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High-Yielding, Versatile, and Practical [Rh(III)Cp*]-Catalyzed *Ortho* Bromination and Iodination of Arenes

Nils Schröder,[‡] Joanna Wencel-Delord,[‡] and Frank Glorius*

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

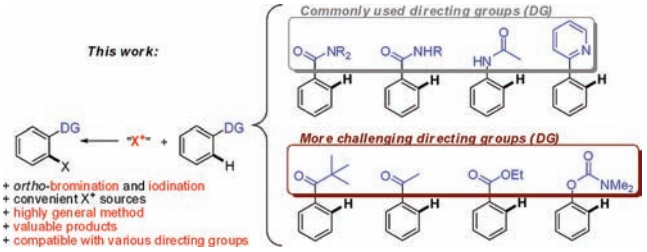
Supporting Information

ABSTRACT: We report a uniquely high-yielding, general, and practical *ortho* bromination and iodination reaction of different classes of aromatic compounds. This reaction occurs by Rh(III)-catalyzed C−H bond activation methodology and is therefore the first example of the application of this cationic catalyst for C−Br and C−I bond formation.

For many decades, aromatic halides have been an important class of compounds, due to their role as precursors for the synthesis of organometallic reagents[1] and for nucleophilic substitution reactions.[2] In addition, with the advent of cross-coupling chemistry,[3] the importance of bromo- and iodoarenes has tremendously increased, and hence they can be classified as the core building blocks of organic synthesis. Consequently, efficient and selective methods to access this class of compounds are highly valuable.

Metal-catalyzed direct functionalization of C−H bonds has emerged over the past decade as a modern and environmentally friendly tool for organic synthesis.[4] Due to the constant effort of many research groups, a plethora of carbon−carbon bond formation reactions have been discovered. However, application of this strategy to create carbon−heteroatom bonds, in particular, carbon−halogen bonds, is still surprisingly underdeveloped. The vast majority of the rare examples of these C−X (X = Cl, Br, I) bond formation reactions use a palladium catalyst.[5] The catalytic systems reported by the groups of Sanford,[6] Yu,[7] Bedford,[8] Shi,[9] Tanabe,[10] Fabis,[11] Xu,[12] and Dong[13] illustrate the major importance of these *ortho*-selective transformations. However, they were generally limited by their scope (the use of a specific directing group such as heteroaromatics or electron-donating directing groups), by their efficiency (moderate yields), or by being suitable for only one type of C−X bond formation. Therefore, a general method enabling the high-yielding and selective formation of valuable and versatile (with regard to further transformations) C−Br and C−I bonds, compatible with a large scope of diverse arenes, is of prime synthetic value.

Recently, Rh(III) has emerged as a highly useful C−H bond activation catalyst. Indeed, it turned out to be a very efficient catalyst for C−H bond activation/olefination,[14] alkynylation,[15] and, more recently, nucleophilic additions[16] and arylation reactions.[17] However, to the best of our knowledge, no application of this catalyst system for carbon−halogen bond formation has been reported before now. Herein, we report a new, high-yielding, versatile, and general method for the synthesis of *ortho*-brominated and -iodinated aromatic compounds using a [Rh(III)Cp*] catalyst. The particular advantage of this strategy is its compatibility with many different, highly useful directing groups, which opens up new possibilities for the synthesis of a panel of aromatic halides.



In order to develop a catalytic system complementary to the already known Pd-catalyzed examples that are especially suited for electron-rich substrates, we selected the rather electron-poor tertiary benzamide **1** as the initial substrate for our study. Moreover, with the aim of discovering halogenation strategies compatible with both bromination and iodination reactions, commercially available, stable, and rather inexpensive *N*-halosuccinimide derivatives were selected as highly promising Br and I sources. We commenced the bromination study using NBS in the presence of $[RhCp^*Cl_2]_2$ (2.5 mol%), $AgSbF_6$ (10 mol%), $Cu(OAc)_2$ as oxidant, and PivOH as additive. No desired product was detected when the reaction was run in dioxane at 140 °C, but we noticed with delight that the simple change of solvent to 1,2-DCE led to the formation of the *ortho*-brominated benzamide **1-Br** with full conversion and 82% isolated yield. Further investigations revealed that $Cu(OAc)_2$ was not required for this transformation and that significantly milder reaction conditions (temperature of only 60 °C) could be successfully applied. Notably, decreasing the catalyst loading to 1 mol% did not affect the efficiency of this transformation. A control reaction showed that omission of the Rh precatalyst resulted in complete inactivity of this catalytic system.

