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PAPER



Copper and Cobalt Co-Catalyzed Aerobic Oxidative Cross-Dehydrogenative Coupling Reaction of (Benzo)Azoles

Yanrong Li,^a Fen Qian,^a Xia Ge,^a Tao Liu,^a Hitesh B. Jalani,^{c,d} Hongjian Lu^{a*} and Guigen Li^{a,b*}

compounds, including bis-benzoazole compounds those were not described in previous catalytic CDC reactions.

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Dehydrogenative cross-coupling (CDC) reaction of diversely substituted azoles, synergistically catalyzed by copper and cobalt is reported. This protocol represents the first example of the use of air as an oxidant to carry out this chemical reaction. The process provides a convenient and economical method for the construction of valuable unsymmetrical bis-heteroaryl

Introduction

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Nitrogen-containing bis-heteroaryl compounds are important structural architectures in a variety of molecules such as commercially available pharmaceuticals, functional materials, ligands and natural products.¹ The transition-metal-catalyzed cross-coupling reaction of two heteroaryl units with different functional groups is one of the traditional approaches for the synthesis of bis-heteroaryl compounds.² Recently, transition metal-catalyzed C-H heteroarylation has emerged as a direct and effective method for the construction of bis-heteroaryl compounds, in which heteroaryl compounds are directly coupled with pre-functionalized aromatic heterocycles.³ The cross-dehydrogenative coupling (CDC) reaction is an ideal strategy for installation of C-C bonds, which circumvents prefunctionalization of starting materials thereby greatly reducing the reaction steps.⁴ However, the use of CDC reactions to synthesize unsymmetrical bis-(benzo)azole compounds faces mainly two challenges:^{4c,e,f} 1) Electron rich (benzo)azoles are prone to be oxidized, but oxidative conditions are generally required in CDC reactions;⁴ and 2) The acidic C-H bonds in (benzo)azoles are likely to be involved in self-coupling, which makes it difficult to obtain unsymmetrical cross-coupled products.⁵ Regardless of these challenges, the CDC strategy has been used often, due to its high efficiency and the important value of the unsymmetrical bis-(benzo)azoles¹ (Scheme 1 A). In 2011, Ofial et al. used the CDC strategy for the first time in the synthesis of bis-(benzo)azoles, wherein they coupled benzthiazoles/benzimidazoles with azoles by using a palladium

catalyst and copper/silver salts as oxidants.⁶ In 2012, You et al. reported a challenging palladium-catalyzed CDC reaction between two structurally similar azoles in presence of a copper salt as an oxidant.⁷ In same year, Wang et al. used a copper salt as an oxidant to achieve coupling reactions of benzoazoles with azoles.⁸ Zhang's group achieved a CDC reaction of benzothiazole with thiazole using catalytic amounts of a copper salt and a stoichiometric quantity of silver carbonate.9 Transition-metalcatalyzed CDC reactions of azoles suffer from a narrow scope of substrates and are mostly limited to the coupling between azoles⁷ and benzoazoles.^{6,8,9} As far as the coupling reactions of two different benzoazoles are concerned, there is only one example wherein the coupling reaction between 5-Brbenzothiazole and 5-Br-benzoxazole has been reported to date.^{10c} However, the isolated yield of desired cross-coupling product and the selectivity between self-coupling and crosscoupling products were not mentioned. In addition, the reported CDC reactions employed a stoichiometric amount of a transition metal oxide as an oxidant, which is non-sustainable from an environmental perspective. Consequently, it is interesting to examine the cross coupling of azoles, especially



Scheme 1. Metal-catalyzed CDC reactions of azoles

^{a.} Institute of Chemistry & BioMedical Sciences, Jiangsu Key Laboratory of Advanced Organic Materials, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, (China) E-mail: hongjianlu@nju.edu.cn; guigenli@nju.edu.cn

^b Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, TX 79409-1061, USA

^{c.} Department for Management of Science and Technology Development, Ton Duc Thang University, Ho Chi Minh City, Vietnam.

^{d.} Faculty of Applied Sciences, Ton Duc Thang University, Ho Chi Minh City, Vietnam.

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between two different benzoazoles, using a catalytic amount of transition-metal salts in the presence of an environmental friendly oxidant.

