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An attractive route to transamidation catalysis: Facile synthesis of new *o*-aryloxide-*N*-heterocyclic carbene ruthenium(II) complexes containing *trans* triphenylphosphine donors

Muthukumaran Nirmala[a], Govindan Prakash[a], Periasamy Viswanathamurthi[a,*], Jan Grzegorz Malecki[b]

[a] Department of Chemistry, Periyar University, Salem 636 011, India
[b] Department of Crystallography, Silesian University, Szkolna 9, 40-006 Katowice, Poland

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ABSTRACT

Well-defined robust ruthenium(II) complexes **3a–d** bearing *o*-aryloxide-*N*-heterocyclic carbene ligands with different wingtip substituents (**3a** (R = Me), **3b** (R = Ph), **3c** (R = ^{i}Pr) and **3d** (R = Mes)) in the imidazole ring were synthesized in good yields by the reaction of imidazolium proligands with metal precursor [RuHCl(CO)(PPh_3)$_3$] by transmetallation from the corresponding silver carbene complexes. All the Ru(II)–NHC complexes have been characterized by elemental analyses, spectroscopic methods as well as ESI mass spectrometry. The molecular structure of the complex **3a** was identified by means of single-crystal X-ray diffraction analysis, which revealed that the complexes possess a distorted octahedral geometry. In order to explore the catalytic potential of the synthesized complexes, all the four [Ru–NHC] complexes [**3a–d**] were tested as catalysts for transamidation of carboxamides with amines. Notably, the complex **3a** was found to be very efficient and versatile catalyst toward transamidation of a wide range of amides with amines.

1. Introduction

The amide functionality is one of the most fundamental chemical building blocks found in nature. It is essential to sustain life, making up the peptide bonds in proteins such as enzymes, and it is also one of the most prolific moieties in pharmaceutical molecules, agrochemicals and natural products (Scheme 1) [1]. The most popular and common methods for the generation of amides involve the reaction of activated carboxylic acid derivatives, such as chlorides, anhydrides or esters, with amines [2,3]. Alternative strategies toward the synthesis of amides are the Staudinger reaction [4], Schmidt reaction [5], Beckmann rearrangement [6], aminocarbonylation of haloarenes [7], alkenes [8] and alkynes [9], oxidative amidation of aldehydes [10], hydrative amide synthesis with alkynes [11] and amidation of thio acids with azides [12]. All of these methods have their own advantages, nonetheless they suffer from certain demerits, such as stoichiometric amount of amidation reagents, harsh reaction conditions, long reaction times, low selectivities, limited substrate scopes etc. Moreover, some of the catalysts have the difficulties in separation from the reaction mass and recycling, making their environmental profile unfavorable. Therefore, there is a clear need for the synthesis of amides with more efficient, under neutral conditions and without the generation of waste, which is a challenging goal [13].

In the search of more atom-economical and cost-effective protocols for amide synthesis, metal-catalyzed organic transformations have been emerged in the last years as attractive alternatives, offering the possibility to develop previously unavailable routes starting from substrates other than carboxylic acids and their derivatives [14]. Since then, a wide range of catalytic systems based on different transition metals have been described as catalysts for the construction of amide bonds. Among them, ruthenium playing a predominant role [14][14g]. For the aforementioned cases, most of the reported catalysts bear ligands containing phosphine coordinating arms usually exhibit much higher catalytic activity due to the steric (bulkiness) and electronic effects (basicity) of the ligand [15]. Our own research group has also succeeded in applying the ruthenium(II) complexes as catalysts for amide synthesis [16].

Alternatively, transamidation is an attractive tool and represents one of the most convenient and straightforward methods for the synthesis of secondary or tertiary amides through tandem processes. Transamidation is a distinct biochemical activity

* Corresponding author. Tel.: +91 944 3775719; fax: +91 427 2345124.
E-mail address: viswanathamurthi72@gmail.com (P. Viswanathamurthi).

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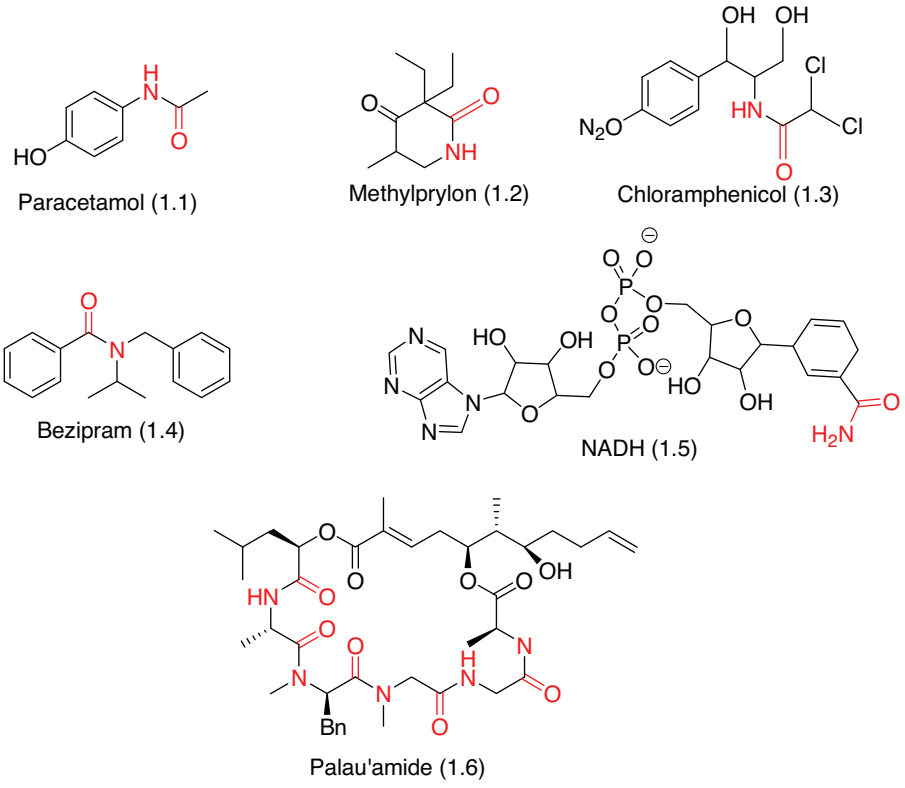


Scheme 1. Amide function in drug molecules [1.1–1[1.1–1.3], agrochemicals [1.4], biological molecules [1.5] and natural products [1.6].

[17] associated with several neurodegenerative disorders such as Alzheimer's and Hungtinton's disease [18]. Recent catalysts explored for transamidation include L-proline, cerium, hydroxylamine hydrochloride, ammonium bromide, and boric acid [19]. There are many reports are available regarding the application of transition metal complexes as catalysts for transamidation reactions [20]. All of the reported catalysts have some drawbacks; they require long reaction times and elevated temperature profile of the reaction.

Recently, a great deal of research efforts have been devoted to the study of transition metal complexes with anion-tethered NHC ligands [21]. Especially, the *o*-hydroxyaryl-substituted NHC 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 [22]. Their distinctive stereo-electronic features, such as strong metal—C_{NHC} bonding, 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. The catalytic activity of the ruthenium complexes containing various *N*-heterocyclic carbene ligands in amide synthesis has been documented as well [23].

Based on the above facts, and continuation of our research on the synthesis, characterization and catalytic applications of transition metal based *N*-heterocyclic carbenes [24], we here in describe new ruthenium(II) complexes bearing *o*-aryloxide *N*-heterocyclic carbene (NHC) ligands with different wingtip substituents in the imidazole ring with chloride and triphenylphosphine as ancillary ligands. It was naturally obvious that the NHC and the phosphorus ligands have different σ-donating or π-back bonding properties. This cooperation has been tuned to increase the efficiency of the metal center [25]. Considering the economic attractiveness and excellent functional group tolerance of ruthenium in homogenous catalysis, we became interested in developing a general transamidation methodology of carboxamides with amines. To the best of our knowledge, [Ru–NHC] catalyzed transamidation reaction has not yet been reported. Herein, we describe our results for the first time.

