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## A nickel precatalyst for efficient cross-coupling reactions of aryl tosylates with arylboronic acids: vital role of dppf

## Feng Hu, Xiangyang Lei\*

Department of Chemistry & Biochemistry, Lamar University, P.O. Box 10022, Beaumont, TX 77710, USA

## A R T I C L E I N F O

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#### ABSTRACT

An air-stable and easy-to-handle nickel precatalyst, (9-phenanthrenyl)Ni(II)(PPh<sub>3</sub>)<sub>2</sub>Cl, was examined for the cross-coupling reactions of aryl tosylates with arylboronic acids. Under the optimized reaction conditions, the catalytic system tolerates a wide range of activated, neutral and deactivated substrates. The selectivity of this cross-coupling reaction towards aryl tosylates and arylboronic acids has been investigated. It is proposed that ligand 1,1'-bis(diphenylphosphino)ferrocene (dppf) plays a key role in the coupling by enforcing a cis geometry in key intermediates and the active Ni(0) species.

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## 1. Introduction

Transition metal-catalyzed Suzuki-Miyaura cross-coupling is one of the most commonly used reactions in the construction of C–C bonds, in which the formation of biarvl/polvarvl motifs is particularly valuable due to its significance in biologically active molecules and chemical materials.<sup>1–4</sup> Pd catalysts have been well studied in this field.<sup>5,6</sup> In the recent decades, however, Ni-based catalytic systems have attracted considerable attention due to their lower cost, high reactivity and lower toxicity.7-13 In this context, the electrophilic substrates involve aryl halides, tosylates, mesylates as well as less common carboxylates, carbamates and sulfamates.<sup>7,14–18</sup> Among them, aryl tosylates have been regarded as excellent substrates due to their high reactivity and wide availability from phenols.<sup>19–22</sup> Recently, Ni(II)  $\sigma$ -aryl complexes, which are air-stable and easy-to-handle, have shown high efficiency as precatalysts in various cross-coupling reactions.<sup>16,20,23-25</sup> Herein, we report the application of (9-phenanthrenyl)Ni(II)(PPh<sub>3</sub>)<sub>2</sub>Cl(1) as a precatalyst in the cross-coupling reactions of aryl tosylates with arylboronic acids.

## 2. Results and discussion

Precatalyst **1** was easily prepared according to the reported procedure.<sup>26</sup> In the preliminary studies, as shown in Table 1, the coupling reaction of tosylate **2a** with phenylboronic acid (**3a**) was

chosen as a model reaction to optimize the reaction conditions. According to the reported Ni-catalyzed Suzuki reactions, the addition of excess phosphine ligand is essential to stabilize the in situ generated Ni(0) catalyst and the intermediate aryl nickel species during the entire catalytic cycle.<sup>27</sup> Therefore, as a regular procedure, some common commercially available ligands were screened. As shown in Table 1, ligand 1,1'-bis(diphenylphosphino) ferrocene (dppf) was the most efficient one with the order of ligand efficiency of dppf>PPh<sub>3</sub>>PCy<sub>3</sub>>1,3-bis(diphenylphosphino) propane (dppp) when other reaction conditions were the same (entries 1-4). Bases K<sub>2</sub>CO<sub>3</sub> and CsF were more efficient than K<sub>3</sub>PO<sub>4</sub>, Cs<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> when the coupling reaction was carried out in toluene with dppf as ligand (entries 4–8). Although K<sub>2</sub>CO<sub>3</sub> and CsF showed the same efficiency, K<sub>2</sub>CO<sub>3</sub> was chosen for further study due to its availability and relatively low price. Among toluene, THF, DMF, EtOH, MeCN and 1,4-dioxane, toluene was the best choice for solvent (entries 4 and 9-13). A short reaction time of 20 h resulted in a yield of 78%, much lower than 95% when the reaction lasted for 30 h (entries 4 and 14). Moreover, the yield decreased from 95% to 43% when the catalyst load was reduced from 5.0 mol % to 2.5 mol % (entries 4 and 15), which indicated that a load of 5.0 mol % of precatalyst 1 was needed to maintain its efficiency. In all cases 2-3% of biphenyl formed by homo-coupling of phenylboronic acid was observed. It should be pointed out that due to the consumption of arylboronic acid in its homo-coupling and in the precatalyst activation process,<sup>25</sup> a slight excess of arylboronic acid over aryl tosylate was required in the crosscoupling reaction. Finally, the optimal reaction conditions were set as entry 4 in Table 1.