Air is a preferred oxidant in various transformations, due to its abundance and environmental friendliness.¹¹ However, the combination of a single transition-metal as a catalyst and oxygen as an oxidant in the coupling reactions of azoles tends to produce self-coupled products.¹⁰ Recently, bimetallic catalysis has emerged as a unique application in CDC reactions, 12,13 and not only controls the reactivity and selectivity of two metalation processes associated with the catalyst cycles, but also synergistically depresses the formation of undesired self-coupling products, thereby improving the overall yields of CDC reactions. In 2006, Li et al. reported the use of cobalt and copper as co-catalysts of the CDC reaction of 1,3-dicarbonyl compounds with allyl compounds.¹⁴ In 2015, Lei et al. developed an interesting CDC reaction of aldehydes and terminal alkynes, using zinc and indium as co-catalysts and triethylamine as a base.¹⁵ In 2018, Zhang et al. reported cobalt and manganese co-catalyzed aerobic oxidative cross-coupling of compounds containing a directing group.¹⁶ Inspired by these bimetallic catalyzed CDC reactions and our continuous research on coupling reactions,¹⁷ we report here a cobalt and copper cocatalyzed CDC reaction of (benzo)azoles using air as an oxidant, ¹⁸ leading to the efficient construction of various unsymmetrical bis-(benzo)azole compounds including benzoazole-benzoazole compounds.

Results and discussion

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Initially, benzothiazole (1a) and benzoxazole (2a) were used as the model substrates in the solvent 1-fluoro-2-(trifluoromethyl)benzene, and several metal oxides were screened (Table 1, entries 1-6). Using 1.5 equivalents of $Cu(OAc)_2 \bullet H_2O$ or $Cu(OAc)_2$ as the additive, the desired product 2-(benzothiazol-2-yl)-benzooxazole (3a) was obtained with 48% and 47% yield, respectively (entries 1 and 2). No product was obtained when CuCl₂, CuBr₂ or AgOAc were used, and only 10% yield of **3a** was obtained with AgNO₃ (entries 3-6), indicating that both copper and acetate ion support the formation of **3a**. Based on our cobalt-catalyzed C-H bond functionalization studies reported previously,17 cobalt catalysts employing 1.5 equivalents of $Cu(OAc)_2 \bullet H_2O$ as the oxidant were screened (entries 7-14), and it was found the yield of 3a could be increased up to 76% by using $Co(NO_3)_2 \bullet 6H_2O$ as a catalyst. Reduction of the amount of Cu(OAc)₂•H₂O to 20 mol % led to a 28% yield of 3a (entry 15). Considering the important role of acetate ion in this reaction, we increased the level of acetate ion by adding sodium acetate. It was found that addition of 1.0 equivalent of sodium acetate greatly enhanced the CDC reaction, producing 3a in a yield of 76% in which Cu(OAc)₂•H₂O and Co(NO₃)₂•6H₂O was used as co-catalysts and air worked as an oxidant (entry 16). Different solvents were then examined. Fluorobenzene has also proved to be one of good choice. While solvent such as chlorobenzene, bromobenzene and xylene could provide desired product 3a in moderate to low yields (entries 17-20). Eventually, no desired product was obtained in DOI: 10.1039/C9GC02464F DMF or DMSO (entries 21-22).

