) naphtholate ligand bind the metal center at O and N forming the six membered chelate ring with bite angle of O(1)–Ru(1)–N(2) 87.49(9) and bond lengths of Ru(1)–O(1) and Ru(1)–N(2) are 2.005(2) and 2.058(2) in **5** respectively. The Ru–Cl bond length is found to be 2.4215(15), 2.4018(9) and 2.4202(8). As all the complexes display similar spectral properties, the other complexes are assumed to have similar structure to that of complexes **1**, **2** and **5**. In half-sandwich complexes of (η^6–*p*–cymene) ruthenium with several nitrogen ligands, Ru–N bond lengths have been reported [38, 39] generally between 2.060, 2.100(2) and 2.156 Å, which are consistent with the present values.

Table 1 Selected bond lengths (Å) and angles (°) in complexes **1, 2 (DFT)** and **5**

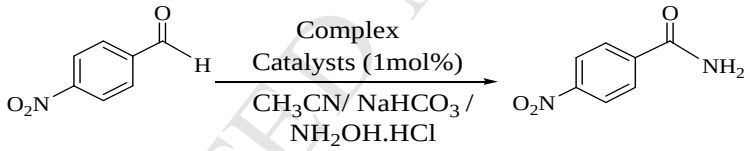
Distances / angles	**1**	**2**	**(DFT)**	**5**
Ru(1)-O(1)	2.059(4)	2.052(2)	(2.047)	2.055(2)
Ru(1)-N(1)	2.103(4)	2.100(2)	(2.101)	2.058(2)
Ru(1)-C(28)	2.173(5)	2.2010(1)	(2.180)	2.182(3)
Ru(1)-Cl(1)	2.4215(15)	2.4018(9)	(2.394)	2.4202(8)
N(2)-N(1)	1.268(6)	1.271(3)	(1.284)	1.251(3)
N(2)-C(8)	1.420(6)	1.4117(1)	(1.401)	1.388(4)
C(1)-O(1)	1.302(7)	1.303(4)	(1.306)	1.272(4)
O(1)-Ru(1)-N(1)	79.10(15)	79.34(9)	(79.47)	87.49(9)
O(1)-Ru(1)-C(28)	129.08(19)	108.56	(107.8)	89.27(10)
O(1)-Ru(1)-Cl(1)	85.52(13)	85.14(7)	(84.94)	84.88(7)
N(1)-Ru(1)-Cl(1)	85.50(11)	84.44(7)	(85.23)	83.94(7)
C(28)-Ru(1)-Cl(1)	144.82(15)	146.09	(145.98)	153.63(9)
N(2)-N(1)-Ru(1)	133.1(3)	132.2(2)	(132.1)	130.5(2)

2.3. Catalytic one-pot conversion of aldehydes to amides

4-nitrobenzaldehyde has been chosen as a model substrate to explore the catalytic activity of the complexes **1-5** under the optimized conditions. Among the tested complexes, complex **1** is highly efficient in the aldehyde to amide with a high conversion of 96%. The result of transformations is given in Table 2. We found that complex **1** showed in high yield than **2**, **3**, **4** and **5** at the same reaction time and at the same temperature. In the results obtained, complex **1** shows good catalytic activity among the other four complexes. Hence, complex **1** was selected as the model catalyst for conversion of 4-nitrobenzaldehyde to 4-nitrobenzamide using $NH_2OH.HCl$ by refluxing in acetonitrile with $NaHCO_3$ as the base.

Table 2

Optimized conditions for the 4-nitrobenzaldehyde to 4-nitrobenzamide conversion using complexes **1-5**[a].



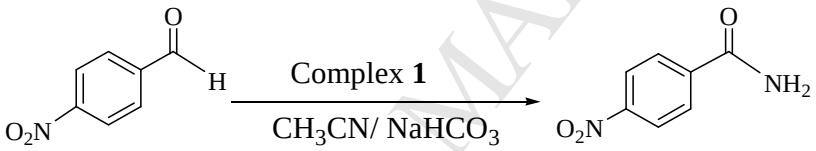
Entry	Complexes	Yield (%)[b]
1	**1**	96
2	**2**	82
3	**3**	79
4	**4**	70
5	**5**	62

[a]Reaction coditions: aldehyde (1 mmol), $NH_2OH.HCl$ (1 mmol), catalyst (1 mol%) and 2 mL of CH_3CN were refluxed for 5 h.
[b]Isolated yield after column chromatography.

In order to optimize the effect of catalyst loading, different catalyst: substrate (C:S) ratios were tested in the one-pot conversion of 4-nitrobenzaldehyde to 4-nitrobenzamide using complex **1** as a catalyst and the results are summarized in Table 3. The reaction proceeds with good isolated yield when the C:S ratio is 1:100. When changing the C:S ratio to 1:200, 1:300, 1:500 and 1:1000, the reaction still proceeds smoothly accompanied by a drop in the isolated yield. Thus, it was concluded that catalyst: substrate ratio of 1:100 is the best compromise between optimal reaction rates in acetonitrile and we obtained 96% yield of amide (entry 1).

Table 3

Effect of catalyst: substrate (C:S) ratio in the one-pot conversion of 4-nitrobenzaldehyde to 4-nitrobenzamide using complex [Ru(*p*–cymene)(Cl)(L_1)] **1**[a]



Entry	Ratio	Yield (%)[b]
1	1:100	96
2	1:200	68
3	1:300	52
4	1:500	41
5	1:1000	35

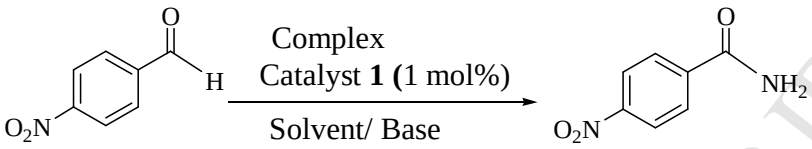
[a]Reaction conditions: Substrate (1 mmol), $NH_2OH.HCl$ (1 mmol) and 2 mL of CH_3CN were refluxed for 5 h.

