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Rhodium(III)-Catalyzed Intermolecular Direct Amidation of Aldehyde C–H Bonds with *N*-Chloroamines at Room Temperature

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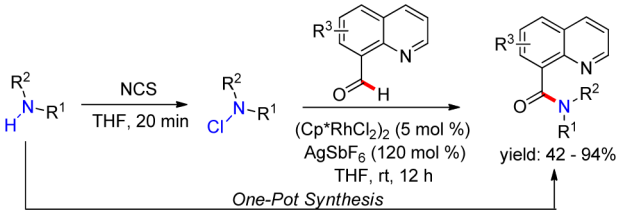
ABSTRACT



A Rh(III)-catalyzed direct aldehyde C–H amidation from aldehydes and *N*-chloroamines, prepared in situ from amines, has been developed via C–H bond activation under very mild reaction conditions. A variety of primary and secondary amines were used to afford the corresponding amides in moderate to excellent yields.

The amide bond is the key chemical connection found in a myriad of natural products, polymers, and pharmaceuticals.[1] Moreover, more than 25% of known drugs contain an amide group.[2] The most straightforward synthetic route to amides is the condensation of carboxylic acids with amines.[3] However, this strategy has the innate drawback derived from the poor atom efficiency and requirement of stoichiometric amounts of activating reagents. A milder and atom-economic alternative approach is the direct amidation of aldehydes which represents an interesting and recent topic in this area.[4] Such approaches include NHC-catalyzed,[5] metal-catalyzed,[6] or metal-free[7] oxidative amidation of aldehydes with amines, the Schmidt reaction,[8] base-mediated amidation of aldehydes with azide,[9] and organocatalytic oxidative amidation of aldehydes with activating reagents.[10] Despite great advances in this area, the development of a catalytic process for amide bond formation under mild reaction conditions remains highly desirable.

Yet, transition-metal-catalyzed functionalizations of unactivated C–H bonds, which enable the efficient construction of carbon–carbon or carbon–heteroatom bonds

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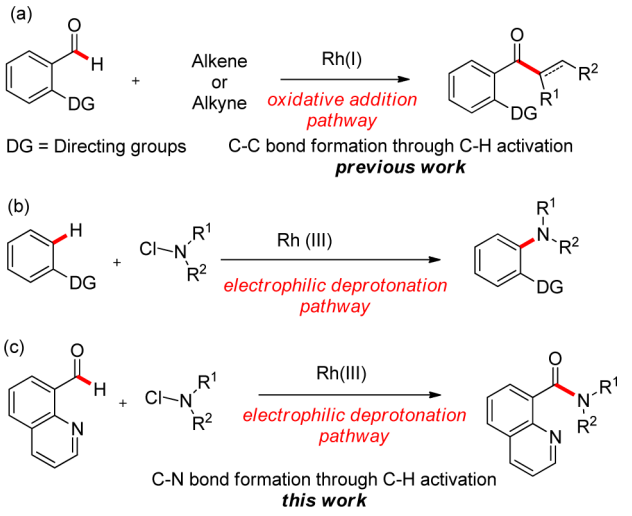
as a highly atom-economical and direct approach, have in recent years attracted significant interest.[11] Although great progress has been made in this emerging field, the selective functionalization of aldehyde C−H bonds is still a great challenge and as of yet limited to coupling with alkenes and alkynes and yielding ketone derivatives through oxidative addition of low-valent transition-metal complexes (especially Rh^{I} catalysts) to aldehyde C−H bonds (Scheme 1a).[12] To the best of our knowledge, catalytic direct C−N bond formation remains a big challenge after a chelation-assisted aldehyde C−H bond activation, with no examples reported.

In this context and inspired by recent reports for the Rh^{III}-catalyzed direct arene C−H amination (Scheme 1b),[13]

Scheme 1. Coupling Reactions through C−H Activation



herein we report the first example of Rh^{III}-catalyzed C−N bond formation through a chelation-assisted aldehyde C(sp^2)−H bond activation (Scheme 1c).[14,15] This catalytic reaction provides a new approach for the construction of amide bonds. Most significantly, the present work also offers novel insights into Rh^{III}-catalyzed C−N cross-coupling reactions after cleavage of an aldehyde C−H bond.

