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# Palladium complex containing two sterically hindered ligands as highly efficient catalyst for Suzuki–Miyaura reaction

# Nasifa Shahnaz and Pankaj Das\*

A new palladium(II) complex containing two sterically hindered ligands, a *P*,*P*-bonded diphosphine and *N*,*N*-bonded Schiff base, within the same coordination sphere has been synthesized and investigated as a catalyst for the Suzuki–Miyaura cross-coupling reactions of aryl halides with arylboronic acids. The reaction was highly efficient with aryl bromides in water at room temperature and aryl chlorides in dimethylformamide under relatively mild conditions. Excellent yields of coupling products were obtained for a wide range of aryl halides including heteroaryl halides with a low loading of catalyst. Copyright © 2015 John Wiley & Sons, Ltd.

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Keywords: palladium complex; DPEphos; Schiff base; Suzuki–Miyaura reaction; water; aryl chloride

## Introduction

Palladium-catalysed Suzuki–Miyaura cross-coupling reactions of aryl halides with boronic acids have become one of the most essential tools in modern chemistry for the construction of unsymmetric biaryls that are used as building blocks in the pharmaceutical, agro-chemical and material industries.<sup>[11]</sup> In recent years, significant efforts have been made towards the synthesis of new and highly efficient palladium catalysts that can promote these reactions in a sustainable way.<sup>[2]</sup> Like many other transition metal-catalysed reactions, in the Suzuki–Miyaura reaction also the nature of ligands coordinated to the palladium centre plays a significant role in the overall performance of a catalyst.

Bulky phosphines are known to be some of the most influential ligands for this reaction. Among various bulky phosphines, biphenyl phosphines,<sup>[3]</sup> phosphapalladacycles,<sup>[4]</sup> phosphabarrelenes,<sup>[5]</sup> hemilabile phosphines,<sup>[6]</sup> indolyl phosphine,<sup>[7]</sup> ferrocenyl phosphines,<sup>[8]</sup> resorcinarenyl phosphines,<sup>[9]</sup> etc., have proven to be of great value in activating difficult substrates including less reactive aryl chlorides. For many years, the ligand bis [2-(diphenylphosphino)phenyl]ether (DPEphos) has been used as a sterically hindered wide-bite-angle diphosphine that has attracted tremendous attention in catalysis because of its commercial availability and interesting chemistry.<sup>[10]</sup> In fact, this ligand has been extensively studied for various transition metal-catalysed reactions including palladium-catalysed cross-coupling reactions like Negishi, Kumada-Corriu, etc.<sup>[11]</sup> Unfortunately, the potentiality of this ligand in the Suzuki-Miyaura cross-coupling reaction is virtually unexplored, although other related bulky diphosphines have shown promising cross-coupling activity.<sup>[4c,9a,12]</sup>

Herein, as a part of our continuing efforts<sup>[13]</sup> to develop efficient Pd catalysts for Suzuki–Miyaura reactions, we report the synthesis of a new Pd complex containing a sterically hindered diphosphine (DPEphos) and a bidentate Schiff base ligand in the same coordination sphere. The efficacy of the complex as a catalyst has been

