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Rhodium(III)-Catalyzed Intermolecular Direct Amination of Aromatic C−H Bonds with *N*-Chloroamines

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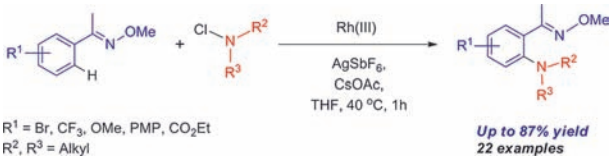
ABSTRACT



A Rh(III)-catalyzed direct aromatic C−H amination is achieved using *N*-chloroamines as a reagent. Furthermore, we also developed a one-pot amination protocol involving in situ chlorination of the secondary amines. The catalytic amination operates at mild conditions with excellent functional group tolerance and regioselectivity.

Catalytic aromatic C−N bond formation[1] via C−H bond activation is an attractive strategy for preparing amino compounds which are commonly found in pharmaceuticals as well as agrochemical and functional materials. Without requiring prefunctionalized arenes, the C−H bond amination approach should improve synthetic efficiency and atom economy.[2] Recent advances have been achieved for some transition metal catalyzed C−H activation/C−C bond formation reactions that exhibit remarkable site selectivity and general substrate scope applications.[3] In contrast, catalytic direct C−N bond formation remains a formidable challenge, and catalytic systems that operate at mild conditions with a wide substrate scope are rare.

Among others,[4] Pd-catalyzed direct amidation of arene C−H bonds has been extensively investigated. Major developments have been made in the intramolecular direct

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(3) For reviews on recent advances of transition metal catalyzed C−H activation/C−C bond formation, see: (a) Yeung, C. S.; Dong, V. M. *Chem. Rev.* **2011**, *111*, 1215. (b) Lyons, T. W.; Sanford, M. S. *Chem. Rev.* **2010**, *110*, 1147. (c) Chen, X.; Engle, K. M.; Wang, D.-H.; Yu, J.-Q. *Angew. Chem., Int. Ed.* **2009**, *48*, 5094. (d) Alberico, D.; Scott, M. E.; Lautens, M. *Chem. Rev.* **2007**, *107*, 174.

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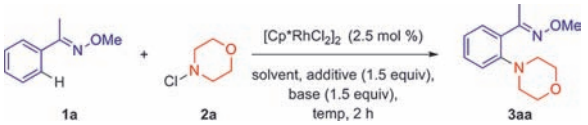
C−N bond formation with amide as coupling partners,[5] and a highly reactive Pd^{IV} intermediate was proposed.[5d−f] Not long ago, we described the Pd-catalyzed intermolecular arene C−H amidation via nitrene intermediates.[6] Despite these efforts, the direct C−N bond formation is largely limited to amides as a coupling partner.[7] A recent breakthrough has been achieved by Yu et al. on the Pd-catalyzed oxidative C−H amination with alkylamines.[7a] Yet, the majority of the Pd-mediated C−N bond formation would require forceful conditions (e.g., high temperature or reactivity reagents), posing serious limitations to the substrate scope and practicality.

Recently, Rh(III)-catalyzed oxidative arene C−H functionalizations leading to C−C bond formation are attracting growing attention.[8] With a directing group (e.g., CO_2H, NHAc, pyridyl, imine), the Rh(III) catalyst would undergo *ortho*-C−H bond metalation to form an aryl-Rh(III) complex.[8o−q] The aryl-Rh(III) has been shown to cross-couple with alkynes,[8k−n] aldehydes[8h,i]/imines,[8e−g] and even CO_2.[8j] Inspired by these findings, herein we report the Rh-(III)-catalyzed direct arene C−H amination with *N*-chloroamines under mild conditions. Our investigation focuses on arylketone oximes as substrates since oximes are known to direct electrophilic C−H metalation.[3b,6b,6e,6g,6i] Furthermore, the oxime group can be easily removed to recover the carbonyl group for further structural transformations.

