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Rh[III]-Catalyzed Direct C−H Amination Using *N*-Chloroamines at Room Temperature

Christoph Grohmann, Honggen Wang, and Frank Glorius*

Westfälische Wilhelms-Universität Münster, Organisch-Chemisches Institut, Corrensstrasse 40, 48149 Münster, Germany

glorius@uni-muenster.de

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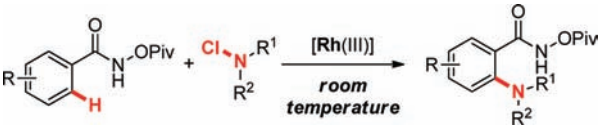
ABSTRACT



An efficient Rh(III)-catalyzed direct C−H amination of *N*-pivaloyloxy benzamides with *N*-chloroamines proceeding at room temperature was achieved. The versatile directing group allows for selective mono- and diamination and can be readily converted to give valuable benzamide or aminoaniline derivatives. Mechanistic studies have been carried out to elucidate the reaction pathway.

The field of C−H activation has seen considerable progress, providing new transformations and improved efficiency.[1] However, many of the developed processes require harsh reaction conditions, thereby restricting their applicability in synthesis. Consequently, the necessity for the design of mild and powerful C−H functionalization methods has become evident.[2] Among the desired transformations, the valuable transition metal catalyzed C−H amination reaction has been unraveled only with limitations.[3] As an alternative to the established Buchwald−Hartwig amination,[4] the corresponding direct transformation of aromatic C−H bonds has been predominantly reported in an intramolecular fashion, mostly using Pd or Cu catalysts.[5] The more challenging intermolecular version had in most cases been limited

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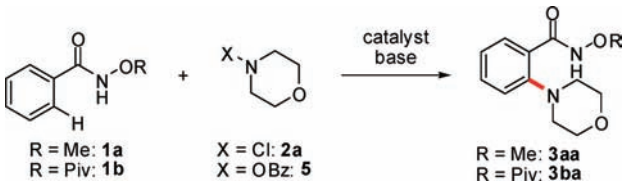
to activated systems such as azoles or polyfluorinated aromatics.[6] Only a few examples of the direct amination of unactivated aromatic C−H bonds have been reported: Pd-catalyzed oxidative amidation of oximes[7a] or anilides[7b] with amides (via reactive nitrene intermediates) or sulfonamides.[7c,d] Yu et al.[8] recently communicated the Pd-catalyzed C−H amination of aromatic C−H bonds using an electron-deficient amide directing group and secondary *N*-benzoyloxyamines. However, the reported Pd-catalyzed methods involve oxidizing conditions at elevated temperatures. Accounting for the need to design more benign and generally applicable processes, it is desirable to develop a mild C−H amination of aromatic substrates using an efficient and versatile directing group, which is (1) readily accessible and (2) easily converted to different valuable functionalities. Herein, we report on a Rh-catalyzed direct C−H amination of aromatic C−H bonds[9] proceeding at rt by usage of the easily installed and versatile *N*-pivaloyloxy amide directing group (DG) CONHOPiv and *N*-chloroalkylamines as a readily accessible nitrogen source.

We[10] and others[11] have previously reported on Rh(III)-catalyzed C−H functionalization reactions proceeding under mild conditions by application of benzhydroxamic acid derived DGs.[12] Encouraged by these results, we approached the C−H amination to build up important arylamines.[13] Therefore, we commenced our study by choosing benzhydroxamic acid derivative **1a** as the substrate, $[RhCp^*Cl_2]_2$ as the catalyst, and CsOAc as the base in methanol at rt (Table 1). As an aminating partner we employed *N*-chloromorpholine **2a**, which has been reported to be efficient in the amination of azoles at rt.[6e,14] To our delight, we observed the aminated product **3aa** in reasonable yield (entry 1). Further optimization revealed the *O*-pivaloyl group of **1b** to be effective at rt: using CsOAc as the base and pivalic acid (PivOH) in substoichiometric amounts, 80% of **3ba** could be isolated (entry 6). Notably, $Pd(OAc)_2$ did not promote this reaction (entry 3) and use of *N*-benzoyloxy morpholine **5** which was reported to be successful in Pd-catalyzed directed C−H amination[8] gave the product in a significantly lower yield (entry 7). When AgOAc was used instead of CsOAc, surprisingly the diamination product **4a** was obtained in 75% isolated yield (entry 8). In accordance with a practical point of view, the catalyst loading can also be lowered to 1 mol % $[RhCp^*Cl_2]_2$ by increasing both the amount of chloroamine to 3 equiv and the reaction temperature to 40 °C (entry 9).

