Iridium-catalyzed Vinylic C–H Borylation of Cyclic Vinyl Ethers by Bis(pinacolato)diboron

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Vinylic C–H borylation of cyclic vinyl ethers by bis(pinacolato)diboron was effectively catalyzed by iridium complexes comprised of $1/2[Ir(OMe)(cod)]_2$ and 4,4′-di-*tert*-butyl-2,2′-bipyridine in hexane or octane to give the corresponding vinylboron compounds in good yields. The reaction of 1,4-dioxene occurred even at room temperature, whereas the reactions of dihydropyran and dihydrofuran derivatives required a temperature above 80 °C. Although dihydropyran and dihydrofuran themselves produced regioisomeric mixtures of α- and β-borylated products, similar substrates possessing substituents at the γ-position selectively underwent borylation at the α-position.

Vinylic boron derivatives are an important class of compounds as versatile intermediates in synthetic organic chemistry, the utility of which has been amply demonstrated in the synthesis of natural products, biologically active compounds, and functional organic materials by application of numerous carbon–carbon bond-forming reactions.[1] Although they have been generally obtained by hydroboration[2] of alkynes or transmetalation[3] between trialkylborates with vinylic lithium or magnesium reagents, transition-metal-catalyzed borylation has emerged as an interesting strategy for their synthesis.[4] Among these methods, vinylic C–H borylation of alkenes by hydroboranes or diborons has attracted considerable attention from the viewpoints of economy, efficiency, and environmental benignity.[5] Recently, we demonstrated that iridium complexes generated from $1/2[IrCl(cod)]_2$ or $1/2[Ir(OMe)(cod)]_2$ and 2,2′-bipyridine (bpy) or 4,4′-di-*tert*-butyl-2,2′-bipyridine (dtbpy) efficiently catalyzed aromatic C–H borylation[6] by bis(pinacolato)diboron (pin_2B_2, pin = $Me_4C_2O_2$) or pinacolborane (pinBH). The combination of $1/2[Ir(OMe)(cod)]_2$ and dtbpy showed a high level of catalytic activity and allowed room-temperature borylation of arenes and heteroarenes with a stoichiometric amount of substrate to produce the corresponding aromatic boron compounds in high yields. This high level of activity prompted us to apply the catalyst to the borylation of alkenes that have sp^2 C–H bonds similar to aromatic substrates. We report herein the vinylic C–H borylation of cyclic vinyl ethers by pin_2B_2 catalyzed by iridium complexes generated from $1/2[Ir(OMe)(cod)]_2$ and dtbpy to

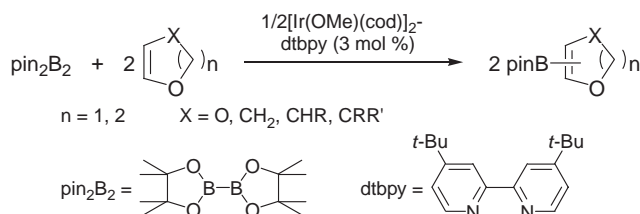afford the corresponding vinylic boron compounds in good yields (Scheme 1).

1,4-Dioxene (2.0 mmol), which does not cause regioselectivity problems, was initially chosen as a substrate, and its reactions with pin_2B_2 (1.0 mmol) were investigated at 25 °C for 8 h in hexane to optimize Ir^I precursors (0.03 mmol/Ir) and ligands (0.03 mmol) (Table 1). Among the catalysts examined, the combination of $1/2[Ir(OMe)(cod)]_2$ and dtbpy, which exhibited a high level of activity toward aromatic C–H borylation,[6] again catalyzed the vinylic C–H borylation to form 2-boryl-1,4-dioxene in 81% yield based on boron atoms in the diboron (Entry 1). The choice of catalyst precursor was crucial for the reaction. Although the combinations of the Ir^I precursor possessing basic hydroxy or phenoxy ligand with dtbpy showed similar catalytic activities (Entries 2 and 3), the less-basic Ir^I acetate complex, the chloride complex, or the cationic complex in combination with dtbpy formed no borylated products (Entries 4–6). The high catalyst efficiency of the alkoxide or hydroxide complex can be attributed to the more facile formation of a tris(boryl)Ir^{III} intermediate,[6,7] which is reactive toward boryla-