[b]Isolated yield after column chromatography.

The catalytic activity of the ruthenium complex **1** was explored for the one-pot synthesis of amides from various aldehydes with hydroxylamine hydrochloride. For the entire optimization, 4-nitrobenzaldehyde was taken as a test substrate for different conditions. To study the influence of solvents in our catalytic system, we have chosen the reaction between 4-nitrobenzaldehyde (1 mmol), $NH_2OH \cdot HCl$ (1 mmol), complex **1** (1 mol%) as the catalyst precursor in the presence of various solvents and $NaHCO_3$ (1 mmol) as the base. Xylene, toluene, Benzene, chloroform, dichloromethane and acetonitrile are taken for our solvent variation study. The extent of conversion is solvent-dependent and low conversions were observed in benzene and xylene as solvent even at a higher temperature. Acetonitrile was found to be the solvent of choice with excellent isolated yield of amide (96%) at a lower temperature. The choice of the base was chosen, as a next step for the optimization in Table 4. It has been observed that in acetonitrile solvent, $NaHCO_3$ and $KHCO_3$ gave excellent isolated yields of 96% (entry 9) and 88% (entry 6) respectively, when compared to a much weaker base like CH_3COONa or Et_3N. Thus, it was concluded that $NaHCO_3$ as a base in acetonitrile solvent at 78 °C is the optimized condition for this conversion.

Table 4

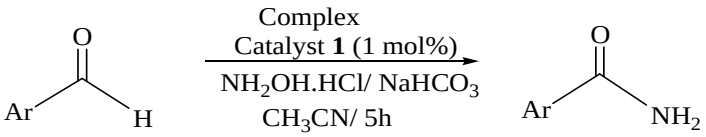
Optimization of solvent and base in the one-pot conversion of 4-nitrobenzaldehyde to 4-nitrobenzamide using complex [Ru(*p*–cymene)(Cl)(L_1)] **1**[a]

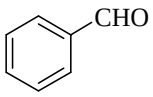
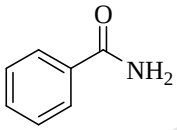
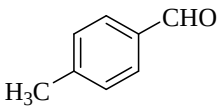
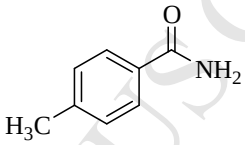
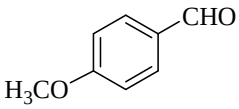
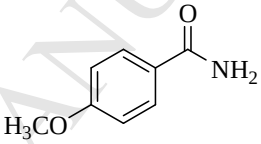
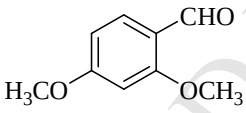
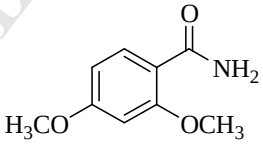
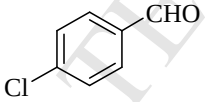
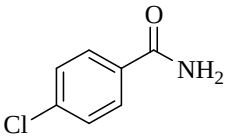
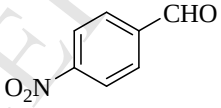
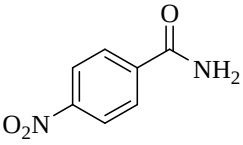
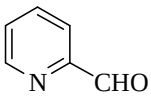
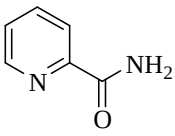
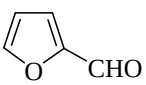
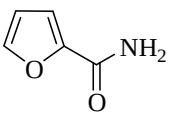
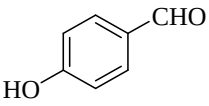
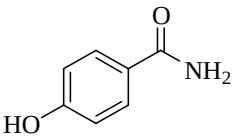


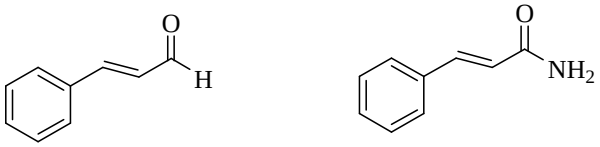
Entry	Solvent	Base	Temp (^oC)	Time (h)	Yield (%)[b]
1	Xylene	$NaHCO_3$	140	24	30
2	Toluene	$NaHCO_3$	110	24	68
3	Benzene	$NaHCO_3$	80	24	28
4	$CHCl_3$	$NaHCO_3$	61	24	32
5	CH_2Cl_2	$NaHCO_3$	40	24	<25
6	CH_3CN	$KHCO_3$	78	5	88
7	CH_3CN	Et_3N	78	5	<20
8	CH_3CN	CH_3COONa	78	5	<20
9	CH_3CN	$NaHCO_3$	78	5	96

[a]Reaction conditions: 4-nitrobenzaldehyde (1 mmol), $NH_2OH.HCl$ (1 mmol), base (1 mmol) and 2 mL of solvent.
[b]Isolated yield after column chromatography.

Table 5 One-pot conversion of aldehydes to amides using complex [Ru(*p*–cymene)(Cl)(L_1)] **1**[a]



Entry	Substrate	Product	Yield (%)[b]
1			93
2			82
3			76
4			71
5			90
6			96
7			72
8			67
9			75



10 70

[a]Conditions: Catalyst (1 mol%), aldehyde (1 mmol), $NH_2OH.HCl$ (1 mmol), $NaHCO_3$ (1 mmol) and 2 mL CH_3CN. [b]Isolated yield after column chromatography.