2. Results and discussion

The ruthenation was accomplished by metalation with Ag_2O to form intermediate silver carbene complexes and subsequent transmetallation with $[RuHCl(CO)(PPh_3)_3]$ indeed, as summarized in Scheme 3

2.1. Synthetic plan

This paper is primarily focused on the carbenes derived from five-membered heterocycles in which the carbene center is flanked by two nitrogen atoms. Carbene center at the 2-position of the imidazole ring would be stable due to electron-donating effects of adjacent nitrogen atoms that provided a conceptual framework for the development of chemistry of these species. The choice is based on the stability and versatility of these species relative to that of the carbenes derived from other nitrogen heterocycles. The synthetic plan to reach the novel ruthenium complexes disclosed herein was initially attempted by deprotonation of imidazolium salts with a strong base (KO^tBu or KHMDS) in THF followed by the addition of metal precursor, but the products were not obtained quantitatively. Hence, the most widely used method of deprotonation by the use of silver base has been used in the syntheses of *N*-heterocylic carbene complexes. Among the various silver bases, Ag_2O is most commonly used as a metal base [26]. Treatment with Ag_2O which act as both base and halide scavenger, under light-free conditions in CH_2Cl_2 at room temperature formed the silver carbene complexes. This method is the direct path for the preparation of the Ru-complexes involving a transmetallation step using the corre-

sponding NHC–silver(I) complex of the bidentate ligands [**1a–d**]. Earlier, this approach has been successfully utilized for a wide variety of transition metals and proved to be a convenient method over other methods under certain conditions [22,26][22i,26].

2.2. Synthetic strategy

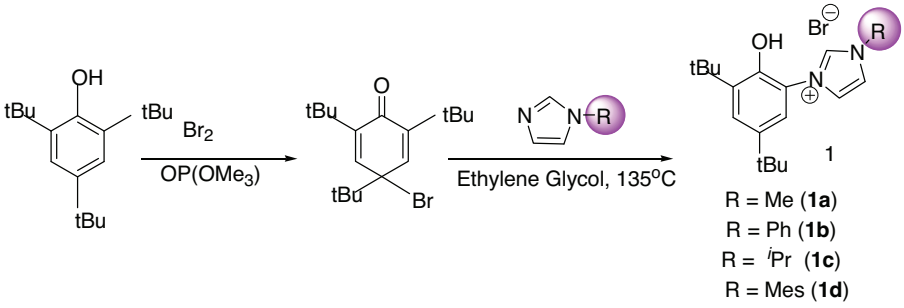
o-hydroxyaryl imidazolium pro-ligands [**1a–d**] were selected as potential ligand platforms of different wingtip substituents on imidazole ring, and were synthesized according to known methods [27], by the reaction of 4-bromo-2,4,6-tri-*tert*-butyl-2,5-cyclohexadiene-1-one with different *N*-substituted imidazoles in about 40% yields (Scheme 2. The NHC–silver complex was prepared by the reaction of **1a–d** with Ag_2O under light free condition at room temperature [28]. The obtained silver complexes are highly air and moisture stable, and soluble in CH_2Cl_2, $CHCl_3$, CH_3CN, DMSO and insoluble in diethyl ether. The NHC–silver complexes are light-sensitive to solution, but light-stable in solid form. The disappearance of ^{1}H NMR signal of the imidazolium ring (NCHN) along with the appearance of a diagnostic silver–bound carbene (NCN–Ag) peak at ~176 ppm in the ^{13}C NMR spectra are the characteristic features of the silver carbene complexes [**2a–d**]. These values are comparable with previously reported Ag–NHC complexes [22,22,28][22c,22h,28]. The Ag–NHC complexes reacted with [RuHCl(CO)(PPh_3)$_3$] in CH_2Cl_2 under dark condition and the reaction mixture was allowed to stir for 24 h at room temperature. The ruthenium complexes [**3a–d**] were isolated upon precipitation with diethyl ether as brown powder in >90% yield and they are extremely soluble in CH_2Cl_2, $CHCl_3$, THF and DMSO. However, they are sparsely soluble in CH_3CN, but hardly insoluble in 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 the complexes [**3a–d**] were fully characterized by ^{1}H, ^{13}C & ^{31}P NMR, mass spectra and elemental analyses. The analytical data (C, H, N) of the [Ru–NHC] complexes are in good agreement with the proposed molecular formulae.

2.3. Spectroscopic description

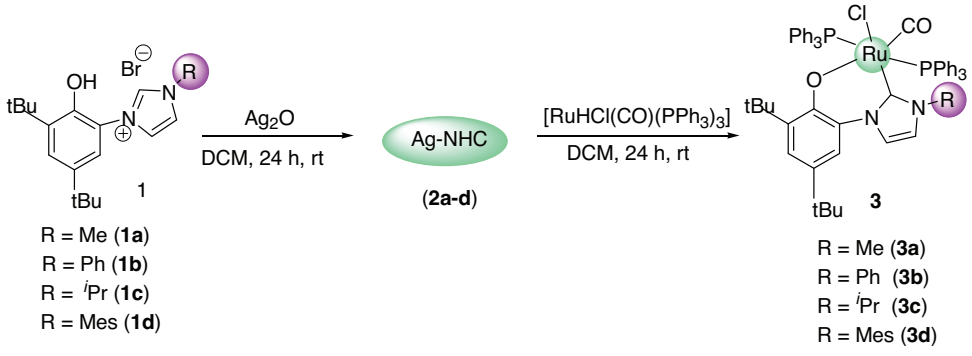
Chelation of the potentially bidentate carbene ligands [**1a–d**] was surmised from spectroscopic measurements in solid and solution. Carbonyl stretching frequencies provide useful comparison of the relative electron-donating abilities of the different ligands. The new [Ru–NHC] complexes [**3a–d**] showed a νCO stretch in the IR spectrum at ~1939 cm^{-1}, indicating considerable back bonding present in this ligand. The imidazolium structures were confirmed by the characteristic bands of 1572–1561 cm^{-1} (N—C—N) and 1617–1610 cm^{-1} (C═C) stretching. The bands located at 1459–1453 cm^{-1} correspond to C—O stretching mode.

The ^{1}H NMR spectra of the complexes [**3a–d**] showed the signals in the expected region (Figs. S1–S4, ESI†). The generation of free carbene and subsequent formation of the [Ru–NHC] complexes were unambiguously confirmed by the absence of the ^{1}H NMR resonances of imidazolium (NCHN) and phenolic (C—OH) protons. The imidazolium ring backbone signals appeared around 7.43–6.69 ppm. Furthermore, the spectra of all the complexes showed a series of signals for aromatic protons at 7.87–7.18 ppm. In addition, a singlet appeared around 3.10–2.22 ppm for complexes **3a, 3c** and **3d** corresponding to terminal—CH_3 group protons. The spectra of the complexes showed a singlet at 1.44–0.84 ppm, which has been assigned to ^{t}Bu protons.

The ^{13}C NMR spectra showed the expected signals in the appropriate region (Figs. S5–S8, ESI†). The ruthenium complexes showed their carbenic carbon resonances at ca. 184.20–180.79 ppm (Ru–$C_{carbene}$), characteristic of the carbenic carbon bound to ruthenium. Normally, Ru–$C_{carbene}$ resonances of Ru–NHC complexes are found in the wide range of 171–197 ppm [29]. It is worth of noting that only one singlet was observed for the carbene carbon in the ^{13}C NMR spectra of these complexes. The C═O carbon resonating at 206.47–200.51 ppm is comparable with earlier observations. The



Scheme 2. General preparation of *o*-hydroxyaryl imidazolium ligands [**1a–d**].



