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ARTICLE

Water-soluble Superbulky (η^6-*p*-cymene) Ruthenium(II) Amine: Active Catalyst in Oxidative Homocoupling of Arylboronic Acids and Hydration of Organonitriles

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Phosphine free water-soluble superbulky amine-ruthenium-arene complex (**2**) encompassing 2,6-bis(diphenylmethyl)-4-methylaniline was synthesised in good yield. **2** was characterized by FT-IR, ^{1}H NMR, ^{13}C NMR spectroscopy, TGA and elemental analyses. Structure of **2** was confirmed by single-crystal X-ray diffraction study. The ruthenium centre in **2** adapts in the *pseudo*-octahedral geometry by η^6-*p*-cymene ring, bulky aniline ligand along with two chloro groups. Besides, the complex **2** was efficaciously employed as catalyst in hydration of organonitriles to amides. This reaction proceeds efficiently for a wide range of substrates in environmentally benign medium and economically reasonable synthetic route to the amides in good yield. In addition, **2** acts as excellent catalyst in oxidative homocoupling of arylboronic acid in water. A range of arylboronic acids undergoes a homocoupling reaction in the presence of catalyst **2** to yield the symmetrical biaryls in reasonable to good yield.

Introduction

Over the last few years, the organometallic compounds have been the subject of profound research due to their affirming applications in catalysis. The most classical compounds of this class, are the so-called "piano-stool" complexes encompassing the dimeric chloro bridges and arene ligands, such as cyclopentadienyl or *p*-cymene, have been explored by many research groups [1-4]. In particular, the half-sandwich complexes of ruthenium have engrossed a reputed position in organometallic chemistry due to their distinctive properties, the lenitive reaction conditions requisite for the synthesis and readiness to form stable complexes with an array of ligands under aqueous conditions [5,6]. Among the half-sandwich complexes, arene ruthenium complexes of the three-legged piano stool type have been recently acknowledged as building blocks for the construction of anticipated architectures due to their versatile applications in different fields of biological science as medicines as well as material science as catalysts [7-17]. Considering these points, the nature of chelating ligands and the leaving groups in these half-sandwich complexes greatly impact their chemical and biological activities and can demonstrate the structural activity relationship [18]. So, the structural adjustments of these organometallic compounds are probed currently, in order to endow a promising relationship between their structural and catalytic activities. Based on the above fact, the expansion of water-soluble arene-ruthenium complexes containing aniline ligands has aroused interest in recent years for various organic transformations [19a-c]. Moreover, these arene-ruthenium-aniline complexes have the capability to execute organic reactions in water, which is inexpensive, harmless and most importantly environment-friendly solvent [20-22]. Typically, anilines are deliberated as a weakly coordinating ligand, wields a considerable role to tune the activity of the catalyst. For instance, the phosphine-free [(η^6-arene)$RuCl_2$(aniline)] complexes exhibits similar or even higher activity than their structurally akin phosphine containing complex [(η^6-arene)$RuCl_2(PPh_3)$] [23-25,19a]. Sanjay *et al.,* have intended that being a simple σ-donor ligand, aniline ligands can form a stable mononuclear ruthenium complex, which is a structural analogue of [(η^6-arene)$RuCl_2(PPh_3)$], but in contradictory to PPh_3, aniline can be simply ectopic by incoming coordinating reactant molecule under catalytic reaction conditions [19c]. Inspirited by these findings, various aniline based ruthenium-arene complexes were accounted [19a-c]. These findings were indeed interesting, as electronic and steric properties of the aniline ligand can be easily fine-tuned by applying several substituents on the phenyl ring. Moreover, the subsequent complexes strategically showed high aqueous solubility and hence accorded an opportunity to accomplish the water-based catalytic reaction [19a].

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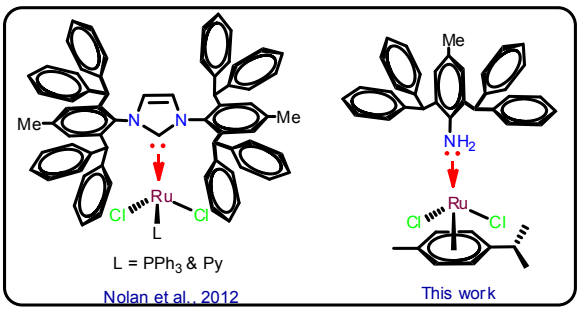


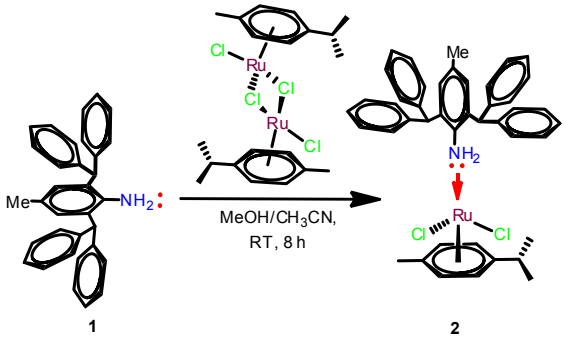
Scheme 1 Known super bulky ruthenium(II) supported by neutral donor ligands.

Motivated by the high activity of arene-Ru(II) complexes for innumerable organic transformations, we engrossed our efforts on developing a new highly flexible yet hindered neutral donor ligand. For example Nolan *et al.*, has isolated two different ruthenium catalysts, $[RuCl_2(IPr^*)(Py)(3\text{-phenylindenylidene})]$ and $[RuCl_2(IPr^*)(PPh_3)(3\text{-phenylindenylidene})]$ from 1,3- bis(2,6-bis(diphenylmethyl)-4-methylphenyl)imidazol-2-ylidene for ring closing and cross-metathesis (Scheme 1) [26]. As of our knowledge $[RuCl_2(IPr^*)(Py)(3\text{-phenylindenylidene})]$ is the only example to be demonstrated towards the effect of steric hindrance at four coordinated Ru(II) to assess influence of sterically encumbered phosphine free neutral donor ligand in catalysis. We believe that these sorts of hefty ligands may attune themselves against the entering substrates in the catalytic cycle [19d]. Thus, in this paper we have studied the impact of super bulky aniline ligand in Ru(II) mediated catalytic reactions. Surprisingly, the new water soluble superbulky 2,6-bis(diphenylmethyl)-4-methylaniline ruthenium(II)-arene complex acts as an efficient catalyst towards the oxidative homocoupling of arylboronic acids and hydration of nitriles in water.

