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Muthukumaran Nirmala, Gandhi Saranya, Periasamy Viswanathamurthi

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Ruthenium(II) complexes incorporating salicylaldiminato-functionalized *N*-heterocyclic carbene ligands as efficient and versatile catalysts for hydration of organonitriles

Muthukumaran Nirmala, Gandhi Saranya, Periasamy Viswanathamurthi,*

Department of Chemistry, Periyar University, Salem-636 011, India.

To whom correspondence should be made, e-mail: viswanathamurthi72@gmail.com;*

Fax: +91 427 2345124

ABSTRACT

We describe a new synthetic procedure for synthesis of ruthenium(II) complexes containing salicyladiminato functionalized mixed *N*-heterocyclic carbene (NHC) ligand and phosphine co-ligand. The complexes (**3a-3d**) have been obtained in good to excellent yields by transmetalation from the corresponding Ag-NHC complexes (**2a-2d**) as carbene transfer reagents. All the [Ru–NHC] complexes have been characterized by elemental analyses, spectroscopic methods as well as ESI mass spectrometry. The ligands **1a-1d** show their versatility by switching to be O,N,C-chelating in these ruthenium(II) complexes. The resulting complexes have been evaluated as potential catalysts for the selective hydration of nitriles to primary amides, and related amide bond forming reactions, in environmentally friendly medium. The reaction tolerated ether, hydroxyl, nitro, bromo, formyl, pyridyl, benzyl and alkyl functional groups. The catalyst was stable for weeks and could be recovered and reused more than six times without significant loss of activity.

Keywords: Salicyladiminato-functionalized NHC ligands, wingtip substituents, [Ru-NHC] complexes, Hydration of nitriles, Recyclable catalyst

1. INTRODUCTION

Amides are one of the most important functional groups in nature, they constitute versatile building blocks in synthetic organic chemistry, and also exhibit a wide range of industrial applications and pharmacological interest [1]. Despite their obvious importance, there has been a great demand to develop novel methodology to synthesize amides. But the conventional synthetic routes [2−4] do not meet the standards of green chemistry, due to the coupling reagents, harsh conditions and chemical wastes. This discrepancy has encouraged efforts towards the identification and development of more atom-efficient, catalytic methods for amide bond formation.

The current methods for amide formation are remarkably general but at the same time widely regarded as expensive and inelegant. One of the straight forward and atom economical ways to synthesize of amide is the hydration of the corresponding organonitriles. The nitrile group is mechanistically intriguing as it is kinetically inert and thermodynamically unstable [5]. Several catalytic hydration of nitriles have been devised utilizing enzyme catalysis [6], transition metal mediated homogeneous catalysis [7], heterogeneous catalysis [8] and nanocatalysis [9]. Various green approaches such as microwave-assisted hydration of nitriles [10], super basic system DMSO−CsOH [11], chitosan-supported ruthenium catalyst [12], and hydroxide-promoted [13] hydrolysis of nitriles have been reported. All of these methods have their own advantages. However, these methods are associated with certain demerits, such as stoichiometric amount of amidation reagents, tedious work-up procedures, harsh reaction conditions, long reaction times, poor selectivity, limited substrate scopes etc. A possible solution to these drawbacks lies with metal catalysis. In this context, remarkable results have been obtained in recent years using homogeneous ruthenium catalysts containing phosphine auxiliary ligand as potential catalysts for nitrile hydration reactions with high substrate tolerance [14, 15-22]. Thereafter, many effective catalytic systems based on ruthenium have been developed [23, 24] because of the fascinating reactivities exhibited by the resultant complexes and the nature of the ligand that dictates the property of those complexes. In this regard, salicylaldiminato functionalized *N*-heterocyclic carbene ligands have potential applications in catalysis and hence their metal complexes have been widely investigated by the researchers as catalysts in various important organic transformations [25]. Their distinctive high σ-donating ability, electronic/steric tunability via the wingtips and admirable stability of the metal–NHC complexes toward heat, air and moisture are considered as the

keys for the success of this versatile class of ligands which has found numerous applications in catalysis. For instance, examination of the ligand topology of substituted *N*-heterocyclic carbene ligands has thrown light on the nature of the steric effects prevailing on these ligands [26]. This being a recurrent theme of our research, we set out to unravel the key attributes of *N*-heterocyclic carbenes with the intent of identifying the underlying hypotheses that oversee the influence of the ligand in catalysis. We desired to critically evaluate the performances of a variety of transition metal based *N*-heterocyclic carbene precatalysts, designed along these underlying hypotheses, in synthetically useful transformations. In this area, our group has been actively engaged in the study on transition metal based *N*-heterocyclic carbene ligands and their catalytic activities in variety of organic transformations [27]. As part of our ongoing investigation in functionalized NHC ligands as the supporting environment for metal complexes and their applications in catalysis [28], we herein report the synthesis and coordination chemistry of new ruthenium(II)-carbene complexes appended with tridentate salicyladiminato functionalized *N*-heterocyclic carbene ligands [$^{t\text{Bu}}$(ONC)$^{-}$], and their catalysis towards the synthesis of amides. To the best of our knowledge, ruthenium(II)-salicylaldiminato functionalized *N*-heterocyclic carbene catalyzed hydration of nitriles has not yet been reported. Accounting this fact, we present the synthesis of complexes containing both NHC and phosphine moieties and their applications in hydration of organonitriles catalysis in this article for the first time.

2. RESULTS AND DISCUSSION

2.1 Synthesis and characterization of salicyladiminato-functionalized N-heterocyclic carbene ligands. Salicyladiminato-functionalized imidazolium salts (**1a-1d**) were synthesized according to known literature procedure [29] (**Scheme 2**). 1-(3-ethylbromide)-3,5-di-tert-butyl salicylaldimine Schiff base was prepared by the reaction of 3,5-di-tert-butyl-2-hydroxy benzaldehyde with 2-bromoethylamine hydrobromide in refluxing ethanol and isolated as yellow solid (**Scheme 1**). The new ligands (**1a-1d**) obtained are highly air and moisture stable. The ligands were fully characterized by ^{1}H and ^{13}C NMR, mass spectra and elemental analysis.

2.2 Synthesis of Precatalysts. All the complexes were synthesized following the carbene transfer route, more precisely the transmetalation route using a silver NHC complex which has proved to be useful in the preparation of a variety of NHC complexes. This procedure is probably one of the most general methods, because it generates an air-stable intermediate

under mild reaction conditions, thus allowing an easy access to a wide range of transition metal complexes. It is often used successfully when other methods fail. The use of Ag-NHC complexes as carbene transfer reagents provides in many cases a convenient way to overcome the difficulties arising from using strong bases, inert atmospheres, and complicated workups. In this study, we employed this route to prepare ruthenium(II) salicyladiminato-functionalized N-heterocyclic carbene complexes **3a**-**3d** (**Scheme 3**). Reacting the imidazolium salts **1a**-**1d** with an excess of Ag_2O in dichloromethane afforded the corresponding silver NHC complexes *in situ*, which were then treated with $[RuHCl(CO)(PPh_3)_3]$ to yield the desired complexes **3a**-**3d** with good yields. Complexes (**3a-d**) are extremely soluble in CH_2Cl_2, $CHCl_3$, THF and DMSO. However, they are sparsely soluble in CH_3CN, but virtually insoluble in non-polar solvents including Et_2O, hexane and pentane. In fact, they were isolated by precipitation from the reaction mixture using Et_2O during the course of their synthesis. All complexes were fully characterized by spectral (^{1}H NMR, ^{13}C NMR, IR, mass) methods. The analytical data (C, H, N) of the [Ru–NHC] complexes are in good agreement with the proposed molecular formulae.

2.3 Spectroscopic studies. The new [Ru–NHC] complexes (**3a–3d**) showed a C≡O stretch in the IR spectrum at ~1975 cm^{-1}, indicating considerable back bonding present in this ligand. A strong vibration observed at 1593–1577 cm^{-1} in the spectra of complexes corresponding to C=C stretching. A sharp band observed at 1542–1527 cm^{-1}, ascribed to N-C-N stretching [30]. In addition, vibrations corresponding to the presence of PPh_3/$AsPh_3$ also appeared in the expected region.