Scheme 3. General synthesis of [Ru–NHC] complexes [**3a–d**].

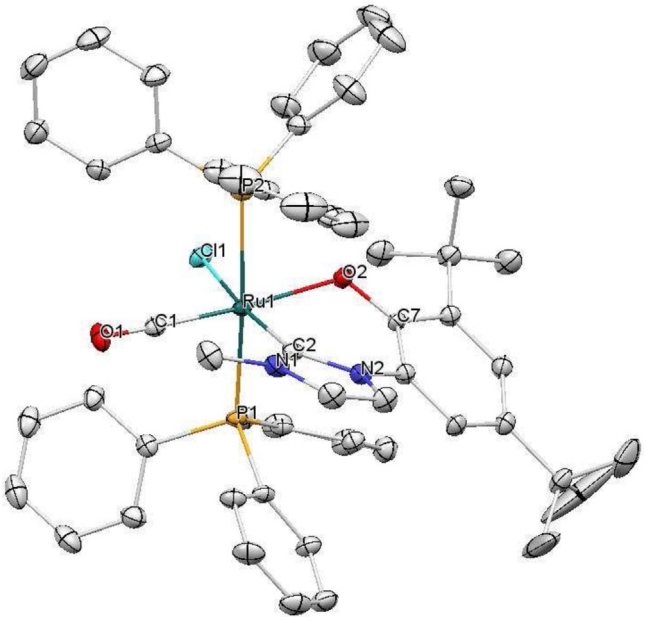


Fig. 1. ORTEP representation of the X-ray crystal structure of **3a** (R = Me). The solvent molecule of crystallization and hydrogen atoms has been omitted for clarity. Thermal ellipsoids are shown at 30% probability. Selected bond lengths (Å) and angles (deg) with standard uncertainties given in parentheses: Ru(1)—C(1) = 1.820(5), Ru(1)—C(2) = 2.012(4), Ru(1)—O(2) = 2.095(3), Ru(1)—P(1) = 2.3966(12), Ru(1)—P(2) = 2.4045(13), Ru(1)—Cl(1) = 2.4549(11), C(1)—Ru(1)—C(2) = 94.11(18), C(1)—Ru(1)—O(2) = 174.96(15), C(2)—Ru(1)—O(2) = 85.03(14), C(1)—Ru(1)—P(1) = 87.15(13), C(2)—Ru(1)—P(1) = 91.33(12), O(2)—Ru(1)—P(1) = 97.83(8), C(1)—Ru(1)—P(2) = 92.14(14), C(2)—Ru(1)—P(2) = 94.38(12), O(2)—Ru(1)—P(2) = 82.98(8), P(1)—Ru(1)—P(2) = 174.29(13), C(1)—Ru(1)—Cl(1) = 95.60(14), C(2)—Ru(1)—Cl(1) = 169.70(12), O(2)—Ru(1)—Cl(1) = 85.59(8), P(1)—Ru(1)—Cl(1) = 85.75(5), P(2)—Ru(1)—Cl(1) = 88.68(5).

presence of peak in the region ~158.21 ppm has been assigned to aryloxy carbon. The signal observed at 143.77–104.29 ppm in the spectra of complexes is due to aromatic carbons. The presence of chemical shifts in the range of 39.34–27.42 ppm belonged to the methyl protons.

^{31}P NMR spectra of the complexes were recorded to confirm the presence of triphenylphosphine groups coordinated to ruthenium center and to determine the geometry of the complexes (Figs. S9–S12, ESI†). All the complexes [**3a–d**] exhibited only one signal at 29.13–24.35 ppm, consistent with the presence of two triphenylphosphine ligands, which were *trans* to each other. ESI-mass spectra of the complexes [**3a–d**] generally showed the molecular ion peak with the loss of a chloride ion $[M–Cl]^+$ (Figs. S13–S15, ESI†).

2.4. X-ray crystal structure description of complex 3a

Even though the analytical and spectral data gave some idea about the molecular formulae of the complexes, they do not indicate the exact coordination of carbene–aryloxygen units in them. To gain additional insight into the coordination chemistry and the structural parameters of the complexes, single crystals of one of the complexes [**3a**] were grown by slow evaporation of the concentrated dichloromethane solution of the respective complex into Et_2O and characterized by X-ray diffraction analysis. The crystallographic and refinement data for the complex **3a** are collated in Table S1 (provided as Supporting information (ESI†)). ORTEP diagram of the complex **3a** is displayed in Fig. 1 along with selected bond angles and inter atomic distances. Packing arrangement of the molecules in the unit cell is shown in supporting information (Fig. S16, ESI†). The complex crystallizes in the monoclinic space group *P*2/c with four units residing at the unit cell. Crystal structure shows that the C/O-functionalized NHC ligand **1a** coordinates to the ruthenium center through the carbenoid-C and the aryloxygen-O donors with Ru(1)—C(2) and Ru(1)—O(2) bond lengths measuring 2.012(4) and 2.095(3) Å, respectively, to form a six-membered chelate ring with a bite angle of 85.03(14)°. The coordination geometry around the Ru(II) ion is slightly distorted octahedron where the basal plane is constructed of a carbene and oxygen atom of the ligand in a uni-negative bidentate CO fashion and one molecule of CO and one molecule of chloride. A pair of triphenylphosphine ligands completes the apical coordination. Though the PPh_3 ligands usually prefer to occupy mutually *cis* positions for better π-interaction, in this complex the presence of CO, a stronger π-acidic ligand, might have forced the bulky PPh_3 ligands to take up mutually *trans* positions for steric reasons. The bond distances are 1.820(5) (Ru(1)—C(1)), 2.4549(11) (Ru(1)—Cl(1)), 2.3966(12) (Ru(1)—P(1)) and 2.4045(13) Å (Ru(1)—P(2)) within the expected range. The chlorido ligand was *trans* to the carbene ligand and the Ru—Cl bond lengths being essentially identical to the six-coordinate cases (~2.452 Å). The CO group occupies the site *trans* to the aryloxygen (C(2)—Ru(1)—P(2) = 94.38(12)). This may be a consequence of strong $Ru^{II} \rightarrow CO$ back donation as indicated by the short Ru(1)—C(1) [1.820(5) Å] bond and the low CO stretching frequency (~1939 cm^{-1}), which prefers σ or π weak donor groups occupying the site opposite to CO to favor the d → π back donation. The bonding parameters around the ruthenium center confirm a slightly distorted octahedral geometry and are in a comparable range to those of the closely related ruthenium complexes in the literature [30]. The results confirmed that the C/O functionalized NHC ligand, Cl and CO as well as the phosphine ligand remain intact at the ruthenium center in **3a**. The *tert*-butyl group on the *o*-aryloxy NHC ligand is slightly distorted away from the metal center as a result of steric repulsion. We tried to grow single crystals in different solvents such as acetonitrile, chloroform, methanol, dimethyl sulfoxide, and dimethylformamide of complexes **3b–d**, unfortunately we have not yet obtained high-quality crystals suitable for X-ray single-crystal diffraction, suggesting that subtle structural factors are critical to stabilizing this species. But the similarity in their spectroscopic characteristics suggests that **3a** is a good structural model for all other three complexes.

To the best of our knowledge, the scaffold of Ru–NHC containing salicylaldimine framework is still meager. Accounting this fact, we present the synthesis of complexes containing both NHC and phosphine moieties and their applications in transamidation catalysis in this article.