Results and discussion

Synthesis and characterization of 2

The superbulky 2,6-bis(diphenylmethyl)-4-methylaniline ligand (**1**) was synthesized in excellent yield as previously described [28]. Treatment of latter (**1**) with $[RuCl_2(p\text{-cymene})_2]_2$ in a mixture of methanol and acetonitrile at room temperature afforded the targeted *pseudo*-octahedral bulky 2,6-bis(diphenylmethyl)-4-methylaniline ruthenium(II)-arene complex (**2**) of general formula $[(\eta^6\text{-}p\text{-cymene})\text{-}RuCl_2(C_6H_2(C_6H_5)_4CH_3NH_2)]$ in good yield (Scheme 2). The complex **2** was highly soluble in polar solvents such as water, methanol ethanol, chloroform and dichloromethane, whereas insoluble in hexane and petroleum ether. The identity of deep red complex **2** was confirmed by elemental analyses, IR, ^1H NMR and ^{13}C NMR spectroscopy. Stability of the **2** was accomplished by thermal gravimetric analysis (TGA) experiments (Fig. 1). The complex **2** exhibits four distinct thermograms. From the TGA curve, it is clear that the complex is stable up to 180 ˚C. After 180 ˚C the complex begins to decompose. The decomposition ends at 700 °C with 14.5 % of initial mass, which corresponds to residual ruthenium metal (Calcd. mass =101.01 g mol^{-1}; mass found = 108 g (calculated for 1 mol)). Moreover, the complex is air stable and no decomposition or structural change of this complex was observed on exposure to air.



Scheme 2 Synthesis of ruthenium-arene complex $[(\eta^6\text{-}p\text{-cymene})\text{-}RuCl_2(C_6H_2(C_6H_5)_4CH_3NH_2)]$ (**2**).

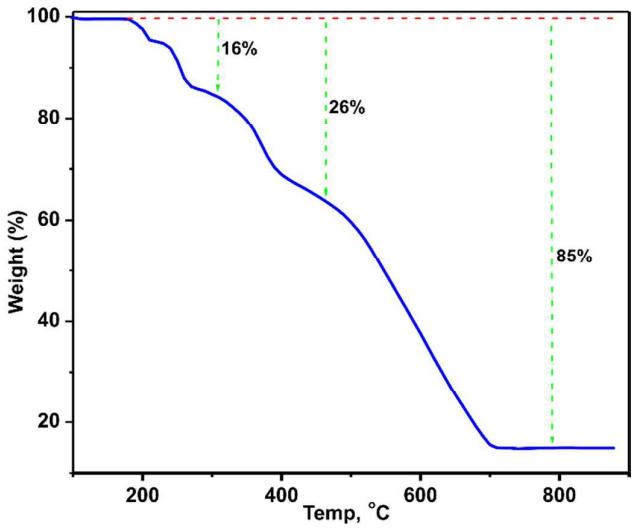


Fig. 1 TGA curve **2** from 100 to 880 °C under a nitrogen atmosphere with a heating rate of 10 °C min^{-1}.

The ^1H NMR spectrum of complex **2** was recorded in deuterated chloroform. The NMR spectrum contains sharp signals in the expected regions, thus ruling out molecular functionality. As the aniline ligand is coordinated to ruthenium, the complex displayed a downfield shift for the protons of aniline ligand as expected. Signals corresponding to aromatic protons of complex **2** were observed from 7.30–6.72 ppm which can be compared to the signals appeared from 7.34–6.48 ppm for the bulky 2,6-bis(diphenylmethyl)-4-methylaniline (**1**). Moreover, a doublet is present for the ruthenium bound η^6-*p*-cymene ring in the range of 5.41–5.26

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ppm. The isopropyl methyl groups resonate at 1.20-1.17 ppm. Analogously, the NH_2 protons resonate at 4.87 ppm as a broad singlet. The -CH_3 protons were observed at 2.11–2.07 ppm, respectively. In the ^{13}C NMR of complex **2**, η^6-*p*-cymene resonates in the region 128.09-126.31 ppm ($CDCl_3$). The peak appeared between 142.60 and 120.81 ppm was attributed to aromatic carbons. The C-N carbon appears at 143.43 ppm and -CH(Ph_2) carbon emerged at 51.80 ppm. In addition, the methyl carbons are resonating in the region 22.16-18.96 ppm.

X-ray crystal structure description of complex 2

The molecular structure of the adumbrative arene-ruthenium(II) amine complex (**2**), was firmly established by the single-crystal XRD analysis of the most congruous crystals developed from a sluggish evaporation of methanol−acetonitrile saturated solution of the complex **2**. X-ray crystallography analyses proclaim **2** crystallize in the triclinic crystal system with *Pī* space group and two complex units residing at the unit cell. The molecular structure, space filling model and packing diagram of **2** are portrayed in figure 2. An elaborated crystal refinement data is collated in table 1, and the selected bond distances and angles of **2** were listed in table 2.

Table 1 Crystal data and structure refinement parameters for complex **2**.

	2
Empirical formula	$C_{43}H_{43}Cl_2NRu$
Formula weight	745.80
T (K)	295
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	*Pī*
Unit cell dimensions	
a (Å)	7.8768(12)
b (Å)	13.917(2)
c (Å)	17.713(3)
α (°)	104.199(4)
β (°)	93.373(4)
γ(°)	105.059(4)
Volume (Å^3)	1802.1 (5)
Z	2
Density (calculated) Mg m^{-3}	1.3743
Absorption coefficient mm^{-1}	0.615
F(000)	770.3401
Scan range for data collection (deg)	3.3831 to 71.0327
Index ranges	-10< = h< = 10 -17< = k< = 17 -22< = l< = 22
Reflections collected/unique, R_{int}	46323/7965/0.0299
Completeness to $theta_{max}$	1
Data/restraints/parameters	7965/0/4298
Goodness-of-fit on F^2	1.0488
Final R indices [I >2σ(I)][a]	R_1 = 0.0299 wR_2 = 0.0827
R indices (all data)	R_1 = 0.0346, wR_2 = 0.0871

[a]Structures were refined on F_o^2: $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$, where $w^{-1} = [\sum(F_o^2) + (aP)^2 + bP]$ and $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

It is clear that the bulky 2,6-bis(diphenylmethyl)-4-methylaniline coordinated to the ruthenium by the nitrogen atom, as akin to the formerly reported arene-ruthenium(II) amine complexes [19a-19c, 27, 29]. As shown in figure 1, the ruthenium centre in **2** is tailored to the *pseudo*-octahedral geometry. The η^6-*p*-cymene ring engaged in the pinnacle position and the bulky aniline ligand along with two chloro groups engrossed the three legs, correspondingly. The η^6-*p*-cymene ring in **2** remains planar and the ruthenium centre is at ectopic by 1.66 Å from the centroid of the η^6-*p*-cymene ring.

