

Letter

Cobalt-Catalyzed C–H lodination of Aromatic Amides with Molecular lodine through the Use of a 2-Aminophenyloxazoline-Based Bidentate-Chelation System

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Supporting Information

ABSTRACT: The cobalt-catalyzed chelation-assisted C–H iodination of aromatic amides using molecular iodine as an iodinating reagent is reported. The reaction is carried out in an atmosphere of air and uses $Co(OAc)_2$ ·4H₂O as an efficient catalyst and 4-chloro-2-(4,5-dihydrooxazol-2-yl)aniline as a directing group. The reaction shows a wide functional group tolerance. Mechanistic



studies suggest that the reaction proceeds through a different mechanism from that of our previously reported transformation in which a Co(II) catalyst/8-amino-5-choloroquinoline chelation system was used.

ransition-metal-catalyzed C–H halogenation is a highly L attractive strategy for the direct introduction of a halogen atom into an organic compound compared with conventional methods, such as lithiation/halogenation.¹ The direct iodination of C-H bonds using molecular I₂ was found to be a fascinating step-economical method for preparing aryl iodides.² In this regard, Pd- and Ni-catalyzed C-H iodination with molecular I₂ has been developed.³ Our recent report regarding the use of molecular I2 in Co-catalyzed C-H iodination reactions was also found to be a major achievement from the standpoint of being cost-effective and involving mild conditions.⁴ However, our previous method suffered somewhat from a relatively lower efficiency and narrow substrate scope. This can be attributed to the stability of the 5,5-membered metallacycle A toward further reaction with I_2 (Figure 1). In addition, C(O)-N bond cleavage also took place to give an acetamide derivative, the formation of which caused a lower



Figure 1. Screening directing groups.

yield of the desired iodination product.⁵ To solve these issues, to develop a mild and more efficient method, and to gain additional insights into the role of the directing group, we concluded that an alternative chelation and catalytic system might be required. It is likely that the efficiency of C-H functionalization reactions is highly dependent on the appropriate combination of the directing group and the metal catalyst that are used.⁶ We hypothesized that structural modification with other heteroatoms in a directing group, as in 1a and 1b, or the use of a 5,6-membered metallacycle, as in 1c, or a 6,6-membered metallacycle, as in 1d, with N,N'-chelation would suppress undesired C-N bond cleavage (Figure 1). Finally, the use of an amide-tethered 2-(4,5-dihydrooxazol-2yl)aniline $(1c)^7$ as a bidentate directing group resulted in a substantial improvement in reactivity when a combination of cobalt complexes was used.

Although substantial progress regarding the use of first-row transition metals such as Mn, Fe, Co, Ni, and Cu has been made in the development of novel C–H functionalization reactions,⁸ these areas continue to be an undeveloped area of research. Among these metals, Co has been of particular interest and has been exploited as a potential alternative for noble-metal catalysts in the field of C–H bond functionalization due to its easy availability, air stability, and unique reactivity.^{9,10} We herein report on the development of an operationally simple and efficient catalytic system, in which inexpensive molecular I₂ is used as an iodinating agent to improve synthetic accessibility. The high efficiency of this C–H iodination hinges on the use of a combination of an amidetethered 2-(4,5-dihydrooxazol-2-yl)aniline as a bidentate directing group and Ag₂CO₃ as an oxidant.

We initiated our studies by investigating potentially suitable directing groups for C–H iodination with I_2 . Various bidentate

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Table 1. Optimization Studies^a

		^{CO} (20 r ^{DG} ^{DG} ^H ^L ^{DG} ^{CO} (20 r ^{OXidant (*)} ^{DCE (0.8)} ¹ ^{DCE (0.8)}	nol %) I equiv) mL) h 2	S= NO	
entry	amide	cobalt catalyst	oxidant	base	yields $(2/1) (\%)^{b}$
1	la	$Co(OAc)_2 \cdot 4H_2O$	Ag ₂ CO ₃		0/0
2	1b	$Co(OAc)_2 \cdot 4H_2O$	Ag_2CO_3		0/10
3	1c	$Co(OAc)_2 \cdot 4H_2O$	Ag_2CO_3		91/0 (87)
4	1d	$Co(OAc)_2 \cdot 4H_2O$	Ag_2CO_3		0/87
5	1e	$Co(OAc)_2 \cdot 4H_2O$	Ag_2CO_3		95/trace (91) ^c
6	1e	$Co(acac)_2 \cdot 2H_2O$	Ag_2CO_3		0/0
7	1e	$Co(acac)_3$	Ag_2CO_3		0/0
8	1e	CoBr ₂	Ag_2CO_3		48/39
9	1e	$CoCl_2$	Ag_2CO_3		36/55
10	1e	$Co(OAc)_2 \cdot 4H_2O$	Ag_2CO_3	NaOAc	42/56
11	1e	$Co(OAc)_2 \cdot 4H_2O$	AgOAc		51/37
12	1e	$Co(OAc)_2 \cdot 4H_2O$	Ag_2SO_4		0/0
13	1e	$Co(OAc)_2 \cdot 4H_2O$	$Mn(OAc)_2 \cdot 4H_2O$		0/18
14	1e	$Co(OAc)_2 \cdot 4H_2O$	$Mn(OAc)_3 \cdot 2H_2O$		8/7
15	1e	$Co(OAc)_2 \cdot 4H_2O$	Ag ₂ O		50/48
16 ^d	1e	$Co(OAc)_2 \cdot 4H_2O$	Ag_2CO_3		20/46
17	1e		Ag_2CO_3		0/82
18	1e	$Co(OAc)_2 \cdot 4H_2O$			0/14

