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Highly efficient synthesis of primary amides via aldoximes rearrangement in water under air atmosphere catalyzed by an ionic ruthenium pincer complex†

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The transformation of aldoximes to primary amides has been evaluated using pincer ruthenium complexes a–c, among which the ionic Ru catalyst a proved to be the most efficient in water under air atmosphere. A variety of (hetero)arene aldoximes proceeded smoothly to afford amides in high yields with good functional group compatibilities. Furthermore, a direct synthetic route of amides from aldehydes, hydroxylamine hydrochloride and sodium carbonate was also described with broad substrates including conjugated and aliphatic aldehydes. This protocol is operationally simple and proceeds with a low catalyst loading (0.5 mol%).

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Introduction

Amide bond formation is one of the most important chemical transformations in organic and biological chemistry, which has been widely utilized in pharmaceuticals, natural products, peptides, and numerous fine materials.¹ The classical methods for amide synthesis involve the reaction of carboxylic acids (at the cost of stoichiometric amounts of coupling reagents such as carbodiimide) or activated carboxylic acid derivatives (*e.g.* chlorides, anhydrides or esters) with amines,² which always suffers from low atom efficiency and environmental issues. Alternatively, Brønsted or Lewis acids-catalyzed Beckmann rearrangement of oximes provides a straightforward method to synthesize *N*-substituted amides.³ However, the use of large amounts of acids, harsh reaction conditions, as well as nitrile generations are the major limitations. In view of this, “amide formation avoiding poor atom economy reagents” was identified as one of the top challenges in organic chemistry.⁴

Recently, transition-metal catalyzed synthetic approaches have appeared as a promising strategy to achieve amide transformations.⁵ Different from Beckmann rearrangement, which

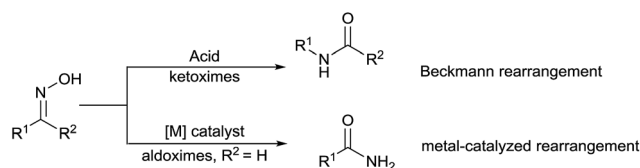
typically generates secondary amides from ketoximes, the rearrangement of aldoximes could be converted into primary amides catalyzed by various transition-metals, such as Fe,⁶ Co/⁷ Zn,⁷ Ni,⁸ Cu,⁹ Zn,¹⁰ Ru,¹¹ Rh,¹² Pd,¹³ In,^{10,14} Ir,¹⁵ Au/Ag¹⁶ (Scheme 1). In special, Ru complexes have been frequently employed for primary amide transformations.^{11,17} However, most of the catalytic systems utilized additional additives,^{11a} organic solvent,^{11a–f} or relatively high catalytic loading.^{11c,g–j} In the search of more environmentally benign protocols, water was recognized as a cheap, nontoxic, and eco-friendly solvent to replace traditional organic solvents.¹⁸ In 2007, Mizuno and co-workers firstly reported the preparation of primary amides using heterogeneous catalyst Rh(OH)_x/Al₂O₃ (4 mol%) at 160 °C in aqueous medium.^{12b} Since 2009, Cadierno and co-workers have also developed the arene–ruthenium(II) complexes (3–5 mol%) to catalyze the same transformations under N₂ in water.^{11g–j} Recently, Li and co-workers described the rearrangement of aldoximes to amides by a relatively expensive Ir complexes [Cp*Ir(H₂O)₃][OTf]₂ (1.5 mol%) under air in water.^{15b} Considering the green and sustainable chemistry, it is highly desirable to develop a new catalytic system with mild conditions, low catalyst loading, and relatively cheap metals.

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Scheme 1 Aldoxime rearrangements to amides.

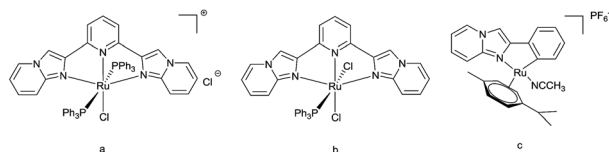


Fig. 1 Ru complexes a–c.

