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# Synthesis of pinacol arylboronates via cross-coupling reaction of bis(pinacolato)diboron with chloroarenes catalyzed by palladium(0)–tricyclohexylphosphine complexes

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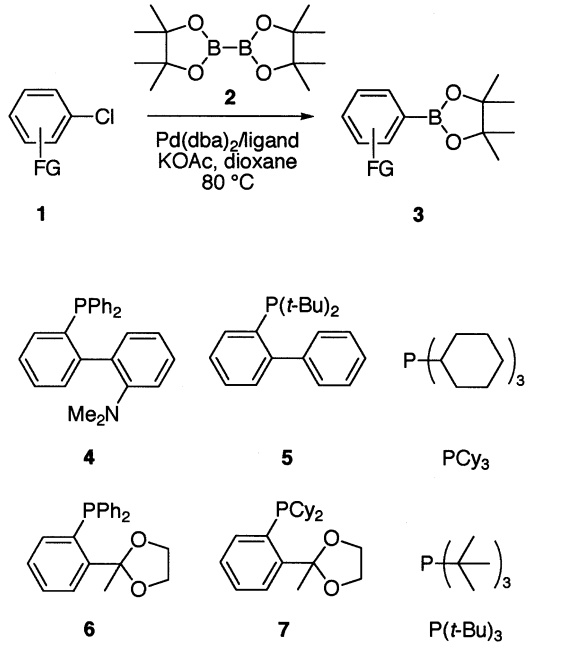
**Abstract**—The cross-coupling reaction of bis(pinacolato)diboron with chloroarenes to yield pinacol arylboronates was carried out in 1,4-dioxane at 80°C in the presence of KOAc (1.5 equiv.) and $Pd(dba)_2$/2.4$PCy_3$ (3–6 mol%). The catalyst was also effective to carry out analogous coupling with aryl bromides or triflates under milder conditions than those of the previous procedures catalyzed by $PdCl_2$(dppf) in DMSO. 

## 1. Introduction

The cross-coupling reaction between tetra(alkoxo)diborons and aryl halides or triflates in the presence of a base and $PdCl_2$(dppf) provides a convenient and direct method for the synthesis of arylboronates from aryl electrophiles.[1] The coupling reaction is feasible with various functional groups, e.g. $CO_2Me$, COMe, $NO_2$, and CN, which need protection–deprotection in the two-step procedure for preparing arylboronic acids or esters from magnesium or lithium reagents.[2] The protocol offers a direct and efficient route to variously functionalized boronic esters, the utility of which has been amply demonstrated in the synthesis of natural products,[3] biologically active compounds,[4] and functional materials.[5] On the other hand, the direct preparation of arylboronic esters from aryl halides or triflates now allows a one-pot, two-step procedure[1b,6] and a solid-phase method[7] for the synthesis of unsymmetrical biaryls. The cross-coupling reaction of pinacolborane with haloarenes in the presence of a palladium catalyst and triethylamine reported by Masuda and Murata is another convenient and economical variant for the preparation of such pinacol arylboronates.[8]

In this paper, we report the palladium-catalyzed coupling reaction of chloroarenes (**1**) with bis(pinacolato)diboron (**2**) for the synthesis of pinacol arylboronates (**3**) (Scheme 1). Chloroarene is a desirable substrate for the cross-coupling reactions in combinatorial synthesis since a large number of derivatives are commercially available. Although their oxidative addition to palladium(0) complexes is very slow, a catalyst in situ generated from $Pd(dba)_2$ and $PCy_3$ efficiently catalyzed the reaction at 80°C. The catalyst can be also effective to carry out the coupling reaction of less reactive aryl bromides or triflates bearing electron-donating substituents under mild conditions.




**Scheme 1.** Synthesis of pinacol arylboronates via cross-coupling reaction of diboron with chloroarenes.

*Keywords*: boron and compounds; coupling reactions; aryl halides; palladium and compounds.

