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Synthetic Methods Hot Paper

Cobalt-Catalyzed Regiodivergent Ring-Opening Dihydroboration of Arylidenecyclopropanes to Access Skipped Diboronates

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Abstract: Ligand-controlled regiodivergent cobalt-catalyzed ring-opening dihydroboration of arylidenecyclopropanes is developed to access synthetically versatile skipped diboronates with catalysts generated in situ from $Co(acac)_2$ and dpephos or xantphos. A variety of arylidenecyclopropanes reacted with pinacolborane (HBpin) to form the corresponding 1,3- or 1,4-diboronates in high isolated yields and with high regioselectivity. Skipped diboronate products from these reactions can undergo various transformations to allow selective installation of two different functional groups along alkyl chains. Mechanistic studies suggest that these reactions combine cobalt-catalyzed ring-opening hydroboration of arylidenecyclopropanes and hydroboration of homoallylic or allylic boronate intermediates.

Introduction

Organoboronates are undoubtedly one class of the most versatile building blocks in chemical synthesis because they are relatively stable, non-toxic, and can undergo a series of well-developed C–B to C–X (X = C, N, O, and halogens) conversions.[1] Among various families of structurally diverse organoboronates, geminal and vicinal diboronates have recently gained increasing attention in multiple step synthesis as their two C–B bonds can be selectively converted.[2] Accordingly, synthetic methods to access geminal and vicinal diboronates have been extensively developed through various metal-catalyzed dihydroboration reactions from readily accessible unsaturated hydrocarbons, such as alkenes, allenes, dienes and alkynes.[3]

Besides geminal and vicinal diboronates, skipped diboronates, such as 1,3- and 1,4-diboronates, are also versatile reagents as they can be employed as synthetic precursors to prepare various 1,3- and 1,4-difunctionalized compounds.[4] More importantly, discrimination of the two boryl sites in these skipped diboronates allows orthogonal molecular functionalization through sequential and selective C–B transformations.[5] As benzylboronates and alkylboronates show different reactivity in various transformations, such as Suzuki–Miyaura cross-coupling and oxidation reactions,[6] skipped diboronates containing both benzyl- and alkyl-substituted boryl sites will be of particular importance for orthogonal synthesis. However, modular and straightforward approaches to synthesize skipped diboronates are limited. For example, homologation of 1,1- or 1,2-diboronates can afford skipped diboronates, but these reactions require boryl-prefunctionalized starting materials and stoichiometric amounts of pyrophoric organolithium reagents.[7] Metal-catalyzed dihydroboration of 1,3-dienes can, in theory, also afford 1,3- and 1,4-diboronates, but it is difficult to develop into useful synthetic methodologies due to regioselectivity issues.[8] Hydroboration of 1,3-dienes occurs readily on one C=C bond to form homoallylic or allylic boronates, however hydroboration of the remaining C=C bond does not occur smoothly.[9] Therefore, it still remains desirable to identify suitable substrates and reliable catalytic conditions for modular synthesis of skipped diboronates.

Arylidenecyclopropanes, which can be conveniently prepared from readily available aryl aldehydes, are very useful reagents in organic synthesis. They possess unique reactivity because ring-opening of their strained cyclopropane rings via transition metal-assisted C–C bond cleavage is facile thermodynamically.[10] For example, the C–C bonds of their cyclopropane rings can undergo oxidative addition to low-valent transition metal complexes to form metallocyclobutane intermediates (Scheme 1A).[10b] Alternatively, insertion of their C=C bonds into organometallic complexes followed by subsequent β-C elimination also leads to ring-opening of the cyclopropane ring and generates allylic or homoallylic metal intermediates, which contain a newly formed C=C bond (Scheme 1B).[10b] Accordingly, various transition metal-catalyzed ring-opening functionalization reactions of arylidenecyclopropanes have been developed and these reactions mainly afford alkene products.[11] Nevertheless, reactions combining ring-opening of cyclopropane rings in arylidenecyclopropanes and hydrofunctionalization of the newly formed C=C bonds are underdeveloped.[12] Recently, the Engle group reported a copper-catalyzed protoboration of arylidenecyclopropanes with B_2pin_2 to synthesize cyclopropylboronates and alkenylboronates (Scheme 1C).[13] However, the alkenylboronate products from these ring-opening protoboration reactions

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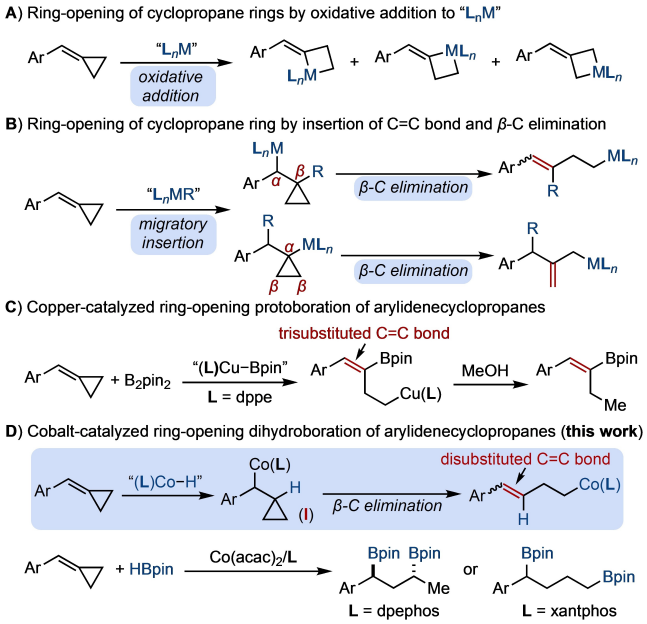


Scheme 1. Ring-opening borylation reactions of arylidenecyclopropanes.

do not undergo second copper-catalyzed protoboration likely because the steric hindrance around the trisubstituted C=C bonds disfavors their migratory insertion into the borylcuprate intermediate (**L**)Cu-Bpin.

