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Zinc-Catalyzed Dual C–X and C–H Borylation of Aryl Halides

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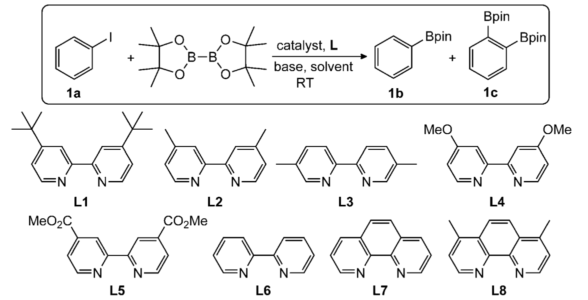
Abstract: *A zinc-catalyzed combined C–X and C–H borylation of aryl halides using B_2pin_2 (pin = $OCMe_2CMe_2O$) to produce the corresponding 1,2-diborylarenes under mild conditions was developed. Catalytic C–H bond activation occurs ortho to the halide groups if such a site is available or meta to the halide if the ortho position is already substituted. This method thus represents a novel use of a group XII catalyst for C–H borylation. This transformation does not proceed via a free aryne intermediate, but a radical process seems to be involved.*

Arylboronic acids and arylboronates are widely used as versatile building blocks in organic synthesis and they are important synthetic intermediates for transition-metal-catalyzed C–C and carbon–heteroatom bond-forming reactions.[1] Traditional methods for their synthesis are based on the reaction of aryl Grignard or lithium reagents with boron electrophiles.[2] More recently, transition-metal-catalyzed borylation of aryl halides[3] and the direct C–H borylation of arenes[4–6] have become increasingly important from the viewpoint of efficiency and functional-group compatibility. The most efficient catalysts for C–H borylation of arenes are based on precious metals such as Rh or Ir.[4–7] Similarly, aryl halide borylation typically utilizes Pd or Ni catalysts,[3a,b] although the inexpensive, abundant, and environmentally more acceptable Cu,[8a–e] Fe,[8f] or even Zn[9] now represent attractive alternatives to the commonly used expensive and toxic noble metals. However, the development of zinc catalysis is still in its infancy.[9–11]

We recently reported an efficient catalytic system using $ZnBr_2$ and 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes) for the cross-coupling of aryl and heteroaryl halides with diboron reagents.[11] We have now found that the combination of $ZnCl_2$ and 4,4′-di-*tert*-butyl-2,2′-bipyridine (dtbpy; **L1**) borylates not only the C–X bond of halobenzenes, but also a C–H bond *ortho* to the halide group, thereby yielding valuable 1,2-bis(Bpin)benzenes[12,13] along with the monoborylated products (Table 1). Classical methods for the preparation of 1,2-disubstituted arenes necessitate the availability of the appropriate dihaloarenes.[12,14] Recently, Yoshida reported that the Pt- or Cu-catalyzed diboration of the

Table 1: Optimization of the reaction conditions for the zinc-catalyzed diborylation of iodobenzene (**1a**).[a]



Entry	Catalyst	Ligand	Base	Solvent [2 mL]	Product Yield [%][b] 1b	1c
1	$ZnCl_2$	**L1**	MeOK	MTBE	56	37[c]
2	$ZnBr_2$	**L1**	MeOK	MTBE	45	20
3	ZnI_2	**L1**	MeOK	MTBE	43	27
4	$ZnEt_2$	**L1**	MeOK	MTBE	84	9
5	$Zn(OAc)_2$	**L1**	MeOK	MTBE	10	0
6	–	**L1**	MeOK	MTBE	0	0
7	$ZnCl_2$	**L2**	MeOK	MTBE	30	15
8	$ZnCl_2$	**L3**	MeOK	MTBE	56	24
9	$ZnBr_2$	**L3**	MeOK	MTBE	50	35[c–e]
10	$ZnCl_2$	**L4**	MeOK	MTBE	trace	0
11	$ZnCl_2$	**L5**	MeOK	MTBE	trace	0
12	$ZnCl_2$	**L6**	MeOK	MTBE	35	14
13	$ZnCl_2$	**L7**	MeOK	MTBE	trace	0
14	$ZnCl_2$	**L8**	MeOK	MTBE	5	0
15	$ZnCl_2$	–	MeOK	MTBE	0	0
16	$ZnCl_2$	**L1**	Cs_2CO_3	MTBE	7	0
17	$ZnCl_2$	**L1**	*t*BuOK	MTBE	trace	0
18	$ZnCl_2$	**L1**	MeONa	MTBE	25	17
19	$ZnCl_2$	**L1**	–	MTBE	0	0
20[f]	CuI	**L1**	MeOK	MTBE	trace	0
21[g]	$NiBr_2$	**L1**	MeOK	MTBE	3	0
22[h]	$Pd(OAc)_2$	**L1**	MeOK	MTBE	26	0
23[i]	$ZnCl_2$	**L1**	MeOK	MTBE	trace	0

