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含吡咯基配体的锌、锂和镁配合物的合成与表征及其对芳基碘代物的硼化反应和醛、酮的硼氢化反应的催化作用

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摘要 用 $ZnEt_2$ 分别与两个含吡咯基的配体 2-(2-((((1*H*-吡咯-2-基)亚甲基)氨基)甲基)-1*H*-吡咯-1-基)-*N*,*N*-二甲基乙烷-1-胺(HL1)和 *N*-((1*H*-吡咯-2-甲基)甲基)-1-(1*H*-吡啶-2-基)甲亚胺(H_2L2)反应，合成了两个化合物[Zn(L1)Et] (**1**)和[$Zn_2(L2)_2(THF)_2$] (**2**). 通过核磁共振波谱、元素分析和单晶 X 射线衍射对配合物进行了表征. 研究了配合物 **1** 和 **2** 对芳基碘与 B_2Pin_2 (B_2Pin_2＝4,4,4',4',5,5,5',5'-八甲基-2,2′-双(1,3,2-二氧杂硼烷))偶联反应的催化作用. 它们都对这类硼化反应有催化活性. 化合物 **1** 显示出比 **2** 更高的活性. 化合物 **1** 催化的这类硼化反应具有温和的条件、宽的底物范围和较好的官能团相容性的特点. 此外，还研究了先前报道的两种已知化合物[$Li_2(L1)_2$] (**3**)和[$Mg(L1)_2(THF)_2$] (**4**)对频哪硼烷(HBpin)和醛、酮的硼氢化反应的催化作用. 配合物 **3** 和 **4** 对该类反应具有较好的催化活性，在很短的时间内以优异的产率生成了一系列硼酸酯.

关键词 硼化反应; 硼氢化反应; 锌化合物; 催化

Synthesis and Characterization of Zinc, Lithium and Magnesium Complexes Containing Pyrrolyl Ligands, and Utilization as Catalysts in Borylation of Aryl Iodides and Hydroboration of Aldehydes and Ketones

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Abstract The reactions of $ZnEt_2$ with two pyrrolyl ligands 2-(2-((((1*H*-pyrrol-2-yl)methylene)amino)methyl)-1*H*-pyrrol-1-yl)-*N*,*N*-dimethylethan-1-amine (HL1) and *N*-((1*H*-pyrrol-2-yl)methyl)-1-(1*H*-pyrrol-2-yl)methanimine (H_2L2) generated a zinc ethyl compound [Zn(L1)Et] (**1**) and a dinuclear complex [$Zn_2(L2)_2(THF)_2$] (**2**). The complexes were characterized by ^1H NMR, ^{13}C NMR, elemental analysis, and single-crystal X-ray diffraction. Complexes **1** and **2** were employed as catalysts for the borylation of aryl iodides with B_2Pin_2 (B_2Pin_2＝4,4,4',4',5,5,5',5'-octamethyl-2,2'-bis(1,3,2-dioxaborolane)). They were both active for this coupling reaction. Complex **1** displays higher activity than that of **2**. This borylation transformation promoted by **1** features mild condition, wide substrate scope and high functional group compatibility. Moreover, the catalytic activities of two known compounds previously reported by our group, namely, [$Li_2(L1)_2$] (**3**) and [$Mg(L1)_2(THF)_2$] (**4**), toward borylation of aryl iodides with B_2Pin_2 were also explored. They cannot catalyze this coupling reaction. Nevertheless, complexes **3** and **4** were catalytically active toward hydroboration of aldehydes and ketones by pinacolborane (HBpin), giving a variety of borate esters in excellent yields in a very short time.

Keywords borylation; hydroboration; zinc complexes; catalysis

1 Introduction

The synthesis of zinc complexes has experienced remarkable renewal and rapid expansion during the last 20 years.[1-12] The motivations of many scientists for the preparation of various zinc complexes have been driven by the extensive applications of these complexes as catalysts for a series of organic reactions. These reactions include hydro-

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alkoxylation cyclization of alkynyl alcohols,[13] hydroamination of alkenes,[14] CO_2/epoxide copolymerization,[15] carboxylic acid ester hydrolysis,[16] asymmetric Michael addition to nitroalkenes,[17] ring-opening polymerization of cyclic esters,[18] and so forth. Particularly, the discoveries that some zinc complexes could catalyze the borylation of aryl halides by B_2Pin_2 [B_2Pin_2 = 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bis(1,3,2-dioxaborolane)] have led to the boost in research activities about zinc-catalyzed borylation reactions.[19-22]

The borylation of organic halides is a very important transformation that could generate aryl borates in a very simple and efficient manner.[23-27] Aryl borates are highly valuable building blocks in organic synthesis, since the boryl group can be transformed into a variety of functional groups.[28-30] The traditional approaches to aryl borates are based on the reactions of organolithium or Grignard reagents with organoboranes.[31] Recent advances in this research field indicated that transition-metal-catalyzed C—H borylation of arenes and borylation of aryl halides are very efficient methodologies for the synthesis of aryl borates.[32-34] Marder[19-21] and Uchiyama[22] have developed a series of catalytic systems based on zinc complexes. These systems are very innovative from the aspects of cheap catalysts, broad aryl halide scope, and high functional group compatibility. Zinc is an earth-abundant, inexpensive, environmentally benign, and biocompatible metal. These characteristics render zinc complexes very promising for utilization as catalysts in organic synthesis.

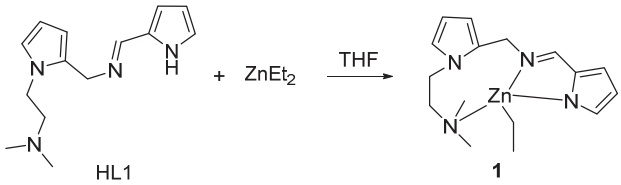
Recently, we reported the synthesis of several zinc compounds supported by *β*-diketiminate ligands and their applications in the cross-coupling of aryl iodides with B_2Pin_2.[35-36] In our continuing efforts in developing efficient zinc-catalyzed systems toward the borylation of aryl halides with organoborane reagents, our attention was turned to preparing zinc complexes incorporating pyrrolyl ligands. The pyrrolyl entity can act as a ligand and is capable of bonding to metals via the η^1-terminal mode, μ_2-bridge mode and μ-η^1:η^5-bridge mode.[37-38] These varied bonding modes may lead to the formation of zinc complexes with diversifying structures. Several zinc complexes containing pyrrolyl ligands have been reported,[39-47] and they are active catalysts in the ring-opening polymerization of cyclic esters,[39-43] copolymerization between CO_2 and epoxides,[44-46] and cyclotrimerization of isocyanates.[47] However, these pyrrolyl ligand-supported zinc complexes have never been used in the borylation of aryl halides.

