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# Room Temperature Ni(0)/PCy<sub>3</sub>-Catalyzed Coupling Reactions of Aryl Arenesulfonates with Bis(pinacolato)diboron

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**Abstract:** Room temperature Ni(0)/PCy<sub>3</sub>-catalyzed cross-coupling reactions of aryl arenesulfonates with bis(pinacolato)diboron are described. The Ni(0)/PCy<sub>3</sub> catalysts, generated from Ni(COD)<sub>2</sub> and PCy<sub>3</sub>, or air-stable 4-MeOC<sub>6</sub>H<sub>4</sub>Ni(II)(PCy<sub>3</sub>)<sub>2</sub>OTs, were efficient catalyst systems for the Miyaura borylation reactions of a variety of aryl arenesulfonates with bis(pinacolato)diboron. The mild reaction condition, the easy availability of the catalysts and good yields make these reactions potentially useful in organic synthesis.

#### Introduction

Arylborons have been extensively employed for bond-forming reactions including the Suzuki cross-coupling reaction.<sup>1</sup> In the past decades, transition metal-catalyzed coupling reactions of aryl (pseudo)halides with diborons has become one of attractive ways for the preparation of arylborons,<sup>2-6</sup> While aryl halides and aryl triflates have been the most common substrates for this borylation reaction, readily available aryl tosylates and mesylates have rarely been used as coupling partners for this reaction.<sup>7</sup> In the few reports of borylation reaction with aryl tosylates or mesylates as substrates, elevated temperatures, 80 °C or higher, were generally needed for the reaction.<sup>7</sup>

In our laboratory, we have been interested in employing aryl arenesulfonates as reaction partners for transition metalcatalyzed bond-forming reactions, particularly under mild reaction conditions. We have documented room temperature Ni(0)/PCy<sub>3</sub>-calayzed cross-coupling reaction of aryl/alkenyl arenesulfonates with arylboronic acids.<sup>8</sup> The mild reaction condition and our understanding of the reaction mechanism prompted us to wonder whether the borylation reaction of aryl arenesulfonates with diborons could be achieved at room temperature with Ni(0)/PCy<sub>3</sub> as the catalyst. Herein our study on room temperature Ni(0)/PCy<sub>3</sub>-catalyzed cross-coupling reactions of aryl arenesulfonates with bis(pinacolato)diboron is reported. **Results and Discussion** 

We have previously showed that  $Ni(0)/PCy_3$  readily undergoes oxidative addition with aryl tosylates and this step should not be a rate-determining step,<sup>8c</sup> we reasoned that the transmetalation of ArNi(II)(PCy<sub>3</sub>)<sub>2</sub>OTs with bis(pinacolato)diboron might likely be the key step for the generation of arylborates. Since the transmetalation step has been reported to be influenced by the base employed,<sup>1</sup> we started our study by examining different bases and our results are listed in Table 1. As KOAc was the best base in reported Pd(OAc)<sub>2</sub>/DPPF system,<sup>3a</sup> KOAc was first tested, but a low conversion was observed (Table 1, entry 1). Other common inorganic bases, K<sub>3</sub>PO<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, KF and *t*-BuOK, were then tested and K<sub>3</sub>PO<sub>4</sub> was found to give a better result (Table 1, entries 2-5). Because the existence of a small amount of water in the reaction system helped Ni(0)/PCy3-catalyzed Suzuki cross-coupling reactions,<sup>8b</sup> we next examined the reaction with only degassed, but not dried THF, higher conversions were observed except for the reaction with t-BuOK as the base (Table 1, entries 6-10), with  $K_3PO_4$  as the best base (Table 1, entry 7). Two other solvents, toluene and dioxane, were also tested and THF was found to be the best solvent (Table 1, entries 6, 11-12). Reducing the amount of the base hindered the reaction and 3-4 equivalents of base gave the best results (Table 1, entries 13-15). The use of 1.5 equivalents of bis(pinacolato)diboron led to a lower conversion (Table 1, entry 16). As a comparison, the reaction without Ni(COD)<sub>2</sub>/PCy<sub>3</sub> was also carried out and no product was observed (Table 1, entry 17).