Table 2 Selected bond lengths (Å) and bond angle (°) for complex **2**.

	Bond lengths (Å)		
Ru(1)-Cl(1)	2.411(6)	Ru(1)-C(35)	2.193(2)
Ru(1)-Cl(2)	2.408(7)	Ru(1)-C(36)	2.202(2)
Ru(1)-N(1)	2.193(15)	Ru(1)-C(37)	2.172(2)
Ru(1)-C(33)	2.199(2)	Ru(1)-C(38)	2.157(2)
Ru(1)-C(34)	2.187(2)	N(1)-C(1)	1.446(2)
	Bond Angle (°)		
Cl(2)-Ru(1)-Cl(1)	86.47(3)	N(1)-Ru(1)-Cl(1)	81.94(4)
N(1)-Ru(1)-Cl(2)	81.31(4)		

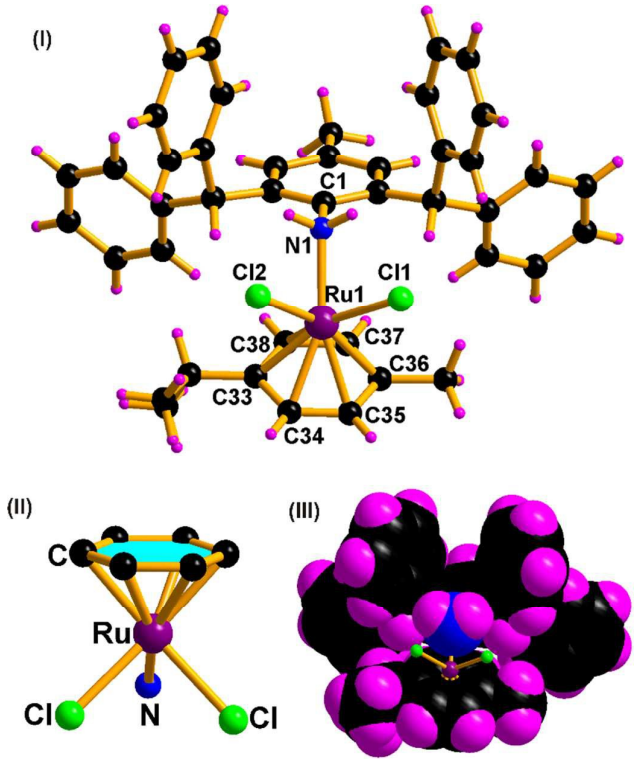

Fig. 2 (I) The solid state structure of **2**. (II) The coordination environment of Ru(II) in **2**. (III) The space filling model of **2**.

Noteworthy that the ruthenium-nitrogen bond length (2.193 Å) is moderately higher for this sterically crowded 2,6-bis(diphenylmethyl)-4-methylaniline encompassing complex **2**, than those for earlier reported similar type complexes [19a-19c]. The phenyl ring of bulky 2,6-bis(diphenylmethyl)-4-methylaniline ligand was located beyond to the metal centre,

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as described from the C(1)-N(1)-Ru(1) bond angle of 121.83° for the complex **2** [19c, 30, 31, 32]. Angles between the legs, Cl(2)-Ru(1)-Cl(1) (86.47°), N(1)-Ru(1)-Cl(1) (81.94°), and N(1)-Ru(1)-Cl(2) (81.31°) for the complex **2** are nearest to those of proclaimed earlier [19a, 19c, 27, 19b, 29]. Notably, the space-filling model of **2** confirms the presence of substituted bulky phenyl rings in the *ortho* position, which in principle should allow the complex to acclimate themselves for the incoming catalytic substrates without much hurdle (Fig. 2) [19d]. In addition, complex **2** contains intermolecular hydrogen bond through C–H· ···Cl and C–H···Ru, respectively (Fig. 3).

Catalytic hydration of organonitriles

Hydration of organonitriles is the most straightforward approach to produce primary amides with a good atom economy. Generally, the hydration reaction was performed under harsh reaction condition and tedious workup procedures. Several transition metal complexes (e.g. Ni, Pt, Rh, Ir, Mo, Au and Ru) have been demonstrated as good catalyst for hydration of nitrile [33-47]. Among them, ruthenium based metal complexes are highly active for nitriles hydration [43-47,48]. Therefore, the ligand effect on the catalytic hydration nitriles has been studied [49,50]. Recently, water was used as the reaction medium by the replacement of organic solvents [40,47,51,52]. Gimeno and his co-workers have reported the half-sandwich ruthenium(II) species $[RuCl_2(\eta^6\text{-arene})(L)]$, containing the hydrosoluble phosphorus donor ligands PTA (1,3,5-triaza-7-phosphatricyclo[3.3.1.13,7]decane), PTABn (1-benzyl-3,5-diaza-1-azonia-7-phosphatricyclo[3.3.1.13,7]decane chloride) and DAPTA (3,7-diacetyl-1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane) are acts as an excellent catalysts for the selective hydration of organonitriles to amides [53-55]. Later, the Gimeno *et al.*, reported the chloro-bridged bis(allyl)-ruthenium(IV)dimer $[\{RuCl(\mu\text{-}Cl)(\eta^3{:}\eta^3\text{-}C_{10}H_{16})\}_2]$ ($C_{10}H_{16}$ = 2,7-dimethylocta-2,6-diene-1,8-diyl) catalyst to catalyze the selective hydration of organonitriles [56]. Oshiki and Breit and their co-workers have proposed the cooperative effect on hydration process through a bifunctional catalysis mechanism, in which, metal acts as a Lewis acid to activate the nitrile, while the nitrogen-containing ligand acts as a Lewis base for the attack of water through hydrogen bonding [57,50]. Therefore, in light of the above, we report here the phosphine-free water soluble bulky 2,6-bis(diphenylmethyl)-4-methylaniline ruthenium(II)-arene complex. Interestingly the catalyst is highly active for the hydration of organonitriles to corresponding amides at a lower temperature, under aqueous-aerobic conditions.

