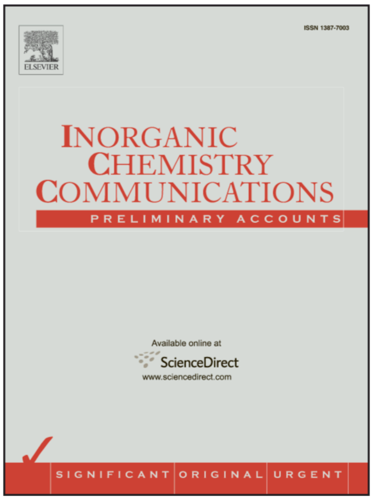

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Arene-Ruthenium(II)-Phosphine Complexes: Green Catalysts for Hydration of Nitriles Under Mild Conditions

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Abstract

Three new arene-ruthenium(II) complexes were prepared by treating [{RuCl(μ-Cl)(η^6-arene)}$_2$] (η^6-arene=p-cymene) dimer with tri(2-furyl)phosphine (PFu$_3$) and 1,3,5-triaza-7-phosphaadamantane (PTA), respectively to obtain [RuCl$_2$(η^6-arene)PFu$_3$] **[Ru]-1**, [RuCl(η^6-arene)(PFu$_3$)(PTA)]BF$_4$ **[Ru]-2** and [RuCl(η^6-arene)(PFu$_3$)$_2$]BF$_4$ **[Ru]-3**. All the complexes were structurally identified using analytical and spectroscopic methods including single-crystal X-ray studies. The effectiveness of resulting complexes as potential homogeneous catalysts for selective hydration of different nitriles into corresponding amides in aqueous medium and air atmosphere was explored. There was a remarkable difference in catalytic activity of the catalysts depending on the nature and number of phosphorus-donor ligands and sites available for catalysis. Experimental studies performed using structural analogues of efficient catalyst concluded a structural-activity relationship for the higher catalytic activity of **[Ru]-1**, being able to convert huge variety of aromatic, heteroaromatic and aliphatic nitriles. The use of eco-friendly water as a solvent, open atmosphere and avoidance of any organic solvent during the catalytic reactions prove the reported process to be truly green and sustainable.

Keywords: Green Chemistry, Homogeneous Catalysis, Organometallic Chemistry, Ru(II)-Arene Complexes

Hydration of nitrile into amide is a key organic transformation, which is utilized extensively to generate pharmaceuticals and other industrial products. Amides have been found to be very essential as the amide linkage paves the way for generation of various polymeric products with versatile industrial applications [1]. The conventional procedure to obtain amides through acid or base catalysis is plagued by drawbacks like overreaction with formation of carboxylic acids and harsh conditions which limits the application in presence of other sensitive functional groups [2, 3]. The formation of amide has been identified as one of the most challenging syntheses in industry and considered as a high-priority research field by ACS GCIPR in 2005. Therefore, developing atom-efficient catalytic procedures for amide formation that avoids the acid/base and/or stoichiometric reagents, is a key goal and highly desirable methodology in modern chemistry [4]. Homogeneous or heterogeneous catalysis involving metal appears to be more attractive and potent alternatives due to their superior substrate scope and easy handling [5]. A huge variety of highly selective homogeneous metal catalysts have been reported for the formation of amide [6-9].