Table 1. Room Temperature Ni(COD)\_2/PCy<sub>3</sub>-Catalyzed Borylation Reaction of p-Tolyl Tosylate with Bis(pinacolato)diboron <sup>a</sup>

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$\neg$	$\rightarrow OTs + OB - BOC + SOC + OCS + OCS$	1000000000000000000000000000000000000	$ = -B_{O}^{O} + $
Entry	Base	Solvent Conv	version (%)
1	KOAc (3 equiv.)	THF (dried & degassed)	6
2	K <sub>3</sub> PO <sub>4</sub> (3 equiv.)	THF (dried & degassed)	33
3	K <sub>2</sub> CO <sub>3</sub> (3 equiv.)	THF (dried & degassed)	6
4	KF (3 equiv.)	THF (dried & degassed)	13
5	KO-t-Bu (3 equiv.)	THF (dried & degrassed)	0
6	KOAc (3 equiv.)	THF (degassed)	10
7	K <sub>3</sub> PO <sub>4</sub> (3 equiv.)	THF (degassed)	77
8	K <sub>2</sub> CO <sub>3</sub> (3 equiv.)	THF (degassed)	23
9	KF (3 equiv.)	THF (degassed)	29
10	KO-t-Bu (4 equiv.)	THF (degassed)	0
11	K <sub>3</sub> PO <sub>4</sub> (3 equiv.)	Toluene (degassed)	12 <sup>c</sup>
12	K <sub>3</sub> PO <sub>4</sub> (3 equiv.)	Dioxane (degassed)	44 <sup>c</sup>
13	K <sub>3</sub> PO <sub>4</sub> (1 equiv.)	THF (degassed)	18 <sup>c</sup>
14	K <sub>3</sub> PO <sub>4</sub> (2 equiv.)	THF (degassed)	47.5 <sup>c</sup>
15	K <sub>3</sub> PO <sub>4</sub> (4 equiv.)	THF (degassed)	95
16	K <sub>3</sub> PO <sub>4</sub> (4 equiv.)	THF (degassed)	46 <sup>d</sup>
17	K <sub>3</sub> PO <sub>4</sub> (4 equiv.)	THF (degassed)	0 <sup>e</sup>

b

a. Reaction conditions: to sylate (1.0 equiv.), diboron (3.0 equiv.),  $\mathrm{Ni}(\mathrm{COD})_2$ 

(5 mol%), PCy3 (20 mol%), base (1-4 equiv.), THF (2 mL), room temperature. b. Conversions based on <sup>1</sup>H NMR analysis. c. Ground base was used. d. 1.5 equiv. of

diboron was used, e. 0% of Ni(COD)/PCv3was used.

By using 4 equivalents of  $K_3PO_4$  as the base and degassed THF as the solvent, we next examined a variety of aryl tosylates for the room temperature Ni(0)/PCy<sub>3</sub>-catalyzed borylation reaction. Our results are summarized in Table 2. As shown in Table 2, the Ni(COD)<sub>2</sub>/PCy<sub>3</sub> system was found to be a general catalyst for both activated and deactivated aryl tosylates, including those with *ortho*-, *meta*- and *para*-substituents. Complete conversions and good isolated yields were observed for all aryl arenesulfonates employed (Table 2, entries 1-14). Aryl benzenesulfonates were also found to be suitable substrates for the reaction and good yields were observed (Table 2, entry 15-17). An aryl mesylate was observed to be less reactive than aryl tosylates, and the reaction involving it as the coupling partner required longer reaction time to go to completion (Table 2, entry 18).