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## 2. Results and discussion

### 2.1. Reaction conditions

Various phosphine ligands are effective in stabilizing the palladium(0) species; however, the stoichiometry of phosphine to palladium and the bulkiness[9] or donating ability[9,10] of phosphine ligands change the reactivity of catalysts toward oxidative addition and transmetalation.[11] Palladium complexes having fewer than four phosphines, a weakly coordinating ligand such as $AsPh_3$,[12] or a bulky phosphine such as P(*o*-tolyl)$_3$,[13] provide a highly reactive catalyst because of the ready formation of the coordinatively unsaturated species. Another role of the ligand is electron donation to the palladium(0) metal center, which was amply demonstrated in the cross-coupling reaction of chloroarenes. Bulky and highly donating ligands, such as P(*t*-Bu)$_3$,[14] *o*-(di-*t*-butylphosphino)biphenyl (**5**),[15] and *N*-heterocyclic carbenes,[16] were recognized to be highly effective for chloroarenes even at room temperature. The high reactivity of the complexes involving these ligands is attributable to the strong electron-donating ability of the ligand to the metal center and the ready dissociation of the ligand to generate a coordinatively unsaturated species. It was also noted that less bulky phosphines, such as (dicyclohexylphosphino)arenes (e.g. **7**)[17] and tricyclohexylphosphine ($PCy_3$),[14,18] are practical ligands giving a more stable complex at high temperature.

A screening of representative phosphine ligands reported in the cross-coupling reactions of chloroarenes is summarized in Table 1. The catalysts were in situ generated by stirring a mixture of Pd(dba)$_2$ (3 mol%) and a phosphine ligand (3.3–7.2 mol%) at room temperature to be used directly for the coupling reaction of diboron (**2**) (1.1 equiv.) and 4-chlorobenzaldehyde (1.0 equiv.) in the presence of KOAc (1.5 equiv.) in dioxane. Use of triarylphosphines commonly resulted in low conversions and low yields due to their low electron-donating ability (entries 2–5), whereas more electron-rich tris(*p*-methoxyphenyl)phosphine exhibited better catalyst activity than triphenylphosphine (entries 2 and 4). Among the four phosphine ligands developed by Buchwald and Guram (**4**–**7**), **4**, **5**, and **7** achieved high yields in a range of 68–78% (entries 6–9). However, a combination of Pd(dba)$_2$ and $PCy_3$ (2.4 equiv.) was finally recognized to be the most efficient catalyst to achieve a quantitative conversion and an almost quantitative yield at 80°C (entry 10). On the other hand, the palladium–P(*t*-Bu)$_3$ complex resulted in low yields at temperatures in the range of 20–80°C (entry 11).

**Table 1.** Effect of ligands in the reaction of bis(pinacolato)diboron (**2**, 1.1 mmol) with 4-chlorobenzaldehyde (1.0 mmol) in dioxane (6 ml) at 80°C for 16 h in the presence of KOAc (1.5 mmol), Pd(dba)$_2$ (3 mol%), and a phosphine ligand (3.3–7.2 mol%)

| Entry | Ligand | Ligand (equiv.)[a] | Yield (%)[b] |
|---|---|---|---|
| 1 | None | | 1 |
| 2 | $PPh_3$ | 2.4 | 19 |
| 3 | P(*o*-Me$C_6H_4$)$_3$ | 2.4 | 36 |
| 4 | P(*p*-Me$OC_6H_4$)$_3$ | 2.4 | 44 |
| 5 | dppf[c] | 1.1 | 18 |
| 6 | **4** | 1.1 | 78 |
| 7 | **5** | 2.4 | 68 |
| 8 | **6** | 1.1 | 10 |
| 9 | **7** | 1.1 | 71 |
| 10 | $PCy_3$ | 2.4 | 94 |
| 11 | P(*t*-Bu)$_3$ | 2.4 | 58 |

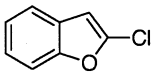
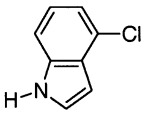
[a] Equivalents to palladium metal.
[b] GC yields based on 4-chlorobenzaldehyde.
[c] 1,1′-Bis(diphenylphosphino)ferrocene.

