C–H Activation

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Cobalt-Catalyzed Oxidative Annulation of Nitrogen-Containing Arenes with Alkynes: An Atom-Economical Route to Heterocyclic Quaternary Ammonium Salts

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Abstract: *Four cobalt-catalyzed oxidative annulation reactions of nitrogen-containing arenes with alkynes proceeds by C–H activation, thus leading to biologically useful quaternary ammonium salts, including pyridoisoquinolinium, cinnolinium, isoquinolinium, and quinolizinium salts, in high yields. The results are comparable to those reactions catalyzed by rhodium and ruthenium complexes. The transformation of the salts into various N-heterocycles has also been demonstrated.*

Transition metal catalyzed oxidative annulations of arenes through C–H bond activation has drawn substantial attention because of their broad synthetic utility in the synthesis of natural products, drugs, and materials.[1] Recently, many nitrogen-containing, group-directed oxidative annulation reactions catalyzed by noble metals such as rhodium, ruthenium, palladium, and iridium, through C–H activation have been developed.[2] However, similar reactions using more abundant, less expensive, and less toxic first-row transition metals as the catalysts are still rare.

Recently, first-row transition metal catalyzed C–H bond activation of arenes has become very attractive because these metals are less expensive, more abundant, and less toxic.[3] Thus, cobalt catalysts have been employed as alternative active C–H activation catalysts for rhodium and ruthenium complexes. In this context, the groups of Kanai,[4a–c] Ackermann,[4d,e] Glorius,[4f,g] Ellman,[4h-i] and Chang[4j,k] reported using high-valent cobalt catalysts for C–H functionalization of arenes by various electrophiles. Recently, Matsunaga, Kanai, and co-workers demonstrated the catalytic activity of [Co^{III}Cp*] and [Rh^{III}Cp*] in the synthesis of pyrroloindolones from N-carbamoyl indoles and alkynes.[4l] Very recently, the groups of Kanai and Matsunaga,[4m] Ackermann,[4n] and Sundararaju[4o] individually reported isoquinoline synthesis by a redox-neutral strategy in the presence of [CoCp*(CO)I_2] as the catalyst. However, there is still no report on the cobalt-catalyzed C–H oxidative annulation of arene with alkyne in the presence of an external oxidant.

N-heterocyclic quaternary ammonium salts such as pyridoisoquinolinium, cinnolinium, pyridinium, and quinolizinium salts are found in the core structures of many bioactive compounds, pharmaceuticals, and organic materials.[5] However, only few synthetic methods are available in the literature, and they generally require prefunctionalized starting materials, multiple steps, and either stoichiometric or catalytic amounts of noble-metal catalysts.[6] Previously, we reported the synthesis of isoquinolinium salts from the annulation of either 2-halobenzaldimines[5b] or 2-iodoketimines[6c] with alkynes catalyzed by low-valent nickel complexes. Later, we used rhodium and ruthenium complexes as the catalysts for preparing the nitrogen salts by C–H bond functionalization.[7] Our continuing interest in metal-catalyzed C–H bond activation[8] and first-row transition metal catalyzed reactions[5b,6c] have stimulated us to investigate the nitrogen-directed *ortho* C–H bond activation of arenes by cobalt complexes, followed by oxidative annulation with alkynes. Herein, we report the synthesis of various quaternary ammonium salts using pyridine, imine, and azo as the directing groups and [CoCp*(CO)I_2] as the catalyst.