To explore the scope of the new catalyst, a range of other substituted aromatic and heterocyclic aldehydes were converted to primary amides using catalyst **1** under the optimized condition. All the reactions were carried out under identical reaction conditions to allow comparison of results. A broad range of amides were successfully synthesized with good to high isolated yields using the above optimized protocol. The results collected from the catalytic reactions are listed in Table 5. The electron donating groups like $–CH_3$, $–OCH_3$ and –OH (entries 2, 3 and 9) on benzaldehyde alters the reactions and the corresponding amides were obtained in good yields of 82%, 76% and 75% respectively and gave slightly lower yields compared with benzaldehyde. On the other hand, electron withdrawing substituents, such as the –Cl, and $–NO_2$ substituents (entries 5 and 6) offering excellent yields (90%, and 96%) when compared to substrate containing electron donating group. The introduction of electron withdrawing substituents to the *para* position of the aryl ring of the aldehyde decreased the electron density on the C=O bond so that the activity was improved giving rise to easier amidation reaction. The conversion proceeded smoothly even in the presence of heteroatoms such as N and O in the substrates (entries 7 and 8) and a range of heterocyclic aromatic amides were obtained in good isolated yields. Further, we believe that the catalytic transformation proceeds via the oxidative addition of the aldoxime N–OH bond to Ru(II), followed by nucleophilic attack on the coordinated imine, then β-elimination of cyclometalated, and finally reductive elimination to give the amide according to the mechanism proposed by Crabtree [40]. The present Ru(II)

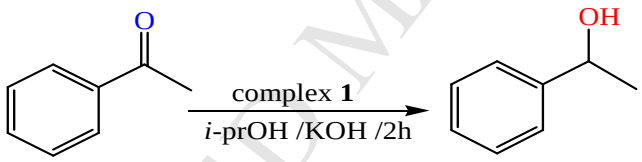
catalyst is more efficient in amidation reaction than the reported ruthenium(II) complexes in terms of reaction time, catalyst loading and isolated yields [41–43].

2.4. Catalytic transfer hydrogenation of ketones

Catalytic transfer hydrogenation reaction in which hydrogen is transferred from one organic molecule to another by ruthenium complexes is well known since one can avoid the use of molecular hydrogen and this prompted us to carry out this type of reactions. Representative types of aliphatic alkyl and aryl ketones were chosen to evaluate the performance of catalyst complex [Ru(*p*–cymene)(Cl)(L_1)] **1** in transfer hydrogenation reaction in the presence of iso-propanol and KOH as promoter.

Table 6

Catalytic transfer hydrogenation of acetophenone using complex **1**.



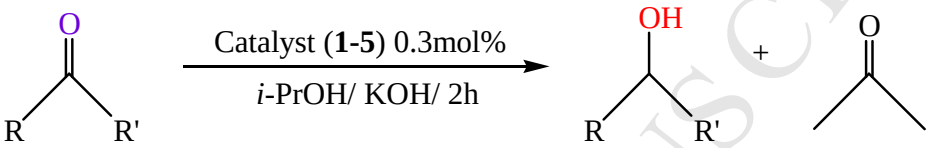
Entry	C/S	Conversion (%)	TON
1	1:900	60	225
2	1:600	75	180
3	1:300	95	285
4	absence of catalyst	product not detected	-

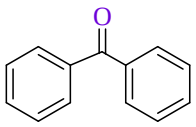
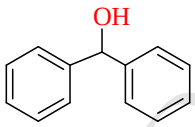
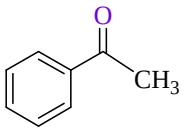
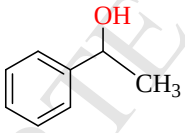
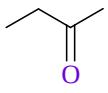
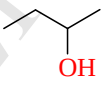
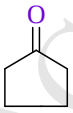
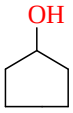
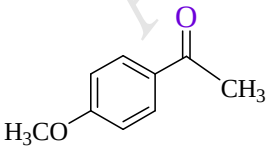
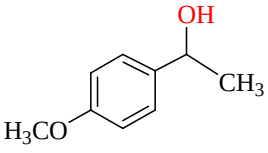
In order to optimize the reaction conditions, different catalyst: substrate ratios were tested and the results are summarized in Table 6. For this initial experiments, acetophenone was selected as a test-substrate and allowed it to react in 2-propanol with catalytic quantities of

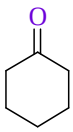
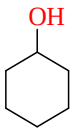
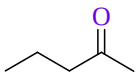
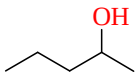
[Ru(*p*–cymene)(Cl)(L_1)] **1** complex in the presence of KOH. When increasing the C:S ratio to 1:300, 1:600 and 1:900 in 2-propanol, the reaction still proceeds smoothly accompanied by a moderate drop in conversion. Thus, it was concluded that catalyst: substrate ratio of 1:300 is the best compromise between optimal reaction rate and C/S ratio.

Table 7

Catalytic Transfer Hydrogenation of Ketones by [Ru(η^6–*p*–cymene)(Cl)($L_{(1-5)}$] **1–5**.