KOAc was found to be the best base for the coupling of diboron (**2**) with bromo- or iodoarenes because a stronger base, such as $K_3PO_4$ and $K_2CO_3$, prompted the further coupling of arylboronates (**3**) with haloarenes, resulting in a competitive formation of homo-coupling biaryls (36–60% yields). The use of KOAc was also significant in the present coupling reaction catalyzed by a palladium–$PCy_3$ complex. The reaction was almost quantitative with KOAc (94%), whereas use of $K_2CO_3$, $K_3PO_4$, and KOPh resulted in 85, 75, and 51% yields, respectively.

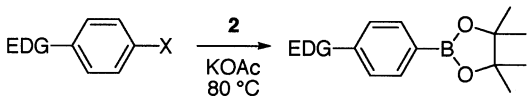
### 2.2. Scope and limitation

The borylation of the representative chloroarenes is summarized in Table 2. The reaction was very fast, completing within 6 h for activated chloroarenes possessing an electron-withdrawing group such as $NO_2$, CN, CHO, and $CO_2$Me (entries 1–6). However, the presence of *ortho*-substituents (entries 2 and 4) or electron-donating substituents (entries 8–13) slowed down the reaction significantly, thus requiring prolongation of the time to 48 h or a higher catalyst loading (6 mol%) to complete the reaction. Analogous to the previous borylation of aryl bromides, iodides, and triflates, the reaction tolerated various functional groups. The reaction is applicable for the borylation of heteroaromatic chlorides such as 3-chloropyridine (entry 16), 2-chlorobenzo[*b*]furan (entry 17), 4-chloroindole (entry 18), and presumably other derivatives reported previously; however, 2-chloropyridine failed to yield the corresponding

**Table 2.** Synthesis of pinacol arylboronates

| Entry | Chloroarene | Mol%[a] | Time (h) | Yield (%)[b] |
|---|---|---|---|---|
| 1 | 4-$O_2NC_6H_4Cl$ | 3 | 4 | 88 |
| 2 | 2-$O_2NC_6H_4Cl$ | 3 | 48 | 72 |
| 3 | 4-$NCC_6H_4Cl$ | 3 | 4 | 98 |
| 4 | 2-$NCC_6H_4Cl$ | 3 | 48 | 72 |
| 5 | 4-$OHCC_6H_4Cl$ | 3 | 6 | 94 |
| 6 | 4-$MeO_2CC_6H_4Cl$ | 3 | 6 | 87 |
| 7 | $C_6H_5Cl$ | 6 | 48 | 91 |
| 8 | 4-$MeC_6H_4Cl$ | 6 | 48 | 92 |
| 9 | 2-$MeC_6H_4Cl$ | 3 | 48 | 86 |
| 10 | 4-$MeOC_6H_4Cl$ | 6 | 48 | 78 |
| 11 | 3-$MeOC_6H_4Cl$ | 6 | 48 | 92 |
| 12 | 2-$MeOC_6H_4Cl$ | 3 | 48 | 70 |
| 13 | 4-$Me_2NC_6H_4Cl$ | 6 | 48 | 73 |
| 14 | 2-Chloronaphthalene | 3 | 48 | 77 |
| 15 | 2-Chloropyridine | 3 | 48 | 0 |
| 16 | 3-Chloropyridine | 3 | 48 | 82 |
| 17 |  | 3 | 48 | 73 |
| 18 |  | 3 | 48 | 72 |

[a] Mol% of catalyst.
[b] GC yields based on chloroarenes.




