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Ruthenium(II) complexes bearing pyridine-functionalized *N*-heterocyclic carbene ligands: Synthesis, structure and catalytic application over amide synthesis

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Abstract. A series of four imidazolium salts was synthesized by the reaction of 2-bromopyridine with 1-substituted imidazoles. These imidazolium salts (**1a–d**) were successfully employed as ligand precursors for the syntheses of new ruthenium(II) complexes bearing neutral bidentate ligands of N-heterocyclic carbene and pyridine donor moiety. The NHC-ruthenium(II) complexes (**3a–d**) were synthesized by reacting the appropriately substituted pyridine-functionalized *N*-heterocyclic carbenes with Ag_2O forming the NHC–silver bromide *in situ* followed by transmetalation with $[RuHCl(CO)(PPh_3)_3]$. The new complexes were characterized by elemental analyses and spectroscopy (IR, UV-Vis, ^1H, ^{13}C, ^{31}P-NMR) as well as ESI mass spectrometry. Based on the spectral results, an octahedral geometry was assigned for all the complexes. The complexes were shown to be efficient catalysts for the one-pot conversion of various aldehydes to their corresponding primary amides with good to excellent isolated yields using $NH_2OH.HCl$ and $NaHCO_3$. The effects of solvent, base, temperature, time and catalyst loading were also investigated. A broad range of amides were successfully synthesized with excellent isolated yields using the above optimized protocol. Notably, the complex **3a** was found to be a very efficient and versatile catalyst towards amidation of a wide range of aldehydes.

Keywords. Pyridine-functionalized carbene ligand; [Ru–NHC] complexes; transmetalation; aldehyde to amide conversion

1. Introduction

Since their discovery over two decades ago, *N*-heterocyclic carbenes (NHCs) have earned a prominent position in the toolbox of the organometallic chemist.[1] Their high σ-donating ability and steric bulk have proven functional in stabilizing transition metal complexes which have found numerous applications in catalysis.[2–10] More recently, a number of novel divalent carbon species have been synthesized that are based on other heterocycles[11–21] offering new avenues to alter one or both of the σ- and π-donor characteristics of the carbene. Many types of interesting NHC containing ligands have been designed to search for new efficient catalysts.[22] In particular, functionalized NHC ligands and catalytic activities of their metal complexes have been the subject of intensive studies.[23] Incorporation of a classical donor into NHC compounds offers vast opportunities in the design of the functionalized NHC ligands.[23a] The non-carbon donor atom would act as a hemilabile arm, capable of reversible dissociation from the metal center. Among the ligands containing various classical donors, the hybrid NHC ligands containing nitrogen donors have attracted considerable interest, particularly the pyridine-functionalized bidentate NHC ligands which have been extensively studied. So far, metal complexes including group 9 (Rh, Ir),[24,25] 10 (Ni, Pd),[26,27] and 11 (Cu, Ag)[28,29] metal complexes of pyridine-functionalized NHC ligands have been reported. They showed efficient catalytic activity towards hydrosilation of acetylenes,[25a] cyclization of acetylenic carboxylic acids,[25a] transfer hydrogenation of ketones,[25a] reduction of nitroarenes,[25b] C-C coupling reactions,[27] and olefin polymerization.[26a,27b] It is of great interest to synthesise and characterize new transition metal complexes other than above metals with pyridine-functionalized NHCs and to study their applications in catalysis.

Amides are a very important class of compounds in chemistry as well as biology that have widely been utilized as intermediate in peptide and protein syntheses, intensifiers of perfume, drugs, fine chemicals, anti-block reagents, colour pigments for ink detergents and lubricants.[30] Over the past few decades, a plethora of

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approaches for the formation of amide compounds have been explored and addressed. Among them, some innovative processes mainly include the direct synthesis of amides from thioesters[31] or azides,[32] amidation of alcohols with amines,[33] and the generation of amides from bromo, nitro compounds with amines.[34] Nevertheless, the majority of these developed approaches for amide synthesis are related to the intermediate utilization of carboxylic acids or activated carboxylic acid derivatives. These methods are low in atom efficiency, often involve potentially explosive molecules as catalysts and generate substantial waste[35,36] making their environmental profile unfavourable. This is the compelling reason for identifying atom-economical, safe, and efficient amide bond formation as a key thrust area of green chemistry research.[37] To address the problem, several transition-metal based catalysts have been developed. Of them, ruthenium complexes have been extensively studied due to their interesting structure[38] and catalytic properties.[39] The earlier reports indicated NHC-promoted Ru catalytic systems showed limited or no activity on the amidation of aldehydes.[40] Later, Muthaiah *et al.,* have reported[41] some [Ru(II)-NHC] complexes generated from *in situ* reaction of $RuH_2(PPh_3)_4$ and an imidazole-based NHC precursors and used as efficient catalysts for amidation of aldehydes and alcohols. In their work, no catalytic activity is observed in the absence of a strong base such as NaH and the reaction required high amounts of NaH, more than for generation of the NHC ligand. The usage of strong base such as NaH leads to the formation of various side products. Apart from that, storing and handling of strong bases such as NaH require special attention and care which make the reaction less convenient to be carried out. Significant efforts have been made in recent years for the development of one-pot process enabling direct formation of primary amides from aldehydes and hydroxylamine derivatives *via* rearrangement of the *in situ* formed aldoximes, which is an elegant alternative pathway. The rearrangement of aldoximes into amides has been reported using transition metal catalysts containing nickel,[42] copper,[43] ruthenium,[44] palladium,[45] iridium,[46] rhodium[47] and zinc.[48]

In contrast to the considerable growth of literature on the chemistry of *N*-heterocyclic carbenes, to the best of our knowledge, there are no reports available for catalytic transformation of aldehydes to amides by ruthenium(II) carbonyl complexes with the pyridine-functionalized *N*-heterocyclic carbene ligands. Herein, we report a simple direct method of [Ru–NHC] catalyzed conversion of aromatic aldehydes into primary amides *via* aldoximes under neat conditions.