The ^{1}H NMR spectra of the complexes (**3a–3d**) showed the signals in the expected region (Figs. S6–S8, ESI†) . The generation of free carbene and subsequent formation of the [Ru–NHC] complexes were unambiguously confirmed by the loss of the C2-proton (NCHN) and phenolic (C-OH) protons. The imidazolium ring backbone signals appeared around 7.39-7.19 ppm. Furthermore, the spectra of all the complexes showed a series of signals for aromatic protons at 7.71–7.53 ppm. In addition, a singlet appeared around 3.09–2.24 ppm for complexes 3a and 3d corresponding to terminal CH_3 group protons. The spectra of the complexes showed a singlet at 1.45–0.84 ppm, which has been assigned to *t*Bu protons .

^{13}C NMR chemical shifts, which provide a useful diagnostic tool for metal carbene complexes, display the expected resonances with a single Ru-$C_{carbene}$ resonance at ca. 197.42–180.79 ppm [31] and the C≡O signal resonating at δ 204.89-203.21 ppm (Figure 1). In

complexes (**3a-3d**), aromatic carbon atoms observed around 139.98–121.99 ppm. The aryloxy carbon signals appear in the regions around 167.16-164.71 ppm. The presence of chemical shifts in the range of 29.90-27.50 ppm belonged to the methyl protons (Figs. S11–S13, ESI†).

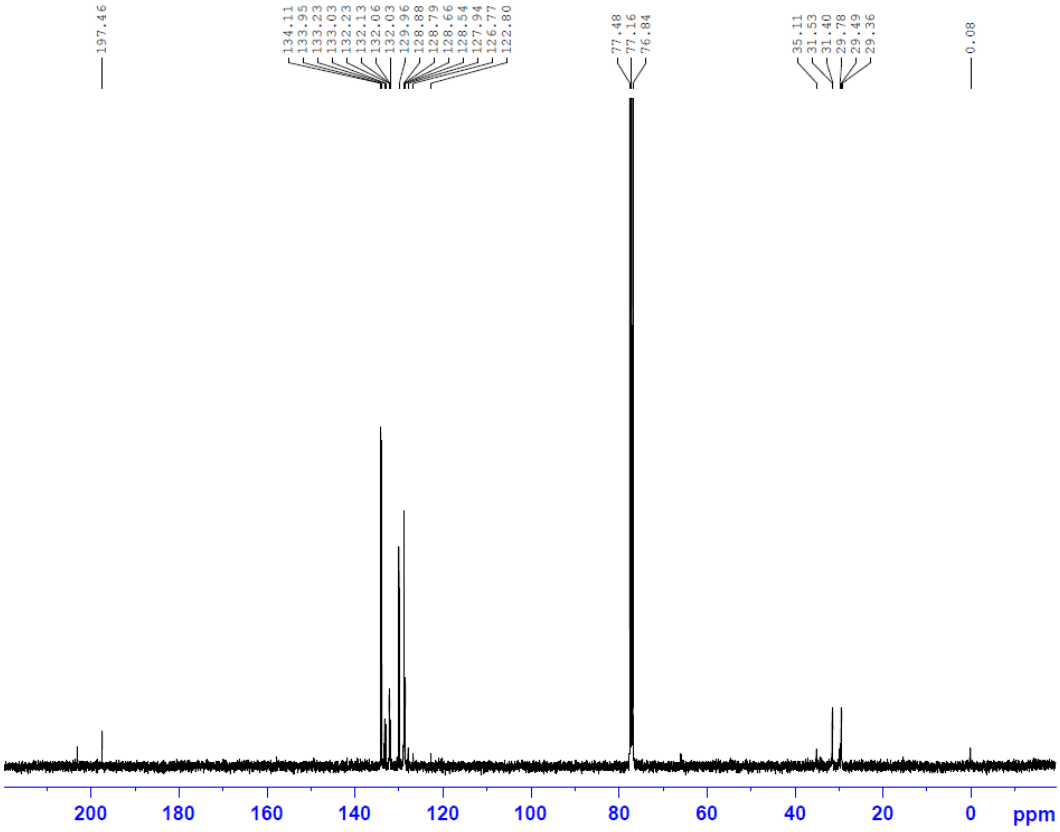

Figure **1.** ^{13}C NMR spectrum for [Ru-NHC] complex **3a**

^{31}P NMR spectra were recorded for all the complexes in order to confirm the presence of triphenylphosphine group. All the complexes (**3a-3d**) exhibited only one signal at 29.45–24.35 ppm, consistent with the presence of only one triphenylphosphine ligand (Figs. S14–S16, ESI†) (Figure 2). ESI-mass spectra of the complexes (**3a–3d**) generally showed the molecular ion peak with the loss of a chloride ion $[M–Cl]^+$(Figs. S20–S23, ESI†). Unfortunately we have not yet obtained high-quality crystals of [Ru-NHC] complexes suitable for X-ray single crystal diffraction, suggesting that subtle structural factors are critical to stabilizing this species.

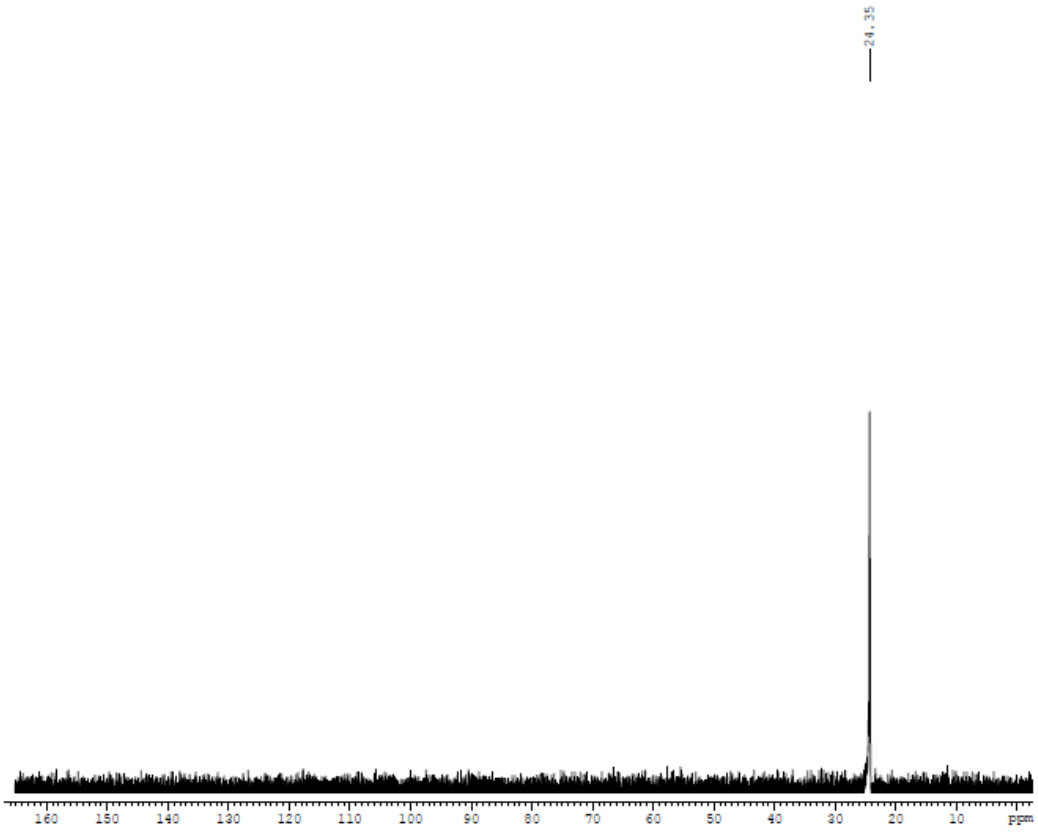

Figure **2.** ^{31}P NMR spectrum for [Ru-NHC] complex **3a**

2.4 Catalytic studies

2.4.1. Catalytic hydration of organonitriles. The catalytic hydration of nitrile is an ideal atom economical reaction and sustainable method for the preparation of amides. Several reports have demonstrated that ruthenium complexes are good catalysts for hydration of nitriles [14, 32-38]. It has also been established that the presence of N-heterocyclic carbene (NHC) in the structure of the catalyst usually provides high stability to the compound. Likewise, conjugated system incorporated with different wingtip substituents in the imidazole ring, may also increase its overall stability of the corresponding NHC complex. Thus with the new carbene complexes in hand, their abilities to catalyze the hydration of nitriles were examined. The reaction conditions for this important process are relatively mild and environment friendly.