Table 1. Optimization of reaction conditions ^a

N ^N 1a	S + N	catalyst (20 mol additive (1.5 equ air, solvent 130 °C, 18 h	%) iv),	S N 3a
Entry	catalyst	additive	solvent	yield
1	-	Cu(OAc) ₂ ·H ₂ O	$1-F-2-CF_3C_6H_4$	48
2	-	Cu(OAc) ₂	$1-F-2-CF_3C_6H_4$	47
3	-	CuCl ₂	$1-F-2-CF_3C_6H_4$	none
4	-	CuBr ₂	$1-F-2-CF_3C_6H_4$	none
5	-	AgNO ₃	$1-F-2-CF_3C_6H_4$	10%
6	-	AgOAc	$1-F-2-CF_3C_6H_4$	none
7	CoCl ₂	Cu(OAc) ₂ ·H ₂ O	$1\text{-}\text{F-}2\text{-}\text{CF}_3\text{C}_6\text{H}_4$	44
8	Co(acac)₂	Cu(OAc) ₂ ·H ₂ O	$1-F-2-CF_3C_6H_4$	52
9	CoCO ₃	Cu(OAc) ₂ ·H ₂ O	$1-F-2-CF_3C_6H_4$	57
10	Co(NO ₃) ₂ ·6H ₂ O	Cu(OAc) ₂ ·H ₂ O	$1\text{-}\text{F-}2\text{-}\text{CF}_3\text{C}_6\text{H}_4$	76
11	Co(ClO ₄) ₂ ·6H ₂ O	Cu(OAc) ₂ ·H ₂ O	$1-F-2-CF_3C_6H_4$	none
12	CoBr ₂	Cu(OAc) ₂ ·H ₂ O	$1-F-2-CF_3C_6H_4$	56
13	Co(acac) ₃	Cu(OAc) ₂ ·H ₂ O	$1\text{-}\text{F-}2\text{-}\text{CF}_3\text{C}_6\text{H}_4$	48
14	Co(OAc) ₂	Cu(OAc) ₂ ·H ₂ O	$1\text{-}\text{F-}2\text{-}\text{CF}_3\text{C}_6\text{H}_4$	54
15	$Co(NO_3)_2 \cdot 6H_2O$ $Cu(OAc)_2 \cdot H_2O^c$		$1-F-2-CF_3C_6H_4$	28
16	Co(NO₃)₂·6H₂O Cu(OAc)₂·H₂O ^c	CH₃COONa ^d	1-F-2-CF ₃ C ₆ H ₄	76
17	Co(NO ₃)₂·6H₂O Cu(OAc)₂·H₂O ^c	CH_3COONa^d	C_6H_5F	74
18	Co(NO ₃) ₂ ·6H ₂ O Cu(OAc) ₂ ·H ₂ O ^c	CH_3COONa^d	C_6H_5CI	35
19	Co(NO ₃)₂·6H₂O Cu(OAc)₂·H₂O ^c	CH_3COONa^d	C_6H_5Br	39
20	Co(NO ₃)₂·6H₂O Cu(OAc)₂·H₂O ^c	CH_3COONa^d	xylene	48
21	Co(NO ₃)₂·6H₂O Cu(OAc)₂·H₂O ^c	CH_3COONa^d	DMF	none
22	Co(NO₃)₂·6H₂O Cu(OAc)₂·H₂O ^c	CH ₃ COONa ^d	DMSO	none

^a Reaction conditions: 1a (0.2 mmol), 2a (0.3 mmol), catalyst (0.04 mmol), 1-fluoro-2-(trifluoromethyl)benzene (0.8 mL), 130 °C, air, 18 h. ^b Crude ¹H NMR yields of desired product **3a** determined by using dibromomethane as an internal standard. ^c Cu(OAc)₂·H₂O (20 mol %). ^d CH₃COONa (1.0 equiv.).

With the optimum reaction conditions, a range of benzothiazole and benzoxazole substrates were screened (Table 2). It was found that benzothiazole reacted not only with benzoxazoles substituted with electron-rich groups (3b, 3c, 3d, 3g), but also with electron-withdrawing groups (3e, 3f), affording the corresponding CDC products in good yields. Benzoxazoles reacted with benzothiazoles substituted with an electron-donating group (3i) or an electron-withdrawing group (3h) to give the desired products with good yields. In addition, benzothiazoles containing different substituents were also found to undergo CDC reactions efficiently with benzoxazoles with different substituents, providing bis-benzoazole compounds with different functional groups (3j-3o). This provides the possibility of further subsequent modification of the bis-heterocyclic products. 4-Cl-Benzoxazole and 7-ClPublished on 03 September 2019. Downloaded by University of Glasgow Library on 9/3/2019 5:55:32 PM

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Table 2. Synthesis of benzoxazole-benzothiazole products a,b

standard 3a. 73% (60%°) **3b**. 71% 3c. 75% 3d. 78% 3f. 69% 3h. 72% 3e. 62% 3g, 74% **3i.** 67% **3i**. 72% 3k. 63% **3I.** 51% Me -Bu 3m, 75% 3n, 73% **30**, 62%

 o Standard conditions: **1** (0.2 mmol), **2** (0.3 mmol), Co(NO₃)₂·6H₂O (0.04 mmol), Cu(OAc)₂·H₂O (0.04 mmol), NaOAc (0.2 mmol), 1-fluoro-2-(trifluoromethyl)benzene (0.8 mL), 130 °C, air, 18 h. ^{*b*} Isolated yield of product **3**, small amount of homo-coupling products were also observed. ^{*c*} With 1.0 mmol scale.

benzoxazole could not react with benzothiazole (1a) under standard conditions, possibly due to the influence of steric hindrance.