We have been interested in developing pincer Ru complexes and their catalytic activities for transfer hydrogenation of ketones.¹⁹ As an continuation of our work to develop Ru-catalyzed reactions, we herein report the employment of an ionic Ru catalyst **a**^{19b} (Fig. 1) for the transformation of aldoximes to amides in water under air. The direct one-pot conversion of aldehydes into primary amides was also attempted. Finally, the reaction mechanism involving a dehydration/rehydration sequence *via* the metal–nitrile species was proposed for this transformation.

Results and discussion

In the search for Ru-catalyzed aldoxime rearrangements to amides, three different ruthenium complexes **a–c** were developed. Tridentate Ru complexes **a** and **b** were synthesized according to previous literature.¹⁹ Bidentate Ru complex **c** was also obtained through a modified synthetic procedure (Experimental section). Commercially available benzaldoxime **1a** was employed as the model substrate to examine the catalytic ability

of Ru complexes **a–c** (Table 1). Initially, the influence of Ru catalysts and solvent (0.4 M) were investigated, and the results were summarized in Table 1. Moderate to high yields were achieved by employing toluene and water as solvent, with Ru catalyst **a** exhibiting the highest reactivity (Table 1, entries 1–6). Compared with toluene, pleasingly, higher yield of 90% could be obtained when water as a green solvent was adopted (Table 1, entry 4). The simple RuCl₃ complex has also been examined to deliver **2a** in 48% yield. The high efficiency of Ru ionic complex **a** is related with itself hydrophilicity, which increases the solubility in water medium. Meanwhile, the presence of phosphine and N[∧]N[∧] ligand can be utilized as the Brønsted base for the nucleophilic attack by aldoxime as a water-surrogate.^{14f} Subsequently, other solvents were also examined as the negative control (Table 1, entries 8–15). Reaction in DMF, 1,4-dioxane, CH₃CN, THF, and CHCl₃ afforded trace, if any, product under Ru catalyst **a**. Interestingly, benzonitrile was obtained as the major byproduct in 65% yield *via* the dehydration of the oxime starting material when the reaction was carried out in CH₃CN.²⁰ Decreased yields were also observed in EtOH, DCE, and PhCF₃ solvent.

On the basis of above analysis, the effects of temperature, concentration, catalyst loading, and reaction time were examined. Conducting the reaction at 110 °C above the boiling point of water was necessary to achieve good yield, which was reduced to 83% and 65% when lowering the temperature to 100 °C and 80 °C, respectively (Table 2, entries 1–2). Elevated temperature of 130 °C also led to decreased yield (Table 2, entry 3). In addition, substrate concentration had some influence on the reaction efficiency, with concentration of 0.4 M providing the highest yield (Table 1, entry 4). Decreased catalytic activities

Table 1 Catalytic behavior of Ru catalyst and solvent in rearrangement of benzaldoxime **1a** to benzamide **2a**^a

Entry	Catalyst	Solvent	Temp (°C)	Yield ^c (%)
1	a	PhMe	110	71
2	b	PhMe	110	39
3	c	PhMe	110	55
4	a	H ₂ O	110	90
5	b	H ₂ O	110	79
6	c	H ₂ O	110	36
7	RuCl₃	H ₂ O	110	48
8 ^b	a	EtOH	78	53
9 ^b	a	DMF	153	N.R.
10 ^b	a	1,4-Dioxane	101	Trace
11 ^b	a	CH ₃ CN	82	Trace
12 ^b	a	THF	66	Trace
13 ^b	a	CHCl ₃	62	Trace
14 ^b	a	DCE	84	22
15 ^b	a	PhCF ₃	103	72

^a The reaction was conducted with **1a** (0.4 mmol) in the presence of Ru complexes (0.5 mol%) in solvent (0.4 M) at 110 °C for 10 h. ^b Boiling point of corresponding solvent was applied. ^c Isolated yield.