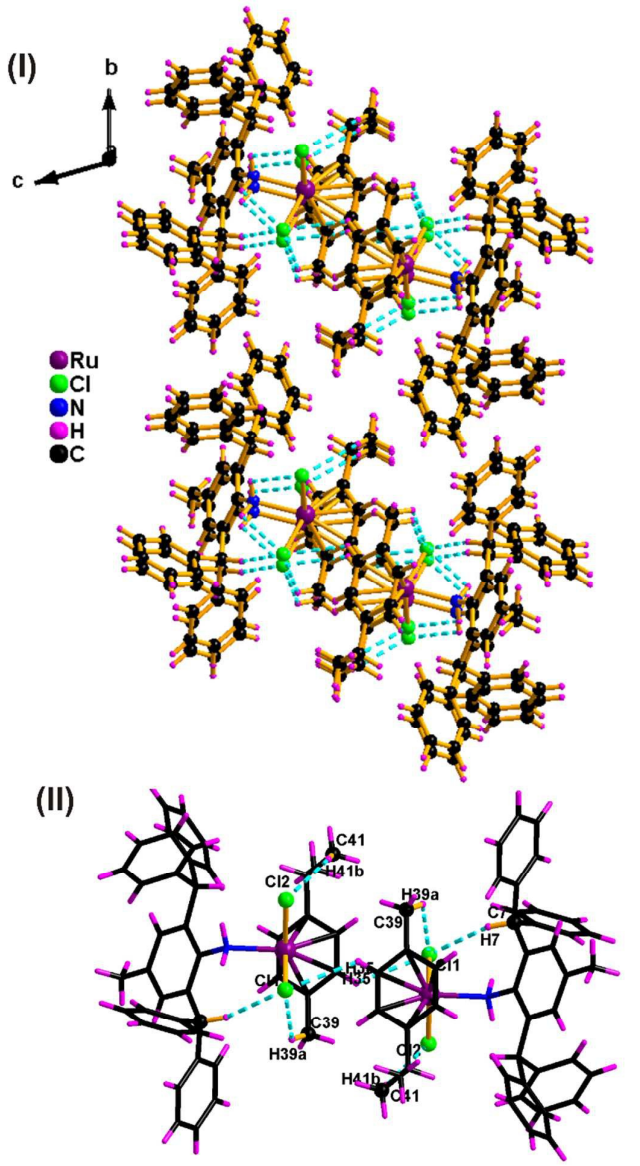

Fig. 3 (I) The solid state packing of **2**. (II) The hydrogen bonding network in **2**.

For the better optimizing condition, the hydration of benzonitrile was chosen as the model reaction. Figure 4 summarizes the influence of catalyst loading and reaction time on the hydration reaction. The reactions were performed by changing the quantity of the catalysts ranging from 1 to 5 mol %. The results revealed that the rate of the catalytic reaction is influenced by the catalyst loading, which is in connection with the reaction time and the production yield. The catalytic loading of 4 mol % is found to be the optimized amount of catalyst to perform the catalytic reaction. No significant increase in the rate and thereby the efficiency of the reaction is observed on further raise of catalyst loading upto 5 mol % and even after a prolonged time (Fig. 4).

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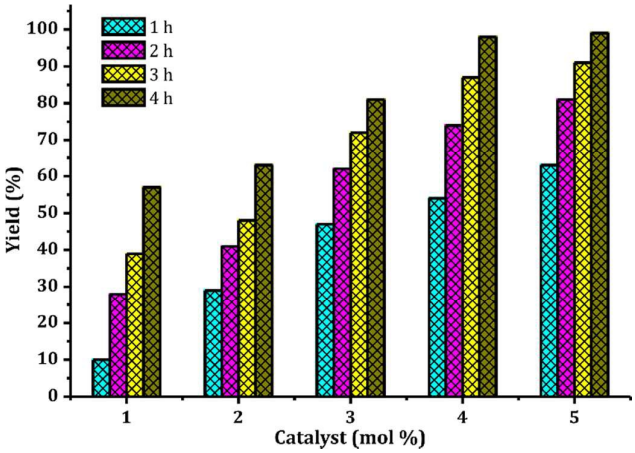

Fig. 4 Effect of catalyst mol % (1 – 5 mol %) with respect to time (1 – 4 h) on hydration of benzonitrile to benzamide.

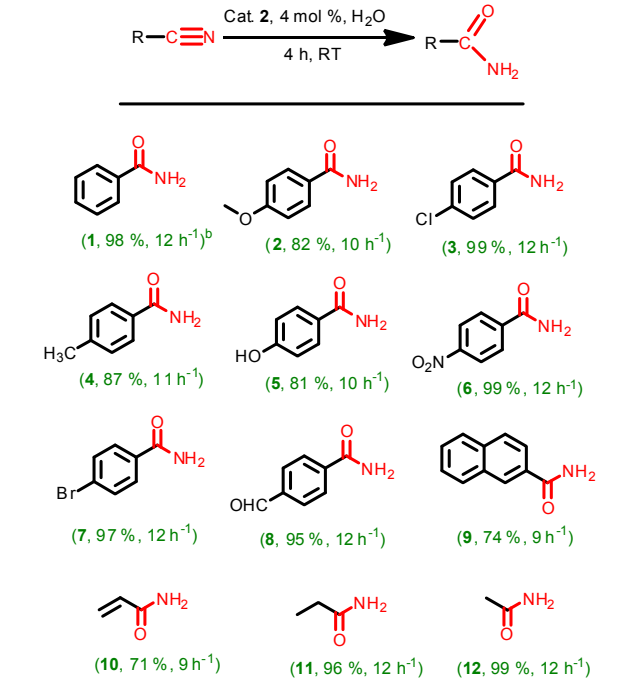

Chart 1 Hydration of organonitriles catalyzed by bulky arene-ruthenium(II)-amine complex **2**. [a]Reaction Conditions: Nitrile (1 mmol), water (5 mL), catalyst loading (4 mol %), time (4 h) at room temperature. [b]Entry number, isolated yield (%) and TOF (h^{-1}) was given in brackets. Turnover frequency ((mol product/mol Ru)/time).

In order to extend the scope of the present catalytic system, the hydration reaction was carried out under optimized conditions on different nitriles possessing various functionalities. Chart 1 summarizes the catalytic activity of 4 mol % **2** on various nitriles at ambient temperature under aqueous and aerobic condition. The reaction time is fixed for 4 h for all the nitriles under investigation. Benzonitriles encompassing electron donating groups gets hydrated efficiently to furnish the corresponding amides in excellent yield (Chart 1, Entries 2, 4 and 5). Furthermore, the benzonitriles incorporating electron withdrawing groups furnished the desired amides with good yield (Chart 1, Entries 3, 6, 7 and 8). The 2-cyanonaphthalene gives the corresponding amide in moderate yield around 74 % (Chart 1, Entry 9). Hydration of acrylonitrile to acrylamide has been efficiently emanated, which is a very significant conversion in industrial point of view (Chart 1, entry 10). The present protocol also effectively hydrates the aliphatic nitriles (Chart 1, Entries 11 and 12). Notably, the TOF of present system is better than the reported TOF for ruthenium complexes [58].

