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Appraisal of Ruthenium(II) complexes of (4-phenoxyphenylazo) ligands for the synthesis of primary amides by dint of hydroxylamine hydrochloride and aldehydes

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ABSTRACT

A new family of O, N donor-functionalized (4-phenoxyphenylazo)-2-naphthol/4-substituted phenol-based ligands (**HL_1-HL_4**) has been synthesized. The prepared ligands were successfully utilized for the access of a series of ruthenium(II) carbonyl complexes of the type $[Ru(L)Cl(CO)(EPh_3)_3]$ (E = phosphine/arsine), (L = 1-(4-phenoxyphenylazo)-2-naphthol (**HL_1**), 2-(4-phenoxyphenylazo)-4-chlorophenol (**HL_2**), 2-(4-phenoxyphenylazo)-4-methylphenol (**HL_3**) and 2-(4-phenoxyphenylazo)-4-methoxyphenol (**HL_4**)). All of the ruthenium(II) carbonyl complexes and ligands have been fully characterized by FT-IR, UV−visible, ^1H NMR, ^{31}P NMR, mass spectrometry and CHN analysis. The ligands have been analyzed by ^{13}C NMR. The UV−visible spectroscopic study reveals that both the ligands and Ru(II) complexes exhibit excellent charge transfer transitions. This is the basic criteria for the oxidative amidation reaction, which is an influential strategy for the transformation of oxygenated organic compounds to the profitable amides. However, this catalytic process makes more impact on the application of new divalent ruthenium(II) azo compounds as catalyst in a single-pot conversion of aldehydes to amides in the presence of $NaHCO_3$.

1. Introduction

Events associated with organoruthenium(II) complexes containing azo ligands have significant interest in recent years [1]. These organoruthenium(II) complexes are extensively used in several industries and biological fields [2–4]. Specifically Ru(II) complexes have found to be catalytic activity of various organic transformations such as hydroxylation, carboxylation, hydroformylation, isomerization, epoxidation, dehalogenation, sulfoxidation, dehydrogenation, polymerization, carbon-carbon bond formation, alcohol and aldehyde reactions [5–10]. The synthesized N-arylamide compounds have emerged as different potential drugs (herbicide, fungicide, insecticide, pesticide, etc.) [11,12]. So, this method of preparation of amide skeleton has become one of the most achievable tasks to the organic chemists. The traditional strategies are used for the preparation of amides via, the coupling of activated carboxylic acid derivatives, viz., acid chloride, anhydride, active esters with a variety of amines. Quite a lot of available methods along with the use of carbonyl compounds (ketones and aldehydes) or carbonyl derivatives (oximes) have been employed for the synthesis of amides [13–16]. Over the years of centenary, Beckmann rearrangement is used to transform oxime into the corresponding amides using an acids or base [17,18].

However, this conversion is quite challenging one due to the formation of undesired nitriles, aldehydes and carboxylic acids during the course of the reaction. These side products might affect the yield of the desired amides when the reactions are scaled up. Hence, the investigation on the synthesis of amides using new catalysts receives more attention. Moreover, metal-mediated methodologies for this conversion by dint of hydroxylamine hydrochloride are sparse [19]. The conversion of aldehydes to amides takes place through the formation of aldoximes. The rearrangement of aldoximes to amides, has been achieved by the usage of various transition metal catalysts possess nickel [20], copper [21], zinc [22] palladium [23], gold/silver [24], iridium [25,26] and rhodium [27]. Williams *et al.*, have reported a ruthenium catalyzed transformation by the results of greater selectivity, appreciable yield and

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low catalyst loading [28]. Moreover, Crabtree and his coworkers have used ruthenium terpyridine complexes as catalysts and achieved the better results without using any acid or base [29]. Ruthenium complexes of thiazolylazo ligands [30], hydrozone ligands [31], P-donor ligand tris(dimethylamino)phosphine [32] and phosphine free ligands [33] have also been utilized for the transfer hydrogenation reactions. Models of ruthenium complexes with different donor sets such as NNN, NNO, SNO, P and N utilized for the amide conversion are shown in Fig. 1.

In kind, $[RuCl_2(DMSO)_4]$ complex has been used as potentially active catalyst for the reactions of aldehydes to primary amides [34].

The previous literature results on ruthenium azo chemistry reveal [35] that, it has great attention owing to its three reasons. At first, the ability of azo functional group in the formation of metal-carbon bonds or metallacycles due to their π-acidic nature [36]. Moreover, the azo functional group (-N=N-) can stabilize the ruthenium ion in lower oxidation states because of its strong π-acidic character, whereas naphtholate/phenolate oxygen being a hard base, which stabilizes the metal ion in higher oxidation states [37]. Secondly, the naphthol/phenol-based systems can act as potential bidentate ligands which coordinate to the metal through N and O donors. Moreover, they have better electron donating activity and provide more steric crowing compared to the phenyl group. Thirdly, a number of ligands can act as tridentate donor systems and can able to produce an additional vacancy at the metal center throughout the catalytic response which facilitates the catalytic cycle. The kind of ligands explored in this work is known to bind with metal atom in a bidentate fashion with mono anionic O, N donors by forming a five membered chelate ring [38].

Herein, we report the synthesis and characterization of ruthenium(II) carbonyl complexes containing triphenylphosphine/triphenylarsine incorporated with (4-phenoxyphenylazo) 2-naphthol/p-substituted phenols. Furthermore, they have been effectively employed as catalysts in the transformation of various aldehydes to amides by following hydroxylamine hydrochloride pathway along with $NaHCO_3$ as an additive.

2. Experimental section

2.1. Materials and measurements

Commercially available $RuCl_3.3H_2O$ was used as supplied from SRL Pvt. Ltd. All the reagents used were chemically pure and analar grade. The solvents were freshly purified using the usual procedures [39]. 4-phenoxyphenylamine, triphenylarsine and triphenylphosphine were purchased from Aldrich. All substituted phenols like 2-naphthol, 4-chlorophenol, 4-methylphenol and 4-methoxyphenol have been received from Merck. The starting precursor $[RuHCl(CO)(PPh_3)_3]$ and $[RuHCl(CO)(AsPh_3)_3]$ have been organized through said literature methods [40,41].

The evaluation of carbon, hydrogen and nitrogen has been completed on VarioEL III CHNS analyzer. FT-IR spectra of ligands and complexes were accomplished on a Bruker 783 spectrometer for the samples in direct utilization. Electronic spectra of the ligands and complexes were recorded in $CHCl_3$ solution with a Cary 300 Bio UV–Vis Varian spectrophotometer in the range 200–800 nm. ^1H, ^{13}C and ^{31}P NMR spectra were recorded in $CDCl_3$ with Bruker 300 MHz tool and the use of TMS as inner reference. Electrospray ionization mass spectra (ESI) have been recorded on ES-MS Q-TOF mass spectrometer.

