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# Polystyrene-supported palladium(II) *N*,*N*-dimethylethylenediamine complex: A recyclable catalyst for Suzuki–Miyaura cross-coupling reactions in water

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#### ABSTRACT

The polystyrene-supported Pd(II) *N,N*-dimethylethylenediamine complex was prepared and characterized by various techniques, including Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), atomic absorption spectroscopy (AAS), and thermal analysis (TG-DTA). This heterogeneous Pd(II) catalyst works efficiently for the Suzuki–Miyaura coupling of arylboronic acids with aryl bromides in aqueous medium. The effect of base, and additives for the C–C coupling reactions were reported. Further, the catalyst can be easily recovered quantitatively by simple filtration and reused up to five times without significant loss in its catalytic activity.

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## 1. Introduction

Palladium catalyzed Suzuki–Miyaura cross-coupling reaction has evolved into one of the most widely used carbon–carbon bond forming processes [1,2]. This cross-coupling reaction of aryl halides with arylboronic acids, represent the most successful method for the preparation of biaryls. Moreover, Suzuki–Miyaura reaction has shown to have a widespread application in the synthesis of natural products, biologically active compounds, and materials science [3–8]. Recently, we have reported homogeneous thiopseudourea palladium complex as catalysts for the cross-coupling reactions [9,10]. There is a thrust for the development of more environmentally benign cross-coupling processes, highly active and easily reusable immobilized catalysts, and the use of water instead of organic solvents [11–16].

Till date, many heterogeneous palladium catalytic systems were developed for the C–C cross-coupling reactions, such as Pd(II)–Schiff base complex supported on multi-walled carbon nanotubes [17], Pd catalyst supported on amine-functionalized glycidylmeth-acrylate gel type terpolymers [18], mesoporous silica-supported Pd catalyst [19], Pd–pyridine complex immobilized on hydrotalcite [20], Pd–grafted porous metal–organic framework material [21], and polymer-supported Pd–NHC complex [22].

So far, chloromethylated polystyrene is one of the most popular polymeric supports used in preparation of heterogeneous transition metal complexes because of its low cost, ready availability, chemical inertness, and facile functionalization. In recent years, a variety of aqueous catalytic systems and polymer-supported metal catalysts for the cross-coupling reactions were reported [23–30].

However, to the best of our knowledge, no Suzuki–Miyaura coupling reactions of arylboronic acid with aryl bromide catalyzed by polystyrene-supported Pd(II) *N*,*N*-dimethylethylenediamine complex was described in the open literature. Herein, we report the synthesis and characterization of a new polystyrene-supported Pd(II) *N*,*N*-dimethylethylenediamine catalyst and its application to Suzuki–Miyaura cross-coupling reactions in water.

#### 2. Experimental

Chloromethylated polystyrene (5.5 mmol/g Cl loading, crosslinked with 5.5% divinylbenzene, particle size of 16–50 mesh) and  $Pd(CH_3CN)_2Cl_2$  were purchased from Aldrich chemical company, and used without further purification.

#### 2.1. Preparation of polymer-bound N,N-dimethylethylenediamine 2

In order to prepare the polymer-supported ligand, we carried out the following reported procedure [31]. A 250 mL round-bottom flask equipped with a magnetic stirrer was charged with CH<sub>3</sub>CN





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(100 mL). To this chloromethylated polystyrene (0.5 g, 2.25 mmol/ Cl), *N*,*N*-dimethylethylenediamine (2.3 mL, 22.5 mmol), and NaI (14.9 mg, 0.1 mmol) were added and the mixture was refluxed for 48 h. The mixture was filtered, and the residue was washed sequentially with CH<sub>3</sub>CN (3 × 20 mL), 1:1 CH<sub>3</sub>OH–1 M aq K<sub>2</sub>CO<sub>3</sub> (3 × 20 mL), 1:1 CH<sub>3</sub>OH–H<sub>2</sub>O (3 × 20 mL), and Et<sub>2</sub>O (2 × 20 mL), and then dried in an oven.

#### 2.2. Preparation of polystyrene-supported palladium complex 3

To the polystyrene-supported ligand, EtOH (100 mL) was added and kept for 30 min. A solution of  $Pd(CH_3CN)_2Cl_2$  (0.25 g) in EtOH (10 mL) was then added, and the mixture was refluxed for 12 h. The brown colored complex, impregnated with the metal, was filtered, washed thoroughly with EtOH (3 × 30 mL), and finally dried in vacuum at 70 °C for 24 h.