2.4.2. Optimization of reaction conditions

The hydration of benzonitrile was selected as the model reaction for establishing the best reaction conditions. It is well-known that the solvent can have a profound effect on the rate of the hydration reaction. Hence, we interested in exploring the solvent-dependent differences in activity of catalyst **3a** on carrying out at the model hydration of nitrile reaction in the most frequently used solvents such as THF, DMSO, EtOH, MeOH, *i*PrOH, DMAc, DMF and toluene. The results are given in Table 1. DMSO, DMAc and DMF invariably gave poor yields (Table 1, entries 2, 6, 8). Whereas THF proved completely futile (Table 1, entry 1). Methanol was found as the best solvent for the hydration of nitrile within 4 h (Table 1, entry 4). While, ethanol, isopropanol and toluene resulted in moderate yields (Table 1, entries 3, 5, 8).

We examined the effect of time on catalyst loading with the aid of [Ru-NHC] catalyst 3a. The reactions were carried out with different amount of catalyst ranging from 0.15-1.0 mol % with different time intervals. The results are collated in Table 2. Aliquots are withdrawn from the reaction mixture at different time intervals and analyzed by GC, giving kinetic data during the course of the reaction. The reaction was not fruitful without the presence of the catalyst. When the catalyst loading was lowered to 0.5 mol % leads to moderate yields. When the catalyst loading was further lowered to 0.25 mol % the complex showed much lower activity (Table 2, entries 6, 7, 8, 9, 10). In the presence of 0.15 mol %, inferior results were observed even after a prolonged time (Table 2, entries 1, 2, 3, 4, 5). An increase in the mol % of catalyst did not improve the yield further (Table 2, entries 15, 16). No considerable conversion was observed without catalyst under similar reaction conditions (Table 2, entry 17).

The following step was done to study the influence of the wingtip substituents on the catalytic activity. The results are summarized in Table 3. All the synthesized complexes are proved to be active catalysts in this transformation, providing benzamide as the unique reaction product (benzoic acid was not detected by GC in the crude reaction mixtures) in 87-98 % GC yield in 4 h. Among them, the [Ru-NHC] complex containing methyl as a wingtip substituent lead to higher yields than those containing phenyl, isopropyl and mesityl at 0.5 mol % of catalyst was used. On the basis of the catalytic performance of catalysts, it was noticed that the influence of electronic and steric factors is in fact minor, for catalyst with phenyl, isopropyl and mesityl as wingtip substituents. However, in the case of catalyst **3a**

containing methyl as a wingtip substituent on nitrogen favours the electronic resonance over the adjacent carbon centers. Thus it enhances the electronic interaction of carbene carbon center of the NHC donor. Therefore, the wingtip methyl substitution favours the catalytic reactions. Moreover, a much less catalytic activity was exhibited by the free ligands when compared to that of their corresponding [Ru-NHC] complexes, which is due to the chelation of them with ruthenium ions. Therefore, our report is a very simple procedure for the hydration of a wide range of organonitriles into their corresponding primary amides by treatment with CH_3OH/H_2O under comparatively mild reaction conditions. The optimization results indicate that catalyst **3a** is the most efficient catalyst among all, because of the presence of electron donating methyl group as a wingtip substituent.

2.4.3. Catalyst Scope. With an optimized catalytic system in hand, to extend the scope and generality of the methodology, we employed several nitriles to evaluate the scope of the catalyst **3a**, using 0.5 mol % of catalyst with the reaction of 4 h at room temperature using methanol as a solvent. Delightfully, a high degree of functional group tolerance for the nitriles was observed and the results are demonstrated in **Table 4**. Among the substituted benzonitriles, those containing electron withdrawing groups (Table 4, entries 3, 7, 8, 9) get hydrated efficiently with good yields than those containing electron donating groups (Table 4, entries 5, 2, 6) [39]. Chloro, nitro and bromo substituted benzonitriles could be converted into the corresponding amides in high yields (Table 4, entries 3, 7, 8). *Trans*-cinnamonitrile hydrated to afford the corresponding amides in excellent yield (Table 4, entry 7). Industrially very important hydration of acrylonitrile also proceeded efficiently to give acrylamide (Table 4, entry 14). The 2-cyanonaphthalene afforded moderate yield around 77 % (Table 4, entry 11). Hydration of dinitriles is a matter of significance as there are equal possibilities of mono- and double hydration.[40-42] In our present catalytic system, only monohydration product was observed for 1, 4-dicyanobenzene (Table 4, entry 12). Catalyst **3a** affords selectively the monohydration product for dinitriles substrate, which appears to be unique example. Transformation of 4-methylbenzylcyanide was converted into corresponding amide with 87 % yield in 4 h. Less reactive aliphatic nitriles such as butyronitrile and acetonitrile were hydrated to afford the corresponding aliphatic amides in excellent yields (Table 4, entries 16, 17). The present protocol also hydrates methoxy acetonitrile and propionitrile efficiently under the optimized reaction condition (Table 4, entries 13, 18).

Further, we have explored the current concise transformation for hydration of heteroaromatic nitriles. Usually, the hydration of heteroaromatic nitriles is more difficult and

the reaction rates are much lower than those of common nitriles because of their strong coordination to the metal centers. The earlier optimized conditions were applied to hydration of heteroaromatic nitriles. Under these conditions, the formation of amide product was quite interesting, and no such reports exist in the salicyladiminato functionalized ruthenium-NHC catalysis. The results are summarized in Table 5. Remarkably, many of the heteroaromatic nitriles containing nitrogen, oxygen, and sulphur atoms were effectively converted into the corresponding amides within 4 h at room temperature, and no accompanying carboxylic acids were detected. In the present study, hydration of cyanopyridines afforded the corresponding amides in quantitative yields (Table 5, entries 1, 2, 3). Even a water-insoluble nitrile, such as 3-quinolinecarbonitrile, was also hydrated to 3-quinolinecarboxamide in a 96% yield (Table 5, entry 4). 2-furancarbonitrile as well as 2-thiophenecarbonitrile is smoothly hydrated to the corresponding amides in excellent yields (Table 5, entries 5, 6). It is notable that pyrazinecarbonitrile was hydrated within 4 h, and the corresponding pyrazinecarboxamide, which is used as a medicine for tuberculosis, was obtained in 98% yield (Table 5, entry 7)

2.4.4. Recyclability of catalyst. For a homogeneous catalyst, it is important to examine its ease of separation, recoverability and reusability. The reusability of the ruthenium catalyst was investigated using benzonitrile and 4-chlorobenzonitrile as model substrates. After each run, the catalyst was recovered easily by the addition of CH_2Cl_2/diethylether mixture. The catalyst was then thoroughly washed with hexane and then dried in air before using in the next run. As seen in **Figure. 3**, the catalyst can be efficiently recycled and reused more than six times without significant loss of the catalytic activity or selectivity in the case of benzonitrile. In the case of 4-chlorobenzylnitrile a decrease in activity was observed after the sixth recycling experiment. We attribute this may be due to incomplete catalyst recovery in the reaction mixture.

In comparison with other reported metal catalysts [43-49] for the nitrile hydration reaction, our present catalysts has been found to exhibit the best activity in terms of low catalyst loading, mild reaction conditions and low reaction time. Moreover, they are easier to prepare and/or cheaper than other systems [45,49,50,51].

The complete elucidation of the mechanism has not been undertaken for this hydration of nitriles reaction. On the basis of the above results and also in accordance with earlier literature reports [52], we believe that the catalytic hydration reaction with salicyladiminato functionalized [Ru-NHC] complex follows the three general steps. (a)

coordination of the nitrile, (b) intermolecular nucleophilic attack of water on the nitrile to form the α-hydroxyimide, and (c) dissociation of the amide product. Efforts are underway to elucidate the mechanistic details of these NH bond forming reactions.