2. Experimental

2.1 *General comments*

All experiments were performed under an atmosphere of dry argon using standard Schlenk techniques and a vacuum-line system. Unless otherwise stated, reagents were used as received from commercial sources. Solvents were deoxygenated immediately prior to use. All Ag_2O reactions were carried out under exclusion of light. Reactions were monitored by thin-layer chromatography using Merck 1.0555 aluminium sheets precoated with silica gel 60 F254, and the spots were examined with UV light at 254 nm or under iodine. Melting points were measured for samples in sealed capillaries on a Technico micro heating table apparatus and are uncorrected. Column chromatography purifications were performed using Merck silica gel 60 (0.063−0.200 mm).

2.2 *Spectroscopy*

IR spectra were recorded on a Nicolet Avatar model FT-IR spectrophotometer (range 4000−400 cm^{-1}) in KBr pellets. ^1H, ^{13}C and ^{31}P NMR spectra were recorded on Bruker AV400 spectrometer at 300 K, using DMSO-d_6 or $CDCl_3$. Chemical shifts (δ, parts per million) are quoted relative to tetramethylsilane or *o*-phosphoric acid (internal standards). ESI-Mass spectra were obtained in the ES+ (electron spray positive ionization) mode for all compounds using liquid chromatography mass spectrometry quadrupole time-of-flight Micro Analyzer (Shimadzu) at SAIF, Punjab University, Chandigarh.

2.3 *Elemental analyses*

Elemental analyses were performed using a Vario EL III elemental analyzer.

2.4 *Materials*

1-Substituted imidazoles[49] and $[RuHCl(CO)(PPh_3)_3]$[50] were prepared according to the previously published procedures.

2.5 *Preparation of NHC ligands*

A solution of 2-bromopyridine (3.80 g, 24 mmol) and 1-substituted imidazole (24 mmol) was stirred neat at 160°C for 20 h. After it was cooled, the mixture was dissolved in CH_2Cl_2 (20 mL) and Et_2O (100 mL) was added. The precipitate was collected and redissolved in

CH_2Cl_2, and precipitated with pentane to give pyridine-functionalized imidazolium salt (**1a–d**) as a pale yellow powder in good yield.

2.5a *Compound **1a** (R =Ph)*: The synthetic procedure of this compound was same as that of the above representative procedure, using 1-phenyl imidazole to give a pale yellow solid **1a**. Yield: 91%; M.p. 79–82°C; Anal. Calcd(%) for $C_{14}H_{12}N_3Br$: C, 55.65; H, 4.00; N, 13.91. Found(%): C, 55.81; H, 4.33; N, 13.62; ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 11.4 (1H, s, NCHN), 8.6 (1H, d, $J = 8.1$ *Hz*, Py–H), 8.3 (1H, m, Py–H), 8.3 (1H, t, imi–H), 8.0 (1H, m, Py–H), 7.9 (1H, t, imi–H), 7.7-7.4 (5H, m, Ar–H), 7.4 (1H, m, Py–H); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 154.2 (C=N), 149.1 (NCHN), 130.4 (Ar–C), 129.4 (Ar–C), 127.9 (Ar–C), 125.9 (Ar–C), 123.6 (imi–C), 122.0 (Ar–C), 119.4 (imi–C), 117.2 (Ar–C), 115.3 (Ar–C), 114.6 (Ar–C); ESI: m/z calcd. For $C_{14}H_{12}N_3Br$ $[M–Br]^+$, 222.23; Found, $[M–Br]^+$, 222.17.

2.5b *Compound **1b** (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 pale yellow solid **1b**. Yield: 89%; M.p. 64–66°C; Anal. Calcd(%) for $C_{11}H_{14}N_3Br$: C, 49.27; H, 5.26; N, 15.67. Found(%): C, 49.44; H, 5.37; N, 15.83; ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 10.8 (1H, s, NCHN), 8.5 (1H, d, $J = 8.2$ *Hz*, Py–H), 8.3 (1H, m, Py–H), 8.2 (1H, t, imi–H), 8.0 (1H, m, Py–H), 7.9 (1H, t, imi–H), 7.6 (1H, m, Py–H), 4.8 (1H, m, $CH(CH_3)_2$), 1.6 (6H, m, $CH(CH_3)_2$); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 153.4 (C=N), 148.2 (NCHN), 129.9 (Ar–C), 127.5 (Ar–C), 124.5 (imi–C), 122.3 (imi–C), 121.4 (Ar–C), 119.4 (Ar–C), 30.2 (CH_3), 29.3 (CH_3); ESI: m/z calcd. For $C_{11}H_{14}N_3Br$ $[M–Br]^+$, 188.25; Found, $[M–Br]^+$, 188.17.