Entry	Substrate	Product	Conversion (%)[a] Complexes **1**	**2**	**3**	**4**	**5**	TON[b] **1**	**2**	**3**	**4**	**5**
1			75	70	87	60	70	225	210	261	180	210
2			95	80	90	85	75	285	240	270	255	225
3[c]			90	82	85	80	60	270	246	255	240	180
4			90	96	92	85	80	270	288	276	255	240
5			82	72	85	80	70	246	270	255	240	210

6			70	73	64	68	75	210	219	192	204	225
7[c]			90	85	80	75	80	270	255	240	225	240

[a]GC analysis; [b]TON = ratio of moles of product obtained the moles of catalyst used; [c]Time 6h

The catalyst performed efficiently in the conversion of ketones to alcohols and the results of this organic transformation are presented in Table 7. Both aliphatic and aromatic ketones are converted into their corresponding secondary alcohols with good conversions and turnover. The efficient conversion (upto 95%) was found in the case of acetophenone (entry 2) among the aromatic ketones with all the complex catalysts **1–5**. The complexes **1–5** efficiently catalyzed the reduction of acyclic ketones such as ethyl methyl ketone and isobutyl methyl ketone to their corresponding alcohols with 90% conversion respectively. These ketones took longer time (entry 3 & 7) to react compared to their cyclic counter parts. Moreover, these catalysts show good activity for the transfer hydrogenation of five and six membered cyclic ketones with excellent conversions upto 96%. This trend of higher conversion of cyclic ketones can be attributable to steric hindrance with respect to access to the C=O bond [44]. The complexes of biphenylazo ligands ($L_{1–5}$) do not differ significantly in catalytic efficiency. The catalytic results obtained are comparable with other ruthenium complexes containg different types of O, N donor ligands [45]. No transfer hydrogenation was observed in the absence of base. In the transfer hydrogenation reaction, the base facilitates the formation of ruthenium alkoxide by abstracting proton from the alcohol and subsequently alkoxide undergoes β-elimination to give ruthenium hydride, which is an active species in this reaction. This is the mechanism proposed by several workers on the

studies of ruthenium catalyzed transfer hydrogenation reaction by metal hydride intermediates [46–50].

3. Conclusion

A family of five half-sandwich ruthenium(II) complexes of the general formula [Ru(η^6–*p*–cymene)(Cl)($L_{1–5}$)] have been synthesized and characterized. The structure of complexes **1**, **2** and **5** were confirmed by single crystal X-ray differaction, to have the pseudo-octahedral three legged piano stool geometry. These ruthenium complexes exhibit a high activity in an exceptionally short reaction time, effective of solvent, base assisted aldehydes to primary amines. Among the five complexes, the complex **1** is the most active one. The ruthenium complexes also effectively catalyze the transfer hydrogenation of various ketones in presence of *i*-prOH.

4. Experimental Procedures

4.1. Materials and physical measurements

Commercial $RuCl_3.3H_2O$ was purchased from Himedia. All the used reagents were chemically pure or analytical reagent grade. Solvents were purified and dried according to standard procedures. The 2–(biphenylazo)phenol and 1–(biphenylazo)naphthol ligands [51] were prepared by diazotization reaction of 2-aminobiphenyl with corresponding *para*-substituted phenols. The metal precursor [{η^6–*p*–cymene)RuCl}$_2$(μ–Cl)$_2$] was prepared by standard procedure [52]. The substrates used in the catalytic studies, were purchased from Merck and Aldrich. The IR spectra of the complexes were recorded on an agilent resolution pro model in 4000–400 cm^{-1} range. Electronic spectra of the complexes were recorded in $CHCl_3$ solution in a Cary 300 Bio UV–Vis Varian spectrophotometer in the range 800–200 nm. The ^{1}H NMR spectra were recorded in $CDCl_3$ with Bruker 300MHz instrument using TMS as internal reference.

*4.2. General method of synthesis of Half-Sandwich Ruthenium complexes (**1–5**)*

The RB flask containing ruthenium precursor $[RuCl_2(p\text{–cymene})]_2$ (0.06g; 0.1mmol) and 2-(biphenylazo)phenol and 1–(biphenylazo)naphthol ligands (HL_1 – HL_5) (0.0568–0.0640g; 0.2mmol) were taken in methanol (20 mL) and the mixture was stirred for 4h. Then, the solvent was removed through vaccum, the dark red mass obtained was dissolved in chloroform (15 mL) and filtered through short path of silica gel column to remove insoluble materials. The red solution was then concentrated into 2 mL, dark-red product separated out an addition of excess hexane and washed with diethyl ether and dried in vaccum.

[Ru(*p*–cymene)(Cl)(L_1)] (**1**)

Yield: 70%; brown solid; M.p.196 ^oC, Anal.Cal. for $C_{29}H_{24}N_2OClRu$: C, 62.92; H, 4.33; N, 5.06; Found: C, 62.94; H, 4.32; N, 5.10. FT–IR (cm^{-1}): 1384 ν(N=N), 1313 ν(C–O). ^{1}H–NMR (300 MHz, $CDCl_3$): δ (ppm) = 6.9–7.9 (m, Ar-H), 4.3 (d 1H, cymene Ar–H), 5.8 (d 1H, cymene Ar–H), 0.9–1.3 (dd, 6H, $2CH_3$ of *p*–cymene), 2.3 (s, CH_3). UV–Vis (λmax, (nm): 450, 340, 250.

[Ru(*p*–cymene)(Cl)(L_2)] (**2**)

Yield: 85%; brownish red solid; M.p. 212 ^oC, Anal. Cal. For $C_{29}H_{26}N_2O_2ClRu$: C, 60.94; H, 4.55; N, 4.90; Found: C, 60.92; H, 4.57; N, 4.88. FT–IR (cm^{-1}): 1388 ν(N=N), 1305 ν(C–O). ^{1}H–NMR (300 MHz, $CDCl_3$): δ (ppm) = 6.7–7.9 (m, Ar-H), 4.15 (d 1H, cymene Ar–H), 5.8 (d 1H, cymene Ar–H), 2.4 (s, 3H, CH_3 of *p*–cymene), 0.8–1.4 (dd, 6H, $2CH_3$ of *p*–cymene), 3.7 (s, OCH_3). UV–Vis (λmax, (nm): 446, 330, 250.