[a] Reaction conditions: C_6H_5I, **1a** (0.5 mmol, 1 equiv), catalyst (10 mol%), ligand (20 mol%), base (1.5 equiv), B_2pin_2 (1.5 equiv), MTBE (2 mL), at room temperature unless otherwise stated. [b] The yields were determined by GC–MS analysis vs. a calibrated internal standard and are averages of two runs. [c] Complete conversion was observed, as determined by GC–MS analysis (see Table S8). [d] The reaction was performed using 2 equiv of B_2pin_2 and 2 equiv of MeOK. [e] The reaction was performed at 50 °C. [f] 2 mol% of CuI catalyst was used. [g] 2 mol% of anhydrous $NiBr_2$ used. A similar result was obtained with $NiCl_2$. [h] 2 mol% of $Pd(OAc)_2$ catalyst was used. [i] 18 μL (1 mmol) of water was added.

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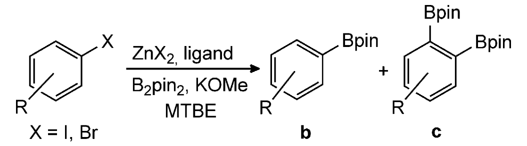
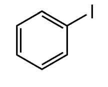
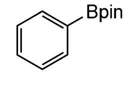
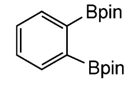
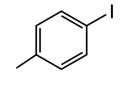
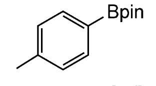
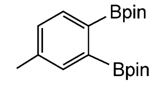
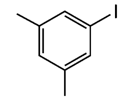
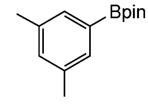
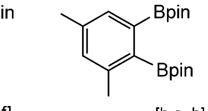
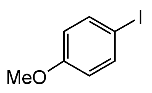
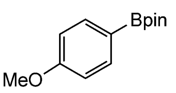
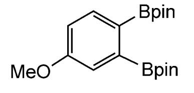
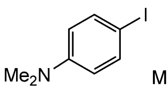
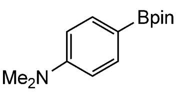
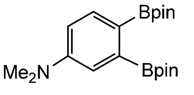
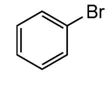
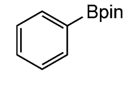
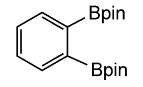
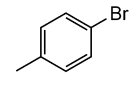
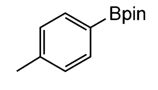
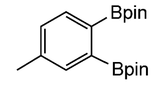
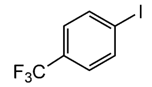
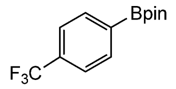
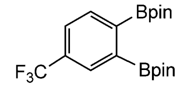
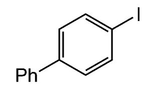
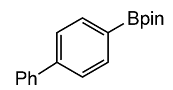
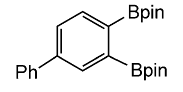
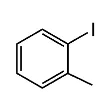
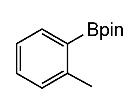
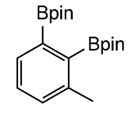
Table 2: Screening of aryl halides for the zinc-catalyzed diborylation reaction.