2.5c *Compound **1c** (R =^{t}Bu)*: The synthetic procedure of this compound was the same as that of above representative procedure, using 1-*tert*-butyl imidazole to give a pale yellow solid **1c**. Yield: 91%; M.p. 68–70°C; Anal. Calcd(%) for $C_{12}H_{16}N_3Br$: C, 51.08; H, 5.72; N, 14.89. Found(%): C, 51.39; H, 5.83; N, 14.62; ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 11.7 (1H, s, NCHN), 8.6 (1H, d, $J = 8.0$ *Hz*, Py–H), 8.5 (1H, dd, $J = 4.8$ *Hz*, $J = 1.0$ *Hz*, Py–H), 8.3 (1H, t, imi–H), 8.1 (1H, m, Py–H), 7.6 (1H, t, imi–H), 7.3 (1H, dd, $J = 7.1$ *Hz*, $J = 4.8$ *Hz*, Py–H), 4.6 (2H, t, ^{t}Bu), 1.9 (2H, m, ^{t}Bu), 1.3 (2H, m, ^{t}Bu), 0.9 (3H, m, ^{t}Bu); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 153.2 (C=N), 149.5 (NCHN), 141.2 (Ar–C), 136.9 (Ar–C), 129.4 (Ar–C), 127.3 (imi–C), 121.1 (imi–C), 115.0 (Ar–C), 50.0 (C, ^{t}Bu), 39.3 (C, ^{t}Bu), 19.4 (C, ^{t}Bu), 14.2 (C, ^{t}Bu); ESI: m/z calcd. For $C_{12}H_{16}N_3Br$ $[M–Br]^+$, 202.28; Found, $[M–Br]^+$, 202.08.

2.5d *Compound **1d** (R = Mes)*: The synthetic procedure of this compound was the same as that of above representative procedure, using 1-mesityl imidazole to give a pale yellow solid **1d**. Yield: 91%; M.p. 72–75°C; Anal. Calcd(%) for $C_{17}H_{18}N_3Br$: C, 59.31; H, 5.27; N, 12.21. Found(%): C, 59.07; H, 5.41; N, 12.39; ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 11.2 (1H, s, NCHN), 8.6 (1H, d, $J = 8.0$ *Hz*, Py–H), 8.3 (1H, m, Py–H), 8.2 (1H, t, imi–H), 8.1 (1H, m, Py–H), 7.9 (1H, t, imi–H), 7.7 (1H, m, Py–H), 2.4 (3H, s, CH_3), 2.2 (6H, s, CH_3); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 152.4 (C=N), 149.4 (NCHN), 129.3 (Ar–C), 126.7 (Ar–C), 123.2 (imi–C), 120.1 (imi–C), 119.5 (Ar–C), 117.4 (Ar–C), 30.2 (CH_3), 28.5 (CH_3), 28.2 (CH_3); ESI: m/z calcd. For $C_{17}H_{18}N_3Br$ $[M–Br]^+$, 264.35; Found, $[M–Br]^+$, 264.17.

2.6 *Syntheses of Pyridine-functionalized N-heterocyclic carbene ruthenium(II) complexes **(3a-d)***

Pyridine-functionalized imidazolium salts (R= Ph (**1a**), *i*Pr (**1b**), *t*Bu (**1c**), Mes (**1d**) (2 mmol) and Silver(I) oxide (0.231 g, 1 mmol) in 25 mL of dichloromethane were stirred in dark at room temperature for 24 h. The unreacted Ag_2O was removed by filtration over a pad of Celite. The resulting yellowish solution was concentrated to 2 mL then Et_2O was added to precipitate the product as a white, flaky solid. The solid was isolated, washed with Et_2O (3 × 5 mL), and dried under reduced pressure to yield the corresponding Ag–NHC complexes as an off-white solid. To the dichloromethane solution (15 mL) of Ag–NHC complex, $[RuHCl(CO)(PPh_3)_3]$ (0.9524 g, 1 mmol) was added, and the mixture was stirred overnight in dark at room temperature. After filtration through a Celite plug to remove the AgBr by-product, the solvent was reduced to 5 mL, and diethyl ether (20 mL) was added to precipitate the crude product. The resulting crude product was purified using column chromatography (SiO_2, 10:1 CH_2Cl_2/acetone).

2.6a *Compound **3a** (R = Ph)*: The synthetic procedure of this compound was the same as that of above representative procedure, using **1a** to give a yellow solid **3a**. Yield: 76%; M.p. 231–234°C; Anal. Calcd(%) for $C_{33}H_{27}N_3OClPRu$: C, 61.06; H, 4.19; N, 6.47. Found(%): C, 61.39; H, 4.42; N, 6.12; IR (KBr disks, cm^{-1}); 1974 (C≡O), 1560 (C=C), 1547 (N–C–N), 1502 (C–C), 1580 (C=N); ^{1}H NMR (300.13 MHz,

$CDCl_3$): δ 8.8–7.6 (4H, m, Py–H), 6.9–6.5 (5H, m, Ar–H), 6.4–6.3 (15H, m, PPh_3), −4.5 (1H, s, Ru–H); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 200.9 (C≡O), 198.6 (Ru–$C_{carbene}$), 152.7 (C=N), 137.2 (Ar–C), 134.9 (Ar–C), 128.5 (Ar–C), 125.8 (Ar–C), 124.4 (Ar–C), 123.8 (Ar–C), 120.1 (Ar–C), 115.1 (Ar–C), 112.5 (Ar–C); ^{31}P NMR (162 MHz, $CDCl_3$), δ 29.9 (s); ESI: m/z calcd. For $C_{33}H_{27}N_3OClPRu$ $[M]^+$, 649.08; Found, $[M]^+$, 649.07.

