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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 equivs) and Pd(dba)₂/2.4PCy₃ (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 PdCl₂(dppf) in DMSO.

Keywords: Boron and compounds; Coupling reactions; Aryl halides; Palladium and compounds

Introduction

The cross-coupling reaction between tetra(alkoxo)diborons and aryl halides or triflates in the presence of a base and PdCl₂(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., CO₂Me, COMe, NO₂, 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 method⁷ 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 is commercially available. Although their oxidative addition to palladium(0) complexes is very slow, a catalyst *in situ* generated from Pd(dba)₂ and PCy₃ 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>>

Results and Discussion

Reaction conditions

Various phosphine ligands are effective in stabilizing the palladium(0) species; however, the stoichiometry of phosphine to palladium and the bulkiness⁹ 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 $\text{P}(o\text{-tolyl})_3$,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 $\text{P}(t\text{-Bu})_3$,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 a practical ligand 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 equivs) and 4-chlorobenzaldehyde (1.0 equiv) in the presence of KOAc (1.5 equivs) 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 PCy₃ (2.4 equivs) 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 °C to 80 °C (entry 11).

<<Table 1>>

KOAc was found to be the best base for the coupling of diboron (**2**) with bromo- or iodoarenes because a stronger base, such as K₃PO₄ and K₂CO₃, 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-PCy₃ complex. The reaction was

almost quantitative with KOAc (94%), whereas use of K₂CO₃, K₃PO₄, and KOPh resulted in 85%, 75%, and 51% yields respectively.

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 NO₂, CN, CHO, and CO₂Me (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. Analogously 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 boronate (entry 15). Since the boronic acids and esters adjacent to a heteroatom are highly susceptible to hydrolytic protodeboration,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 protodeboration 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).

<<Table 2>>

The use of such highly electron-donating ligand (PCy₃) 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 PdCl₂(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/PCy₃ completed the reactions of both 4-methoxy and 4-dimethylamino derivatives within 7 h. Although the efficiency of Pd(dba)₂/PCy₃ 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 PdCl₂(dppf).

<<Scheme 2>>

Experimental

Reagents

Pd(dba)₂²⁰ and bis(pinacolato)diboron²¹ 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*.

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 (PCy₃, 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 MgSO₄. Kugelrohr distillation gave an analytically pure sample.

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

2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzotrile (entry 4). ¹H NMR (400 MHz, CDCl₃, TMS) δ 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); ¹³C NMR (100 MHz, CDCl₃, TMS) δ 24.77, 84.77, 117.24, 118.96, 131.06, 131.54, 133.40, 135.82; ¹¹B NMR (128 MHz, CDCl₃, BF₃•OEt₂) δ 30.74; exact mass calcd for C₁₃H₁₆BNO₂ 229.1274, found 229.1270.

3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)anisole (entry 11). ¹H NMR (400 MHz, CDCl₃, TMS) δ 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) δ 24.85, 55.24, 83.82, 117.91, 118.64, 127.17, 128.93, 159.02; ^{11}B NMR (128 MHz, CDCl_3 , $\text{BF}_3\cdot\text{OEt}_2$) δ 30.56; exact mass calcd for $\text{C}_{13}\text{H}_{19}\text{BO}_3$ 234.1427, found 234.1432.

3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (entry 16). ^1H NMR (400 MHz, CDCl_3 , TMS) δ 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) δ 24.84, 84.20, 123.05, 142.18, 151.98, 155.48; ^{11}B NMR (128 MHz, CDCl_3 , $\text{BF}_3\cdot\text{OEt}_2$) δ 31.00; exact mass calcd for $\text{C}_{11}\text{H}_{16}\text{BNO}_2$ 205.1274, found 205.1281.

2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[*b*]furan (entry 17). ^1H NMR (400 MHz, CDCl_3 , TMS) δ 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) δ 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 , $\text{BF}_3\cdot\text{OEt}_2$) δ 27.51; exact mass calcd for $\text{C}_{14}\text{H}_{17}\text{BO}_3$ 244.1270, found 244.1264.

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)indole (entry 18). ^1H NMR (400 MHz, CDCl_3 , TMS) δ 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) δ 24.97, 83.38, 104.50, 113.96,

