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J. Am. Chem. Soc., Just Accepted Manuscript • DOI: 10.1021/jacs.7b13049 • Publication Date (Web): 09 Mar 2018 Downloaded from http://pubs.acs.org on March 9, 2018

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Cobalt(II)-Catalyzed Electroo**xidative C–H** Amination of Arenes with Alkylamines

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Supporting Information Placeholder

ABSTRACT: An environmentally friendly electrochemical protocol about cobalt-catalyzed C-H amination of arenes has been developed, which offers a simple way to access synthetically useful arylamines. In divided cells, a wide variety of arenes and alkylamines are examined to afford C-N formation products without using external oxidants, which avoids the formation of undesired byproducts and exhibits high atom economy. Importantly, the reaction can also be extended to gram level with moderate efficiency. KIE experiment indicates that C-H bond cleavage might not be involved during the rate-limiting step.

Transition-metal-catalyzed C-H functionalization has been recognized as one of powerful strategies to construct C-C and C-X (X=N, O, P, S etc.) bonds.¹ Compared with some noble metals, cobalt exhibited various advantages in low cost and toxicity, unique catalytic reactivity.² In recent years, cobalt-catalyzed C-H alkoxylation,³ amination⁴ and arylation⁵ have been widely reported. However, high consumption of material and severe metal residue were inevitable since a large excess of silver and manganese salts were needed for the dehydrogenative process.⁶ Therefore, it is highly desirable to seek for a more efficient oxidant-free Co-catalytic system.

The development of efficient and environmentally friendly methods is an important topic in organic synthesis. As an ideal alternative to chemical oxidants, electrochemical anodic oxidation can serve as an environmentally friendly synthetic tool in organic chemistry.7 Under electrolytic conditions, substrates could be oxidized at anode directly⁸ or indirectly.⁹ Nevertheless, most metal catalysts are prone to be reduced at cathode and lose catalytic reactivity. For this reason, continuous efforts have been devoted to developing transition-metal-catalyzed electrooxidative C-H functionalization under divided cell.¹⁰ In 2007, Jutand and co-workers firstly reported Pd-catalyzed electrooxidative C(sp²)-H alkenylation.^{10a} Subsequently, Kakiuchi and co-workers developed Cu-catalyzed electrooxidative C(sp³)-H chlorination.^{10e} Overall, transition-metal-catalyzed electrooxidative C-H functionalization was mainly limited to Pd-catalyzed reactions.¹¹ Therefore, it would make sense to develop cheaper transition-metal-catalyzed electrooxidative C-H functionalization. Herein, we demonstrated cobalt-catalyzed electrooxidative C-H amination between arylamides and alkylamines under divided electrolytic conditions (Fig. 1). The replacement of oxidants with electricity made organic reactions proceed efficiently.



Figure 1. Electrochemical Cobalt-Catalyzed C-H Amination.

Table 1. Effect of the Reaction Parameters.^a



Entry	Variation from standard conditions	Yield (%)
1	none	74
2	CoCl ₂ ·6H ₂ O	67
3	Co(acac) ₂	14
4	NaOAc at anode	67
5	HOPiv at anode	46
6	DMF instead of MeCN	54
7	CF ₃ CH ₂ OH instead of MeCN	n.d.
8	H ₂ O instead of MeOH	68
9	5 mA, 6 h	68
10	15 mA, 2 h	68
11	undivided cell	n.d.
12	without Co(OAc) ₂ ·4H ₂ O	n.d.
13	no electric current	n.d.

^{*a*} Reaction conditions: **1a** (0.25 mmol), **2a** (2.0 equiv.), Co(OAc)₂·4H₂O (20 mol%), NaOPiv·H₂O (1.0 equiv.), "Bu₄NBF₄ (2.0 equiv.), MeCN (10.0 mL) [anode], and NaOPiv·H₂O (2.0 equiv.), HOPiv (8.0 equiv.), MeOH (10.0 mL) [cathode] in H-type divided cell with carbon cloth anode (15 mm×15 mm×0.36 mm), nickel plate cathode (15 mm×15 mm×1.0 mm) and a AMI-7001-30 membrane, constant current = 10.0 mA ($j_{anode} = 4.4$ mA/cm²), nitrogen balloon, 65 °C, 3 h (4.5 F). Isolated yields are shown.