Under these optimized conditions, the scope of benzamides bearing diverse substituents on the arene ring was examined (Table 1). Electron-rich substituents such as Me or OMe in both *para* and *meta* positions were well tolerated, leading to the formation of the desired products with excellent yields. However, when **5** was used as a substrate, the small steric hindrance of the methoxy group was not sufficient to control the selectivity of this reaction, and two easily separable regioisomers of **5-Br** were obtained in almost equal amounts.

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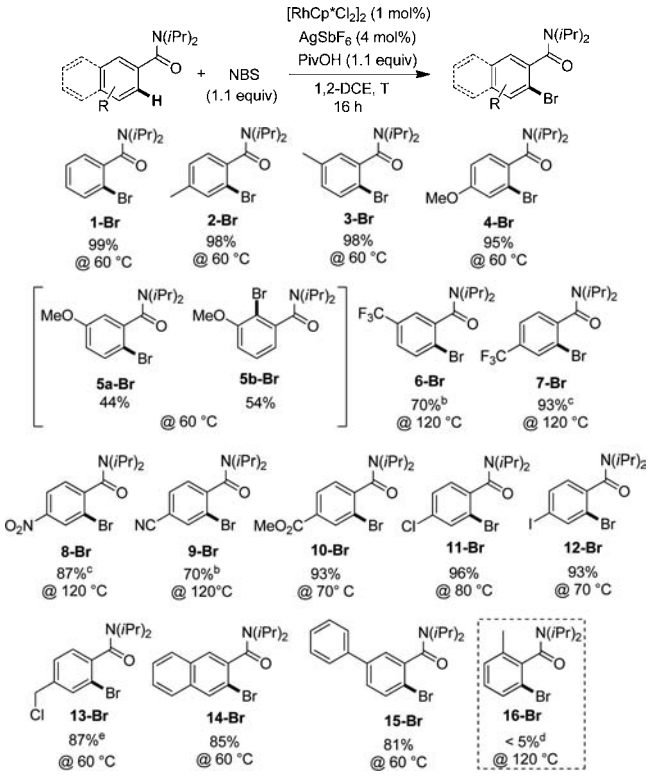
Table 1. *Ortho* Bromination of Benzamides[a]

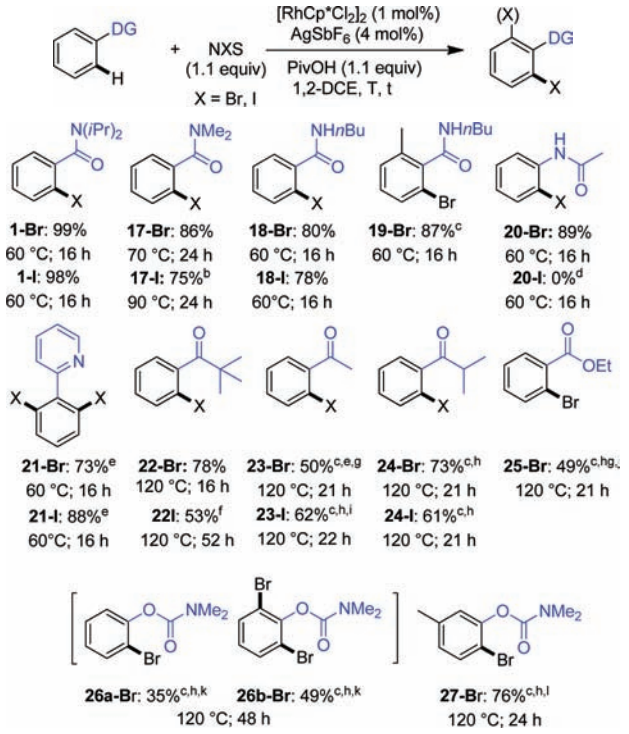


[a]Isolated yields, reaction run on a 1 mmol scale. [b]48 h reaction time and 2 equiv of NBS. [c]24 h reaction time and 2 equiv of NBS. [d]Only traces of brominated product could be detected by ESI analysis of the crude mixture. [e]2.5 mol% $[RhCp^*Cl_2]_2$ and 10 mol% $AgSbF_6$.