explored for the Suzuki-Miyaura reactions of aryl bromides in water at room temperature and aryl chlorides in dimethylformamide (DMF) under slightly harsh conditions. It is pertinent to mention that there are a few reports of the employment of Schiff base ligands in Suzuki-Miyaura reactions;<sup>[13,14]</sup> however, to the best of our knowledge, this is the first example of a Pd complex containing both bulky phosphine and bidentate Schiff base ligands within the same coordination sphere. It is expected that the introduction of two bulky ligands within the same coordination sphere would increase the steric congestion around the Pd centre which would facilitate both the oxidative addition and reductive elimination steps in the cross-coupling mechanism. It is worth mentioning that, barring a few examples,<sup>[13a,14c]</sup> the majority of the reported Pd-Schiff base catalysts were not effective in water as a reaction medium. In fact, from environmental and economic perspectives, water is the most desirable solvent for organic syntheses, and hence many research groups including those of Leadbeater,<sup>[15a,b]</sup> Eppinger,<sup>[15c]</sup> Zhang,<sup>[15d]</sup> Vanelle,<sup>[15e]</sup> Bora,<sup>[15f]</sup> SanMartin and Domínguez,<sup>[15g,h]</sup> Luo,<sup>[15i]</sup> Plenio<sup>[15j]</sup> and Shao<sup>[15k]</sup> have developed some excellent catalytic systems for Suzuki reactions in water. However, the majority of those protocols required either severe reaction conditions<sup>[15a]</sup> and/or addition of phase transfer catalyst<sup>[15a,b,d,e]</sup>/additive<sup>[15f]</sup> or high catalyst loading,<sup>[15f]</sup> which limits the applications of these catalytic systems on an industrial scale. Thus, developments of new catalytic systems that can effectively perform the cross-coupling reactions in aqueous media, especially under mild conditions without using any additive, are of great significance.

Correspondence to: Pankaj Das, Department of Chemistry, Dibrugarh University, Dibrugarh 786004, Assam, India. E-mail: pankajd29@yahoo.com

Department of Chemistry, Dibrugarh University, Dibrugarh 786004, Assam, India

## **Experimental**

### Chemicals, instrumentation and analysis

PdCl<sub>2</sub> and DPEphos were purchased from Acros Organics. Silver perchlorate was purchased from Sigma-Aldrich. The substrates and other chemicals used for the experiments were procured from Sigma-Aldrich, Merck, Spectrochem and Rankem. The solvents were purchased from various Indian firms and distilled prior to use. Fourier transform infrared (FT-IR) spectra were recorded with a Shimadzu IR Prestige-21 FTIR spectrophotometer. The <sup>1</sup>H NMR and <sup>31</sup>P NMR spectra of the complex were recorded with a Bruker Avance II 400 and <sup>13</sup>C NMR spectra with a JEOL ECS-400. The mass spectrum of the complex was obtained with a Waters ZQ-4000 ESI/MS. The <sup>1</sup>H NMR spectra of the products were recorded with an AV400 and a Bruker Avance III 500. Gas chromatographic studies of the products were carried out using an Agilent 7820A GC system.

### Preparation of palladium catalyst

A solution of ligand DPEphos (0.175 g, 0.325 mmol) in 15 ml of dichloromethane was added dropwise to a solution of complex **1** (0.15 g, 0.325 mmol) in 15 ml of dichloromethane. To this solution, AgClO<sub>4</sub> (0.135 g, 0.65 mmol) was added in small portions and then stirred at room temperature for 4 h. A curdy white precipitate of AgCl deposited at the bottom of the solution which was filtered off to afford a yellow solution. After evaporation of the solvent under reduced pressure and washing with hexane, complex **2** was isolated as a bright yellow solid which was recrystallized from dichloromethane.

Yield 90%. Anal. Calcd for  $C_{56}H_{44}N_2P_2CI_2O_9Pd$  (%): C, 59.62; H, 3.93; N, 2.48. Found (%): C, 59.76; H, 3.94; N, 2.49. ESI-MS (CH<sub>2</sub>Cl<sub>2</sub>): *m/z* 1164 [M + 2NH<sub>4</sub>]<sup>2+</sup>, 1185 [M + NH<sub>4</sub> + K]<sup>2+</sup>. FT-IR (KBr, cm<sup>-1</sup>): 1589 (v<sub>C</sub>=<sub>N</sub>: imine). <sup>1</sup>H NMR (400 MHz, CDCI<sub>3</sub>,  $\delta$ , ppm): 8.05 (2 H, s, CH=N), 6.59–7.74 (42 H, br m, Ph). <sup>13</sup>C{<sup>1</sup>H} NMR (400 MHz, CDCI<sub>3</sub>,  $\delta$ , ppm): 159.17 (CH=N), 134.27, 134.10, 132.33, 131.56, 130.88, 130.23, 129.66, 129.28, 129.11, 128.94, 126.37, 126.03 (Ph). <sup>31</sup>P{<sup>1</sup>H} NMR (161.97 MHz, CDCI<sub>3</sub>,  $\delta$ , ppm): 2.08 (2P, s).