Stimulated by our earlier finding that $[Rh(COD)Cl]_2$ would catalyze the coupling reaction of arylboronate, α-aryldiazoactates, and *N*-chloromorpholine to form an α-aminoacetate,[6c] we hypothesized that *N*-chloroamines could be viable reagents for direct C−H amination.[4e,9] First, acetophenone *N*-methyloxime (**1a**) was treated with $[Cp^*RhCl_2]_2$ (2.5 mol %), *N*-chloromorpholine (**2a**), and $AgSbF_6$ (1.2 equiv) in THF at 80 °C for 2 h, producing **3aa** in <5% yield (Table 1, entry 1). We were aware that carboxylate would be needed for the Rh(III)-mediated C−H activation; however, poor **3aa** formation was observed with AgOAc and CsOAc as additives (entries 2—3). After several trials, a combination of $AgSbF_6$ (1.5 equiv) and CsOAc (1.5 equiv) was found to give **3aa** in 38% yield (entry 4). The molecular structure of **3aa**, isolated as a hydrochloride salt, has been established by X-ray crystallography.[10] It is noteworthy that no **3aa** formation was observed in the absence of $[Cp^*RhCl_2]_2$ (entry 5). In this work, *N*-benzoyloxymorpholine was found to be an ineffective reagent, and only a trace amount of **3aa** was formed under the Rh(III)-catalysis (entry 6). As expected, morpholine, instead of the *N*-chloro derivative, failed to yield any **3aa** formation (entry 7).

To optimize the amination protocol, we extensively screened various experimental parameters. When we performed the amination reaction at 40 °C, **3aa** was formed in 73% yield (entry 8). The lower temperature probably slowed down the self-decomposition of the *N*-chloromorpholine in the reaction mixture. Among the solvents being tested, THF was the solvent of choice (entries 9—14). Compared to CsOAc, KOAc and Cs_2CO_3 are ineffective additives, whereas the silver salts of some noncoordinating anions such as PF_6^-, BF_4^-, OTf^- produced less satisfactory results (entries 15−19).

Table 1. Reaction Optimization[a,b]



entry	additive (equiv)	base (equiv)	solvent	temp (°C)	yield (%)
1[c]	$AgSbF_6$ (1.2)	–	THF	80	<5
2[c]	AgOAc (1.2)	–	THF	80	<5
3[c]	–	CsOAc (1.2)	THF	80	0
4[c]	$AgSbF_6$	CsOAc	THF	80	(38%)[d]
5[c,e]	$AgSbF_6$	CsOAc	THF	80	0
6[f]	$AgSbF_6$	CsOAc	THF	80	0
7[g]	$AgSbF_6$	CsOAc	THF	40	<5
8	$AgSbF_6$	CsOAc	THF	40	(72)[d]
9	$AgSbF_6$	CsOAc	dioxane	40	<5
10	$AgSbF_6$	CsOAc	*t*-AmyOH	40	<5
11	$AgSbF_6$	CsOAc	DMF	40	15
12	$AgSbF_6$	CsOAc	DCE	40	12
13	$AgSbF_6$	CsOAc	toluene	40	0
14	$AgSbF_6$	CsOAc	MeCN	40	8
15	$AgSbF_6$	KOAc	THF	40	43
16	$AgSbF_6$	Cs_2CO_3	THF	40	40
17	$AgPF_6$	CsOAc	THF	40	64
18	$AgBF_4$	CsOAc	THF	40	21
19	AgOTf	CsOAc	THF	40	40
20	$AgSbF_6$ (0.3)	CsOAc	THF	40	<5
21[h]	**$AgSbF_6$**	**CsOAc (0.3)**	**THF**	**40**	**(85)**[d]
22[i]	$AgSbF_6$	CsOAc (0.3)	THF	40	(81)[d]
23[j,k]	$AgSbF_6$	CsOAc (0.3)	THF	40	61

[a] Conditions: **1a** (0.2 mmol), **2a** (1.2 equiv), $[Cp^*RhCl_2]_2$ (2.5 mol %), solvent (1 mL), 2 h. [b] Yields determined by ^1H NMR. [c] **2a** (1.5 equiv). [d] Isolated yields in parentheses. [e] No $[Cp^*RhCl_2]_2$. [f] Morpholine (1.5 equiv) was used. [g] *N*-Benzoyloxymorpholine (1.5 equiv) was used. [h] Reaction time = 1 h. [i] $[Cp^*RhCl_2]_2$ (1 mol %). [j] $[Cp^*RhCl_2]_2$ (0.5 mol %). [k] Reaction time = 3 h.