Guided by our previous studies on oxidative annulation by C–H activation, we started examining the reaction of 2-phenylpyridine (**1a**) with diphenylacetylene (**2a**) under various reaction conditions (Table 1). The reaction of **1a** (0.10 mmol) with **2a** (0.15 mmol) in the presence of [CoCp*(CO)I_2] (10 mol %), AgOAc (10 mol %), $NaHCO_3$ (0.12 mmol), and $AgBF_4$ (0.20 mmol) in DCE at 130 °C under N_2 for 24 hours gave the pyrido-[2,1-*a*]isoquinolin-5-ium salt **3aa** in 89% yield (entry 7). The compound was carefully characterized and the structure was confirmed by comparison to data in our previous reports.[7] The choice of additive, oxidant, and solvent are crucial to obtaining high product yields. Particularly, the selection of the OAc^- source is important for the present C–H functionalization. It is well-known that a coordinated OAc group acts as a proton acceptor in cobalt-catalyzed C–H activation reactions.[4b–h,j–q] In addition, the silver salts AgOAc and $AgBF_4$ serve to remove I^- as an oxidant to regenerate the cobalt(III) active species, and as an anion source (BF_4^-) for the final product. It should be noted that $AgBF_4$ is used in a stoichiometric amount relative to the substrates. Initial studies showed that AgOAc afforded **3aa** in 72% yield, while other salts such as KOAc, NaOAc, and $Cu(OAc)_2$, are much less effective (entries 4–6). The addition of $NaHCO_3$ (1.2 equiv) to the reaction solution increases the yield of **3aa** from 72 to 89%, but the use of other bases such as Na_2CO_3, K_2CO_3, and Cs_2CO_3 reduces the product yield (entries 8–10). It is noteworthy that the chlorinated solvents 1,2-dichloroethane (DCE) and chlorobenzene are suitable for this reaction (entries 7 and 11), while others such as alcohol and ether solvents are totally ineffective for the product formation. Finally, various cobalt(II) and cobalt(III) complexes were

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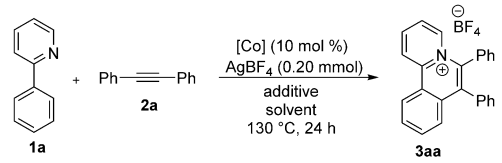
Table 1: Optimization of cobalt-catalyzed oxidative annulation.[a]



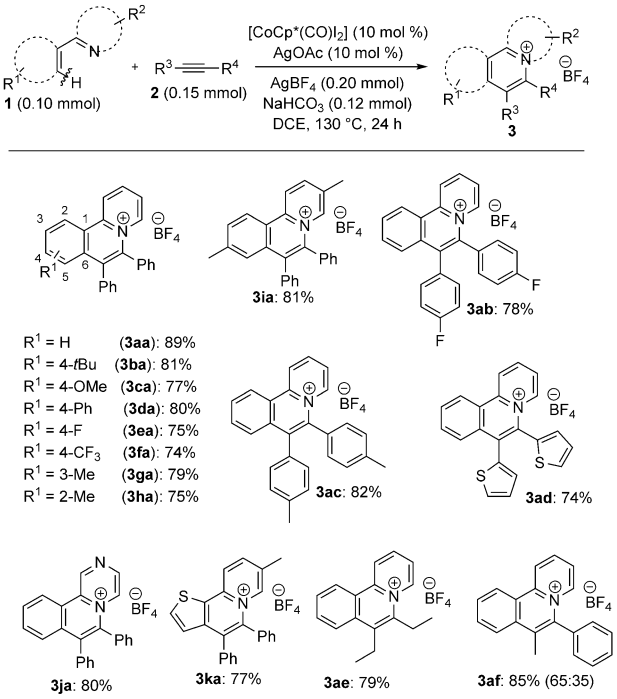
Entry	Catalyst	Additive	Solvent	Base	Yield [%][b]
1[c]	$[CoCp^*(CO)I_2]$	–	DCE	–	15
2[c]	$[CoCp^*(CO)I_2]$	AgOAc	DCE	–	57
3	$[CoCp^*(CO)I_2]$	AgOAc	DCE	–	72
4	$[CoCp^*(CO)I_2]$	KOAc	DCE	–	6
5	$[CoCp^*(CO)I_2]$	NaOAc	DCE	–	13
6	$[CoCp^*(CO)I_2]$	$Cu(OAc)_2$	DCE	–	10
7	$[CoCp^*(CO)I_2]$	AgOAc	DCE	$NaHCO_3$	89
8	$[CoCp^*(CO)I_2]$	AgOAc	DCE	Na_2CO_3	66
9	$[CoCp^*(CO)I_2]$	AgOAc	DCE	K_2CO_3	58
10	$[CoCp^*(CO)I_2]$	AgOAc	DCE	Cs_2CO_3	26
11	$[CoCp^*(CO)I_2]$	AgOAc	PhCl	$NaHCO_3$	35
12	$[CoCp^*(CO)I_2]$	AgOAc	EtOH	$NaHCO_3$	–
13	$[CoCp^*(CO)I_2]$	AgOAc	*t*-AmylOH	$NaHCO_3$	–
14	$[CoCp^*(CO)I_2]$	AgOAc	1,4-dioxane	$NaHCO_3$	–
15	$[CoCp^*(CO)I_2]$	AgOAc	PhMe	$NaHCO_3$	–
16	CoI_2	AgOAc	DCE	$NaHCO_3$	–
17	$CoBr_2$	AgOAc	DCE	$NaHCO_3$	–
18	$Co(OAc)_2$	AgOAc	DCE	$NaHCO_3$	–
19	$[Co(acac)_3]$	AgOAc	DCE	$NaHCO_3$	–