2.6b *Compound* ***3b*** *(R = ^{i}Pr)*: The synthetic procedure of this compound was the same as that of above representative procedure, using **1b** to give a yellow solid **3b**. Yield: 81%; M.p. 212–216°C; Anal. Calcd(%) for $C_{30}H_{29}N_3OClPRu$: C, 58.58; H, 4.75; N, 6.83. Found(%): C, 58.81; H, 4.92; N, 6.51; IR (KBr disks, cm^{-1}); 1981 (C≡O), 1564 (C=C), 1552 (N–C–N), 1510 (C–C), 1586 (C=N); ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 8.7–7.8 (4H, m, Py–H), 6.8–6.2 (15H, m, PPh_3), 4.7 (1H, m, $CH(CH_3)_2$), 1.7 (6H, m, $CH(CH_3)_2$) −4.54 (1H, s, Ru–H); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 202.4 (C≡O), 197.4 (Ru-$C_{carbene}$), 154.7 (C=N), 138.1 (Ar–C), 135.7 (Ar–C), 129.2 (Ar–C), 127.3 (Ar–C), 125.7 (Ar–C), 123.6 (Ar–C), 122.8 (Ar–C), 119.1 (Ar–C), 118.2 (Ar–C), 116.4 (Ar–C), 107.7 (Ar–C), 31.3 (CH_3), 29.4 (CH_3); ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.9 (s); ESI: m/z calcd. For $C_{30}H_{29}N_3OClPRu$ $[M]^+$, 615.07; Found, $[M]^+$, 615.65.

2.6c *Compound* ***3c*** *(R = ^{t}Bu)*: The synthetic procedure of this compound was the same as that of above representative procedure, using **1c** to give a yellow solid **3c**. Yield: 78%; M.p. 209–211°C; Anal. Calcd(%) for $C_{31}H_{31}N_3OClPRu$: C, 59.19; H, 4.97; N, 6.68. Found(%): C, 59.42; H, 4.63; N, 6.89; IR (KBr disks, cm^{-1}); 1979 (C≡O), 1572 (C=C), 1549 (N–C–N), 1504 (C–C), 1574 (C=N); ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 8.9–7.6 (4H, m, Py–H), 6.7–6.4 (15H, m, PPh_3), 1.7 (2H, m, ^{t}Bu), 1.7 (2H, m, ^{t}Bu), 1.2 (2H, m, ^{t}Bu), 0.9 (3H, m, ^{t}Bu), –4.4 (1H, s, Ru–H); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 203.6 (C≡O), 195.3 (Ru–$C_{carbene}$), 154.7 (C=N), 137.9 (Ar–C), 136.4 (Ar–C), 133.1 (Ar–C), 129.3 (Ar–C), 128.7 (Ar–C), 127.2 (Ar–C), 126.7 (Ar–C), 124.3 (Ar–C), 123.4 (Ar–C), 122.9 (Ar–C), 108.4 (Ar–C), 51.3 (C, ^{t}Bu), 38.3 (C, ^{t}Bu), 18.4 (C, ^{t}Bu), 16.2 (C, ^{t}Bu); ESI: m/z calcd. For $C_{31}H_{31}N_3OClPRu$ $[M]^+$, 629.09; Found, $[M]^+$, 629.05.

2.6d *Compound* ***3d*** *(R = Mes)*: The synthetic procedure of this compound was the same as that of above representative procedure, using **1d** to give a yellow solid **3d**. Yield: 82%; M.p. 230–234°C; Anal. Calcd(%) for $C_{36}H_{31}N_3OClPRu$: C, 62.56; H, 4.81; N, 6.08. Found(%): C, 62.83; H, 4.57; N, 6.43; IR (KBr disks, cm^{-1}); 1984 (C≡O), 1576 (C=C), 1543 (N–C–N), 1512 (C–C), 1581 (C=N); ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 7.7–7.4 (4H, m, Py–H), 6.8–6.4 (15H, m, PPh_3), 3.4 (3H, s, CH_3), 2.7 (3H, s, CH_3), 2.1 (3H, s, CH_3), –4.78 (1H, s, Ru-H); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 204.1 (C≡O), 195.2 (Ru–$C_{carbene}$), 147.1 (C=N), 131.5 (Ar–C), 130.1 (Ar–C), 128.6 (Ar–C), 127.3 (Ar–C), 126.5 (Ar–C), 123.2 (Ar–C), 108.9 (Ar–C), 35.1 (CH_3), 33.9 (CH_3), 25.7 (CH_3); ESI: m/z calcd. For $C_{36}H_{33}N_3OClPRu$ $[M]^+$, 691.16; Found, $[M]^+$, 691.46.