Table 2 Optimization of the concentration, catalyst loading and reaction time of amide formation^a

Entry	Conc (M)	Ru (mol%)	Time (h)	Yield ^e (%)
1 ^b	0.4	0.5	10	65
2 ^c	0.4	0.5	10	83
3 ^d	0.4	0.5	10	82
4	0.8	0.5	10	77
5	0.2	0.5	10	80
6	0.1	0.5	10	76
7	0.4	1	10	86
8	0.4	2	10	83
9	0.4	0.3	10	61
10	0.4	0.5	8	63
11	0.4	0.5	12	97
12	0.4	0.5	16	94

^a The reaction was conducted with **1a** (0.4 mmol) in the presence of Ru **a** in solvent at 110 °C. ^b The reaction was conducted at 80 °C. ^c The reaction was conducted at 100 °C. ^d The reaction was conducted at 130 °C. ^e Isolated yield.

were observed at either higher concentration (Table 2, entry 4) or lower concentrations (Table 2, entries 5 and 6). Increasing the catalyst loading from 0.5 mol% to 1 mol% and 2 mol% led to slightly decreased efficiency (Table 2, entries 7 and 8), while only 61% yield was achieved for 0.3 mol% of catalyst loading (Table 2, entry 9). Finally, prolonged reaction time is beneficial for nearly complete conversion. A yield of 97% was successfully accomplished when extending the reaction time to 12 h (Table 2, entry 11). Based on the above discussion, the optimal reaction conditions employed 0.5 mol% Ru **a** as the catalyst in water at 110 °C for 12 h.

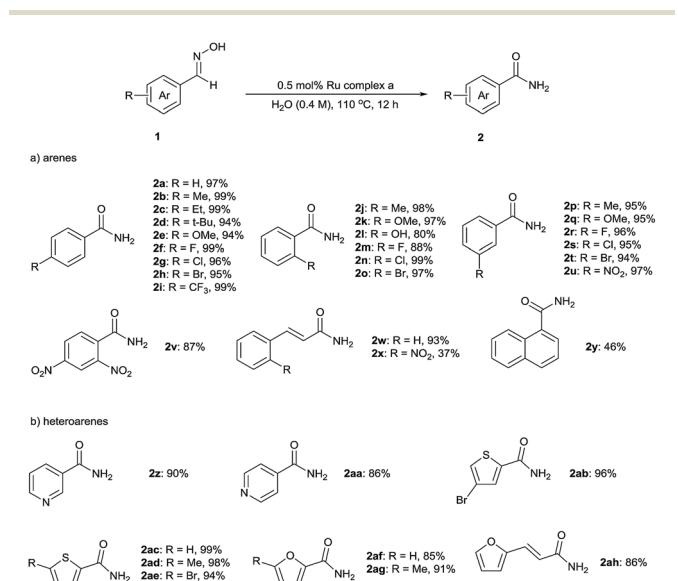
With the optimized conditions established (Table 2, entry 11), a broad range of aromatic aldoximes were investigated for primary amide formation reactions (Scheme 2). Benzaldoximes bearing electron-donating and electron-withdrawing groups at *ortho*, *meta*, or *para* positions all proceeded smoothly to afford the corresponding products **2a–u** in 80–99% yields. Multiple functional groups, including halogen, ether, nitro, trifluoromethyl and even *ortho*-hydroxyl substituents, were well tolerated. High yield of 87% were also achieved for 2,4-dinitro-substituted aldoximes into primary amide **2v**. Meanwhile, the α,β -unsaturated cinnamaldoxime was proven to be suitable substrates to deliver the desired products **2w** in 93% yield. To our disappointment, *ortho*-nitro substituted aldoxime only provided amide **2x** in 37% yield. Moderate transformation was observed for 1-naphthaldoxime, which generated 1-naphthamide **2y** in 46% yield. The present catalytic system was not limited to arene substrates. Heteroarene substrates, such as pyridyl, thienyl, and furanyl moieties, all furnished the primary amides **2z–ah** in high yields of 85–99%. It is noteworthy that excellent yields could still be achieved for thiophene carboxaldoximes **2ab–ae**, despite sulfur species are detrimental for homogeneous catalysts due to the formation of strong metal-sulfur bonds.²¹