#### General procedure for Suzuki-Miyaura reaction

A 50 ml round-bottomed flask was charged with a mixture of aryl halide (0.5 mmol), arylboronic acid (0.75 mmol),  $K_2CO_3$  (1.5 mmol) and Pd catalyst (0.1 mol% for aryl bromide or 0.5 mol% for aryl chloride). The mixture was stirred for required times at room temperature in water (4 ml) for aryl bromides or at 80°C in DMF (4 ml) for aryl chlorides. The progress of the reaction was monitored using TLC with aluminium-coated TLC plates (Merck) under UV light or using GC. After completion, the reaction mixture was diluted with water (20 ml) and extracted with ether (3 × 20 ml). The combined extract was washed with brine (3 × 20 ml) and dried over Na<sub>2</sub>SO<sub>4</sub>. After evaporation of the solvent under reduced pressure, the residue was chromatographed (silica gel, ethyl acetate–hexane 1:9) to obtain the desired product. Finally the separated products were characterized using <sup>1</sup>H NMR and mass spectral analyses.

## **Results and discussion**

## Synthesis and characterization of catalyst

The new Pd complex **2** was prepared via halide abstraction reaction with a previously reported complex  $\mathbf{1}^{[13b]}$  according to Scheme 1. The identity of the complex was confirmed using elemental



**Scheme 1.** Synthetic pathway for the preparation of complex **2**.

analyses, ESI-MS and FT-IR, <sup>1</sup>H NMR, <sup>13</sup>C{<sup>1</sup>H} NMR and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopies. In the FT-IR spectrum of complex **2**, the C=N stretching band appears at 1589 cm<sup>-1</sup> which is significantly lower than the C=N stretching band of complex **1** (1609 cm<sup>-1</sup>). The imine signal in the <sup>1</sup>H NMR spectrum of complex **2** appears at 8.05 ppm, which, compared to the parent complex, is an upfield shift of 0.78 ppm. In the <sup>13</sup>C NMR spectrum, a downfield shift of 5.04 ppm in the imine-carbon signal is observed. The <sup>31</sup>P NMR spectrum of the complex shows a singlet at 2.05 ppm.

#### Suzuki-Miyaura cross-coupling reactions

In order to investigate the efficacy of our complex as a catalyst, we performed the cross-coupling reaction using 4-bromoanisole and phenylboronic acid as model substrates. The reaction was performed in water at room temperature using K<sub>2</sub>CO<sub>3</sub> as base with 0.2 mol% of complex 2. We were delighted to find that the reaction proceeds smoothly in water and almost quantitative formation of cross-coupling product is achieved after 8 h of reaction time (Fig. 1). In order to investigate the efficacy of our catalytic system, we performed the model reaction using complex 2, parent Schiff base complex 1 and the phosphine complex Pd(DPEphos)Cl<sub>2</sub> (3) as catalysts using various inorganic bases (Fig. 1). Interestingly, under the same set of experimental conditions, complex 2 shows higher performance than complexes 1 and 3 which may be attributed to the presence of both Schiff base and DPEphos ligands in the same complex. With complex **2** as catalyst,  $K_2CO_3$  is found to be the most efficient base (Fig. 1). Good yields are also obtained with NaHCO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub>. On optimizing the catalyst quantity we find that 0.1 mol% of complex 2 is sufficient to achieve reaction completion (Table 1, entry 2).