Initially, we chose *N*-(quinolin-8-yl)thiophene-2-carboxamide (1a) and morpholine (2a) as standard substrates. After unremitting efforts, under constant-current electrolysis at 10 mA for 3 h, 74 % isolated yield of the desired product (**3aa**) could be obtained in the presence of 20 mol% Co(OAc)₂·4H₂O and 1 equiv. NaOPiv·H₂O in MeCN at 65 °C (Table 1, entry 1). Replacing Co(OAc)₂·4H₂O by CoCl₂·6H₂O or Co(acac)₂ would lead to the decreased yields (Table 1, entries 2 and 3). While we attempted to use NaOAc or HOPiv as additive at anode, lower yields would be obtained in this transformation (Table 1, entries 4 and 5). Then we investigated the effect of different solvents, MeCN exhibited the best transformation compared with DMF and CF₃CH₂OH (Table 1, entries 6 and 7). The yield would decrease slightly when replacing MeOH by H₂O

Scheme 1. Substrate Scope of Amides.^a

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^{*a*} Reaction conditions: **1a** (0.25 mmol), **2a** (2.0 equiv.), Co(OAc)₂·4H₂O (20 mol%), NaOPiv·H₂O (1.0 equiv.), "Bu₄NBF₄ (2.0 equiv.), MeCN (10.0 mL) [anode], and NaOPiv·H₂O (2.0 equiv.), HOPiv (8.0 equiv.), MeOH (10.0 mL) [cathode] in H-type divided cell with carbon cloth anode (15 mm×15 mm×0.36 mm), nickel plate cathode (15 mm×15 mm×1.0 mm) and a AMI-7001-30 membrane, constant current = 10 mA ($j_{anode} = 4.4$ mA/cm²), nitrogen balloon (1 atm.), 65 °C, 3.5 h (5.2 F). Isolated yields are shown. ^{*b*} Constant current = 10 mA ($j_{anode} = 4.4$ mA/cm²), 3.0 h (4.5 F).

at cathode (Table 1, entry 8). Keeping constant electric quantity, increasing or decreasing electric current resulted in lower yields (Table 1, entries 9 and 10). In addition, this reaction couldn't occur under undivided cell (Table 1, entry 11). Finally, the control experiment indicated that both $Co(OAc)_2 \cdot 4H_2O$ and electricity were essential for this reaction (Table 1, entries 12 and 13).

With the optimized protocols in hand, the substrate scope of amides was screened next (Scheme 1). Firstly, we explored the reacti vity of various aromatic amides. Thiophene-2-carboxamide, furan-2-carboxamide, benzothiophene-2-carboxamide and naphthalene-1-carboxamide were compatible in the reaction (3aa-3ca, 3pa), 8aminoquinolinebenzamide could afford 61 % yield (3da). Benzamide possessing para or ortho methyl could furnish the desired product in moderate yield (3ea and 3fa). As for the benzamide possessing meta methyl, exclusive product could be obtained in lower yield at the less hindered ortho position (3ga). To our delight, other electron-neutral substituents, such as fluoride, chloride and bromide group, as well as phenyl group, could also be tolerated and gave desirable yields (3ha-3ka). Benzamide bearing electron-rich groups, such as methoxyl, showed moderate efficiency in the transformation (3la). Moreover, benzamide possessing electronwithdawing groups participated in the reaction smoothly, obtained in acceptable yields (3ma-3oa).

Scheme 2. Substrate Scope of Alkylamines.^a



^{*a*} Reaction conditions: **1a** (0.25 mmol), **2a** (2.0 equiv.), Co(OAc)₂·4H₂O (20 mol%), NaOPiv·H₂O (1.0 equiv.), "Bu₄NBF₄ (2.0 equiv.), MeCN (10.0 mL) [anode], and NaOPiv·H₂O (2.0 equiv.), HOPiv (8.0 equiv.), MeOH (10.0 mL) [cathode] in H-type divided cell with carbon cloth anode (15 mm×15 mm×0.36 mm), nickel plate cathode (15 mm×15 mm×1.0 mm) and a AMI-7001-30 membrane, constant current = 10 mA ($j_{anode} = 4.4$ mA/cm²), nitrogen balloon (1 atm.), 65 °C, 3.0 h (4.5 F). Isolated yields are shown. ^{*b*} Constant current = 12 mA ($j_{anode} = 4.4$ mA/cm²), 3.5 h (6.3 F). ^{*c*} The yield was determined by ¹H NMR spectroscopy with CH₂Br₂ as the internal standard.