#### 2.3. General experimental procedure for Suzuki–Miyaura crosscoupling reaction

Catalyst **3** (10 mg, 0.004 mmol of Pd), arylboronic acid (0.75 mmol), aryl bromide (0.5 mmol), K<sub>2</sub>CO<sub>3</sub> (138 mg, 1 mmol), cetyltrimethylammonium bromide (36 mg, 0.1 mmol), and water (3 mL) were added to a reaction vessel. The resulting mixture was stirred at 80 °C for 6 h, then cooled to room temperature and catalyst was filtered, the crude residue was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were extracted with water, saturated brine solution, and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The organic layers were evaporated under reduced pressure and the resulting crude product was purified by column chromatography by using ethyl acetate/hexane (1:9) as eluent to give the corresponding product.

#### 2.4. General procedure for catalyst recycling

After the completion of every repeated Suzuki–Miyaura coupling reaction (bromobenzene with phenylboronic acid), the polystyrene-supported Pd catalyst was recovered from the reaction mixture by filtration and washed with distilled water  $(2 \times 15 \text{ mL})$ , ethanol  $(2 \times 15 \text{ mL})$  and diethyl ether  $(2 \times 15 \text{ mL})$ . The washed catalyst was dried at 60 °C under vacuum for 12 h.

#### 3. Results and discussion

#### 3.1. Catalyst characterization

Firstly, polystyrene-supported *N*,*N*-dimethylethylenediamine **2** was prepared by treating chloromethylated polystyrene with an appropriate quantity of *N*,*N*-dimethylethylenediamine **1** in refluxing acetonitrile for 48 h. Product **2** was characterized by FTIR. Then, the ligand-functionalized polystyrene-supported Pd(II) complex **3** was prepared by a suspension of **2** in a solution of Pd(CH<sub>3</sub>CN)<sub>2</sub>Cl<sub>2</sub> in EtOH and was refluxed for 12 h (Scheme 1). The catalyst **3** was characterized by FTIR, SEM–EDX, and AAS. The amount of palladium incorporated into the polymer was determined by atomic absorption spectroscopy (AAS), which showed a value of 4.23% (0.39 mmol/g).

In the IR spectrum of chloromethylated polystyrene, the two characteristic peaks at 1263 and 670 cm<sup>-1</sup> were due to stretching and bending vibrations of C–Cl group (Fig. S1a). They were practically eliminated after the introduction of *N*,*N*-dimethylethylenediamine (Fig. S1b), and palladium onto the polymer (Fig. S1d). Compared to the IR spectrum of Pd(CH<sub>3</sub>CN)<sub>2</sub>Cl<sub>2</sub> (Fig. S1c), the peaks at 2330 cm<sup>-1</sup> (C= $\mathbb{N}$ , CH<sub>3</sub>CN), and 2918 cm<sup>-1</sup> (C– $\mathbb{H}$ , CH<sub>3</sub>CN) are absent in the case of complex; as the NH group of polystyrene-sup-



Scheme 1. Preparation of polystyrene-supported Pd(II) complex 3.

ported ligand in the IR spectrum is 3427 cm<sup>-1</sup>, the NH group of polystyrene-supported palladium complex **3** in the IR spectrum is 3454 cm<sup>-1</sup> indicating the formation Pd–N bond (Fig. S1d).

Morphological features of the polymeric ligand and Pd(II) complex were investigated by making use of scanning electron microscopy. SEM-EDX of the polymeric ligand and their Pd(II) complex are given in Fig. 1. The scanning electron micrographs (Fig. 1, A&C) of the polymer supported ligand and Pd(II) catalyst clearly show the morphological change which occurred on the surface of polystyrene after loading of metal on it. SEM of the polymeric ligand has rough surface. The voids/channels present in the polymeric ligand are responsible for the swelling of the polymer and the active sites buried in the polymer matrix. For the polymeric ligand and Pd(II) complex, the surface was found to be composed of regions of white flake-like appearance. This white flake-like appearance is higher in the case of DVB-crosslinked Pd(II) complex. Also the voids present in the uncomplexed resin are more as compared to the complexed resin. This may arise from the contraction of the voids by the cooperative contribution of the ligands for complexation with Pd(II) ions or the disappearance of the voids in the rearrangement of polymer chains for complexation with metal ions. Energy dispersive X-ray spectroscopy (EDX) analysis data for the polymer anchored ligand and palladium catalyst are given in Fig. 1 (B and D). The EDX data also infers the attachment of palladium metal on the surface of the polymer matrix.