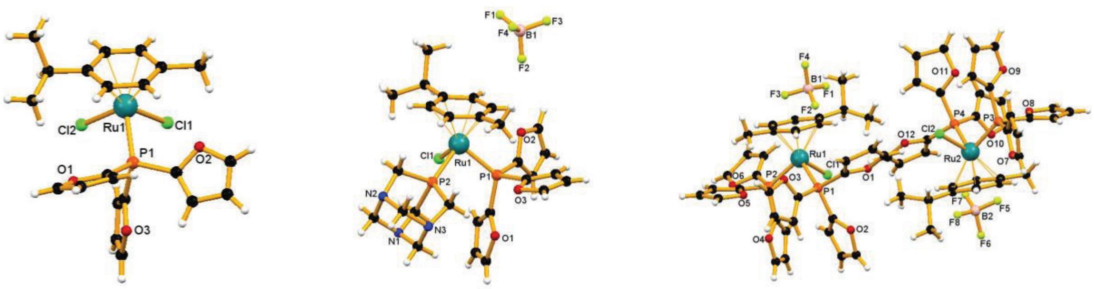
Amongst all transition metal based catalysts, ruthenium is considered as one of the highest explored metals for transformation of nitrile to amide because few of the highly efficient catalysts containing ruthenium, are reported with high substrate acceptance toward the nitrile hydration [5e, 10-16] especially, with phosphine containing ligands [8, 9, 10, 17-22] Most of these catalysts work only in organic media with or without the presence of water and operate in an inert atmosphere like nitrogen and argon [18]. Therefore, to develop safer and more eco-friendly procedures, some groups are working since last few years to explore the possibility of development of new homogeneous catalysts, which are able to perform the selective hydration of nitriles to amides in aqueous medium [6,10,12,13,15,23]. It is important to note that development of organic transformations in aqueous medium has become one of the key requirements in contemporary chemistry in line with the increasing interest of academia and industry in satisfying the principles of “Green Chemistry”, [24, 25] being water the most suitable solvent that can be thought of in terms of safety, accessibility, cost and environmental impact [26].

In view of this, we present the synthesis of three new ruthenium(II)-arene complexes where tri(2-furyl) phophine (PFu_3) has been utilized as co-ligand which has already shown remarkable impact in various transition metal based organic transformation [27]. The three new compounds $[RuCl_2(\eta^6\text{-arene})PFu_3,]$ **[Ru]-1**, $[RuCl(\eta^6\text{-arene})(PFu_3)(PTA)]BF_4$ **[Ru]-2** **[**PTA = 1,3,5-triaza-7-phosphaadamantane] and $[RuCl(\eta^6\text{-arene})(PFu_3)_2]BF_4$, **[Ru]-3** have shown excellent selective hydration of different nitrile derivatives to their corresponding amides using these complexes in aqueous media and relatively mild condition in open atmosphere with excellent yield.

Though ruthenium based organometallic complexes have been studied for organic transformation of nitrile to amide, there are only few reports where water soluble complexes act as homogeneous catalyst in aqueous medium. One such report has highlighted the use of PTA based ruthenium compounds for efficient hydrolysis of nitriles in water medium [19a].

Our research has been initiated for alternative phosphine based ligands, which in conjunction with ruthenium can be effective hydrolytic catalyst. Tris(2-furyl)phosphine (PFu_3) with additional electronegative heteroatoms is an automatic choice as it is reported to be poorer σ-donor and relatively easily dissociable, which may be the prerequisite for improved catalytic activity. The PFu_3 coordinated arene-ruthenium(II) complexes [$RuCl_2(\eta^6$-arene)PFu_3], **[Ru]-1** and [$RuCl(\eta^6$-arene)$(PFu_3)_2$]BF_4 **[Ru]-3** were achieved in excellent yield by the reaction of arene-ruthenium dimer [{(η^6-arene)$RuCl_2$}$_2$], with PFu_3 in methanol-dichloromethane solvent mixture. Furthermore, substitution of ruthenium bonded chloride in **[Ru]-1** with PTA furnished [$RuCl(\eta^6$-arene)(PFu_3)(PTA)BF_4] **[Ru]-2** in mild condition (Scheme S1 in ESI**).**