During our continuous efforts to develop catalytic synthesis of structurally diverse multiple organoboronates from unsaturated hydrocarbons,[14] we became interested in developing selective modular synthesis of skipped diboronate compounds from readily accessible starting materials in the presence of first-row transition metal catalysts. As shown in Scheme 1D, we envisioned that, with a suitable cobalt catalyst (**L**)Co–H, arylidenecyclopropane would undergo regioselective migratory insertion into (**L**)Co–H to form a benzylcobalt intermediate (**I**) and subsequent β-C elimination would generate a disubstituted C=C bond, which could undergo second hydroboration. Therefore, arylidenecyclopropanes would be ideal substrates for syntheses of skipped diboronates. However, there are some challenges that need to be considered to achieve high chemo- and regioselectivity for this ring-opening dihydroboration. For example, insertion of arylidenecyclopropane into (**L**)Co–H needs to be facile and regioselective, and β-C elimination of benzylcobalt intermediate (**I**) needs to be faster than its σ-bond metathesis with HBpin to minimize direct hydroboration of arylidenecyclopropanes (Scheme 1D). Herein, we report the first ligand-controlled cobalt-catalyzed regiodivergent ring-opening dihydroboration of arylidenecyclopropanes that afford synthetically versatile 1,3- and 1,4-diboronates with high chemo- and regioselectivity.

Results and Discussion

We chose the reaction of 4-methylbenzylidenecyclopropane (**1a**) with HBpin to identify cobalt catalysts and reaction conditions for selective production of 1,3-diboronate **2a** or 1,4-diboronate **3a**. Cobalt catalysts employed in this study were generated by mixing $Co(acac)_2$ and bisphosphine ligands and activated in situ by their reaction with HBpin. We evaluated various bisphosphine ligands, solvents, concentrations, and additives for this reaction, and the results of selected experiments are summarized in Table 1 (see the Supporting Information for the detailed evaluation). In general, the reactions were performed with 5 mol % $Co(acac)_2$ and 6 mol % ligand in various solvents at 50 °C.

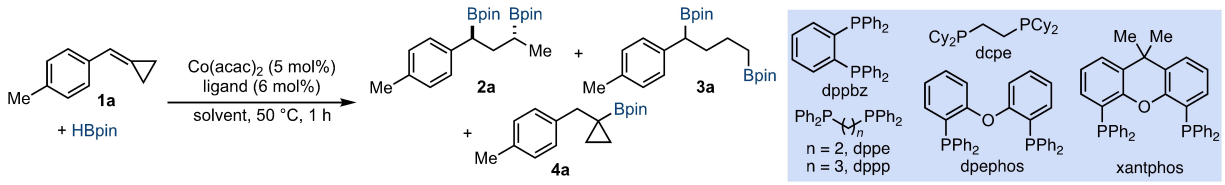
The reactions catalyzed by the combination of $Co(acac)_2$ and bisphosphine ligand, such as dppe, dppp, dcpe, and dppbz, in THF did not produce detectable amounts of diborylalkane **2a** or **3a** (entry 1 in Table 1), as shown by the GC-MS analysis on the reaction mixtures. Instead, these reactions formed a complex mixture of various boron-containing compounds. To our delight, the reaction catalyzed by $Co(acac)_2$ and dpephos in THF formed 1,3-diborylalkane **2a** as the major product in 54 % GC yield, together with a trace amount of 1,4-diborylalkane **3a** (entry 2 in Table 1). However, the corresponding reaction conducted with $Co(acac)_2$ and xantphos in THF afforded 1,4-diborylalkane **3a** as the major product, albeit in modest yield (48 %, entry 3 in Table 1).

To improve the $Co(acac)_2$/dpephos-catalyzed ring-opening dihydroboration of **1a** with HBpin, we then tested the reaction in various solvents, such as THF, 1,4-dioxane, toluene, DMA, and hexane (entries 2 and 4–7 in Table 1). The results of these reactions showed that the solvents did not influence the ratio of **2a** to **3a** significantly but had a noticeable effect on the GC yield of **2a**. The reaction in hexane afforded 1,3-diborylalkane **2a** in 77 % GC yield (entry 6 in Table 1).