2.2. Synthesis of 4-phenoxyphenylazo ligands

2.2.1. Synthesis of 1-(4-phenoxyphenylazo)-2-naphthol (HL_1)

4-phenoxyphenylamine (1.85 g; 10 mmol) was mixed with 3 mL concentrated sulphuric acid and diazotized at 0–5 °C with sodium nitrite (0.685 g; 10 mmol). The diazonium salt that formed was coupled with an alcoholic 10% sodium hydroxide solution (50 mL) of 2-naphthol (1.08 g; 10 mmol) at the same reaction temperature. The reaction was completed just after 30 min. A dark red precipitate was obtained and dried in vacuum. The product was recrystallized from methanol. Yield: 84%; Anal. calcd (%) for $C_{22}H_{16}N_2O_2$: C, 77.63; H, 4.74; N, 8.23. Found: C, 77.59; H, 4.71; N, 8.19. FT-IR (cm^{-1}): 3418 (ν_{O-H}), 1449 ($\nu_{N=N}$); 1124 ($\nu_{(C-O)}$); UV–Vis {Chloroform, $\lambda_{max,}$ nm}: 316, 418; ^1H NMR (300 MHz, $CDCl_3$): δ 9.28 (s, ArOH, 1H); 8.19–6.90

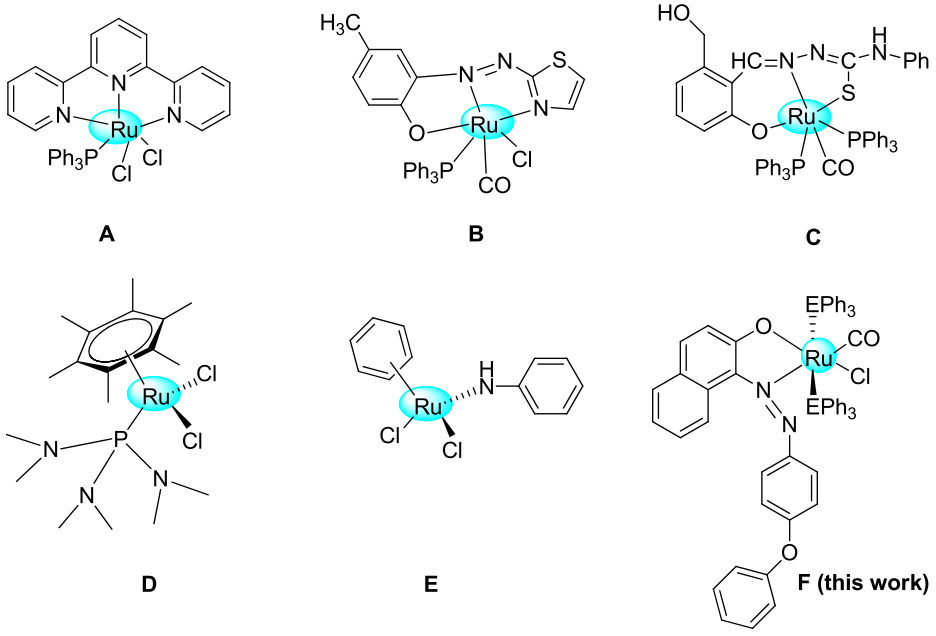


Fig. 1. Models of ruthenium-complexes for the amide conversion.

(m, ArH, 15H); ^{13}C NMR (75 MHz, $CDCl_3$): 156.37, 155.50, 154.05, 136.38, 131.86, 127.17, 126.70, 125.23, 124.72, 123.88, 121.06, 120.50, 119.18, 118.18, 116.88, 107.62. ESI-MS, *m/z*: 340 $[MH]^+$. The phenoxyphenylazo ligands, (**HL_{2-4}**), were synthesized by following the above procedure.

2.2.2. Synthesis of 2-(4-phenoxyphenylazo)-4-chlorophenol (HL_2)

Yield: 67%; Colour: Yellow solid; Anal. calcd (%) for $C_{18}H_{13}ClN_2O_2$: C, 66.57; H, 4.03; N, 8.63. Found: C, 66.50; H, 4.00; N, 8.54. FT-IR (cm^{-1}): 3435 (ν_{O-H}), 1412 ($\nu_{N=N}$); 1189 ($\nu_{(C-O)}$); UV–Vis {Chloroform, $\lambda_{max,}$ nm}: 308, 358; ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.14 (s, ArOH, 1H); 7.63–6.73 (m, ArH, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): 159.21, 157.08, 150.30, 145.86, 133.53, 128.48, 126.51, 125.67, 124.72, 122.79, 121.83, 120.70, 118.92, 118.88. ESI-MS, *m/z*: 324 $[MH]^+$.

2.2.3. Synthesis of 2-(4-phenoxyphenylazo)-4-methylphenol (HL_3)

Yield: 81%; Colour: Brown solid; Anal. calcd (%) for $C_{19}H_{16}N_2O_2$: C, 74.98; H, 5.30; N, 9.20. Found: C, 74.94; H, 5.28; N, 9.17. FT-IR (cm^{-1}): 3403 (ν_{O-H}), 1432 ($\nu_{N=N}$); 1138 ($\nu_{(C-O)}$); UV–Vis {Chloroform, $\lambda_{max,}$ nm}: 312, 364; ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.64 (s, ArOH, 1H); 7.87–6.79 (m, ArH, 12H); 2.38 (s, $ArCH_3$, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 158.82, 155.19, 149.31, 144.97, 135.74, 132.62, 129.62, 128.73, 127.72, 122.81, 119.29, 118.73, 117.49, 115.80, 19.02. ESI-MS, *m/z*: 304 $[MH]^+$.

2.2.4. Synthesis of 2-(4-phenoxyphenylazo)-4-methoxyphenol (HL_4)

Yield: 82%; Colour: Orange solid; Anal. calcd (%) for $C_{19}H_{16}N_2O_3$: C, 71.24; H, 5.03; N, 8.74. Found: C, 71.20; H, 5.00; N, 8.71. FT-IR (cm^{-1}): 3436 (ν_{O-H}), 1431 ($\nu_{N=N}$); 1155 ($\nu_{(C-O)}$); UV–Vis {Chloroform, $\lambda_{max,}$ nm}: 312, 362; ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.39 (s, ArOH, 1H); 7.87–6.69 (m, ArH, 12H); 3.86 (s, $ArOCH_3$, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 158.86, 157.14, 156.22, 152.08, 145.73, 141.27, 136.18, 129.31, 127.35, 123.38, 122.01, 120.36, 119.57, 112.63, 55.11. ESI-MS, *m/z*: 320 $[MH]^+$.

2.3. Synthesis of ruthenium(II) phenoxyphenylazo complexes

2.3.1. Synthesis of [Ru(L_1)Cl(CO)(PPh_3)$_2$] (1)

To a solution of [RuHCl(CO)(EPh_3)$_3$] (E = P & As) (0.1 g, 1.0 mmol) benzene (20 mL), HL_1 (0.04 g, 1.0 mmol) was added and the reaction mixture was refluxed for 8 h under N_2 atmosphere to yield green solution. The solvent was then removed under reduced pressure. The residue was checked by thin layer chromatography and purified by column chromatography. Chloroform have been used as eluent in the column chromatography and the green coloured band was collected and dried. Yield: 78%; Colour: green solid; m.p.: 102 °C; Anal. calcd (%) for $C_{59}H_{45}ClN_2O_3P_2Ru$: C, 68.90; H, 4.41; N, 2.72. Found: C, 68.87; H, 4.38; N, 2.69. FT-IR (cm^{-1}): 1924 (ν_{CO}), 1434 ($\nu_{N=N}$), 1230 ($\nu_{Ar(C-O)}$); UV–Vis {Chloroform, $\lambda_{max,}$ nm}: 260, 338, 430, 537; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.71–7.08 (m, ArH, 45H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 24.35 (s, 2P). ESI-MS, *m/z*: 1028 $[MH]^+$. The Ru(II) complexes **2**–**8** were prepared by following the above procedure using the phenoxyphenylazo ligands (**HL_{2-4}**).