Initially, our study focused on the reaction of **8**-quinolinecarbaldehyde (**1a**) and *N*-chloromorpholine (**2a**) to optimize the reaction conditions (Table 1). To our delight, the desired product **3a** was observed in a 15% yield with $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ as the catalyst in toluene at 60 °C despite the low conversion (entry 1). Different catalysts were tested (entries 1−5), and $(Cp^*Rh(OAc)_2)_2$ showed a similar result (entry 2). $(Cp^*RhCl_2)_2$ (5 mol %) in the presence of $AgSbF_6$ (120 mol %) turned out to be more reactive, and the yield of **3a** was increased to 68% in toluene at 60 °C (entry 3). Surprisingly, other transition metal catalysts such as $Pd(OAc)_2$ and ruthenium complexes were completely ineffective in this C(sp^2)−H amidation reaction (entries 4−5). Subsequently, we examined the role of each reactant through a series of control experiments. Notably, in the absence of $AgSbF_6$ or $[Cp^*RhCl_2]_2$, we recovered the starting materials (entries 6 and 7). Moreover, we also tested morpholine as the substrate, and it failed to give the product **3a** (entry 8). Replacement of 8-quinolinecarbaldehyde with 1-naphthaldehyde failed to yield any desired coupling product, suggesting a critical role for the N-directing group for C−H activation (entry 9).

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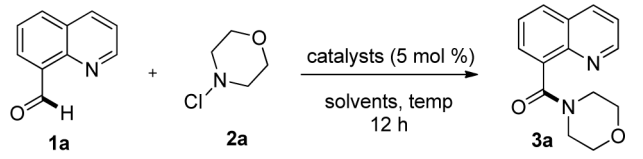
A substoichiometric amount (30 mol %) of $AgSbF_6$ led to a low yield of the product **3a** (entry 10).

To optimize the amidation protocol, the influence of the solvent on this reaction was studied next (entries 3, 11−13) and the most satisfactory yield was obtained in THF (entry 13). Next, various temperatures were screened (entries 13−15), and the best result was obtained by lowering the reaction temperature to rt (entry 15). Indeed, the catalytic reaction can also be carried out with good efficiency in the presence of 3 mol % of catalyst by simply lengthening the reaction time to 24 h (entry 16). Notably, compared to previously reported procedures for amidation of aldehydes with *N*-chloroamines,[16] this catalytic method proceeds in the absence of external oxidants under very mild reaction conditions.

Table 1. Reaction Optimization[a]