In contrast to electron-donating groups, strongly electron-withdrawing groups, such as CF_3, on either the *para* or *meta* position had a significant influence on the activity of this catalytic system, and an increased reaction temperature (120 °C) was required to complete this transformation. Similarly, other electron-deficient benzamides bearing a NO_2 or CN substituent in the *para* position could undergo the bromination reaction sufficiently, but more sluggishly, leading to the formation of **8-Br** and **9-Br** in 87 and 70% yield, respectively. Notably, this catalytic system turned out to be efficient and totally selective even when benzamide **10** bearing an additional ester substituent, potentially a second chelating group, was submitted to the reaction conditions. Halo-substituted benzamides **11** and **12** were also well tolerated, and therefore the highly valuable bromo-chloro- and bromo-iodo-substituted arenes could be obtained in excellent yield (96 and 93%). Moreover, bromination of the benzamide bearing a chloromethyl substituent (**13**) was also possible, leading to formation of the *ortho*-brominated product in 87% yield. Expanding the scope from the phenyl to the naphthyl system (**14**) was also possible, leading to the formation of **14-Br**. The presence of an additional aromatic ring on the substrate was tolerated as well, leading to the regioselective formation of **15-Br**. However, it is important to note that, for this sterically demanding tertiary benzamide directing group, an *ortho* substitution turned out to be detrimental for this transformation: only trace amounts of brominated product **16-Br** could be detected by ESI-HR analysis of the crude mixture.[14j,k]

To additionally establish the power of this methodology, we examined the possibility of performing the iodination reaction (Table 2). We were pleased to observe that the simple replacement of NBS by NIS under otherwise identical conditions led to the formation of the *ortho*-iodinated compound **1-I** in an excellent yield of 98%. Encouraged by these results, we turned our attention to arenes bearing other directing groups. These bromination and iodination reactions proved to be highly versatile. First, the highly sterically demanding isopropyl substituent on the benzamide group could be replaced by less sterically demanding and less electron-rich methyl groups, leading to the formation of the corresponding brominated and iodinated compounds **17-Br** and **17-I** in 86 and 75% yields. Moreover, the tertiary amide group could be efficiently replaced by a secondary amide group, leading to the formation of **18-Br** and **18-I** with good yields of 80 and 78%. Notably, the use of the secondary amide directing group obviated the intolerance of the tertiary benzamide toward *ortho* substituents; **19** underwent the bromination reaction smoothly, leading to the formation of **19-Br** in 87% yield. For a highly activated arene, like acetanilide, *ortho* bromination occurred smoothly under the standard conditions. However, interestingly, this reaction failed when the stronger electrophile NIS was used. In this case, the *para*-iodinated product was selectively obtained, which presumably results from the non-rhodium-catalyzed electrophilic aromatic substitution pathway (the control reaction run in the absence of rhodium gave an identical result). When unsubstituted phenylpyridine **21** was used in the presence of 2.2 equiv of

Table 2. *Ortho* Bromination and Iodination of Various Arenes[a]



[a]Isolated yields, reactions run on a 1 mmol scale. [b]1.6 equiv of NIS. [c]2.5 mol% $[RhCp^*Cl_2]_2$ and 10 mol% $AgSbF_6$. [d]Instead the 4-iodoacetanilide (82%) from S_E-Ar-reaction was formed [e]2.2 equiv of NXS. [f]2.5 equiv of NIS was added in 5 portions. [g]1.1 equiv $Cu(OAc)_2$ instead of PivOH. [h]2.2 equiv $Cu(OAc)_2$ instead of PivOH. [i]1.4 equiv of NIS. [j]2.0 equiv of NBS was added in 4 portions. [k]2.0 equiv of NBS. [l]1.5 equiv of NBS.

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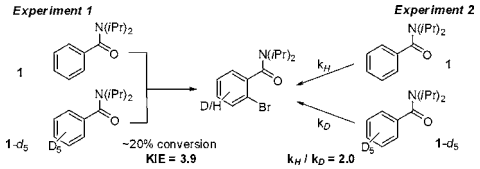
the halogenating agent, selective dihalogenation was observed for either the bromination or the iodination reaction. Thereafter, we focused our attention on highly valuable substrates such as ketones or esters, which are known to be challenging in C−H activation processes. Under standard reaction conditions with the increased reaction temperature (120 °C), bromination of the *tert*-butyl phenyl ketone occurred smoothly, leading to the formation of the desired **22-Br** in 78% yield. In contrast, the iodination reaction turned out to be troublesome, and successive addition of NIS in small portions was required to allow the successful execution of this transformation. Encouraged by these results, we submitted a simple acetophenone substrate to our halogenation reaction. Disappointingly, no desired product was formed, and a noncatalyzed bromination of the methyl group occurred. Replacement of the PivOH additive by CsOPiv led to the total inhibition of the reaction. However, we were delighted to discover that when copper acetate was used instead of pivalic acid, the desired *ortho*-brominated acetophenone could be isolated in 50% yield. These modified reaction conditions turned out to be key to the successful halogenation reaction of other enolizable isopropyl phenyl ketone and benzoic ester substrates. Thus, the corresponding halogenated products were obtained in moderate yields, probably due to the instability of the substrates at the high reaction temperature, required for the less efficient C−H activation event. Finally, the potential of a phenyl dimethylcarbamate to undergo the C−H bond activation/C−X bond formation sequence was examined. The bromination reaction run at 120 °C, with 5 mol% catalyst loading and 2 equiv of NBS, led to the formation of the mixture of mono- and dihalogenated product. The two species could be separated, leading to the isolation of **26a-Br** and **26b-Br** in 35 and 49% yields.