**Figure 1.** Effect of base on the catalytic activities of complexes **1**, **2** and **3** (reaction conditions: 4-bromoanisole (0.5 mmol), phenylboronic acid (0.75 mmol), base (1.5 mmol), catalyst (0.2 mol%),  $H_2O$  (4 ml), room temperature, 8 h).

<b>Table 1.</b> Effects of catalyst quantity in Suzuki–Miyaura reactions of 4- bromoanisole with phenylboronic acid using complex <b>2</b> as catalyst <sup>a</sup>				
Br $ OCH_3 + $ $B(OH)_2 \frac{Complex 2 (0.025-0.2 mol%)}{K_2CO_3, H_2O, rt} - OCH_3$				
Entry	Catalyst (mol%)	Time (h)	Yield (%) <sup>b</sup>	
1	0.2	8	100	
2	0.1	11	100	
3	0.075	15	89	
4	0.05	24	74	
5	0.025	48	61	
<sup>a</sup> Reaction conditions: 4-bromoanisole (0.5 mmol), phenylboronic acid (0.75 mmol), K-CO <sub>2</sub> (1.5 mmol), H-O (4 ml)				

<sup>b</sup>GC yields.

In order to widen the scope of our catalyst, various aryl bromides including heteroaryl bromides were coupled with arylboronic acids, using 0.1 mol% of complex 2 in aqueous media. The results are summarized in Table 2. Usually, para-substituted aryl bromides with electron-withdrawing groups (-CHO, -COCH<sub>3</sub>, -COPh) as well as electron-donating groups (-CH<sub>3</sub>, -OCH<sub>3</sub>) give excellent yields (Table 2, entries 1-3, 7, 9). Surprisingly, the coupling reaction between *para*-nitrobromobenzene and phenylboronic acid gives a relatively poor yield in water. However, the yield can be substantially increased by using <sup>i</sup>PrOH as co-solvent with water (entry 4). Interestingly, our catalyst can also tolerate sterically demanding substrates like 3-bromoanisole, 2-bromobenzaldehyde and 1bromo-2,5-dimethoxybenzene and gives the desired products in good yields (entries 5, 6 and 10, respectively). It may be noted that heteroaryl halides are usually difficult to activate in Suzuki-Miyaura reactions and often produce poor yields.<sup>[16]</sup> However, in our case, the heteroaryl bromides 5-bromopyrimidine and 2-bromo-3methylthiophene give reasonably good yields in neat water which can be further enhanced by using <sup>i</sup>PrOH as co-solvent with water (entries 11 and 12). Also, in addition to phenylboronic acid, our catalyst can also tolerate other representative boronic acids like 4-chlorophenylboronic acid (entry 13) and 4-tolylboronic acid (entry 14). The coupling reaction with heteroarylboronic acid, however, results in moderate yield (entry 16).

Encouraged by the results of coupling reactions of aryl bromides, we extended the scope of our catalyst for the cross-coupling reactions of aryl chlorides. To evaluate the efficiency of our complex as a catalyst for the Suzuki-Miyaura reaction of aryl chlorides, we chose 4-chloronitrobenzene and phenylboronic acid as model substrates. Studies of the effect of various inorganic bases and solvents on the reaction reveal that K<sub>2</sub>CO<sub>3</sub> is the most effective base and DMF is the most effective solvent. Using this combination, guantitative biaryl formation is achieved with 4-chloronitrobenzene (Fig. 2) with 1 mol% catalyst loading at 80°C. Unfortunately, unlike aryl bromides, in this case the coupling reaction does not seem to proceed very well in neat water and poor yields are observed. Optimization of temperature and catalyst quantity was also done and the results are summarized in Table 3. Our results indicate that 0.5 mol% catalyst loading is enough to achieve quantitative biaryl formation at 80°C (entry 4). Further reduction of catalyst quantity and temperature causes the product yields to decrease considerably. It is worth mentioning that activation of aryl chloride as substrate is guite challenging due to the higher Ar-Cl bond strength and generally harsh reaction conditions are required.