In addition, we have examined the current catalytic system for hydration of heteroaromatic nitriles under the prior optimized conditions. The formation of amide product for this type was quite interesting, and no such reports exist in the water soluble bulky ruthenium-arene-amine catalysis. The results are summarized in chart 2. Surprisingly, the heteroaromatic nitriles containing sulphur, oxygen and nitrogen has been efficaciously transformed to the corresponding amides within 4 h at ambient temperature, and no concomitant carboxylic acids were identified (Chart 2, Entries 1-7). The hydration of isonicotinonitrile and nicotinonitrile afforded the corresponding amides in 97-99 % yield (Chart 2, Entries 1 and 2). Even, 3-quinolinecarbonitrile was hydrated within 4 h, and gives the corresponding 3-quinolinecarboxamide in 93 % yield (Chart 2, Entry 3), which is usually carried out in 12 h to 24 h [59a]. Noteworthy that the pyrazine carboxamide, a drug against tuberculosis was produced in 96 % yield (Chart 2, Entry 4). Subsequently, the hydration of 2-furancarbonitrile and 2-thiophenecarbonitrile underwent smoothly to provide the amide product in 96-98 % yield (Chart 2, Entries 5 and 6). To our delight, the sterically hindered ethyl 2-chloro-3-cyano-6-methyl-5-nitrosoisonicotinate hydrated well under our optimized condition and furnishes 79 % of 2-chloro-4-(ethoxycarbonyl)-6-methyl-5-nitroso-3-pyridine carboxamide (Chart 2, Entry 7). Interestingly, the isolated yield under the present synthetic methodology is more convenient and energy efficient than the most efficient (isolated 94 %) catalytic route demonstrated using MnO_2 under very high pressure (100 psi) and high temperature (60 °C) [59b].

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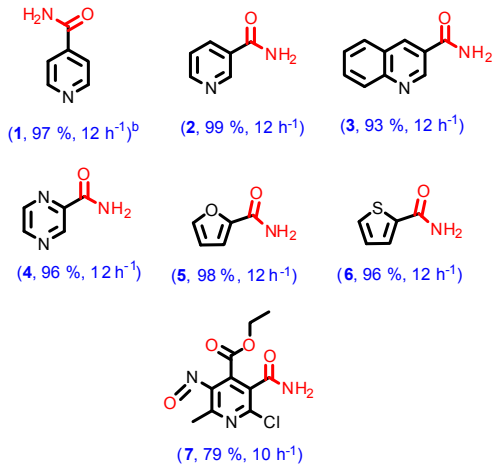
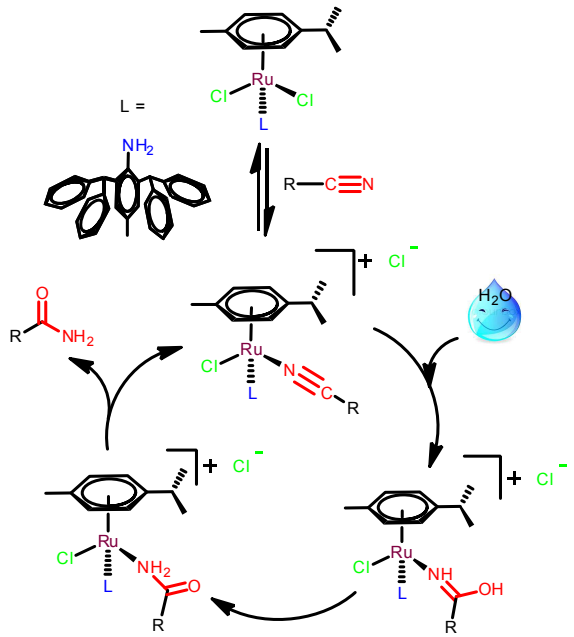


Chart 2 Hydration of heteroaromatic nitriles catalyzed by bulky arene-ruthenium(II)-amine complex 2. [a]Reaction Conditions: Heteroaromatic nitrile (1 mmol), water (5 mL), catalyst loading (4 mol %), time (4 h) at room temperature. [b]Entry number, isolated yield (%) and TOF (h^{-1}) was given in brackets. Turnover frequency ((mol product/mol Ru)/time)

On the basis of the above results and also in conformity with previous literature reports [60], we trust that the catalytic nitrile hydration of bulky 2,6-bis(diphenylmethyl)-4-methylaniline ruthenium(II)-arene catalyst follows three steps (Scheme 3). Step 1: coordination of the nitrile to the ruthenium centre. Step 2: Then, formation of α-hydroxyimide by the intermolecular nucleophilic attack of water on the nitrile and step-3: dissociation of the amide product.



Scheme 3 Proposed general mechanism for **2** catalyzed hydration of nitriles.

Oxidative homo-coupling of arylboronic acids

For our initial catalytic investigation, the homo-coupling of phenylboronic acid in the presence of **2** was fixed as the model reaction in water at room temperature and the results are depicted in figure 5. In order to assess the crucial function of base in advancing the generation of intermediates all along the catalytic cycle, the effect of bases on the desired homocoupling reaction was studied by various bases such as K_2CO_3, Na_2CO_3, K_3PO_4, Cs_2CO_3 and NaOAc. Among the bases employed, K_3PO_4 was found to be the best and led to higher yield for this reaction at room temperature. To make sure the catalytic role, a control experiment was executed without the base or the catalyst. As expected, there was no reaction even after an extended reaction time. The catalytic loading of 4 mol % is found to be the optimized amount of catalyst to perform the catalytic reaction. No significant increase in the rate and thereby the efficiency of the reaction is observed on further raise of catalyst loading to 5 mol %. In the latest reports, akin catalytic reaction was executed at 70 °C using K_2CO_3 base in water/methanol mixture and $Cu(OAc)_2$ as additive [19a]. In order to decreases the reaction temperature, we treated the phenylboronic acid with K_3PO_4 base and $Cu(OAc)_2$ additive in water at room temperature and without any inert gas fortification and in the presence of 4 mol % of catalyst **2**.