2.7 *Representative procedure for ruthenium-catalyzed aldehydes to amides conversion*

The reaction vessel was charged with aldehyde (1 mmol), $NH_2OH{\cdot}HCl$ (1 mmol), $NaHCO_3$ (1 mmol), [Ru–NHC] catalyst (0.5 mol %) and the mixture was placed under an atmosphere of N_2. About 2 mL of dry and degassed toluene was added and the mixture was stirred for 15 min at room temperature followed by reflux for 8 h. On completion of the reaction, 2–3 mL methanol was added to the mixture followed by filtration through Celite to remove the catalyst and $NaHCO_3$. The crude product was then purified by column chromatography ($MeOH/CH_2Cl_2$, 1:1) using silica (200–400 mesh) as solid phase provided the amide in good yield. The resultant amide solution was subjected to GC analysis and the product was identified in comparison with authentic samples

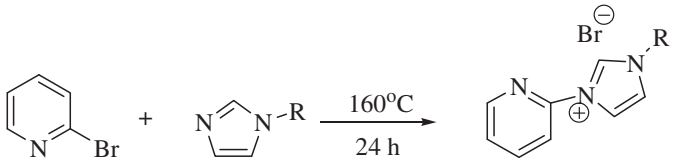
3. Results and Discussion

3.1 *Synthesis and characterization of pyridine-functionalized N-heterocyclic carbene ligands*

Pyridine-functionalized imidazolium salts (**1a–d**) were synthesized according to known literature procedure[51] (Scheme 1) by the reaction of 2-bromopyridine with 1-substituted imidazole stirred at 160°C for 20 h. The new ligands (**1a–d**) obtained are highly air and moisture stable. The ligands were fully characterized by ^{1}H and ^{13}C NMR, mass spectra and elemental analysis.

3.2 *Synthesis of Precatalysts*

The synthetic plan to achieve the new ruthenium complexes disclosed herein was initially attempted *via* the



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

Scheme 1. General preparation of pyridine-functionalized imidazolium salts (**1a–1d**).

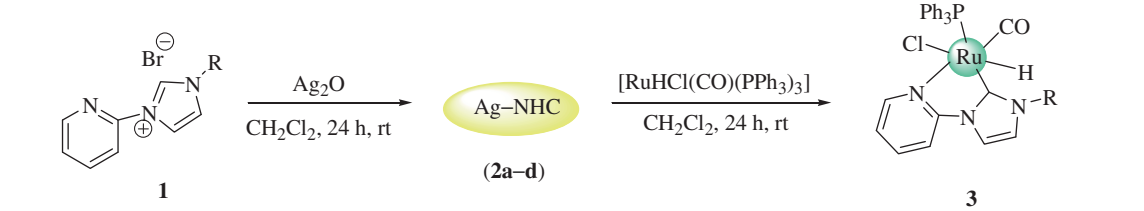
free carbene route. Imidazolium deprotonation using a strong base such as *t*−BuOK or *n*−BuLi and subsequent ruthenium coordination yielded the desired products in low yield with significant amounts of unidentified impurities. Hence, the mild silver base (Ag_2O) has been used for the deprotonation in the syntheses of N-heterocyclic carbene complexes. This procedure is probably one of the most general methods, because it generates an air-stable intermediate under mild reaction conditions, thus allowing a straightforward access to a wide range of transition metal complexes. It is often used successfully when other methods failed. The use of Ag–NHC complexes as carbene transfer reagents provide a convenient way to overcome the difficulties arising from using strong bases, inert atmospheres, and complicated workups. All the desired [Ru–NHC] complexes (**3a–d**) were synthesized following the carbene transfer route, more precisely transmetalation of the *in situ* generated NHC-silver(I) bromide complexes with the [$RuHCl(CO)(PPh_3)_3$] precursor (Scheme 2). All the complexes (**3a–d**) are highly soluble in CH_2Cl_2, $CHCl_3$, THF and DMSO but insoluble in diethyl ether and hydrocarbon solvents. They were fully characterized by spectral (^{1}H NMR, ^{13}C NMR, IR, mass) and elemental analysis studies.

3.3 *Spectroscopic description*

IR spectra of free ligand were compared with new complexes in order to confirm the coordination of ligand to ruthenium metal. The new [Ru–NHC] complexes (**3a–d**) show a νCO stretch in the IR spectrum at ∼1981 cm^{-1}. The complexes showed a strong band in the region 1552–1543 cm^{-1} due to ν(N–C–N). A strong vibration was observed at 1576–1560 cm^{-1} in the spectra of complexes corresponding to C=C stretching. In all the ruthenium complexes, the band due to terminal ν(C=N) group appeared at 1586–1581 cm^{-1}. In addition to the above vibrations, the characteristic bands due to triphenylphosphine group were also present in the expected region.[52]

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) proton. The imidazolium ring backbone signals appeared around 8.2–7.6 ppm, the pyridine protons appeared in the region of 8.9–7.4 ppm. A signal at high field (∼–4.8 ppm) indicated the presence of the hydride ligand. Furthermore, the spectra of all the complexes showed a series of signals for aromatic protons at 7.4–6.4 ppm. In addition, a singlet appeared around 3.4–2.2 ppm for complexes **3a** and **3d** corresponding to terminal CH_3 group protons. The spectra of the complexes showed a singlet at 1.7–0.9 ppm, which has been assigned to *t*Bu protons (Figures S1–S4, in Supplementary Information).