3. CONCLUDING REMARKS

In summary, We have disclosed the synthesis and characterization of the novel air stable ruthenium(II) complexes bearing salicyladiminato functionalized mixed N-heterocyclic carbene (NHC) ligand phosphine co-ligand (**3a-3d**) , in which the wingtip substituents was present on one imidazole nitrogen. The ruthenation was accomplished by metalation with Ag_2O and subsequent transmetallation with $[RuHCl(CO)(PPh_3)_3]$. The yields were promising. The [Ru–NHC] complexes (**3a-3d**) displayed excellent stability toward air and moisture which are the additional advantages for a better catalyst. The efficiency of complexes (**3a-3d**) as catalyst for selective hydration of organonitriles to primary amides has been established. The present catalytic system efficiently converts nitriles to amides in mild reaction condition with tolerance of air and a variety of functional groups. Remarkably, in all the catalytic transformations studied, activities superior to those described previously. Advantages of the catalytic system discussed here include easy catalyst preparation, simple reaction setup, and the use of solvent (CH_3OH/H_2O). The catalyst is robust and highly recyclable under atmospheric conditions (no inert atmosphere required). The wingtip groups have a direct impact on the catalytic activity. We have shown that the selectivity of the reaction strongly depends on the nature of the wingtip substituent present in the imidazole ring. Alkyl wingtip providing the most active species while aryl wingtip groups shows lower activity. To the best of our knowledge, the protocol has been applied for the first time successfully to ruthenium(II) complexes bearing salicyladiminato functionalized mixed N-heterocyclic carbene (NHC) ligand and phosphine co-ligand. All these taken together make the catalyst especially useful for practical applications in organic synthesis. Further work on other applications of the present catalytic system is in progress.

4. EXPERIMENTAL SECTION

4.1 General comments. All operations were performed under a dry argon atmosphere using Schlenk techniques and a vacuum-line system. Silver reactions were conducted in the absence of light. All commercial chemicals were used as purchased. Solvents were dried, distilled, and degassed before use. Thin-layer chromatography (TLC) was performed on Merck 1.0555 aluminum sheets precoated with silica gel 60 F254, and the spots were

visualized with UV light at 254 nm or under iodine. Column chromatography purifications were performed using Merck silica gel (200-400 mesh). Melting points were checked in open capillary tubes on a Technico micro heating table and are uncorrected.

4.2 Spectroscopy. Infrared spectra of the ligands and the metal complexes were recorded as KBr discs in the range of 4000–400 cm^{-1} using a Nicolet Avatar model FT-IR spectrophotometer. ^{1}H (300.13 MHz), ^{13}C (75.47 MHz) and ^{31}P NMR (162 MHz) spectra were taken in DMSO-d_6 or $CDCl_3$ at room temperature with a Bruker AV400 instrument with chemical shifts relative to tetramethylsilane (^{1}H, ^{13}C) and *o*-phosphoric acid (^{31}P). Electrospray ionization mass spectra were recorded by liquid chromatography mass spectrometry quadrupole time-of-flight Micro Analyzer (Shimadzu) at SAIF, Panjab University, Chandigarh.

4.3 Elemental analyses. Microanalyses of carbon, hydrogen and nitrogen were carried out using a Vario EL III elemental analyzer.

4.4 Materials. 1-Substituted imidazoles [53], 1-(3-ethylbromide)-3,5-di-*tert*-butyl salicylaldimine Schiff base [29] and $[RuHCl(CO)(PPh_3)_3]$ [54] were prepared according to the previously published procedures.

4.5 Preparation of NHC ligands

The preparation of new salicylaldiminato-functionalized *N*-heterocyclic carbene ligand involve two stages

4.5.1. Stage 1. Synthesis of 1-(3-ethylbromide)-3,5-di-*tert*-butyl salicylaldimine Schiff base [3,5-tBu$_2$-2-(HO)C_6H_2CH=NCH_2CH_2Br]

1-(3-ethylbromide)-3,5-di-*tert*-butyl salicylaldimine Schiff base was prepared according to the literature procedure [32]. To a solution of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (6.10 g, 50.0 mmol) in 20 mL of 95% alcohol was added to 2-bromoethylamine hydrobromide (10.80 g, 52.7 mmol) in 20 mL of H_2O. When the solution was heated to 50°C, NaOH (2.20 g, 55.0 mmol) in 2 mL of H_2O was added with stirring. Recrystallization from 95% alcohol afforded the target product as yellow crystals. Yield: 80 %. M.p. 69–71°C. Anal. Calcd for $C_{17}H_{26}BrNO$: C, 60.00; H, 7.70; N, 4.12. Found: C, 60.08; H, 7.73; N, 4.14 %. ^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 13.4 (1H, s, OH), 8.4 (1H, s, CH=N),

7.4 (1H, s, ArH), 7.1 (1H, s, ArH), 4.0 (2H, m, NCH_2), 3.9 (2H, m, CH_2Br), 1.5 (9H, s, $CH(CH_3)_3$), 1.3 (9H, s, $CH(CH_3)_3$).

4.5.2. Stage 2. Synthesis of salicylaldiminato-functionalized imidazolium salts (**1a-1d)**

To a solution of 1-(3-ethylbromide)-3,5-di-*tert*-butyl salicylaldimine (10.20 g, 30.0 mmol) in 20 mL of hexane was added to 1- substituted imidazole (3.30 g, 30.0 mmol) in 20 mL of Et_2O. After refluxing for 4 days, the suspension solution was cooled to room temperature and filtered. The salicylaldiminato-functionalized imidazolium salts (**1a-1d**) were obtained as a pale yellow powder in good yield.

4.5.3. Compound **1a** (R = Me): The synthetic procedure of this compound was the same as that of above representative procedure, using 1-methyl imidazole to give a yellow solid **1a.** Yield: 95%. M.p. 122–124°C. Anal. Calcd for $C_{21}H_{32}N_3OBr$: C, 59.71; H, 7.64; N, 9.95. Found: C, 59.81; H, 7.91; N, 9.79 %. ^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 13.1 (1H, s, OH), 10.6 (1H, s, NCHN), 8.5 (1H, s, CH=N), 7.4-7.5 (2H, m, ArH), 7.2 (1H, s, NCH), 7.0 (1H, d, NCH), 4.8 (2H, m, NCH_2), 4.2 (2H, m, NCH_2), 1.4 (9H, s, $CH(CH_3)_3$), 1.2 (9H, s, $CH(CH_3)_3$). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 167.6 (C-O), 157.6 (-CH=N), 139.9 (C_{quat}, aryl), 136.5 (C_{quat}, aryl), 127.0 (C_{quat}, aryl), 125.8 (C_{quat}, aryl), 117.3 (C_{quat}, aryl), 60.4 ((NCH_2), 34.7 (C_{quat}, *t*Bu), 33.8 (C_{quat}, *t*Bu), 31.7 (C_{quat}, *t*Bu), 31.1 (C_{quat}, *t*Bu), 29.1 (N-CH_3). ESI: *m/z* calcd. For $C_{21}H_{32}N_3OBr$ $[M–Br]^+$, 342.496; Found, $[M–Br]^+$, 342.17.

4.5.4. Compound **1b** (R = Ph): The synthetic procedure of this compound was the same as that of above representative procedure, using 1-phenyl imidazole to give a yellow solid **1b.** Yield: 87%. M.p. 132–136°C. Anal. Calcd for $C_{25}H_{34}N_3OBr$: C, 64.46; H, 7.07; N, 8.67. Found: C, 64.13; H, 7.45; N, 8.86 %. ^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 13.1 (1H, s, OH), 10.8 (1H, s, NCHN), 8.5 (1H, s, CH=N), 7.7-7.8 (2H, m, ArH), 7.5-7.6 (2H, m, ArH), 7.4-7.5 (2H, m, ArH), 7.1-7.4 (1H, m, ArH), 7.2 (1H, s, NCH), 7.1 (1H, d, NCH), 4.3 (2H, m, NCH_2), 4.0 (2H, m, NCH_2), 1.4 (9H, s, $CH(CH_3)_3$), 1.3 (9H, s, $CH(CH_3)_3$). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 166.5 (C-O), 149.8 (-CH=N), 139.8 (C_{quat}, aryl), 138.2 (C_{quat}, aryl), 136.4 (C_{quat}, aryl), 131.1 (C_{quat}, aryl), 127.3 (C_{quat}, aryl), 126.7 (C_{quat}, aryl), 121.7 (C_{quat}, aryl), 108.2 (C_{quat}, aryl), 60.4 ((NCH_2), 38.7 (C_{quat}, *t*Bu), 33.8 (C_{quat}, *t*Bu), 24.1 (C_{quat}, *t*Bu), 21.6 (C_{quat}, *t*Bu). ESI: *m/z* calcd. For $C_{25}H_{34}N_3OBr$ $[M–Br]^+$, 407.57; Found, $[M–Br]^+$, 408.25.