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<sup>\*</sup> Corresponding author. E-mail address: xlei@lamar.edu (X. Lei).

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## Table 1

Optimization of reaction conditions<sup>a</sup>



Entry	Ligand	Base	Solvent	Time (h)	Yield <sup>b</sup> (%)
1	PPh <sub>3</sub> <sup>c</sup>	K <sub>2</sub> CO <sub>3</sub>	Toluene	30	72
2	PCy <sub>3</sub> <sup>c</sup>	K <sub>2</sub> CO <sub>3</sub>	Toluene	30	40
3	dppp	K <sub>2</sub> CO <sub>3</sub>	Toluene	30	27
4	dppf	K <sub>2</sub> CO <sub>3</sub>	Toluene	30	95
5	dppf	CsF	Toluene	30	95
6	dppf	K <sub>3</sub> PO <sub>4</sub>	Toluene	30	90
7	dppf	Cs <sub>2</sub> CO <sub>3</sub>	Toluene	30	89
8	dppf	Na <sub>2</sub> CO <sub>3</sub>	Toluene	30	15
9 <sup>d</sup>	dppf	K <sub>2</sub> CO <sub>3</sub>	THF	30	58
10 <sup>d</sup>	dppf	K <sub>2</sub> CO <sub>3</sub>	DMF	30	8
11 <sup>d</sup>	dppf	K <sub>2</sub> CO <sub>3</sub>	EtOH	30	13
12 <sup>d</sup>	dppf	K <sub>2</sub> CO <sub>3</sub>	MeCN	30	41
13 <sup>d</sup>	dppf	K <sub>2</sub> CO <sub>3</sub>	1,4-Dioxane	30	7
14	dppf	K <sub>2</sub> CO <sub>3</sub>	Toluene	20	78
15 <sup>e</sup>	dppf	K <sub>2</sub> CO <sub>3</sub>	Toluene	30	43

Reaction conditions: 2a (1.0 mmol), 3a (1.2 mmol), 1 (0.05 mmol), ligand (0.05 mmol), base (3.0 mmol), solvent (3 mL), 110 °C.

b Determined by GC using hexadecane as the internal standard.

0.10 mmol. <sup>d</sup> 100 °C.

1 (0.025 mmol) and dppf (0.025 mmol).

With the optimized catalytic system in hand, we explored the scope of aryl tosylates by examining the coupling reactions of phenylboronic acid with aryl tosylates with various electronic and steric properties. During this study the reactions were monitored by thin-layer chromatography. When the reaction was judged complete by the disappearance of aryl tosylate from the reaction mixture, it was stopped. As shown in Table 2, aryl tosylates bearing electron-donating groups, such as methoxy, methyl and acetylamino groups can efficiently couple with phenylboronic acid to yield the corresponding biaryls in good to excellent yields (68-95%, entries 1-6). Aryl tosylates with electron-withdrawing groups also gave the corresponding biaryls in good to excellent yields (70–97%, entries 7-15) except for the nitro-substituted aryl tosylate (entry 16), which didn't yield any detectable cross-coupling product at all. This is because that the catalyst may form a stable (nitroso)nickel(II) species and lose its activity.<sup>28,29</sup> The successful coupling of 4formylphenyl tosylate with phenylboronic acid (entry 11) indicates that our catalytic system is more compatible than that of a similar catalytic system using a Ni(II)  $\sigma$ -aryl complex as precatalyst.<sup>23</sup> In addition, pyridyl and quinolyl tosylates, respectively, were coupled with phenylboronic acid in good to excellent yields (86% and 97%. entries 17 and 18). This catalytic protocol was also efficient for the formation of polyaryls as indicated by the successful coupling of ditosylates with phenylboronic acid (entries 19 and 20). The catalytic system is not very sensitive to the steric hindrance of aryl tosylates with relatively small substituents, such as methyl and acetyl groups, as their ortho-, meta- and para-substituted isomers gave similar yields (entries 2–4 and 13–15). More obvious steric effects were observed under more bulky situations (entries 6, 9 and 19).