3. Catalytic studies

3.1. Catalytic transamidation of carboxamides with amines

There are numerous reports have demonstrated that ruthenium complexes are good catalysts for the synthesis of amides [31]. It has also been established that the introduction of NHC ligand to the metal center would enhance the catalytic activity. Thus, with the new carbene complexes in hand, their abilities to catalyze transamidation of carboxamides with amines were studied. In principle, the transamidation of primary amides should be synthetically useful because it can provide a route to higher amides through expulsion of a molecule of ammonia. Thanks to its low boiling point, this can readily be removed from the reaction, providing secondary or tertiary amides efficiently.

3.2. Evaluation of conditions for transamidation reaction

At the outset of our investigations, a screen was performed for a model reaction between acetamide and aniline and the results are

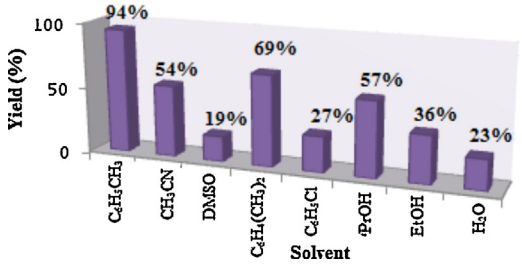


Fig. 2. Effect of solvent on transamidation of carboxamide with amine.

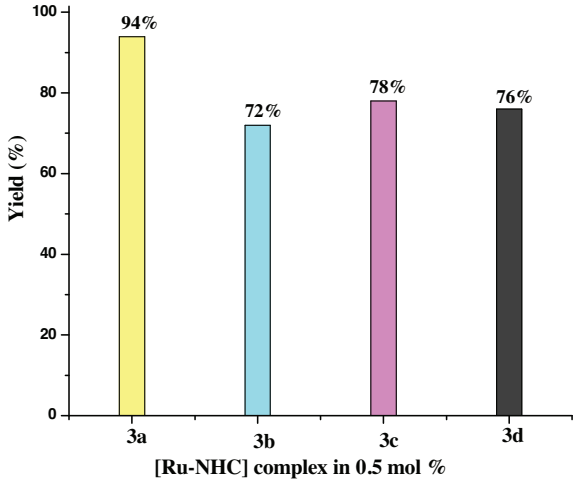
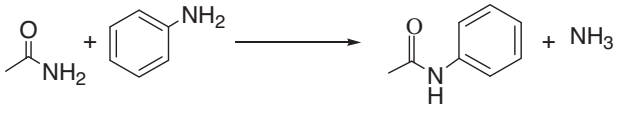


Fig. 3. Influence of wingtip substituents and catalyst loading on the catalytic activity of [Ru–NHC] complexes.

depicted in Table 1. To ensure its catalytic role, the control experiment was performed in the absence of [Ru–NHC] and as expected, no further gain in the conversion was obtained after a prolonged reaction time up to 24 h (Table 1, entries 1, 2). Addition of [Ru–NHC] complex **3a** (0.5 mol%) to the reaction mixture resulted in the desired transformation, but these conditions were not very active. An increase in the mol% of catalyst did not improve the yield further (Table 1, entry 17). Conversely, a decrease in the catalyst (mol%) led to diminish the yield of the product considerably (Table 1, entries 3, 4). It is well known that the solvent can have profound effect on the transamidation reaction. We are interested in exploring the solvent-dependent differences in the activities of catalysts on carrying out the model reaction in the most frequently used solvents such as, toluene, xylene, chlorobenzene, acetonitrile, DMF, DMSO, *n*-$C_5H_{11}OH$, *i*PrOH, EtOH and H_2O (Fig. 2). Aromatic hydrocarbon

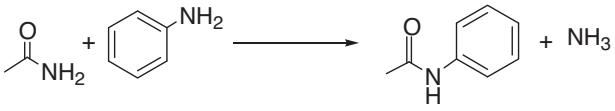
Table 2
Influence of wingtip substituents and catalyst loading on the catalytic activity of [Ru–NHC] complexes[a].



Entry	Catalyst	Amount of catalyst (mol%)	Wingtip (R)	Time (h)	Yield (%)[b]
1	**3a**	**0.5**	**Me**	**8**	94
2	**3b**	0.5	Ph	8	72
3	**3c**	0.5	^{i}Pr	8	78
4	**3d**	0.5	Mes	8	76
5	–	–	–	24	–

[a] Reaction conditions: acetamide (5 mmol), aniline (5 mmol).
[b] Yields were calculated after isolation of the amide product through column chromatography using silica gel (200–400 mesh).

Table 1
Evaluation of conditions for the model reaction using complex **3a**[a].



Entry	Catalyst (mol%)	Solvent	Temp. (°C)	Time (h)	Yield (%)[b]
1	–	–	110	24	Nil
2	–	Toluene	110	24	Nil
3	0.15	Toluene	110	24	45
4	0.25	Toluene	110	12	56
5	0.5	Toluene	110	6	74
6	**0.5**	**Toluene**	**110**	**8**	**94**
7	0.5	Toluene	rt	24	Nil
8	0.5	Acetonitrile	110	24	54
9	0.5	DMF	110	24	<5
10	0.5	DMSO	110	24	19
11	0.5	*p*-Xylene	110	24	69
12	0.5	Chlorobenzene	110	24	27
13	0.5	*n*-$C_5H_{11}OH$	110	24	Nil
14	0.5	*i*PrOH	100	24	57
15	0.5	EtOH	100	24	36
16	0.5	H_2O	100	24	23
17	1.0	Toluene	110	24	94

[a] Reaction conditions: acetamide (5 mmol), aniline (5 mmol).
[b] Yields were calculated after isolation of the amide product through column chromatography using silica gel (200–400 mesh).

solvents such as toluene and *p*-xylene (Table 1, entries 6, 11) were found to be better reaction media than polar aprotic (DMF, DMSO; Table 1, entries 9, 10) or protic solvents (Table 1, entries 14–16), whereas *n*-$C_5H_{11}OH$ proved completely futile (Table 1, entry 13). Pleasingly, toluene was found to be the solvent of choice, giving 94% yield in 8 h, whereas acetonitrile were inferior (Table 1, entries 6, 8).

3.3. Influence of wingtip substituents and catalyst loading

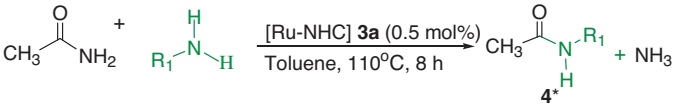
We continued the transamidation reaction optimization process to study the influence of the wingtip substituents and catalyst loadings on the catalytic activity (Fig. 3). The results are summarized in Table 2. It indicates that the lower catalyst loadings lead to moderate yields and longer reaction times are required to achieve maximum conversion. Further, the [Ru–NHC] complex containing Methyl (Table 2, entry 1) as a wingtip substituent lead to higher yields than those containing phenyl, isopropyl or mesityl at 0.5 mol% of catalyst was used. This behavior indicates that steric effects may be played an important role in the catalytic activity. In addition, significantly shorter reaction times are needed to complete all the transamidation process.