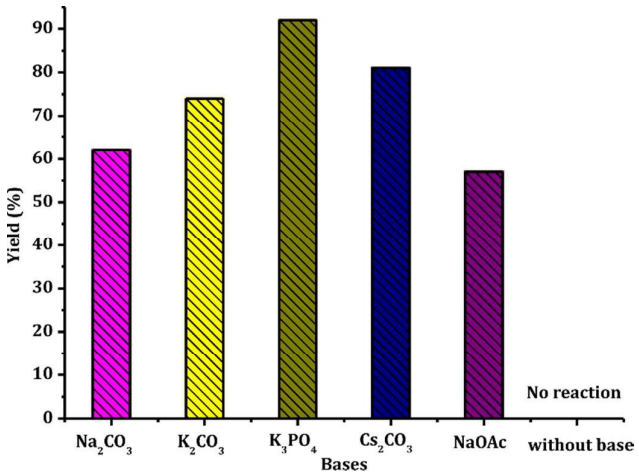


Fig. 5 Effect of the base (NaOAc, K_2CO_3, Cs_2CO_3, K_3PO_4 and Na_2CO_3) on homocoupling of biphenyl.

In order to decreases the reaction temperature, we treated the phenylboronic with K_3PO_4 base and $Cu(OAc)_2$ additive in the presence of 4 mol % of catalyst **2** in water at room temperature under aerobic condition. In order to explicate the role of $Cu(OAc)_2$, we did the controlled experiments by varying the amount of $Cu(OAc)_2$ (0.1–1.5 equiv.) (Table 3, Entries 1-11). Results inferred that a lower content of $Cu(OAc)_2$ gave poor yield of biphenyl (Table 3, Entries 1, 2, 3). There is no conversion of biaryls was observed for the reaction performed in the absence of base (Table 3, Entry 7). Notably, the reactions performed without additive $Cu(OAc)_2$ resulted in

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moderate yield (61 %, Table 3, Entry 8). Moreover, the $Cu(OAc)_2$ additive in the absence of O_2 (under N_2 atm) did not give better results (Table 5, Entry 10). Awfully, the complex **2** endows a good yield (92 %) of biphenyl, implying the vital role of $Cu(OAc)_2$ as an oxidant to restore the Ru(II) species and impede catalyst decomposition during the catalytic cycle (Scheme 5) [61]. However, the $Cu(OAc)_2$ is an efficient oxidant in this transformation. Additionally, the results indicate that the aerial oxygen is a very active partner to render an efficient Cu/O_2 oxidative system. Complex **2** shows excellent stability in an aerobic environment. This may be due to the presence of super bulky aniline at ruthenium centre. Hence, we carried out all the catalytic reactions under aerobic circumstances. With these novel features, the present catalytic system is much better than the known protocols documented in the literature [19a, 62, 61i, 61j, 61n].

With a dynamic catalyst in hand and unswerving reaction conditions are identified. Consequently, we examined the scope of various arylboronic acids that undergoes the oxidative homocoupling reactions. The results are collated in chart 3 from which we can find that all the reactions take place gently and furnished the corresponding biphenyls in moderate to good yield (Chart 3, Entries 1-10). Results confirmed that having sterically bulky 2,6-diphenylmethane aniline ligand, **2** afforded the moderate to good yield of biarlys in 4 h as compared to the earlier reported catalytic systems containing aniline ligand [19a]. Catalyst **2** is able to endure the range of functional groups and substitutions like methyl, ethyl, methoxy, chloro, bromo, trifluoro methyl, and thiophene (Chart 3, Entries 1-10). Conversely, electron withdrawing group substituted phenyl boronic acids were fruitfully transformed to the corresponding products in excellent yields (Chart 3, Entries 2, 3 and 8). The *p*-C_2H_5-substituted phenylboronic acid furnishes 82 % yield for 4,4'-diethyl-1,1'-biphenyl (Chart 3, Entry 7). The electron donating phenylboronic acids afforded the desired biphenyls in good yields (Chart 3, Entries 4, 5 and 6). Similarly, the (4-trifluoromethyl)phenylboronic acid homocoupled gave the expected biaryl in very good yield (Chart 3, Entry 9). Thiophen-3-yl boronic acid also fruitfully achieved the moderate yield of desired biaryl in 4 h (Chart 3, Entry 10).

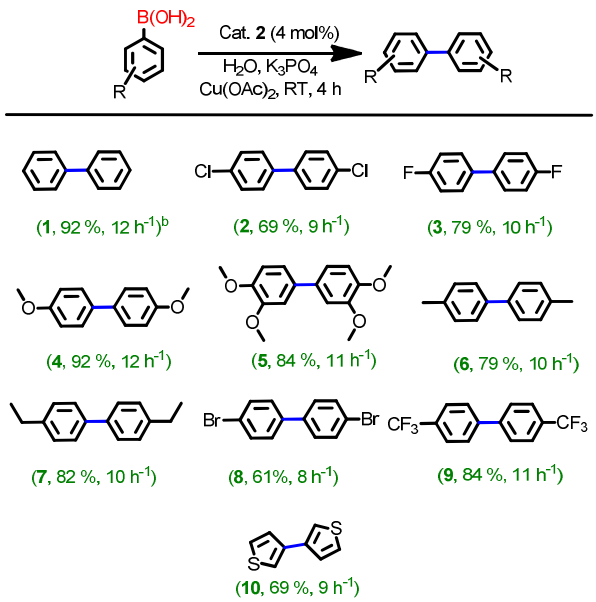
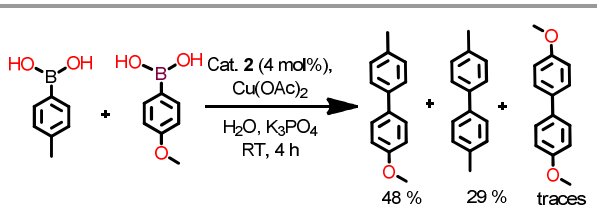


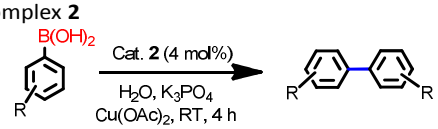
Chart 3 Homocoupling of arylboronic acids catalyzed by bulky arene-ruthenium(II)-amine complex **2**. [a]Reaction conditions: arylboronic acid (1 mmol), K_3PO_4 (2 mmol), $Cu(OAc)_2$ (1.5 mmol), water (5 mL), catalyst loading (4 mol %), time (4 h) at room temperature. [b]Entry number, isolated yield (%) and TOF (h^{-1}) was given in brackets. [c] Turnover frequency ((mol product/mol Ru)/time).