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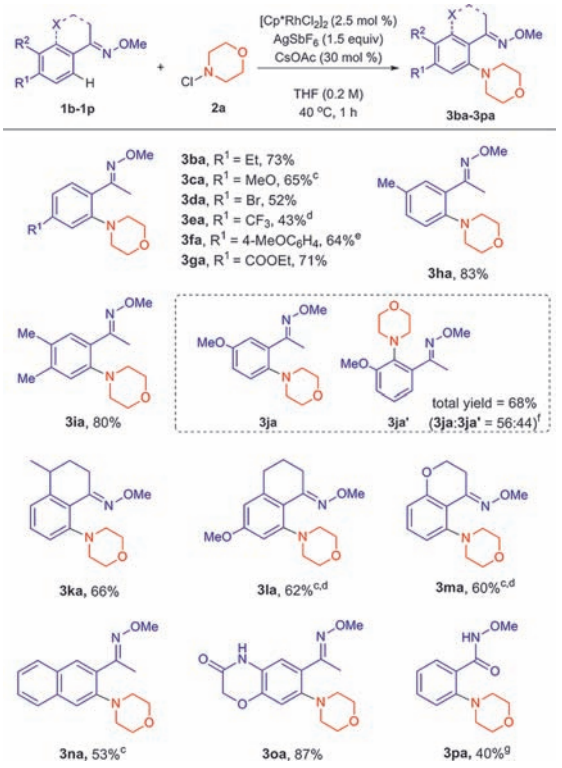
(7) For an example of Pd-catalyzed intermolecular C−H amination, see: (a) Yoo, E. J.; Ma, S.; Mei, T.-S.; Chan, K. S. L.; Yu, J.-Q. *J. Am. Chem. Soc.* **2011**, *133*, 7652. For other examples of Pd-catalyzed intermolecular C−H amidation, see: (b) Sun, K.; Li, Y.; Xiong, T.; Zhang, J.; Zhang, Q. *J. Am. Chem. Soc.* **2011**, *133*, 1694. (c) Xiao, B.; Gong, T.-J.; Xu, J.; Liu, Z.-J.; Liu, L. *J. Am. Chem. Soc.* **2011**, *133*, 1466. (d) Xiong, T.; Li, Y.; Lv, Y.; Zhang, Q. *Chem. Commun.* **2010**, *46*, 6831.

Table 2. Substrate Scope[a,b]



[a] Conditions: substrate (0.2 mmol), **2a** (1.2 equiv), $[Cp^*RhCl_2]_2$ (2.5 mol %), CsOAc (30 mol %), $AgSbF_6$ (1.5 equiv), THF (1 mL), 40 °C, 1 h. [b] Isolated yields. [c] **2a** was slowly added over 30 min. [d] Reaction temperature = 60 °C. [e] THF (3 mL). [f] The regioisomeric ratio was determined by NMR analysis. [g] CsOAc (1.5 equiv).

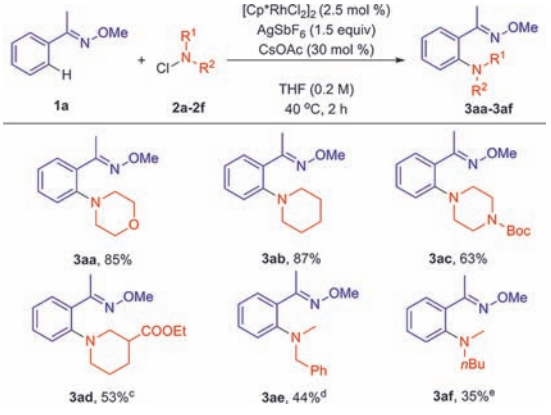
Employing a substoichiometric amount (30 mol %) of $AgSbF_6$ resulted in poor **3aa** formation (< 5%, entry 20). Notably, the best result (**3aa**: 85%) was attained under the conditions $[Cp^*RhCl_2]_2$ (2.5 mol %), $AgSbF_6$ (1.5 equiv), and CsOAc (30 mol %) in THF at 40 °C (entry 21). Indeed, the catalytic system remained operational at lower catalyst loadings (1−0.5 mol %) with **3aa** being obtained in 61−81% yield (entries 22−23).