[Ru(*p*–cymene)(Cl)(L_3)] (**3**)

Yield: 60%; brown solid; M.p. 206 ^oC, Anal.Cal. For $C_{32}H_{35}N_2OClRu$: C, 64.10; H, 5.84; N, 4.67; Found: C, 64.12; H, 5.85; N, 4.61. FT–IR (cm^{-1}): 1389 ν(N=N), 1317 ν(C–O). ^{1}H–NMR (300 MHz, $CDCl_3$): δ (ppm) = 6.4–7.9 (m, Ar-H), 4.1 (d 1H, cymene Ar–H), 5.3 (d

1H, cymene Ar–H), 2.3 (s, 3H, CH_3 of *p*–cymene), 1.1–1.3 (dd, 6H, $2CH_3$ of *p*–cymene), 2.9 (m, $(CH_3)_3C$). UV–Vis (λmax, (nm): 444, 325, 255.

[Ru(*p*–cymene)(Cl)(L_4)] (**4**)

Yield: 75%; brown solid; M.p. 142 ^oC, Anal. Cal. For $C_{28}H_{27}N_2OCl_2Ru$: C, 58.13; H, 4.67; N, 4.84; Found: C, 58.10; H, 4.70; N, 4.82. FT–IR (cm^{-1}): 1388 ν(N=N), 1310 ν(C–O). ^{1}H–NMR (300 MHz, $CDCl_3$): δ (ppm) = 6.6–7.7 (m, Ar-H), 4.15–5.6 (d 1H, cymene Ar–H), 2.2 (s, 3H, CH_3 of *p*–cymene), 0.9–1.2 (dd, 6H, $2CH_3$ of *p*–cymene). UV–Vis (λmax, (nm): 455, 330, 260.

[Ru(*p*–cymene)(Cl)(L_5)] (**5**)

Yield: 80%; brown solid; M.p. 240 ^oC, Anal. Cal. For $C_{32}H_{24}N_2OClRu$: C, 65.18; H, 4.07; N, 4.75; Found: C, 65.19; H, 4.09; N, 4.76. FT–IR (cm^{-1}): 1384 ν(N=N), 1323 ν(C–O). ^{1}H–NMR (300 MHz, $CDCl_3$): δ (ppm) = 6.6–7.8 (m, Ar-H), 4.2 (d 1H, cymene Ar–H), 5.8 (d 1H, cymene Ar–H), 2.5–2.8 (s, 3H, CH_3 of *p*–cymene), 0.85–1.3 (dd, 6H, $2CH_3$ of *p*–cymene). UV–Vis (λmax, (nm): 448, 330, 250.

4.3. Typical procedure for the one-pot conversion of aldehydes to amides

To an oven-dried round-bottom flask equipped with magnetic stirring bar was added complex (1) (1 mol%), the aldehyde (1 mmol), $NH_2OH.HCl$ (1 mmol) and $NaHCO_3$ (1 mmol) and the mixture was placed under an atmosphere of N_2. Dry and degassed MeCN (2 mL) was added and the reaction mixture was refluxed for the time specified under an N_2 atmosphere. The reaction was cooled to room temperature and the solvent evaporated. The residue was dissolved in CH_2Cl_2, filtered and the solvent removed. The crude product was then purified using silica gel

chromatography ($CHCl_3$/MeOH) giving the amides in high isolated yields. Characterization details for each amide are given in the supporting information S16-S20.

4.4. General procedure for catalytic transfer hydrogenation reaction

A solution of the ketone (3.75mmol), KOH (0.03mmol) and the catalyst complexes **1–5** (0.0125mmol) was heated under reflux (80 ^oC) in 5 mL of 2-propanol for 2h. The solvent was removed under vaccum, and an aliquot of the remaining product was extracted with diethylether, filtered through a short column of silica gel. The column was washed with diethylether. The filtrate and washings of the column were mixed and evaporated on a rotary evaporator and analyzed by GC.

4.5. X-ray crystallography

Single crystals of [Ru(η^6–*p*–cymene)(Cl)(L_1)] (**1**), [Ru(η^6–*p*–cymene)(Cl)(L_2)] (**2**) and [Ru(η^6–*p*–cymene)(Cl)(L_5)] (**5**) were grown by slow evaporation of a chloroform–pentane solution at room temperature. Crystals were mounted on a Stoe Mark II-Image Plate diffractometer using monochromated Mo Kα radiation (λ = 0.71073). Data were collected at 296 K. Structures were solved with direct method using SHELXS [53] and were refined by full-matrix least-squares method [54] on F^2 with SHELXL. Non hydrogen atoms were refined with anisotropy thermal parameters.

Acknowledgments

The authors express sincere thanks to Single Crystal X–ray Diffraction Facility, SAIF Guwahati University, for providing X–ray data collection.

Appendix A. Supplementary data

FT-IR, UV-Vis and ^{1}H-NMR spectra of representative complexes. CCDC 1868196, CCDC 1915333 and CCDC 1863103 contain the supplementary crystallographic data for complex **1, 2** and **5**. These data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK (fax: +44 1223 336033; email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Reference

[1] (a) S. Medici, M. Peana, V. M. Nurchi, J. I. Lachowicz, G. Crisponi, M. A. Zoroddu, Coord. Chem. Rev. 284 (2015) 329–350;

(b) W. Su, Z. Tang, P. Li, Mini-Rev. Med. Chem. 16 (2016) 787–795;

(c) B. S. Murray, M. V. Babak, C. G. Hartinger, P. J. Dyson, Coord. Chem. Rev. 306 (2016) 86–114;

(d) J. M. Stubbs, R. J. Hazlehurst, P. D. Boyle, J. M. Blacquiere, Organometallic 36 (2017) 1692–1698;

(e) M. Simonetti, G. J. P. Perry, X. C. Cambeiro, F. Julia-Hernandez, J. N. Arokianathar, I. Larrosa, J. Am. Chem. Soc. 138 (2016) 3596–3606;

(f) A. O. Ogweno, S. O. Ojwach and M. P. Akerman, Dalton Trans. 43 (2014) 1228-1237.