^{*a*}Reaction conditions: amide 1 (0.15 mmol), I₂ (0.3 mmol), cobalt catalyst (0.03 mmol), an oxidant (0.15 mmol), solvent (0.8 mL) at 120 °C for 7 h in air. ^{*b*}Yields were determined by ¹H NMR analysis of the crude reaction mixture using 1,1,2,2-tetrachloroethane as an internal standard. ^{*c*}Number in parentheses represents the yield of the isolated product. ^{*d*}Ag₂CO₃ (0.4 equiv).

chelation systems, such as the N,O-bidentate 1a, N,S-bidentate 1b, and N,N-bidentate 1c and 1d in the presence of $Co(OAc)_2$ ·4H₂O (20 mol %) as a catalyst and Ag₂CO₃ (1 equiv) as an oxidant in 1,2-dichloroethane (DCE) at 120 °C for 7 h were examined (Table 1). The substrates 1a, 1b, and 1d failed to furnish the desired iodination products (entries 1, 2, and 4). The use of the N.N-bidentate chelation system 1c, however, gave the ortho-iodination product 2c in good yield, along with a trace amount of a remote (4-position) C-H iodination product (entry 3). The amide 1e, which contains a chloro group at the four-position in 1c, produced an excellent yield of 2e as a single product (entry 5). Various cobalt salts were screened as catalysts in the reaction of 1e (entries 6-9), and $Co(OAc)_2 \cdot 4H_2O$ was found to be the catalyst of choice. Next, various oxidants were screened (entries 10–15). Among them, Ag_2CO_3 was found to be a suitable oxidant for use in this reaction. It is noteworthy that the yield of 2e decreased with a lower loading of Ag₂CO₃ (entry 16). No product was formed in the absence of the catalyst (entry 17) and Ag₂CO₃ (entry 18). After screening a series of solvents (PhCl, TFE, dioxane, and hexafluoroisopropanol (HFIP)), we concluded that none were superior to DCE, and we concluded that it is the optimal solvent. (See Table S1 for details.)

With the optimized conditions in hand, we next examined the scope of aromatic amides (Scheme 1). The reaction showed a wide functional group tolerance, including halides (F, Cl, and Br), $-CF_3$, -OMe, and esters groups. Whereas aromatic amides containing both an electron-withdrawing group and an electron-donating group at the ortho position reacted smoothly with I₂ to give excellent yields of the corresponding products, amides containing an electron-withdrawing group, as in **1g**–**j**, required longer reaction times (15– 24 h) to produce excellent product yields. It appears that electron-donating groups facilitate the reaction. The reaction

Scheme 1. Substrate Scope for Iodination



^aI₂ (0.45 mmol), Ag₂CO₃ (0.3 mmol). ^bAmide 1 (1.0 mmol), I₂ (2.0 mmol), Co(OAc)₂ 4H₂O (0.03 mmol), Ag₂CO₃ (2.0 mmol), DCE (10 mL) at 120 $^{\circ}$ C for 24 h in air.

with a simple benzoic amide, as in 1k, gave a mixture of monoand di-iodination products of 29 and 52%, respectively. The

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use of more I_2 and Ag_2CO_3 gave di-iodination product $2\mathbf{k}'$ as a major product. Meta-substituted aromatic amides with an electron-donating group (OMe), as in **1m**, gave the di-iodination product as the major product, which could easily be isolated in the pure form by column chromatography. In contrast, the reaction of an electron-deficient (CF₃)-substituted amide **1o** gave the monoiodination product **2o** exclusively in excellent yield (87%), in which the reaction took place exclusively at the less hindered position. The naphthylderived amide **1v** and thiophene-derived amide **1x** were also compatible with the reaction conditions. This cobalt-catalyzed iodination was successfully carried out on a 1 mmol scale reaction. The reaction of **1f** (1 mmol) with I_2 gave **2f** in 79% isolated yield.

Deuterium labeling experiments were carried out in an attempt to gain insights into the reaction mechanism (Scheme 2). When the amide $1e-d_7$ was reacted with I₂ under the



standard reaction conditions for 2 h, no hydrogen atoms were incorporated into the recovered deuterated amide. No H/D exchange was detected, even in the absence of I₂. These results indicate that C-H bond cleavage is an irreversible step in this reaction. It should also be noted that the metallacyclic intermediate C- d_{13} was isolated by column chromatography and was structurally characterized by HRMS and ¹H NMR. (This is discussed more fully in Scheme 3.)