Table 2. Room Temperature Ni(COD)\_2/PCy\_3-Catalyzed Borylation Reaction of Aryl Arenesufonates with Bis(pinacolato)diboron  $^{\rm a}$ 

4=-080	$\rightarrow 0$ $0 \neq 3\%$ Ni(0	3%Ni(COD) <sub>2</sub> /12% PCy <sub>3</sub> 0 /	
Ar-OSC	$V_2 A r + O O O K_3 PO$	AI -B. O	
Entry	Ar-OSO <sub>2</sub> Ar'	Yield (%) <sup>b</sup>	
1	- $OTs(1a)$	87	
2	<b>OTs</b> (1b)	85	
3	MeO - OTs (1c)	88	
4	OTs (1d)	79 <sup>c</sup>	
5	$\rightarrow OTs$ (1e)	82	
6	$\sim$ OTs(1f)	87	
7	O - O - OTs (1g)	90	
8	$OT_{a}$	83	
9		82 <sup>c</sup>	
10	O $O$ $OTs(1j)$	87	
11	$Ph - OTs(\mathbf{1k})$	85	
12	$F_{3}C$ (11)	87	
13	$MeO_2C$ $OTs^{(1m)}$	88	
14	$\frac{\text{MeO}_2\text{C}}{\text{MeO}} \rightarrow \text{OTs}^{(1n)}$	85	
15		80	
16	SOSO <sub>2</sub> Ph (1p)	77	
17	$MeO - OSO_2Ph$ (1q)	82	
18	-OMs (1r)	73 <sup>c</sup>	

a. Reaction conditions: aryl sulfonates (0.2 mmol), bis(pinacolato)diboron (3 equiv.), K<sub>3</sub>PO<sub>4</sub> (4 equiv.), THF (1 mL), room temperature. b. Isolated yields. c. Reaction time: 24 h.

As Ni(COD)<sub>2</sub>/PCy<sub>3</sub>, especially Ni(COD)<sub>2</sub>, are very air-sensitive, we wondered whether air-stable Ni(II) complexes could be employed as operationally convenient catalysts for this Miyaura borylation reaction. Because 4-MeOC<sub>6</sub>H<sub>4</sub>Ni(II)(PCy<sub>3</sub>)<sub>2</sub>OTs, the oxidative addition adduct of 4-MeOC<sub>6</sub>H<sub>4</sub>OTs with Ni(COD)<sub>2</sub>/PCy<sub>3</sub>, is readily accessible and air-stable, and has been established as Ni(0)/PCy<sub>3</sub> source for the cross-coupling reactions of aryl acids,8 arylboronic arenesulfonates with 4-MeOC<sub>6</sub>H<sub>4</sub>Ni(II)(PCy<sub>3</sub>)<sub>2</sub>OTs naturally emerged as our choice for this exploration. We found that by using 4-MeOC<sub>6</sub>H<sub>4</sub>Ni(II)(PCy<sub>3</sub>)<sub>2</sub>OTs as the catalyst, the cross-coupling reactions of aryl arenesulfonates with bis(pinacolato)diboron occurred smoothly and good to high yields were obtained (Table 3). These results suggested that 4-MeOC<sub>6</sub>H<sub>4</sub>Ni(II)(PCy<sub>3</sub>)<sub>2</sub>OTs as well as its analogs could be an operationally convenient substitute for the Ni(COD)<sub>2</sub>/PCy<sub>3</sub> catalyst system for the room temperature cross-coupling reactions of aryl arenesulfonates with bis(pinacolato)diboron.

Table 3. Room Temperature 4-MeOC\_6H\_4Ni(II)(PCy\_3)\_2OTs-Catalyzed Cross-Couplings of Aryl Arenesulfonates with Bis(pinacolato)diboron  $^{\rm a}$ 

Ar-OSO	$_{2}\text{Ar'}$ + 0 $_{O}\text{B}$ -B $_{O}$ + $\frac{5\% 4 \cdot \text{MeOC}_{e}\text{H}_{4}\text{Ni}(II)(\text{PC})}{K_{3}\text{PO}_{4}, \text{THF},}$ r, 12-24 h	$Ar = B_0^{O}$
Entry	Ar-OSO <sub>2</sub> Ar'	Yield (%) <sup>b</sup>
1		89
2	<b>OTs</b> (1b)	87
3	$MeO \langle - \rangle OTs (1c)$	95
4	$\bigcirc$ -OTs (1d)	72
5	$\rightarrow$ -OTs (1e)	80
6	$\sim$ OTs(1f)	86
7	$0 \rightarrow 0 \text{ or } 1g$	81
8	$OTs(\mathbf{lh})$	81
9	OTs (1i)	83 <sup>c</sup>
10	O $O$ $OTs(1j)$	81
11	Ph = O OTs(1k)	79
12	$\sim$ $OTs$ (1m)	78
13	$\frac{\text{MeO}_2\text{C}}{\text{MeO}} - \frac{1}{\sqrt{2}} - OTs(1n)$	80
14	$\frac{\text{MeO}_2\text{C}}{\text{OTs}(10)}$	77
15		78
16	∠>OSO <sub>2</sub> Ph (1q)	79
17	$MeO \sim OSO_2 Ph$ (1r)	92
18	- OMs (1s)	70 <sup>c</sup>