4.5.5. Compound **1c** (R = ^{i}Pr): The synthetic procedure of this compound was the same as that of above representative procedure, using 1-isopropyl imidazole to give a yellow solid **1c.** Yield: 91%. M.p. 128–131°C. Anal. Calcd for $C_{23}H_{36}N_3OBr$: C, 61.33; H, 8.06; N, 9.33.

Found: C, 61.26; H, 8.08; N, 9.35 %. ^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 13.0 (1H, s, OH), 10.8 (1H, s, NCHN), 8.5 (1H, s, CH=N), 7.9-7.4 (2H, m, ArH), 7.2 (1H, s, NCH), 7.1 (1H, d, NCH), 4.9 (2H, m, NCH_2), 4.8 (1H, m, $CH(CH_3)_2$), 4.3 (2H, m, NCH_2), 1.6 (6H, m, $CH(CH_3)_2$), 1.4 (9H, s, $CH(CH_3)_3$), 1.3 (9H, s, $CH(CH_3)_3$). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 166.8 (C-O), 154.8 (-CH=N), 138.9 (C_{quat}, aryl), 135.8 (C_{quat}, aryl), 126.6 (C_{quat}, aryl), 125.4 (C_{quat}, aryl), 116.9 (C_{quat}, aryl), 60.7 (NCH_2), 35.1 (C_{quat}, *t*Bu), 34.2 (C_{quat}, *t*Bu), 31.9 (C_{quat}, *t*Bu), 31.1 (C_{quat}, *t*Bu), 30.2 (CH_3), 29.3 (CH_3).

4.5.6. Compound **1d** (R = Mes): The synthetic procedure of this compound was the same as that of above representative procedure, using 1-mesityl imidazole to give a yellow solid **1d.** Yield: 89%. M.p. 121–124°C. Anal. Calcd for $C_{29}H_{40}N_3OBr$: C, 61.32; H, 8.06; N, 9.32. Found: C, 61.26; H, 8.08; N, 9.35 %. ^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 13.2 (1H, s, OH), 10.7 (1H, s, NCHN), 8.5 (1H, s, CH=N), 7.9-7.5 (2H, m, ArH), 7.1 (1H, s, NCH), 4.8 (4H, m, NCH_2), 2.3 (3H, s, Ar-CH_3), 2.2 (6H, s, Ar-CH_3), 1.4 (9H, s, $CH(CH_3)_3$), 1.3 (9H, s, $CH(CH_3)_3$). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 168.2 (C-O), 154.3 (-CH=N), 137.3 (C_{quat}, aryl), 134.2 (C_{quat}, aryl), 127.6 (C_{quat}, aryl), 125.6 (C_{quat}, aryl), 116.7 (C_{quat}, aryl), 61.2 (NCH_2), 35.3 (C_{quat}, *t*Bu), 34.2 (C_{quat}, *t*Bu), 32.3 (C_{quat}, *t*Bu), 30.4 (C_{quat}, *t*Bu), 30.1 (CH_3), 29.7 (CH_3), 29.3 (CH_3). ESI: *m/z* calcd. For $C_{29}H_{40}N_3OBr$ $[M–Br]^+$, 442.62; Found, $[M–Br]^+$, 442.92.

4.6 Syntheses of salicylaldiminato-functionalized *N*-heterocyclic carbene ruthenium(II) complexes (3a-3d). The milder conditions of the "transmetalation" pathway make it an attractive choice for the synthesis of ruthenium complexes. Salicylaldimino-functionalized imidazolium salts (R= Me (**1a**), Ph (**1b**), *i*Pr (**1c**), Mes (**1d**) 2 mmol) was dissolved in 25 mL of dichloromethane and transferred into a Schlenk vessel. Silver(I) oxide (0.231 g , 1 mmol) was added, and the mixture was stirred for 24 h at room temperature under argon atmosphere. The unreacted Ag_2O was filtered through a plug of Celite, and in most cases the solution was directly applied for further synthetic steps. The product can be isolated by removing the solvent under reduced pressure to give a solid, stable to oxygen and water. $[RuHCl(CO)(PPh_3)_3]$ (0.9524 g, 1 mmol) was taken up in 5 mL of dichloromethane and added to a solution of Ag complex in 10 mL of CH_2Cl_2. A white precipitate (AgBr) formed, and the mixture was stirred overnight at room temperature. After filtration in air, the solvent was removed in vacuum to give a brown waxy substance. The waxy substance was triturated with diethyl ether. The final compound is stable in air. The crude product was purified by column chromatography (SiO_2, 10:1 CH_2Cl_2/Acetone).

4.6.1. Compound **3a** (R = Me): The synthetic procedure of this compound was the same as that of above representative procedure, using **1a** to give a yellow solid **3a.** Yield: 81%. M.p. 210–214°C. Anal. Calcd for $C_{40}H_{45}N_3O_2ClPRu$: C, 62.61; H, 5.91; N, 5.48. Found: C, 62.82; H, 6.37; N, 5.11. IR (KBr disks, cm^{-1}); 1975 (C≡O), 1593 (C=C), 1542 (N-C-N), 1496 (C-C), 1433 (C-O). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 8.3 (1H, s, CH=N), 7.4-7.5 (2H, m, ArH), 7.4 (m, 8H, ArH), 7.2 (m, 7H, ArH), 3.1 (s, 3H, CH_3), 1.3 (s, 9H, $C(CH_3)_3$), 0.8 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 203.5 (C≡O), 197.5 (Ru-$C_{carbene}$), 134.1 (C_{quat}, aryl), 133.9 (C_{quat}, aryl), 133.2 (C_{quat}, aryl), 133.0 (C_{quat}, aryl), 132.2 (C_{quat}, aryl), 132.1 (C_{quat}, aryl), 132.1 (C_{quat}, aryl), 132.0 (C_{quat}, aryl), 129.9 (C_{quat}, aryl), 128.9 (C_{quat}, aryl), 128.8 (C_{quat}, aryl), 128.7 (C_{quat}, aryl), 128.5 (C_{quat}, aryl),128.9 (C_{quat}, aryl), 127.9 (C_{quat}, aryl), 126.8 (C_{quat}, aryl), 122.9 (C_{quat}, aryl), 35.1 (C_{quat}, *t*Bu), 31.5 (C_{quat}, *t*Bu), 31.4 (C_{quat}, *t*Bu), 29.8 (C_{quat}, *t*Bu), 29.4 (N-CH_3). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 24.4 (s). ESI: *m/z* calcd. For $C_{40}H_{45}N_3O_2ClPRu$ [M–Cl] $^+$, 731.85; Found, [M–Cl] $^+$, 732.13.