Table 2 depicts the results of the substrate scope study using **2a** as a coupling partner. In general, functionalized oximes can be transformed to their respective arylamines **3ba**−**3ga** in 43−73% yields with excellent *ortho*-selectivity. While electron-neutral and -deficient arenes can be aminated with the Rh(III)-catalyzed reaction, slightly lower yields (ca. 50%) were obtained with electron-deficient arenes. Nevertheless, the Rh(III)-catalyzed reaction exhibits better tolerance to electron-withdrawing groups (Br, CF_3, CO_2Et) than the Pd(II)-catalyzed intermolecular amidations.[6a] Tolerance to the bromo and ester functions is especially noteworthy since they are useful for subsequent cross-coupling reactions.

To scrutinize further the regioselectivity, the amination reaction of *meta*-substituted oxime **1h** occurred exclusively to the more open C−H bond (**3ha**: 83%). Likewise, **1i** bearing two methyl substituents was converted to **3ia** selectively. However, the analogous reaction of the *meta*-methoxy-substituted oximes **1j** produced inseparable regioisomeric products **3ja** and **3ja′** in a ratio of 56:44 based on NMR analysis. Assuming the aryl-Rh(III) complexes as the intermediate, our findings are compatible with an earlier report by Jones and co-workers that C−H rhodation by $[Cp^*RhCl_2]_2$ occurred nonregioselectively with *meta*-methoxy-substituted 2-arylpyridines.[8o] In this work, other bicyclic oximes such as those containing tetralone (**1k**−**l**) and chromalone (**1m**) scaffolds are effective substrates for the direct amination reactions. Successful amination of the naphthalene and 2*H*-1,4-bezoxazin-3(4*H*)-one scaffolds have also been accomplished to afford **3na** and **3oa** in 53% and 87% yields. We found that *N*-methoxybenzamide can be aminated to give **3pa** in 40% yield.

Employing **1a** as the substrate, the amination scope has been further extended to other *N*-chloroamines (Table 3).

Table 3. Amine Scope[a,b]

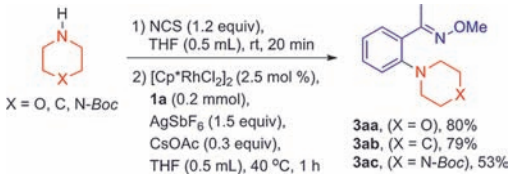


[a] Conditions: **1a** (0.2 mmol), *N*-chloroamine (1.2 equiv), $[Cp^*RhCl_2]_2$ (2.5 mol %), CsOAc (30 mol %), $AgSbF_6$ (1.5 equiv), THF (1 mL), 40 °C, 2 h. [b] Isolated yields. [c] Reaction was carried out at rt for 15 h. [d] $[Cp^*RhCl_2]_2$ (5 mol %). [e] *N*-Chloro-*N*-methylbutylamine (**2f**) was added slowly over 30 min.

