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Aromatic C–H Borylation Catalyzed by Hydrotris(pyrazolyl)borate Complexes of Rhodium and Iridium

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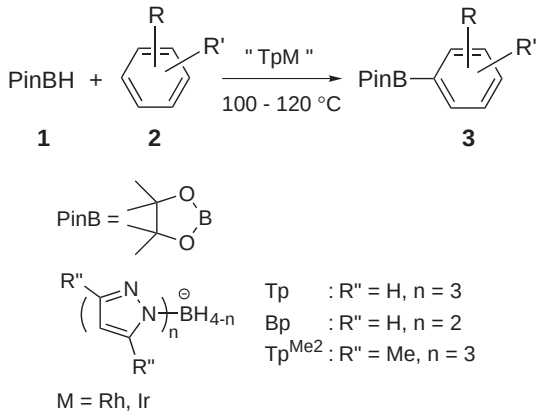
Dehydrogenative coupling of 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (pinacolborane) with arenes occurred in good yield in the presence of a catalytic amount of [Rh(Tp^{Me2})(cod)] (Tp^{Me2} = hydrotris(3,5-dimethylpyrazolyl)borate, cod = 1,5-cyclooctadiene), [Ir(Tp)(cod)] (Tp = hydrotris(pyrazolyl)borate), and related (pyrazolyl)borate complexes. The catalytic activity was strongly affected by substituents on the pyrazolyl rings.

Aryldialkoxyboranes are useful intermediates in organic synthesis, particularly, for reactions involving carbon–carbon bond formation through the palladium-catalyzed Suzuki–Miyaura cross-coupling reaction.[1] They can be easily prepared by the palladium-catalyzed borylation of aryl halides with tetra(alkoxo)diborons[2] or with dialkoxyboranes, such as 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1**, pinacolborane).[3] From environmental and economical points of view, however, direct borylation of aromatic C–H bonds of arenes **2** is more attractive. Therefore, much attention has been focused on the C–H borylation of aromatic hydrocarbons **2** using bis(pinacolato)diboron or **1** as a boron source, and numerous catalyst systems, such as [Ir(Cp*)H(PMe$_3$)(BO$_2$C$_2$Me$_4$)] (Cp* = η^5-pentamethylcyclopentadienyl),[4] [Rh(Cp*)(η^4-C$_6$Me$_6$)],[5] [{RhCl$_2$(Cp*)}$_2$],[6] [RhCl(N$_2$){P(*i*-Pr)$_3$}$_2$],[6] [{IrCl(cod)}$_2$]/2,2′-bipyridine (cod = 1,5-cyclooctadiene),[2,7] and [Ir(η^5-indenyl)(cod)]/diphosphine,[8] have been reported to affect this dehydrogenative coupling reaction.

Hydrotris(pyrazolyl)borate (Tp) and a series of derivates with different substitutions on the pyrazolyl rings have become versatile ligands in organometallic chemistry.[9] They have some interesting features: the κ^3 isomer of Tp is isoelectronic with η^5-cyclopentadienyl, and a nitrogen-based chelate structure results from κ^3–κ^2 isomerism. The structural similarity with Cp* and 2,2′-bipyridine suggested to us that Tp derivatives could be also efficient as supporting ligands for the borylation of arenes **2**. Additionally, activation of C–H bonds by hydrotris(pyrazolyl)borate complexes of rhodium(I) or iridium(I) have been reported.[10] In this paper, we wish to report the aromatic C–H borylation using pinacolborane (**1**) in the presence of a catalytic amount of rhodium(I) or iridium(I) complexes coordinated with (pyrazolyl)borate derivatives (Scheme 1).



Scheme 1. Aromatic C–H borylation using pinacolborane.

Table 1. Screening of Various Catalysts[a)]

Entry	Catalyst	Temp /°C	Yield /%[b)]
1	1/2[{RhCl(cod)}$_2$]/TpK	100	74
2	1/2[{RhCl(cod)}$_2$]/BpK	100	24
3	1/2[{RhCl(cod)}$_2$]/Tp^{Me2}K	100	80
4	[Rh(Tp^{Me2})(cod)]	100	88
5	1/2[{RhCl$_2$(Cp*)}$_2$]	100	28
6	1/2[{IrCl(cod)}$_2$]/TpK	100	40
7	1/2[{IrCl(cod)}$_2$]/TpK	120	71
8	[Ir(Tp)(cod)]	120	88
9	1/2[{IrCl(cod)}$_2$]/BpK	120	77
10	1/2[{IrCl(cod)}$_2$]/Tp^{Me2}K	120	20
11	1/2[{IrCl$_2$(Cp*)}$_2$]	120	2

a) Reaction conditions: **1** (0.5 mmol), **2a** (5 mmol), catalyst (0.005 mmol), 100–120 °C, 16 h. b) GC yields are based on **1**.