[2] (a) M. J. Clarke, Coord. Chem. Rev. 236 (2003) 209-233;

(b) W. H. Ang, P. J. Dyson, Eur. J. Inorg. Chem. (2006) 4003-4018;

(c) N. Song, J. J. Concepcion, R. Binstead, J. Rudd, A. K. Vannucci, C. J. Dares, M. K. Coggins and T. J. Meyer, Proc. Natl. Acad. Sci. U. S. A., 112 (2015) 4935–4940;

(d) M. Yamamoto, L. Wang, F. Li, T. Fukushima, K. Tanaka, L. Sun, H. Imahori, Chem. Sci. (2016) 1–10;

(e) D. Zell, S. Warratz, D. Gelman, S. J. Garden, L. Ackermann, Chem. Eur. J. 22 (2016)

1248–1252;

(f) J. Malineni, H. Keul, M. Moller, Dalton Trans. 44 (2015) 17409–17414.

[3] (a) A. G. Walden, A. J. M. Miller, Chem. Sci. 6 (2015) 2405–2410;

(b) M. V. Sheridan, B. D. Sherman, Z. Fang, K. R. Wee, M. K. Coggins and T. J. Meyer, ACS Catal. 5 (2015) 4404–4409;

(c) J. J. Concepcion, M. K. Tsai, J. T. Muckerman, T. J. Meyer, J. Am. Chem. Soc. 132 (2010) 1545–1557;

(d) F. Sepulveda, M. C. Carrion, A. D. Phillips, F. A. Jalon, P. J. Dyson, B. R. Manzano, Eur. J. Inorg. Chem. (2017) 630–638;

(e) K. M. Steward, E. C. Gentry, J. S. Johnson, J. Am. Chem. Soc. 134 (2012) 7329–7332.

[4] (a) C. J. Cramer, V. S. Batista, A. Llobet, Angew. Chem., Int. Ed., 53 (2014) 205–209;

(b) L. Tong, Y. Wang, L. Duan, Y. Xu, X. Cheng, A. Fischer, M. S. G. Ahlquist, L. Sun, Inorg. Chem. 51 (2012) 3388–3398;

(c) L. Tong, A. K. Inge, L. Duan, L. Wang, X. Zou and L. Sun. Inorg. Chem. 52 (2013) 2505–2518;

(d) R. E. Morris, R. E. Aird, P. Murdoch del, S. H. Chen, J. Cummings, N. D. Hughes, S. Parsons, A. Parkin, G. Boyd, D. I. Jodrell, P. J. Sadler, J. Med. Chem. 44 (2001) 3616–3621.

[5] (a) P. Singh, A. K. Singh, Organometallics 29 (2010) 6433–6442;

(b) G. Venkatachalam, N. Raja, D. Pandiarajan, R. Ramesh, Spectrochim. Acta, Part A. 71 (2008) 884–891;

(c) S. Kannan, R. Ramesh, Polyhedron 25 (2006) 3095–3103;

(d) D. Chatterjee, A. Mitra, S. Mukherjee, J. Mol. Catal. A: Chem. 165 (2001) 295;

(e) S. Campestrini, M. Carraro, U. Tonellato, M. Pagliaro, R. Ciriminna, Tetrahedron Lett. 45 (2004) 7283.

[6] (a) N. Sathya, G. Raja, N. Padma Priya, C. Jayabalakrishnan, Appl. Organometal. Chem. 24 (2010) 366–373;

(b) S. K. Sarkar, M. S. Jana, T. K. Mondal, C. Sinha, J. Organomet. Chem. 716 (2012) 129–137;

(c) S. J. Bozorghi, H. Esfandiari, H. Saravani, F. R. Charati, B. W. Skelton, M. Makha, J. Coord. Chem. 65 (2012) 994–1003;

(d) M. U. Raja, N. Gowri, R. Ramesh, Polyhedron 29 (2010) 1175–1181.

[7] (a) M. Sivagamasundari, R. Ramesh, Spectrochim. Acta, Part A. 66 (2007) 427–433;

(b) R. W. Murray, K. Iyanar, J. X. Chen, J. Wearing, Tetrahedron Lett. 36 (1995) 6415;

(c) V. Kesavan, D.B. Delpon, J.P. Begue, A. Srikanth, S. Chandrasekaran, Tetrahedron Lett. 41 (2000) 3327;

(d) T. Nishimura, T. Onoue, K. Ohe, S. Uemura, J. Org. Chem. 64 (1999) 6750.

[8] (a) H. Brunner, Adv. Organomet. Chem. 18 (1980) 151–206;

(b) M. H. Bennett, Coord. Chem. Rev. 166 (1997) 225;

(c) D. Tyagi, C. Binnani, R. K. Rai, A. D. Dwivedi, K. Gupta, P. –Z. Li, Y. Zhao, S. K. Singh, Inorg. Chem. 55 (2016) 6332– 6343;

(d) W. –G. Jia, H. Zhang, T. Zhang, S. Ling, Inorg. Chem. Commun., 66 (2016) 15–18;

(e) J. H. Rigby, M. A. Kondratenko, Top. Organomet. Chem. 7 (2004) 181–204;

(f) F. Ding, Y. G. Sun, F. Verpoort, Eur. J. Inorg. Chem. (2010) 1536-1543;

[9] (a) W. Y. Wong, W. T. Wong, Coord. Chem. Rev. 146 (1995) 307;

(b) G. Winkhaus, H. Singer, J. Organomet. Chem. 7 (1967) 487–491;

(c) G. Pampaloni, Coord. Chem. Rev. 254 (2010) 402–419.

[10] (a) M. G. Richard, Coord. Chem. Rev. 141 (1995) 63.