With these conditions in hand, the scope of the amine partner was explored (Scheme 1). All of the present chloroamines are readily accessible from the corresponding

Table 1. Reaction Optimization[a]



entry	substrate	amine	catalyst	base	yield (%)[b]
1	**1a**	**2a**	$[RhCp^*Cl_2]_2$	CsOAc	27, **3aa**
2[c]	**1a**	**2a**	$[RhCp^*Cl_2]_2$	CsOAc	35, **3aa**
3[c]	**1a**	**2a**	$Pd(OAc)_2$	CsOAc	<5, **3aa**
4	**1b**	**2a**	$[RhCp^*Cl_2]_2$	CsOAc	80, **3ba**
5	**1b**	**2a**	$[RhCp^*Cl_2]_2$	CsOPiv	83, **3ba**
6[d]	**1b**	**2a**	$[RhCp^*Cl_2]_2$	CsOAc, PivOH	85 (80), **3ba**
7	**1b**	**5**	$[RhCp^*Cl_2]_2$	CsOAc	56, **3ba**
8	**1b**	**2a**	$[RhCp^*Cl_2]_2$	AgOAc	(75), **4a**
9[e]	**1b**	**2a**	$[RhCp^*Cl_2]_2$	CsOAc	72, **3ba**

[a] Reaction conditions: substrate **1a** or **1b** (0.2 mmol), *N*-substituted morpholine (0.4 mmol), catalyst (5 mol %), base (0.4 mmol), dry MeOH (1 mL), rt, 16 h. [b] Determined by ^1H NMR of crude product using CH_2Br_2 (7.04 μL) as internal standard; isolated yields in parentheses. [c] 100 °C, 0.2 mmol of CsOAc. [d] 0.4 mmol of CsOAc, 0.1 mmol of PivOH. [e] 0.6 mmol of **2a**, 1 mol % $[RhCp^*Cl_2]_2$, 0.6 mmol of CsOAc, 40 °C.

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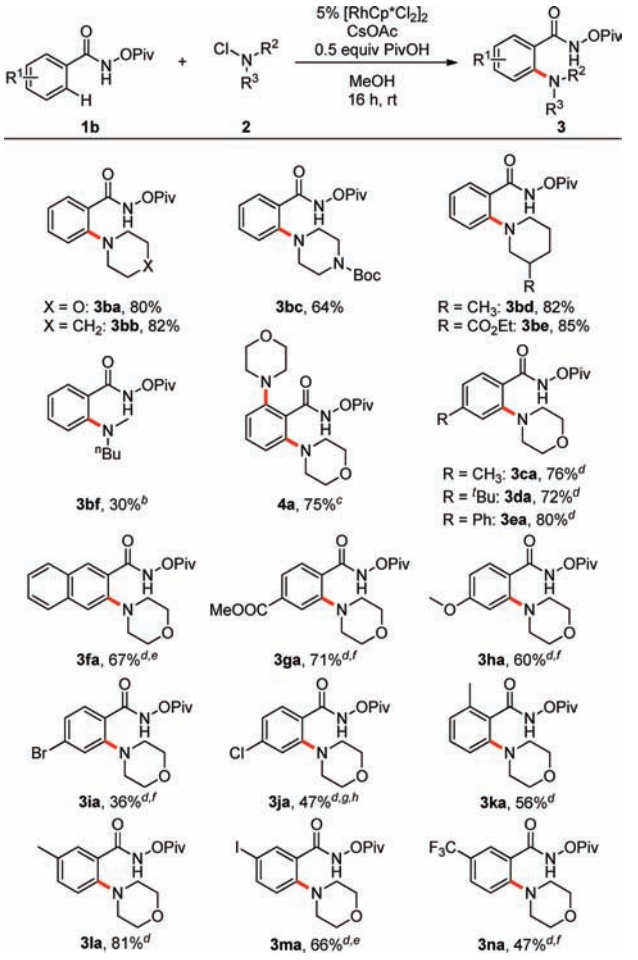
Scheme 1. Substrate Scope[a]



[a] Reaction conditions: **1b** (1.0 mmol), *N*-chloroamine (**2**) (2.0 mmol), $[RhCp^*Cl_2]_2$ (5 mol %), CsOAc (2.0 mmol), PivOH (0.5 mmol), MeOH (5 mL), rt, 16 h. Isolated yields. [b] At 60 °C. [c] AgOAc (2.0 equiv) instead of CsOAc and PivOH, 3 h, rt. [d] Reaction conditions: *N*-pivaloyloxy benzamide **1** (0.5 mmol), **2a** (1.5 mmol), CsOAc (1.5 mmol), PivOH (0.25 mmol), $[RhCp^*Cl_2]_2$ (5 mol %), MeOH (2.5 mL), rt, 16 h. [e] 4 equiv of CsOAc and **2a**. [f] 5 equiv of CsOAc and **2a**. [g] 10 equiv of CsOAc and **2a**. [h] 10 mol % $[RhCp^*Cl_2]_2$.