Entry	Aryl-X	Arylboronates (yield [%])		ArH [%][a]
1	 **1a**	 **1b** (56)[b,c]	 **1c** (37)[b,c]	[5]
2	 **2a**	 **2b** (50)[c,d]	 **2c** (34)[c,d]	[8]
3	 **3a**	 **3b** (52)[b,e,f]	 **3c** (28)[b,e–h]	[8]
4	 **4a**	 **4b** (48)[d–f]	 **4c** (37)[d–g]	[6]
5	 **5a**	 **5b** (39)[d–f]	 **5c** (28)[d–g]	[21]
6	 **6a**	 **1b** (53)[b,c,f]	 **1c** (18)[b,c,f]	[11]
7	 **7a**	 **2b** (45)[c,d,f]	 **2c** (11)[c,d,f]	[12]
8	 **8a**	 **8b** (64)[d–f]	 **8c** (12)[d–f]	[6]
9	 **9a**	 **9b** (52)[d–f]	 **9c** (19)[d–g]	[15]
10	 **10a**	 **10b** (40)[c,d,f]	 **10c** (34)[c,d,f]	[9]

[a] Approximate ArH yields were estimated by GC–MS analysis.
[b] Reaction conditions (A): aryl halide (0.5 mmol, 1 equiv), B_2pin_2 (1.5 equiv), $ZnCl_2$ (10 mol%), Ligand: **L1** (20 mol%), MeOK (1.5 equiv), MTBE (2 mL), at room temperature unless otherwise stated. [c] Yields were determined by GC–MS analysis vs. a calibrated internal standard and are averages of two experiments. [d] Reaction conditions (B): aryl halide (0.5 mmol, 1 equiv), B_2pin_2 (2 equiv), $ZnBr_2$ (10 mol%), Ligand: **L3** (20 mol%), MeOK (2 equiv), MTBE (2 mL), at room temperature unless otherwise stated. [e] Yield was determined by ^{1}H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard. [f] The reaction was performed at 50 °C for 12 h. [g] GC–MS analysis of the crude reaction mixture revealed the presence of a small amount of one more isomer of the diborylation product. [h] The structure of **3c** was confirmed by single-crystal X-ray diffraction (see Figure S7).

highly reactive C≡C bond of arynes at elevated temperatures (Pt catalyst at 80 °C, Cu catalyst at 100 °C) yielded 1,2-diborylarenes.[13] This route entails preparing the appropriate *ortho*-(trimethylsilyl)aryl triflate derivative from a suitable precursor.[15] Our novel Zn-catalyzed diborylation of aryl halides via both C–X and C–H activation under mild conditions represents a new type of catalytic process.

Using **1a** as the substrate, we screened a range of conditions, zinc sources, ligands, bases, and solvents to assess the scope and limitations of this diborylation reaction (Table 1; see Tables S1–S7 in the Supporting Information for details). Diborylated product **1c** was obtained in the highest yield using 1.5 equivalents of B_2pin_2 and MeOK in the presence of $ZnCl_2$ as the catalyst and **L1** (dtbpy) as the ligand at ambient temperature in methyl *tert*-butyl ether (MTBE), with complete conversion after 8 h (entry 1), while $ZnBr_2$ and ZnI_2 provided the product in lower yields (entries 2 and 3). $ZnEt_2$[9b] yielded predominantly the monoborylation product **1b**, and $Zn(OAc)_2$ showed very low catalytic activity (entries 4 and 5). In the absence of a Zn source, the borylation reaction does not occur at either the C–X or the C–H bond (entry 6) in this solvent.[3d]

The choice of ligand is crucial for this unusual diborylation reaction. Several substituted 2,2′-bipyridine and 1,10-phenanthroline ligands were investigated (**L2**, **L4–L8**), which provided lower yields than **L1** and **L3** (entries 7–14). The 5,5′-di-Me-bpy (**L3**) ligand displayed comparable reactivity to **L1** when used in combination with 2 equiv of B_2pin_2 and MeOK (entry 9). Ligand is essential for this catalytic process; no borylated products were observed when the ligand was omitted (entry 15). Next, the effects of the base were examined (entries 16–19). The replacement of MeOK by Cs_2CO_3 or *t*BuOK resulted in limited or no reaction, whereas MeONa was only somewhat less effective than MeOK (entries 16–18). There was no reaction in the absence of a base (entry 19).