^{13}C NMR chemical shifts, which provide a useful diagnostic tool for metal carbene complexes, display the expected resonances with a single Ru–$C_{carbene}$ resonance at *ca.* 198.5–195.2 ppm[52] and the C≡O signal



1 (**2a–d**) **3**

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

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

Scheme 2. General synthesis of [Ru–NHC] complexes (**3a–3d**).

resonating at δ 204.1–200.9 ppm. In complexes (**3a–d**), aromatic carbon atoms observed around 136.4–108.3 ppm. The presence of a peak at 154.2–147.1 ppm region was assigned to C=N group. The presence of chemical shifts in the range of 33.9–25.7 ppm belonged to the methyl protons (Figures S5–S8, in Supplementary Information).

^{31}P NMR spectra were recorded for the complexes in order to confirm the presence of triphenylphosphine group. The complexes **3a** and **3b** exhibited only one signal at 29.9 and 29.9 ppm, consistent with the presence of only one triphenylphosphine ligand (Figures S9 and S10, in Supplementary Information).

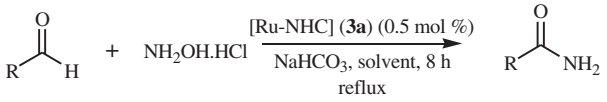
The molecular ion peaks (M^+) observed with *m*/*z* values 222.17, 188.17, 202.08, 264.17, 649.07, 615.65 and 629.05 corresponding to the ligands **1a–d** and [Ru–NHC] complexes **3a, 3b**, **3c** and **3d**, respectively, in the ESI-MS spectra of the ligands and complexes, support the proposed molecular formulae (Figures S11–S18, ESI). Unfortunately, we have not yet obtained high-quality crystals of Ru–NHC complexes suitable for X-ray single-crystal diffraction, suggesting that subtle structural factors are critical to stabilizing this species.

3.4 *Catalytic studies*

3.4a *Catalytic aldehyde to amide conversion*: The synthesized [Ru–NHC] complexes **3a–d** were employed as catalysts for the conversion of aldehydes to their corresponding amides. In order to optimize the reaction conditions, the effect of solvents was tested and the results are summarized in Table 1. For the initial experiments, benzaldehyde was selected as a test-substrate and allowed to react in different solvents with catalytic quantities of [Ru–NHC] complex **3a** in the presence of $NaHCO_3$ additive. Benzene, DMF, DMSO, Toluene, THF, Xylene, $CHCl_3$, CH_3CN and CH_2Cl_2 are taken for our solvent variant study. Out of different solvents tested during the course of optimization, the solvents such as benzene, DMF, DMSO, Xylene, CH_2Cl_2 and $CHCl_3$ could bring about only a little conversion (Table 1, Entries 1, 5, 6, 7, 10, 11). THF was found to be ineffective. However, acetonitrile gives a good yield of 84 and 89%. When the reaction was carried out in toluene, 98 and 99% isolated product yield at the temperature of 110°C (Table 1, Entries 3, 4) was observed. It is interesting to note that toluene could not afford any conversion at 90°C, hence implicating a crucial temperature effect on the reaction. A 20°C rise in temperature caused a spectacular effect on the reaction.

The choice of base was made, as the next step for optimization. No conversion was observed in the absence of base (Table 2). It has been observed that in toluene solvent, $NaHCO_3$ and $KHCO_3$ gave excellent isolated yields of 98 and 93%, respectively (Table 2, Entry 4, 6) when compared to a much weaker base like CH_3COONa and Et_3N (Table 2, Entry 9, 10). Thus it was concluded that $NaHCO_3$ as a base in toluene solvent at 110°C is the optimized condition for this conversion.

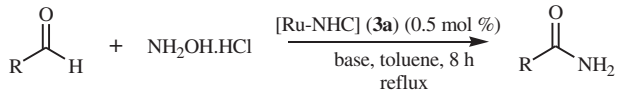
Table 1. Effect of solvents on amidation of benzaldehyde to benzamide catalyzed by [Ru–NHC] complex **3a**[a].



Entry	Solvent	Temp (°C)	Time (h)	(%) conversion[b]
1	Benzene	80	12	32
2	THF	66	12	n.r
3	Toluene	90	12	n.r
3	**Toluene**	**110**	**8**	**98**
4	**Toluene**	**110**	**12**	**99**
5	DMF	153	12	27
6	DMSO	189	12	42
7	Xylene	144	12	37
8	**Acetonitrile**	**82**	**8**	**84**
9	**Acetonitrile**	**82**	**12**	**89**
10	Dichloromethane	40	12	47
11	Chloroform	61	12	31

[a]Reaction Conditions: aldehyde (1 mmol), $NH_2OH{\cdot}HCl$ (1 mmol), $NaHCO_3$ (1 mmol), [Ru–NHC] catalyst **3a** (0.5 mol%) under N_2, reflux for 8-12 h; [b]Conversion determined by GC.