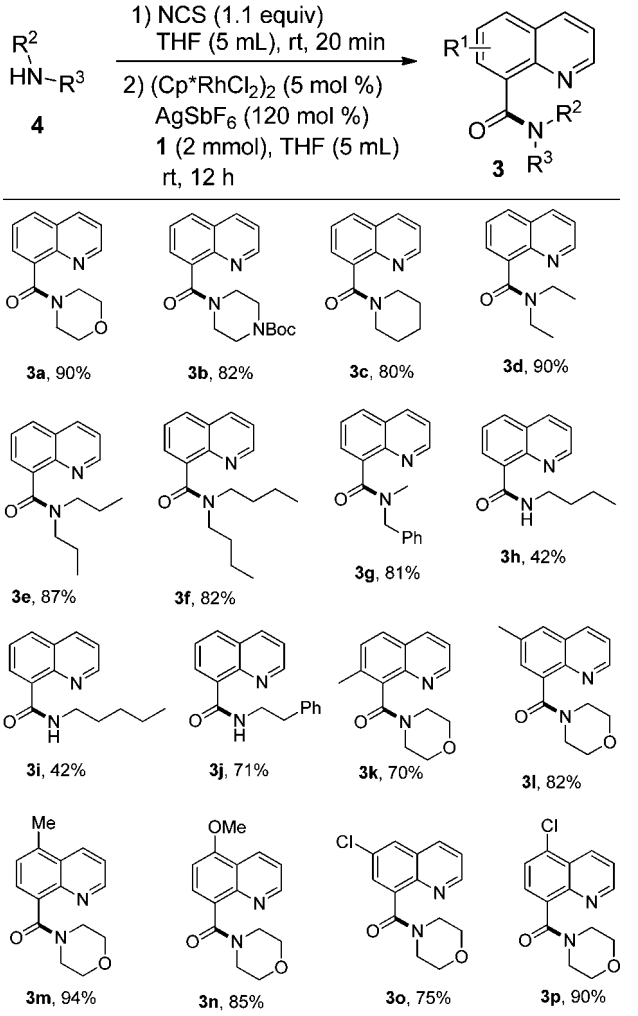
1a 2a 3a

entry	catalysts (mol %)	solvents	temp (°C)	yield (%)[b]
1	$[Cp^*Rh(MeCN)_3](SbF_6)_2$ (5)	toluene	60	15 (80)
2	$(Cp^*Rh(OAc)_2)_2$ (5)	toluene	60	16 (80)
3	$(Cp^*RhCl_2)_2$ (5)/$AgSbF_6$ (120)	toluene	60	68
4	$Pd(OAc)_2$ (5)	toluene	60	<5
5	$[Ru(p\text{-cymene})Cl_2]_2$ (5)/$AgSbF_6$ (120)	toluene	60	<5
6	$(Cp^*RhCl_2)_2$ (5)	toluene	60	0
7	$AgSbF_6$ (120)	toluene	60	0
8[e]	$(Cp^*RhCl_2)_2$ (5)/$AgSbF_6$ (120)	toluene	60	0
9[d]	$(Cp^*RhCl_2)_2$ (5)/$AgSbF_6$ (120)	toluene	60	0
10	$(Cp^*RhCl_2)_2$ (5)/$AgSbF_6$ (30)	toluene	60	25
11	$(Cp^*RhCl_2)_2$ (5)/$AgSbF_6$ (120)	DCM	60	66
12	$(Cp^*RhCl_2)_2$ (5)/$AgSbF_6$ (120)	DCE	60	60
13	$(Cp^*RhCl_2)_2$ (5)/$AgSbF_6$ (120)	THF	60	76
14	$(Cp^*RhCl_2)_2$ (5)/$AgSbF_6$ (120)	THF	40	80
15	$(Cp^*RhCl_2)_2$ (5)/$AgSbF_6$ (120)	THF	20	90
16[e]	$(Cp^*RhCl_2)_2$ (3)/$AgSbF_6$ (120)	THF	20	85

[a] Reaction conditions: 2 mmol of **1a**, 2.4 mmol of **2a**, 0.1 mmol of catalyst, and 10 mL of solvent at the indicated temperature for 12 h. [b] Yield of isolated product. Yield in parentheses is based on recovered starting material. [c] Morpholine was used. [d] Using 1-naphthaldehyde as the substrate. [e] Reaction time is 24 h.

With the success of the Rh-catalyzed amidation reaction, we attempted to develop a one-pot synthesis of amide from aldehydes and amines (Scheme 2). Toward this end, treatment of amines **4** with NCS in THF for 20 min gave the *N*-chloroamines. Then aldehyde **1**, $[Cp^*RhCl_2]_2$, and $AgSbF_6$ were added to this THF solution, and the mixture was stirred at rt for 12 h. To our delight, a broad scope of amines (**3a**−**3j**) can be coupled under standard reaction conditions. First, a number of cyclic and acyclic *N*,*N*-dialkylamines were tested. Analogous to **3a**, the Rh-catalyzed coupling of 4-Boc-piperazine and piperidines gave products **3b**−**3c** in good yields. Acyclic secondary amines were also well tolerant providing the desired products **3d**−**3g** in moderate to good yields. Notably, primary amines were effective coupling partners providing the corresponding *N*-monosubstituted amides **3h**−**3j** in moderate yields. The substrate scope was further extended to a variety of aldehydes. It was found that the electronic nature of the substituents on the quinoline ring did not play a key role in this catalytic reaction. Aldehydes with both electron-donating groups, such as methyl (**3k**−**3m**) and methoxy groups (**3n**), and electron-withdrawing groups, such as the chloro group (**3o** and **3p**), were well tolerated providing the desired amides in moderate to excellent yields. Notably, the tolerance of the chloro group offers the opportunity for further functionalization.

Scheme 2. One-Pot Direct Amidation[a]



[a] Reaction conditions: 2 mmol of **1**, 2.4 mmol of **4**, 2.6 mmol of NCS, 0.1 mmol of $(Cp^*RhCl_2)_2$, 2.4 mmol of $AgSbF_6$, and 10 mL of THF at rt for 12 h. Yield of isolated product.

We then tried to gain some insight into the mechanism by conducting a series of experiments (Scheme 3).

