



Cobalt-catalyzed annulation of aryl iodides with alkynes



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ABSTRACT

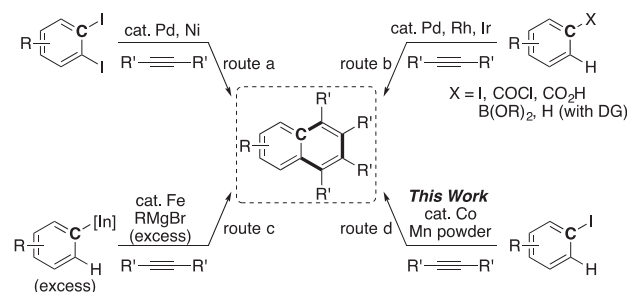
A cobalt-catalyzed approach for the concise synthesis of naphthalenes by the annulation of aryl iodides with alkynes is disclosed. In the reaction, manganese reductant and MeCN solvent are necessary to proceed efficiently, which tolerates various functional groups, for example, boronate ester. Mechanistic investigation indicates that the transformation employs electrophilic aromatic substitution (S_EAr) in the aromatic C–H bond replacement step.

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Selective and practical construction of naphthalenes and other polyaromatic hydrocarbons has been an important subject in organic synthesis because of their potential utility as π -conjugated materials.¹ Among several synthetic methods for naphthalenes, transition metal-catalyzed annulation of aromatic compounds with two alkynes has attracted much attention due to its simplicity, flexibility, and modularity. Among them, the double-functionalization of 1,2-dihaloarenes with alkynes using Pd- and Ni catalysts has been demonstrated (Scheme 1, route a).² In contrast, a similar annulation of mono-functionalized aromatic substrates such as aryl iodides,³ aryl chlorides,⁴ benzoic acids,⁵ arylboronic acids,⁶ and simple arenes having a directing group (DG),⁷ has also been reported (route b). These methods are not only synthetically attractive from atom economy and structural diversity points of view, but also mechanistically intriguing because the reaction involves the C–H bond replacement. However, these procedures use expensive and rare transition metal catalysts such as Pd, Rh, and Ir. As the improved method, Yoshikai recently developed the Fe-catalyzed annulation of arylindiums with alkynes (route c).⁸ However, the method requires a large excess of arylindiums and Grignard reagents, which would restrict the use of some reactive substituents in the annulation reaction.

In consideration of the background and related information, we noticed that vinyl-transition metal species **A** or **A'** are common key intermediates in routes b and c, which were followed by the second alkyne insertion and sequential C–H replacement, and/or

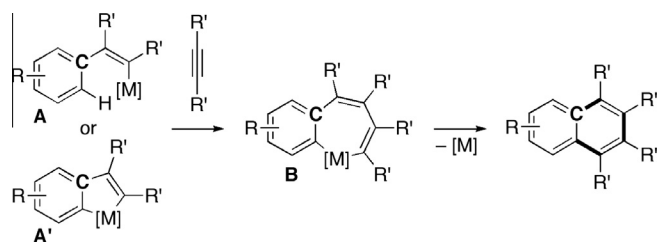
reductive elimination via **B** to afford naphthalenes (Scheme 2, bottom). On the other hand, inexpensive and abundant cobalt salts have been extensively used as catalysts in the $C(sp^2)$ – $C(sp^2)$ couplings,⁹ wherein the generation of the aryl-Co by the oxidative addition is involved as a key step. Furthermore, the aryl-Co is known to be an active species for the alkyne insertion to give a vinyl-Co similarly to the carbocobaltation,¹⁰ cyclotrimerization,¹¹ and other related reactions.¹² But, the generated aryl-Co and vinyl-Co are quickly transmetalated to give thermally more stable vinyl-zinc complexes by the residual salts or organozinc reagents during the reaction.¹³ In contrast, manganese (Mn) powder works effectively as a reductant in the aryl-Co generation step;¹⁴ noteworthy, the transmetalation of the generated aryl-Co with residual manganese salts does not occur.^{14c} Based on these results, we envisaged that Co/Mn system might induce the annulation (route d). Herein, we would like to report a cobalt-catalyzed annulation



Scheme 1. Transition metal-catalyzed annulations of mono- and bi-functionalized arenes with alkynes.

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Scheme 2. Common key intermediates in the transition metal-catalyzed annulation.

of aryl iodides with 2 equiv of unactivated alkynes in the presence of Mn powder.

To prove the feasibility of the hypothesis, we first examined the reaction of 4-iodotoluene (**1a**) with 4-octyne (**2a**) under various reaction conditions (Table 1). When **1a** was treated with 2.2 equiv of **2a** in the presence of CoBr₂ (10 mol %), 1,2-bis(diphenylphosphino)ethane (DPPE, 10 mol %) and Mn powder (2.0 equiv) in MeCN for 3 h at 50 °C, the desired adduct **3aa** was obtained in 52% yield, along with hydroarylation product **4** in 11% yield (entry 1).¹⁵ The similar bidentate phosphine ligand such as 1,1'-bis(diphenylphosphino)ferrocene (DPPF) was also an effective ligand (entry 2), but xantphos completely prevented the reaction (entry 3). 2,2'-Bipyridine (Bipy) afforded the lower yield (entry 3).