In light of the above-mentioned consideration, we synthesized two zinc complexes of compositions [Zn(L1)Et] (**1**) and [$Zn_2(L2)_2(THF)_2$] (**2**) (HL1 = 2-(2-((((1*H*-pyrrol-2-yl)methylene)amino)methyl)-1*H*-pyrrol-1-yl)-*N*,*N*-dimethylethan-1-amine, H_2L2 = *N*-((1*H*-pyrrol-2-yl)methyl)-1-(1*H*-pyrrol-2-yl)methanimine). They were both active toward the borylation of aryl iodides with B_2Pin_2. We also found that our previously reported complexes[48] [$Li_2(L1)_2$] (**3**) and [$Mg(L1)_2(THF)_2$] (**4**) were highly active toward the hydroboration of aldehydes and ketones by pinacolborane (HBpin). Herein, we report the synthesis and characterization of **1** and **2** and the catalytic behaviors of **1**～**4** toward the borylation of aryl iodides and hydroboration of aldehydes and ketones.

2 Results and discussion

2.1 Synthesis and structure of 1

Treatment of a THF solution of HL1 with a solution of $ZnEt_2$ (1.0 mol/L in hexane) generated [Zn(L1)Et] (**1**) as a light pink solid in high yield (91%, Scheme 1). Colorless single crystals of **1** suitable for X-ray single crystal diffraction were obtained from a saturated toluene solution at −35 ℃ after one week.



Scheme 1 Synthesis of [Zn(L1)Et] (**1**)

X-ray single crystal diffraction analysis of **1** showed that it crystalizes in the monoclinic space group *P*21/*c*. The molecular structure of **1** is presented in Figure 1.

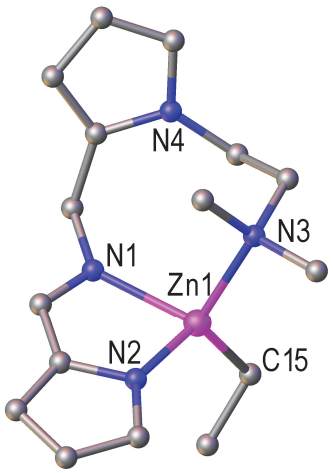


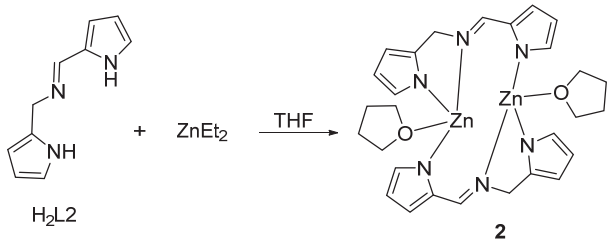
Figure 1 Molecular structure of [Zn(L1)Et] (**1**)
The bond distances are listed as follows: Zn(1)—N(1) 0.2110(2) nm; Zn(1)—N(2) 0.2018(2) nm; Zn(1)—N(3) 0.2135(2) nm; Zn(1)—C(15) 0.1981(3) nm

Compound **1** is mononuclear and consists of one Zn^{II} ion, one $L1^-$ ligand and an ethyl group. The Zn^{II} ion is coordinated by one pyrrolyl nitrogen atom, one aminomethyl nitrogen atom, one imine nitrogen atom, and one carbon atom of the ethyl group. The continuous shape measure (CShM) method[49] was utilized to calculate the coordination geometry of the Zn^{II} ion. It was calculated that the four-coordinated Zn^{II} ion exhibits tetrahedron geometry with a shape value of 2.196. The Zn—$N_{pyrrolyl}$, Zn—$N_{aminomethyl}$, and Zn—N_{imine} bond distances are 0.2018(2), 0.2110(2) and 0.2135(2) nm, respectively. The Zn—C bond

length is 0.1981(3) nm.

2.2 Synthesis and structure of $[Zn_2(L2)_2(THF)_2]$ (**2**)

Compound **2** was prepared in a similar method to that of **1**. Transalkylation between a tetrahydrofuran (THF) solution of H_2L2 and a hexane solution of $ZnEt_2$ gave a light-yellow solid of **2** in 90% yield (Scheme 2). Colorless single crystals of **2** were recrystallized from a mixture of THF and hexane.



Scheme 2 Synthesis of $[Zn_2(L2)_2(THF)_2]$ (**2**)

Compound **2** has a quasi-centrosymmetric binuclear structure. Complex **2** is composed of two $L2^{2-}$ ligands, two tetrahydrofuran molecules and two Zn^{II} ions (Figure 2a). Two Zn^{II} ions have the same coordination environments, and each of them is four-coordinated by two pyrrolyl nitrogen atoms, one imine nitrogen atom and one oxygen atom from tetrahydrofuran. Each Zn^{II} ion displays tetrahedron geometry with a shape value of 2.794. The bond lengths of Zn—$N_{pyrolyl}$ are 0.19249(15) and 0.19810(16) nm. The Zn—N_{imine} bond distance is 0.20431(15) nm, and the Zn—O bond length is 0.20434(13) nm. Two zinc atoms are connected by four nitrogen atoms and four carbon atoms from two $L2^{2-}$ ligands to form a ten-membered ring. Thus, compound **2** displays a saddle-like topology (Figure 2b).