2.3.2. Synthesis of [Ru(L_2)Cl(CO)(PPh_3)$_2$] (2)

Yield: 62%; Colour: green solid; m.p.: 80 °C; Anal. calcd (%) for $C_{55}H_{42}Cl_2N_2O_3P_2Ru$: C, 65.22; H, 4.18; N, 2.77. Found: C, 65.19; H, 4.15; N, 2.74. FT-IR (cm^{-1}): 1943 (ν_{CO}), 1433 ($\nu_{N=N}$), 1236 ($\nu_{Ar(C-O)}$); UV–Vis UV–Vis {Chloroform, $\lambda_{max,}$ nm}: 303, 370, 411, 525; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.35–6.57 (m, ArH, 42H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.13 (s, 2P). ESI-MS, *m/z*: 1012 $[MH]^+$.

2.3.3. Synthesis of [Ru(L_3)Cl(CO)(PPh_3)$_2$] (3)

Yield: 75%; Colour: green solid; m.p.: 84 °C; Anal. calcd (%) for $C_{56}H_{45}ClN_2O_3P_2Ru$: C, 67.77; H, 4.57; N, 2.82. Found: C, 67.74; H, 4.55; N, 2.78. FT-IR (cm^{-1}): 1929 (ν_{CO}), 1433 ($\nu_{N=N}$), 1241 ($\nu_{Ar(C-O)}$); UV–Vis UV–Vis {Chloroform, $\lambda_{max,}$ nm}: 307, 333, 448, 534; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.87–6.79 (m, ArH, 42H); 2.38 (s, $ArCH_3$, 3H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 25.61 (s, 2P). ESI-MS, *m/z*: 992 $[MH]^+$.

2.3.4. Synthesis of [Ru(L_4)Cl(CO)(PPh_3)$_2$] (4)

Yield: 80%; Colour: green solid; m.p.: 82 °C; Anal. calcd (%) for $C_{56}H_{45}ClN_2O_4P_2Ru$: C, 66.70; H, 4.50; N, 2.78. Found: C, 66.67; H, 4.48; N, 2.72. FT-IR (cm^{-1}): 1926 (ν_{CO}), 1434 ($\nu_{N=N}$), 1239 ($\nu_{Ar(C-O)}$); UV–Vis {Chloroform, $\lambda_{max,}$ nm}: 302, 369, 443, 665; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.97–6.84 (m, ArH, 42H); 3.85 (s, $ArOCH_3$, 3H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 24.98 (s, 2P). ESI-MS, *m/z*: 1008 $[MH]^+$.

2.3.5. Synthesis of [Ru(L_1)Cl(CO)($AsPh_3$)$_2$] (5)

Yield: 73%; Colour: green solid; m.p.: 118 °C; Anal. calcd (%) for $C_{59}H_{45}As_2ClN_2O_3Ru$: C, 68.90; H, 4.41; N, 2.72. Found: C, 68.87; H, 4.38; N, 2.69. FT-IR (cm^{-1}): 1943 (ν_{CO}), 1432 ($\nu_{N=N}$), 1232 ($\nu_{Ar(C-O)}$); UV–Vis {Chloroform, $\lambda_{max,}$ nm}: 260, 341, 435, 534; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.81–7.10 (m, ArH, 45H). ESI-MS, *m/z*: 1116 $[MH]^+$.

2.3.6. Synthesis of [Ru(L_2)Cl(CO)($AsPh_3$)$_2$] (6)

Yield: 67%; Colour: green solid; m.p.: 98 °C; Anal. calcd (%) for $C_{55}H_{42}As_2Cl_2N_2O_3Ru$: C, 60.01; H, 3.85; N, 2.54. Found: C, 59.98; H, 3.82; N, 2.51. FT-IR (cm^{-1}): 1920 (ν_{CO}), 1431 ($\nu_{N=N}$), 1221 ($\nu_{Ar(C-O)}$); UV–Vis {Chloroform, $\lambda_{max,}$ nm}: 257, 353, 405, 531; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.32–6.60 (m, ArH, 42H). ESI-MS, *m/z*: 1101 $[MH]^+$.

2.3.7. Synthesis of [Ru(L_3)Cl(CO)($AsPh_3$)$_2$] (7)

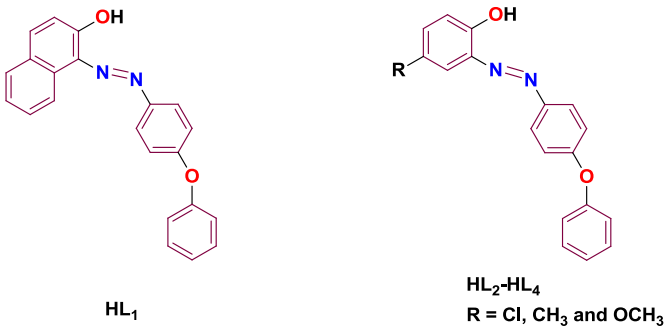
Yield: 87%; Colour: green solid; m.p.: 126 °C; Anal. calcd (%) for $C_{56}H_{45}As_2ClN_2O_3Ru$: C, 62.26; H, 4.20; N, 2.59. Found: C, 62.23; H, 4.18; N, 2.54. FT-IR (cm^{-1}): 1919 (ν_{CO}), 1432 ($\nu_{N=N}$), 1218 ($\nu_{Ar(C-O)}$); UV–Vis {Chloroform, $\lambda_{max,}$ nm}: 259, 354, 414, 530; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.86–6.80 (m, ArH, 42H); 2.38 (s, $ArCH_3$, 3H). ESI-MS, *m/z*: 1080 $[MH]^+$.

2.3.8. Synthesis of [Ru(L_4)Cl(CO)($AsPh_3$)$_2$] (8)

Yield: 79%; Colour: green solid; m.p.: 112 °C; Anal. calcd (%) for $C_{56}H_{45}As_2ClN_2O_4Ru$: C, 61.35; H, 4.14; N, 2.56. Found: C, 61.32; H, 4.12; N, 2.52. FT-IR (cm^{-1}): 1919 (ν_{CO}), 1433 ($\nu_{N=N}$), 1227 ($\nu_{Ar(C-O)}$); UV–Vis {Chloroform, $\lambda_{max,}$ nm}: 254, 350, 412, 561; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.96–6.69 (m, ArH, 42H); 3.85 (s, $ArOCH_3$, 3H). ESI-MS, *m/z*: 1096 $[MH]^+$.