121.30, 124.58, 127.84, 132.49, 135.09; ¹¹B NMR (128 MHz, CDCl₃, BF₃•OEt₂) δ 31.05; exact mass calcd for C₁₄H₁₈BNO₂ 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)benzotrile (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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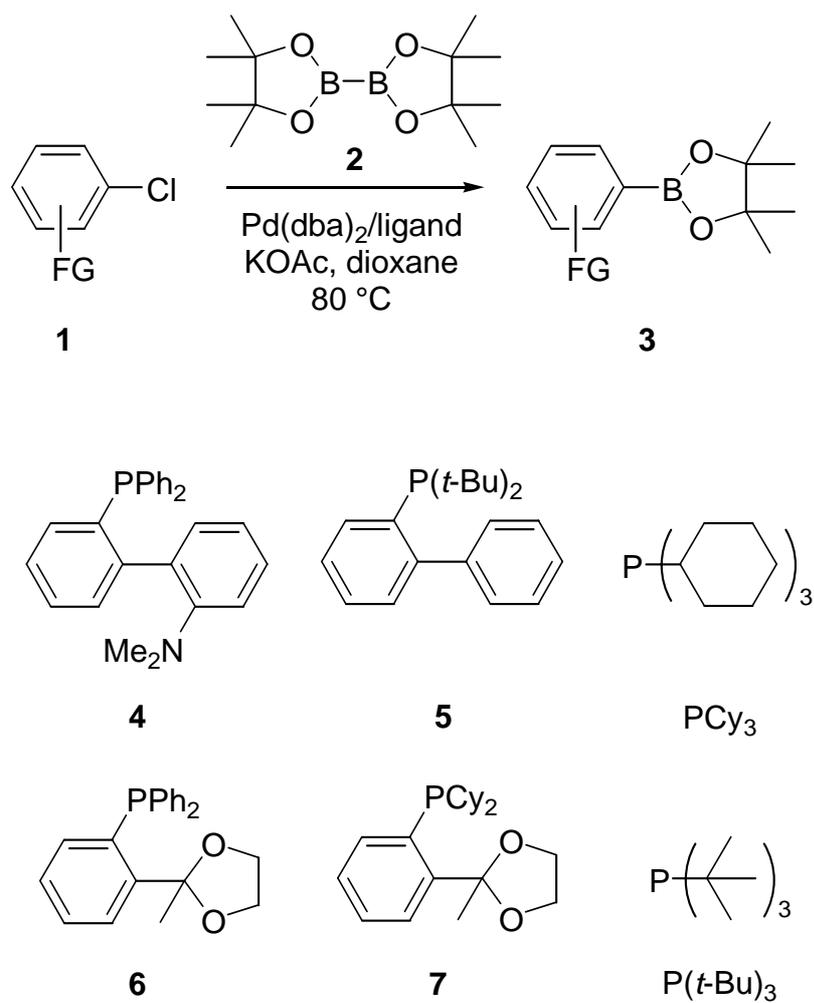
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Scheme 1. Synthesis of pinacol arylboronates via cross-coupling reaction of diboron with chloroarenes.

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%)

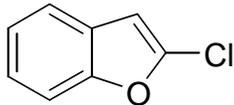
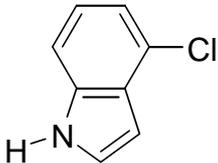
entry	ligand	ligand/equivs ^a	yield/% ^b
1	none		1
2	PPh ₃	2.4	19
3	P(<i>o</i> -MeC ₆ H ₄) ₃	2.4	36
4	P(<i>p</i> -MeOC ₆ H ₄) ₃	2.4	44
5	dppf ^c	1.1	18
6	4	1.1	78
7	5	2.4	68
8	6	1.1	10
9	7	1.1	71
10	PCy ₃	2.4	94
11	P(<i>t</i> -Bu) ₃	2.4	58

^aEquivalents to palladium metal.

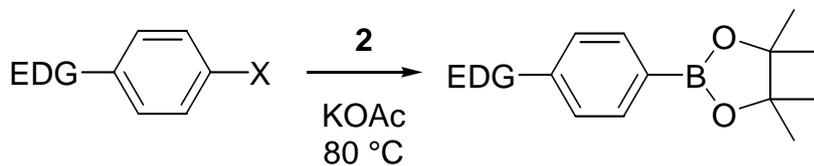
^bGC yields based on 4-chlorobenzaldehyde.

^c1,1'-bis(diphenylphosphino)ferrocene.

Table 2. Synthesis of pinacol arylboronates

entry	chloroarene	mol% ^a	time/h	yield/% ^b
1	4-O ₂ NC ₆ H ₄ Cl	3	4	88
2	2-O ₂ NC ₆ H ₄ Cl	3	48	72
3	4-NCC ₆ H ₄ Cl	3	4	98
4	2-NCC ₆ H ₄ Cl	3	48	72
5	4-OHCC ₆ H ₄ Cl	3	6	94
6	4-MeO ₂ CC ₆ H ₄ Cl	3	6	87
7	C ₆ H ₅ Cl	6	48	91
8	4-MeC ₆ H ₄ Cl	6	48	92
9	2-MeC ₆ H ₄ Cl	3	48	86
10	4-MeOC ₆ H ₄ Cl	6	48	78
11	3-MeOC ₆ H ₄ Cl	6	48	92
12	2-MeOC ₆ H ₄ Cl	3	48	70
13	4-Me ₂ NC ₆ H ₄ Cl	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

^aMol% of catalyst.^bGC 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 ₂ N	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 diboron with electron-rich aryl electrophiles.