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## Diaminophosphine Oxides as Preligands for Ni-Catalyzed Suzuki Cross-Coupling Reactions of Aryl Chlorides with Arylboronic Acids

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**Graphic Abstract** 

 $Ar-Cl + Ar'-B(OH)_2 \xrightarrow{\text{precatalyst, preligand, K_3PO_4}}_{\text{toluene, 110 °C, 18 h}} Ar-Ar' \xrightarrow{\text{Cl}}_{\text{precatalyst}} Ph_3P-Ni-PPh_3$ 

### Abstract

The first investigation of air- and moisture-stable diaminophosphine oxides as preligands in the Ni-catalyzed Suzuki cross-coupling reactions of aryl chlorides with arylboronic acids has been reported. The results show that under the optimized reaction conditions, the new catalytic system with a Ni(II)  $\sigma$ -aryl complex as precatalyst and a diaminophosphine oxide as preligand tolerates a variety of functional groups and is efficient for both electron-rich and electron-deficient aryl chlorides, though it shows higher efficiency for activated arylboronic acids than deactivated ones. Steric effects were observed for both aryl chlorides and arylboronic acids.

**Keywords**: Diaminophosphine oxides; Ni(II)  $\sigma$ -aryl complexes; Suzuki cross-coupling reactions; Aryl chlorides; Arylboronic acids

Transition metal-catalyzed Suzuki cross-coupling reactions are powerful tools in synthetic chemistry.<sup>1-4</sup> Among transition metal catalysts, Ni-based catalytic systems, due to their low cost, low toxicity, and high reactivity, have played an important role in the construction of C-C bonds, especially in the formation of biaryl/polyaryl motifs that have been proven to be significant in biological molecules and chemical materials.<sup>5-13</sup> In order to achieve high catalytic efficiency, ligands have been employed as a key controlling element in transition metal catalysis. Although various ligands have been

used in Ni-catalyzed cross-couplings, the electron-rich mono- and bi-dentate phosphine ligands, which are often prone to oxidation, are predominantly employed.<sup>5,6</sup> A notable development of phosphorus-based ligands was reported by Li in 2001,<sup>14,15</sup> showing that air-stable alkyl-substituted secondary phosphine oxides (SPOs) allow for the transformation of less reactive aryl chlorides in a variety of cross-coupling reactions. However, with alkyl-substituted SPOs, it is difficult to modify the electronic property of the respective phosphine oxide without altering its steric property at the same time. Recently, heteroatom-substituted SPOs, specifically diaminophosphine oxides whose electronic and steric properties can be finely tuned, have attracted considerate attention as preligands in a variety of reactions, such as Pd-catalyzed Suzuki cross-coupling reactions,<sup>16-18</sup> Pd-<sup>19</sup> or Ni-catalyzed<sup>17,18,20,21</sup> Kumada cross-coupling reactions, Ir-<sup>22</sup> or Pd-catalyzed<sup>23,24</sup> asymmetric allylic amination and alkylation, Ru-catalyzed arylation via C-H bond functionalization,<sup>17,25,26</sup> and Ni-catalyzed asymmetric hydrocarbamoylations of alkenes.<sup>27</sup> To our best knowledge, however, diaminophosphine oxides have not been used as preligands in the Ni-catalyzed Suzuki cross-coupling reactions. As a continuation of our research interest in Ni-catalyzed cross-coupling reactions,<sup>28-30</sup> herein, we report the first investigation of air- and moisture-stable diaminophosphine oxides as preligands with air-stable and easy-to-handle Ni(II) σ-aryl complexes as precatalysts in the Suzuki cross-coupling reactions of aryl chlorides with arylboronic acids.