Next, the cross-coupling reactions of 4-methoxyphenyl tosylate (2a) with various arylboronic acids were examined to determine the scope of arylboronic acids, and the results are summarized in Table 3. Phenylboronic acids bearing electron-donating groups and naphthylboronic acids were successfully coupled with 4methoxyphenyl tosylate to give the cross-coupling products in good to excellent yields (83-92%, entries 1-6). Arylboronic acids bearing weak electron-withdrawing groups, such as the fluoro and

#### Table 2 Scope of aryl tosylates<sup>a</sup>

	Ar = OTs + Ph = B	(OH) <sub>2</sub> pre-	cat. 1, dppf	r-Ph
	2 3	$K_2CO_3$ ,	toluene, 110 °C	4
Entry	Ar-OTs	Time (h)	Product	Yield <sup>b</sup> (%)
1	MeO-	DTs 30	MeO-Ph 4a	93
2		<sup>°s</sup> 24	-∕Ph 4b	95
3	$\sim$ OTs 2c	24	Ph 4c	92
4		24	∠Ph 4d	90
5	AcNH-	OTs <sub>18</sub>	AcNH- Ph	84
6	OMe OMe OMe 2f	30	OMe Ph OMe 4f	68
7	F <sub>3</sub> CO-2g	OTs 12	$F_3CO - Ph$	92
8	F <sub>3</sub> C 	Гs 30	$F_{3}C$ $Ph$ $4h$	78
9	CF <sub>3</sub> OTs 2i	30	CF <sub>3</sub> —Ph 4i	70

(continued on next page)

Table 2 (continued)

Entry	Ar-OTs	Time (h)	Product	Yield <sup>b</sup> (%)
10	EtOOC-	20	EtOOC-Ph 4j	87
11	OHC	20	OHC-Ph	95
12	NC - OTs	15	NC- Ph	97
13	$\sim - 0$ 2m $- 0$ Ts	30	$\sim \sim $	90
14	O O O O Ts <b>2n</b>	18	→ Ph 4n	95
15		24	O Ph 40	90
16	$O_2N - OTs$ <b>2p</b>	30	$O_2N - Ph$	0
17	$\sim 10^{N}$ OTs $2q$	12	NPh 4q	86
18	$\sim$ OTs N 2r	18	Ph N 4r	98
19 <sup>c</sup>	OTs OTs 2s	18	Ph 4s	80
20 <sup>c</sup>	TsO OTs	18	Ph 4t	90

 $^a$  Reaction conditions: 2 (1.0 mmol), 3a (1.2 mmol), 1 (0.05 mmol), dppf (0.05 mmol), K\_2CO\_3 (3.0 mmol), toluene (3 mL), 110  $^\circ C$  .

<sup>b</sup> Isolated yields.

<sup>c</sup> **3a** (2.4 mmol) was used.

methoxycarbonyl groups also produced the corresponding diaryls in good vields under the optimal reaction conditions (78-88%. entries 7–9), though strong electron-withdrawing groups, such as the formyl and cyano groups significantly deactivated the corresponding arylboronic acids and no cross-coupling product was obtained (entries 10 and 11). Likewise, the coupling of electrondeficient pyridin-4-ylboronic acid with 4-methoxyphenyl tosylate did not yield any detectable cross-coupling product (entry 12). However, it is likely that biaryls 4d'-f' can be synthesized by the cross-coupling reactions of electron-deficient 4-formylphenyl tosylate, 4-cyanophenyl tosylate and 4-pyridyl tosylate with electron-rich 4-methoxyphenylboronic acid, respectively, under the optimal reaction conditions. Steric effects were observed as the yields followed the sequence of *p*-tolylboronic acid>*m*-tolylboronic acid>o-tolylboronic acid (entries 1–3). It should be pointed out that dppf proved again to be the optimal ligand as it gave much higher yields than PPh<sub>3</sub> and dppp in the same reactions under otherwise same reaction conditions (entries 8 and 9).