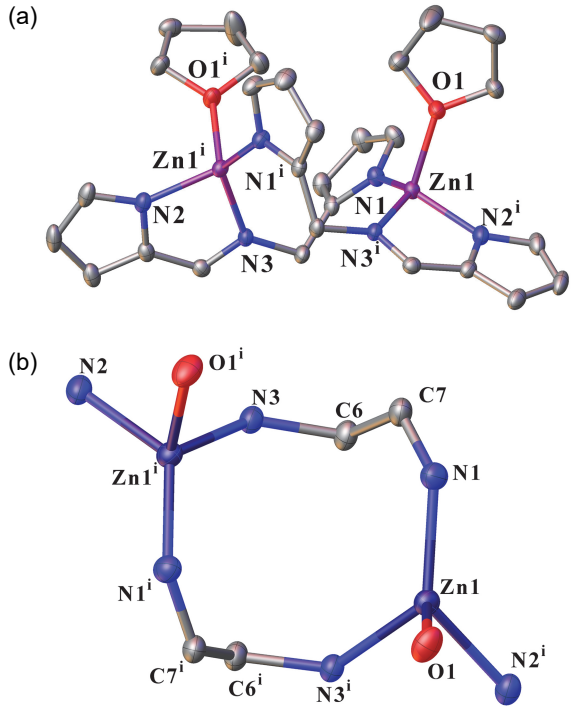


Figure 2 Molecular structure of **2** (a) and the ten-membered ring in **2** (b)

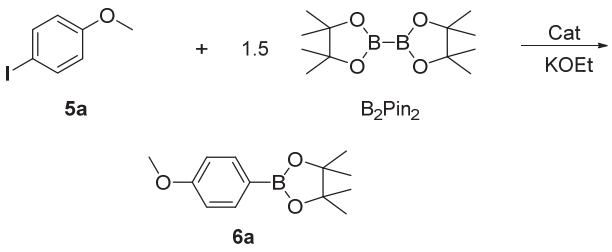
The bond distances are listed as follows: O(1)—Zn(1) 0.20434(13) nm; N(1)—Zn(1) 0.19249(15) nm; Zn(1)—N(21) 0.19810(16) nm; Zn(1)—$N(3)^i$ 0.20431(15) nm; N(2)—$Zn(1)^i$ 0.19810(16) nm; N(3)—$Zn(1)^i$ 0.20431(15) nm.

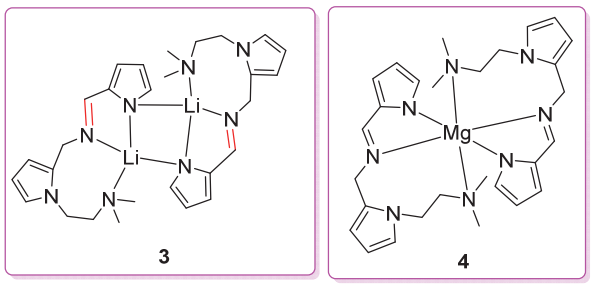
2.3 Borylation of aryl iodides by B_2pin_2 catalyzed by **1** and **2**

Motivated by the previous works of Marder,[19-21] Uchiyama,[22] and our group[35-36] which showed that some zinc complexes could effectively catalyze the borylation reactions between aryl halides and B_2pin_2, we postulated that the synthesized complexes **1** and **2** may be utilized as catalysts for the borylation of aryl iodides.

We embarked on our studies by investigating the borylation of 1-iodo-4-methoxybenzene with B_2pin_2 in the presence of KOEt in THF.[35-36] The reactions in the presence of 10 mol% complexes **1** and **2**, respectively, at 75 ℃ for 12 h gave the corresponding borylated product **6a** in >99% NMR yield (Table 1, Entries 1 and 2). Lowering the catalyst loading to 1 mol% afforded **6a** in 50% and 66% NMR

Table 1 Optimization of reaction conditions[a]





Entry	Cat. (mol%)	Base	Time/h	Temp./℃	Solvent	Yield[b]/%
1	**1** (10)	KOEt	12	75	THF	>99
2	**2** (10)	KOEt	12	75	THF	54
3	**1** (1)	KOEt	12	75	THF	50
4	**2** (1)	KOEt	12	75	THF	66
5	**1** (5)	KOEt	12	60	THF	31
6	**1** (5)	KOEt	6	75	THF	51
7	**3**[c] (10)	KOEt	12	75	THF	0
8	**4**[c] (10)	KOEt	12	75	THF	0
9	^{n}BuLi	NaOEt	12	75	THF	0
10	$^n Bu_2Mg$	NaOEt	12	75	THF	0
11	Et_2Zn	NaOEt	12	75	THF	0

[a] Conditions: B_2Pin_2 (0.375 mmol, 1.5 equiv.), KOEt (0.0375 mmol, 1.5 equiv.), and aryl iodides (0.25 mmol, 1 equiv.) in 1 mL of solvent, 75 ℃, 12 h. [b] Yield determined by ^{1}H NMR using 1,2-dichloroethane as an internal standard. [c] Structures of **3** and **4**.

yields (Table 1, Entries 3 and 4), respectively. Considering that complex **2** has a dinuclear structure, complex **1** is apparently more active than complex **2**. When the catalyst loading of **1** was changed to 5 mol%, and the temperature was reduced from 75 ℃ to 60 ℃, decreased yield of 31% was obtained (Table 1, Entry 5). Shortening the reaction time from 12 to 6 h produced **6a** in 51% NMR yield (Table 1, Entry 6).

Intrigued by the observation that complexes **1** and **2** could catalyze the borylation reaction between 1-iodo-4-methoxybenzene and B_2pin_2, we examined the reaction of 1-iodo-4-methoxybenzene and B_2pin_2 (Table 1, Entries 7 and 8) catalyzed by two compounds $[Li_2(L1)_2]$ (**3**) and $[Mg(L1)_2]$ (**4**), which were reported recently by our group.[48] Unfortunately, the borylation transformation did not occur.

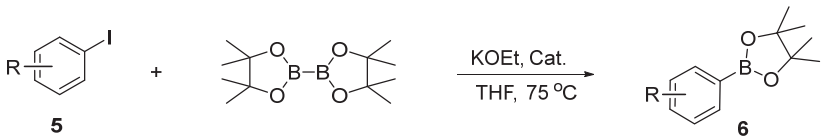
The catalytic activities of ^{n}BuLi, ^{n}Bu$_2$Mg, and Et$_2$Zn (the catalyst loading is 10 mol%) toward the borylation reaction were also tested (Table 1, Entries 9～11). None of the borylation products were detected.