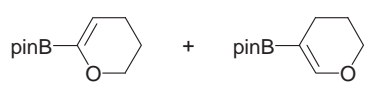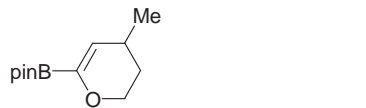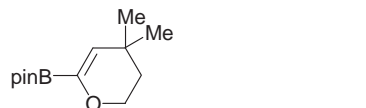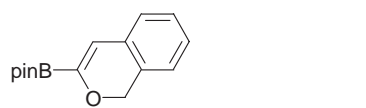**Table 1.** Reaction conditions for 1,4-dioxene[a]
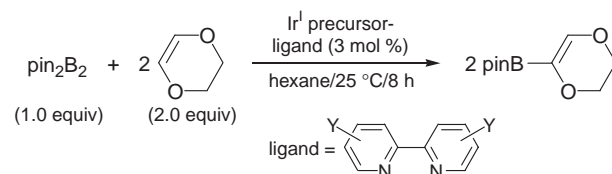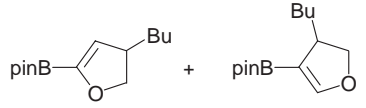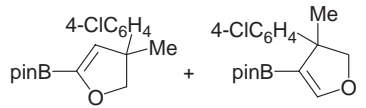
Entry	Ir^I precursor	Ligand	Yield/%[b]
1	$1/2[Ir(OMe)(cod)]_2$	dtbpy	81
2	$1/2[Ir(OH)(cod)]_2$	dtbpy	71
3	$1/2[Ir(OPh)(cod)]_2$	dtbpy	72
4	$1/2[Ir(OAc)(cod)]_2$	dtbpy	0
5	$1/2[IrCl(cod)]_2$	dtbpy	0
6	$[Ir(cod)_2]BF_4$	dtbpy	0
7	$1/2[Ir(OMe)(cod)]_2$	none	0
8	$1/2[Ir(OMe)(cod)]_2$	bpy	50
9	$1/2[Ir(OMe)(cod)]_2$	3,3′-di-Me-bpy	0
10	$1/2[Ir(OMe)(cod)]_2$	4,4′-di-Me-bpy	75
11	$1/2[Ir(OMe)(cod)]_2$	5,5′-di-Me-bpy	55
12	$1/2[Ir(OMe)(cod)]_2$	6,6′-di-Me-bpy	0
13	$1/2[Ir(OMe)(cod)]_2$	4,4′-di-MeO-bpy	71
14	$1/2[Ir(OMe)(cod)]_2$	4,4′-di-Cl-bpy	0
15	$1/2[Ir(OMe)(cod)]_2$	4,4′-di-O_2N-bpy	0

[a]A mixture of a pin_2B_2 (1.0 mmol), 1,4-dioxene (2.0 mmol), an Ir precursor (0.03 mmol/Ir), a ligand (0.03 mmol), and hexane (6 mL) was stirred at 25 °C for 8 h. [b]GC yields based on boron atom in pin_2B_2.

Scheme 1.

Table 2. C–H borylation of cyclic vinyl ethers[a]

Entry	Product	Yield/%[b]
1	pinB—⬡—O + pinB—⬡—O	64 (75:25)
2	pinB—⬡(Me)—O	61
3	pinB—⬡(Me,Me)—O	65
4	pinB—⬡—O (benzofused)	81
5	pinB—⬠—O + pinB—⬠—O	75 (49:51)
6	pinB—⬠(Bu)—O + pinB—⬠(Bu)—O	71 (86:14)
7	pinB—⬠(4-ClC₆H₄,Me)—O + pinB—⬠(4-ClC₆H₄,Me)—O	73 (95:5)

[a]All reactions were carried out at 80 °C for 8 h by using pin$_2$B$_2$ (1.0 mmol), a cyclic vinyl ether (3.0 mmol), [Ir(OMe)(cod)]$_2$ (0.015 mmol), dtbpy (0.03 mmol), and octane (6 mL) in a sealed tube. [b]GC yields based on boron atom in pin$_2$B$_2$.

tion of vinylic C–H bonds. 2,2′-Bipyridine and derivatives of this structure were particularly effective as ligands for Ir (Entry 7). Catalysts bearing dtbpy, bpy, 4,4′-di-Me-bpy, and 5,5′-di-Me-bpy displayed similar reactivity (Entries 1, 8, 10, and 11), but there was no reaction in the case of catalysts bearing 3,3′-di-Me-bpy and 6,6′-di-Me-bpy (Entries 9 and 12). These results indicated the importance of a parallel arrangement of two pyridine rings and a relatively unhindered coordination sphere at Ir.

Reactions catalyzed by complexes containing electron-rich derivatives of bpy generated more active catalysts than did reactions catalyzed by complexes containing electron-poor derivatives (Entries 1, 10, and 13–15). The results described above are comparable to those observed in aromatic C–H borylation.[6]

Representative results of vinylic C–H borylation of dihydropyran, dihydrofuran, and their derivatives by pin$_2$B$_2$ catalyzed by the combination of 1/2[Ir(OMe)(cod)]$_2$ and dtbpy are summarized in Table 2. Since these substrates were less reactive than

1,4-dioxene, the reactions were carried out by using 3.0 equiv of the substrates at 80 °C in octane in a sealed tube. At that time, we assumed that the borylation of these substrates selectively proceeds at the α-position, because an electronegative oxygen atom would activate the α-C–H bond. However, dihydropyran and dihydrofuran themselves produced regioisomeric mixtures of α- and β-borylated products in ratios of 75:25 and 49:51, respectively (Entries 1 and 5). Our previous studies on aromatic C–H borylation demonstrated that the reaction does not occur at sterically hindered C–H bonds ortho to a substituent.[6] Thus, we examined substrates possessing substituents at the γ-position to increase the α-selectivity of the borylation. Actually, introduction of substituents at the γ-position sufficiently improved the α-selectivity. The reactions of γ-substituted and γ,γ-disubstituted dihydropyran derivatives yielded α-borylated products as single isomers (Entries 2–4), while those of the corresponding dihydrofuran derivatives still yielded small amounts of β-borylated products (Entries 6 and 7). It notable that substrates having both vinylic and aromatic C–H bonds selectively underwent borylation at the vinylic C–H bond to produce only vinylboron compounds (Entry 4).

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