To provide step-economic access to primary amides, the one-pot synthesis from aldehydes and hydroxylamine

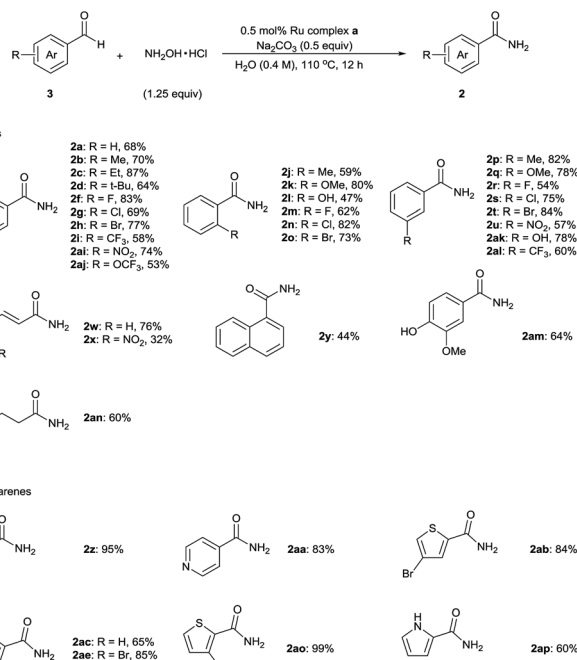
hydrochloride was conducted in the presence of sodium carbonate and Ru catalyst *via* a condensation/rearrangement cascade (Scheme 3). To our delight, a variety of aldehydes, including aromatic, unsaturated, aliphatic and heterocyclic ones, could couple with hydroxylamine hydrochloride smoothly to afford the corresponding amides in moderate to high yields, with unsaturated amide **2w** in 76% yield and aliphatic amide **2an** in 60% yield. Also, disubstituted vanillin could be transformed into corresponding product **2am** in 64% yield. Notably, heteroarene-containing primary amides **2z–ab**, **2ae**, and **2ao** could be efficiently prepared in high to excellent yields. Compared with aldoxime reactants, decreased yields were obtained from corresponding aldehydes. Nevertheless, the results were acceptable considering the catalyst loading as low as 0.5 mol%, as well as tandem one-pot synthesis.

Intrigued by the substrate versatility and efficiency of the Ru-catalyzed rearrangement of aldoximes to amides, we conducted mechanistic studies to obtain information for this reaction. In the transformation of benzaldoxime **1a** to benzamide **2a**, GC was used to monitor the reaction process and no benzonitrile was found. Furthermore, benzamide wasn't detected when benzonitrile was treated with 0.5 mol% Ru catalyst **a** in water at 110 °C for 12 h [eqn (1)]. However, when 1 equivalent of **1z** was added in the previous reaction under the same conditions, benzamide **2a** was obtained in 68% yield, accompanied with formation of **4** in 11% yield [eqn (2)].

Two different reaction pathways have been proposed based on mechanistic investigations. The first one involves the initial dehydration of aldoxime and subsequent hydration by the water released in the previous step *via* a metal-nitrile

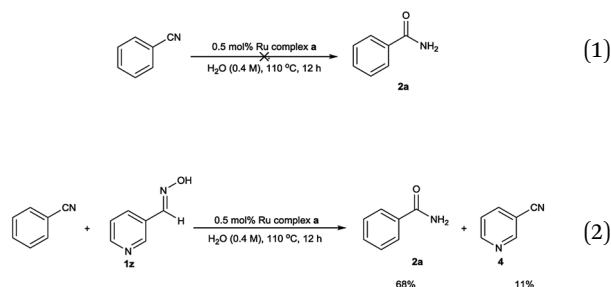


Scheme 2 Reaction of (hetero)arene carboxaldoximes **1** to amides **2**.