[a] Unless otherwise mentioned, all reactions were carried out using **1a** (0.10 mmol), **2a** (0.15 mmol), [Co] (10 mol %), additive (10 mol %), base (0.12 mmol), and solvent (2.0 mL) at 130 °C for 24 h. [b] Yield of isolated product. [c] At 120 °C. acac = acetylacetonate, $Cp^* = C_5Me_5$, DCE = 1,2-dichloroethane.

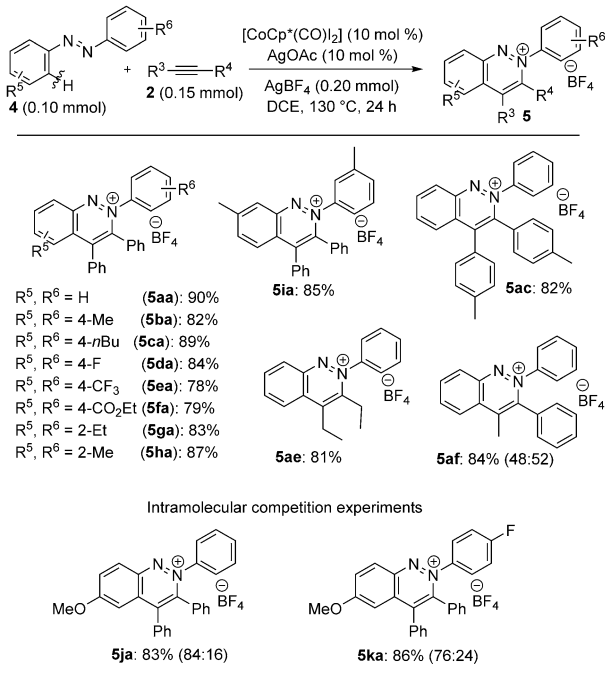
tested, but only $[CoCp^*(CO)I_2]$ is active. The other complexes, including CoI_2, $CoBr_2$, $Co(OAc)_2$, and $[Co(acac)_3]$ are totally ineffective (entries 16–19).

This oxidative annulation protocol was then applied to a variety of 2-arylpyridines (**1**; Scheme 1). Thus, the substrates **1b–i**, with either electron-donating or electron-withdrawing groups present on the aryl, underwent the oxidative annulation reactions with **2a** effectively to provide the corresponding pyridoisoquinolinium salts **3ba–ia** in 74 to 81% yields (Scheme 1). For the substrate 3-methylphenylpyridine (**1g**), selective C–H activation occurred only at C6 to give the annulation product **3ga**. No product with C–H activation at C2 was found, probably because of the steric effect of methyl group at C3. Similarly, the reaction of 2-phenylpyrazine (**1j**) with **2a** gave the expected salt **3ja** in 80% yield. Other symmetrical aromatic alkynes (**2b–d**) were also tested as the annulation partners to give the corresponding salts in good yields (**3ab–ad**). It is noteworthy that the aliphatic alkyne **2e** also reacted smoothly to provide **3ae** in 79% yield. For the unsymmetrical alkyne **2f**, the reaction gave two regioisomeric salts with a 65:35 ratio in an 85% combined yield (**3af**).

We then extended the catalytic reaction to substrates with different nitrogen directing groups (Scheme 2). We found that the azobenzene **4a** reacted with **2a** under similar catalytic conditions to give the cinnolinium salt **5aa** in 90% yield. There is also no report on oxidative annulation reactions, through C–H activation, of azobenzenes with alkynes in the



Scheme 1. Cobalt-catalyzed synthesis of isoquinolinium salts.



Scheme 2. Cobalt-catalyzed synthesis of cinnolinium salts.