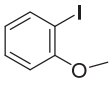
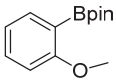
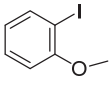
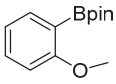
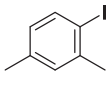
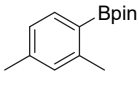
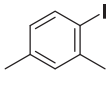
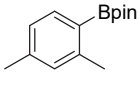
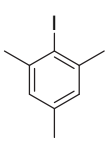
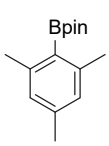
Next, the scope of this transformation was screened under the conditions of Entry 1 in Table 1. A series of aryl iodides were subjected to this borylation (Table 2) by employing **1** as the catalyst. The borylation of 1-iodo-2-methoxybenzene (**5b**) to **6b** proceeded in 82% NMR yield (Table 2, Entry 1). Two or three methyl substituents at the different positions of the phenyl ring were well tolerated, generating borylation products (**6c** and **6d**) in good to moderate yields. Anthranthyl iodide reacted well to provide **6e** in 89% isolated yield. The benzene group could also be tolerated, affording **6f** in 71% isolated yield. Iodobenzene with an electron-withdrawing CF_3 group turned out to be a good substrate for the borylation reaction, producing **6g** in good yield. 1-Iodo-4-hydroxybenzene (**5h**) could not be borylated under the standard conditions. The borylation of 1-iodobenzene (**5i**) occurred smoothly to give borylated product **6i** in 63% isolated yield. Iodobenzenes bearing methyl groups (**5k**, **5l**) worked well to generate the corresponding borylated products in moderate yields.

Unfortunately, when 1-iodobenzene was replaced by 1-bromobenzene and 1-chlorobenzene, respectively, the borylation reactions did not occur (Table 2, Entries 19 and 20).

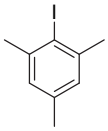
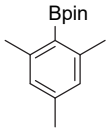
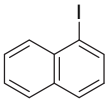
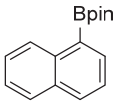
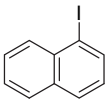
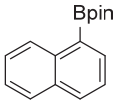
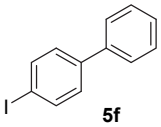
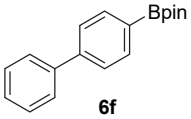
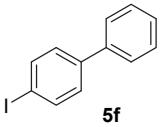
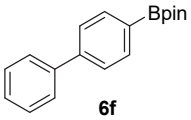
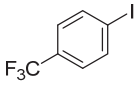
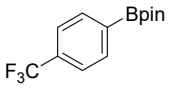
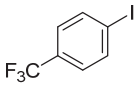
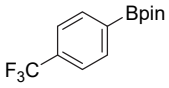
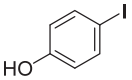
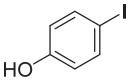
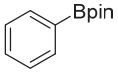
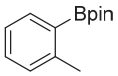
We were very pleased to find that under the same conditions complex **2** could catalyze the borylation of a series of aryl iodides (Table 2, Entries 1～14). However, complex **2** is less active than **1**. We reasoned that the bond distances around each Zn^{II} ion of **2** are shorter than those of **1**, resulting in the more crowded environment of the Zn^{II} ion. Thus, complex **2** is less active.

Table 2 Scope of the borylation of aryl iodides by B_2Pin_2 catalyzed by **1** and **2**[a]

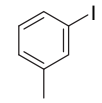
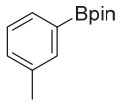
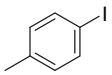
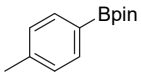


Entry	Reactant	Time/h	Cat. (mol%)	Product	Yield/%
1	 **5b**	12	**1** (5)	 **6b**	82[b]
2	 **5b**	12	**2** (10)	 **6b**	43[b]
3	 **5c**	12	**1** (10)	 **6c**	75[c]
4	 **5c**	12	**2** (10)	 **6c**	64[b]
5	 **5d**	12	**1** (10)	 **6d**	64[c]

Continued

Entry	Reactant	Time/h	Cat. (mol%)	Product	Yield/%
6	 **5d**	12	**2** (10)	 **6d**	83[b]
7	 **5e**	12	**1** (10)	 **6e**	89[c]
8	 **5e**	12	**2** (10)	 **6e**	65[b]
9	 **5f**	12	**1** (10)	 **6f**	71[c]
10	 **5f**	12	**2** (10)	 **6f**	44[b]
11	 **5g**	12	**1** (5)	 **6g**	99[b]
12	 **5g**	12	**2** (10)	 **6g**	71[b]
13	 **5h**	12	**1** (5)	—	NP
14	 **5h**	12	**2** (10)	—	NP
15	 **5i**	12	**1** (10)	 **6i**	63[c]
16	 **5j**	12	**1** (10)	 **6j**	75[c]

Continued

Entry	Reactant	Time/h	Cat. (mol%)	Product	Yield/%
17	 **5k**	12	**1** (10)	 **6k**	41[b]
18	 **5l**	12	**1** (10)	 **6l**	39[c]
19	 **5j**	12	**1** (10)	—	NP[d]
20	 **5k**	12	**1** (10)	—	NP[d]

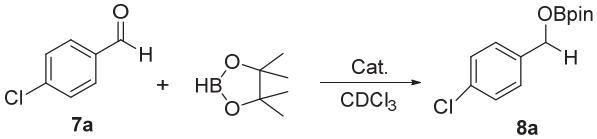
[a] Conditions: B_2Pin_2 (0.375 mmol, 1.5 equiv.), KOEt (0.0375 mmol, 1.5 equiv.), and aryl iodides (0.25 mmol, 1 equiv.) in 1 mL of solvent. 75 ℃, 12 h. [b] Yield determined by ^{1}H NMR using 1,2-dichloroethane as an internal standard. [c] Isolated yield. [d] The reactions were performed using NaOEt as a base.

Mechanistic investigation of the borylation of aryl iodides employing complexes **1** and **2** as catalysts is ongoing. In light of the observation that the borylation of 1-iodo-4-methoxybenzene (**5a**) by B_2Pin_2 proceeded relatively fast and that the reaction was completed in 12 h (＞99% NMR yield; Table 1, Entry 1), we anticipated that the radical mechanism is plausible for this coupling reaction.[35-36] To test this hypothesis, the reactions by adding radical scavengers were carried out. For the coupling reaction of 1-iodo-4-methoxybenzene (**5a**) and B_2Pin_2, product **6a** was not produced (0% yield) when TEMPO (2 equiv.) was utilized as the radical scavenger under the conditions given in Table 2 of Entry 1. Similarly, when another radical scavenger ethene-1,1-diyldibenzene (2 equiv.) was added to the borylation reaction of 1-iodo-4-methoxybenzene (**5a**) by B_2Pin_2, product **6a** was not afforded. These results confirmed the radical mechanism of this borylation transformation.