| EDG | X= | catalyst/solvent | time/h | yield/% |
|---|---|---|---|---|
| MeO | I | $PdCl_2$(dppf)/DMSO | 2 | 82 |
| | Br | $PdCl_2$(dppf)/DMSO | 24 | 69 |
| | Br | $Pd(dba)_2$-$PCy_3$/dioxane | 7 | 81 |
| | OTf | $PdCl_2$(dppf)-dppf/dioxane | 13 | 93 |
| | OTf | $Pd(dba)_2$-$PCy_3$/dioxane | 2 | 83 |
| $Me_2N$ | I | $PdCl_2$(dppf)/DMSO | 6 | 90 |
| | Br | $PdCl_2$(dppf)/DMSO | 24 | 23 |
| | Br | $Pd(dba)_2$-$PCy_3$/dioxane | 6 | 81 |

**Scheme 2.** Cross-coupling reaction of dibron with electron-rich aryl electrophiles.

boronate (entry 15). Since the boronic acids and esters adjacent to a heteroatom are highly susceptible to hydrolytic protodeboronation,[19] the coupling reaction can be often followed by hydrolytic boron–carbon bond cleavage. Although the reaction in dioxane can be much more insensitive to such protodeboronation than that in DMSO, the 2-borylpyridine was quantitatively led to free pyridine. Such side-reaction giving the reduction product of haloarenes in small amounts was also observed in the reactions of 2-chloronitrobenzene and 2-chlorobenzonitrile (entries 2 and 4).

The use of such highly electron-donating ligand ($PCy_3$) was also advantageous to significantly shorten the reaction times of the borylation of electron-rich aryl bromides or triflates (Scheme 2). The borylation of iodoarenes is fast under the previous conditions using $PdCl_2$(dppf) in DMSO, even for a dimethylamino derivative; however, analogous reactions of the bromides or triflates are significantly slow. In contrast to the palladium–dppf complex, $Pd(dba)_2$/$PCy_3$ completed the reactions of both 4-methoxy and 4-dimethylamino derivatives within 7 h. Although the efficiency of $Pd(dba)_2$/$PCy_3$ has not yet been studied in detail for other halides or triflates, the catalyst would serve to achieve complete conversions within shorter reaction times than those of the previously reported procedure using $PdCl_2$(dppf).

## 3. Experimental

### 3.1. Reagents

$Pd(dba)_2$[20] and bis(pinacolato)diboron[21] were synthesized by the reported procedures. All phosphine ligands purchased from Strem were used directly without further purification. 1,4-Dioxane was distilled from sodium and KOAc was dried in vacuo.

### 3.2. Representative procedure (Table 2)

A 25 ml flask assembled a magnetic stirring bar, a septum inlet, and a condenser was charged with $Pd(dba)_2$ (0.017 g, 0.03 mmol, 3 mol%) and tricyclohexylphosphine ($PCy_3$, 0.020 g, 0.072 mmol), and flushed with nitrogen. Dioxane (6 ml) was added and the resulting mixture was then stirred for 30 min at room temperature. Bis(pinacolato)diboron (**2**, 0.279 g, 1.1 mmol), KOAc (0.147 g, 1.5 mmol), and a chloroarene (1.0 mmol) were added successively. After being stirred at 80°C for the period shown in Table 2, the reaction mixture was treated with water (5 ml) at room temperature. The product was extracted with benzene, washed with brine, and dried over $MgSO_4$. Kugelrohr distillation gave an analytically pure sample.

The following arylboronates were prepared by the general procedure, unless otherwise noted.