An initial screening was performed using metal precursors [{MCl(cod)}$_2$] (M = Rh and Ir) and additional (pyrazolyl)borate ligands for the dehydrogenative coupling of benzene **2a** and **1**. The results are summarized in Table 1. These complexes and potassium salts are commercially available and can be handled in air. Treatment of **1** with **2a** (10 molar amounts) in the presence of 0.01 molar amount of a metal complex prepared in situ from [{RhCl(cod)}$_2$] (0.005 molar amount) and TpK (0.015 molar amount) was found to lead to the corresponding phenylpinacolborane **3a** in 74% yield (Entry 1). Using an excess amount of **2a**, the formation of diborylated products was completely suppressed. Although dihydrobis(pyrazolyl)borate (Bp) was less efficient than Tp as a supporting ligand under the same conditions (Entry 2), the use of potassium hydrotris(3,5-dimethylpyrazolyl)borate (Tp^{Me2}K) showed improved reactivity, affording phenylboronate **3a** in 80% yield (Entry 3). When the catalyst [Rh(Tp^{Me2})(cod)] was isolated and used for the aromatic C–H borylation,[11] product **3a** was obtained in 88% yield (Entry 4). [Rh(Tp^{Me2})] system had higher catalytic activity than the previous Rh(Cp*) system, as [{RhCl$_2$(Cp*)}$_2$] was less effective at 100 °C (Entry 5).[5,6]

The present borylation was also performed using iridium(I) analogues. The iridium(I) catalysts coordinated with a Tp ligand[12] reacted with **2a** and afforded **3a** in 71–88% yields (Entries 7 and 8), although a reaction temperature of 120 °C

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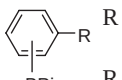
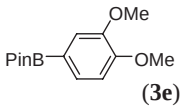
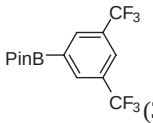
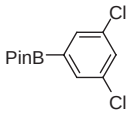
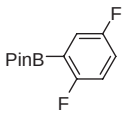
Table 2. Isomer Distributions for C–H Borylation[a)]

Entry	Product **3**	Yield/% (*o*:*m*:*p*)[b)]	
		[Rh(Tp^{Me2})(cod)]	[Ir(Tp)(cod)]
1	 R = Me (**3b**)	74[c)] (0:62:38)	81 (0:64:36)
2	BPin R = OMe (**3c**)	57 (4:63:33)	74 (3:66:31)
3	R = CF_3 (**3d**)	54 (0:70:30)	99 (0:68:32)
4	 (**3e**)	30	72 [66][d)]
5	 (**3f**)	10	86 [84][d)]
6		trace	65 [61][d)]
7	 (**3h**)	29	88 [85][d)]

a) Reaction conditions: **1** (0.5 mmol), **2** (5 mmol), catalyst (0.005 mmol), 120 °C, 16 h. b) Yield and isomer ratio were determined by GC analysis. c) A 23% yield of $PhCH_2BPin$ was also obtained. d) Isolated yield.

was required (Entries 6 and 7). In contrast to the rhodium(I)-catalyzed reactions, the use of Tp^{Me2} gave quite lower yield (Entry 10), whereas Bp was found to be an effective ligand for this reaction (Entry 9). Presumably, the formation of the κ^2 isomer is essential for the Ir(Tp) system to catalyze the C–H borylation, and the steric hindrance around the iridium center would have a profound influence on the catalytic activity.