The orange-brown to red-brown coloured complexes **[Ru]-1-3** were characterized by ^{1}H, ^{13}C and ^{31}P NMR (Figs. S1-S9 in ESI) spectroscopy, elemental analysis and ESI-MS techniques (Figs. S10-S12 in ESI). ^{1}H NMR spectra of all the complexes, The ^{1}H NMR spectra of all the complexes showed the downfield shift of the protons of PFu_3 in comparison with the free uncoordinated ligand, which is consistent with the coordinated P-donor ligands to Ru centre. The ^{1}H NMR peaks for coordinated aromatic group upfield shift is also observed as expected. Compound **[Ru]-2** shows typical peaks for coordinated PTA ligand within the range 5.81-4.17 ppm [19a]. All the complexes were further structurally confirmed by single-crystal X-ray studies with the most suitable crystals of the synthesized complexes (Fig. 1, and Tables S1-S3 in ESI). The ruthenium centre exhibits pseudo-octahedral three legged piano-stool geometry in which the η^6-arene ring occupies apical position and remaining three positions are occupied by one phosphorus atom of ligand PFu_3 and two chloride ligand in **[Ru]-1**, one phosphorus atom of ligand PFu_3, one phosphorus atom of ligand PTA and one chloride ligand in **[Ru]-2** and two phosphorus atoms of two PFu_3 and one chloride ligand in **[Ru]-3**. The Ru-P bond distances for the coordinated PFu_3 are 2.3176(11) Å and 2.2998(9) Å in **[Ru]-1** and **[Ru]-2**, respectively. Compound **[Ru]-3** crystallizes in crystallographically two different units. The Ru-P bond distances in **[Ru]-3** for coordinated PFu_3 ligands are 2.333(4) Å and 2.306(5) Å in one unit whereas 2.330(4) Å and 2.302(4) Å in other. The Ru-P bond distance due to PTA coordination in **[Ru]-2** is 2.313(11) Å. The Ru-C bond distances are also comparable with other analogous complexes. The bond angles Cl(1)-Ru-P(1) (82.90(5)), Cl(1)-Ru-P(2) (90.23(4)), and Cl(1)-Ru-Cl(2) (87.38(6)), and those between the centre of the *p*-cymene ring and the legs, showed typical values for [$RuCl_2(\eta^6$-arene)(PFu_3)] species.



[Ru]-1 **[Ru]-2** **[Ru]-3**

Fig. 1. ORTEP diagram of the ruthenium(II)-arene complexes (50% probability thermal ellipsoids).

In the beginning, the hydration of nitriles into amides was investigated using ruthenium catalysts, **[Ru]-1-3**, in water under moderate reaction conditions. Benzonitrile was selected as a model substrate for its conversion into benzamide in the presence of synthesized arene-ruthenium(II) catalysts. In classical experiment, the ruthenium catalyst (different mol%) was added to the solution of benzonitrile (1 mmol) in water (3 mL) and the reaction was heated in an oil bath at desired temperature. The progress of the reaction was examined by taking regular samples and analysing by gas chromatography (GC). As depicted in Table S4, all the synthesized complexes were able to catalyse the hydration of benzonitrile to benzamide. Within the group of synthesized catalysts, the reaction of benzonitrile with **[Ru]-1** catalyst resulted in complete conversion with >99% selectivity for benzamide at 80°C in 4 h (Table S4, entries 6-10). The reaction mixture was analysed by ^{31}P NMR after 4 hrs which showed the presence of phosphorus of tri phenyl phosphine after the reaction (Fig. S13). Some traces of triphenyl phosphine and triphenyl phosphine oxide were observed in case of **[Ru]-3**, lowering the selectivity of **[Ru]-3** to amide. However, drastic decrease in the catalytic conversion of benzonitrile was observed when the temperature was decreased to 60°C or lower (Table 1, entries 1-5). Remarkably, complete conversion of benzonitrile to benzamide was attained at 80°C, which was able to produce benzamide quantitatively in only 4 h (Table S4, entry 8). However, with decrease in the amount of catalyst even after increasing time resulted in lower catalytic conversion of benzonitrile to benzamide (Table S4, entries 6, 7). As previously observed in case of certain Ruthenium(II)-arene complexes [12, 19a], in this case also no traces of benzoic acid were noticed by GC in the reaction mixtures with any catalyst.