2.4 Hydroboration of aldehydes and ketones by HBpin catalyzed by **3** and **4**

In light of recent reports by several groups that lithium and magnesium complexes could successfully catalyze the hydroboration reactions of aldehydes and ketones,[48,50-53] we were interested in the catalytic activities of **3** and **4** toward the hydroboration reactions of aldehydes and ketones. To this end, we commenced our investigation by examining the hydroboration of *p*-chlorobenzaldehyde (**7a**) with pinacolborane (HBpin) by utilizing **3** and **4** as catalysts (10 mol% catalyst loading), in $CDCl_3$ at room temperature, respectively (Table 3, Entries 1, 2). We were very pleased to find that *p*-chlorobenzaldehyde can be hydroborated to give *p*-ClC_6H_4OBpin (**8a**) in nearly quantitative yield (99%) after 120 min. Keeping the catalyst loading at 10 mol% and shortening the reaction time to 60 min still furnished **8a** in ＞99% NMR yield (Table 3, Entries 3 and 4). Further shortening the reaction time to 30 min also gave **8a** in ＞99% NMR yield. Efficient hydroboration occurred even at low catalyst loadings (5 and 1 mol%), leading to **8a** in 99% NMR yield (Table 3, Entries 7～10).

Table 3 Optimization of reaction conditions[a]



7a **8a**

Entry	Catalyst	Amt (mol%)	Time/min	Yield[b]/%
1	**3**	10	120	＞99
2	**4**	10	120	＞99
3	**3**	10	60	＞99
4	**4**	10	60	＞99
5	**3**	10	30	＞99
6	**4**	10	30	＞99
7	**3**	5	30	＞99
8	**4**	5	30	＞99
9	**3**	1	30	＞99
10	**4**	1	30	＞99

[a] Conditions: **7a** (0.035 g, 0.25 mmol), HBpin (0.032 g, 0.25 mmol), $CDCl_3$ (0.5 mL) as the solvent, r.t. [b] Yields were determined by ^{1}H NMR spectroscopy.

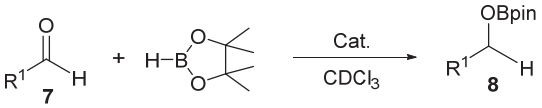
Intrigued by these results, the scope of this hydroboration reaction under a catalyst loading of 1 mol% within 30 min was screened. The excellent applicability of complexes **3** and **4** for the hydroboration of several very challenging aldehyde substrates is shown in Table 4.

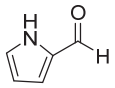
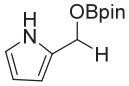
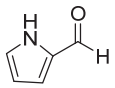
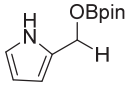
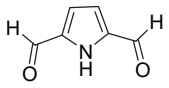
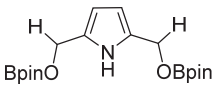
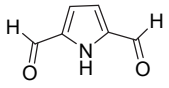
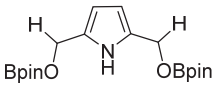
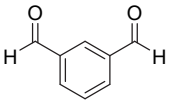
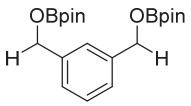
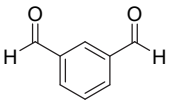
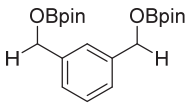
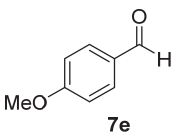
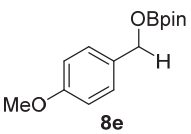
For pyrrole-2-aldehyde (**7b**), excellent chemoselectivity was determined. It was found that only the aldehyde group was hydroborated, leaving the pyrrolyl hydrogen unattacked (Table 4, Entries 1 and 2) by HBpin. The hydrobora-

tion of 1*H*-pyrrole-2,5-dicarbaldehydepyrrole with 2 equiv. of HBpin proceeded smoothly to exclusively afford dihydroborated compound **8c** (Table 4, Entries 3 and 4). Similarly, isophthalaldehyde (**7d**) underwent efficient hydroboration, producing **8d** in ＞99% NMR yield by employing 2 equiv. of HBpin (Table 4, Entries 7 and 8). Benzene aldehydes with electron-donating groups (**7e**, **7f**) were completely transformed into the corresponding borate esters **8e** and **8f** (Table 4, Entries 9 and 10).

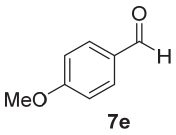
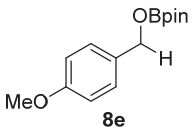
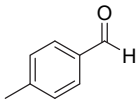
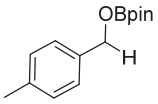
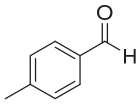
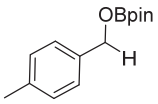
Naturally, the hydroboration of ketones and HBpin catalyzed by **3** and **4** was next studied (Table 5). Previous investigations by several groups indicated that the hydroboration of ketones and HBpin was slower than that of aldehydes.[51,53] Surprisingly, the hydroboration of the examined ketones proceeded rapidly, generating the corresponding borate esters almost qualitatively (＞99% NMR yield) within 30 min under a catalyst loading of 1 mol%. Acetophenones underwent smooth hydroboration and the electron-withdrawing chloro group and electron-donating methyl group were well tolerated (**9a**, **9b**). Diary ketones worked well to yield the corresponding hydroborated compounds in excellent yields. It is noteworthy that hydroboration of the extraordinary sterically challenging substrates proceeded well, as illustrated by the exclusive transformation of several benzophenone substrates (**9c**, **9d**, **9e**) into the corresponding borate esters even though electron-withdrawing [*p*-Cl (**9e**)] and electron-donating [*p*-Me (**9d**)] substituents were attached.