The scope of the other types of heterocyclic substrates was explored with the optimal reaction conditions (Table 3). The substrates underwent coupling reactions with similar substrates. For example, benzoxazole coupled with 5-'Bubenzoxazole (**3p**), 5-Me-benzoxazole reacted with 5-'Bubenzoxazole (**3q**) or 6-Me-benzoxazole (**3r**), and benzothiazole reacted with 6-MeO-benzothiazole (**3s**). In addition, the previously reported⁵⁻⁸ cross-coupling reactions of benzoazoles with azoles were also examined and the desired products were isolated in moderate to good yields. For example, benzoxazoles (**3t**-**3y**), benzothiazoles could react with oxazoles and thiazoles (**3z**, **3a'**, **3b'**) and finally, thiazoles and oxazoles could couple with one another (**3c'**, **3d'**).

Several control experiments were conducted in an attempt to understand the mechanism of this CDC reaction (Table 4). When the reaction was performed in an oxygen atmosphere, the yield of the cross-coupling reaction was reduced to 56%, the yield of self-coupling product 2,2'-bibenzothiazole (**4a**) was increased to 22% and the yield of the self-coupling product 2,2'-



 Table 3. Scope of other substrates a,b



^{*a*} Standard conditions, same as note in Table 2. ^{*b*} Isolated yield of product **3**, small amount of homo-coupling products were also observed.

yields of both cross-coupling and self-coupling products were reduced, indicating that oxygen present in the air participated in the reaction (entry 3). To further understand the influence of Cu(OAc)₂•H₂O, Co(NO₃)₂•6H₂O and NaOAc in this reaction, control experiments were conducted (entries 4-7). It was found that no product 3a was formed in the absence of Cu(OAc)₂•H₂O (entry 4), and the selectivity to the cross-coupling product 3a was reduced in the absence of Co(NO₃)₂•6H₂O and/or NaOAc (entries 5-7).^{10c} When the reaction was performed with a stoichiometric amount of Cu(OAc)₂ but with no Co(NO₃)₂•6H₂O, 3a was produced in 42% yield with good selectivity between cross-coupling and self-coupling reactions (entry 8). In order to assess the selectivity of the cross-coupling reaction more clearly, the reaction was conducted with a one-to-one ratio of substrates 1a and 2a, and it was found in this case that the yield of the product (3a) was slightly reduced to 54%, but the selectivity was acceptable. The yields of self-coupling products were 8% (4a) and 16% (5a), respectively (entry 9). Additionally, the solvent screening experiments showed good selectivity in 1fluoro-2-(trifluoromethyl)benzene and fluorobenzene (entries 1, 10-15). These control experiments demonstrate that a catalytic amount of Cu(OAc)2•H2O is indispensable for the formation of the cross-coupling product, and a catalytic amount

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of $Co(NO_3)_2 \bullet 6H_2O$ and the solvent of fluoro-2-(trifluoromethyl)benzene or fluorobenzene are good for the

Table 4.	Control	experiments
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1a + - 2a (1.5 equiv)	standard conditions	-S N 4a	+ ~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	N 5a
entry	change from standard conditions	3 a	4a	5a
1	-	76	8	34
2	oxygen instead of air	56	22	12
3	argon instead of air	8	10	6
4	no Cu(OAc) ₂ •H ₂ O	0	0	0
5	no Co(NO ₃) ₂ •6H ₂ O	34	trace	39
6	no Co(NO ₃) ₂ •6H ₂ O, no NaOAc	26	trace	22
7	no NaOAc	28	trace	10
8	$Cu(OAc)_2 \cdot H_2O$ (1.5 equiv),	42	12	5
	no Co(NO ₃) ₂ •6H ₂ O			
9	b	54	8	16
10	C_6H_5F	74	10	33
11	C ₆ H ₅ Cl	35	12	34
12	C ₆ H ₅ Br	39	10	29
13	xylene	48	18	32
14	DMF	0	0	0
15	DMSO	0	0	0

^a Crude ¹H NMR yields of products **3a**, **4a** and **5a** determined by using dibromomethane as an internal standard. ^b **2a** (1.0 equiv).

selectivity of the cross-coupling product, and the acetate ion increases the efficiency of this cross-coupling reaction.