a. Reaction conditions: aryl sulfonates (0.2 mmol), bis(pinacolato)diboron (3 equiv.), K<sub>3</sub>PO<sub>4</sub> (4 equiv.), THF (1 ml), room temperature. b. Isolated yields. c. Reaction time: 48 hours.

### Conclusions

We have demonstrated that room temperature Miyaura borylation reaction of readily available aryl arenesulfonates with bis(pinacolato)diboron occurred smoothly with the Ni(0)/PCy<sub>3</sub> catalyst system. Ni(COD)<sub>2</sub>/PCy<sub>3</sub> was found to be an efficient catalyst system for the Miyaura borylation reactions of a variety of aryl arenesulfonates with bis(pinacolato)diboron. To circumvent the air-sensitivity issue associated with the Ni(COD)<sub>2</sub>/PCy<sub>3</sub> catalyst system, we explored to use air-stable 4-MeOC<sub>6</sub>H<sub>4</sub>Ni(II)(PCy<sub>3</sub>)<sub>2</sub>OTs, the oxidative addition adduct of Ni(COD)<sub>2</sub>/PCy<sub>3</sub> with 4-MeOC<sub>6</sub>H<sub>4</sub>OTs, as the catalyst for the borylation reaction. We found 4-MeOC<sub>6</sub>H<sub>4</sub>Ni(II)(PCy<sub>3</sub>)<sub>2</sub>OTs was as efficient as Ni(COD)<sub>2</sub>/PCy<sub>3</sub>. The mild reaction condition, the easy availability of the catalyst systems, and good coupling yields make this Ni(0)/PCy3-catalyzed borylation reaction potentially useful in organic synthesis.

#### **Experimental Section**

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General Procedure for Ni(COD)<sub>2</sub>/PCy<sub>3</sub>-Catalyzed Cross-Coupling Reactions of Aryl Arenesulfonates with Bis(pinacolato)diboron: In a alovebox with an N<sub>2</sub>-atmosphere, to а vial containing bis(pinacolato)diboron (1.5 mmol, 3 equiv.), potassium phosphate (2.0 mmol, 4 equiv.), THF (5 mL), bis(1,5-cyclopentadiene) nickel(0) (0.025 mmol, 5 mol%) and tricyclohexylphosphine (0.1 mmol, 20 mol%), aryl tosylate or aryl benzenesulfonate (0.5 mmol, 1.0 equiv.) was added. The mixture was allowed to react at the room temperature for 6-24 h. After quenching with water, the reaction mixture was extracted with ethyl acetate. The organic layer was washed with brine and then evaporated under vacuum. Flash chromatography on silica gel yielded the desired products.

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**Keywords:** aryl arenesulfonates • bis(pinacolato)diboron • nickel(0) • tricyclohexylphosphine • cross-coupling

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## **Entry for the Table of Contents**

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B-BO 3%Ni(COD)2/12%PCy ArOSO<sub>2</sub>Ar' + or 4-MeOC<sub>6</sub>H<sub>4</sub>Ni(PCy<sub>3</sub>)<sub>2</sub>OTs K<sub>3</sub>PO<sub>4</sub>, THF, r.t., 6-48 h Ó Ó 70-92%

Room temperature  $Ni(0)/PCy_3$ -catalyzed cross-coupling reactions of aryl arenesulfonates with bis(pinacolato)diboron to form arylborates are described.

## Borylation

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Room temperature Ni(0)/PCy<sub>3</sub>-Catalyzed Coupling Reactions of Aryl Arenesulfonates with Bis(pinacolato)diboron