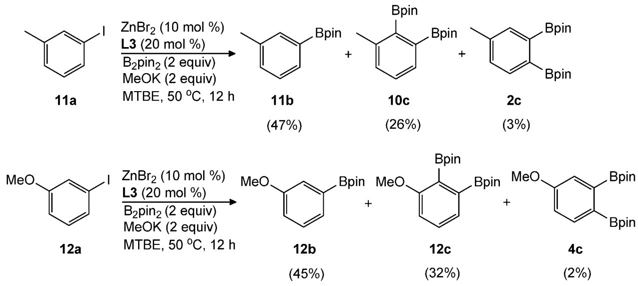
The possible involvement of copper, nickel, or palladium contamination in the catalyst was eliminated by the observation that copper[8a–e] and nickel[3a] salts provided trace or very small amounts of **1b** and no **1c** (entries 20 and 21), and $Pd(OAc)_2$ provided a low yield of monoborylation product **1b** and no diborylation product **1c** under the standard reaction conditions (entry 22). The reaction is moderately sensitive to air[16] but very sensitive to moisture; after the addition of 2 equiv of water, no significant amounts of the arylboronic esters were formed (entry 23).

Further screening of metal salts, ligands, and bases identified the two best catalyst systems. System A comprises $ZnCl_2$, **L1**, and 1.5 equiv of B_2pin_2 and MeOK in MTBE (entry 1), and system B comprises $ZnBr_2$, **L3**, and 2 equiv of B_2pin_2 and MeOK in MTBE (entry 9).

With optimized reaction conditions in hand, we examined the substrate scope of the diborylation reaction (Table 2).

Substituted aryl halides underwent diborylation reactions exclusively at the position *ortho* to the halide group, irrespective of the electronic nature of the substituent. Aryl halides possessing electron-donating substituents, such as *p*-methyl, 3,5-di-methyl, *p*-methoxy, and *p*-*N*,*N*-dimethylamino groups (**2a**–**5a**), are well tolerated, providing 1,2-diborylarenes in moderate yields. Aryl bromides (**6a** and **7a**) are less reactive, with the yields of the bis(boronate) being lower even at higher temperature. An electron-withdrawing CF_3 group (**8a**) at the *para* position yielded diborylation product **8c** in lower yield, along with the monoborylation product **8b**. The sterically congested, *ortho*-tolyl derivative **10a** was diborylated in 34 % yield.

In the absence of a combination of directing groups and specific catalysts,[5] the regioselectivity of the Rh- or Ir-catalyzed C–H borylation of arenes is primarily controlled by steric effects[6] and, consequently, the reactions typically occur at unhindered sites.[4–7] To study the steric effect of the substituents in our zinc-catalyzed reaction, we investigated the diborylation of *meta*-substituted aryl halides (Scheme 1).



Scheme 1. Borylation of 1-iodo-3-methylbenzene (**11a**) and 1-iodo-3-methoxybenzene (**12a**; the structure of **12c** was confirmed by single-crystal X-ray diffraction; see Figure S8).

Significantly, the zinc-catalyzed diborylation of **11a** occurred preferentially at the more hindered site, *ortho* to the substituent, thereby yielding 1,2-bis(Bpin)-3-methylbenzene (**10c**) accompanied by a small amount of 1,2-bis(Bpin)-4-methylbenzene (**2c**). A similar result was observed for the corresponding 1-iodo-3-methoxybenzene (**12a**), thus providing further evidence that the regioselectivity of the C–H borylation is not dominated by steric effects of the substituents.

The mechanism of this Zn-catalyzed diborylation of aryl halides is not immediately obvious. To probe the possibility of a two-step process, in which the C–X borylation product subsequently undergoes *ortho* C–H borylation, we monitored the reaction of **2a** by GC–MS analysis. As shown in Figure S1 in the Supporting Information, the monoborylated product **2b** and diborylated product **2c** were formed in maximum yields of 50 % and 34 %, respectively, within 8 h. The roughly similar shapes of the graphs for the time dependence of the formation of the two products indicate that both products are formed concurrently under the standard reaction conditions, so a two-step process is unlikely. Indeed, the isolated monoborylated product **2b**, which would arise from initial C–X borylation, did not undergo a second (C–H) borylation reaction under the standard conditions. We do note that there is an induction period for the formation of both products.

