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Homogeneous Catalysis

Cobalt-Catalyzed Addition of Arylzinc Reagents to Alkynes to Form *ortho*-Alkenylarylzinc Species through 1,4-Cobalt Migration**

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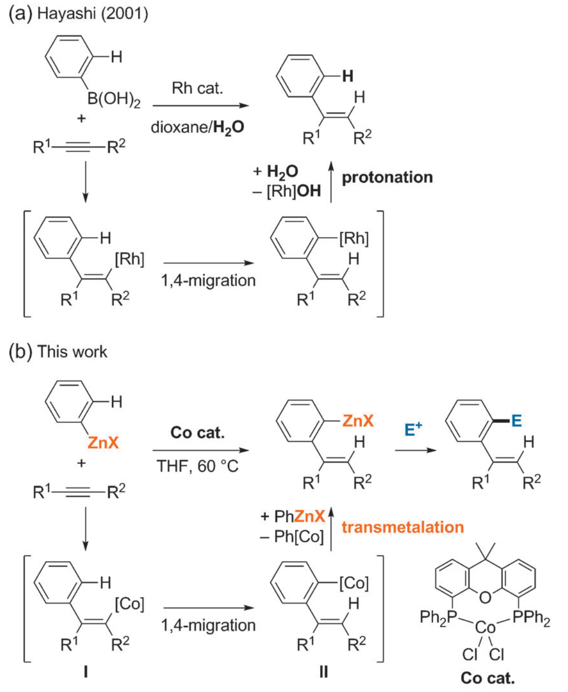
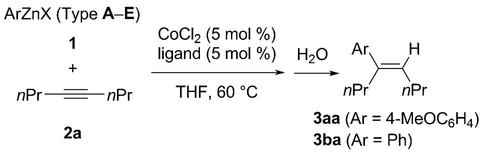
Metal migration reactions through C–H bond activation, 1,4-migrations in particular, have attracted significant attention in organorhodium and organopalladium chemistry not only as mechanistically intriguing processes but also as entries to novel remote C–H bond functionalization reactions.[1–3] After the first observation of 1,4-rhodium migration in the reaction of an arylboronic acid with norbornene by Miura et al.,[4] Hayashi and co-workers reported that a rhodium-catalyzed hydroarylation reaction of an alkyne with an arylboronic acid involves insertion of the alkyne into an arylrhodium species, vinyl-to-aryl 1,4-rhodium migration, and protonation of the resulting *ortho*-alkenylarylrhodium species (Scheme 1 a).[5] These seminal studies set the stage for the subsequent development of domino cyclization reactions involving 1,4-rhodium migration followed by trapping of the arylrhodium species with an internal electrophile (e.g., carbonyl group).[2] Herein, we report on a cobalt-catalyzed reaction of an arylzinc reagent with an alkyne that involves a similar vinyl-to-aryl 1,4-cobalt migration but is unique in that the 1,4-migration is followed by transmetalation with the arylzinc reagent (Scheme 1 b). Trapping of the resulting *ortho*-alkenylarylzinc species with external electrophiles allows access to a variety of 1-alkenyl-arenes functionalized in the 2-position, many of which are not readily accessible by existing synthetic methods.



Scheme 1. a) Rhodium-catalyzed alkyne hydroarylation involving 1,4-rhodium migration, and b) cobalt-catalyzed alkyne arylzincation involving 1,4-cobalt migration.

Recently, we reported the use of a $CoCl_2$–Xantphos[6] complex for the catalysis of a zinc insertion reaction into aryl iodides, bromides, and chlorides that allows efficient and convenient preparation of arylzinc reagents.[7] During this study, we found that the Co–Xantphos catalyst promoted an addition reaction of the thus-prepared arylzinc reagent to an unactivated internal alkyne. Thus, a 4-methoxyphenylzinc reagent **1a** prepared from 4-iodoanisole and Zn·LiCl with the cobalt catalyst in THF (denoted as type **A** reagent) reacted with 4-octyne (**2a**) at 60°C, and on quenching with water afforded the *syn*-addition product **3aa** in 70% yield (Scheme 2 and entry 1 in Table 1). Despite the recent report of Oshima and co-workers on an arylzincation reaction of an unactivated alkyne catalyzed by $CoBr_2$ alone,[8] this initial observation attracted our attention because their reaction proceeded in acetonitrile but not at all in THF.