To determine the rate-determining step, we conducted experiments that were designed to detect possible kinetic isotope effects (KIEs) for C–H iodination (Figure 2). Two parallel experiments were carried out using 1e and 1e- d_7 , and the results revealed a KIE of 0.53, which is in sharp contrast with previous reports.^{3,4} This observed inverse secondary KIE suggests that the involvement of C–H bond cleavage as the rate-determining step can be ruled out in this reaction and clearly points to the fact that the cleavage of a C–H (C–D) bond undergoes sp²–sp³ rehybridization in the rate-determining step, similar to an aromatic electrophilic substitution mechanism.¹¹

As shown in Scheme 1, the iodination of aromatic amides with an electron-withdrawing substituent required a longer reaction time to produce a high product yield, suggesting the putative involvement of an aromatic electrophilic mechanism. To probe the electronic effects on the iodination reaction, a Hammett analysis for the relative rate of aromatic C–H iodination on different *p*-substituted amides 11, 1m, 1n, and 10 versus an unsubstituted amide 1k was performed (Figure 3).¹² A nearly linear correlation of the corresponding to log(conv. of R/conv. of H) against the Hammett constant (σ_p) with a negative slope ($\rho = -3.22$) was observed, indicating that the

Scheme 3. Synthesis of Co(III)-Metallacyclic Species C and Its Reactivity



Figure 2. Kinetic isotopic effect studies: parallel experiments.

rate-determining transition state is stabilized by electrondonating substituents. It therefore appears that an aromatic electrophilic substitution mechanism is involved in this reaction.¹¹

To gain additional information regarding the mechanism for this reaction, we isolated the metallacycle by following a literature procedure (Scheme 3).¹³ When the amide **1e** was treated with one equivalent of $Co(OAc)_2$ ·4H₂O and Ag₂CO₃ in DCE at 120 °C for 2 h, the cobalt complex C was successfully isolated (16%) by column chromatography and was characterized by HRMS and ¹H NMR spectroscopy (see the SI for details).¹⁴ When the catalytic reaction for C–H iodination was next carried out using C as a catalyst (5 mol %)

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Figure 3. Hammett plot.

under the standard reaction conditions, **2e** was produced in 43% yield. The reaction of **C** with two equivalents of I₂ in DCE at 120 °C for 7 h gave moderate yields of the iodinated product along with a significant amount of unidentified byproducts. When one equivalent of Ag_2CO_3 was added, the yield of **2e** increased to 83%, and no byproducts were detected. These experiments reveal that the Co(III)-metallacyclic intermediate **C** shows catalytic activity and that Ag_2CO_3 is an essential component of the reaction for promoting the iodination and eliminating the formation of byproducts. However, we do not think that the complex **C** is a key intermediate, but it exists as a resting state.

The results of the kinetic studies (Figure 2) and the Hammett plot (Figure 3) suggest that the reaction proceeds through a stepwise electrophilic aromatic substitution mechanism. On the basis of literature reports^{4,11,15} and our experimental results, we propose a plausible mechanistic pathway (Scheme 4). The coordination of amide 1 to the





Co(II) species, followed by oxidation by Ag(I) gives the Co(III) species **D**, which functions as a key catalytic species.^{15a} A stepwise electrophilic substitution pathway through the formation of an arenium ion intermediate **E** gives the metallacycle **F**, which reacts with 1 to give the metallacyclic intermediate **C**' as an off-cycle species (corresponding to **C** in

Scheme 3). The redox neutral Co(III)/Co(III) pathway operates via the transition state **G**. In this process, the electrophilic attack of I_2 on the Co(III) species **F** gives **H** directly through the transition state **G**. ^{15b,c} The protonation of intermediate **H** with exchange with **1** gives the iodination product **2** with the regeneration of the Co(III) species. On the basis of the obtained results, it appears that the present reaction proceeds through a stepwise electrophilic aromatic substitution, although we have no direct evidence of this at this time.

In summary, we report on an efficient catalytic system for C-H iodination using molecular I_2 as an iodinating agent. The reaction tolerated a wide variety of functional groups. The amide-tethered 2-(4,5-dihydrooxazol-2-yl) aniline was found to be an efficient directing group. Kinetic studies and a Hammett study revealed that the present C-H iodination process likely proceeds through a stepwise electrophilic aromatic substitution mechanism. The Ag₂CO₃ not only functions for the oxidation of Co(II) to Co(III) but also greatly reduces the formation of byproducts. Further mechanistic studies will be needed to uncover the precise mechanism of this C-H iodination. Our findings clearly indicate the importance of the use of a metaldirecting group for designing new types of C-H functionalizations and provides useful insights for the use of directing group design in the future. We conclude that the findings reported in this study will stimulate the development of additional novel types of transformations in the near future.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.or-glett.9b02109.

Experimental procedure, synthesis of starting materials, and characterization of compounds (PDF)

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Notes

The authors declare no competing financial interest.

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