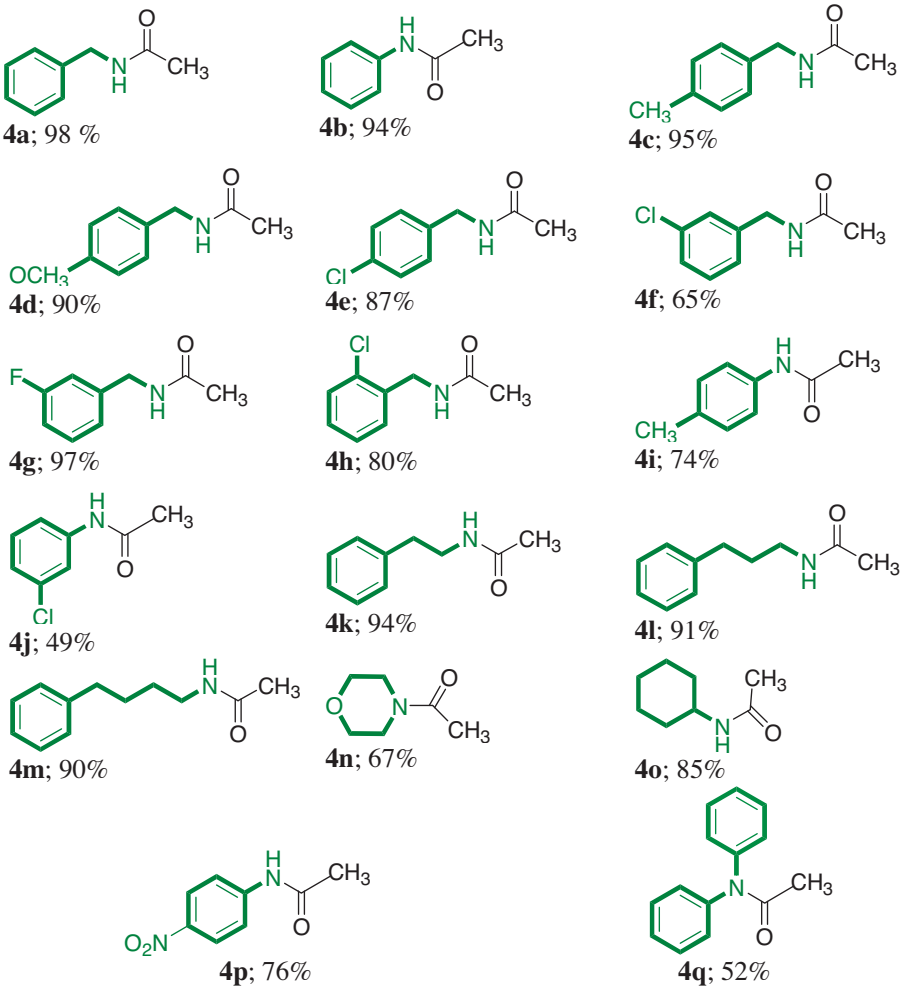
The optimization process led us toward the determination of the best reaction conditions to analyze the substrate scope. Catalyst **3a** was proved to be the most efficient complex for the transamidation of carboxamides with amines in terms of yield and selectivity.

3.4. Transamidation of acetamide with various amines

After we established suitable reaction conditions, a number of structurally diverse amides and amines were coupled to evaluate the reliability of the reaction and the results are summarized in Tables 3–5. We were pleased to see that all the reactions proceeded smoothly and afforded the desired products in reasonable to excellent yields upon isolation. The transamidation of acetamide with various amines demonstrate (Table 3) that the catalytic process is able to tolerate a variety of functional groups and substituents including CH_3, OCH_3, NO_2 and Cl. Various amines having both electron donating and electron withdrawing groups underwent the reaction smoothly and gave rise to good to excellent product yields

Table 3
Transamidation of acetamide with various amines[a].





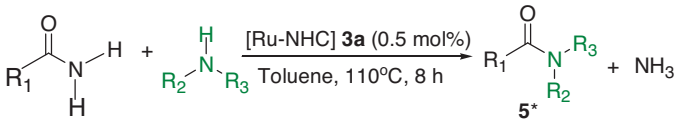
*Yields were calculated after isolation of the amide product through column chromatography using silica gel (200–400 mesh).
[a] Reaction conditions: amide (5 mmol), amine (5 mmol), [Ru–NHC] **3a** (0.5 mol%), toluene (5 mL), reflux.

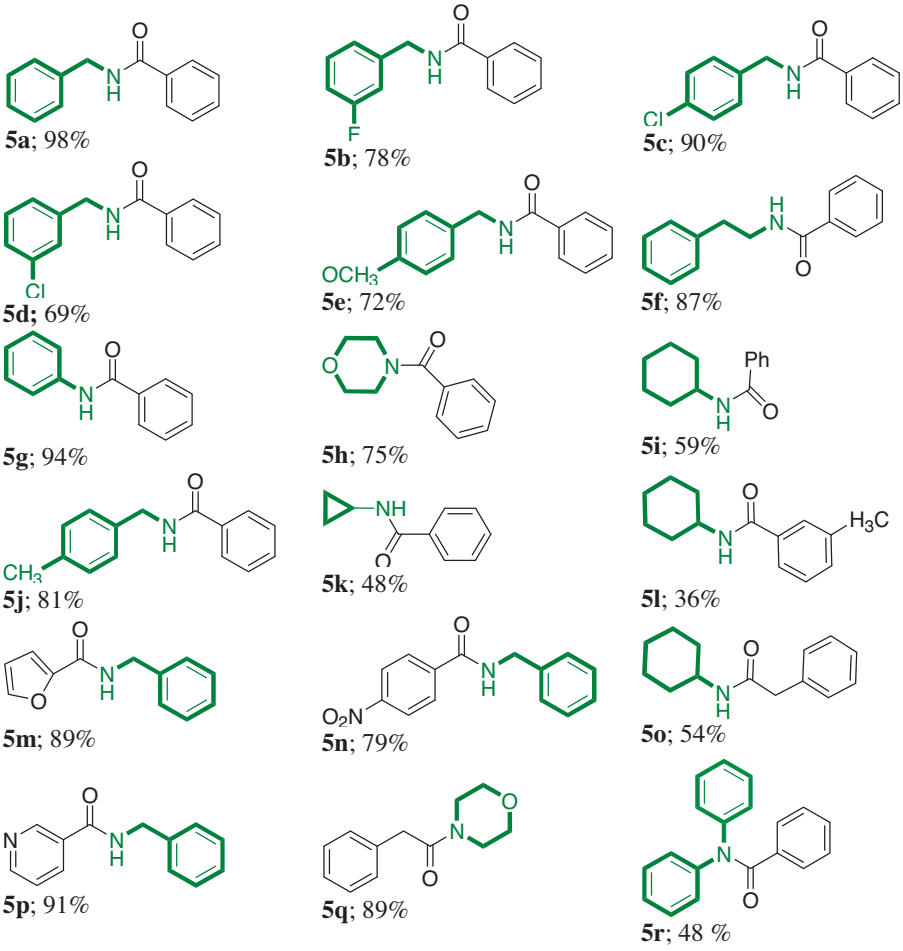
regardless of the substituted positions (Table 3, entry 4a, 4c–h). The less nucleophilic aniline, methyl aniline and 3-chloroaniline, provide good to moderate yields (Table 3, entry 4b, 4i, 4j). We assume this may be due to the delocalization of the nitrogen lone pair of electrons on the aromatic ring, which is apparent according to the literature [19][19c]. But in the case of *p*-nitro aniline, as expected due to its decreased nucleophilicity, the reaction was very slow and gave a yield of 76% in 8 h (Table 3, entry 4p). Acetamide could be transamidate with aromatic amines like phenethylamine, 3-phenyl propylamine and 3-phenyl butylamine to gave the corresponding amides in high yield (Table 3, entries 4k–m), but in the case of morpholine, the reaction was very slow and gave 67% yield in 8 h (Table 3, entry 4n). Similarly, acetamide was successfully transamidate with cyclohexylamine, gave 85% yield in 8 h (Table 3, entry 4o). As for as the steric effects are concerned, we have also examined the effectiveness of the current catalytic system for the amidation of hindered secondary amine such as *N*,*N*-diphenylamine. The desired amide product was obtained as moderate yield (Table 3, entry 4q). Notably, alkyl aromatic, aliphatic and secondary amides were also successfully accomplished under our investigated conditions, albeit at a somewhat higher temperature.