After investigating the scope of amides, we explored varieties of alkylamines under optimized conditions (Scheme 2). Some cyclic alkylamines could participate in the reaction, such as piperidine, 1

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thiomorpholine and 1,2,3,4-tetrahydroisoquinoline; afforded medium yields (**3ab-3ad**). When piperidine or piperazine was substituted with some electron-withdrawing groups, desired products would be obtained in moderate to good yields (**3ae-3ag**). It was observed that hydroxyl could also be tolerated in this transformation (**3ah**); no by-product was observed by C-H/O-H coupling. Unfortunately, when we investigated different chain amines, only *N*methylbenzylamine could give desired product in inferior yield (**3ai**); other chain amines, such as diethylamine and dibutylamine, would afford homo-coupling product of thiophene-2-carboxamide. Primary alkylamines were not suitable for this transformations, which might result from the coordination to Co(II) and over-oxidation of primary alkylamines.

The scalability of electrochemical cobalt-catalyzed C-H amination was evaluated in a 5.0 mmol scale (Scheme 3). The reaction between **1a** and **2a** furnished the desired product in 59 % yield, which shows great potential of this electrochemical cobalt-catalyzed C-H/N-H cross-coupling.

Scheme 3. Gram Scale Experiment.



To gain some insights into this reaction mechanism, we carried out kinetic isotope effect experiment and cyclic voltammetry experiment. Firstly, we demonstrated intermolecular competition experiment between **1d** and **[D₅]-1d** (Scheme 4, a), the ratio of C-H bond amination products **3da** and **[D₄]-3da** is 1.13:1. The intramolecular competition experiment has been demonstrated in this transformation (Scheme 4, b). Reaction of the monodeuterated substrate 1d led to an 63:37 ratio of product isotopologues (KIE= 1.70). These results indicated that C–H bond cleavage might not be involved during the rate-limiting step.



Furthermore, we carried out cyclic voltammetry experiment (see ESI, Fig: S1). The naught potential E^{012} of $Co(OAc)_2 \cdot 4H_2O$ was 1.269 V. Then we added 1e and $Co(OAc)_2 \cdot 4H_2O$ together; the naught potential E^0 turned to 1.460 V. Finally, we performed chronoamperometry to proof the hypothesis for the oxidation of Co(II)

occurring in the electrolysis (Fig. 2). In blank experiment, current density was close to nought. After addition of $Co(OAc)_2 \cdot 4H_2O$, current density was big at first and then experienced the fast decay to reach relatively steady state. This result indicated that the current decay arose from consumption of Co(II).

Based on the experimental results and literature reports,^{5b,6c,6d,13} we attempted to propose two plausible mechanism. Path I: Co(II) was oxidized to Co(III) at anode; then Co(III) coordinated to *N*-(quinolin-8-yl)benzamide to get Co(III)-complex B. Path II: In the presence of base, Co(II) coordinated to *N*-(quinolin-8-yl)benzamide to get Co(II)-complex A before electrolysis. This Co(II)-complex A was oxidized at anode to furnish Co(III)-complex B. In the presence of base, C-H activation took place and Co(III)-complex B, followed by reductive elimination of Co(III)-complex C to release the desired product and Co(I) species. Co(I) species was reoxidized to Co(II) at anode to complete the whole catalytic cycle of Co.

Scheme 5. Proposed Mechanism.

In conclusion, we have developed cobalt-catalyzed electrooxidative C-H amination of arenes in divided cells. Various functional groups are tolerated in this transformation. Compared with previous cobalt-catalyzed C-H functionalization, no external oxidants are needed; lower temperature and good scalability are also beneficial to actual industrial production. Our further efforts are to develop more first row transition-metal-catalyzed C-H functionalization via anodic oxidation.

ASSOCIATED CONTENT

Supporting Information

The experimental procedure, characterization data, and copies of ¹H and ¹³C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

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Author Contributions

‡Xinlong Gao and Pan Wang contributed equally.

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The authors declare no competing financial interests.

ACKNOWLEDGMENT

This work was supported by the National Natural Science Foundation of China (21390400, 21520102003, 21272180, 21302148), the Hubei Province Natural Science Foundation of China (2013CFA081), the Research Fund for the Doctoral Program of Higher Education of China (20120141130002), and the Ministry of Science and Technology of China (2012YQ120060). The Program of Introducing Talents of Discipline to Universities of China (111 Program) is also appreciated.

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