Precatalysts 1-2 (Fig. 1)<sup>30,31</sup> and preligands L1-L3 (Fig. 2)<sup>18</sup> were easily prepared according to literature procedures. In the preliminary study, we examined the cross-coupling reaction of *p*-chloroanisole (**3a**) with phenylboronic acid (**4a**) to optimize the reaction conditions. As shown in Table 1, when complex 1 was employed as precatalyst with  $K_2CO_3$  as base and toluene as solvent at 110 °C, sterically hindered preligand L3, which bears aromatic substituents on nitrogen atoms, showed higher efficiency than preligands L1 and L2 (entries 1-3). Similarly, preligand L3 was the most efficient one when complex 2 was used as precatalyst under the same reaction conditions (entries 4-6).



Figure 1. Structures of Ni(II)  $\sigma$ -aryl complexes used in this study.



Figure 2. Structures of diaminophosphine oxides used in this study.

#### Table 1

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

	``	Cl + (	$\begin{array}{c} B(OH)_2  \text{prec}\\ \hline 4a \end{array}$	se, solvent	5a	6
Entry	Precat.	Preligand	Base	Solvent	$T(^{o}C)$	Yield (%) <sup>b</sup>
1	1	L1	K <sub>2</sub> CO <sub>3</sub>	Toluene	110	37
2	1	L2	$K_2CO_3$	Toluene	110	65
3	1	L3	K <sub>2</sub> CO <sub>3</sub>	Toluene	110	73
4	2	L1	$K_2CO_3$	Toluene	110	32
5	2	L2	$K_2CO_3$	Toluene	110	56
6	2	L3	$K_2CO_3$	Toluene	110	64
7	1	L3	$K_3PO_4$	Toluene	110	96
8	2	L3	$K_3PO_4$	Toluene	110	79
9	1	L3	$Cs_2CO_3$	Toluene	110	43
10	1	L3	CsF	Toluene	110	26
11	1	L3	Na <sub>2</sub> CO <sub>3</sub>	Toluene	110	6
12	1	L3	K <sub>3</sub> PO <sub>4</sub>	THF	80	4
13	1	L3	K <sub>3</sub> PO <sub>4</sub>	EtOH	80	9
14	1	L3	K <sub>3</sub> PO <sub>4</sub>	DMF	110	45
15	1	L3	K <sub>3</sub> PO <sub>4</sub>	MeCN	80	58
16	1	L3	K <sub>3</sub> PO <sub>4</sub>	DMSO	110	11
17	1	L3	K <sub>3</sub> PO <sub>4</sub>	1,4-Dioxane	80	73
18 <sup>c</sup>	1	L3	$K_3PO_4$	Toluene	110	56

<sup>a</sup> Reaction conditions: **3a** (1.0 mmol), **4a** (1.2 mmol), precat. (0.05 mmol), preligand (0.10 mmol), base (3.0 mmol), solvent (3 mL), 18 h.

<sup>b</sup> GC yields using hexadecane as the internal standard.

<sup>c</sup> **1** (0.025 mmol), **L3** (0.05 mmol), 24 h.

These results are consistent with the reported efficiency sequence of preligands L1-L3 in the Ni-catalyzed Kumada cross-coupling reactions.<sup>20</sup> Between complexes 1 and 2, precatalyst 1 is more efficient (entries 1 and 4, 2 and 5, 3 and 6), and its higher efficiency was further confirmed when  $K_3PO_4$  was used as base with L3 as preligand (entries 7 and 8). Base  $K_3PO_4$  was more efficient than  $K_2CO_3$ ,  $Cs_2CO_3$ , CsF, and  $Na_2CO_3$  (entries 3, 7, and 9-11). Among toluene, THF, EtOH, DMF, MeCN, DMSO, and 1,4-dioxane, toluene is the best choice for solvent (entries 7 and 12-17). In addition, the yield decreased from 96% to 56% when the precatalyst loading was reduced from 5.0 to 2.5 mol% (entry 18).

Finally, the optimal reaction conditions were set as entry 7 in Table 1. It is worthy to point out that under the optimal reaction conditions, the cross-coupling of **3a** with **4a** catalyzed by  $NiCl_2 \cdot 6H_2O$  yielded only trace amount of cross-coupling product **5a**.