With the purpose of ensuring the flexibility of our catalyst, we have studied the chemoselectivity of coupled products between two different arylboronic acids (Scheme 4). Under the optimized reaction condition, the reaction was carried out using an equimolar amount of two different arylboronic acids. The selectivity towards the cross- and homocoupled biaryls was confirmed by ^1H NMR. Results proved that the reaction of 4-methoxyphenylboronic acid with 4-methylphenylboronic shows the higher selectivity of 4-methyl-4'-methoxy-1,1'-biphenyl cross-coupled product (48 % for 4-methyl-4'-methoxy-1,1'-biphenyl) together with the homocoupled products of both of the arylboronic acids.



Scheme 4 C–C coupling reactions of different arylboronic acids by **2**.

Table 3 Effect of additive and oxidant on Homocoupling of arylboronic acids catalyzed by bulky arene-ruthenium(II)-amine complex **2**



Entry	Base	Additive	Oxidant	Time	Yield (%)[g]

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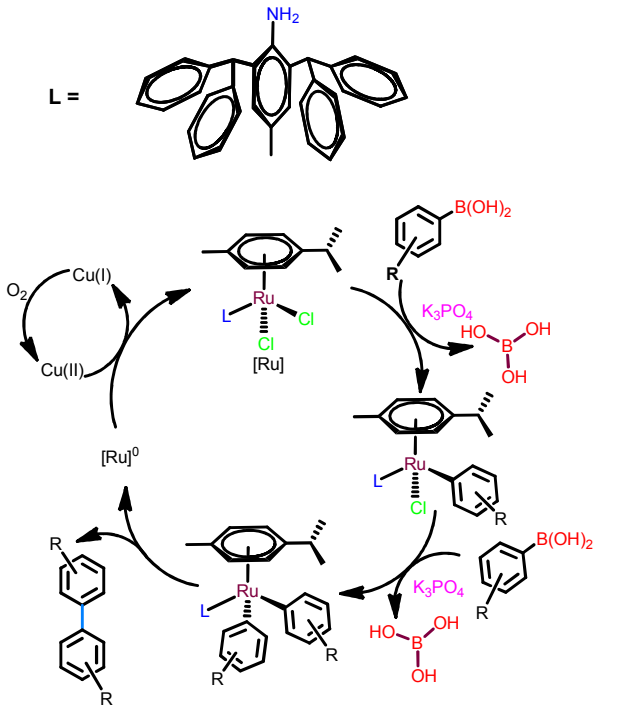
1[a]	K_3PO_4	$Cu(OAc)_2$ (0.1 equiv.)	O_2	8 h	17 %
2[a]	K_3PO_4	$Cu(OAc)_2$ (0.4 equiv.)	O_2	8 h	28 %
3[a]	K_3PO_4	$Cu(OAc)_2$ (0.8 equiv.)	O_2	8 h	46 %
4[a]	K_3PO_4	$Cu(OAc)_2$ (1.2 equiv.)	O_2	8 h	77 %
5[a]	K_3PO_4	$Cu(OAc)_2$ (1.5 equiv.)	O_2	4 h	92 %
6[a]	K_3PO_4	$Cu(OAc)_2$ (1.5 equiv.)	O_2	12 h	94 %
7[b]	-	$Cu(OAc)_2$ (1.5 equiv.)	O_2	4 h	No reaction
8[c]	K_3PO_4	-	O_2	4 h	61 %
9[d]	K_3PO_4	-	O_2	8 h	No reaction
10[e]	K_3PO_4	$Cu(OAc)_2$ (1.5 equiv.)	-	4 h	58 %
11[f]	K_3PO_4	$Cu(OAc)_2$ (1.5 equiv.)	O_2	4 h	32 %

[a] Arylboronic acid (1 mmol), water (5 mL), K_3PO_4 (2 mmol), $Cu(OAc)_2$ (1.5 mmol), catalyst loading (4 mol %), time (4-12 h) at room temperature. [b] Without base. [c] Without additive. [d] Without catalyst and additive. [e] Arylboronic acid (1 mmol), water (5 mL), K_3PO_4 (2 mmol), $Cu(OAc)_2$ (1.5 mmol), catalyst loading (4 mol %), time (4 h) at room temperature under N_2 atm. [f] Without catalyst, arylboronic acid (1 mmol), water (5 mL), K_3PO_4 (2 mmol), $Cu(OAc)_2$ (1.5 mmol), time (4 h) at room temperature. [g] Isolated yield.

On the basis of earlier literature report [19a], we believe that the bulky ruthenium(II)-arene-amine complex forms a σ-aryl-Ru(II) intermediate by the reaction of aryl boronic acid (Scheme 5). We consider that this may be due to the presence of the bulkier diphenylmethane substituents on the *ortho* positions of phenyl ring (of amine ligand) pushes out the chloride ligand and thereby easily forms the vacancy on the ruthenium complex. This vacancy allowed the complex to accommodate the catalytic substrate to initiate the catalytic cycle. Afterwards, the second molecule of arylboronic acid coordinates with the latter intermediate to form a new transmetalated di(σ-aryl)-Ru(II) intermediate. In the final step, the biaryl was produced *via* the reductive elimination of di(σ-aryl)-Ru(II) intermediate with the generation of the Ru^0 species, which can be reoxidized to restore the active ruthenium species Ru^{II} by the Cu(II)/aerial O_2 oxidative system to complete the catalytic cycle [19a].



Scheme 5 Proposed general mechanism for **2** catalyzed homocoupling of arylboronic acids.

Experimental

Materials and methods

All reactions involving the synthesis of metal complex were carried out in oven dried glassware with magnetic stirrer and without inert gas protection. All commercial chemicals were used as purchased. 2,6-bis(diphenylmethyl)-4-methylaniline [28] and $[(p\text{-cymene})RuCl_2]_2$ were prepared according to the earlier proclaimed methods [63]. FT-IR measurement (neat) was carried out on a Bruker Alpha-P Fourier transform spectrometer. Microanalyses of carbon, hydrogen and nitrogen were carried out using a Euro EA - CHNSO Elemental Analyzer. NMR spectra were recorded on Bruker Ultrashield-400 spectrometers at 25 °C unless otherwise stated. Chemical shifts are given relative to TMS and were referenced to the solvent resonances as internal standards.