**3.2.1. 2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-benzonitrile (entry 4).** $^1$H NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 1.39 (s, 12H), 7.52 (dt, $J$=1.5, 7.4 Hz, 1H), 7.57 (dt, $J$=1.5, 7.4 Hz, 1H), 7.70 (dd, $J$=1.5, 7.3 Hz, 1H), 7.88 (d, $J$=7.3 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS) $\delta$ 24.77, 84.77, 117.24, 118.96, 131.06, 131.54, 133.40, 135.82; $^{11}$B NMR (128 MHz, $CDCl_3$, $BF_3$·$OEt_2$) $\delta$ 30.74; exact mass calcd for $C_{13}H_{16}BNO_2$ 229.1274, found 229.1270.

**3.2.2. 3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-anisole (entry 11).** $^1$H NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 1.35 (s, 12H), 3.84 (s, 3H), 7.01 (dd, $J$=2.7, 8.1 Hz, 1H), 7.30 (t, $J$=7.8 Hz, 1H), 7.33 (d, $J$=2.7 Hz, 1H), 7.40 (d, $J$=7.1 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS) $\delta$ 24.85, 55.24, 83.82, 117.91, 118.64, 127.17, 128.93, 159.02; $^{11}$B NMR (128 MHz, $CDCl_3$, $BF_3$·$OEt_2$) $\delta$ 30.56; exact mass calcd for $C_{13}H_{19}BO_3$ 234.1427, found 234.1432.

**3.2.3. 3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-pyridine (entry 16).** $^1$H NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 1.36 (s, 12H), 7.28 (ddd, $J$=0.9, 4.9, 7.6 Hz, 1H), 8.05 (dt, $J$=7.6, 1.8 Hz, 1H), 8.67 (dd, $J$=2.0, 4.9 Hz, 1H), 8.95 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS) $\delta$ 24.84, 84.20, 123.05, 142.18, 151.98, 155.48; $^{11}$B NMR (128 MHz, $CDCl_3$, $BF_3$·$OEt_2$) $\delta$ 31.00; exact mass calcd for $C_{11}H_{16}BNO_2$ 205.1274, found 205.1281.

**3.2.4. 2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-benzo[*b*]furan (entry 17).** $^1$H NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 1.39 (s, 12H), 7.23 (t, $J$=7.4 Hz, 1H), 7.34 (dt, $J$=1.2, 7.8 Hz, 1H), 7.40 (s, 1H), 7.57 (d, $J$=8.5 Hz, 1H), 7.63 (d, $J$=7.8 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS) $\delta$ 24.77, 84.68, 111.97, 119.53, 121.88, 122.71, 125.93, 127.48, 157.51; $^{11}$B NMR (128 MHz, $CDCl_3$, $BF_3$·$OEt_2$) $\delta$ 27.51; exact mass calcd for $C_{14}H_{17}BO_3$ 244.1270, found 244.1264.

**3.2.5. 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)indole (entry 18).** $^1$H NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 1.39 (s, 12H), 7.06 (ddd, $J$=1.0, 2.1, 3.0 Hz, 1H), 7.21 (dd, $J$=7.1, 8.1 Hz, 1H), 7.26 (t, $J$=2.8 Hz, 1H), 7.50 (d, $J$=8.1 Hz, 1H), 7.64 (dd, $J$=0.7, 7.1 Hz, 1H), 8.17 (br s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS) $\delta$ 24.97, 83.38, 104.50, 113.96, 121.30, 124.58, 127.84, 132.49, 135.09; $^{11}$B NMR (128 MHz, $CDCl_3$, $BF_3$·$OEt_2$) $\delta$ 31.05; exact mass calcd for $C_{14}H_{18}BNO_2$ 243.1430, found 243.1422.

Syntheses of 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nitrobenzene (entry 1),[1,8] 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nitrobenzene (entry 2),[1] 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile (entry 3),[1,8] 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (entry 5),[1] methyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (entry 6),[1] (4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (entry 7),[1,8] 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)toluene (entry 8),[8] 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)toluene (entry 9),[8] 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)anisole (entry 10),[1,8] 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)anisole (entry 12),[1] *N*,*N*-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (entry 13),[1,8] and 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalene (entry 14)[8] were previously reported.

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