## Table 3

Scope of arylboronic acids<sup>a</sup>

p-Me	$\begin{array}{r} \text{OPh-OTs} + \text{Ar-B(OH)}_2 = \\ \mathbf{2a} \qquad 3 \end{array}$	$\frac{\text{precat. 1, dppf}}{\text{K}_2\text{CO}_3, \text{ toluene, } 110 ^{\circ}\text{C}} \blacktriangleright p-1$	MeOPh-Ar 4
Entry	ArB(OH) <sub>2</sub>	Product	Yield <sup>b</sup> (%)
1		<i>p</i> -MeOPh-	90
2	B(OH) <sub>2</sub>	<i>p</i> -MeOPh	87
3	B(OH) <sub>2</sub> 3d	<i>p</i> -MeOPh-	83
4	$MeO - B(OH)_2$	$p$ -MeOPh $\longrightarrow$ OMe $4x$	88
5	B(OH) <sub>2</sub> 3f	p-MeOPh 4y	92
6	B(OH) <sub>2</sub> 3g	p-MeOPh 4z	92
7	$F - \underbrace{ - B(OH)_2}{3h}$	p-MeOPh-F 4a'	81
8	$F$ $B(OH)_2$ $F$ $3i$	<i>p</i> -MeOPh	88 42 <sup>c</sup> 28 <sup>d</sup>
9	$MeOOC - \underbrace{ B(OH)_2}{3j} - B(OH)_2$	<i>p</i> -MeOPh-COOMe	78 12 <sup>c</sup> 41 <sup>d</sup>
10	$OHC - B(OH)_2$ 3k	<i>p</i> -MeOPhСНО <b>4d'</b>	0
11	NC $ B(OH)_2$ $3l$	<i>p</i> -MeOPh-CN 4e'	0
12	$N = B(OH)_2$ 3m	p-MeOPh-N 4f'	0

 $<sup>^</sup>a$  Reaction conditions: 2a (1.0 mmol), 3 (1.2 mmol), 1 (0.05 mmol), dppf (0.05 mmol), K\_2CO\_3 (3.0 mmol), toluene (3 mL), 110  $^\circ C$ , 30 h.

<sup>b</sup> Isolated yields.

<sup>c</sup> PPh<sub>3</sub> (0.10 mmol).

<sup>d</sup> dppp (0.05 mmol).

In order to determine the selectivity of this cross-coupling reaction towards aryl tosylates, an equimolar mixture of tosylates **2a** and **2l** was treated with an excess of phenylboronic acid (**3a**) under the optimal reaction conditions. As shown in Scheme 1, crosscoupling products **4a** and **4l** were obtained in 44% and 42% yields, respectively, using tosylates **2a** and **2l**. Meanwhile, the intermolecular competition between arylboronic acids **3a** and **3j** to couple with tosylate **2a**, as shown in Scheme 2, yielded solely biaryl **4a** in an 84% yield with no detectable biaryl **4c**', though arylboronic acid **3j** can smoothly couple with tosylate **2a** on its own (entry 9 in Table **3**). These results indicate that the efficiency of the crosscoupling reaction depends on electronic factors in the arylboronic acids and not the aryl tosylates. This is probably because that arylboronic acids participate in both the precatalyst activation



Scheme 2. Intermolecular competition between arylboronic acids.

process and the rate-determining transmetalation step in the main catalytic cycle,<sup>25</sup> and electron-withdrawing groups on arylboronic acids may retard these two steps.