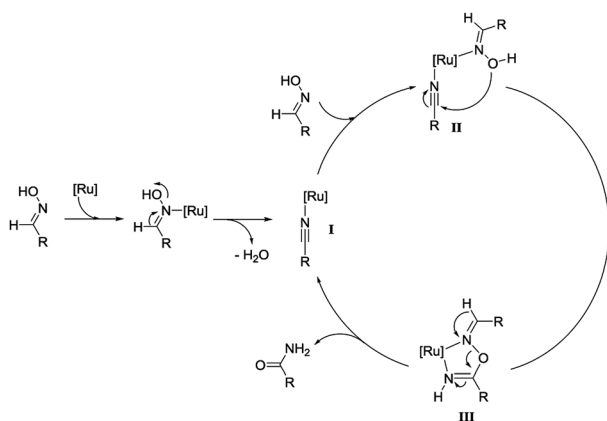


Scheme 3 One-pot synthesis of amides from aldehydes, hydroxylamine hydrochloride and sodium carbonate.

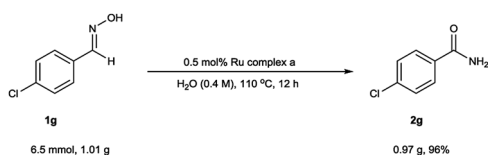
intermediate.^{11a,12a} In the second mechanism, the generated metal–nitrile specie was attacked by another aldoxime through a five-membered metallacyclic intermediate, which was evidenced with isotopically labeled substrates.²² Based on our preliminary mechanism investigation, the plausible catalytic cycle was proposed (Scheme 4). The process commences with metal-induced dehydration of the substrate to form metal–nitrile species **I**, which coordinates with another aldoxime to generate intermediate **II**. The second aldoxime acts as a water-surrogate to attack the metal–nitrile species to form a five-membered metallacyclic intermediate **III**. Decomposition of the intermediate **III** will lead to the formation of the primary amide product and regeneration of species **I** to continue the catalytic cycle.



To highlight the synthetic potential for this protocol, a gram-scale reaction was conducted using **1g** as the substrate, to afford the primary amide **2g** in 96% yield (Scheme 5). This pleasing result demonstrates the high efficiency and promising applicability of this catalytic system for the production of valuable primary amides.



Scheme 4 Proposed catalytic cycle.



Scheme 5 Gram-scale synthesis.

Conclusions

In conclusion, an ionic ruthenium pincer catalyst **a** was applied, which exhibited high efficiency for the rearrangement of aldoximes to amides in water under an air atmosphere. In addition, catalyst **a** was applicable for the one-pot synthesis of amides from aldehydes and hydroxylamine hydrochloride *via* a condensation/rearrangement cascade. Various substrates, including aromatic and heteroaromatic, were well tolerated with high functional group compatibilities. It is noteworthy to mention that this protocol exhibited some advantages such as low catalyst loading, environmental benignity and operational convenience without any ligands or additives.

Experimental section

General experimental details

Solvents were dried with standard methods and freshly distilled prior to use if needed. Ru catalyst **a** and **b** were synthesized according to previous reports.¹⁹ Unless otherwise indicated, all reactions for amide syntheses were run under an atmosphere of air. Melting points were measured on an XT4A melting point apparatus. Infrared spectra were obtained by a PerkinElmer FT-IR Spectrophotometer. ¹H NMR and ¹³C NMR spectra were recorded at 400 MHz or 600 MHz using Bruker spectrometers with TMS as an internal standard. Data are reported as follows: chemical shift (δ ppm), multiplicity (s = single, d = doublet, t = triplet, q = quartet, m = multiplet), integration, and coupling constants (J) in hertz (Hz). HRMS were determined on a Q-ToF Micro MS/MS System ESI spectrometer. Flash column chromatography was performed on silica gel (200–300 mesh). Analytical and preparative thin-layer chromatography (TLC) plates coated with commercial silica gel were used to monitor the reactions and purify amide products.