3.5. Expanded substrate scope

In order to check the versatility of our catalysts, we decided to study the expanded substrate scope of the catalyst **3a** with a variety of benzylic, aromatic, aliphatic, propargylic, heteroaromatic and secondary amines with other amides. The results showed in Table 4 summarize the effect of the substrates on the yield and selectivity of the catalytic reaction using a 0.5 mol% loading of catalyst in toluene at 110 °C. Benzamide containing electron-donating or electron-with drawing functionalities underwent facile reactions with various amines, including aniline, benzylamine and phenethylamine giving the corresponding amides in good to moderate yields (Table 4, entry 5a–h, 5j). The reaction of aliphatic amines with variety of aromatic amides led to reduction in yield due to losses in product isolation (Table 4, entry 5i, 5k, 5l, 5o). Similarly, the reaction was also found to be slow between *p*-nitrobenzamide, carrying an electron withdrawing group and benzylamine, gave yield of 79%

Table 4
Expanded substrate scope of transamidation method[a].





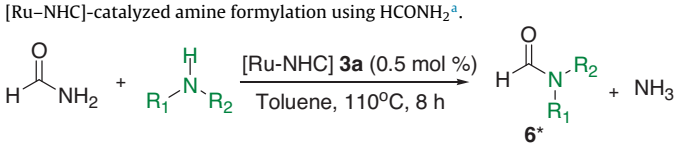
*Yields were calculated after isolation of the amide product through column chromatography using silica gel (200–400 mesh).
[a] Reaction conditions: amide (5 mmol), amine (5 mmol), [Ru–NHC] **3a** (0.5 mol%), toluene (5 mL), reflux.

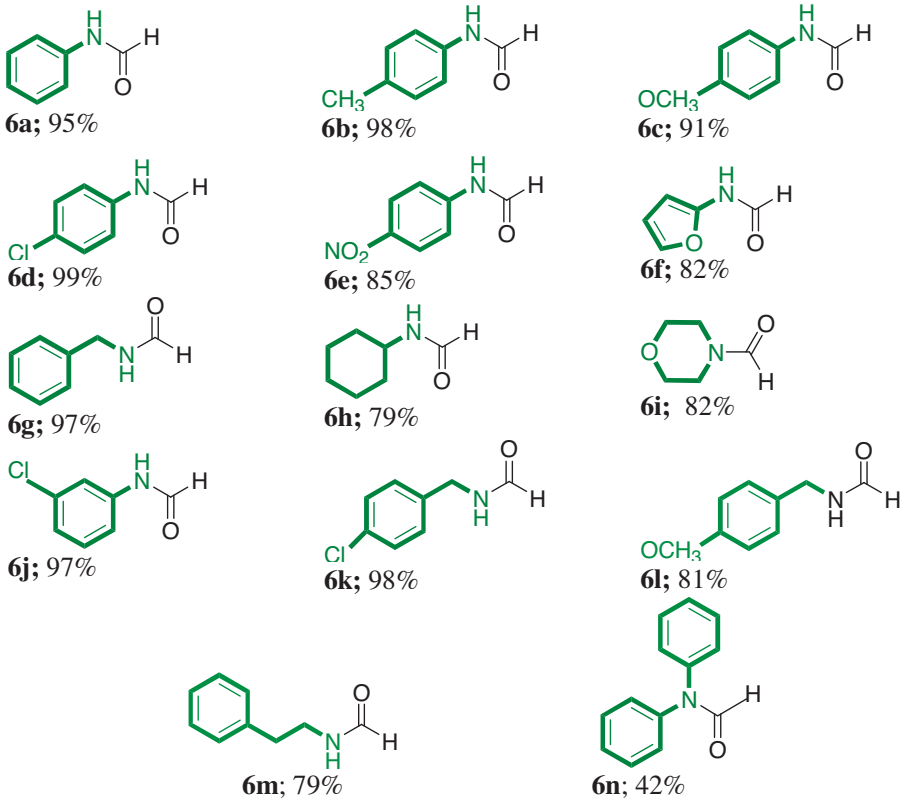
in 8 h (Table 4, entry 5n). Furthermore, it was found that 2-furamide an acid labile heterocyclic amide, which is difficult to transamidate under homogeneous catalysis, reacted smoothly with benzylamine and gave very good yield (Table 4, entry 5m). Phenyl acetamides were transamidate using nicotinamide and morpholine, in these cases, the reaction was smooth and gave the corresponding amides in good yields (Table 4, entry 5p, 5q). A sterically hindered secondary amine such as *N*,*N*-diphenylamine gave the corresponding amide product in lower yield (Table 4, entry 5r).

3.6. *N*-formylation of amines

Encouraged by these promising results, we turned our attention to the *N*-formylation of amines through transamidation using formamide. The *N*-formylation of amines is one of the most important reactions in organic and industrial chemical synthesis. We were particularly intrigued by the high reactivity of unsubstituted formamide toward different amines under [Ru–NHC] **3a** catalyzed conditions. As expected, the results were good, with a series of different amines coupled with formamide and gave good yields. Typically, the *N*-formylation of amine is carried out using hazardous, toxic, and unstable reagents (mixed formic/acetic anhydride, cyanomethyl formate, pentafluorophenyl formate, and formyl fluoride). This led us to carry out a more comprehensive study of scope and limitation of formylation using the present methodology (Table 5). The formylation of amines is a useful synthetic procedure for the preparation of *N*-formyl protected amides and therefore the *N*-formylation of formamide with various aliphatic, aromatic, alicyclic, benzylic, and hetero-aromatic amines were studied in detail (Table 5, entries 6a–m). With regards to the reactivities of the amines (Table 5, entry 6h), the aliphatic amines performed better, where as both the furylamine and morpholine worked well in these transamidation reaction (Table 5, entries 6f, 6i). We have explored an effective transamidation of formamide with different amine partners containing electron withdrawing substituents afford diverse carboxamides in reasonably good to excellent yields (Table 5, entries 6d, 6e, 6j, 6k). The reaction with benzylamine proceeded smoothly at temperature of 110 °C to furnish excellent yields (Table 5, entry 6g). Concerning the reactivity of aromatic primary amines, those having electron-donating groups performed better in these transamidation reactions, afforded the clean conversion without formation of side products (Table 5, entry

Table 5
[Ru–NHC]-catalyzed amine formylation using $HCONH_2$[a].





*Yields were calculated after isolation of the amide product through column chromatography using silica gel (200–400 mesh).
[a] Reaction conditions: amide (5 mmol), amine (5 mmol), [Ru–NHC] **3a** (0.5 mol %), toluene (5 mL), reflux.

6b, 6c, 6l). For the reaction of *N*,*N*-diphenylamine with formamide to gave the corresponding amide product in lower yield under optimized condition (Table 5, entry 6n). It is worth mentioning that the complex **3a** can also catalyze the transamidation of formamide with different amines, which is more sustainable for the synthesis of amides.

Based on previous literature report [20][20k], the reaction of ^{15}N-labeled benzamide with unlabeled benzylamine led to the exclusive formation of unlabeled secondary amide product, and it is proposed that, the [Ru–NHC] catalyzed transamidation reaction was also take place by the addition of amine–amide.