In order to probe the select ty of this reaction, several Co/Cu co-catalyzed oxidative coupling reactions were performed (Scheme 2). When o of the starting compounds, either 1a or 2a was allowed to re under standard conditions, it was found that self-coupling oducts were obtained with yields of only 10% (4a) and 38%), respectively (Scheme 2A). It was clear that the reaction cor tions used tend to inhibit the self-coupling reaction and pre entially generate a crosscoupling product. When the rea on was performed in the



Scheme 3. Proposed catalytic cycle

c

presence of 1.0, 2.0 or 3.0 equiv. of (2, 2, 6, 6 tetramethylpiperidin-1-yl)oxyl (TEMPO), а free radical scavenger, the yields of 3a remained mainly unaffected (Scheme 2B), suggesting that a radical mechanism is not involved in the reaction. Intermolecular experiments showed that benzoxazole substituted with an electron-donating group takes preference in the reaction and very little cross-coupling of benzoxazoles 2b and 2e was observed (Scheme 2C).

Cu(OAc)₂

в

Based on our experimental results and previous related reports,^{4,14} a possible reaction mechanism is proposed and is shown in Scheme 3. Since that it is known that the reaction can be initiated by a concerted metalation-deprotonation process of the relatively more acidic heteroarene's C-H bond,^{8,20} the copper is prone to react with benzoxazole first to form the intermediate (A) with the assistance of sodium acetate. Then, A reacts with Cu(OAc)₂ to produce a Cu(III) intermediate (B).²¹ The second concerted metalation-deprotonation process of benzothiazole's C-H bond promoted by B results in the key heterocoupling intermediate species C, which might be ratedetermining procedure in the reaction and prone to carry out. $^{\rm 22,23}$ Subsequently, ${\bm C}$ undergoes reductive elimination to form the cross-coupling product (3a) and CuOAc. Finally, the CuOAc is oxidized by the cobalt (III) species which is produced by the air oxidation of cobalt (II),¹⁶ and the addition of sodium

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acetate may make up for the reduction of acetate ion, regenerating $Cu(OAc)_2$ and continuing the next cycle.

Conclusions

In summary, we have developed a CDC reaction of (benzo)azoles with a co-catalytic system of $Co(NO_3)_2 \cdot 6H_2O$ and $Cu(OAc)_2 \cdot H_2O$. With the assistance of CH_3COONa , the reaction uses air as an oxidant and produces cross-coupling products with good selectivity and moderate to good isolated yields. This co-catalytic system avoids the use of stoichiometric amounts of metal oxidants, thereby providing an economical and environmentally acceptable method for the construction of important unsymmetrical bis-heteroaryl compounds, including bis-benzoazoles which were not observed in previously reported catalytic CDC reactions. Further work on this newlydeveloped CDC, possibly providing access to other interesting heterocycles, is currently underway and will be reported in due course.

Experimental

A 35 mL oven-dried pressure tube was charged with benzothiazole (**1a**) (27.0 mg, 0.2 mmol), benzoxazole (**2a**) (35.8 mg, 0.3 mmol), Cu(OAc)₂·H₂O (8 mg, 0.04 mmol), Co(NO₃)₂·6H₂O (11.7 mg, 0.04 mmol), CH₃COONa (16.4 mg, 0.2 mmol), and 1-fluoro-2-(trifluoromethyl)benzene (0.8 mL). The tube was sealed and stirred vigorously at 130 °C for 18 h, then, cooled to room temperature, diluted with ethyl acetate, filtered through a celite pad and concentrated under reduced pressure. The residue was purified by silica gel chromatography (dichloromethane/hexane (v/v): 10/1 to 1/1) to give the desired benzothiazol-2-yl)benzoxazole (**3a**) (45 mg, 73% yield).

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Conflicts of interest

There are no conflicts to declare.

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realized by copper and cobalt co-catalysis under air conditions.