Type **A**: ArBr or ArI + Zn•LiCl, 5 mol % $CoCl_2$–Xantphos
Type **B**: $ZnCl_2$•TMEDA + ArMgBr
Type **C**: $ZnCl_2$•TMEDA + 2 ArMgBr
Type **D**: ArBr or ArI + Zn•LiCl, 5 mol % $CoCl_2$–Xantphos, then Me_3SiCH_2MgCl
Type **E**: $ZnCl_2$•TMEDA + ArMgBr + Me_3SiCH_2MgCl

Scheme 2. Cobalt-catalyzed addition of arylzinc reagents to 4-octyne and types of arylzinc reagent used in this study. For type A and D reagents, the $CoCl_2$–Xantphos catalyst that was used to promote the zinc insertion was also used for the addition reaction.

A subsequent study revealed that Xantphos is a uniquely effective ligand for the present reaction (Table 1). Not

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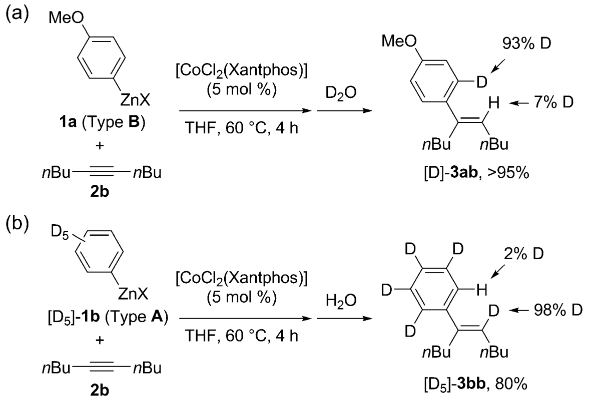
Table 1: Addition of ArZnX to 4-octyne (**2a**).[a]

Entry	Ar, reagent type (equiv)	Ligand	Yield [%][b]
1[c]	4-MeOC$_6$H$_4$, **A** (3)	Xantphos	70
2	Ph, **B** (1.1)	Xantphos	90 (90)
3	Ph, **B** (1.4)	DPEphos	3
4	Ph, **B** (1.4)	dppe	0
5	Ph, **B** (1.4)	dppp	2
6[d]	Ph, **B** (1.4)	PPh$_3$	1
7	Ph, **B** (1.4)	None	1
8[e]	Ph, **B** (1.1)	Xantphos	69
9[f]	Ph, **B** (1.1)	Xantphos	7
10	Ph, **C** (0.55)	Xantphos	74
11[c]	4-MeOC$_6$H$_4$, **D** (1.5)	Xantphos	99 (94)
12	Ph, **E** (1.5)	Xantphos	77

[a] Reaction conditions: CoCl$_2$ (5 mol%), ligand (5 mol%), **2a** (0.3 or 0.6 mmol), ArZnX, THF, 60°C, 4 h. See Scheme 2 for the type of the arylzinc reagent. [b] Determined by GC using *n*-tridecane as an internal standard. The *E*/*Z* ratio was >50:1 as determined by ^{1}H NMR spectroscopy and GC analysis. The yield of isolated product is shown in parentheses. [c] CoCl$_2$–Xantphos catalyst was used for both the zinc insertion and addition reactions. [d] PPh$_3$ (10 mol%) was used. [e] Performed in THF/toluene (1:1). [f] Performed in THF/MeCN (1:1).