Next, we examined the cross-coupling reactions of a variety of aryl chlorides with phenylboronic acid to determine the scope of aryl chlorides. As shown in Table 2, aryl chlorides bearing

### Table 2

Scope of aryl chlorides<sup>a</sup>

2

Entry	ArCl	Product	Yield $(\%)^{b}$
1	<i>p</i> -MeO-Ph-Cl ( <b>3a</b> )	p-MeO-Ph-Ph (5a)	94
2	<i>p</i> -Me-Ph-Cl ( <b>3b</b> )	<i>p</i> -Me-Ph-Ph ( <b>5b</b> )	84
3	o-Me-Ph-Cl (3c)	<i>o</i> -Me-Ph-Ph ( <b>5</b> c)	76
4 <sup>c</sup>	2,5-Dimethoxy-Ph-Cl (3d)	2,5-Dimethoxy-Ph-Ph- <i>p</i> -OMe ( <b>5d</b> )	69
5	p-HOCH <sub>2</sub> -Ph-Cl ( <b>3e</b> )	p-HOCH <sub>2</sub> -Ph-Ph ( <b>5e</b> )	22
6	Ph-Cl ( <b>3f</b> )	Ph-Ph ( <b>5f</b> )	88
$7^{\rm c}$	1-Cl-naphthalene ( <b>3g</b> )	1-( <i>p</i> -MeO-Ph)-naphthalene ( <b>5</b> g)	66
8	o-MeO <sub>2</sub> C-Ph-Cl ( <b>3h</b> )	$o-MeO_2C-Ph-Ph$ ( <b>5h</b> )	80
9	o-MeO <sub>2</sub> C-Ph-Cl ( <b>3i</b> )	$o-MeO_2C-Ph-Ph$ (5i)	91
10	<i>p</i> -OHC-Ph-Cl ( <b>3j</b> )	<i>p</i> -OHC-Ph-Ph ( <b>5j</b> )	87
11	<i>p</i> -NC-Ph-Cl ( <b>3k</b> )	<i>p</i> -NC-Ph-Ph ( <b>5</b> k)	90
12	<i>p</i> -PhOC-Ph-Cl ( <b>3l</b> )	<i>p</i> -PhOC-Ph-Ph ( <b>5l</b> )	72
13 <sup>c</sup>	<i>p</i> -F-Ph-Cl ( <b>3m</b> )	p-F-Ph-Ph- $p$ -OMe ( <b>5m</b> )	85
14 <sup>c</sup>	3,5-Difluoro-Ph-Cl ( <b>3n</b> )	3,5-Difluoro-Ph-Ph- <i>p</i> -OMe ( <b>5n</b> )	83
15	<i>o</i> -O <sub>2</sub> N-Ph-Cl ( <b>30</b> )	<i>o</i> -O <sub>2</sub> N-Ph-Ph ( <b>50</b> )	0
16	p-O <sub>2</sub> N-Ph-Cl ( <b>3p</b> )	p-O <sub>2</sub> N-Ph-Ph ( <b>5p</b> )	0
17	<i>p</i> -Ph-Ph-Cl ( <b>3q</b> )	$p$ -Ph-Ph-Ph ( <b>5</b> $\mathbf{q}$ )	88
18 <sup>d</sup>	<i>p</i> -Cl-Ph-Cl ( <b>3r</b> )	<i>p</i> -Ph-Ph-Ph ( <b>5q</b> )	70
19 <sup>e</sup>	1,3,5-Trichlorobenzene (3s)	1,3,5-Tri( <i>p</i> -MeO-Ph)benzene ( <b>5r</b> )	67

	0
	G
$Ar-Cl + Ph-B(OH)_2$	$1, L3, K_3PO_4 \rightarrow Ar^-Ph$

<sup>a</sup> Reaction conditions: **3** (1.0 mmol), **4a** (1.2 mmol), **1** (0.05 mmol), **L3** (0.10 mmol), K<sub>3</sub>PO<sub>4</sub> (3.0 mmol), toluene

(3 mL), 110 °C, 18 h.