Table 4 Scope of the hydroboration of aldehydes by HBPin catalyzed by **3** and **4**[a]



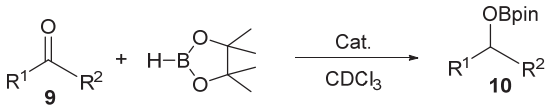
Entry	Reactant	Time/min	Cat.	Product	Yield[b]/%
1	 **7b**	30	**3**	 **8b**	＞99
2	 **7b**	30	**4**	 **8b**	＞99
3	 **7c**	30	**3**	 **8c**	—
4	 **7c**	30	**4**	 **8c**	＞99
5	 **7d**	30	**3**	 **8d**	＞99
6	 **7d**	30	**4**	 **8d**	64
7	 **7e**	30	**3**	 **8e**	＞99

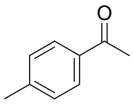
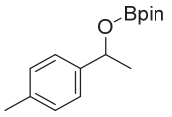
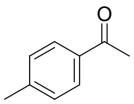
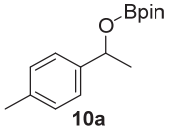
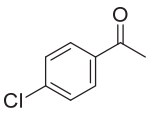
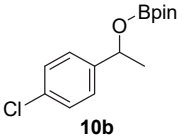
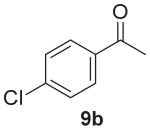
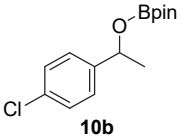
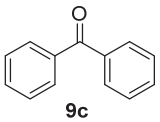
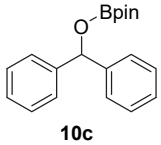
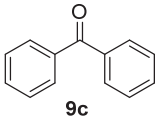
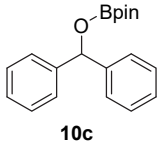
Continued

Entry	Reactant	Time/min	Cat.	Product	Yield[b]/%
8	 **7e**	30	**4**	 **8e**	>99
9	 **7f**	30	**3**	 **8f**	>99
10	 **7f**	30	**4**	 **8f**	>99

[a] Conditions: Cat. (1 mol%), aldehyde (0.25 mmol), HBpin (0.032 g, 0.25 mmol), $CDCl_3$ (0.5 mL), r.t.; [b] yields were determined by ^1H NMR spectroscopy.

Table 5 Scope of the hydroboration of ketones by HBpin catalyzed by **3** and **4**[a]



Entry	Reactant	Time/min	Cat.	Product	Yield[b]/%
1	 **9a**	30	**3**	 **10a**	>99
2	 **9a**	30	**4**	 **10a**	>99
3	 **9b**	30	**3**	 **10b**	>99
4	 **9b**	30	**4**	 **10b**	>99
5	 **9c**	30	**3**	 **10c**	>99
6	 **9c**	30	**4**	 **10c**	>99

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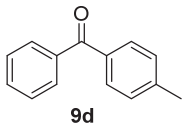
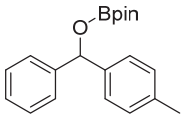
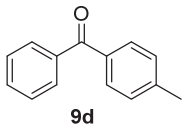
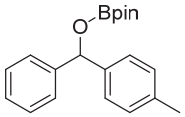
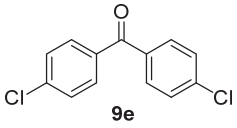
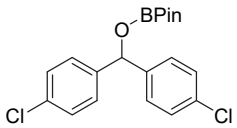
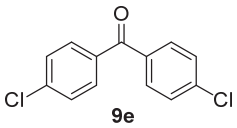
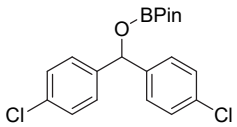
7	 9d	30	**3**	 10d	>99
8	 9d	30	**4**	 10d	>99
9	 9e	30	**3**	 10e	>99
10	 9e	30	**4**	 10e	>99

Conditions: [a] Cat. (1 mol%), ketone (0.25 mmol), HBpin (0.032 g, 0.25 mmol), $CDCl_3$ (0.5 mL), r.t. [b] Yields were determined by ^1H NMR spectroscopy.

3 Conclusions

In conclusion, the syntheses and structures of two zinc complexes [Zn(L1)Et] (**1**) and [$Zn_2(L2)_2(THF)_2$] (**2**) were described. Complex **1** is a mononuclear zinc ethyl compound and complex **2** is a bis-ligated dinuclear molecule. The borylation of aryl iodides by B_2pin_2 promoted by **1** and **2** was investigated. They were both catalytically active to this borylation transformation. Meanwhile, the catalytic behavior of two known compounds [$Li_2(L1)_2$] (**3**) and [$Mg(L1)_2(THF)_2$] (**4**) reported by our group toward the hydroboration of aldehydes and ketones by pinacolborane (HBpin) was also explored. Complexes **3** and **4** were feasible catalysts for this hydroboration reaction. We are now studying the detailed mechanisms of the borylation reactions catalyzed by **1** and **2**. These works are in progress and will be reported soon.

4 Experimental section

4.1 General methods

All reactions were carried out in a glove box filled with nitrogen. Tetrahydrofuran, hexane, and toluene were distilled by drying benzophenone and sodium filaments, and stored in a nitrogen-filled 4 Å molecular sieve. $^nBu_2Mg$, ^{n}BuLi and Et_2Zn were purchased from J&K and Macklin and used directly. Deuterated chloroform was obtained by distillation under reduced pressure after two days of drying with CaH_2 and stored in a nitrogen-filled 4 Å molecular sieve. The ^1H NMR spectra were tested at ambient temperature on instruments with Aglient 400 MHz and Aglient 300 MHz, and the spectra were referenced using TMS signals (δ 0). The ^{13}C NMR spectra were obtained at ambient temperature on a Bruker Avance-III 600 MHz NMR spectrometer. The elemental analyses of C, H and N were performed with a Perkin-Elmer 2400 elemental analyzer. The crystal data were tested at low temperatures with a Bruker AXS tricycle goniometer with a CCD detector and the crystal structures were analyzed using OLEX2 crystal resolution software. CCDC 1887901 (**1**) and 2018590 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html.

4.2 Synthesis of [Zn(L1)Et] (1)

A THF (2 mL) solution of the HL1 ligand (0.2444 g, 1.0 mmol) was slowly added to $ZnEt_2$ solution (1.0 mol/L in *n*-hexane, 1 mL) at −35 ℃. The reaction mixture was allowed to warm to room temperature and stirred overnight. Then the volatiles were removed under reduced pressure to give a light pink solid with 0.307 g (91% yield). Colorless single crystals of **1** suitable for X-ray single crystal diffraction were obtained from a saturated toluene solution at −35 ℃ after one week. ^1H NMR (600 MHz, chloroform-*d*) δ: 8.06 (d, J=0.9 Hz, 1H), 7.13 (q, J=1.1 Hz, 1H), 6.76 (dd, J=3.4, 1.0 Hz, 1H), 6.72 (dd, J=2.9, 1.8 Hz, 1H), 6.39 (dd, J=3.4, 1.6 Hz, 1H), 6.20 (t, J=3.2 Hz, 1H), 6.08 (dd, J=3.5, 1.8 Hz, 1H), 4.69 (s, 2H), 4.40 (s, 2H), 2.90 (t, J=5.1 Hz, 2H), 2.02～1.70 (m, 6H), 1.39 (t, J=8.1 Hz, 3H), 0.26 (q, J=8.1 Hz, 2H); ^{13}C NMR (151 MHz, chloroform-*d*) δ: 159.26, 136.97, 134.60, 131.88, 119.84, 115.96, 111.80, 109.15, 107.42, 60.78, 52.24, 46.22, 13.57, −3.20. Anal. calcd for $C_{16}H_{24}N_4Zn$: C 56.89, H 7.16, N 16.59; found C 56.74, H 7.33, N 16.16.