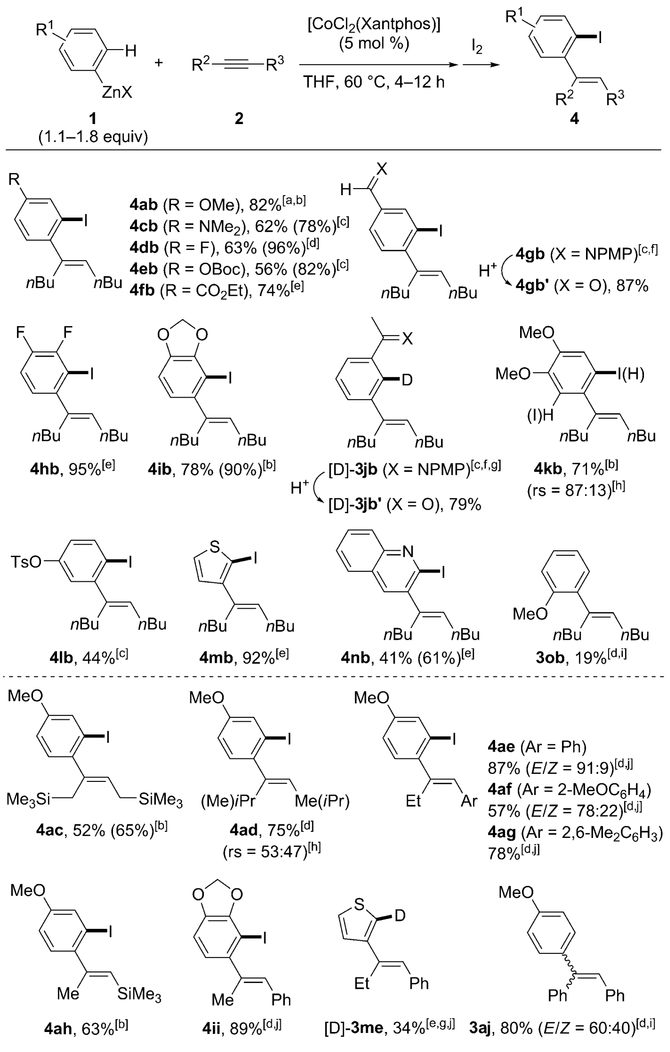
unexpectedly, the CoCl$_2$–Xantphos catalyst promoted the reaction of a phenylzinc reagent prepared from equimolar amounts of ZnCl$_2$·TMEDA and PhMgBr (type **B** reagent) with **2a** to afford the *syn*-adduct **3ba** in 90% yield (Table 1, entry 2). A preformed [CoCl$_2$(Xantphos)] complex exhibited an equally high catalytic activity as the catalyst generated in situ. In contrast, no measurable catalytic activity was obtained using other common phosphine ligands, such as DPEphos, dppe, dppp, and PPh$_3$,[6] or performing the reaction under ligand-free conditions (Table 1, entries 3–7), while a trace amount (1–3%) of the cyclotrimerization product of **2a** was observed. The reaction was slightly slower in a THF/toluene solvent mixture (Table 1, entry 8) and was significantly retarded by the use of MeCN as a cosolvent (entry 9). A diphenylzinc reagent (0.55 equiv) prepared from a 1:2 mixture of ZnCl$_2$·TMEDA and PhMgBr (type **C** reagent) afforded **3ba** in 74% yield (Table 1, entry 10), thus indicating transfer of both phenyl ligands on the zinc atom. Moreover, the reactivity of the type **A** arylzinc reagent was enhanced upon transmetalation with one equivalent of Me$_3$SiCH$_2$MgCl (type **D** reagent),[9] thus resulting in the formation of **3aa** in a near quantitative yield (Table 1, entry 11). Naturally, a mixed arylzinc reagent prepared from ZnCl$_2$·TMEDA, PhMgBr, and Me$_3$SiCH$_2$MgCl (type **E** reagent) was also reactive (Table 1, entry 12). Note that the use of PhMgBr instead of the phenylzinc reagents afforded only a trace amount of the adduct **3ba**, although alkyne **2a** was consumed by unidentified side reactions.