Table 2.	Suzuki-Miyaura reactions of various aryl and heteroaryl bro-
mides wit	h arylboronic acids using complex <b>2</b> as catalyst <sup>a</sup>

$R=Br+R'=B(OH)_{2} \xrightarrow{Complex 2 (0.1 mol%)}_{K_{2}CO_{3}, H_{2}O, rt} R=R'$				
Entry	R–Br	R'	Time (h)	Yield (%) <sup>b</sup>
1	4-CHOC <sub>6</sub> H <sub>4</sub> Br	C <sub>6</sub> H₅	11	95
2	4-COCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> Br	C <sub>6</sub> H <sub>5</sub>	8	94
3	4-OCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> Br	C <sub>6</sub> H <sub>5</sub>	8	97
4	$4-NO_2C_6H_4Br$	C <sub>6</sub> H <sub>5</sub>	8	68/96 <sup>c</sup>
5	3-OCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> Br	C <sub>6</sub> H <sub>5</sub>	14	87
6	2-CHOC <sub>6</sub> H <sub>4</sub> Br	C <sub>6</sub> H <sub>5</sub>	19	86
7	4-CH <sub>3</sub> C <sub>6</sub> H₄Br	C <sub>6</sub> H <sub>5</sub>	12	94
8	C <sub>6</sub> H₅Br	C <sub>6</sub> H <sub>5</sub>	12	91
9	4-COPhC <sub>6</sub> H <sub>4</sub> Br	C <sub>6</sub> H <sub>5</sub>	20	93
10	2,5-OCH <sub>3</sub> C <sub>6</sub> H <sub>3</sub> Br	C <sub>6</sub> H <sub>5</sub>	20	81
11	5-Bromopyrimidine	C <sub>6</sub> H <sub>5</sub>	20	72/96 <sup>c</sup>
12	2-Bromo-3-methylthiophene	C <sub>6</sub> H <sub>5</sub>	20	74/92 <sup>c</sup>
13	$4-NO_2C_6H_4Br$	4-CIC <sub>6</sub> H <sub>4</sub>	20	91
14	$4-NO_2C_6H_4Br$	$4-CH_3C_6H_4$	20	98
15	C <sub>6</sub> H₅Br	$3-NO_2C_6H_4$	20	90
16	C <sub>6</sub> H₅Br	2-Thenylboronic acid	20	58

<sup>a</sup>Reaction conditions: aryl bromide (0.5 mmol), arylboronic acid (0.75 mmol),  $K_2CO_3$  (1.5 mmol),  $H_2O$  (4 ml).

<sup>b</sup>Isolated yields (average of two runs).

<sup>c</sup>iPrOH–H<sub>2</sub>O (1:1) used as solvent.



**Figure 2.** Effect of base and solvent on the conversion of 4chloronitrobenzene (reaction conditions: 4-chloronitrobenzene (0.5 mmol), phenylboronic acid (0.75 mmol), base (1.5 mmol), complex **2** (1 mol%), solvent (4 ml), 80°C, 5 h).

To study the scope and limitations of our present catalytic system, a series of Suzuki coupling reactions of a wide range of electronically and sterically diverse aryl chlorides with arylboronic acids were performed under the optimized conditions (DMF,  $K_2CO_3$ , 80°C, 0.5 mol% complex **2**). As evident from Table 4, both electron-rich and electron-poor aryl chlorides are successfully coupled with boronic acids resulting in the desirable products in good to excellent yields. Usually, aryl chlorides bearing electron-withdrawing *para* substituent groups like –CHO and –NO<sub>2</sub> give excellent yields (94 and 98%, respectively) in 6 h

Table 3.	Optimization of	temperatu	re an	d catalyst quantity for Su	zuki–
Miyaura	cross-coupling	reaction	of	4-chloronitrobenzene	with
phenylboronic acid with complex <b>2</b> as catalyst <sup>a</sup>					

CI				
Entry	Catalyst (mol%)	Temp. (°C)	Time (h)	Yield (%) <sup>b</sup>
1	1	26	24	34
2	1	60	12	76
3	1	80	6	100
4	0.5	80	6	100
5	0.25	80	12	57
6	0.1	80	12	32

<sup>a</sup>Reaction conditions: 4-chloronitrobenzene (0.5 mmol), phenylboronic acid (0.75 mmol),  $K_2CO_3$  (1.5 mmol), DMF (4 ml). <sup>b</sup>GC yields.