Synthesis of of $[(\eta^6\text{-}p\text{-cymene})\text{-}RuCl_2(C_6H_2(C_6H_5)_4CH_3NH_2)]$ complex (2)

The methanolic solution of $[RuCl_2(p\text{-cymene})_2]_2$ (0.044 g, 0.1 mmol) was added to the solution of **1** (0.0612 g, 0.1 mmol) made in CH_3CN (4 mL). The mixture was stirred for 8 h at room temperature. The resulting deep red solution was filtered and kept for crystallization. Single crystals of **2** suitable for X-ray diffraction were obtained in a mixture of CH_3OH and CH_3CN (v/v, 1:1). Yield: 76% (based on **1**). Anal. Calcd for $C_{43}H_{43}NCl_2Ru$: C, 69.25; H, 5.81; N, 1.88 %. Found: C, 69.49; H, 5.56; N, 1.68 %. FT-IR (cm^{-1}, neat): 3039(w), 2958(m), 2148(m),

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2004(w), 1734(w), 1445(m), 1256(s), 1080(m), 1014(s), 868(m), 793(s), 691(m). ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.30-7.28 (d, *J* = 7.2 Hz, 2H, Ar-*H*), 7.21 (s, 2H, Ar-*H*), 7.15-7.11 (m, 2H, Ar-*H*), 7.07-7.05 (d, *J* = 8 Hz, 2H, Ar-*H*), 7.04-7.01 (d, *J* = 10 Hz, 4H, Ar-*H*), 7.006-6.99 (d, *J* = 4.8 Hz, 2H, Ar-*H*), 6.98-6.97 (d, *J* = 6 Hz, 2H, Ar-*H*), 6.76 (s, 2H, Ar-*H*), 6.74-6.72 (t, 2H, Ar-*H*), 5.41-5.39 (d, *J* = 9.6 Hz, 2H, Ar-*H*), 5.33 (s, C*H*, 2H), 5.28-5.26 (d, *J* = 8 Hz, 2H, Ar-*H*), 5.05 (bs, 2H, NH_2), 2.87-2.80 (s, CH, 1H, C*H*(CH_3)$_3$), 2.11 (s, 3H, CH_3), 2.07 (s, 3H, CH_3), 1.20-1.17 (d, 6H, (CH(CH_3)$_2$). ^{13}C NMR (100 MHz, DMSO-d_6) *δ*: 143.43 (C-N), 142.60 (Ar-*C*), 141.49 (Ar-*C*), 139.31 (Ar-*C*), 133.76 (Ar-*C*), 130.90 (Ar-*C*), 130.27 (Ar-*C*), 130.04 (Ar-*C*), 129.76 (Ar-*C*), 128.29 (Ar-*C*), 128.09 (Ar-*C*), 126.93 (Ar-*C*), 126.50 (Ar-*C*), 126.44 (Ar-*C*), 126.31 (Ar-*C*), 120.81 (Ar-*C*), 51.80 (CH(Ph_2)) 30.77 (CH), 22.16 ((CH_3)$_2$), 18.96 (CH_3).

General procedure for the homocoupling of arylboronic acids to form biaryls

The arene-ruthenium- catalyzed homocoupling of arylboronic acids was carried out according to the previously reported method [19a]. To a mixture of arylboronic acid (1 mmol), tri-potassium phosphate (0.425 g, 2 mmol) and Cu(OAc)$_2$ (0.300 g, 1.5 mmol), [Ru]-catalyst **2** (0.029 g, 4 mol %) in water (5 mL) was added. The reaction mixture was stirred for the preferred reaction time at room temperature. The procession of reaction was examined by TLC. After completion of the reaction, it was extracted with ethyl acetate (3 × 10 mL). The organic layer was alienated and dried with anhydrous Na_2SO_4 to expel moisture. The solvent was evaporated under reduced pressure to get the desired product. The product formation was identified by ^{1}H NMR. Isolated yield was computed by using column chromatography with Hexane: EtOAc (99:1 or 95:5 v/v) as eluent.

General procedure for the hydration of nitriles

To a stirred solution of ruthenium(II) complex [(η^6-*p*-cymene)-$RuCl_2(C_6H_2(C_6H_5)_4CH_3NH_2)$] (**2**) (0.029 g, 0.04 mmol, 4 mol %, dissolved in 5 ml of water) in a round bottom flask, was added a nitrile (1 mmol) under open air conditions. The reaction mixture was stirred at room temperature for a pertinent period of time. After culmination of the reaction, the reaction mixture was extracted with dichloromethane. The organic layer was alienated and dried with sodium sulfate to expel moisture. The product was filtered and evaporated under reduced pressure. The crude reaction mixture was purified by column chromatography using diethyl ether as eluent. The identity of the resulting amides was assessed by ^{1}H NMR spectroscopy.

Crystallography

The crystal structure of **2** was measured on a Bruker D8 QUEST diffractometer with graphite monochromated radiation of Mo Kα (λ= 0.71073 Å) from a micro focus source at 273 K. The X-ray generator was operated at 50 kV and 1 mA and the data collection was monitored by the APEX2 program. The frames were integrated with the Bruker SAINT Software package using a narrow-frame algorithm. All data were corrected for absorption effects using the multi-scan method (SADABS) [64]. The molecular structure of **2** was solved by direct method using the Olex program [65] and refined via full-matrix least-squares method based on F2 using the SHELXL-97 program [66, 67].

Conclusions

In conclusion, we have conferred the synthesis and structural characterization of phosphine free water-soluble bulky amine-ruthenium-arene complex (**2**). The structural identity of the complex **2** was confirmed by single crystal XRD studies which unveiled that the complex adopts a *pseudo*-octahedral geometry. The 2,6-bis(diphenylmethyl)-4-methylaniline ligand interacts with the metal through the amine group, the *pseudo*-octahedral geometry being compensated by a η^6-coordinated *p*-cymene ring and by two chloride ligands. The complex **2** was successfully employed for the hydration of organonitriles to amides and oxidative homocoupling of arylboronic acids to corresponding biaryls in water under moderate reaction conditions and short reaction time. The present catalytic system bestowed the hydration of a broad scope of nitriles, together with aromatic, heteroaromatic and aliphatic substrates. In the catalytic activity of homo coupling of aryl boronic acids, an incredible effect of the coordinating bulky aniline ligands was noted on the selectivity toward biaryls, where moderate to good yields of the corresponding biaryls were achieved. Indeed, the outcomes of the current work will significantly endow towards the exploration and growth of highly active water-soluble new catalytic system for the synthesis of biaryls and amides. Further explorations in this direction are in progress.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

‡ ^{1}H and ^{13}C NMR spectra of the synthesized complex. Catalysis protocols and characterization data of catalytic products. CCDC 1855045. These data can be obtained free of charge from the Cambridge Crystallographic Data center via www.ccdc.cam.ac.uk/data_request/cif.

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Table of Contends

The synthesis and catalytic applications of water-soluble superbulky (η^6-*p*-cymene) ruthenium(II) amine complex in oxidative homocoupling of arylboronic acids and hydration of organonitriles are reported.