With an attempt to improve the $Co(acac)_2$/xantphos-catalyzed ring-opening dihydroboration of **1a**, we also tested the reaction in various solvents and found that the solvent effects were profound for this reaction. For example, the reactions performed in nonpolar solvents, such as 1,4-dioxane, toluene, and hexane, provided cyclopropylboronate **4a** as the major product, together with small amounts of 1,4-diboronate **3a** (entries 8–10 in Table 1), and the reactions in polar solvents, such as THF and DMA, favored the formation of **3a** (entries 3 and 11). Evaluation of concentrations of **1a** revealed that reactions conducted with high concentration of **1a** afforded **3a** in lower yields but **4a** in higher yields (entries 3, and 12–14 in Table 1). Upon screening various lithium salts as additives for this reaction (see the Supporting Information for the detailed evaluation), we discovered that the reaction performed in 0.2 mL THF in the presence of 10 mol % LiCl as an additive formed 1,4-diborylalkane **3a** in 75 % GC yield with high regioselectivity (entry 15 in Table 1).

With the identified cobalt catalysts and reliable conditions in hand (entries 6 and 15 in Table 1), we studied the substrate scope of these cobalt-catalyzed ring-opening dihy-

Table 1: Evaluation of conditions for cobalt-catalyzed ring-opening double hydroboration of 1-(cyclopropylidenemethyl)-4-methylbenzene **1a**.[a]



Entry	Ligand	Solvent (mL)	Conv. [%][b]	Yield [%][b]			2a:3a:4a
				2a	3a	4a	
1	dppe/dppp/dcpe/dppbz	THF (2)	>99[c]	0	0	<1	–:–:–
2	dpephos	THF (2)	>99	54	3	<1	95:5:–
3	xantphos	THF (2)	>99	4	48	<1	9:91:–
4	dpephos	1,4-dioxane (2)	>99	59	5	<1	92:8:–
5	dpephos	toluene (2)	>99	64	5	<1	93:7:–
6	**dpephos**	**hexane (2)**	>99	**77** (70[d])	**5**	**<1**	**93:7:–**
7	dpephos	DMA (2)	>99	44	3	<1	92:8:–
8	xantphos	1,4-dioxane (2)	>99	4	15	63	5:18:77
9	xantphos	hexane (2)	>99	3	10	66	4:13:84
10	xantphos	toluene (2)	>99	4	12	61	5:16:79
11	xantphos	DMA (2)	>99	4	28	14	9:61:30
12	xantphos	THF (1)	>99	5	44	25	7:59:34
12	xantphos	THF (0.2)	>99	<1	21	60	–:26:74
14	xantphos	–	>99	<1	9	68	–:12:88
15[e]	**xantphos**	**THF (0.2)**	>99	**5**	**75**(69)	**<1**	**6:94:–**

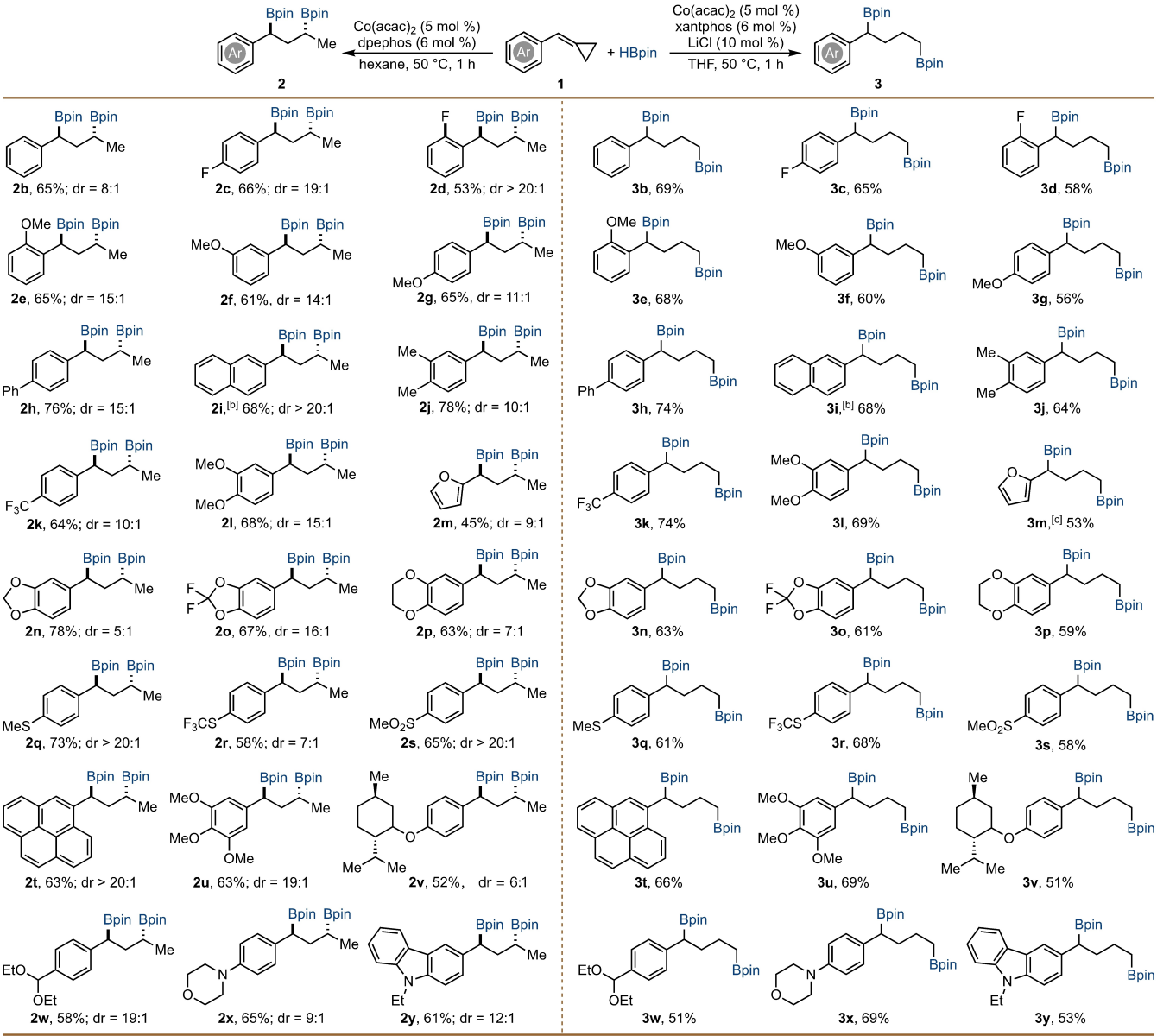
[a] Reaction conditions: **1a** (0.200 mmol), HBpin (0.800 mmol), $Co(acac)_2$ (10 μmol), ligand (12 μmol), solvent (2 mL), 50 °C, 1 h; [b] The yields of **2a**, **3a**, and **4a** were determined with gas chromatography (GC) analysis with tridecane as internal standard and the yields in parathesis are isolated yields; [c] The reaction afforded a complex mixture of various boron-containing compounds; [d] The stereochemistry of **2a** was assigned as *anti* by oxidizing **2a** to the corresponding 1,3-diol and comparing its NMR spectroscopic data with an authentic sample;[15] [e] LiCl (20 μmol) was added.