4.3 Synthesis of $[Zn_2(L2)_2(THF)_2]$ (**2**)

A THF (2 mL) solution of the H_2L2 ligand (0.173, 1.0 mmol) was slowly added to a solution of $ZnEt_2$ (1.0 mmol/L in *n*-hexane, 1 mL) at −35 ℃. The reaction mixture was allowed to warm to room temperature and stirred overnight. Volatiles were removed under reduced pressure to obtain a white solid with 0.277 g (90% yield). The white solid was dissolved in tetrahydrofuran/*n*-hexane solution and stood still at −35 ℃ to give colorless crystals. ^{1}H NMR (300 MHz, pyridine-C_5D_5N) δ: 8.01 (s, 1H), 7.26 (s, 1H), 6.97 (s, 1H), 6.68 (s, 1H), 6.60 (s, 1H), 6.41 (s, 1H), 6.30 (s, 1H), 4.69 (s, 2H), 3.65 (s, 4H), 1.61 (s, 4H); ^{13}C NMR (151 MHz, pyridine-C_5D_5N) δ: 156.98, 134.45, 133.95, 133.11, 125.32, 115.66, 111.29, 107.19, 66.10, 54.10, 29.98, 24.08, 21.12, 12.5. Anal. calcd for $C_{28}H_{34}O_2N_6Zn_2$: C 54.47, H 5.55, N 13.61; found C 53.63, H 5.55, N 13.61.

4.4 General procedure for the borylation reaction of aryl iodides

In a glove box, a mixture of B_2Pin_2 (95.2 mg, 0.375 mmol), KOEt (32.0 mg, 0.375 mmol), complex **1** (18.3 mg, 0.025 mmol), and THF (1 mL) was added to a 25 mL Schlenk flask. The reaction mixture was stirred at room temperature for half an hour. Then an aryl iodide (0.25 mmol) was added. The Schlenk flask was removed from the glove box, and the reaction mixture was heated to 75 ℃ for 12 h. The volatiles were removed under reduced pressure to obtain a crude product. The crude product was purified by column chromatography using ethyl acetate/petroleum ether as the eluent.

2-(4-Methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6a**):[35] A colorless oil (99% determined by ^{1}H NMR using 1,2-dichloroethane as internal standard). ^{1}H NMR (400 MHz, Chloroform-*d*) δ: 7.77 (d, *J*=6.8 Hz, 2H), 6.91 (d, *J*=7.2 Hz, 2H), 3.82 (s, 3H), 1.33 (s, 12H).

2-(2-Methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6b**):[35] A colorless oil (82% yield determined by ^{1}H NMR using 1,2-dichloroethane as internal standard). ^{1}H NMR (400 MHz, Chloroform-*d*) δ: 7.66 (d, *J*=6.0 Hz, 1H), 7.40 (t, *J*=7.0 Hz, 1H), 6.93 (t, *J*=7.0 Hz, 1H), 6.84 (d, *J*=8.0 Hz, 1H), 3.82 (s, 3H), 1.35 (s, 12H).

2-(2,4-Dimethylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6c**):[35] A colorless oil (75%). ^{1}H NMR (300 MHz, Chloroform-*d*) δ: 7.65 (s, 1H), 7.03～6.92 (m, 2H), 2.50 (s, 3H), 2.31 (s, 3H), 1.33 (s, 12H).

2-(2,4,6-Trimethylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6d**):[35] A colorless oil (64%). ^{1}H NMR (300 MHz, Chloroform-*d*) δ: 6.77 (s, 2H), 2.36 (s, 6H), 2.23 (s, 3H), 1.37 (s, 12H).

4,4,5,5-Tetramethyl-2-(naphthalen-1-yl)-1,3,2-dioxaborolane (**6e**):[35] A light-yellow solid (89%). ^{1}H NMR (300 MHz, Chloroform-*d*) δ: 8.68 (d, *J*=8.4 Hz, 1H), 7.99 (d, *J*=7.1 Hz, 1H), 7.83 (d, *J*=8.3 Hz, 1H), 7.73 (d, *J*=8.1 Hz, 1H), 7.44 (t, *J*=6.0 Hz, 1H), 7.40 (d, *J*=9.0 Hz, 2H), 1.32 (s, 12H).

2-([1,1'-Biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6f**):[35] A white solid (71%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ: 7.94 (d, *J*=7.0 Hz, 2H), 7.65 (*J*=7.0, 4H), 7.47 (t, *J*=7.0 Hz, 2H), 7.39 (t, *J*=7.0 Hz, 1H), 1.39 (s, 12H).

4,4,5,5-Tetramethyl-2-(4-(trifluoromethyl)phenyl)-1,3,2-dioxaborolane (**6g**):[35] A white solid (99% determined by ^{1}H NMR using 1,2-dichloroethane as internal standard). ^{1}H NMR (400 MHz, Chloroform-*d*) δ: 7.92 (d, *J*=8.0 Hz, 2H), 7.61 (d, *J*=8.0 Hz, 2H), 1.35 (s, 12H).

4,4,5,5-Tetramethyl-2-phenyl-1,3,2-dioxaborolane (**6i**):[35] A colorless oil (63%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ: 7.81 (d, *J*=7.0 Hz, 2H), 7.45 (t, *J*=7.0 Hz, 1H), 7.38 (t, *J*=7.0 Hz, 2H), 1.36 (s, 12H).