The thermal stability of the complex was investigated by TG-DTA. The negligible weight loss below 200 °C is due to the physically adsorbed solvent molecules. The complex **3** is stable up to 286 °C and further weight loss at a higher temperature (above 286 °C) was attributed to the decomposition of complex Fig. S2 (supporting information). The catalytic activity of the diaminefunctionalized polystyrene-supported palladium complex **3** was tested for the Suzuki–Miyaura cross-coupling reactions.

#### 3.2. Catalytic Suzuki-Miyaura cross-coupling reaction

Initial studies were performed upon the Suzuki–Miyaura crosscoupling reaction of 2-naphthylboronic acid with 4-bromoanisole as a model reaction using **3** (10 mg, 0.004 mmol/Pd) as the catalyst in water at 80 °C for 6 h (Table 1). The reaction was significantly affected by the nature of base and the additive used. Of all the bases and additives tested, the K<sub>2</sub>CO<sub>3</sub>-CTAB was found to be the best combination (Table 1, entry 3). When the reaction was conducted at room temperature, trace amount of product was observed (Table 1, entry 11). Cross-coupling reaction of 2-naphthylboronic acid with 4-chloroanisole did not result in expected yield (Table 1, entry 12). When the catalyst **3** loading was



Fig. 1. SEM-EDX of polystyrene-supported N,N-dimethylethylenediamine ligand 2 (A and B) and polystyrene-supported Pd(II) complex 3 (C and D).

#### Table 1

Screening reaction conditions for Suzuki coupling reaction between 2-naphthylboronic acid and 4-bromoanisole.



Entry	Base	Additive	Yield (%) <sup>a</sup>
1	K <sub>2</sub> CO <sub>3</sub>	-	72
2	K <sub>2</sub> CO <sub>3</sub>	TBAB	80
3	K <sub>2</sub> CO <sub>3</sub>	CTAB	82
4	K <sub>2</sub> CO <sub>3</sub>	PEG-400	76
5	K <sub>3</sub> PO <sub>4</sub>	CTAB	79
6	KF·H <sub>2</sub> O	CTAB	74
7	LiOH·H <sub>2</sub> O	CTAB	76
8	NaOAc	CTAB	70
9	KHCO <sub>3</sub>	CTAB	64
10	KO <sup>t</sup> Bu	CTAB	81
11	K <sub>2</sub> CO <sub>3</sub>	CTAB	Trace <sup>b</sup>
12	K <sub>2</sub> CO <sub>3</sub>	CTAB	Trace <sup>c</sup>
13	K <sub>2</sub> CO <sub>3</sub>	CTAB	68 <sup>d</sup>
14	K <sub>2</sub> CO <sub>3</sub>	CTAB	82 <sup>e</sup>

Reaction conditions: 2-naphthylboronic acid (0.75 mmol), base (1 mmol), 4-bromoanisole (0.5 mmol), catalyst **3**(10 mg, 0.004 mmol/Pd), water (3 mL), additive (0.1 mmol), 80 °C, 6 h. <sup>a</sup> Isolated vield.

<sup>b</sup> Reaction was done at room temperature.

<sup>c</sup> Reaction was done by 4-chloroanisole.

<sup>d</sup> Catalyst **3** (5 mg, 0.002 mmol/Pd) was used.

<sup>e</sup> Catalyst 3 (20 mg, 0.008 mmol/Pd) was used.

decreased to 0.002 mmol, or increased to 0.008 mmol from 0.004 mmol (Table 1, entries 13 and 14) for the coupling reaction of 4-bromoanisole, no improvement in the yield was observed.

Using the optimized reaction conditions, we explored the general applicability of catalyst **3** for cross-coupling reactions with different arylboronic acids and aryl bromides containing electron withdrawing or donating substituent, and the results were summarized in Table 2. High catalytic activity was observed in the coupling of 2-naphthylboronic acid with various aryl bromides, i.e. para and meta positions of methoxy group (entries 1 and 3), para positions of NO<sub>2</sub>, CF<sub>3</sub>, and CN (entries 6, 9, and 10). With 2-bromoaniline, no reaction took place (entry 7). We also investigated the activity of catalyst **3** for simple and substituted (p-methyl and methoxy) phenylboronic acids with aryl bromides and the results were given in Table 2 (entries 11–23). In this case, the yields are comparable with reported values.