droboration reactions, and the results are summarized in Scheme 2. In general, a variety of arylidenecyclopropanes containing electronically varied aryl groups (**1b**–**1y**) reacted smoothly with HBpin in the presence of 5 mol % $Co(acac)_2$ and 6 mol % dpephos in hexane at 50 °C and produced the corresponding 1,3-diborylalkanes (**2b**–**2y**) in 52–78 % yields with moderate to high diastereoselectivity (5:1 to >20:1 d.r.). Meanwhile, ring-opening dihydroboration reactions of these arylidenecyclopropanes (**1b**–**1y**) catalyzed by 5 mol % $Co(acac)_2$ and 6 mol % xantphos in the presence of 10 mol % LiCl in THF at 50 °C gave the corresponding 1,4-diborylalkanes (**3b**–**3y**) in 51–74 % isolated yields. The GC-MS analysis on the crude mixtures showed that these reactions also generated 5–10 % of borylcyclopropane by-products, which were derived from direct hydroboration of arylidenecyclopropanes without ring-opening. The desired skipped diboronate products could be purified by column chromatography on silica, however, their instability on silica significantly lowered their isolated yields.

Data in Scheme 2 demonstrates that the substitution patterns of aryl groups do not have significant influences on these cobalt-catalyzed ring-opening dihydroboration reactions. For example, arylidenecyclopropanes (**1e**–**1g**) containing a methoxy group at the *ortho*-, *meta*-, and *para*-positions of the phenyl group reacted under both sets of conditions to provide the corresponding 1,3- and 1,4-diborylalkane products (**2e**–**2g** and **3e**–**3g**) in similar isolated yields. These cobalt-catalyzed reactions can tolerate various reactive groups, such as fluoro (**2c**/**3c** and **2d**/**3d**), trifluoromethyl (**2k**/**3k**), sulfide (**2q**/**3q**), trifluoromethylthio (**2r**/**3r**), sulfonyl (**2s**/**3s**), and acetal (**2w**/**3w**) moieties. In addition, arylidenecyclopropanes containing fused rings, such as naphthalene (**2i**/**3i**), benzodioxole (**2n**/**3n** and **2o**/**3o**), benzodioxane (**2p**/**3p**), pyrene (**2t**/**3t**), and carbazole (**2y**/**3y**), also reacted to afford the corresponding diborylalkane products in 53–78 % isolated yields. However, alkylidenecyclopropanes did not react to yield the desired skipped diboronates under both sets of reaction conditions.

To highlight the synthetic utility of this cobalt-catalyzed ring-opening dihydroboration of arylidenecyclopropanes, we carried out the reaction of **1b** with HBpin on a 5-mmol scale under both sets of conditions with a reduced catalyst loading (2 mol %), and these reactions provided gram-scale synthesis of 1,3- and 1,4-diborylalkanes **2b** and **3b** in 55 % and 67 % isolated yields, respectively (Scheme 3A). In addition, we also conducted further transformations of **2b** and **3b** by converting their C–B bonds. For example, both **2b** and **3b** reacted with vinylmagnesium bromide in the presence of I_2 to afford 1,6-diene **5** and 1,7-diene **6**,[16] which underwent Ru-catalyzed ring-closing metathesis to provide cyclic alkenes **7** and **8** in high isolated yields, respectively (Scheme 3B).[17] Double homologation reactions of diboronates **2b** and **3b** in the presence of $LiCH_2Br$ generated 1,5- and 1,6-diboronates **9** and **10**, respectively, albeit in modest isolated yields (Scheme 3C).[7a]