amines and bleach.[15] The reaction proceeds smoothly for secondary (hetero)cyclic *N*-chloroamines and gives the monoaminated products in good to excellent yields. Gratifyingly, ester and Boc protecting group are well tolerated (**3bc**, **3be**). However, a decrease in yield was observed, when acyclic substrates were engaged (**3bf**), probably due to their increased steric demand. Next, we examined the arene partner for the influence of functional groups and the substitution pattern of the aromatic ring on the reaction course (Scheme 1). Alkyl (**3ca**, **3da**) and phenyl substituents (**3ea**) in the *para* position to the DG do not alter the reaction outcome. Remarkably, the naphthamide derived substrate (**3fa**) is aminated in the less sterically hindered position in good yield. The methyl ester (**3ga**) and methoxy group (**3ha**) in the *para* position are also tolerated well, providing good yields with an excess

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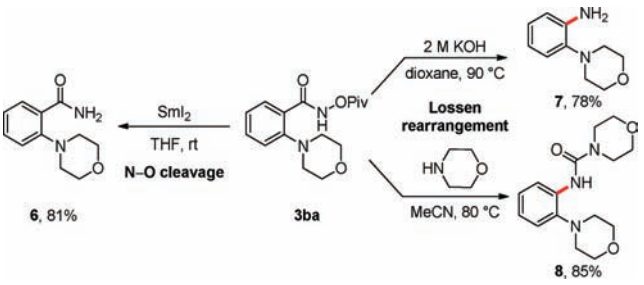
Scheme 2. Derivatization of the *N*-Pivaloyloxy Amide Directing Group



amount of chloromorpholine **2a**. Also, *meta* (**3la**) and *ortho* (**3ka**) substituents could be applied successfully in this method. Interestingly, halide substituents (**3ia**, **3ja**) seem to hamper the reaction, although the reason for this drop in reactivity remains to be elucidated.[16] In contrast, substrates bearing the strongly electron-withdrawing trifluoromethyl group (**3na**) and the reactive C(aryl)–I bond (**3ma**) could be aminated successfully using this protocol. This is remarkable, since aryliodides represent synthetically very useful moieties, allowing for further transformation.

To get access to valuable amino benzamides **6**, the N–O bond of the *N*-pivaloyloxy amide in **3ba** can be easily cleaved using SmI_2 as a reductant (Scheme 2).[17] Importantly, heating under basic conditions causes the *N*-pivaloyloxy amide group to undergo a Lossen rearrangement.[18] This fact might be particularly useful, since valuable 2-aminoaniline derivatives can be readily obtained from the aminated products **3**, as could be demonstrated in the synthesis of 1-morpholinoaniline **7** from **3ba**. Furthermore, by reaction of **3** with amines, urea functionalities can be installed into the molecule, providing access to biologically interesting structures (**8**).[19]

We then tried to gain some insight into the mechanism by conducting a series of experiments.[20] To check the reversibility of the C–H activation step, a reaction using substrate **1b** was carried out in MeOH-d_4 with omission of *N*-chloromorpholine **2a** (Scheme 3, I). The deuterium incorporation was monitored by ESI-MS analysis and revealed significant deuteration of **1b** already after 30 min. Furthermore, after 18 h only 2% undeuterated **1b** was left, displaying an efficient reversible cyclometalation of **1b**

(16) In the cases of **3ia** and **3ja**, the reaction did not reach complete conversion, even though an excess of *N*-chloromorpholine **2a** was used. Prolonged reaction time and heating did not improve the yield.

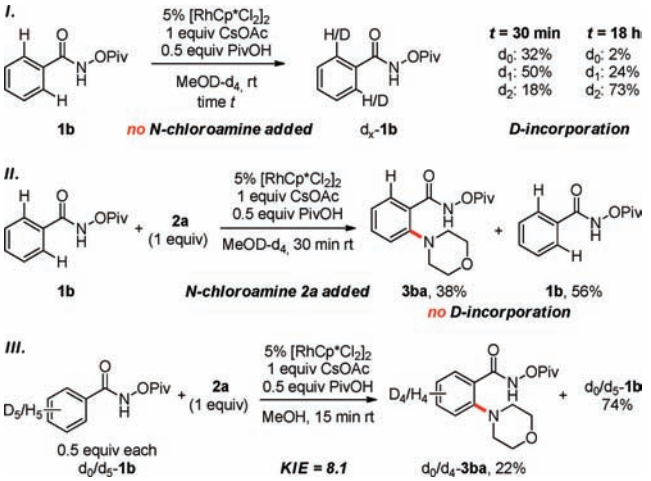
(17) For N–O cleavage using SmI_2, see: (a) Keck, G. E.; Wager, T. T.; McHardy, S. F. *Tetrahedron* **1999**, *55*, 11755.