4.6.2. Compound **3b** (R = Ph): The synthetic procedure of this compound was the same as that of above representative procedure, using **1b** to give a yellow solid **3b.** Yield: 83%. M.p. 237–240°C. Anal. Calcd for $C_{45}H_{47}N_3O_2ClPRu$: C, 64.17; H, 5.71; N, 5.07. Found: C, 64.43; H, 6.08; N, 5.29. IR (KBr disks, cm^{-1}); 1973 (C≡O), 1577 (C=C), 1527 (N-C-N), 1435 (C-C), 1413 (C-O). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 8.2 (1H, s, CH=N), 7.7 (2H, m, ArH), 7.5-7.6 (2H, m, ArH), 7.4-7.5 (2H, m, ArH), 7.1-7.4 (1H, m, ArH), 7.7 (m, 5H, ArH), 7.7 (m, 2H, ArH), 7.7 (m, 8H, ArH), 1.3 (s, 9H, $C(CH_3)_3$), 1.5 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 203.2 (C≡O), 197.4 (Ru-$C_{carbene}$), 165.1 (C-O), 159.2 (CH=N), 138.6 (C_{quat}, aryl), 136.7 (C_{quat}, aryl), 134.1 (C_{quat}, aryl), 133.9 (C_{quat}, aryl), 133.1 (C_{quat}, aryl), 133.0 (C_{quat}, aryl), 132.9 (C_{quat}, aryl), 132.2 (C_{quat}, aryl), 132.1 (C_{quat}, aryl), 132.0 (C_{quat}, aryl), 129.9 (C_{quat}, aryl), 129.7 (C_{quat}, aryl), 128.8 (C_{quat}, aryl), 128.5 (C_{quat}, aryl),, 127.9 (C_{quat}, aryl), 122.8 (C_{quat}, aryl), 37.0 (C_{quat}, *t*Bu), 35.1 (C_{quat}, *t*Bu), 34.3 (C_{quat}, *t*Bu), 34.2 (C_{quat}, *t*Bu). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 29.2 (s). ESI: *m/z* calcd. For $C_{45}H_{47}N_3O_2ClPRu$ [M–Cl] $^+$, 793.92; Found, [M–Cl] $^+$, 794.15.

4.6.3. Compound **3c** (R = ^{i}Pr): The synthetic procedure of this compound was the same as that of above representative procedure, using **1c** to give a yellow solid **3c.** Yield: 81%. M.p. 219–223°C. Anal. Calcd for $C_{42}H_{49}N_3O_2ClPRu$: C, 63.42; H, 6.21; N, 5.28. Found: C, 64.73; H, 6.53; N, 5.05. IR (KBr disks, cm^{-1}); 1989 (C≡O), 1591 (C=C), 1522 (N-C-N), 1493 (C-C), 1389 (C-O). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 8.2 (1H, s, CH=N), 7.8-7.7 (2H, m, ArH), 7.6 (m, 6H, ArH), 7.3-7.5 (m, 8H, ArH), 7.2 (m, 4H, ArH), 4.8 (1H, m, $CH(CH_3)_2$), 4.2 (2H, m,

NCH_2), 1.6 (6H, m, $CH(CH_3)_2$), 1.4 (9H, s, $CH(CH_3)_3$), 1.2 (9H, s, $CH(CH_3)_3$). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 204.2 (C≡O), 180.8 (Ru-$C_{carbene}$), 167.2 (C-O), 162.1 (CH=N), 140.0 (C_{quat}, aryl), 136.2 (C_{quat}, aryl), 135.3 (C_{quat}, aryl), 134.3 (C_{quat}, aryl), 132.9 (C_{quat}, aryl), 131.2 (C_{quat}, aryl), 124.9 (C_{quat}, aryl), 122.0 (C_{quat}, aryl), 37.7 (C_{quat}, *t*Bu), 30.3 (C_{quat}, *t*Bu), 30.0 (C_{quat}, *t*Bu), 29.9 (CH_3). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 29.5 (s). ESI: *m/z* calcd. For $C_{42}H_{49}N_3O_2ClPRu$ $[M–Cl]^+$, 759.90; Found, $[M–Cl]^+$, 760.06.

4.6.4. Compound **3d** (R = Mes): The synthetic procedure of this compound was the same as that of above representative procedure, using **1d** to give a yellow solid **3d.** Yield: 84 %. M.p. 229–232°C. Anal. Calcd for $C_{48}H_{55}N_3O_2ClPRu$: C, 66.00; H, 6.35; N, 4.81. Found: C, 66.33; H, 6.45; N, 4.42. IR (KBr disks, cm^{-1}); 1981 (C≡O), 1595 (C=C), 1528 (N-C-N), 1491 (C-C), 1387 (C-O). ^1H NMR (300.13 MHz, $CDCl_3$): δ 8.3 (1H, s, CH=N), 7.5-7.4 (2H, m, ArH), 7.6 (s, 2H, ArH), 7.0 (d, J = 1.8 Hz, 2H, ArH), 6.8 (d, J = 2.1 Hz, 4H, ArH), 4.8 (2H, m, NCH_2), 4.5 (2H, m, NCH_2), 2.5 (s, 3H, Ar-CH_3), 2.2 (s, 6H, Ar-CH_3), 1.9 (9H, s, $CH(CH_3)_3$), 1.6 (9H, s, $CH(CH_3)_3$). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 204.9 (C≡O), 196.8 (Ru-$C_{carbene}$), 164.7 (C-O), 161.0 (CH=N), 129.4 (C_{quat}, aryl), 128.4 (C_{quat}, aryl), 128.2 (C_{quat}, aryl), 126.5 (C_{quat}, aryl), 123.7 (C_{quat}, aryl), 122.1 (C_{quat}, aryl), 121.9 (C_{quat}, aryl), 120.0 (C_{quat}, aryl), 38.7 (C_{quat}, *t*Bu), 37.6 (C_{quat}, *t*Bu), 35.1 (CH_3, *t*Bu), 32.3 (CH_3, *t*Bu), 30.7 (CH_3, *t*Bu), 29.4 (CH_3), 28.4 (CH_3), 27.5 (CH_3). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 28.9 (s). ESI: *m/z* calcd. For $C_{48}H_{55}N_3O_2ClPRu$ $[M–Cl]^+$, 838.02; Found, $[M–Cl]^+$, 837.98.

4.7 General procedure for the hydration of nitriles to amides

Organic nitrile (1 mmol) and distilled water (1 mL) were sequentially added to 3 mL methanol solution of the [Ru-NHC] catalyst (0.5 mol %) and the reaction mixture was stirred at room temperature. The progress of the reaction in each case was monitored by TLC analysis. After completion of reaction the catalyst was extracted from the reaction mixture by the addition of CH_2Cl_2/petroleum ether followed by filtration. The filtrate was subjected to GC analysis and the product was identified with authentic samples.

SUPPORTING INFORMATION

Representative NMR (^1H, ^{13}C, ^{31}P) and ESI-MS spectra of ligands and the complexes.

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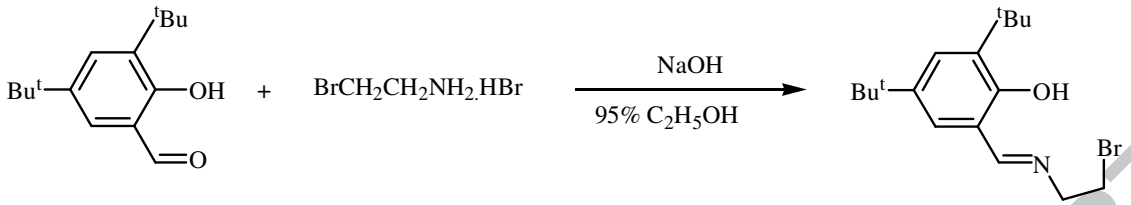
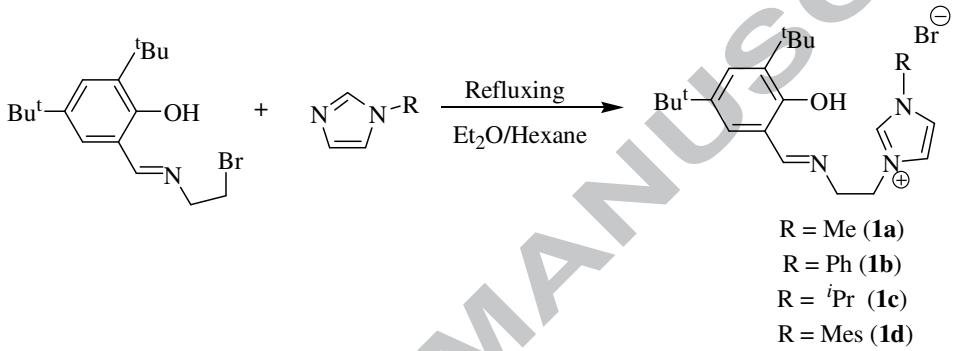
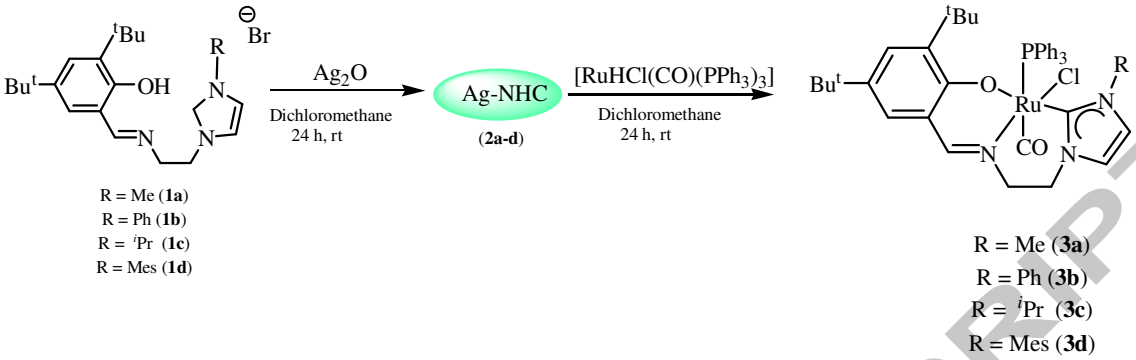