(8) For reviews on the Rh-catalyzed C−H activation/C−C bond formation, see: (a) Colby, D. A.; Bergman, R. G.; Ellman, J. A. *Chem. Rev.* **2010**, *110*, 624. (b) Satoh, T.; Miura, M. *Chem.—Eur. J.* **2010**, *16*, 11212. For recent selected examples of the Rh-catalyzed aromatic C−H bond functionalizations, see: (c) Patureau, F. W.; Besset, T.; Glorius, F. *Angew. Chem., Int. Ed.* **2011**, *50*, 1064. (d) Rakshit, S.; Grohmann, C.; Besset, T.; Glorius, F. *J. Am. Chem. Soc.* **2011**, *133*, 2350. (e) Hesp, K. D.; Bergman, R. G.; Ellman, J. A. *J. Am. Chem. Soc.* **2011**, *133*, 11430. (f) Tsai, A. S.; Tauchert, M. E.; Bergman, R. G.; Ellman, J. A. *J. Am. Chem. Soc.* **2011**, *133*, 1248. (g) Li, Y.; Li, B.-J.; Wang, W.-H.; Huang, W.-P.; Zhang, X.-S.; Chen, K.; Shi, Z.-L. *Angew. Chem., Int. Ed.* **2011**, *50*, 2115. (h) Park, J.; Park, E.; Kim, A.; Lee, Y.; Chi., K.-W.; Kwak, J. H.; Jung, Y. H.; Kim, I. S. *Org. Lett.* **2011**, *13*, 4390. (i) Yang, L.; Correia, C. A.; Li, C.-J. *Adv. Synth. Catal.* **2011**, *353*, 1269. (j) Mizuno, H.; Takaya, J.; Iwasawa, N. *J. Am. Chem. Soc.* **2011**, *133*, 1251. (k) Too, P. C.; Chua, S. H.; Wong, S. H.; Chiba, S. *J. Org. Chem.* **2011**, *76*, 6159. (l) Hyster, T. K.; Rovis, T. *J. Am. Chem. Soc.* **2010**, *132*, 10565. (m) Stuart, D. R.; Alsabeh, P.; Kuhn, M.; Fagnou, K. *J. Am. Chem. Soc.* **2010**, *132*, 18326. (n) Guimond, N.; Gouliaras, C.; Fagnou, K. *J. Am. Chem. Soc.* **2010**, *132*, 6908. For more detailed studies of cyclorhodated Aryl−Rh(III) complexes, see: (o) Li, L.; Brennessel, W. W.; Jones, W. D. *Organometallics* **2009**, *28*, 3492. (p) Li, L.; Brennessel, W. W.; Jones, W. D. *J. Am. Chem. Soc.* **2008**, *130*, 12414. (q) Davies, D. L.; Al-Duaij, O.; Fawcett, J.; Giurdiello, M.; Hilton, S. T.; Russell, D. R. *Dalton Trans.* **2003**, 4132.

Analogous to **2a**, the Rh-catalyzed coupling of *N*-chloropiperidine and 4-*Boc*-*N*-chloropiperazine gave **3ab** (87%) and **3ac** (63%) effectively. The analogous reaction of *N*-chloroethyl nipecotate afforded **3ad** in 53% yield. Yet, the reactions of aliphatic *N*-chlorodialkylamines furnished the desired products (e.g., **3ae** and **3af**) in moderate yields (35−44%).

Scheme 1. One-Pot Direct Amination

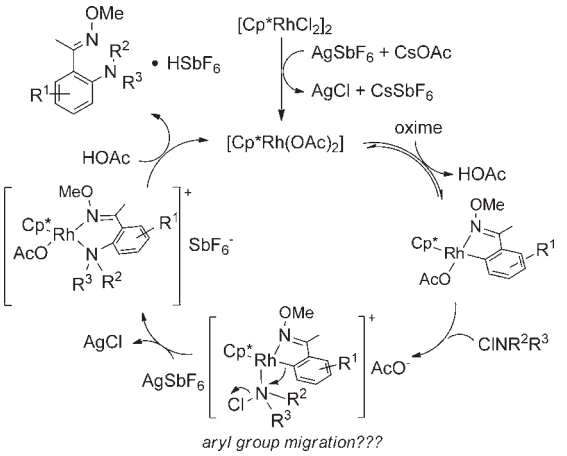


Development of a one-pot direct amination protocol without isolating the *N*-chloroamines would be attractive for synthetic application. In this work, we prepared **2a** by treating morpholine with NCS in THF for 20 min in the dark. Afterward, the mixture was added to the THF solution containing **1a**, $[Cp^*RhCl_2]_2$, $AgSbF_6$, and CsOAc (Scheme 1), and **3aa** was obtained in 80% yield. The one-pot protocol can be applied to the couplings of piperidine and *N*-*Boc*-piperazine. To illustrate the practicality of our protocol, we demonstrated that the *O*-methyl oxime can be easily removed by heating **3aa** in 6 M HCl to afford *N*-(2-acetylphenyl)morpholine in 89% yield. According to the literature, 2-aminoacetophenones are useful scaffolds in some medicinally active compounds.[10,11]