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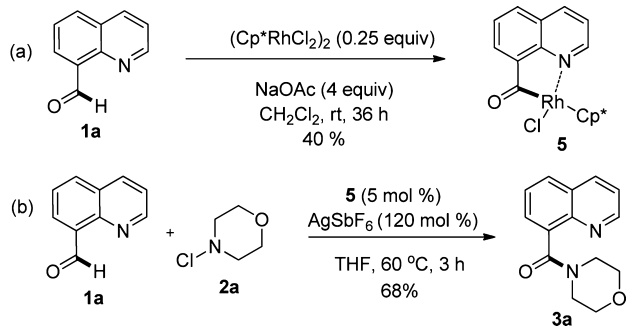
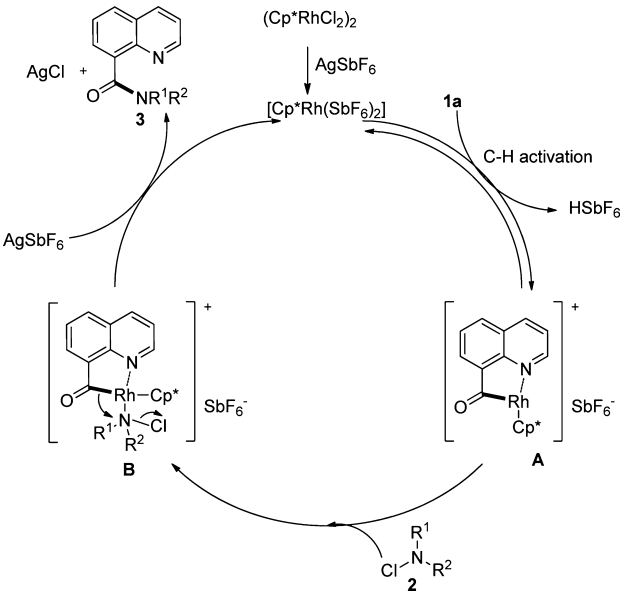
Scheme 3. Preliminary Mechanistic Studies



8-Quinolinecarbaldehyde **1a**, $(RhCp^*Cl_2)_2$, and NaOAc reacted smoothly to give rhodacycle **5**, which was further characterized by X-ray crystallography (Scheme 3a).[17] More importantly, complex **5** successfully catalyzed the coupling of **1a** with **2a** (Scheme 3b), suggesting the plausible intermediacy of a cyclometalated complex in the catalytic cycle. Although Rh(III) catalysts have been widely applied in C−H activation, reports on isolated stable organorhodium(III) intermediates are still limited,[18] especially for acyl-rhodium(III) intermediates.[19]

Based on the above observed data, a plausible catalytic cycle is presented in Scheme 4. First, treatment of the $[RhCp^*Cl_2]_2$ precursor with the $AgSbF_6$ additive provides a cationic Rh(III) species. A cyclometalation process through C−H bond activation gives five-membered cyclometalated acyl-Rh(III) complexes **A** with a loss of an acid.[20] Coordination of the *N*-chloroamine to the acyl-Rh(III) complex gives the intermediate **B**. Then the chloride abstraction with Ag^+ promotes the migration of the

Scheme 4. Proposed Catalytic Cycles



acyl group to the nitrogen which provides the amides and regenerates the catalysts.[21]

In summary, we have developed a Rh(III)-catalyzed directed amidation of aldehyde C−H bonds with *N*-chloroamines, prepared in situ from amines, proceeding in the absence of external oxidants at rt. A variety of primary and secondary amines were used to afford the corresponding amides in moderate to excellent yields. More importantly, this process may provide a new direction for direct C−N bond formation from aldehyde C−H bond activation. Further studies into the scope, mechanism, and synthetic application are ongoing in our laboratory.[22]

Supporting Information Available. Experimental procedures, characterization of products, and copies of ^1H and ^{13}C NMR spectra are provided. The material is available free of charge via the Internet at http://pubs.acs.org.

(17) CCDC 935272 (**5**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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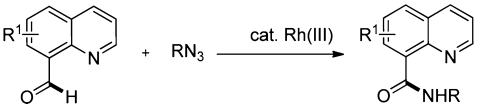
(22) A related work using azides as nitrogen sources to give primary amides was submitted to *Chem.—Eur. J.* by our group at this time; see:



The authors declare no competing financial interest.