Table 2. Effect of base on amidation of benzaldehyde to benzamide catalyzed by [Ru–NHC] complex **3a**[a].



Entry	Base	(%) conversion[b]
1	NaOH	48
2	K_2CO_3	69
3	KO*t*Bu	37
4	**$NaHCO_3$**	**98**
5	KOH	41
6	$KHCO_3$	93
7	NaO*t*Bu	72
8	Na_2CO_3	27
9	Et_3N	93
10	CH_3COONa	24
11	Without base	n.r

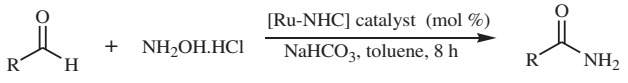
[a]Reaction Conditions: aldehyde (1 mmol); $NH_2OH{\cdot}HCl$ (1mmol), base (1 mmol); [Ru–NHC] catalyst **3a** (0.5 mol%) under N_2, reflux for 8 h; [b]Conversion determined by GC.

In order to optimize the catalyst loading, the amidation reaction was performed at catalyst loading in the range of 0.15–0.5 mol% (Table 3). The reactions proceed with high conversion of benzaldehyde to benzamide when 0.5 mol% is used. Further, the catalyst works well with low catalyst loading of 0.15 mol% and 0.25 mol%, showing a yield of 68–77% and 73–84% respectively. Since, the isolated yields are good with appreciable turnover numbers when catalyst loading is 0.5 mol%. Catalyst with phenyl wingtip substituent exhibits higher activity when compared to others. Hence, the order of catalytic activity with respect to different wingtip substituents has been observed as **3a**>**3d**>**3b**>**3c**.

In order to ensure the generality of this finding, a range of aromatic aldehydes were converted to amides using catalyst **3a** under the optimized condition. A broad range of amides were successfully synthesized with good to high isolated yields using the above optimized protocol. The results collected from the catalytic reactions are listed in Table 4. The electron donating groups like $-CH_3$, $-OCH_3$ and $-OH$ on benzaldehyde alters the reaction and the corresponding amides were obtained in excellent yields of 93, 96 and 91% respectively (Table 4, Entries 2, 3, 4) and gave slightly lower yields compared with benzaldehyde (Table 4, Entry 1). On the other hand, electron withdrawing substituents, such as $-NO_2$, $-Cl$ and $-Br$ substituents also offer good yields (Table 4, Entries 6, 7, 8). The reaction of napthaldehyde in presence of toluene afforded the desired amide product in excellent yield (Table 4, Entry 8). The catalyst shows good catalytic activity for the conjugated aldehyde such as, cinnamaldehyde which was converted to the corresponding conjugated amides in 92% yield (Table 4, Entry 9). Interestingly, the amidation reaction with aliphatic aldehyde gave good yield (Table 4, Entry 10).

Further, to explore the scope of the catalyst, a range of heteroaromatic aldehydes were converted to primary heteroaromatic amides using catalyst **3a** under the optimized condition. Results show all the aldehydes reacted well and resulted in excellent yield of the products (Table 5). The complex efficiently catalyzes the reaction of thiophene and substituted thiophene aldehydes to their corresponding carboxamides in good yield (Table 5, Entry 1, 2). The pyridine carbaldehydes yielded the corresponding amide product in 76% and 81% yields (Table 5, Entries 3, 4). Moderate yields of amide products could be obtained for the reaction involving indole-2-carbaldehyde and

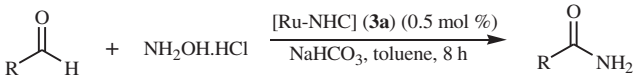
Table 3. Effect of catalyst screening on amidation of benzaldehyde to benzamide catalyzed by [Ru–NHC] complexes **3a–3d**[a].

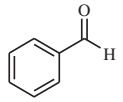
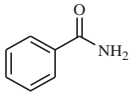
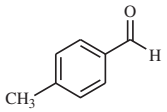
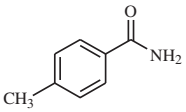
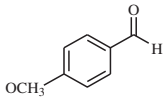
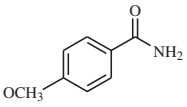
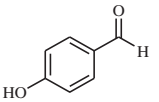
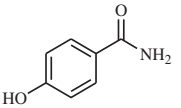
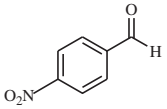
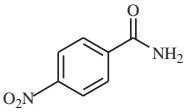
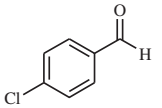
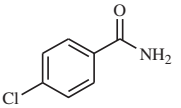
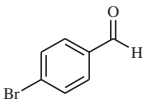
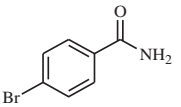
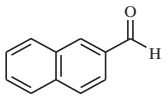
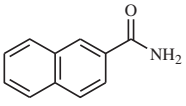
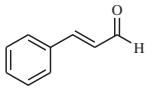
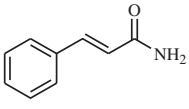
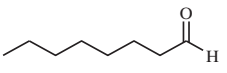
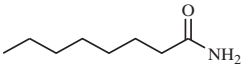