In comparison with **[Ru]-1** catalyst, **[Ru]-2** and **[Ru]-3** catalysts appeared to be less effective (Fig.2), as the complete catalytic conversion of benzonitrile to benzamide was not attained with **[Ru]-2** or **[Ru]-3** catalysts even at 80°C for 12 h (Table S4, entries, 11-30). However, lower conversion and selectivity were observed with decrease in temperature (60°C). The efficiency of **[Ru]-1** was found to be much greater than other two catalysts under analogous conditions. Moreover, the time for completion of reaction can be reduced by increasing the temperature to 90°C or 100°C.

The Hg(0) is able to poison metal-particle heterogeneous catalysts and is extensively used test [28]. This test is carried out by adding Hg(0) to the reaction mixture. The decrease in catalytic activity by Hg(0) is an evidence for a heterogeneous catalyst and no significant change in the catalytic activity suggests homogeneous catalysis. We have performed the mercury poisoning test to understand whether the reaction is homogeneous or heterogeneous. The test was performed with catalyst **[Ru]-1** in the presence of excess Hg(0) (Table S4, entry 31). The results confirmed no significant decrease in the catalytic conversion of benzonitrile to benzamide, confirming no involvement of heterogeneous ruthenium nanoparticles/colloids and the hydration of nitrile was predominantly homogeneous in nature [28].

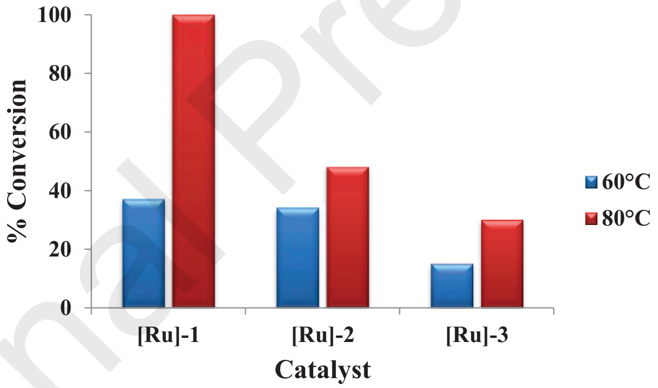


Fig. 2. Effect of temperature on the catalytic hydration of benzonitrile to benzamide by arene-ruthenium(II) catalysts. Reaction Conditions: benzonitrile (1.0 mmol), catalyst (3 mol%), T = 60°C (blue)/80°C (red) and water (3 mL).

The coordination of the substrate onto ruthenium(II) arene complexes involves Cl release from one Ru-Cl bond. In accordance with this, to explore the effect of unique structural benefits with **[Ru]-1** catalyst on its catalytic efficacy, catalytic activity of **[Ru]-1** was compared by using structurally similar ruthenium catalysts with PTA (**[Ru]-2**) and with another extra PFu_3 (**[Ru]-3**) ligands, in place of one of the two chlorides, for the catalytic hydration of benzonitrile using optimized reaction conditions. Interestingly, replacement of one chloride with PTA and PFu_3 in ruthenium catalysts **[Ru]-2** and **[Ru]-3**, respectively, resulted in noticeable decrease in the activity in the order of **[Ru]-1** > **[Ru]-2** > **[Ru]-3** for the catalytic hydration of benzonitrile to benzamide (as shown in Fig. 3 and Table S5 in ESI). These results clearly illustrated that replacement of the labile chloro group using bulky PTA in **[Ru]-2** or PFu_3 in **[Ru]-3** demonstrated significant decrease in the catalytic hydration suggesting dissociation of one of the attached chloro group during the reaction to deliver vacant sites for the coordination of nitrile (Fig. 3).