Table 1
Screening of reaction conditions

Entry	Catalyst	Ligand	Reductant	Yield ^a (%)	
				3aa	4 ^b
1	CoBr ₂	DPPE	Mn	52	11
2	CoBr ₂	DPPF	Mn	53	14
3	CoBr ₂	Xantphos	Mn	No reaction	
4	CoBr ₂	Bipy	Mn	40	24
5 ^c	CoBr ₂	IMes·HCl ^d	Mn	No reaction	
6 ^e	CoBr ₂	DPPE	Mn	51	10
7	CoBr ₂	P(<i>n</i> -Bu) ₃	Mn	49	5
8	CoBr ₂	P(<i>t</i> -Bu) ₃	Mn	56	5
9	CoBr ₂	P(Mes) ₃ ^f	Mn	52	4
10	CoBr ₂	PPh ₃	Mn	69	8
11	CoBr ₂	PPh ₃ ^g	Mn	62	14
12	CoBr ₂	—	Mn	54	4
13	CoBr ₂	PPh ₃	Zn	12	25
14	CoCl ₂	PPh ₃	Mn	60	9
15	CoI ₂	PPh ₃	Mn	62	13
16	Co(acac) ₂	PPh ₃	Mn	No reaction	
17	NiCl ₂	PPh ₃	Mn	No reaction	
18	FeCl ₂	PPh ₃	Mn	No reaction	
19 ^h	CoBr ₂	PPh ₃	Mn	70 (68)	4

^a Determined by GC using decane as an internal standard. Value in parenthesis indicates isolated yield.

^b Hydroarylation products were formed with ca. 50:50 *E/Z* ratio.

^c With Cs₂CO₃ (15 mol %).

^d *N,N'*-Bis(2,4,6-trimethylphenyl)imidazolium hydrochloride.

^e With Cs₂CO₃ (100 mol %).

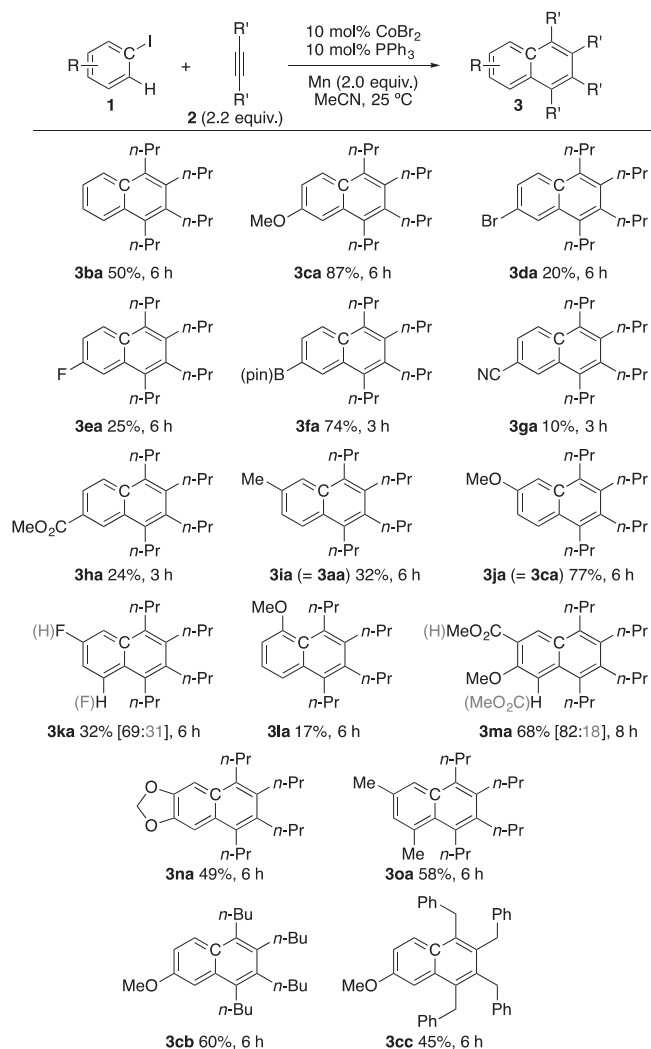
^f Tris(2,4,6-trimethylphenyl)phosphine.

^g 20 mol % of PPh₃ was used.

^h The reaction was carried out at 25 °C for 6 h.

4). An *N*-heterocyclic carbene ligand (IMes: 1,3-bis(mesityl)-imidazol-2-ylidene), which was generated in situ from the reaction of its salt with Cs₂CO₃, did not take effect (entry 5), but Cs₂CO₃ did not control the reaction progress (entry 6). In contrast, monodentate phosphine ligands, P(*n*-Bu)₃, P(*t*-Bu)₃, P(Mes)₃, and PPh₃ were totally more effective than bidentate ones because of restraining the formation of hydroarylation products (entries 7–10). Finally, simple and ubiquitous PPh₃ was proved to be the most effective ligand (entry 10). 20 mol % of PPh₃ led to the similar result (entry 11). In contrast, the absence of PPh₃ caused a slightly lower yield (entry 12). In the Co-catalyzed annulation, Mn reductant was necessary to effect the annulation efficiently, that is, Zn powder mainly gave the hydroarylation product (entry 13). Other cobalt complexes such as CoCl₂ and CoI₂ showed the similar catalytic activity (entries 14 and 15), but Co(acac)₂ and other transition metal complexes, NiCl₂ and FeCl₂, did not convert both substrates to the products at all (entries 16–18). Additionally, we found that CoBr₂/PPh₃ complex could effect the annulation under ambient temperature (25 °C) for 6 h, giving rise to the corresponding naphthalene **3aa** in 70% yield (entry 19). The metal salt catalyst, reductant, and MeCN solvent were crucial in the transformation. Other

Table 2
Scope of aryl iodides **1** and alkynes **2** in the co-catalyzed annulation^a



^a The indicated yields were isolated yields. Gray color indicates the minor isomer and its ratio.

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