2.4. Representative procedure for the rearrangement of aldehydes to amides

Conversion of aldehydes to amides was carried out using the procedure described in the literature [34]. Under nitrogen atmosphere, the corresponding aldehyde (1 mmol), $NH_2OH{\cdot}HCl$ (1 mmol), $NaHCO_3$ (1 mmol), toluene (3 mL) and ruthenium(II) catalyst **1** (0.01 mmol) were introduced into a RB flask, and the reaction mixture was stirred at 120 °C in an oil bath for 12 h. After the completion of reaction, 2–3 mL of MeOH was added to the reaction mixture. The catalyst and $NaHCO_3$ which settled down the flask was removed by filtration through Celite. The filtrate has been dried and the crude product was purified by the use of column chromatography ($MeOH/CH_2Cl_2$). Finally, the isolated amide was characterized by the aid of ^{1}H NMR.



Scheme 1. Synthesis of phenoxyphenylazo ligands.

3. Results and discussion

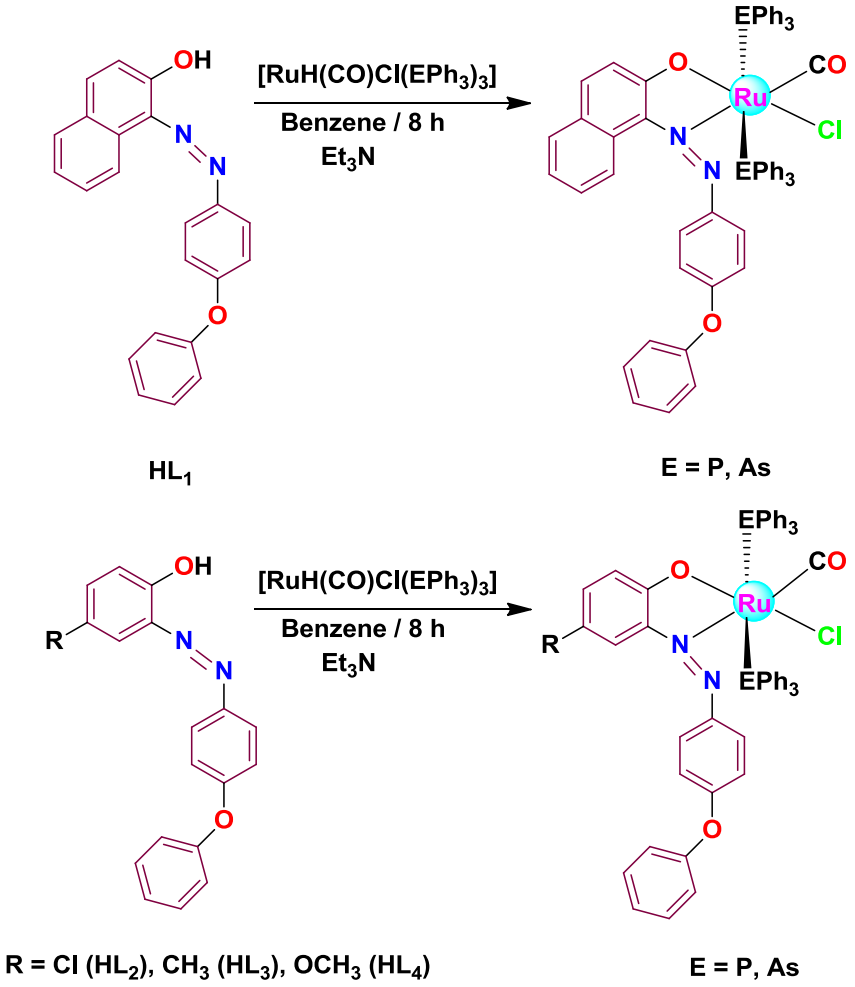
Phenoxyphenylazo ligands have been prepared in good yields by diazotization of 2-naphthol/4-substituted phenol with 4-phenoxyphenylamine at 0–5 °C (Scheme 1).

On the complexation of Ru(II) precursor, $[RuHCl(CO)(EPh_3)_3]$ (E = Phosphorous and Arsine), with azo ligands in benzene led to the synthesis of ruthenium(II) phenoxyphenylazo complexes (**1**–**8**) of general formula $[Ru(L)Cl(CO)(EPh_3)_2]$ (Scheme 2).

The ligands and complexes have been characterized by IR, UV–visible, ^1H NMR, ^{13}C NMR, ^{31}P NMR, mass spectral analysis as well as elemental analysis. The complexes were formed by the coordination of ruthenium ion to the azo nitrogen and phenolic oxygen in the monoanionic bidentate donor set of our ligands (**HL_1-HL_4**), which leads to the formation of five membered chelate ring due to its strong π-acidic character [42–44]. All the ruthenium(II) complexes (**1**–**8**) are air and moisture stable. And the complexes are all completely soluble in common organic solvents like benzene, dichloromethane, chloroform, dimethyl sulfoxide, dimethylformamide, toluene, acetonitrile and methanol. These complexes were utilized as catalysts in the catalytic activity for the conversion of aldehydes to primary amides in a single-pot reaction. Then, the reaction was carried out by taking the substrates, aldehyde and $NH_2OH{\cdot}HCl$, along with the base $NaHCO_3$ in the presence of ruthenium catalyst **1**. The catalytic activity of ruthenium(II) complexes (**1**–**8**) have been optimized under different conditions.

3.1. Infrared spectra

Infrared spectra of the ligands and ruthenium(II) complexes exhibit many characteristic features within 4000–400 cm^{-1}. Sharp stretching vibrations around 3436-3403 cm^{-1}, 1449-1431 cm^{-1} and 1189-1124 cm^{-1} in the infrared spectra of the free ligands, **HL_1-HL_4**, are assigned to the naphtholic/phenolic (ν_{O-H}), phenoxyphenylazo ($\nu_{N=N}$) and phenolic (ν_{C-O}) groups respectively [45]. The disappearance of naphtholic, phenolic O–H band and increase in the C–O stretching frequencies in the region 1241-1230 cm^{-1} indicates



Scheme 2. Synthesis of ruthenium(II) 1-(4-phenoxyphenylazo)-2-naphtholate/2-(4-phenoxyphenylazo)-4-phenolate complexes.

the coordination of the metal through naphtholic/phenolic oxygen in the complexes. The bands appeared around 1940 cm^{-1} and 1433 cm^{-1} indicate the existence of metal carbonyls and azo groups respectively in the complexes [46–48]. All the ruthenium(II) complexes are shown strong vibrational bands corresponding to M – P/M – As, M – O and M – N in the region 694-613 cm^{-1}/689-607 cm^{-1}, 530-515 cm^{-1} and 453-410 cm^{-1} respectively [47,49,50].

3.2. Electronic spectra

The electronic spectra of the phenoxyphenylazo ligands, **HL_1-HL_4**, and organoruthenium(II) complexes (**1**–**8**) have been carried out in chloroform solvent. The ligands display intense peaks due to the π-π* and n-π* transitions at 316-308 nm and 418-358 nm respectively. Ruthenium(II) complexes display a high-intensity π-π* transition at 307-254 nm and low-intensity n-π* transition at 370-333 nm. All the complexes are shown metal to ligand, (Ru(dπ)-to-(Lπ*)), charge transfer transition in the region 448-405 nm [51] and d-d transitions are observed at around 665-525 nm. Furthermore, ruthenium(II) complexes are affirmed by octahedral geometry [52] and representative electronic spectra of the Ru(II) complexes (**5**–**8**) are exhibited in Fig. 2.