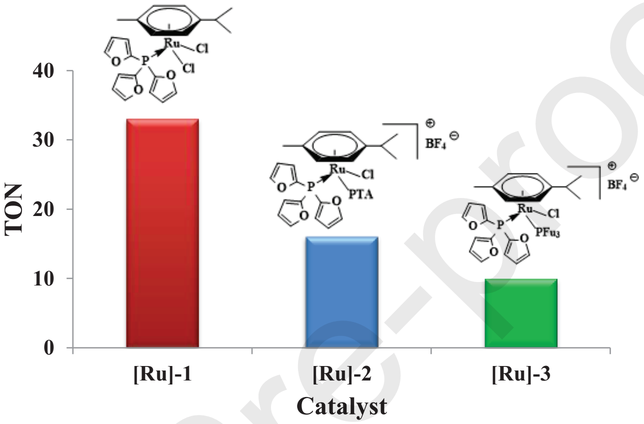
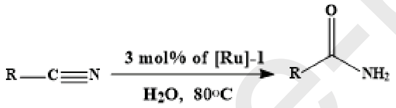


Fig. 3. Effect of the structure of catalyst on the catalytic hydration of benzonitrile to benzamide using different arene-ruthenium(II) catalysts. Reaction Conditions: benzonitrile (1.0 mmol), catalyst (3 mol%), T = 80°C and water (3 mL).

After getting encouraging results for **[Ru]-1** with benzonitrile, variety of nitriles having different substituents was subjected to the catalytic action of **[Ru]-1** using optimized reaction conditions. Selected results are depicted in Table 1. As detected for benzonitrile, which was transformed into benzamide with 99% GC yield after 4 h of heating (Table 1, entry 1), most of the other substituted nitriles could be converted to the corresponding primary amides in excellent yields after 2−24 h irrespective of their substitution arrangement and electronic nature.

A minor impact of the electronic property of the aromatic ring was observed, with substrates having electron-donating groups resulting in comparatively a low reactivity (e.g., entry 12 vs 13). A lesser efficient hydration (entry 8 vs 18) was observed in ortho substituted derivatives. Interestingly, no traces of the corresponding benzoic acid in any case were noticed by GC in the reaction mixtures. However, probably due to steric hindrance, ortho-substituted substrates displayed a lower reactivity compared to their meta- or para-substituted derivatives (e.g., 2 vs 11; 3 vs 5, 23; 7 vs 26, 14 or 8 vs 6, 18). Remarkably, the presence of common functional groups, like halide, hydroxyl, amino, nitro or ether was tolerated confirming the high potential of **[Ru]-1** for practical applications. It is worth to note about the conversion of nitrile even having thiomethyl group, since sulfur species form strong metal-sulfur bond which is a poison for homogeneous catalysts (entry 28 in Table 1) [29]. Thus, as detected for benzonitrile, substituted benzonitriles (e.g., entries 6-9, 12, 14, 18 and 19) having electron-withdrawing groups resulted in the corresponding amides in high yields and short reaction times. Chromatographic workup using silica gel and solvent removal gave pure samples of amides, which were identified by comparing their ^{1}H and ^{13}C NMR data with previously reported in the literature.

Table 1. Catalytic hydration of nitrile derivatives into corresponding amides by **[Ru]-1** in aqueous medium.



Entry	Substrate	Time (h)	Yield[a]/Sel. %	TOF(h^{-1})[b]
1	R=Ph	4	>99/>99	8.3
2	R=2-$C_6H_4NH_2$	24	44/>99	0.6
3	R=2-C_6H_4OH	8	>99/>99	4.2
4	R=2-Pyridyl	24	44/>99	0.6
5	R=3-C_6H_4OH	6	98/>99	5.4
6	R=3-C_6H_4Cl	4	>99/>99	8.3
7	R=2-C_6H_4Br	8	90/>99	3.7
8	R=2-C_6H_4Cl	8	92/>99	3.8
9	R=2-C_6H_4F	8	95/>99	3.9
10	R=3-Pyridyl	4	>99/>99	8.3
11	R=4-$C_6H_4NH_2$	8	>99/>99	4.2
12	R=4-$C_6H_4NO_2$	4	>99/>99	8.3
13	R=4-C_6H_4OMe	8	>99/>99	4.2
14	R=4-C_6H_4Br	2	>99/>99	16.6
15	R=2-C_6H_4Me	12	85/>99	2.4
16	R=4-C_6H_4BrMe	24	45/87	0.6
17	R=3-C_6H_4Me	4	>99/>99	8.3
18	R=4-C_6H_4Cl	2	>99/>99	16.6
19	R=3-C_6H_4F	6	>99/>99	5.5
20	R=4-C_6H_4CHO	24	86/98	1.2
21	R=4-C_6H_4COOH	8	90/98	3.7
22	R=4-C_6H_4Me	2	>99/>99	16.6
23	R=4-C_6H_4OH	2	>99/>99	16.6
24	R=4-Pyridyl	2	>99/>99	16.6
25	R=3-$C_6H_4NH_2$	4	>99/>99	8.3