(18) For Lossen rearrangement, see: (a) Lossen, H. *Liebigs Ann. Chem.* **1869**, *150*, 314. (b) Lossen, W. *Liebigs Ann. Chem.* 1872, *161*, 347; **1877**, *186*, 1; **1889**, *252*, 170; **1894**, *281*, 169. For review, see: (c) Bauer, L.; Exner, O. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 376.

(19) For AVE2865, a structurally related potent glycogen phosphorylase inhibitor, see: Anderka, O.; Loenze, P.; Klabunde, T.; Dreyer, M. K.; Defossa, E.; Wendt, K. U.; Schmoll, D. *Biochemistry* **2008**, *47*, 4683.

(20) See Supporting Information for further experimental details and analytical data.

Scheme 3. Deuteration Experiments Probing the Reversibility of the C−H Activation Step and the Kinetic Isotope Effect



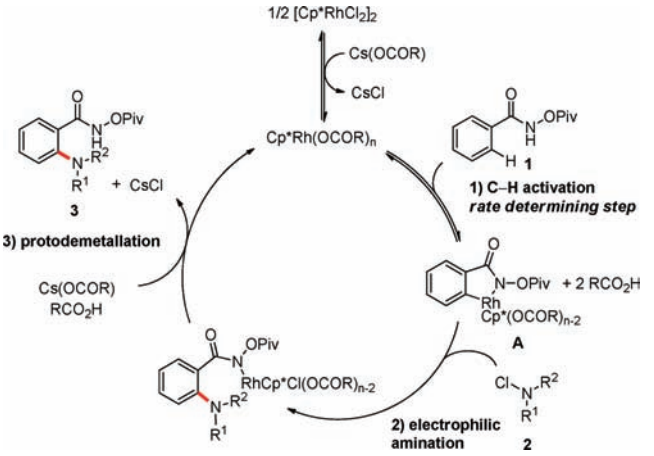
with the Rh-catalyst. When the same experiment was run in the presence of 1 equiv of *N*-chloromorpholine **2a** (Scheme 3, II) and stopped after 30 min, 38% of **3ba** and 56% **1b** could be isolated. Analysis by ^{1}H NMR and ESI-MS showed no deuterium incorporation in both starting material and product, suggesting the C−N bond formation to be significantly faster than the back reaction of the C−H activation step.[21] Next, in determining the rate-determining step of the catalytic cycle, the deuterium kinetic isotope effect was measured (Scheme 3, III). Therefore, substrate d_5-**1b** was synthesized and together with **1b** submitted to the Rh-catalyzed C−H amination. After 15 min, the reaction was stopped and the products were analyzed by ^{1}H NMR and ESI-MS. A large k_H/k_D value of 8.1 was observed, indicating the C−H/C−D bond dissociation event as the rate-determining step of the reaction pathway.

From these results, we would like to propose the following mechanistic scenario (Scheme 4): After dissociation of the rhodium dimer, ligand exchange of the monomer with the present cesium salts provides a rhodium-carboxylate species.[22] Precomplexation to the directing *N*-pivaloyloxy amide moiety is followed by C−H activation to form rhodacyle **A**; C−H activation is the slow step in the catalytic cycle and is reversible in the absence and irreversible in the

(21) For a related mechanistic investigation of an Rh-catalyzed isoquinolone synthesis, see: Hyster, T. K.; Rovis, T. *J. Am. Chem. Soc.* **2010**, *132*, 10565.

(22) Li, L.; Brennessel, W. W.; Jones, W. D. *Organometallics* **2009**, *28*, 3492.

Scheme 4. Proposed Mechanism



presence of *N*-chloroamine **2**. The next steps in the catalytic cycle are comparably fast but can only be presumed. *N*-Chloro amine **2** might undergo an electrophilic amination[14] of rhodacycle **A** to give metalated species **B**, which upon protodemetalation affords the amination product **3** and the Rh(III)-catalyst.

In conclusion we have developed a Rh(III)-catalyzed directed amination of aromatic C−H bonds with *N*-chloroamines proceeding at rt. The use of a versatile *N*-pivaloyloxy amide directing group is attractive, since it allows for further diversification of the arylamine products into valuable benzamide and 1-aminoaniline derivatives. Mechanistic studies revealed the C−H activation event as the slow and irreversible step of the catalytic cycle. This novel method constitutes an extension to known Pd-catalyzed C−H amination processes and benefits the design of new synthetic approaches to important arylamine structures.

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Supporting Information Available. Experimental procedures and full spectroscopic data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.