A critical difference between the present reaction and the CoBr$_2$-catalyzed arylzincation reported by Oshima and coworkers[8] became clear from the results of deuterium-labeling experiments. When the reaction of 4-methoxyphenylzinc reagent with 5-decyne was quenched with D$_2$O, predominant deuteration of the *ortho* position of the aryl group (93%) rather than the vinylic position (7%) was observed (Scheme 3a). Furthermore, the reaction of a pentadeuteriophenylzinc reagent with 5-decyne followed by quenching with H$_2$O afforded the product [D$_5$]-**3bb**, where one of the *ortho*-deuterium atoms of the zinc reagent had almost completely transferred to the vinylic position (Scheme 3b). These results are reminiscent of Hayashi's rhodium-catalyzed hydroarylation reaction (Scheme 1a),[5] and suggest a catalytic cycle consisting of the following steps (Scheme 1b): 1) insertion of the alkyne into an arylcobalt species generated from the cobalt precatalyst and the arylzinc reagent,[8,10] 2) 1,4-cobalt migration of the resulting alkenylcobalt species **I** to generate an *ortho*-alkenylarylcobalt species **II**, and 3) transmetalation between **II** and the arylzinc reagent to afford an *ortho*-alkenylarylzinc species and regenerate the arylcobalt species.



Scheme 3. Deuterium-labeling experiments.

The unique feature of this "migratory arylzincation" reaction compared with the rhodium-catalyzed hydroarylation reaction is that the product bears a reactive aryl–zinc bond, which can be intercepted by an external electrophile. Thus, we explored the generality of the addition–migration process using I$_2$ as the electrophile (Scheme 4). A variety of arylzinc reagents participated in the reaction with 5-decyne to afford the corresponding 1-iodo-2-alkenylarenes in moderate to good yields (**4ab**–**4nb**). Electron-donating, electron-withdrawing, and potentially sensitive functional groups including dimethylamino (**4cb**), carbonate (**4eb**), ester (**4fb**), aldimine (**4gb**), and tosyloxy (**4lb**) groups as well as heterocycles, such as thienyl (**4mb**) and quinolinyl (**4nb**), groups were tolerated,[11] while the reaction of an *ortho*-substituted arylzinc reagent was rather sluggish (**3ob**). Cobalt 1,4-migration was also feasible for different alkynes including dialkyl-, arylalkyl-, and silylalkylalkynes (see the corresponding products **4ac**–**4ah**, **4ii**, **3me**). Note that the reaction of arylalkylalkynes required the use of P(OPh)$_3$ (10 mol%) as a coligand to suppress *E*/*Z* isomerization. Without it, the reaction was accompanied by a substantial degree of *E*/*Z* isomerization (ca. 6:4–7:3). The reaction of diphenylacetylene afforded, upon protonation, the adduct **3aj** with a modest *E*/*Z* ratio, which was not improved by the addition of P(OPh)$_3$.[12] Terminal alkynes such as phenylacetylene and 1-octyne and sterically hindered alkynes such as bis(trimethylsilyl)acetylene did not participate in the reaction. While virtually no regioselectivity was observed for 4-methylpent-2-yne (see the corresponding product **4ad**), arylalkyl- and silylalkylalkynes underwent regioselective arylation on the acetylenic carbon