<sup>b</sup> Isolated yields.

<sup>c</sup> *p*-MeOPhB(OH)<sub>2</sub> (1.2 mmol).

<sup>d</sup> 4a (2.4 mmol), 1 (0.10 mmol), L3 (0.20 mmol), K<sub>3</sub>PO<sub>4</sub> (6.0 mmol), and toluene (4 mL).

<sup>e</sup> *p*-MeOPhB(OH)<sub>2</sub> (3.6 mmol), **1** (0.15 mmol), **L3** (0.30 mmol), K<sub>3</sub>PO<sub>4</sub> (9.0 mmol), and toluene (6 mL).

electron-donating groups such as methoxy and methyl groups can efficiently couple with phenylboronic acid to provide the corresponding biaryl products in good to excellent yields (entries 1–3). The coupling of aryl chloride **3d** with phenylboronic acid resulted in a crude product that is difficult to purify. Substitution of phenylboronic acid by 4-methoxyphenylbonoric acid in the reaction facilitated the purification of product by column chromatography and gave a good yield (entry 4). Probably due to the effect of the active hydroxyl group, the coupling of aryl chloride **3e** with phenylboronic acid gave a low yield (entry 5). Neutral chlorobenzene (3f) and 1-chloronaphthalene (3g) coupled efficiently with phenylboronic acid and 4-methoxylphenylbonoric acid, respectively (entries 6 and 7). Aryl chlorides containing electron-withdrawing groups such as methoxycarbonyl, formyl, cyano, and fluoro groups yielded the corresponding biaryl products in good to excellent yields (entries 8-14), though nitro-substituted aryl chlorides 30 and 3p did not give any detectable cross-coupling product. This result is consistent with literature and is probably due to the deactivation of the catalyst by the nitro group by the formation of a stable (nitroso)nickel(II) species.<sup>29</sup> The coupling of 4-chlorobiphenyl (**3q**) and 1,4-dichlorobenzene (3r) with phenylboronic acid, respectively, gave *p*-terphenyl in good yields (entries 17 and 18). The coupling of 1.3,5-trichlorobenzene (3s) with 4-methoxylphenylbonoric acid also gave the corresponding polyphenyl in a good yield (entry 19). These results demonstrated that this catalytic protocol was efficient for the formation of polyaryls. Steric effects were observed as the ortho-substituted aryl chlorides generally gave lower yields than their para-substituted analogs (entries 1 and 4, 2 and 3, 8 and 9, respectively).

In order to determine the scope of arylboronic acids, the cross-coupling reactions of *p*-chloroanisole (**3a**) with various arylboronic acids (**4**) were examined. As shown in Table 3, phenylboronic acids bearing electron-donating groups and naphthylboronic acids successfully coupled with *p*-chloroanisole to give the cross-coupling products in good to excellent yields (entries 1–6). The yield sequences of *p*-tolylboronic acid > *m*-tolylboronic acid > *o*-tolylboronic acid (entries 2-4) and 2-naphthylboronic acid > 1-naphthylboronic acid (entries 5 and 6) are probably due to steric effects. Except for arylboronic acids containing electron-withdrawing groups such as methoxycarbonyl, cyano, and formyl groups gave no cross-coupling product at all (not shown). This is because electron-deficient boronic acids are generally less reactive than electron-rich ones due to the rate-determining transmetalation step of the catalytic cycle.<sup>32,33</sup> Other possible reasons include the poor solubility of some arylboronic acids in