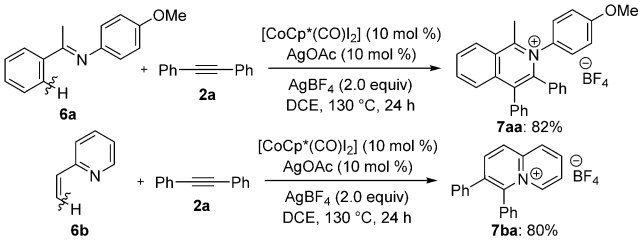
presence of cobalt(III) complexes. In this reaction, no extra base, such as $NaHCO_3$, is required to furnish the product.[4r] The presence of an electron-donating group on **4** increases the product yield up to 89%, while electron-withdrawing substituents such as F, CF_3, and CO_2Et, on the azobenzenes **4d–f** provide the corresponding functionalized cinnolinium salts

5da–fa in 78–84%. The substituent at either the *ortho* or *meta* position does not much affect the reaction outcome (**5ga–ia**). Notably, this cobalt-catalyzed azo-directed C–H activation reaction appears similar in reactivity and selectivity to the pyridine directed reaction. We also conducted an intramolecular competition reaction using unsymmetrical the azo arenes **4j** and **4k**. The results (**5ja** and **5ka**) reveal that the C–H activation occurs more favorably at the electron-rich aryl group of these two substrates.

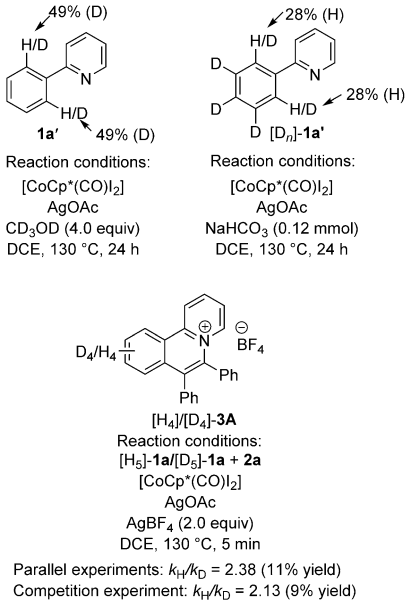
To further demonstrate the power of this cobalt catalytic system, we tested the C–H activation and annulation of the ketoimine **6a** with **2a** (Scheme 3). The reaction proceeded smoothly to give the expected product 1-methyl isoquinolinium salt **7aa** in 82% yield. In a similar way, 2-vinylpyridine reacted with **2a** to afford the quinolizinium salt **7ba** in 80% yield.

To gain insight into the catalytic mechanism, we conducted a series of deuterium-labeling experiments (Scheme 4). Heating **1a** in the presence of CD_3OD and $[D]_5$-**1a** in the presence of $NaHCO_3$ showed significant H/D scrambling, thus indicating the cyclometallation step is reversible in nature. Finally, we conducted the deuterium-labeled competition experiments between $[D_5]$-**1a** and **1a** with **2a** to give intermolecular KIE (k_H/k_D) of 2.38 (for parallel experiments) and 2.13 (for competition experiment). The observed KIE values suggested that the C–H bond-cleavage step is plausibly involved in the rate-determining step (see the Supporting Information for details on the deuterium-labeling experiments).

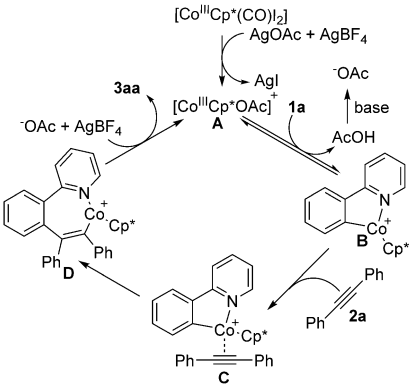
Based on the known cobalt chemistry and the present observations, a reasonable mechanistic rationale of the oxidative annulation of 2-phenyl pyridine (**1a**) with diphenylacetylene (**2a**) is proposed in Scheme 5. The catalytic reaction is probably initiated by the exchange of iodide ligands in $[CoCp^*(CO)I_2]$ with AgOAc to give $[Cp^*Co(OAc)]^+$ (**A**). Then, nitrogen-directed reversible *ortho* C–H bond cleavage forms the five-membered cobaltacycle **B**. Further, π coordination of the alkyne to form **C** and subsequent insertion provides the seven-membered cobaltacyclic intermediate **D**. The latter then undergoes reductive elimination followed by oxidation of cobalt(I) by $AgBF_4$ to give the quaternary ammonium salt **3aa** and cobalt(III) species. In the catalytic reaction, a stoichiometric amount of the BF_4 anion is required to isolate the final salt.