3.7. Mechanistic study

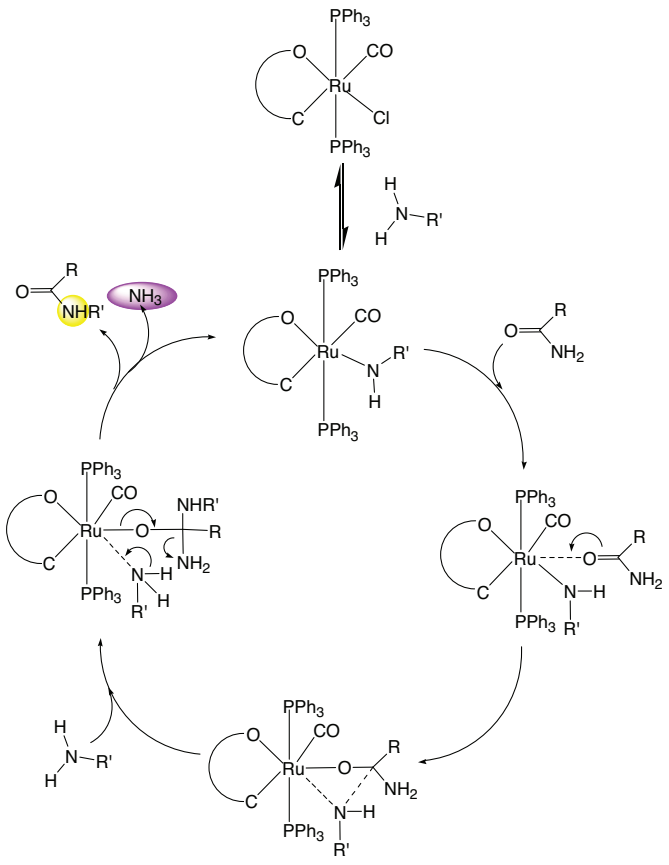
On the basis of previous investigations, a possible mechanism was proposed for [Ru–NHC] catalyzed transamidation, which has been schematically represented (Scheme 4). Catalyst forms a ruthenium amide complex (Ru–NHR′) by the ligand exchange reaction of amine with catalyst. We consider that this amide complex enhance the addition of amide with the catalyst. This is evident from the second order kinetics of the reaction with amine. The obtained intermediate undergone inter ligand reaction as shown in Scheme 4. Addition of new amine restores the (Ru–NHR′) complex with the liberation of *N*-substituted amide and ammonia. Although the complete elucidation of the mechanism has not been undertaken, we have conducted some control experiments to ascertain the specific role of catalyst and exact nature of the catalytic intermediate for these novel transamidation reactions. Efforts are underway to elucidate the mechanistic details of these NH bond forming reactions.

To our knowledge, these results provide the first demonstration of [Ru–NHC] catalyzed transamidation under moderate conditions. The data provide several insights regarding the identity of successful catalysts. Gratifyingly, all the reactions proceeded efficiently and furnished all types of substituted amides in good to excellent yields.

4. Summary and outlook

Our study has furnished the following results. The combination of phosphine and NHC in one unique metal complex has led to important discoveries in organometallic chemistry, providing catalytic improvements. In this paper, we designed and synthesized new *o*-aryloxide-*N*-heterocyclic carbene ruthenium(II) complexes [**3a–d**] containing *trans* triphenylphosphine donors in two consecutive steps. The ruthenation was accomplished by metalation with Ag_2O to form intermediate silver carbene complexes and subsequent transmetallation with $[RuHCl(CO)(PPh_3)_3]$. The yields were promising. The [Ru–NHC] complexes [**3a–d**] displayed excellent stability toward air and moisture which are the additional advantages for a better catalyst.

In addition, transamidation catalysis was explored for the one-pot synthesis of amides from carboxamides with amines. This



Scheme 4. Possible mechanism for [Ru–NHC] catalyzed transamidation.

method has a great potential for the preparation of amides, because it tolerates a wide range of substrates with excellent yield. To our knowledge, these results provide the first demonstration of [Ru–NHC] catalyzed transamidation under moderate conditions with lower catalyst loadings. We were delighted to find that the catalytic activities observed are unprecedented and represented a substantial step toward a long-range goal of conducting transamidation reactions with carboxamides under mild reaction conditions. In the catalysis reaction the complex **3a** has proven to be a versatile and efficient catalyst under mild reaction condition in comparison with other three ruthenium complexes [**3a–d**]. The steric effect of wingtip substituents at the NHCs slightly influenced the catalytic activities. Efforts are currently underway in our research group to expand the scope of this method to a library of different functionalized substrates and elucidation of mechanistic principles underlying these novel transamidation reactions with even greater activity.

5. Experimental

5.1. General comments

All reactions involving the syntheses of metal complexes were carried out in oven- or flame dried glassware with magnetic stirrer under argon atmosphere with anhydrous solvents, using standard Schlenk techniques. Silver reactions were conducted in the absence of light. All commercial chemicals were used as purchased. 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.

5.2. Materials

1-Substituted imidazoles [32], 4-bromo-2,4,6-tri-*tert*-butyl-2,5-cyclohexadien-1-one [33], *o*-hydroxyaryl-substituted imidazolium salts [**1a–d**] [22][22a] and [$RuHCl(CO)(PPh_3)_3$] [34] were prepared according to the previously published procedures.

5.3. 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. ^1H (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 (^1H, ^{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.

5.4. Elemental analyses

Microanalyses of carbon, hydrogen and nitrogen were carried out using a Vario EL III elemental analyzer at SAIF, Cochin, India.

5.5. Representative syntheses

The milder conditions of the "transmetalation" pathway make it an attractive choice for the synthesis of ruthenium complexes. *o*-hydroxyaryl-substituted imidazolium ligands (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, 10:1CH_2Cl_2/Acetone). Single crystal of the compound **3a** was obtained by slow diffusion of diethyl ether onto a concentrated solution of the yellow powder isolated via column chromatography in dichloromethane.

5.5.1. Compound *3a* (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 **3a**. Yield: 92%, R_f (CH_2Cl_2/acetone, 10/1). M. pt: 210–213 °C. Anal. Calcd for $C_{55}H_{55}N_2O_2ClP_2Ru$: C, 67.79; H, 5.69; N, 2.87%. Found: C, 67.54; H, 5.42; N, 2.61%. IR (KBr disks, cm^{-1}); 1937 (C≡O), 1610 (C═C), 1572 (N—C—N), 1458 (C—C), 1416 (C—O). ^1H NMR (300.13 MHz, $CDCl_3$): δ = 7.49–7.44 (m, 5H, aryl-H), 7.43 (m, 8H, aryl-H), 7.25 (m, 7H, aryl-H), 7.21 (m, 8H, aryl-H), 7.18 (s, 2H, aryl-H), 7.09 (d, 1H, J = 2.2 Hz, imi-H), 6.69 (d, 1H, J = 2.8 Hz, imi-H), 3.09 (s, 3H, CH_3), 1.25 (s, 9H, $C(CH_3)_3$), 0.84 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 206.5 (C≡O), 180.8 (Ru–$C_{carbene}$), 162.1 (C—O), 143.8 (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), 59.2 (NCH_2), 45.2 (C_{quat}, *t*Bu), 44.9 (C_{quat}, *t*Bu), 36.6 (CH_3, *t*Bu), 35.6 (CH_3, *t*Bu), 35.1 (CH_3, *t*Bu), 30.3 (N-CH_3). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 24.35 (s). ESI: *m*/*z* calcd. For $C_{55}H_{55}N_2O_2ClP_2Ru$ $[M–Cl]^+$, 939.057; Found, $[M–Cl]^+$, 939.12.