Synthesis of the cationic ruthenium complex **c**²³

A suspension of [RuCl₂(*p*-cymene)₂] (36.8 mg, 0.06 mmol), 2-phenyl-imidazo[1,2-*a*]pyridines (25.6 mg, 0.132 mmol), NaOH (4.8 mg, 0.12 mmol), and KPF₆ (44.2 mg, 0.24 mmol) in CH₃CN (5 mL) were stirred at 45 °C for 3 h. The reaction mixture was passed through vacuum filtration apparatus to remove the solvent. Solid was collect and immediately dried *in vacuo*. The residue was purified by silica gel column chromatography with ethyl acetate as eluent to give complex **c** (36.9 mg, 45.5%). MP: 105–107 °C. IR: ν 2965, 1637, 1597, 1504, 1293, 1016, 828, 748, 555 cm⁻¹. ¹H NMR (600 MHz, CDCl₃) δ 8.28 (d, J = 6.7 Hz, 1H), 8.03 (d, J = 7.4 Hz, 1H), 7.95 (d, J = 9.1 Hz, 1H), 7.85 (s, 1H), 7.54 (t, J = 8.5 Hz, 2H), 7.14 (t, J = 7.3 Hz, 1H), 7.08 (t, J = 7.3 Hz, 1H), 6.97 (t, J = 6.7 Hz, 1H), 6.03 (d, J = 5.9 Hz, 1H), 5.86 (d, J = 5.8 Hz, 1H), 5.70 (d, J = 5.9 Hz, 1H), 5.50 (d, J = 5.9 Hz, 1H), 2.19–2.15 (m, 1H), 2.02 (s, 3H), 2.00 (s, 3H), 0.85 (d, J = 6.9 Hz, 6H). ¹³C NMR (151 MHz, CDCl₃) δ 169.9, 152.4, 145.4, 139.7, 138.7, 128.4, 128.1, 127.7, 124.0, 122.7, 122.3, 114.8, 114.2, 106.1, 100.9, 100.7, 91.7, 90.5, 87.0, 84.2, 31.0, 22.2, 22.0, 18.7, 3.5. HRMS (positive ESI, m/z): [M – PF₆ – CNMe]⁺ calcd for C₂₃H₂₃N₂Ru 429.0905, found 429.0904.

General procedure for the rearrangement of aldoximes to amides in water catalyzed by Ru complex a

To a flame-dried 15 mL sealed tube were added aldoxime (0.4 mmol), catalyst a (0.002 mmol, 0.5 mol%) and H₂O (1 mL) under air atmosphere. The reaction mixture was heated at 110 °C for 12 h and then cooled to room temperature. The reaction mixture was directly evaporated and the residue was purified by preparative TLC plates to provide the desired product. ¹H and ¹³C NMR spectra were used to characterize amide products, and their analytical data are given in the ESI.†

The one-pot synthesis of amides from aldehydes, hydroxylamine hydrochloride and sodium carbonate catalyzed by Ru complex a

To a flame-dried 15 mL sealed tube were added aldoxime (0.4 mmol), hydroxylamine hydrochloride (1.25 equiv.), and Na₂CO₃ (0.5 equiv.), catalyst a (0.002 mmol, 0.5 mol%) and H₂O (1 mL) under air atmosphere. The reaction mixture was heated at 110 °C for 12 h and then cooled to room temperature. The reaction mixture was directly evaporated and the residue was purified by preparative TLC plates to provide the desired product. ¹H and ¹³C NMR spectra were used to characterize amide products, and their analytical data are given in the ESI.†

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