Similar to other cross-coupling reactions using Ni(II)  $\sigma$ -aryl complexes as precatalysts,<sup>16,25</sup> the catalytic mechanism is believed to start with the activation of precatalyst  $\mathbf{1}$  to form the active Ni(0) species, and the subsequent main catalytic cycle involves oxidative addition, transmetalation and reductive elimination. Complex 5, shown in Fig. 1, is believed to be the active Ni(0) species. It is proposed that precatalyst 1 has ligand exchange with dppf to form complex 6, which undergoes transmetalation with activated arylboronic acid to give complex 7. The reductive elimination of complex 7 yields active Ni(0) species 5 as well as side product 9arylphenanthrene (8), which has been isolated and characterized.<sup>25</sup> The argument of complex **5** as the active Ni(0) species is supported by the results of Hartwig that the reaction of dppfligated cinnamylnickel(II) chloride with 2-thienyl boronic acid with K<sub>3</sub>PO<sub>4</sub> as a base in THF in the presence of 1 equiv of dppf generated (dppf)<sub>2</sub>Ni(0) quantitatively in 10 min at room temperature.<sup>30</sup> It is further supported by the recent results reported by Buchwald that complex (Ph<sub>3</sub>P)<sub>2</sub>Ni(o-tolyl)Cl can easily exchange its two triphenylphosphine ligands with dppf in THF at room temperature to form (dppf)Ni(o-tolyl)Cl in an 83% yield, and the latter is an efficient precatalyst for the amination of a variety of aryl and heteroaryl electrophiles.<sup>15</sup> This argument is also supported by our experimental results that dppf is a more efficient ligand than PPh<sub>3</sub>, PCy<sub>3</sub> and dppp under otherwise the same reaction conditions (entries 1-4 in Table 1, entries 8 and 9 in Table 3). It is believed that ligand dppf plays a key role in the precatalyst activation process by enforcing a cis geometry of the 9-phenanthrenyl and chloro or aryl groups in complexes 6 and 7, respectively, and facilitating the reductive elimination step. The cis geometry of complex 5 is beneficial to the subsequent main catalytic cycle in the same way.

arylboronic acids. The catalytic system is compatible with various aryl tosylates bearing electron-donating or electron-withdrawing groups. Coupling with arylboronic acids with weak electron-withdrawing groups under the optimal reaction conditions also gave the corresponding diaryls in good yields, though strong electron-withdrawing groups significantly deactivated the corresponding arylboronic acids and no cross-coupling product was obtained. This coupling reaction is highly selective towards arylboronic acids, but not selective towards aryl tosylates. It is proposed that ligand dppf plays a key role in the coupling by enforcing a cis geometry in key intermediates and the active Ni(0) species. All isolated cross-coupled biaryl products have been characterized by <sup>1</sup>H and <sup>13</sup>C NMR, and their spectral data are consistent with those reported.

## 4. Experimental section

## 4.1. General

Precatalyst **1** was prepared according to a literature method.<sup>26</sup> Aryl tosylates were prepared according to our unpublished procedures.<sup>31</sup> Bases (Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, Cs<sub>2</sub>CO<sub>3</sub> and K<sub>3</sub>PO<sub>4</sub>) were ground into powder and dried under vacuum at 125 °C for 4 h prior to use. Toluene and THF were refluxed over Na/benzophenone and distilled under nitrogen, respectively. All other reagents and solvents were purchased from commercial suppliers and used as received. NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer in CDCl<sub>3</sub> and referenced to the residual solvent signals (<sup>1</sup>H: 7.26 ppm; <sup>13</sup>C: 77.16 ppm). Peaks were characterized as singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublet (dd), triplet of triplet (tt) and multiplet (m). An Agilent 6890N Network Gas Chromatograph, equipped with a capillary column (HP-5) and a TCD detector, was used to assay the reaction yields for the opti-



Fig. 1. Proposed mechanism for the formation of the active Ni(0) species (Phen=9-phenanthrenyl).

## 3. Conclusions

We have demonstrated that complex **1** is an efficient precatalyst for the Suzuki–Miyaura cross-coupling of aryl tosylates with mization of reaction conditions. All glasswares were dried in an oven at 120 °C for 8 h and cooled under nitrogen atmosphere in a desiccator before use. Column chromatography was performed with 300-400 mesh silica gel.

# 4.2. General procedure for the Suzuki cross-coupling reactions

Aryl tosylate (1.0 mmol), arylboronic acid (1.2 mmol), precatalyst **1** (0.05 mmol), ligand (0.05 mmol) and base (3.0 mmol) were added to a Schlenk tube equipped with a magnetic stirring bar, a septum and a reflux condenser. After the tube was evacuated and refilled with nitrogen gas three times, degassed solvent (3 mL) was added via a syringe. The reaction mixture was heated to the described temperature for the required time. After the reaction cooled to room temperature, water (10 mL) was added to the reaction mixture. The resulting mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3×10 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated to dryness. The remaining residue was analyzed by GC (Table 1) or purified by flash chromatography on silica gel with ethyl acetate—hexanes (0–20% ethyl acetate in hexanes) of as eluents (Tables 2 and 3).

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## Supplementary data

Experimental procedures, spectra data and NMR spectra. Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2014.04.059.

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