<b>Table 4.</b> Suzuki–Miyaura reactions of various aryl and heteroaryl chlo-rides and arylboronic acids with complex <b>2</b> as catalyst <sup>a</sup>					
R−Cl+R'−B(OH) <sub>2</sub> Complex <b>2</b> (0.5 mol%) K <sub>2</sub> CO <sub>3</sub> , DMF, 80 °C					
Entry	R–Cl	R'	Time (h)	Yield (%) <sup>b</sup>	
1	4-CHOC <sub>6</sub> H <sub>4</sub> Cl	C <sub>6</sub> H₅	6	94	
2	4-COCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> Cl	$C_6H_5$	6	88	
3	4-OCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> Cl	C <sub>6</sub> H <sub>5</sub>	8	89	
4	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> Cl	C <sub>6</sub> H₅	6	98	
5	2-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> Cl	C <sub>6</sub> H <sub>5</sub>	8	62	
6	4-CH <sub>2</sub> OHC <sub>6</sub> H <sub>4</sub> Cl	C <sub>6</sub> H₅	6	82	
7	3-CH <sub>2</sub> OHC <sub>6</sub> H <sub>4</sub> Cl	C <sub>6</sub> H₅	8	75	
8	3-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> Cl	C <sub>6</sub> H₅	8	81	
9	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> Cl	C <sub>6</sub> H₅	6	83	
10	C <sub>6</sub> H₅Cl	C <sub>6</sub> H₅	6	85	
11	3-Chloropyridine	C <sub>6</sub> H₅	8	91	
12	2-Chlorothiophene	C <sub>6</sub> H₅	8	94	
13	4-OCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> Cl	4-CIC <sub>6</sub> H <sub>4</sub>	8	84	
14	4-OCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> Cl	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	8	86	
15	C <sub>6</sub> H₅Cl	2-Thenylboronic acid	20	34	
<sup>a</sup> Reaction conditions: aryl chloride (0.5 mmol), arylboronic acid (0.75 mmol), $K_2CO_3$ (1.5 mmol), DMF (4 ml). <sup>b</sup> Isolated yields (average of two runs).					

reaction time (entries 1 and 4) and electron-donating *para* substituent groups such as  $-OCH_3$  and  $-CH_3$  give good yields (89 and 83%, respectively) in 8 h reaction time (entries 3 and 9). The *meta*-substituted aryl chlorides 3-chlorobenzyl alcohol and 3-chloronitrobenzene give moderate yields (entries 7 and 8) and *ortho*-substituted 2-chloroanisole gives lower yield probably due to steric hindrance in a reaction time of 8 h (entry 5). To our delight, excellent yields of cross-coupling products are observed with the heteroaryl chlorides 3-chloropyridine and 2-chlorothiophene (entries 11 and 12). Coupling reactions of 4-chloroanisole with 4-Cl- and 4-CH<sub>3</sub>-substituted phenylboronic acids proceed smoothly resulting in high product yields (entries 13 and 14). However, a lower yield (34%) is obtained with heteroarylboronic acid (entry 15). In summary, we have developed a highly stable Pd complex composed of phosphine and Schiff base ligands, and successfully performed the cross-coupling reactions of various aryl bromides in water and aryl chlorides in DMF with a low catalyst loading (<0.5 mol %). The catalytic system could also effectively activate sterically demanding aryl halides.

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## **Supporting information**

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