Addition of anthracene, 9,10-dimethylanthracene, 1,3-diphenylisobenzofuran, or 2,5-dimethylfuran as benzyne traps did not generate Diels–Alder adducts, thus indicating that our diborylation reaction does not generate a free benzyne intermediate resulting from base-promoted dehydrohalogenation. However, careful analysis of the crude reaction mixture with added anthracene revealed the formation of a small amount of 9-phenyl-9,10-dihydroanthracene,[17] suggesting the possibility of a radical mechanism (Scheme S1 in the Supporting Information). Furthermore, no *vic*-diborylbenzene (**1c**) was observed by GC–MS analysis when benzyne, generated in situ from 2-(trimethylsilyl)phenyl triflate and KF/[18]crown-6, was reacted with B_2pin_2 in the presence of $ZnCl_2$ and **L1** as the ligand.[9b,13]

The borylation of sterically congested iodomesitylene (**13a**), which is substituted at both *ortho* positions, afforded the unexpected 1,3-diborylarene product **13c**, as confirmed by X-ray diffraction (Figure 1). It is significant that in the case of **13a**, the C–H activation took place at a remote aryl C–H bond rather than a weaker benzylic C–H bond (compare **2a**, **3a**, **7a**, and **10a**). The formation of **13c** further excluded the possibility of an aryne intermediate.

When the reaction was performed in the presence of 1 equiv of the radical inhibitor 9,10-dihydroanthracene, the desired products were obtained in lower yields (**1b**: 26 %; **1c**: 18 %). Increasing the radical inhibitor to 7 equiv shuts down the reaction almost completely (4 % of **1b** and no **1c** detected by GC–MS) and a similar result was obtained when using 3 equiv of 2,2,6,6-tetramethylpiperidin-1-yloxyl (TEMPO) as the inhibitor. It thus seemed that the borylation reaction might involve one-electron processes. A radical-clock experiment using substrate **14a** under the standard conditions afforded the major acyclic mono and diborylation products **14b** and **14c** in 42 and 26 % yield, respectively, and no 5-*exo*-trig cyclization product **14d** was detected (Scheme 2; a trace amount of one more isomeric diborylation product was also observed by GC–MS analysis). However, an experiment using 1-bromo-2-(but-3-en-1-yl)benzene (**15a**; Scheme 3) gave monoborylated product **15b**, along with cyclized (borylmethyl)indane (**15d**); no diborylation product **15c** was detected by GC–MS (small amounts of hydrodehalogenation byproducts 4-phenyl-1-butene and 1-methylindane were also

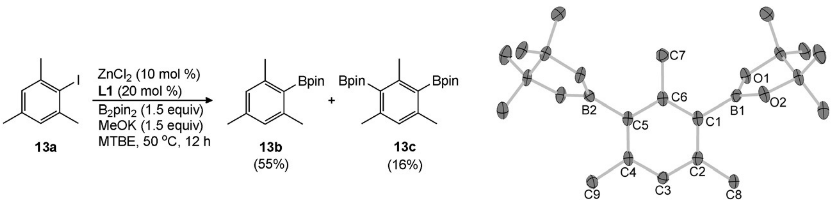
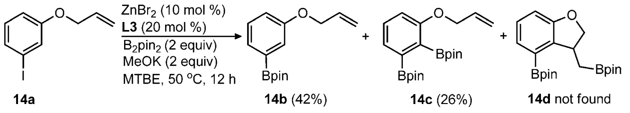
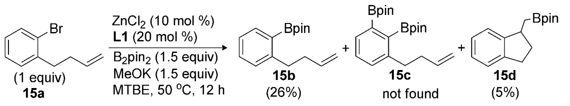


Figure 1. Borylation of 1-iodo-2,4,6-trimethylbenzene (**13a**) along with the molecular structure of **13c** (see Figure S9 for details).



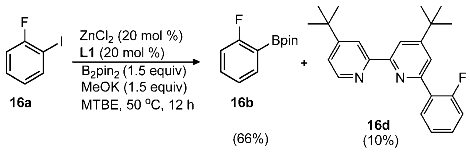
Scheme 2. Borylation of 1-(allyloxy)-3-iodobenzene (**14a**).



Scheme 3. Borylation of 1-bromo-2-(but-3-en-1-yl)benzene (**15a**).

observed). Formation of the cyclized product **15d** supports the possibility of a radical mechanism.