3.3. ^{1}H and ^{31}P NMR spectra

NMR spectra of the ligands and complexes are further supported to their assigned structures. The proton NMR spectra of the free ligands, **HL_1-HL_4**, show peaks which appeared as single resonance around 12.64–9.14 ppm in the naphtholic/phenolic protons screened as a singlet (Ar-OH) and aromatic protons (ArH) appeared as multiplets at 8.19–6.69 ppm. The methoxy protons (Ar-OCH_3) in **HL_4** and methyl protons (Ar-CH_3) in **HL_3** ligands are exhibited at 3.86 ppm and 2.38 ppm respectively. The absence of the peak due to free naphtholic/phenolic (Ar-OH) protons in the ruthenium(II) complexes (**1**–**8**) indicates the coordination of the naphtholate/phenolate oxygen atom to the ruthenium(II) ion by the proton displacement of OH group. The aromatic protons are appeared as multiplets in the region 8.35–6.57 ppm in the spectra of all the complexes. The methoxy protons in the complexes (4, 8) and the methyl protons in the complexes (3, 7) are appeared as singlets at 3.85 ppm and 2.38 ppm respectively. The ruthenium(II) complexes (**1**–**8**) are diamagnetic (S = 0) in nature. The selected ^{1}H NMR spectra of the Ru(II) complexes are displayed in Fig. 3.

^{31}P NMR spectra of the complexes (**1**–**4**), show a sharp singlet at 29.13–24.35 ppm which confirms the coordination of two triphenylphosphine groups to ruthenium present in the complexes.

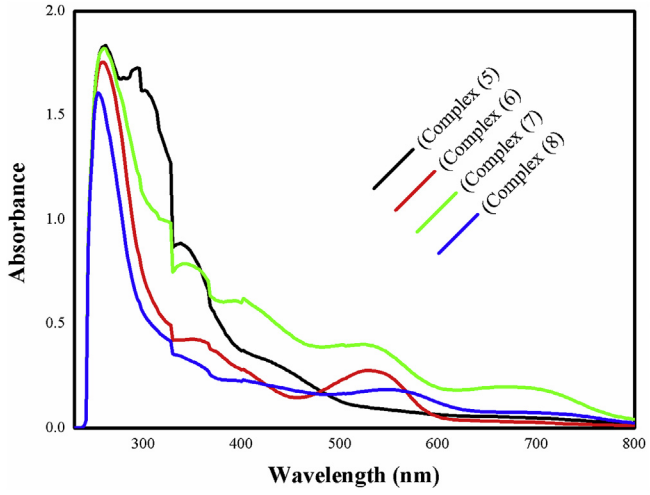


Fig. 2. Electronic spectra of ruthenium(II) complexes (**5**–**8**).

3.4. ^{13}C NMR and mass spectra

The ^{13}C NMR spectra of the phenoxyphenylazo ligands, **HL_1-HL_4**, show the downfield shift of azo naphtholic/phenolic carbons (145.73–153.67 ppm) and upfield shift of Ar-OCH_3 (55.11 ppm), Ar-CH_3 (19.02 ppm) carbons and are further support the assigned structure of the ligands. The mass spectral peaks of ligands and complexes are shown fine agreement with their experimental molecular ion peaks and are further support the assigned structure. The mass spectrum of complex **7** is shown in Fig. 4.

3.5. Catalytic studies for the synthesis of primary amides via aldehydes with hydroxylamine hydrochloride

We have utilized our synthesized complexes as catalysts to realize a few valuable chemical reactions. Due to the rapid growth of using Ru(II) complexes in a variety of catalytic transformations, we are intrigued to assess the catalytic activity of ruthenium catalysts in amide synthesis reaction from the most interesting sustainable materials, aldehyde and hydroxylamine hydrochloride. Subsequently, we have achieved in finding powerful catalysts with high yield both from economic and environmental perspectives. Moreover, the catalytic activity of the ruthenium complexes will be enhanced by the presence of a ligand with a bulky group. We have well accomplished the screening of the specifications such as solvent, base and catalyst loading. The present framework has accompanying the huge preferences: 1) appropriateness to different kinds of substrates, 2) the need of only one equivalent of hydroxylamine hydrochloride, 3) the utilization of toluene as solvent, 4) a basic workup strategy, to be specific catalyst/product separation by filtration, 5) the utilization of an easily synthesized ruthenium azo complex **1** that is easy to handle and 6) water as a sole by-product.

3.6. Effect of solvent, base and low catalyst loading

We have examined the catalytic reactions using a range of solvents and bases in Tables 1 and 2. We started from the reaction of benzaldehyde with $NH_2OH.HCl$ in presence of base ($NaHCO_3$) and catalyst **1** using both polar and non-polar solvents like methanol, acetonitrile, dichloromethane, dimethyl sulfoxide, dimethylformamide, benzene and toluene. The reaction in toluene has shown excellent conversion (98%) whereas in acetonitrile has shown good yield (86%) [34]. Methanol medium has given moderate yield (63%) while the other solvents benzene, DCM, DMSO and DMF have provided poor yields (40-18%). From this, we have concluded that toluene is the best shot as a medium for the conversion of amides. Then we have carried out the reaction in toluene using the catalyst **1** without any base and are found with poor yield (9%). Hence, we have tended to optimize the base. By varying the bases in the catalytic reactions, we have concluded that $NaHCO_3$ (98% yield) is the most suitable base than the other ones (86-12% yield).

Moreover, we have performed the catalyst loading trials using benzaldehyde as a test substrate in the optimized solvent, toluene, and base, sodium bicarbonate. A sequence of reaction conditions has been opted for the amide conversion using different catalyst:substrate (C:S) ratios (1:50, 1:100, 1:150, 1:200 and 1:250.) and the results are given in Table 3. While increasing the C/S ratio from 1:50 to 1:100, the conversion has also been increased (entry 1 and 2). However, on further increase in the ratio from 1:150 to 1:200 followed by 1:250, the conversion has been decreased gradually (entry **3**–**5**). Thus, we have accomplished that the catalyst:substrate ratio of about 1:100 is the best compromise with 98% yield

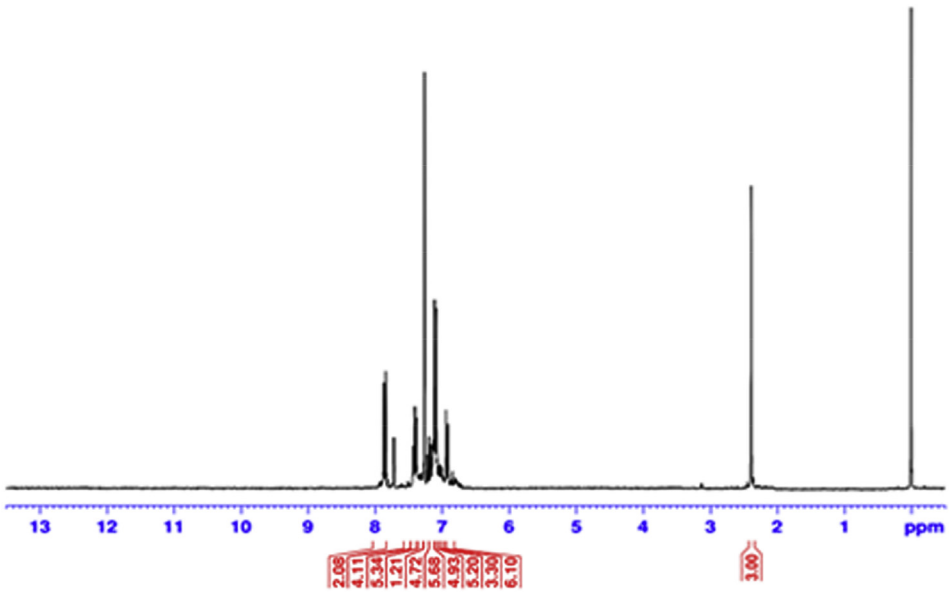


Fig. 3. ^{1}H NMR spectrum of ruthenium(II) carbonyl complex (**3**).