26	R=3-C_6H_4Br	4	>99/>99	8.3
27	R=4-C_6H_4F	12	90/>99	2.5
28	R=4-C_6H_4SMe	24	89/97	1.2
29	R= -CH=CHPh	8	>99/>99	4.2
30	R=^{n}Propyl	2	>99/>99	16.6
31	R=Pyrazyl	4	98/>99	8.2
32	R=Me	2	>99/>99	16.6
33	R=^{n}Pentyl	2	>99/>99	16.6
34	R=piperonyl	2	>99/>99	16.6
35	R= 2-Pyrimidyl	2	>99/>99	16.6

Conditions: nitrile (1.0 mmol), catalyst (3 mol%), T = 80°C and water (3 mL). [a] Yield was determined by GC (uncorrected GC area). [b] Turnover frequency ((mol product/mol Ru)/time) was calculated at the time indicated in each case.

The extensive scope of the reaction was also evaluated by using another types of nitriles like heteroaromatic (entries 4, 10, 24, 31, 35), aliphatic (entries 30, 32, 33) and α, β-unsaturated (entry 29), which were all easily and completely hydrated with higher reactivity with respect to the previously reported examples [18, 19] Complex **[Ru]-1** was particularly found to be most effective in case of heteroaromatic nitriles. In addition, for this specific class of substrates, noticeable difference in activity was observed, based on the position of the heteroatom and the C=N unit. Notably, poor conversion of 2-cyanopyridine to picolinamide was observed at even after heating for 24 h with **[Ru]-1**. However, 3-cyanopyridine and 4-cyanopyridine were almost converted into nicotinamide and isonicotinamide, respectively, after only 2−4 h of heating (entries 10 and 24). Steric hindrance could be the possible reason for the difference in catalytic activity observed as in 2-cyanopyridine, 3-cyanopyridine and 4-cyanopyridine. Extremely fast reactions were witnessed in case of 3-pyrimidinecarbonitrile and pyrazinecarbonitrile (entries 31 and 35). In particular, hydration of pyrazinecarbonitrile resulted in pure anti-tuberculosis drug pyrazinamide in excellent yield. The catalyst **[Ru]-1** was also active for the hydration of aliphatic nitriles with good yields in 2 h only confirming the extensive scope of the catalytic hydration (entries 30, 32, 33). It is important to note that neither polymerization process nor hydration of C=C bond were observed in these reactions.

Studies on the conversion of nitrile derivatives into corresponding amides have been carried out particularly in inert atmosphere using N_2 or Ar gas. It should be noted that even after avoiding the use of any inert gas, we attained complete conversion of many nitriles into their corresponding amides with excellent yields in aqueous medium at 80°C using arene-ruthenium(II) complexes containing Phosphorus-donor, which is so far one of the best results obtained to the best of our knowledge [19]. A table comparing the data of similar results in water are included in the supplementary information (Table S6 in ESI).