Scheme 1. Preparation of 1-(3-ethylbromide)-3,5-di-*tert*-butyl salicylaldimine Schiff base



Scheme 2. General preparation of salicylaldiminato-functionalized imidazolium salts (**1a-1d**)



R = Me (**1a**)
R = Ph (**1b**)
R = ^{i}Pr (**1c**)
R = Mes (**1d**)

R = Me (**3a**)
R = Ph (**3b**)
R = ^{i}Pr (**3c**)
R = Mes (**3d**)

Scheme 3. General synthesis of [Ru-NHC] complexes (**3a-3d**)

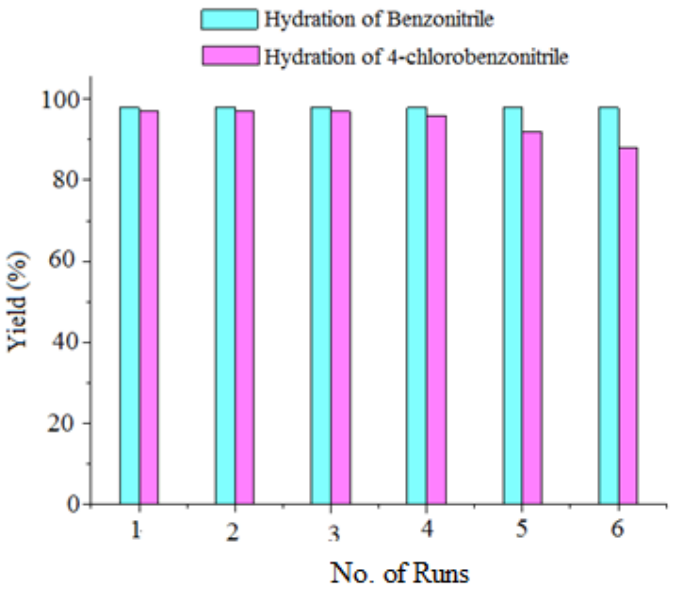
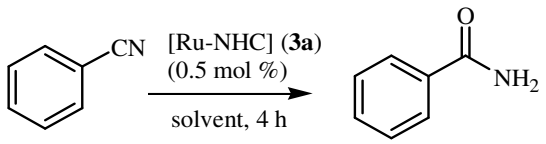


Figure 3. Recyclability test of [Ru-NHC] catalyst using benzonitrile and 4-chlorobenzonitrile

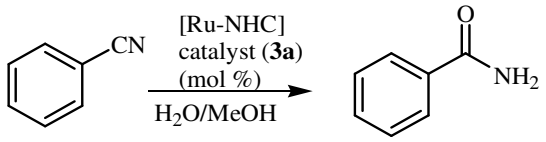
Table 1. Effect of solvent on benzonitrile hydration catalyzed by [Ru-NHC] complex **3a**[a]



Entry	Solvent	TON[b]	TOF[c]	% Conversion[d]
1	THF	-	-	n.r
2	DMSO	78	20	39
3	EtOH	154	39	77
4	**MeOH**	**196**	**49**	**98**
5	*i*PrOH	138	35	69
6	DMAc	62	16	31
7	DMF	66	17	33
8	Toluene	106	27	53
9	Without solvent	-	-	-

[a]Reaction Conditions: Benzonitrile (1 mmol), solvent (3 mL), water (1 mL), catalyst loading (0.5 mol %) at room temperature for 4 h.
[b]Turnover number (TON) = (mmol of product)/(mmol of catalyst) after time t.
[c] TOF = TON/time
[d] Conversion determined by GC

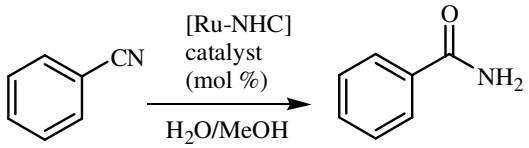
Table 2. Effect of time on catalyst loading for benzonitrile hydration catalyzed by [Ru-NHC] complex **3a**[a]



Entry	Catalyst (mol %)	Time (h)	TON[b]	TOF[c]	%Conversion[d]
1	0.15	1	63	63	<10
2	0.15	2	220	110	33
3	0.15	3	340	113	51
4	0.15	4	429	107	67
5	0.15	5	480	96	72
6	0.25	1	132	132	33
7	0.25	2	189	95	47
8	0.25	3	248	83	62
9	0.25	4	312	78	78
10	0.25	5	320	64	81
11	0.5	1	84	84	42
12	0.5	2	106	53	53
13	0.5	3	148	49	74
14	**0.5**	4	**196**	**49**	**98**
15	0.5	5	198	40	>99
16	1.0	8	198	25	>99
17	-	8	-	-	-

[a]Reaction Conditions: Benzonitrile (1 mmol), MeOH (3 mL), water (1 mL), catalyst loading (0.15-0.5 mol %), time (1-8 h) at room temperature.
[b]Turnover number (TON) = (mmol of product)/(mmol of catalyst) after time t.
[c] TOF = TON/time
[d] Conversion determined by GC

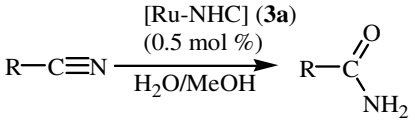
Table 3. Influence of wingtip substituents and catalyst loading on benzonitrile hydration catalyzed by new [Ru-NHC] complexes **3a-3d**[a]

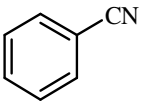
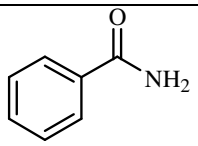
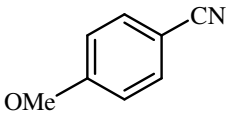
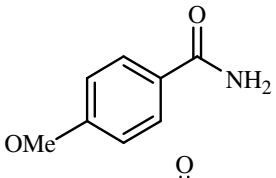
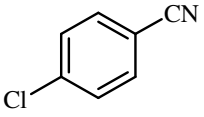
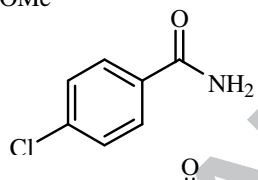
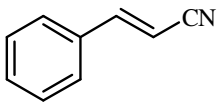
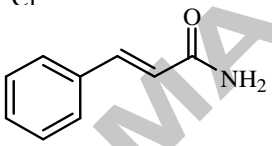
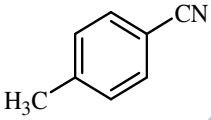
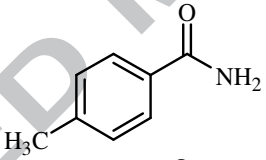
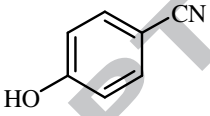
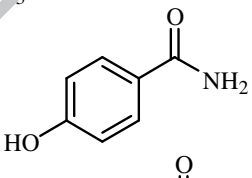
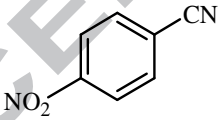
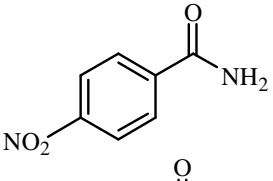
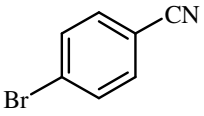
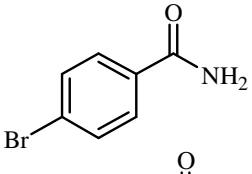
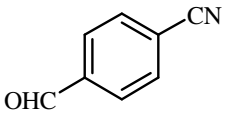
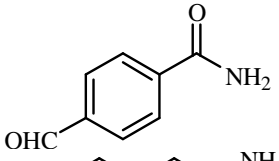
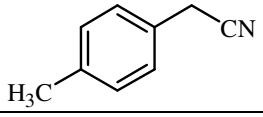
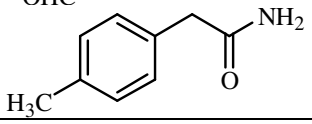