#### 3.3. Recyclability test

The reusability of the catalyst is a very important theme, especially for commercial applications. Therefore, the recovery and reusability studies of the catalyst were done by conducting the reaction of phenylboronic acid with bromobenzene. Not much decrease in the activity of catalyst was observed even after five cycles (Fig. 2).

After every cycle, leaching of the palladium content from the catalyst **3** was determined by AAS. After the first run, a 0.23% of palladium weight loss was observed. A 5% Pd loss was noticed after five times usage of our catalyst.

#### Table 2

Suzuki cross coupling reaction of arylboronic acids with aryl bromides using polystyrene-supported Pd(II) complex **3**.

Arylboronic acids	+	Aryl bromide

$$\begin{array}{c} \text{catalyst } \mathbf{3} \\ \hline K_2 \text{CO}_3, \text{CTAB}, \text{H}_2 \text{O} \\ 80 \text{ }^\circ\text{C}, 6 \text{ h} \end{array} \end{array} \text{Product}$$

Entry	Arylboronic acids	Aryl bromide	Product	Yield (%) <sup>a</sup>	TON <sup>b</sup>
1	(4a) B(OH) <sub>2</sub>	4-OCH₃C <sub>6</sub> H₄Br	OCH3	82	102.5
2	4a	$2\text{-OCH}_3\text{C}_6\text{H}_4\text{Br}$		65	81.2
3	4a	3-OCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> Br	OCH3	84	105.0
4	4a	3-CNC <sub>6</sub> H₄Br		78	97.5
5	4a	1-naphthyl bromide		72	90.0
6	4a	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> Br		88	110.0
7	4a	2-NH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> Br		00	00
8	4a	C <sub>6</sub> H₅Br	NH <sub>2</sub>	82	102.5
9	4a	4-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> Br	CF <sub>3</sub>	86	107.5
10	4a	4-CNC <sub>6</sub> H <sub>4</sub> Br		85	106.0
11	B(OH) <sub>2</sub>	C <sub>6</sub> H₅Br		98	122.5
12	(4b) 4b	4-ClC <sub>6</sub> H <sub>4</sub> Br	CI	92	115.0
13	4b	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> Br		96	120.0
14	4b	$4-CH_3C_6H_4Br$	CH3	94	117.5
15	4b	4-OCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> Br	CCH3	93	116.0
16	4b	4-SCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> Br	SCH3	88	110.0

(continued on next page)

Table 2 (continued)

Entry	Arylboronic acids	Aryl bromide	Product	Yield (%) <sup>a</sup>	TON <sup>b</sup>
17	4b	2-OCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> Br	H <sub>3</sub> CO	83	103.7
18	4b	3-BrC₅H₄N		86	107.5
19	$H_3C \longrightarrow B(OH)_2$	4-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> Br	H <sub>3</sub> C	88	110.0
20	4c	$4-CH_3C_6H_4Br$	H <sub>3</sub> C — CH <sub>3</sub>	92	115.0
21	4c	4-OCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> Br	H <sub>3</sub> C — OCH <sub>3</sub>	90	112.5
22	4c	4-SCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> Br	H <sub>3</sub> C-SCH <sub>3</sub>	86	107.5
23	EtO	$4-OCH_3C_6H_4Br$	EtO	78	97.5
	B(OH)2		CH3		

Reaction conditions: arylboronic acids (0.75 mmol), aryl bromide (0.5 mmol), catalyst (10 mg, 0.004 mmol/Pd), K<sub>2</sub>CO<sub>3</sub> (1 mmol), CTAB (0.1 mmol), water (3 mL), 80 °C, 6 h. <sup>a</sup> Isolated yield.

<sup>b</sup> Turnover number (TON).



Fig. 2. Efficiency of recyclable catalyst for Suzuki cross coupling reaction of phenylboronic acid with bromobenzene.

#### 4. Conclusion

We have developed a clean and safe protocol for the Suzuki– Miyaura cross-coupling reaction catalyzed by the **3** complex. The present system is highly air and moisture stable and the catalyst can be synthesized readily from inexpensive and commercially available starting materials. Moreover, the catalyst could be reused for five consecutive cycles without noticeable loss of its catalytic activity. These advantages make the process highly valuable from the synthetic and environmental points of view.

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#### **Appendix A. Supplementary material**

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2014.07.044.

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