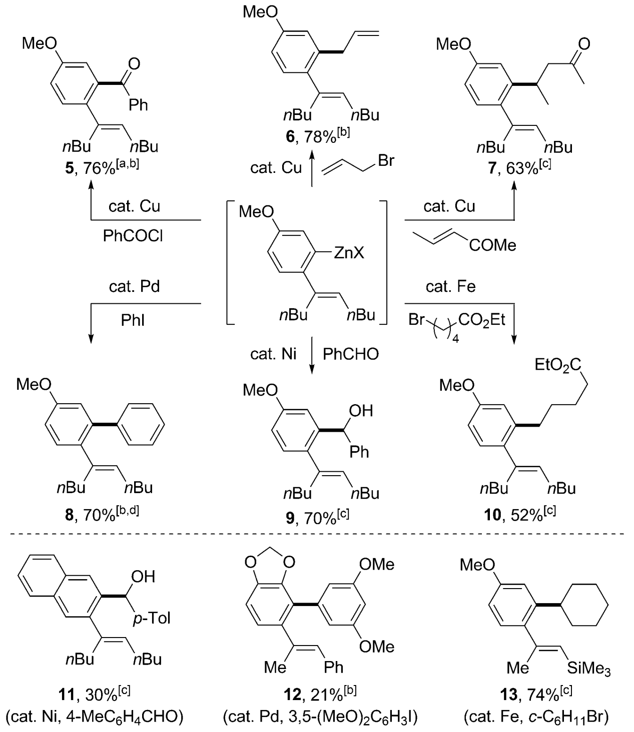


Scheme 4. Scope of the migratory arylzincation (0.6–1 mmol scale unless otherwise noted). The yields in parentheses refer to the yields of hydroarylation products obtained by quenching with H_2O. Ts = toluenesulfonyl, Boc = *tert*-butyloxycarbonyl [a] 5 mmol scale. [b] Reagent type = **B**. [c] Reagent type = **A**. [d] Reagent type = **C**. [e] Reagent type = **D**. [f] PMP = *p*-methoxyphenyl. The product was isolated after hydrolysis of the imine. [g] The reaction was quenched with D_2O. [h] rs = regioselectivity. [i] The reaction was quenched with H_2O. [j] $P(OPh)_3$ (10 mol%) was added.

atom proximal to the alkyl group (see the corresponding products **4ae–4ah**, **4ii**, and **3me**); this is the same regioselectivity as commonly observed for carbometalation of alkynes.[13,14] Note that, owing to partial decomposition during isolation, the yields of the iodinated products were generally lower than those of the corresponding hydroarylation products obtained by quenching with H_2O (see yields shown in parentheses).

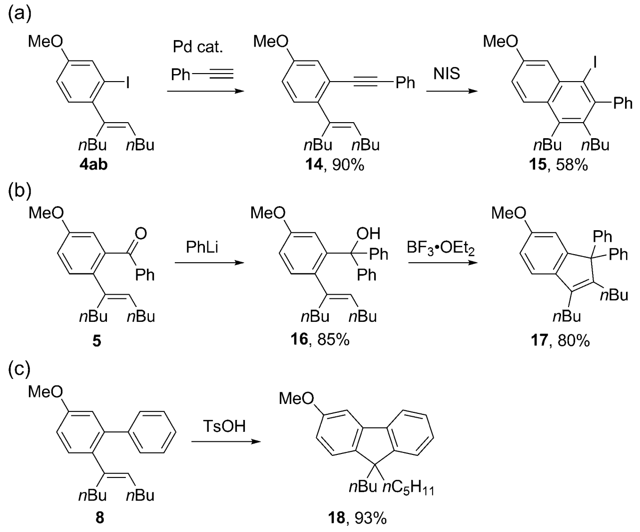
The regioselectivity of 1,4-cobalt migration deserves some comments. The presence of a difluoro- or methylenedioxy moiety at the *meta* and *para* positions resulted in exclusive 1,4-migration to the *ortho* position proximal to the functional group (**4hb** and **4ib**); this selectivity may be ascribed to the stabilizing effect of the fluorine atom on the *ortho* aryl–metal bond (for **4hb**)[15] and/or coordination of the *meta*-fluorine/oxygen atom to the cobalt center during the migration process.[16,17a] An *N*-aryl imine group at the *meta* position also served as a directing group ([D]-**3jb**).[17] In contrast, the reactions of 3,4-dimethoxy- and 3-tosyloxyphenylzinc reagents resulted in preferential metal migration to the less hindered *ortho* position (**4kb** and **4lb**), presumably because coordination of the *meta*-oxygen atom was not feasible owing to the increased bulkiness[16] and/or the reduced Lewis basicity (for **4lb**). Regioselective migration to the C2-position was observed in the reaction of 3-thienyl- and 3-quinolinylzinc reagents (see the corresponding products **4mb** and **4nb**), while correlation of the regioselectivity to specific parameters such as acidity is not clear to date.[18]