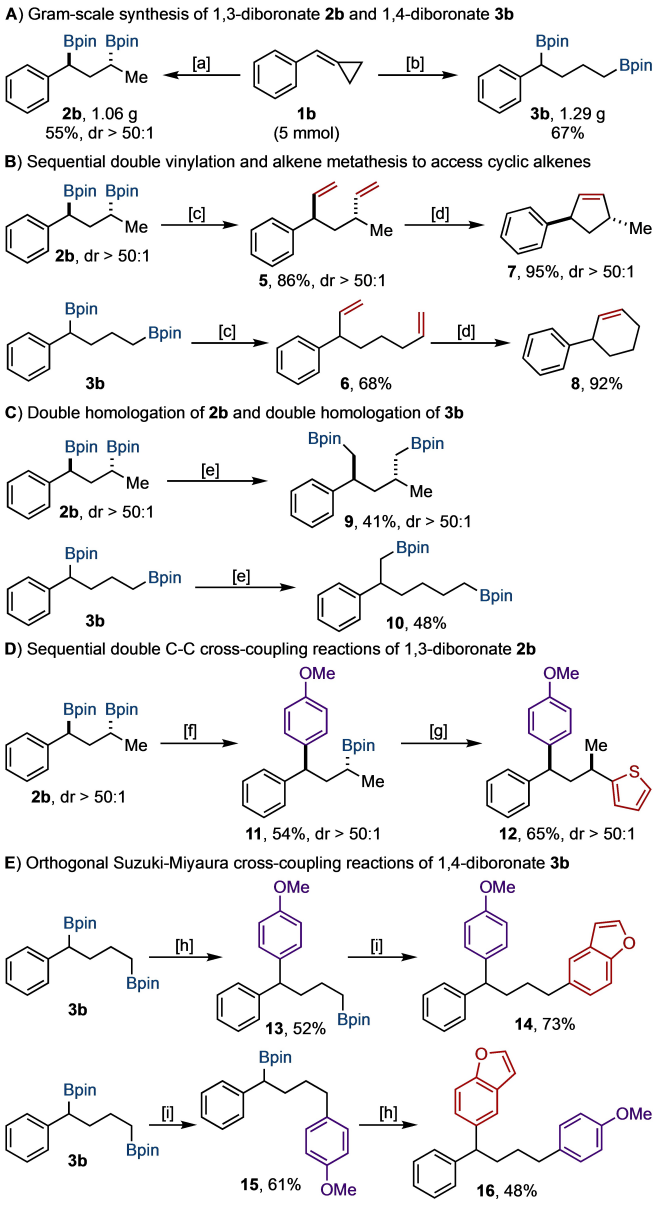
The $Pd_2(dba)_3/PPh_3$-catalyzed Suzuki–Miyaura coupling of 1,3-diboronate **2b** with 4-iodoanisole occurred selectively at the benzylic site to form a secondary alkylboronate **11**,



Scheme 2. Scope of arylidenecyclopropanes for the cobalt-catalyzed ring-opening double hydroboration reactions. Conditions: benzylidenecyclopropane **1** (0.300 mmol), HBpin (1.20 mmol), $Co(acac)_2$ (15.0 μmol), dpephos or xantphos (18.0 μmol), hexane (3 mL) or THF (0.3 mL), 50 °C, 1 h, yields of isolated products, and the *dr* values of 1,3-diborylalkane products were determined by ^{1}H NMR spectroscopic analysis on the crude mixtures of the reactions; [b] The reaction was conducted at 70 °C; [c] The reaction was conducted with 10 mol % cobalt catalyst.

which could undergo oxidative coupling with 2-thienyllithium and NBS to form compound **12** in 65 % isolated yield (Scheme 3D).[18] Attempts to perform Pd-catalyzed Suzuki–Miyaura coupling with secondary alkylboronate **11** led to protodeboronation of **11**. Different from 1,3-diboronate **2b**, 1,4-diboronate **3b** can undergo Pd-catalyzed Suzuki–Miyaura coupling at benzylboronate and alkylboronate sites selectively, which allows orthogonal functionalization of 1,4-diboronates.[19] For example, Suzuki–Miyaura coupling of **3b** with 4-iodoanisole catalyzed by $Pd_2(dba)_3$/PPh_3 with Ag_2O as a base proceeded at the benzylboronate site to produce alkylboronate **13** in 52 % isolated yield, and the second Suzuki–Miyaura coupling between **13** and 5-iodobenzofuran occurred in the presence of $Pd_2(dba)_3$, Ruphos, and NaO^{t}Bu to form compound **14** in 73 % isolated yield (Scheme 3E). Alternatively, these orthogonal Suzuki–Miyaura reactions of 1,4-diboronate **3b** could also be achieved through first coupling at the alkylboronate site to form benzylboronate **15** followed by second coupling at the benzylboronate site to produce compound **16**.