Scheme 3. Cobalt-catalyzed synthesis of 1-methylisoquinolinium and quinolizinium salts.



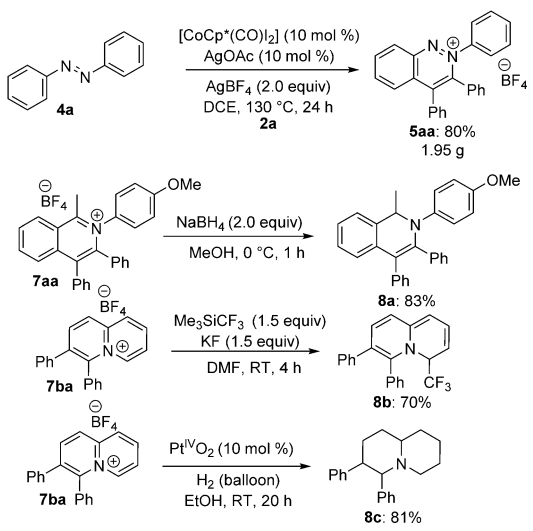
Scheme 4. Deuterium-labeling experiments.



Scheme 5. A plausible reaction mechanism.

Finally, to demonstrate the synthetic potential of this methodology, we briefly explored the applications of the present oxidative annulation reactions (Scheme 6). This cobalt-catalyzed reaction is convenient for practical use as supported by the scale-up experiment for the synthesis of **5aa** in 80% (1.95 g) yield. In addition, we found that **7aa** could be readily reduced by $NaBH_4$ to give the addition product 1,2-dihydroisoquinoline **8a** in 83% yield and **7ba** reacted with Me_3SiCF_3 to afford the CF_3 addition product 4-(trifluoromethyl)-4*H*-quinolizine (**8b**) in 70% yield. Similarly, the reduction of **7ba** by platinum(IV) oxide gave an unusual quinolizidine product in 81% yield.

Additionally, we also studied the photophysical properties of the selected cinnolinium salts. The emission spectra of these salts in dichloromethane are depicted in Figure 1. The photoluminescence spectra of **5aa**, **5ca**, **5fa**, **5ga**, and **5ae** show intense peaks between $\lambda = 430$–550 nm, which reveals violet-to-green fluorescence emissions depending on the functional group present in the salts. Surprisingly, the product



Scheme 6. Applications of C–H activation products. DMF = *N*,*N*-dimethylformamide.

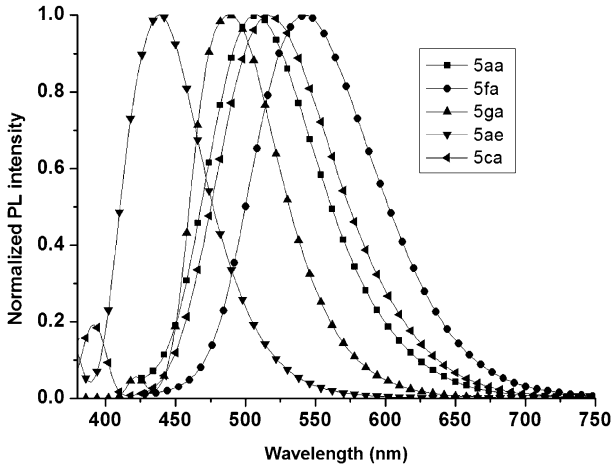


Figure 1. Photoluminescence spectra of selected cinnolinium salts (**5aa**, **5ca**, **5fa**, **5ga**, and **5ae**) in DCM (1.0×10^{-5} M).

5ga shows strong blue photoluminescence with a narrow bandwidth at $\lambda = 490$ nm. We have also been interested in finding new blue organic light-emitting diodes (OLEDs),[9] which are rarely developed in organic materials. In this respect, our compounds are useful in the preparation of blue-light-emitting diodes and ionic dopants.[9c–d]

In summary, we have successfully developed a cobalt-catalyzed oxidative annulation of 2-arylpyridines, azobenzenes, aryl ketimines, and 2-vinylpyridines with alkynes by C(sp^2)–H activation to give various quaternary heteroaromatic ammonium salts including pyridoisoquinolinium, 1-substituted isoquinolinium, cinnolinium, and quinolizinium salts, in high yields. The results show that a cobalt complex under suitable reaction conditions can also catalyze oxidative annulation reactions just as the noble-metal rhodium and ruthenium complexes.

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