The *ortho*-alkenylarylzinc species generated from the 4-methoxyphenylzinc reagent and 5-octyne was amenable to a variety of transition-metal-catalyzed C–C bond-forming reactions (Scheme 5). Thus, copper-catalyzed acylation, allylation, and conjugate addition,[19] palladium-catalyzed Negishi coupling, nickel-catalyzed addition to an aldehyde,[20] and iron-catalyzed cross-coupling with an alkyl halide[9] produced 1-alkenyl-2-functionalized arenes **5–10**, respectively, in moderate to good yields. The feasibility of such electrophilic trapping was further demonstrated by three additional examples (see products **11–13**), albeit with modest yields for the first two cases, which could be improved on by optimizing the trapping conditions (compare the yields of **4ii** and **12**). Note that the 1,4-migration reaction starting from a 2-naphthylzinc reagent took place exclusively at the less hindered aromatic carbon (see **11**).



Scheme 5. Transition-metal-catalyzed transformation of *ortho*-alkenylarylzinc species (1 mmol scale unless otherwise noted). See the Supporting Information for details of the reaction conditions. [a] 5 mmol scale. [b] Reagent type = **B**. [c] Reagent type = **E**. [d] 3 mmol scale.

The present 1,2-difunctionalization protocol opens the way for the divergent synthesis of benzo-fused carbocycles through manipulation of the alkenyl and other functional groups as synthetic handles. The feasibility of this idea was readily demonstrated by three sets of transformations: 1) naphthalene synthesis (**15**) from 1-iodo-2-alkenylarene **4ab** through Sonogashira coupling followed by NIS-mediated iodocarbocyclization (Scheme 6a),[21] 2) indene synthesis (**17**) from 1-benzoyl-2-alkenylarene **5** through phenyllithium addition followed by BF_3-mediated cyclization (Scheme 6b), and 3) fluorene synthesis (**18**) from 1-phenyl-2-alkenylarene **8** through Friedel–Crafts cyclization (Scheme 6c).



Scheme 6. Transformation of 1-alkenyl-arenes functionalized in the 2-position. See the Supporting Information for details of the reaction conditions. NIS = *N*-iodosuccinimide. TsOH = *p*-toluenesulfonic acid.

In summary, we have developed a cobalt-catalyzed addition reaction of an arylzinc reagent to an internal alkyne that involves 1,4-cobalt migration followed by cobalt-to-zinc transmetalation to afford an *ortho*-alkenylarylzinc species, which serves as a versatile synthetic intermediate. It is an interesting observation that the Co–Xantphos catalyst performs best for the zinc insertion reaction as well as for the migratory arylzincation reaction, while the origin of its unique catalytic activity remains elusive. To our knowledge, the present reaction represents the first example of 1,4-cobalt migration in cobalt-catalyzed C−C-bond forming reactions,[22] and represents a new example of C−H bond functionalization using cobalt catalysts.[17,23,24] Further synthetic application of the 1,2-difunctionalization protocol and development of other cascade catalytic reactions based on cobalt migration are currently under investigation.

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[6] Abbreviations: Xantphos = 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene, TMEDA = *N,N,N′,N′*-tetramethylethylenediamine, DPEphos = bis[2-(diphenylphosphino)phenyl]ether, dppe = 1,2-bis(diphenylphosphino)ethane, dppp = 1,3-bis(diphenylphosphino)propane.

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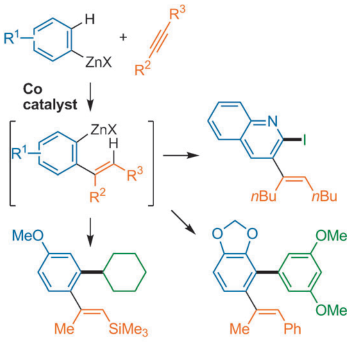
Communications

Homogeneous Catalysis



Migratory carbometalation: A cobalt–Xantphos complex catalyzes the addition of an arylzinc reagent to an unactivated internal alkyne; the reaction most likely involves insertion of the alkyne into an arylcobalt species and vinyl-to-aryl 1,4-cobalt migration, followed by transmetalation with the arylzinc reagent. Interception of the resulting *ortho*-alkenylarylzinc species with electrophiles allows access to 1-alkenyl arenes functionalized in the 2-position.