5.5.2. Compound **3b** (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 **3b**. Yield: 90%, R_f (CH_2Cl_2/acetone, 10/1). M. pt: 224–226 °C. Anal. Calcd for $C_{60}H_{57}N_2O_2ClP_2Ru$: C, 69.52; H, 5.54; N, 2.70%. Found: C, 69.81; H, 5.21; N, 2.42%. IR (KBr disks, cm^{-1}); 1939 (C≡O), 1614 (C═C), 1569 (N—C—N), 1453 (C—C), 1412 (C—O). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.77 (d, 1H, *J* = 7.5 Hz, aryl-H), 7.74 (m, 5H, aryl-H), 7.71 (m, 2H, aryl-H), 7.65 (m, 8H, aryl-H), 7.58 (m, 8H, aryl-H), 7.55 (m, 8H, aryl-H), 7.47 (m, 3H, aryl-H), 7.46 (s, 1H, aryl-H), 7.44 (d, 1H, *J* = 1.8 Hz, imi-H), 7.29 (d, 1H, *J* = 1.8 Hz, imi-H), 7.22–7.19 (m, 3H, aryl-H), 1.28 (s, 9H, $C(CH_3)_3$), 1.45 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 202.1 (C≡O), 184.2 (Ru–$C_{carbene}$), 153.3 (C—O), 141.3 (C_{quat}, aryl), 139.9 (C_{quat}, aryl), 138.3 (C_{quat}, aryl), 137.4 (C_{quat}, aryl), 136.2 (C_{quat}, aryl), 131.1 (C_{quat}, aryl), 127.2 (C_{quat}, aryl), 121.3 (C_{quat}, aryl), 109.1 (C_{quat}, aryl), 101.8 (C_{quat}, aryl), 104.3 (C_{quat}, aryl), 55.1 (NCH_2), 41.3 (C_{quat}, *t*Bu), 40.0 (C_{quat}, *t*Bu), 39.3 (CH_3, *t*Bu), 36.4 (CH_3, *t*Bu), 35.4 (CH_3, *t*Bu). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 25.61 (s).

5.5.3. Compound **3c** (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 **3c**. Yield: 94%, R_f (CH_2Cl_2/Acetone, 10/1). M. pt: 219–222 °C. Anal. Calcd for $C_{57}H_{59}N_2O_2ClP_2Ru$: C, 68.29; H, 5.93; N, 2.79%. Found: C, 69.59; H, 5.62; N, 2.57%. IR (KBr disks, cm^{-1}); 1938 (C≡O), 1617 (C═C), 1564 (N—C—N), 1457 (C—C), 1417 (C—O). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.85 (m, 6H, aryl-H), 7.81 (m, 8H, aryl-H), 7.74 (m, 4H, aryl-H), 7.54 (m, 5H, aryl-H), 7.51 (m, 6H, aryl-H), 7.43 (d, 1H, *J* = 1.8 Hz, imi-H), 7.34 (d, 1H, *J* = 2.1 Hz, imi-H), 7.31 (d, 1H, *J* = 2.2 Hz, aryl-H), 7.24 (d, 1H, *J* = 2.1 Hz, aryl-H), 2.82 (m, 1H, $CH(CH_3)_3$), 2.17 (d, 3H, *J* = 6.7 Hz, CH—CH_3), 1.91 (d, 3H, *J* = 6.7 Hz, CH—CH_3), 1.44 (s, 9H, $C(CH_3)_3$), 1.01 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 201.3 (C≡O), 183.8 (Ru–$C_{carbene}$), 149.9 (C—O), 142.9 (C_{quat}, aryl), 139.9 (C_{quat}, aryl), 138.5 (C_{quat}, aryl), 136.3 (C_{quat}, aryl), 133.6 (C_{quat}, aryl), 131.1 (C_{quat}, aryl), 128.5 (C_{quat}, aryl), 128.2 (C_{quat}, aryl), 127.7 (C_{quat}, aryl), 127.4 (C_{quat}, aryl), 126.0 (C_{quat}, aryl), 125.7 (C_{quat}, aryl), 107.7 (C_{quat}, aryl), 51.9 (NCH_2), 39.5 (C_{quat}, *t*Bu), 38.2 (C_{quat}, *t*Bu), 34.9 ($CHCH_3$), 34.1 ($CHCH_3$), 32.7 (CH_3, *t*Bu), 30.9 (CH_3, *t*Bu), 31.2 (CH_3, *t*Bu). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 26.01 (s). ESI: *m*/*z* calcd. For $C_{57}H_{59}N_2O_2ClP_2Ru$ $[M–Cl]^+$, 967.107; Found, $[M–Cl]^+$, 967.15.

5.5.4. Compound **3d** (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 **3d**. Yield: 89%, R_f (CH_2Cl_2/acetone, 10/1). M. pt: 226–228 °C. Anal. Calcd for $C_{63}H_{63}N_2O_2ClP_2Ru$: C, 70.15; H, 5.89; N, 2.60%. Found: C, 69.89; H, 5.64; N, 2.49%. IR (KBr disks, cm^{-1}); 1937 (C≡O), 1615 (C═C), 1561 (N═C—N), 1459 (C—C), 1421 (C—O). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.87 (d, 1H, *J* = 2.4 Hz, aryl-H), 7.58 (m, 6H, aryl-H), 7.49 (m, 7H, aryl-H), 7.46 (d, 1H, aryl-H), 7.40 (m, 9H, aryl-H), 7.38 (m, 9H, aryl-H), 7. 35 (d, 1H, *J* = 2.5 Hz, imi-H), 7.21 (d, 1H, *J* = 2.1 Hz, imi-H), 2.48 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 1.91 (s, 3H, CH_3), 1.44 (s, 9H, $C(CH_3)_3$), 1.07 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 200.5 (C≡O), 182.4 (Ru–$C_{carbene}$), 158.2 (C—O), 147.4 (C_{quat}, aryl), 137.5 (C_{quat}, aryl), 135.6 (C_{quat}, aryl), 133.9 (C_{quat}, aryl), 129.1 (C_{quat}, aryl), 128.7 (C_{quat}, aryl), 128.3 (C_{quat}, aryl), 126.3 (C_{quat}, aryl), 123.7 (C_{quat}, aryl), 120.1 (C_{quat}, aryl), 49.6 (NCH_2), 38.7 (C_{quat}, *t*Bu), 37.4 (C_{quat}, *t*Bu), 35.8 (CH_3, *t*Bu), 31.8 (CH_3, *t*Bu), 29.9 (CH_3, *t*Bu), 28.8 (CH_3), 28.3 (CH_3), 27.4 (CH_3). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 29.13 (s). ESI: *m*/*z* calcd. For $C_{63}H_{63}N_2O_2ClP_2Ru$ $[M–Cl]^+$, 1043.207; Found, $[M–Cl]^+$, 1043.31.

5.6. Representative procedure for transamidation reaction

A mixture of amide (5 mmol), amine (5 mmol), [Ru–NHC] complex (0.5 mol%) and toluene (5 mL) was stirred in a sealed tube under nitrogen atmosphere at 110 °C for 8 h. After cooling down to room temperature, the reaction solvent was removed under vacuum. After removal of the solvent, the crude reaction mixture was dissolved in CH_2Cl_2 and purified by column chromatography on silica gel (200–400 mesh) eluting with heptane:ethanol [25:1] to give corresponding amides as a white solid. The yields are mentioned in Tables 3–5. The product was confirmed by NMR spectroscopy. Reported isolated yields are an average of two runs.

5.7. Crystal structure determination

Crystals of complex **3a** were mounted on glass fibers used for data collection. Crystal data were collected at 295 K using a Gemini A Ultra Oxford Diffraction automatic diffractometer. Graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) was used throughout. The absorption corrections were performed by the multi-scan method. Corrections were made for Lorentz and polarization effects. The structure was solved by direct methods using the program SHELXS [35]. Refinement and all further calculations were carried out using SHELXL [35]. The H atoms were included in calculated positions and treated as riding atoms using the SHELXL default parameters. The non-hydrogen atoms were refined anisotropically using weighted full-matrix least squares on F^2. Atomic scattering factors were incorporated into the computer programs.

Supporting information

CCDC reference number 985755 contains the supplementary crystallographic data for **3a**. The 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, U.K.; fax: +44 1223 336 033; or email: Representative NMR 1H, 13C, 31P and ESI MS spectra of complexes, the unit cell packing diagram for the complex **3a**, detailed experimental procedure and spectral data for amide products.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2015.03.015.

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