(b) R. Castarlenas, C. Vovard, C. Fischmeister, P. H. Dixneuf, J. Am. Chem. Soc. 128 (2006) 4079–4089;

(c) F. A. Beckford, G. Leblanc, J. Thessing, M. Shaloski, B. J. Frost, L. Li, N. P. Seeram, Inorg. Chem. Commun., 12 (2009) 1094–1098;

(d) A. M. Pizarro, M. Melchart, A. Habtemariam, L. Salassa, F. P. A. Fabbiani, S. Parsons, P. J. Sadler, Inorg. Chem. 49 (2010) 3310–3319.

[11] (a) S. Dayan N. K. Ozpozan, N. Özdemir, O. Dayan J. Organomet. Chem. 770 (2014) 21-28;

(b) J. M. Gichumbi, H. B. Friedrich, B. Omondi, J. Organomet. Chem. 808 (2016) 87–96;

(c) S. Dayan, N. Kayac, N. O. Kalaycioglu, O. Dayan, E. C. Ozturk, Inorg. Chimi. Acta. 401 (2013) 107–113.

[12] (a) A. Kanchanadevi, R. Ramesh, D. Semeril, Inorg. Chem. Commun, 56 (2015) 116–119;

(b) M. Ramesh, G. Venkatachalam, Chemistry Select, 3 (2018) 9056–9061;

(c) N. Raja, B. Therrien J. Organomet. Chem, 765 (2014) 1-7;

(d) R. N. Prabhu, R. Ramesh, RSC Adv, 2 (2012) 4515–4524.

[13] (a) N. Raja, M. U. Raja, R. Ramesh, Inorg. Chem. Commun, 19 (2012) 51–54;

(b) L. Perreux, A. Loupy, F. Voltron, Tetrahedron 58 (2002) 1215;

(c) C. L. Allen, A. R. Chhatwal, J. M. J. Williams, Chem. Commun. 48 (2012) 666–668.

[14] (a) W.-G. Jia, H. Zhang, T. Zhang, D. Xie, S. Ling, E.-H. Sheng Organometallics, 35(4) (2016) 503–512;

(b) I. Sorribes, G. Wienhöfer, C. Vicent, K. Junge, R. Llusar, M. Beller, Angew. Chem., Int.

Ed. 51 (2012) 7794−7798;

(c) N. S. Sanjini, S. Velmathi, RSC Adv. 4 (2014) 15381−15388;

(d) M. Paul, N. Pal, A. Bhaumik, Eur. J. Inorg. Chem. (2010) 5129−5134.

[15] (a) W.-G. Jia, S. Ling, H.-N. Zhang, E.-H. Sheng, R. Lee, Organometallics, 37(1) (2018) 40–47;

(b) S. K. Mohapatra, S. U. Sonavane, R. V. Jayaram, P. Selvam, Tetrahedron Lett. 43 (2002) 8527−8529;

(c) R. V. Jagadeesh, G. Wienhöfer, F. A. Westerhaus, A.-E. Surkus, H. Junge, K. Junge, M. Chem. Eur. J. 17 (2011) 14375−14379;

(d) G. Wienhöfer, I. Sorribes, A. Boddien, F. Westerhaus, K. Junge, H. Junge, R. Llusar, M. J. Am. Chem. Soc. 133 (2011) 12875−12879.

[16] (a) W.-G. Jia, Z.-B. Wang, X.-T. Zhi, J.-Q. Han, Y. Sun, J. Coord. Chem 70 (2017) 848-858;

(b) S. Hohloch, L. Suntrup, B. Sarkar, Organometallics 32 (2013) 7376−7385;

(c) S. Gowda, D. C. Gowda, Tetrahedron 58 (2002) 2211−2213.

[17] C. E. Mabermann, in: J. I. Kroschwitz (Ed.), Encyclopedia of Chemical Technology, vol. 1, Wiley, New York, (1991) 251–266.

[18] D. Lipp, in: J. I. Kroschwitz (Ed.), Encyclopedia of Chemical Technology, vol. 1, Wiley, New York, (1991) 266–287.

[19] R. Opsahl, in: J. I. Kroschwitz (Ed.), Encyclopedia of Chemical Technology, vol. 2, Wiley, New York, (1991) 346–356.

[20] E. C. Horning, V. L. Stromberg, J. Am. Chem. Soc. 74 (1952) 5151–5152.

[21] R. E. Gawly, Org. React. 35 (1988) 1.

[22] A. Loupy, S. Regnier, Tetrahedron Lett. 40 (1999) 6221–6224.

[23] (a) D. Gnanamgari, R. H. Crabtree, Organometallics 28 (2009) 922–924;

(b) S. T. Chill, R. H. Mebane, Synth. Commun. 40 (2010) 2014–2017.

[24] J. W. Faller, J. Parr, Organometallics 19 (2000) 1829–1832.

[25] (a) Y. Miyaki, T. Onishi, H. Kurosawo, Inorg. Chim. Acta. 300 (2000) 369–377;

(b) D. P. Halbach, C. G. Hamaker, J. Organomet. Chem. 691 (2006) 3349–3361;

(c) K. Severin, Corr. Org. Chem. 10 (2006) 217–224;

(d) L. Delande, A. Demonceau, A. F. Noels, Curr. Org. Chem. 210 (2006) 203.

[26] C. M. Thomas, R. Mafia, B. Thesrian, E. Rusanov, H. S. Evans, G. S. Fink, Chem. Eur. J. 8 (2002) 3343–3352.

[27] K. Sui, S. M. Peng, S. Bhattacharya, Polyhedron 18 (1999) 631–640.

[28] R. Noyori, H. Akaya, Acc. Chem. Res. 23 (1990) 345–350.

[29] P. Dani, T. Karlen, R. A. Gossage, S. Gladiali, G. Van Koten, Angew. Chem., Int. Ed. 112 (2000) 759–761.