For obtaining more mechanistic insight, a deuteration experiment was conducted (Scheme 1). Treatment of a 1:1

Scheme 1. Deuteration Experiments

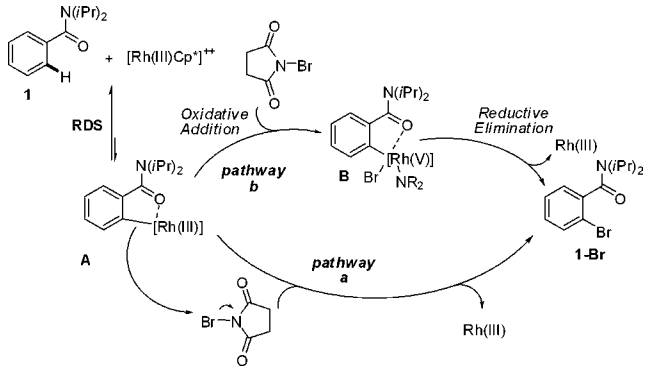


mixture of **1** and **1-d_5** under the typical reaction conditions revealed a kinetic isotopic effect (KIE) of 3.9 for the initial reaction rate (conversion of 20%, Experiment 1). This value is typical for the C−H activation process. Moreover, in order to investigate the nature of the rate-determining step, the initial rate of the reaction with **1** and **1-d_5** was measured and revealed a k_H/k_D of 2.0 (Experiment 2). This result suggests that the C−H bond activation is a rate-determining step. In addition, the analysis of the recovered starting material showed significant H/D-scrambling, which indicates the reversible character of the C−H activation step.[18]

Additionally, ^{1}H NMR studies were undertaken in order to characterize some key intermediates. **1** was added at 60 °C to a preformed cationic catalyst $[RhCp^*(MeCN)_3](SbF_6)_2$ in a stoichiometric and substoichiometric ratio. The ^{1}H NMR analysis did not reveal any significant change of spectra in comparison to the spectrum of **1** alone. Subsequent addition of NBS and PivOH resulted in the immediate initiation of the expected reaction; however, no intermediate species could be detected. These observations suggest that an equilibrium between substrate + catalyst and the rhodacycle is in operation in the absence of NXS and that this equilibrium is shifted in the direction of the substrate. In the presence of NBS, the halogenation step would be fast, leading to rapid conversion of the intermediate rhodacycle to the desired product. Furthermore, a kinetic study of the reaction revealed that this transformation requires no incubation time.[19]

Based on these results, we propose two different mechanistic pathways (Scheme 2). Both of them start with the reversible

Scheme 2. Proposed Catalytic Pathways



C−H activation and formation of rhodacycle **A**. Following pathway a, rhodacycle **A** can undergo a nucleophilic addition type reaction to NBS to directly lead to product **1-Br**. On the other hand, similar to some palladium-catalyzed halogenations, intermediate **A**, in the presence of NBS, could potentially be oxidized to Rh(V) complex **B**, which then would undergo reductive elimination to form product **1-Br** and regenerate the Rh(III) catalyst.

In conclusion, a general and practical strategy for the *ortho* bromination *and* iodination of arenes by a cationic Rh(III) catalyst has been developed. This transformation is compatible not only with tertiary benzamide substrates bearing a variety of electron-rich and electron-poor groups such as ester, chloro, or methoxy substituents but also with other classes of arenes, such as secondary benzamides, acetamides, and phenylpyridines. Moreover, this reaction is the first example of the direct halogenations of simple ketones and benzoic esters occurring via C−H bond activation. Due to its versatility, efficiency, and, in many cases, fairly mild reaction conditions,[4c] this reaction should be of high synthetic value.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental and characterization details. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

glorius@uni-muenster.de

Author Contributions

‡N.S. and J.W.-D. contributed equally.

Notes

The authors declare no competing financial interest.

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