Entry	Catalyst	Amount of catalyst (mol %)	TON[b]	TOF (h^{-1})[c]	(%) conversion[b]
1	**3a**	**0.15/0.25/0.5**	**513/332/196**	**64/42/25**	**77/83/98**
2	**3b**	0.15/0.25/0.5	493/336/174	62/42/22	74/84/87
3	**3c**	0.15/0.25/0.5	413/292/162	52/37/20	62/73/81
4	**3d**	0.15/0.25/0.5	453/296/178	57/37/22	68/74/89

[a]Reaction Conditions: aldehyde (1 mmol), $NH_2OH{\cdot}HCl$ (1 mmol), $NaHCO_3$ (1 mmol), [Ru–NHC] catalyst **3a–3d** (0.15–0.5 mol%) under N_2 reflux for 8 h. [b]Turnover number (TON) = (mmol of product)/(mmol of catalyst) after time t; [c] Turnover frequency (TOF) = TON/time (h); [d]Conversion determined by GC.

Table 4. One pot synthesis of amides from aldehydes catalyzed by [Ru–NHC] complex **3a**[a].



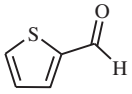
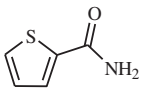
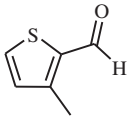
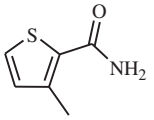
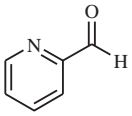
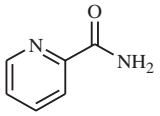
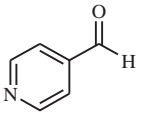
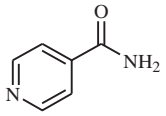
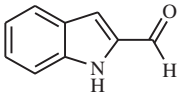
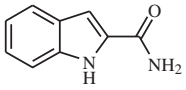
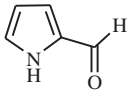
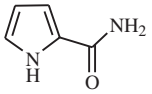
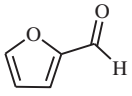
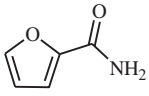
Entry	Aldehyde	Amide	TOF (h^{-1})[b]	(%) conversion[c]
1			25	98
2			23	93
3			24	96
4			23	91
5			22	89
6			24	94
7			23	93
8			25	99
9			23	92
10			20	81

[a]Reaction Conditions: aldehyde (1 mmol), $NH_2OH{\cdot}HCl$ (1 mmol), $NaHCO_3$ (1 mmol), [Ru–NHC] catalyst **3a** (0.5 mol%) under N_2 reflux for 8 h; [b]Turnover frequency (TOF) = TON/time (h); [c]Conversion determined by GC.

pyrrole-2-carbaldehyde (Table 5, Entries 5, 6). However, when furan-2-carbaldehyde was used as a substrate, higher yield was obtained (Table 5, Entry 7). It is worth noting that by-products such as nitriles or carboxylic acids are not observed in this protocol, indicating that this reaction differs from the Beckmann rearrangement.

Further, we believe that the catalytic transformation proceeds *via* the oxidative addition of the aldoxime N–OH bond to Ru(II)–NHC complex, followed by nucleophilic attack on the coordinated imine, and then β-elimination of cyclometalated compound, and finally reductive elimination to give the amide according to the proposed mechanism by Crabtree and his coworkers.[44a] In this reaction, water cannot be eliminated as a by-product indicating the absence of nitrile products. The present [Ru–NHC] catalyst is more efficient in amidation reaction than the reported ruthenium(II)

Table 5. One pot synthesis of amides from heteroaromatic aldehydes catalyzed by [Ru-NHC] complex **3a**[a].

Entry	Aldehyde	Amide	TOF (h^{-1})[b]	(%) conversion[c]
1			24	97
2			22	87
3			19	76
4			20	81
5			18	73
6			20	79
7			22	88

[a]Reaction Conditions: aldehyde (1 mmol), $NH_2OH{\cdot}HCl$ (1 mmol), $NaHCO_3$ (1mmol), [Ru–NHC] catalyst **3a** (0.5 mol%) under N_2 reflux for 8 h; [b]Turnover frequency (TOF) = TON/time (h); [c]Conversion determined by GC.

complexes in terms of reaction time, catalyst loading and isolated yields.[44a,53]

4. Conclusions

A new series of imidazolium salts (**1a–d**) was designed and successfully used for the preparation of ruthenium(II) complexes bearing neutral bidentate ligands of *N*-heterocyclic carbene and pyridine donor moiety. The ruthenation was accomplished by metalation with Ag_2O to form intermediate silver carbene complexes and subsequent transmetalation with $[RuHCl(CO)(PPh_3)_3]$. Promising yields were obtained. The [Ru–NHC] complexes (**3a–d**) displayed excellent stability toward air and moisture which are the additional advantages for a better catalyst. Based on the spectral results, an octahedral geometry was assigned for all the complexes. The catalytic ability of the present system for the conversion of aldehydes to amides has been studied and the conversions are found to be excellent. Notably, the complex **3a** was found to be a very efficient and versatile catalyst towards amidation of a wide range of aldehydes.

Supplementary Information (SI)

Representative NMR (^1H, ^{13}C, ^{31}P) and ESI-MS spectra of ligand and complexes (Figures S1–S18) are given in the supporting information, available at www.ias.ac.in/chemsci.

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