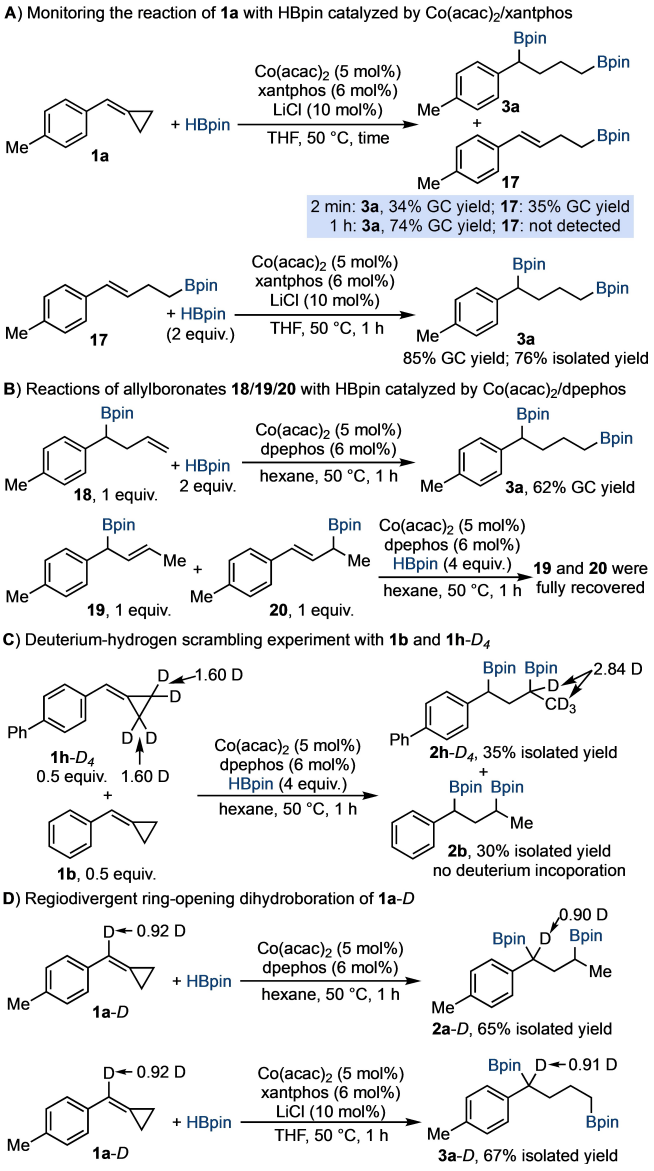
To gain insight into the cobalt-catalyzed regiodivergent ring-opening dihydroboration reactions of arylidenecyclopropanes, we monitored by GC analysis the reactions of **1a** with HBpin under both sets of conditions. For the reaction catalyzed by $Co(acac)_2$ and dpephos, substrate **1a** was converted rapidly to the desired 1,3-diboronate **2a** with no



Scheme 3. Gram-scale synthesis of skipped diboronates **2b** and **3b** and their further transformations. Conditions: [a] **1a** (5.00 mmol), HBpin (20.0 mmol), $Co(acac)_2$ (0.100 mmol), dpephos (0.125 mmol), 50 °C, 2 h; [b] **1a** (5.00 mmol), HBpin (20.0 mmol), $Co(acac)_2$ (0.100 mmol), xantphos (0.125 mmol), LiCl (0.500 mmol), THF, 50 °C, 2 h; [c] vinylmagnesium bromide (6 equiv), I_2/MeOH (6 equiv), THF, −78 °C, 2 h; [d] Grubbs 2nd catalyst (7.5 mol%), CH_2Cl_2, RT, 2 h; [e] $BrCH_2Cl$ (10 equiv), ^{n}BuLi (10 equiv), THF, −78 °C-RT, 6 h; [f] $Pd(dba)_2$ (5 mol%), PPh_3 (50 mol%), 4-iodoanisole (1.2 equiv), K_2CO_3 (1.5 equiv), Ag_2O (1.5 equiv) THF, 100 °C, 8 h; [g] 2-thienyllithium (3 equiv), NBS (1.2 equiv), THF/MeOH, −78 °C-RT, 3 h; [h] $Pd(dba)_2$ (10 mol%), PPh_3 (1 equiv), 4-iodoanisole (2 equiv) for the synthesis of **13** and 5-iodobenzofuran (2 equiv) for the synthesis of **16**, Ag_2O (1.5 equiv) THF, 100 °C, 12 h; [i] $Pd_2(dba)_3$ (2.5 mol%), Ruphos (5 mol%), 5-bromobenzofuran (2 equiv) for the synthesis of **14** and 4-iodoanisole (1.5 equiv) for the synthesis of **15**, NaO^{t}Bu (4 equiv), toluene/H_2O, 100 °C, 12 h. NBS = N-bromosuccinimide.

intermediates detected by GC analysis. However, for the reaction catalyzed by $Co(acac)_2$ and xantphos, GC analysis showed that substrate **1a** was nearly fully consumed within 2 minutes and the reaction produced 1,4-diboronate **3a** (34 % GC yield) and (*E*)-homoallylic boronate **17** (35 % GC yield) at this stage (Scheme 4A). However, the reaction formed 1,4-diboronate **3a** in 76 % GC yield in 1 h and monoboronate **17** was not detected (Scheme 4A). We then isolated monoboronate **17** and subjected it to the reaction catalyzed by 5 mol % $Co(acac)_2$ and 6 mol % xantphos. Indeed, it reacted smoothly to afford 1,4-diboronate **3a** in 85 % GC yield (Scheme 4B), which suggested the competence of monoboronate **17** as a potential intermediate for the formation of 1,4-diboronate **3a**.