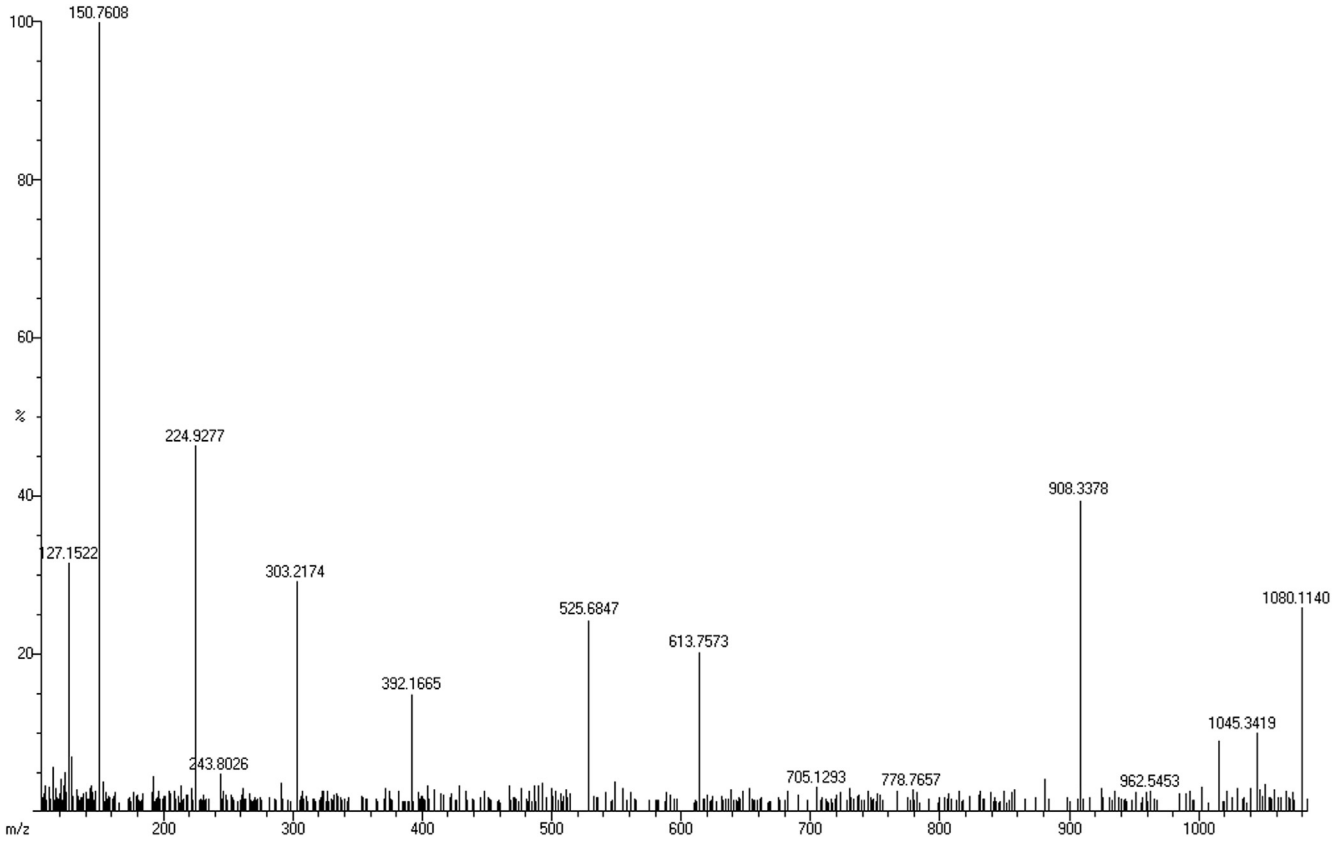


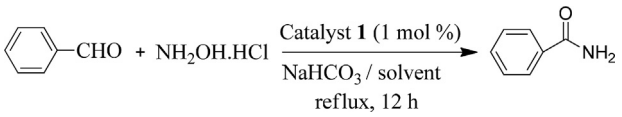
Fig. 4. Mass spectrum of ruthenium(II) carbonyl complex (**7**).

and 9800 TON.

3.7. Substrate scope of the amidation reaction from aldehydes and hydroxylamine hydrochloride

We have exploited the reaction of a series of aliphatic, aryl and heterocyclic aldehydes with hydroxylamine hydrochloride under the above optimized conditions. Initially, we have subjected all the complexes (1–8) as catalysts for this conversion. From these results, we have optimized that the complex 1 showed a better catalytic activity than the rest and the data are shown in Table 4. In general, the conversion of amide products has shown good to excellent

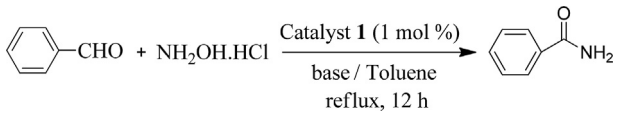
Table 1
Screening of different solvents for the synthesis of primary amides catalyzed by ruthenium complex 1.[a].



Entry	Solvents	Conversion[b] %
1	Methanol	63
2	Benzene	40
3	Toluene	98
4	Acetonitrile	86
5	Dichloromethane	32
6	DMSO	34
7	DMF	18

[a] Reaction conditions: Benzaldehyde (1 mmol), $NH_2OH.HCl$ (1 mmol), $NaHCO_3$ (1 mmol), Catalyst **1** (1 mol %) and Solvent (3 mL).
[b] Isolated yield.

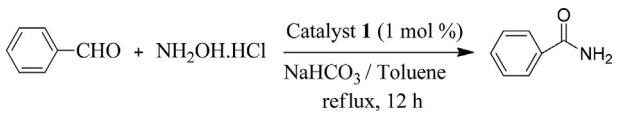
Table 2
Screening of different bases for the preparation of primary amides catalyzed by ruthenium complex 1.[a].



Entry	Base	Conversion[b] %
1	Et_3N	12
2	$KHCO_3$	86
3	K_2CO_3	58
4	$NaHCO_3$	98
5[c]	–	09
6[d]	$NaHCO_3$	12
7	Na_2CO_3	63

[a] Reaction conditions: Benzaldehyde (1 mmol), $NH_2OH.HCl$ (1 mmol), bases (1 mmol), Catalyst **1** (1 mol %) and toluene (3 mL).
[b] Isolated yield.
[c] Absence of base.
[d] Absence of catalyst.