#### Table 3

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

	$\frac{Cl}{3a} + Ar - B(0)$	OH) <sub>2</sub> $(1, L3, K_3PO_4)$ toluene, 110 °C, 18 h	Ar
Entry	ArB(OH) <sub>2</sub>	Product	Yield (%) <sup>b</sup>
1	p-MeO-PhB(OH) <sub>2</sub> ( <b>4b</b> )	p-MeO-Ph-Ph- $p$ -OMe ( <b>5</b> s)	93
2	p-Me-PhB(OH) <sub>2</sub> ( <b>4</b> c)	p-Me-Ph- $p$ -OMe ( <b>5t</b> )	90
3	m-Me-PhB(OH) <sub>2</sub> ( <b>4d</b> )	m-Me-Ph-Ph- $p$ -OMe ( <b>5u</b> )	83
4	o-Me-PhB(OH) <sub>2</sub> ( <b>4e</b> )	o-Me-Ph-Ph-p-OMe (5v)	75
5	$1-B(OH)_2$ -naphthalene (4f)	1-( <i>p</i> -MeO-Ph)-naphthalene ( <b>5</b> g)	70
6	2-B(OH) <sub>2</sub> -naphthalene (4g)	2-( <i>p</i> -MeO-Ph)-naphthalene ( <b>5w</b> )	78
7	p-F-PhB(OH) <sub>2</sub> ( <b>4h</b> )	<i>p</i> -F-Ph-Ph- <i>p</i> -OMe ( <b>5m</b> )	78
8	3-B(OH) <sub>2</sub> -furan ( <b>4i</b> )	3-( <i>p</i> -MeO-Ph)-furan ( <b>5</b> x)	68
9	3-B(OH) <sub>2</sub> -pyridine ( <b>4j</b> )	3-( <i>p</i> -MeO-Ph)-pyridine ( <b>5</b> y)	0

<sup>a</sup> Reaction conditions: **3a** (1.0 mmol), **4** (1.2 mmol), **1** (0.05 mmol), **L3** (0.10 mmol), K<sub>3</sub>PO<sub>4</sub> (3.0 mmol), toluene

(3 mL), 110 °C, 18 h.

<sup>b</sup> Isolated yields.

toluene, the strong coordination ability of functional groups (such as COOMe and CN) to the active Ni(0) species, and the enhanced protodeboronation of arylboronic acids due to the presence of electron-withdrawing groups.<sup>34</sup> The coupling of heteroarylboronic acid **4i** with *p*-chloroanisole resulted in a good yield (entry 8), while heteroarylboronic acid **4j** did not yield any cross-coupling product (entry 9).

Similar to the other cross-coupling reactions using Ni(II)  $\sigma$ -aryl complexes as precatalysts,<sup>29,35</sup> the catalytic mechanism is believed to start with the activation of precatalyst **1** to form the active Ni(0) species, and the observation of a small amount of 1-arylnaphthalene confirmed the precatalyst activation process. The subsequent main catalytic cycle involves three basic steps: oxidative addition, transmetalation, and reductive elimination. In solution, diaminophosphine oxides exist in equilibrium between pentavalent phosphorus tautomer **6** and trivalent phosphinous acid **7** (Fig. 3).<sup>36,37</sup> At room temperature pentavalent tautomer **6** predominates. In the presence of base and Ni catalyst at elevated temperature, the equilibrium is believed to shift and yield predominantly complex **8**. It is proposed that in complex **8** a phosphinous and a phosphinito ligand is associated by a strong hydrogen bond. Therefore, the high catalytic activity achieved with diaminophosphine oxides as preligands is probably

due to the generation and subsequent deprotonation of the phosphinous acid nickel complex.



Figure 3. Generation and subsequent deprotonation of the phosphinous acid nickel complex (R = aryl or alkyl group).

In summary, with air-stable and easy-to-handle Ni(II)  $\sigma$ -aryl complexes as precatalysts, air- and moisture-stable diaminophosphine oxides are efficient preligands for the Suzuki cross-coupling reactions of aryl chlorides with arylboronic acids. The new catalytic system tolerates a variety of functional groups and works for both electron-rich and electron-deficient aryl chlorides under the optimal reaction conditions, though it shows higher efficiency for activated arylboronic acids than deactivated ones. Steric effects were observed for both aryl chlorides and arylboronic acids.

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### Supplementary data

Supplementary data (experimental procedures, spectra data, and NMR spectra) associated with this article can be found, in the online version, at....

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