As monoboronate intermediates were not observed for the reaction of **1a** with HBpin catalyzed by $Co(acac)_2$ and dpephos, we prepared three allylboronate compounds **18**, **19**, and **20**, which can potentially act as intermediates and undergo cobalt-catalzyed hydroboration with HBpin to form



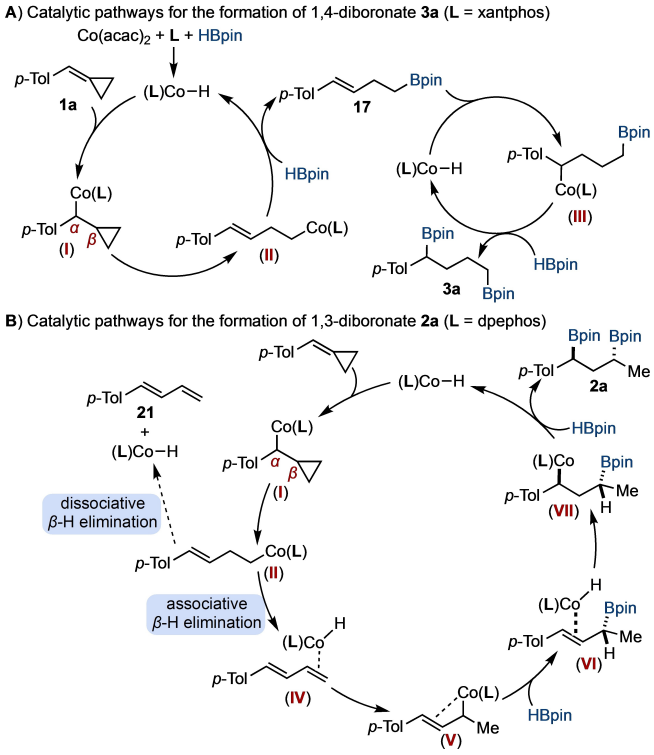
Scheme 4. Control experiments and deuterium-labelling experiments.

1,3-diboronate **2a** (Scheme 4B). However, homoallylboronate **18** reacted to provide 1,4-diboronate **3a** in 62% GC yield and allylboronates **19** and **20** did not react under these conditions. The results of these reactions suggest that the substrate is coordinated to the cobalt catalyst throughout the process of installing both Bpin groups in 1,3-diboronate **2a**. To test this possibility, we carried out a crossover experiment of $Co(acac)_2$/dpephos-catalyzed ring-opening dihydroboration using a 1:1 mixture of substrates **1b** and **1h**-D_4 and found that this reaction did not afford any H/D scrambled products (Scheme 4C). In addition, we also conducted deuterium-labelling reactions of substrate **1a**-D_1 under both sets of conditions, and deuterium atoms were retained at the benzylic positions in both diboronate products **2a**-D_1 and **3a**-D_1 (Scheme 4D).

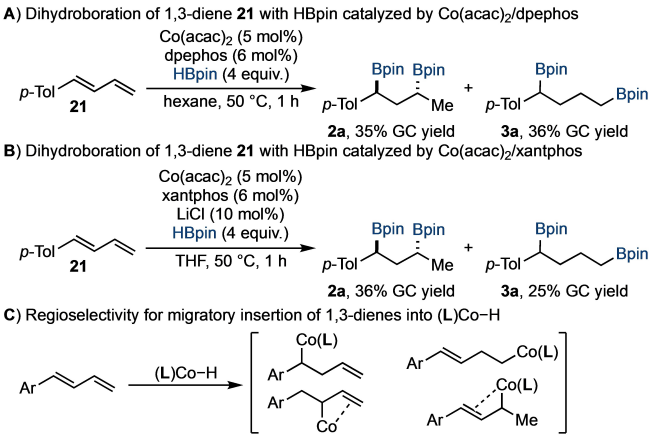
Based on the results of the above mechanistic experiments and the precedent for cobalt-catalyzed hydroboration reactions of unsaturated hydrocarbons,[20] we proposed plausible pathways for the cobalt-catalyzed ring-opening dihydroboration reactions of arylidenecyclopropane **1a** with HBpin (Scheme 5). Activation of $Co(acac)_2$ with HBpin in the presence of a bisphosphine ligand produces a cobalt hydride species (**L**)Co–H. Regioselective migratory insertion of **1a** into (**L**)Co–H forms a benzylcobalt intermediate **I**, which undergoes β-C elimination to produce a homoallylic cobalt species **II**.[10b] For the $Co(acac)_2$/xantphos-catalyzed ring-opening dihydroboration of **1a** (Scheme 5A), intermediate **II** reacts with HBpin to generate a homoallylic boronate **17**. Migratory insertion of **17** into (**L**)Co–H produces a benzylcobalt intermediate **III**, which reacts with HBpin to afford 1,4-diboronate product **3a** and regenerates the (**L**)Co–H species. For the $Co(acac)_2$/xantphos system, the rigid ligand backbone of xantphos likely prevents cobalt intermediate **II** from adopting the conformation required for β-H elimination and thus favours σ-bond metathesis with HBpin to form homoallylic boronate **17**, a key intermediate to 1,4-diboronate **3a**.