The results obtained with arenes **2**, giving arylpinacolboranes **3** similarly as above, are listed in Table 2. The yields and product ratios were determined by GC analysis of crude reaction mixtures. The presence of functional groups did not interfere with the outcome of the iridium(I)-catalyzed reaction. However, the rhodium(I)-catalyzed reaction lacked wide applicability to functionalized substrates **2**, presumably due to coordination of hetero atoms to the rhodium metal center yielding an inactive species (Entries 2–6). Furthermore, the present C–H borylation using Tp complexes showed the following common features: (i) benzylic activation of toluene (**2b**) increased for the rhodium catalyst system versus the iridium analogue (Entry 1);[4b,7f] (ii) the reaction of monosubstituted arenes **2b**–**2d** resulted in a 2:1 mixture of meta and para isomers and electronic characteristics of the substituent on **2** hardly affected the statistical meta/para ratios (Entries 1–3); and (iii) disubstituted arenes **2e**–**2h** were functionalized regioselectively for steric reasons (Entries 4–6).[4b,5b,7a–d,8]

In conclusion, we have demonstrated that rhodium(I) complexes coordinated with Tp derivatives and analogous iridium(I) complexes catalyzed the dehydrogenative coupling of arenes **2** with pinacolborane (**1**). Above all, [Rh(Tp^{Me2})(cod)] and [Ir(Tp)(cod)] showed high catalytic activities in the aromatic C–H borylation; however, the mechanism for this borylation is unclear at the present stage. Further investigations of this and related C–H functionalizations are currently underway in our laboratory.

Experimental

All the experiments were carried out under a nitrogen atmosphere in oven-dried (120 °C) glassware. Pinacolborane (**1**) and all arenes **2** were purchased from commercial sources and purified by distillation before use. [{RhCl(cod)}$_2$], [{IrCl(cod)}$_2$], Tp$^-$K$^+$, Bp$^-$K$^+$, Tp^{Me2-}K$^+$, [{RhCl$_2$(Cp*)}$_2$], and [{IrCl$_2$(Cp*)}$_2$] were purchased and used without purification. [Rh(Tp^{Me2})(cod)][12] and [Ir(Tp)(cod)][13] were prepared by literature methods.

Typical Procedure for Synthesis of Dialkoxyarylborane. [Ir(Tp)(cod)] or [Rh(Tp^{Me2})(cod)] (5 μmol) was added to a resealable Schlenk tube. The tube was evacuated and backfilled with nitrogen and then charged with arene **2** (5 mmol) and pinacolborane (**1**) (0.50 mmol). After being stirred at 120 °C for 18 h, the reaction mixture was analyzed by GC and GC-MS. The product was extracted with ether, washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by Kugelrohr distillation to afford the desired dialkoxyarylborane **3**. **3a**: identical spectroscopic data to those previously described.[3b] **3b**: the above procedure afforded an inseparable mixture of *m*-, *p*-**3b**, and $PhCH_2BPin$. By comparing with the retention time of the prepared authentic **3b** (isomer mixture, $m:p = 69:31$)[7a] and $PhCH_2BPin$,[13] the product distribution was determined by GC and GC-MS analysis of the crude product. **3c**: the above procedure afforded an inseparable mixture of *o*-, *m*-, and *p*-**3c**. By comparing with the retention time of the prepared authentic mixture of **3c** (isomer mixture, $o:m:p = 1:74:25$),[7a] the product distribution was determined by GC and GC-MS analysis of the crude product. **3d**: the above procedure afforded an inseparable mixture of *m*- and *p*-**3d**. By comparing with the retention time of the prepared authentic **3d** (isomer mixture, $m:p = 70:30$),[7a] the product distribution was determined by GC and GC-MS analysis of the crude product. **3e**: identical spectroscopic data to those previously described.[5b] **3f**: identical spectroscopic data to those previously described.[5b] **3g**: identical spectroscopic data to those previously described.[7a] **3h**: ^{1}H NMR ($CDCl_3$): δ 1.36 (s, 12H), 6.98 (br s, 1H), 7.10 (br s, 1H), 7.39 (br s, 1H). ^{13}C NMR ($CDCl_3$): δ 24.77, 84.21, 116.54 (dd, $J = 8.3$ and 26.9 Hz), 119.69 (dd, $J = 9.3$ and 24.8 Hz), 122.22 (dd, $J = 9.3$ and 22.8 Hz), 158.84 (d, $J = 242.1$ Hz), 162.92 (d, $J = 247.3$ Hz). HR-MS (EI): m/z calcd for $C_{12}H_{15}O_2F_2B$ [M$^+$]: 240.1133; found: 240.1131.

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