Table 3
Effect of catalyst/substrate ratio for the conversion of the benzaldehyde to primary amides using complex 1.[a].



Entry	C:S ratio	Time (h)	Conversion[b] %	TON[c]
1	1:50	12	88	8800
2	1:100	12	98	9800
3	1:150	12	85	8500
4	1:200	12	75	7500
5	1:250	12	67	6700

[a] Reaction conditions: Benzaldehyde (1 mmol), $NH_2OH.HCl$ (1 mmol), $NaHCO_3$ (1 mmol), Catalyst **1** (1 mol %) and Solvent (3 mL).
[b] Isolated yield.
[c] Turnover number (TON) = (mmol of product)/(mmol of catalyst) after time t.

yields. The reaction of benzaldehyde was well-tolerated in this procedure and has given an excellent conversion 98% (entry 1) which may be due to resonance stabilization. When comparing the conversion of aldehydes with electron donating *p*-substituents to electron withdrawing *p*-substituents, the conversion of later cases are greater than the former ones. The conversion of aldehydes with electron withdrawing *p*-substituents, i.e., $-NO_2$, Cl & Br has shown higher yields 95%, 93% and 92% (entry 5, 6 & 7) respectively.

This protocol is also successful for the utilization of aryl aldehydes with electron donating *p*-substituents, i.e., $-OCH_3$, $-CH_3$ and –OH has shown good yields 86%, 82% & 79% (entry 2, 3 and 4) respectively. The conversion against the conjugated aldehyde, cinnamaldehyde (entry 8) 84% yield) is less superior to that of benzaldehyde, because of the presence of extended conjugated double bond in the former one. In addition heterocyclic amide compounds were also synthesized in this Beckmann rearrangement utilizing catalyst 1 with appreciable yield. The heterocyclic aldehydes with N and S atoms viz., pyrrole-2-carboxaldehyde, 2-pyridinecarboxaldehyde and thiophene-2-carboxaldehyde (entry 9, 10 & 11) have shown good yields 93%, 91% and 89% respectively. We have also carried out the amide conversion of aliphatic aldehydes, yields are lesser than aromatic aldehydes. The conversion of ethanal, propanal, 3-methylbutanal and n-butanal (entry 12–15) are 78%, 74%, 73% and 68% respectively.

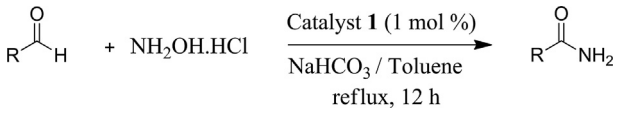
The plausible mechanism for the transformation of aldehyde to amide in the presence of ruthenium catalyst (Scheme 3) is followed by the reported metal catalyzed reactions [53]. In first step, oxidative addition of aldehyde with OH group to form oxime [29]. It get coordinated to the ruthenium(II) catalyst (1) and to form species I followed by the elimination of HCl. In second step, the elimination of nitrile from species (I) and gives the intermediate (II) [28]. At the concurrent nucleophilic attack of nitrile over the coordinated hydroxide resulted a ruthenium iminolate species (III) in third step [53a,b]. Finally, the hydrolysis of ruthenium iminolate species (III) leads to revitalize the catalyst with the formation of the product.

Though there are similar catalytic systems involving octahedral Ru(II) complexes containing polydentate N-, O- and/or S-donor ligands with azo group [30,31], we have utilized 4-phenoxyaniline, instead of aniline, with 4-substituted phenol/2-naphthol for the synthesis of our azo system. Among our four catalysts, the catalyst that contains 2-naphthol moiety (1) shows better results than others, bearing phenolic moiety (2–4). As the coordination mode and environment of all these four ligands are similar, the better efficiency of the optimized ligand may be due to the influence of bulkiness of the former one when compared to the later. Moreover, we have compared the efficiency of our optimized catalyst with other literature reports including the one with similar kind of 2-naphthol moiety and found that our catalyst has shown comparable or better than the rest (see Table 5). It is interesting to compare the activity of our catalyst with the one reported by Ramesh et al., based on the ligand moiety [48a]. The later one has three units of *p*-substituted (-CH_3, $-OCH_3$, Br, NO_2) (phenylazo)naphthol moiety with six coordinated ruthenium(III) ion, whereas our catalyst has *p*-(phenoxyphenylazo)naphthol moiety along with $(PPh_3)_2$, CO and Cl with six coordinated Ru(II) ion. It reveals that our catalyst has shown greater efficiency than the other, that may be due to influence of 2-naphthol moiety along with mixed ligands in our systems.

4. Conclusion

We report here, the synthesis of eight new ruthenium(II) carbonyl complexes that contains bidentate oxygen and nitrogen chelating phenoxyphenylazo ligands. All the ligands and complexes

Table 4
Scope of the oxidative primary amides of various aldehydes with hydroxylamine hydrochloride using catalyst 1.[a].