For the $Co(acac)_2$/dpephos-catalyzed reaction (Scheme 5B), the flexible backbone of dpephos enables the homoallylic cobalt intermediate **II** to readily adopt the confirmation with Co–C–C–H coplanar, and thus intermediate **II** can undergo associative β-H elimination to form a diene-coordinated cobalt hydride species **IV**. Subsequent reinsertion of the coordinated diene in intermediate **IV** into the Co–H bond generates an allylcobalt species **V**, which then reacts with HBpin to produce an allylboronate-coordinated cobalt hydride species **VI**, where the cobalt fragment binds to allylboronate from the less hindered face of its double bond. Subsequent intramolecular insertion of the coordinated allylboronate into the Co–H bond of **VI** generates a benzylcobalt intermediate **VII**, where the cobalt fragment stays *anti* to the Bpin group. Intermediate **VII** then undergoes σ-bond metathesis with HBpin to form 1,3-diboronate product *anti*-**2** with the regeneration of the catalytically active species (**L**)Co–H.

If dissociative β-H elimination from **II** occurs as the major pathway in the formation of allylcobalt intermediate **V**, 1,3-diene **21** will be a key intermediate in the $Co(acac)_2$/dpephos-catalyzed ring-opening dihydroboration of **1a**, as shown in Scheme 5B. To rule out this possibility, we carried out the dihydroboration reaction of 1,3-diene **21** with HBpin in the presence of 5 mol% $Co(acac)_2$ and 6 mol% dpephos. However, this reaction proceeded with poor regioselectivity and produced approximately equal amounts of 1,3-diboronate **2a** and 1,4-diboronate **3a** (Scheme 6A). In addition, we also conducted the dihydroboration of **21** catalyzed by 5 mol% $Co(acac)_2$ and 6 mol% of xantphos. Similarly, this reaction also afforded a mixture of diboronates **2a** and **3a** with a GC ratio of 59:41 (Scheme 6B). The obtained low regioselectivity for these two dihydroboration reactions of



Scheme 5. Proposed pathways for the cobalt-catalyzed regiodivergent ring-opening dihydroboration reactions of arylidenecyclopropanes.



Scheme 6. Dihydroboration of 1,3-diene **21** catalyzed by $Co(acac)_2$/dpephos and $Co(acac)_2$/xantphos.

1,3-diene **21** might be due to the poor regioselectivity for the migratory insertion step of 1,3-dienes into a cobalt hydride intermediate (Scheme 6C). These results suggest that β-C elimination from benzylcobalt intermediate **I** to form a single homoallylic cobalt species **II**, as shown in Scheme 5A and B, is crucial for achieving high selectivity for these ring-opening dihydroboration reactions of arylidenecyclopropanes.

Conclusion

In summary, we have developed convenient and effective protocols to access 1,3- and 1,4-diboronate compounds through ligand-controlled regiodivergent cobalt-catalyzed ring-opening dihydroboration reactions of arylidenecyclopropanes with HBpin. A variety of arylidenecyclopropanes reacted with HBpin in the presence of $Co(acac)_2$ and dpephos to afford the corresponding 1,3-diboronates with high regioselectivity and diastereoselectivity, These arylidenecyclopropanes reacted to form 1,4-diboronates when $Co(acac)_2$ and xantphos were employed as a catalyst. The diborylalkane products from these reactions can undergo various selective transformations by converting their two C–B bonds. Mechanistic studies suggest that the selective formation of a single homoallylic cobalt intermediate via β-C elimination to open the cyclopropane ring is crucial for achieving high regioselectivity for both 1,3- and 1,4-dihydroboration reactions.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

Keywords: Arylidenecyclopropane · Cobalt Catalysis · Regiodivergence · Ring-Opening · Skipped Diboronate

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Research Articles

Synthetic Methods

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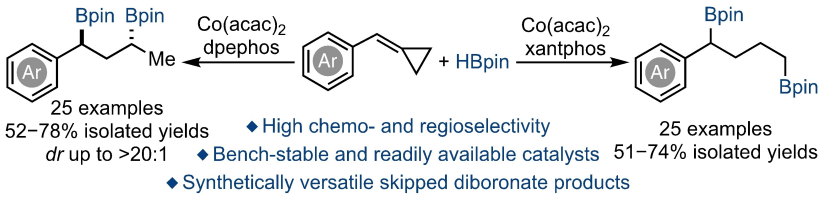
Cobalt-Catalyzed Regiodivergent Ring-Opening Dihydroboration of Arylidenecyclopropanes to Access Skipped Diboronates



Regiodivergent cobalt-catalyzed ring-opening dihydroboration of arylidenecyclopropanes with pinacolborane is developed to access synthetically versatile 1,3- and 1,4-diboronates. The catalysts are generated in situ from $Co(acac)_2$/dpephos and $Co(acac)_2$/xantphos, respectively. The ring-opening of arylidenecyclopropanes to form single homoallylic cobalt intermediates via β-C elimination is crucial for the obtained high regioselectivity.