Though there are various advantages of homogeneous catalysis, the recovery of catalyst from the reaction mixture has some limitations. However, due to good solubility of **[Ru]-1** in water during the catalytic process on heating, we were able to recover the catalyst easily from the reaction mixture and reuse in further hydration of nitrile without any substantial loss in the catalytic activity. After each catalytic run, the extraction of amides from the reaction mixture was carried out using suitable organic solvent, whereas catalyst persisted in the aqueous phase. After adding appropriate amount of distilled water to aqueous phase to make it 3 mL, it was further used for next catalytic run. In a typical run, 1 mmol of benzonitrile was further added to the aqueous phase and the reaction was carried out at optimized conditions. Fig. 4 shows an excellent recyclability of **[Ru]-1** for the hydration of nitrile to primary amide upto 4 catalytic runs without significant loss in the catalytic activity. A slight decrease in catalytic activity observed after individual catalytic run was due to the incompletion of catalyst recovery during the transfer of the aqueous phase, which was visible to the naked eye from the light yellow colour of the product.

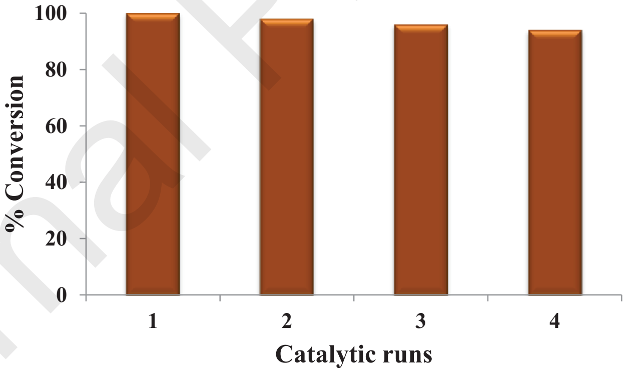


Fig. 4. Recyclability of **[Ru]-1** catalyst for the catalytic hydration of benzonitrile to benzamide. Reaction Conditions: benzonitrile (1.0 mmol), catalyst (3 mol%), T = 80°C and water (3 mL).

In summary, we have successfully explored the catalytic efficiency of arene-ruthenium(II) complexes bearing tri-(2-furyl)phosphine ligand, **[Ru]-1-3**, for the highly selective hydration of nitriles to their corresponding amides under challenging reaction conditions, *i.e.*, in an aqueous medium and open air atmosphere. Among the three complexes screened, **[Ru]-1** with two chloride and one PFu_3 ligands, was found to be the best for catalytic systems with high selectivity and conversion. The reaction has been carried out for a wide variety of substrates, including aromatic, heteroaromatic, aliphatic and α, β-unsaturated ones. The varied scope and great acceptance toward functional groups exhibited by the ruthenium catalyst **[Ru]-1,** make this catalytic process an attractive synthesis for the formation of amides avoiding the use of classical organic solvent and inert atmosphere. To the best of our knowledge, **[Ru]-1** is so far one of the most efficient ruthenium catalysts for the transformation of nitriles in aqueous medium and air atmosphere reported till date in the literature. Exploration of the catalytic efficiency of structurally analogues of arene-ruthenium(II) complex, highest efficiency of **[Ru]-1** catalyst revealed a unique structure-activity relationship. Due to the presence of two labile chloro groups, superior catalytic activity of **[Ru]-1** has been observed through dissociation of chloride ligand from coordination sphere. Moreover, the catalytic studies of ruthenium catalyst revealed high recyclability of the catalyst up to 4 runs. We anticipate that this study could offer insights toward the synthesis of simple yet efficient catalyst for the hydration of nitrile to precious amides and could be applicable to many other industrially important catalytic transformations.

Supporting Information

The supporting information includes experimental details, all spectral data as well as catalytic data and copies of NMR spectra of the synthesized amides. CCDC 1551675, 1840409 and 1840408 contain the supplementary crystallographic data for **[Ru]-1**, **[Ru]-2** and **[Ru]-3**, respectively. The crystallographic data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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- Three new arene-ruthenium(II) complexes with phosphine ligands have been prepared.
- All the complexes have been structurally identified using analytical and spectroscopic methods including single-crystal X-ray studies.
- The effectiveness of resulting complexes for selective hydration of different nitriles in aqueous medium and air atmosphere is explored.

Arene-Ruthenium(II)-Phosphine Complexes: Green Catalysts for Hydration of Nitriles Under Mild Conditions

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Graphical abstract