4,4,5,5-Tetramethyl-2-(*o*-tolyl)-1,3,2-dioxaborolane (**6j**):[35] A colorless oil (75%). ^{1}H NMR (300 MHz, Chloroform-*d*) δ: 7.77～7.75 (m, 1H), 7.34～7.29 (m, 1H), 7.17～7.14 (m, 2H), 2.54 (s, 3H), 1.34 (s, 12H).

4,4,5,5-Tetramethyl-2-(*m*-tolyl)-1,3,2-dioxaborolane (**6k**):[35] A colorless oil (41% determined by ^{1}H NMR using 1,2-dichloroethane as internal standard). ^{1}H NMR (300 MHz, Chloroform-*d*) δ: 7.64 (d, *J*=7.9 Hz, 2H), 7.28～7.26 (m, 2H), 2.35 (s, 3H), 1.35 (s, 12H).

4,4,5,5-Tetramethyl-2-(*p*-tolyl)-1,3,2-dioxaborolane (**6l**):[35] A colorless oil (39%). ^{1}H NMR (300 MHz, Chloroform-*d*) δ: 7.56 (d, *J*=7.5 Hz, 2H), 7.20 (d, *J*=7.5 Hz, 2H), 2.28 (s, 3H), 1.45～1.17 (m, 25H).

4.5 General procedure for the hydroboration of aldehydes and ketones

In a glove box, a mixture of aldehyde or ketone (0.25 mmol), HBpin (0.032 g, 0.25 mmol), compound **3** or **4** (1 mol%, 0.0025 mmol), and $CDCl_3$ (0.5 mL) was loaded to a J. Y. NMR tube at room temperature. The hydroboration product was characterized by measuring its ^{1}H NMR spectrum. The yield of the product was calculated by comparing the area of Bpin of the product with that of the unreacted HBpin. The products were not isolated. The colors and states of the hydroboration products were referenced from the literature. The identifies of the hydroboration products were confirmed by comparing the obtained NMR spectra with those of in the literature. The obtained NMR spectra were identical to those reported in the literature.[54-62]

2-((4-Chlorobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**8a**):[54] A colorless oil (99% determined by ^{1}H NMR using 1,2-dichloroethane as internal standard). ^{1}H NMR (400 MHz, Chloroform-*d*) δ: 7.29 (d, *J*=9.7 Hz, 4H), 4.88 (s, 2H), 1.26 (s, 12H).

2-(((4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)-1*H*-pyrrole (**8b**):[55] 99% determined by ^{1}H NMR. ^{1}H NMR (400 MHz, Chloroform-*d*) δ: 8.67 (s, 1H), 6.76 (t, *J*=4.0 Hz, 1H), 6.17～6.12 (m, 2H), 4.85 (s, 2H), 1.29 (s, 12H).

2,5-Bis(((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)-1*H*-pyrrole (**8c**):[55] 99% determined by ^{1}H NMR. ^{1}H NMR (400 MHz, Chloroform-*d*) δ: 8.86 (s, 1H), 6.03～5.98 (m, 2H), 4.79 (s, 4H), 1.26 (s, 24H).

1,3-Bis(((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)benzene (**8d**):[56] 99% determined by ^{1}H NMR.

^{1}H NMR (400 MHz, Chloroform-*d*) δ: 7.33～7.22 (m, 4H), 4.92 (s, 4H), 1.26 (s, 24H).

2-((4-Methoxybenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**8e**):[57] 99% determined by ^{1}H NMR. ^{1}H NMR (400 MHz, Chloroform-*d*) δ: 7.27 (d, J=7.9 Hz, 2H), 6.85 (d, J=7.9 Hz, 2H), 4.84 (s, 2H), 3.78 (s, 3H), 1.25 (s, 12H).

4,4,5,5-Tetramethyl-2-((4-methylbenzyl)oxy)-1,3,2-dioxaborolane (**8f**):[54] A colorless oil (99% determined by ^{1}H NMR). ^{1}H NMR (400 MHz, Chloroform-*d*) δ: 7.27 (d, J=6.6 Hz, 2H), 7.17 (d, J=6.5 Hz, 2H), 4.91 (s, 2H), 2.36 (s, 3H), 1.29 (s, 12H).

4,4,5,5-Tetramethyl-2-(1-(*p*-tolyl)ethoxy)-1,3,2-dioxaborolane (**10a**):[58] A colorless oil (99% determined by ^{1}H NMR). ^{1}H NMR (600 MHz, Chloroform-*d*) δ: 7.28 (d, J=8.0 Hz, 2H), 7.15 (d, J=7.9 Hz, 2H), 5.24 (m, 1H), 2.35 (s, 3H), 1.50 (d, J=6.5 Hz, 3H), 1.25 (s, 12H).

2-(1-(4-Chlorophenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**10b**):[59] A colorless oil (99% determined by ^{1}H NMR). ^{1}H NMR (600 MHz, Chloroform-*d*) δ: 7.30～7.22 (m, 4H), 5.19 (m, 1H), 1.44 (d, J=6.5 Hz, 3H), 1.21 (s, 12H).

2-(Benzhydryloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**10c**):[60] A white solid (99% determined by ^{1}H NMR). ^{1}H NMR (600 MHz, Chloroform-*d*) δ: 7.42 (d, J=7.6 Hz, 4H), 7.32 (t, J=7.6 Hz, 4H), 7.25 (t, J=7.3 Hz, 2H), 6.23 (s, 1H), 1.23 (s, 12H).

4,4,5,5-Tetramethyl-2-(phenyl(p-tolyl)methoxy)-1,3,2-dioxaborolane (**10d**):[61] A white solid (99% determined by ^{1}H NMR). ^{1}H NMR (600 MHz, Chloroform-*d*) δ: 7.37 (d, J=7.4 Hz, 2H), 7.27 (dd, J=7.4 Hz, 4H), 7.19 (t, J=7.3 Hz, 1H), 7.09 (d, J=7.9 Hz, 2H), 6.15 (s, 1H), 2.28 (s, 3H), 1.18 (s, 12H).

2-(Bis(4-chlorophenyl)methoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**10e**):[62] A white solid (99% determined by ^{1}H NMR). ^{1}H NMR (600 MHz, Chloroform-*d*) δ: 7.30～7.24 (m, 8H), 6.11 (s, 1H), 1.19 (s, 12H).

Supporting Information General procedures for the borylation of aryl iodides, and hydroboration of aldehydes and ketones. Crystallographic data of complexes **1** and **2**. NMR spectra of complexes **1** and **2**, and borylation and hydroboration products. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn.

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