Itami and co-workers have reported a transition-metal-free *t*BuOK-promoted coupling of electron-deficient nitrogen heterocycles with aryl iodides.[18a] Recently, Jutand and Lei et al. reported that the interaction between 1,10-phenanthroline (Phen) and *t*BuOK generates the 1,10-phenanthroline radical anion Phen$^{\bullet-}$ and the *t*BuO$^{\bullet}$ radical.[18b] Furthermore, Phen serves as a relay for the reduction of phenyl bromide to the phenyl radical via Phen$^{\bullet-}$. Echegoyen et al. reported $[Ru(bpy)_3]^0$, formed by reductive electrocrystallization of $[Ru(bpy)_3](PF_6)_2$, and the crystal structure provides evidence that the extra electrons reside on the bpy ligands.[18c] Interestingly, the borylation of 2-fluoroiodobenzene afforded monoborylated product **16b**, along with the arylated dtbpy product **16d**; no diborylated product was observed by GC–MS (Scheme 4). The formation of coupling product **16d** suggested the possibility of dtbpy reduction followed by attack at the aryl iodide. In the absence of a Zn source, neither the borylation nor arylation occurred (see Table S9), thus suggesting the intermediacy of a Zn-dtbpy complex. Running the reaction with **1a** under standard conditions but in the dark (Table S7, entry 9) had no effect on the conversion or product distribution; therefore, the borylations are not triggered by a photoexcited state.



Scheme 4. Borylation of 2-fluoroiodobenzene (**16a**).

To account for the observed products, we speculate that there are two independent pathways occurring. One pathway (A) gives monoborylated products via metathesis between a (dtbpy)Zn^{II}-boryl complex and ArX.[8b,11] In the second pathway (B; Figure 2) leading to the diborylated products, MeOK reacts with B$_2$pin$_2$ to generate the adduct $K^+[B_2pin_2OMe]^-$,[19a,b] which reduces a (dtbpy)nZn^{II}XY complex ($n=1$ or 2; X,Y = OMe, Bpin or both) to produce a Zn^{II}-stabilized [dtbpy]$^{\bullet-}$ radical. This can pass the electron to ArX to form ArX$^{\bullet-}$ (**II**), which reacts with $K^+[B_2pin_2OMe]^-$ (in either a step-wise or concerted (**III**) fashion), giving diborylated arene and regenerating the [Zn-dtbpy]$^{\bullet-}$ radical anion. The regioselectivity shown in Scheme 1 can be explained by a concerted mode, in which ArX$^{\bullet-}$ undergoes nucleophilic substitution (releasing X$^-$), which in turn promotes the electrophillic substitution (**III**).[19c] For the formation of **13c**, the regioselectivity can be explained by a fast, step-wise addition process.

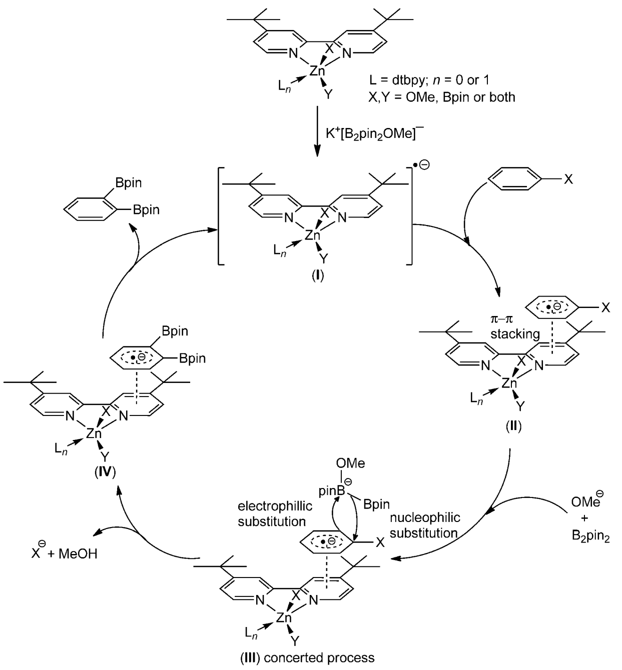


Figure 2. A plausible mechanism for pathway (B).

We have discovered a novel process that yields 1,2-diborylarenes via Zn-catalyzed C–X and C–H activation of aryl halides under mild conditions. Preliminary investigations show that the C–X/C–H diborylation reaction does not involve a free aryne, but one-electron processes seem to be involved.

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