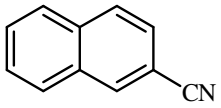
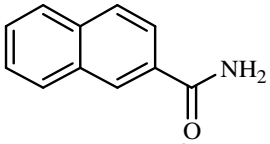
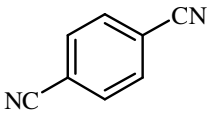
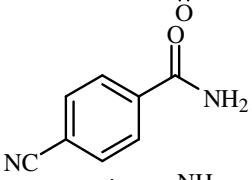
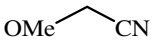
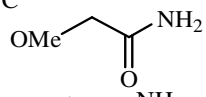
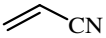
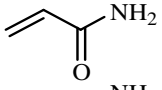
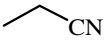
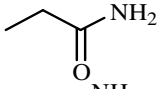
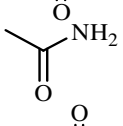
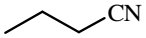
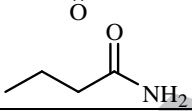
Entry	catalyst	Amount of catalyst (mol %)	Wingtip (R)	Time (h)	TON[b]	TOF[c]	% Conversion[d]
1	**1a**	0.5	Me	4	34	9	17
2	**1a**	0.5	Me	8	68	9	33
3	**1b**	0.5	Ph	8	50	6	25
4	**1c**	0.5	^{i}Pr	8	42	5	21
5	**1d**	0.5	Mes	8	56	7	28
6	**3a**	**0.5**	**Me**	**4**	**196**	**49**	**98**
7	**3b**	0.5	Ph	4	168	42	89
8	**3c**	0.5	^{i}Pr	4	174	44	87
9	**3d**	0.5	Mes	4	180	45	90
10	**-**	-	-	8	-	-	-

[a]Reaction Conditions: Benzonitrile (1 mmol), MeOH (3 mL), water (1 mL), catalyst loading (0.5 mol %), time (4-8 h) at room temperature.
[b]Turnover number (TON) = (mmol of product)/(mmol of catalyst) after time t.
[c] TOF = TON/time
[d] Conversion determined by GC

Table 4. Catalytic hydration of organonitriles catalyzed by [Ru-NHC] complex **3a**[a]

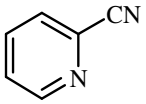
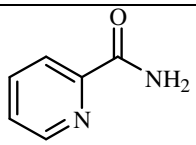
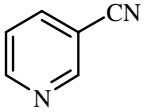
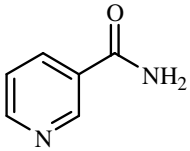
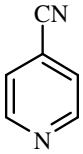
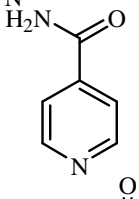
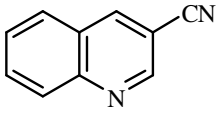
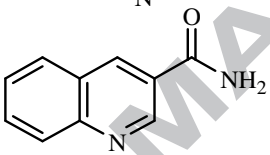
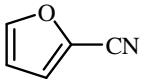
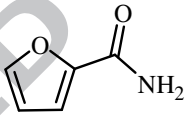
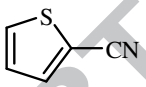
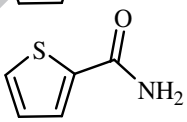
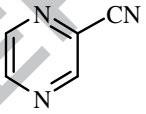
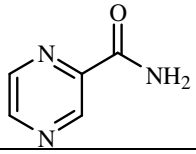


Entry	Nitrile	Amide	TON[b]	TOF[c]	% Conversion[d]
1			196	49	98
2			156	39	78
3			194	49	97
4			186	47	93
5			178	45	89
6			166	42	83
7			196	49	98
8			190	48	95
9			186	47	93
10			174	44	87

11			154	39	77
12			194	49	97
13			188	47	94
14			128	32	64
15			166	42	83
16	MeCN		196	49	98
17			162	41	81

[a]Reaction Conditions: Nitrile (1 mmol), MeOH (3 mL), water (1 mL), catalyst loading (0.5 mol %), time (4 h) at room temperature.
[b]Turnover number (TON) = (mmol of product)/(mmol of catalyst) after time t.
[c] TOF = TON/time
[d] Conversion determined by GC

Table 5. Hydration of various heteroaromatic nitriles catalyzed by [Ru-NHC] complex **3a**[a]

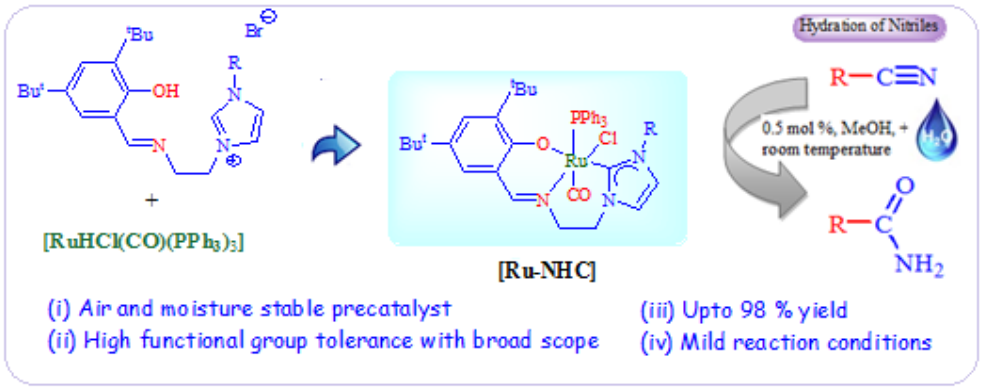
Entry	Nitrile	Amide	TON	TOF[c]	% Conversion[d]
1			196	49	98
2			188	47	94
3			196	49	98
4			192	48	96
5			196	49	98
6			194	49	97
7			196	49	98

[a]Reaction Conditions: heteroaromatic nitrile (1 mmol), MeOH (3 mL), water (1 mL), catalyst loading (0.5 mol %), time (4 h) at room temperature.
[b]Turnover number (TON) = (mmol of product)/(mmol of catalyst) after time t.
[c] TOF = TON/time
[d] Conversion determined by GC

Graphical abstract synopsis

A new air-stable Ru(II) complexes (3a-3d) containing salicyladiminato functionalized mixed N-heterocyclic carbene (NHC) ligand and phosphine co-ligand was synthesized and characterized by FT-IR, NMR and ESI-Mass. The resulting complexes have been evaluated as potential catalysts for the selective hydration of nitriles to primary amides, and related amide bond forming reactions. This method has a great potential for the preparation of amides, because it tolerates a wide range of substrates with excellent yield.

Graphical abstract pictogram



Research Highlights

- New ruthenium(II) complexes containing salicyladiminato functionalized mixed N-heterocyclic carbene (NHC) ligand and phosphine co-ligand have been synthesized and characterized.
- Analytical and spectral data confirm the structure of the new complexes.
- The resulting complexes have been evaluated as potential catalysts for hydration of nitriles.