[30] R. L. Chowdhury, J. E. Backvall, J. Chem. Soc., Chem. Commun., (1991) 1063–1064.

[31] (a) W. Ferstl, I. K. Sakodinskaya, N. B. Sutter, G. L. Borgne, M. Pfeffer, A. D. Ryabov, Organometallics 16 (1997) 411–418;

(b) Y. Miyaki, T. Onishi, S. Ogoshi, H. Kurosawa, J. Organomet. Chem. 616 (2000) 135–139;

(c) M. Ramesh, M. Kalidass, M. Jaccob, D. Kaleeswaran, G. Venkatachalam, J. Organomet. Chem. 830 (2017) 33–41;

(d) S. Basu, S. Halder, I. Pal, S. Samanta, P. Karmakar, Michael G. B. Drew, S. Bhattacharya, Polyhedron 27 (2008) 2943–2951;

(e) P. Gupta, S. Dutta, F. Basuli, S. M. Peng, G. H. Lee, S. Bhattacharya, Inorg. Chem. 45 (2006) 460.

[32] P. Byabartta, P. K. Santra, T. K. Misra, C. Sinha, C. H. L. Kennard, Polyhedron 20 (2001) 905–913.

[33] S. Goswami, R. Mukerjee, A. Chakravorty, Inorg. Chem. 22 (1983) 2825–2832.

[34] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley Interscience, New York, (1971).

[35] A. Ceulemans, L. G. Vanquickenborne, J. Am. Chem. Soc. 103 (1981) 2238–2241.

[36] A. B. P. Lever, Inorganic Electronic Spectroscopy, second ed., Elsiever, New York, (1984).

[37] (a) A. J. Welch, Crystals 7 (2017) 234;

(b) B. S Krishnamoorthy, A. Thakur, K. K. V. Chakrahari, S. K. Bose, P. Hamon, T. Roisnel, S. Kahlal, S. Ghosh, J.-F. Halet, Inorg. Chem., 51 (2012) 10375.

[38] (a) T. Bugareic, A. Habtemariam, R. J. Deeth, F. P. A. Fabbiani, S. Parsons, P. J. Sadler, Inorg. Chem. 48 (2009) 9444–9453;

(b) S. Adhikari, W. Kaminsky, M. R. Kollipara, J. Organomet. Chem. 848 (2017) 95–103;

(c) S. Adhikari, O. Hussain, R. M. Phillips, M. R. Kollipara, J. Organomet. Chem. 854 (2018) 27–37.

[39] (a) A. Bacchi, P. Pelagatti, C. Pelizzi, D. Rogolino, J. Organomet. Chem. 694 (2009) 3200–3211.

(b) P. Govindaswamy, Y. A. Mozharivskyj, M. R. Kollipara, J. Organomet. Chem. 689 (2004) 3265–3274

[40] J. F. Hull, S. T. Hilton, R. H. Crabtree, Inorg. Chim. Acta 363 (2010) 1243–1245.

[41] D. Gnanamgari, R. H. Crabtree, Organometallics 28 (2009) 922–924.

[42] D. Tyagi, R. K. Rai, A. D. Dwivedi, S. M. Mobin, S. K. Singh, Inorg. Chem. Front. 2 (2015) 116–124.

[43] S. T. Chill, R. C. Mebane, Synth. Commun. 40 (2010) 2014–2017.

[44] M. D. Bala, M. I. Ikhile, J. Mol. Catal. A: Chem. 385 (2014) 98–105.

[45] (a) M. Ramesh, G. Prabusankar, G. Venkatachalam, Inorg. Chem. Commun. 79 (2017) 89–94;

(b) S. Kannan, R. Ramesh, Y. Liu, J. Organomet. Chem. 692 (2007) 3380–3391;

(c) R. N. Prabhu, R. Ramesh, J. Organomet. Chem. 718 (2012) 43–51;

(d) K. Mandal, A. R. Chakravarty, Polyhedron 11 (1992) 823-827;

(e) N. Mohan, R. Ramesh, Appl. Organomet. Chem. (2016) 1–9.

[46] J. -E. Backvall, J. Organomet. Chem. 652 (2002) 105–111.

[47] R. Noyori, S. Hashiguchi, Acc. Chem. Res. 30 (1997) 97–102.

[48] H. Doucet, T. Ohkuma, K. Murata, T. Yokozawa, M. Kozawa, E. Katayama, F. A. England, T. Ikariya, R. Noyori, Angew. Chem. Int. Ed. 37 (1998) 1703–1707.

[49] E. P. Kelson, P. P. Phengsy, J. Chem. Soc., Dalton Trans. (2000) 4023–4024.

[50] H. Zhang, C. B. Yang, Y. Y. Li, Z. R. Donga, Z. X. Gao, H. Nakamura, K. Murata, K. Ikariya, Chem. Commun. (2003) 142–143.

[51] (a) R. Nandhini, M. Ramesh, G. Prabusankar, G. Venkatachalam, Inorg. Chem. Commun. 85 (2017) 84–88;

(b) M. Ramesh, M. Deepan kumar, M. Jaccob, B. Therrien, G. Venkatachalam, Inorg. Chim. Acta. 477 (2018) 40-50.

[52] M. A. Bennett, A. K. Smith, J. Chem. Soc., Dalton Trans. (1974) 233–241.

[53] G. M. Sheldrick, Acta Cryst. A. 64 (2008) 112.

[54] L. J. Farrugia, J. Appl. Cryst. 30 (1997) 565.

Highlights

- A family of *p*-cymene Ruthenium(II) complexes have been synthesized.
- Molecular structure of the complexes was confirmed by single crystal XRD.
- These complexes were used an efficient catalysts for aldehyde to primary amines and transfer hydrogenation reaction of various ketones.