The catalytic amination reaction should involve initially electrophilic metalation of the *ortho*-arene C−H bond of the oximes to afford an aryl-Rh(III) species (Scheme 2). The Rh(III)-mediated C−H metalation should be reversible. In this work, treating **1a**-d_5 with $[Cp^*RhCl_2]_2$ (5 mol %), $AgSbF_6$ (1.5 equiv), and CsOAc (0.3 equiv) in MeOH at 40 °C for 20 min in the absence of haloamine led to a 47% loss of *ortho*-deuteriums.[10] This finding is comparable to the previous results reported by Fagnou et al.[8m,n] By means of competitive experiments with **1a** and **1a**-d_5 as substrates, a primary kinetic isotope effect (k_H/k_D) = 2.7 was observed, suggesting that the C−H bond cleavage is rate-limiting.[12]

The mechanism of the C−N bond coupling step remains to be elucidated. In this work, treating the cyclorhodated 2-phenylpyridine (2PP) complex [Cp*RhCl(2-PP)] with **2a** (1.1 equiv) and $AgSbF_6$ (2.2 equiv) at 40 °C for 3 h afforded the corresponding amination product in 52% yield.[10] This result suggested that the reaction is likely to go through the

Scheme 2. Proposed Mechanism



cyclometalated aryl-Rh(III) complexes. A possible pathway for the C−N bond coupling may involve prior coordination of the *N*-chloroamine to the aryl-Rh(III) complex. Migration of the aryl group to the nitrogen prompted by the chloride abstraction with Ag^+ would result in the C−N bond formation .[13] Compatible with this notion, a stoichiometric amount of Ag salt is needed for the amination reaction. Moreover, changing the halide leaving group to benzoate is also detrimental to the reaction.

In summary, we developed a Rh(III)-catalyzed intermolecular *ortho*-C−H amination of acetophenone *O*-methyl oximes using *N*-chloroamines, and a one-pot protocol using amines directly for the C−H amination is also developed. The Rh-catalyzed reaction exhibits high functional group tolerance, regioselectivity, and broad substrate scope under relatively mild conditions. Mechanistic studies and application of the Rh-catalyzed reaction to other substrate classes will be reported in due course.

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Supporting Information Available. Experimental details, characterization data, and copies of ^1H, ^{13}C NMR spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

(9) For a review on *N*-haloamines, see: (a) Kovacic, P.; Lowery, M. K.; Field, K. W. *Chem. Rev.* **1970**, *70*, 639. For recent examples using *N*-chloroamines as reagents, see: (b) Hatakeyama, T.; Yoshimoto, Y.; Ghorai, S. K.; Nakamura, M. *Org. Lett.* **2010**, *12*, 1516. (c) Barker, T. J.; Jarvo, E. R. *J. Am. Chem. Soc.* **2009**, *131*, 15598.

(10) See Supporting Information for detailed experimental.

(11) (a) Tulp, M.; Bohlin, L. *Trends Pharmacol. Sci.* **2005**, *26*, 175. (b) Bellamy, F. D.; Chazan, J. B.; Dodey, P.; Dutartre, P.; Ou, K.; Pascal, M.; Robin, J. *J. Med. Chem.* **1991**, *34*, 1545.

(12) Intermolecular primary KIE (k_H/k_D) values of 2.2−4.2 have been reported for Rh-catalyzed *ortho*-C−H activation of arenes; for examples, see refs 8e, 8m, and 8n.

(13) The analogous reaction of chloroamines with organoboranes was proposed to occur via anionotropic migration of an alkyl group from boron to nitrogen; see: Kabalka, G. W.; McCollum, G. W.; Kunda, S. A. *J. Org. Chem.* **1984**, *49*, 1656.