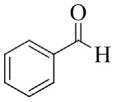
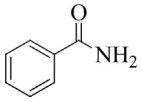
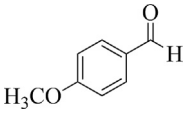
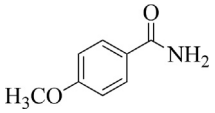
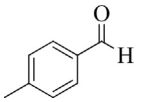
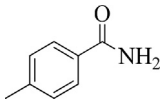
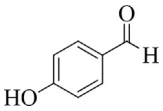
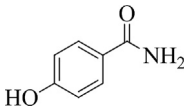
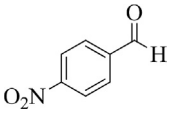
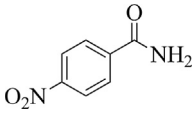
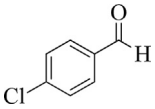
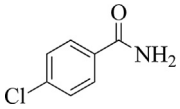
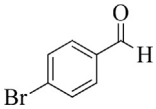
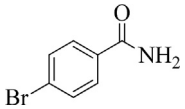
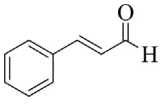
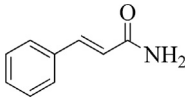
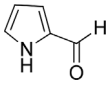
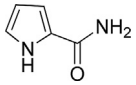
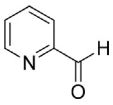
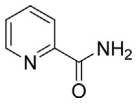
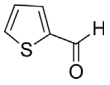
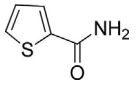
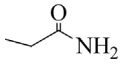
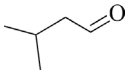
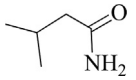
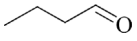
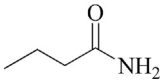
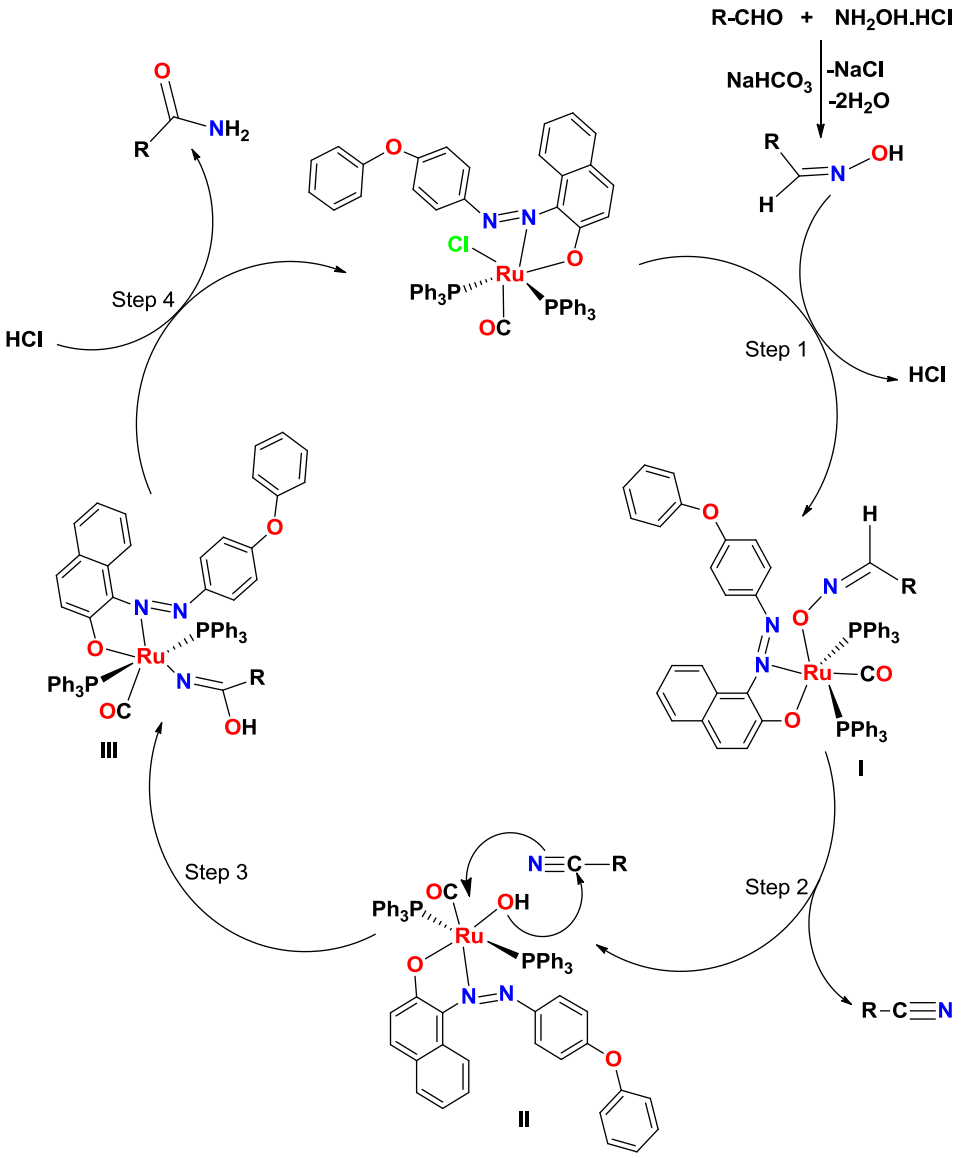
Entry	Aldehydes	Amides	Convresion[b] %	TON[c]	TOF[d]
1			98	9800	817
2			86	8600	717
3			**82**	8200	683
4			**79**	7900	658
5			95	9500	792
6			93	9300	775
7			**92**	9200	767
8			84	8400	700
9			91	9100	758
10			93	9300	775
11			89	8900	742
12			**78**	7800	650
13			**74**	7400	614
14			**73**	7300	608

Table 4 (*continued*)

Entry	Aldehydes	Amides	Convresion[b] %	TON[c]	TOF[d]
15			**68**	6800	567

[a] General conditions: Aldehyde (1 mmol), $NH_2OH.HCl$ (1 mmol), $NaHCO_3$ (1 mmol), Catalyst **1** (1 mol %) and Toluene (3 mL).
[b] Isolated yield.
[c] Turnover number (TON) = (mmol of product)/(mmol of catalyst) after time t.
[d] Turnover frequency (TOF) = TON/time.



Scheme 3. Plausible mechanism for the ruthenium(II) catalytic (1) conversion of aldehydes to amides.

were well characterized by spectral and analytical methods. The studies confirmed the coordination of naphtholic/phenolic oxygen and azo nitrogen of the ligand to the ruthenium(II) ion which is present in an octahedral environment. The thorough investigation in the present work shows, ruthenium complex **1** is the best catalyst for the conversion of aldehydes to primary amides. Catalytic activity for an expansive scope of substrates was assessed utilizing 1 mol % of catalyst **1** for 12 h our catalyst is not only well suited for different classes of aldehydes viz., aliphatic aldehydes, aryl aldehydes with electron donating or electron withdrawing substituents, conjugated aldehydes and heterocyclic aldehydes, but also it has shown better activity against all of them. These results reveal that

Table 5
Comparsion of catalytic efficiency of our present ruthenium catalyst (1) with previously reported catalytic systems for aldehyde to amide transformations.[a].

Entry	Catalyst	Conditions	Yield (%) References[b]
1	Cu(II), (20 mg)	H_2O, 100 °C, Cs_2CO_3, 12 h	95 [54]
2	Ru(II), (0.1 mol%)	CH_3CN, 78 °C, $NaHCO_3$, 5 h	88 [31]
3	Ru(III), (1 mol%)	PhMe, 110 °C, $NaHCO_3$, 18 h	84 [48a]
4	Ru(II), (3.75 mol%)	MeOH:H_2O, 95–100 °C, K_2CO_3, 24 h	96 [55]
5	Ru(II), (0.1 mol%)	PhMe, 100 °C, NaOH, 12 h	95 [56]
6	Ru(II), (0.2 mol%)	PhMe, 110 °C, $NaHCO_3$, 2 h	90 [57]
7	Ru-(nano), (5 mol%)	H_2O, 120 °C, $NaHCO_3$, 7 h	88 [58]
8	Ru(II), (5 mol%)	H_2O, 60 °C, $NaHCO_3$, 24 h	99 [33]
9	Ru(II), (1 mol%)	PhMe, 110 °C, $NaHCO_3$, 18 h	92 [59]
10	Ru(II), (1 mol%)	PhMe, 110 °C, $NaHCO_3$, 12 h	98[This work]

[a] Reaction conditions: Benzaldehyde (1 mmol), $NH_2OH.HCl$ (1 mmol), $NaHCO_3$ (1 mmol), Catalyst **1** (1 mol %) and Toluene (3 mL).
[b] Previous reports.

the bulkiness of the ligand as well as the mixed ligand system on these kind of catalytic amidation reactions might lead to better efficiency.

Acknowledgement

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[1] (a) P.J. Chirik, K. Wieghardt, Science 327 (2000) 794–795;
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(c) V. Lyaskovskyy, B. de Bruin, ACS Catal. 2 (2012) 270–279;
(d) H. Gruetzmacher, Angew. Chem. Int. Ed. 47 (2008) 1814–1818;
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