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### COMMUNICATION



## A simple, quick and novel protocol for biaryl synthesis using LiCl-promoted *in situ*-generated Pd nanoparticles

Parmita Phukan<sup>1</sup> | Preeti Rekha Boruah<sup>1</sup> | Praveen Singh Gehlot<sup>2</sup> | Arvind Kumar<sup>2</sup> | Diganta Sarma<sup>1</sup>

<sup>1</sup>Department of Chemistry, Dibrugarh University, Dibrugarh 786004 Assam, India

<sup>2</sup>Academy of Scientific and Innovative Research (AcSIR)-Central Salt and Marine Chemicals Research Institute, Council of Scientific and Industrial Research (CSIR), G. B. Marg, Bhavnagar 364002 Gujarat, India

Correspondence

D. Sarma, Department of Chemistry, Dibrugarh University, Dibrugarh 786004, Assam, India. Email: dsarma22@gmail.com

### Abstract

This paper describes a simple and a very quick protocol for biaryl synthesis using the Suzuki–Miyaura cross-coupling reaction. A quintessential role of salting-out agent LiCl was observed in the Suzuki–Miyaura cross-coupling reaction that enhanced the reduction rate of Pd (II) to a considerable extent, resulting in the formation of nanosized palladium in a few seconds. The isolated Pd nanoparticles were characterized with X-ray diffraction, dynamic light scattering, TGA, transmission electron microscopy and scanning electron microscopydispersive X-ray spectroscopy. The Suzuki–Miyaura cross-coupling reaction proceeded very well with the *in situ*-generated Pd nanocatalysts furnishing the desired biaryl adducts with excellent yields.

### KEYWORDS

green chemistry, LiCl, nanoparticles, palladium chloride, Suzuki-Miyaura reaction

### **1** | INTRODUCTION

Nanoparticles of noble metals have received great attention in recent years because of their wide applications in various fields, as well as their considerable structural stability. Nanostructured transition metal particles have characteristic properties that are strikingly different from those of the bulk, as a result of which they have gained attention from both fundamental and technological points of view.<sup>[1,2]</sup> Palladium, being one of the most versatile metals, has been extensively used in the area of palladium nanoparticle catalysis. Among the diverse metal nanoparticles, palladium nanoparticles are of particular interest in the field of nanocatalysis owing to their unique properties and wide potential in a variety of organic reactions and transformations,<sup>[3]</sup> including their applications in the field of medicine, material science, sensor design applications, etc. Nanosized palladium crystals act as strong and efficient catalysts for a large number of important catalytic reactions, such as hydrogenation reactions,<sup>[4]</sup> electrochemical reductions and oxidations,<sup>[5–7]</sup> oxidation of hydrocarbons in automobiles,<sup>[8,9]</sup> carboncarbon bond-forming reactions,<sup>[10]</sup> such as Heck,<sup>[11]</sup> Suzuki,<sup>[12]</sup> and Stille,<sup>[13]</sup> along with C-N coupling reactions.<sup>[14]</sup> Synthetic methodologies have been reported in recent years, regarding the preparation of stable palladium nanoparticles that can be used as catalysts. In general, nanostructured catalysts are prepared chemically by the reduction of Pd (II) salts using various reducing agents. It has been observed that the methodologies adopted during the synthesis of palladium nanoparticle catalysts usually employ high-performance technologies, such as sonochemical method,<sup>[15]</sup> sonoelectrochemical method,<sup>[16]</sup> microemulsion technique,<sup>[17]</sup>  $\gamma$ -irradiation,<sup>[18]</sup> UV-irradiation,<sup>[19]</sup> polyol reduction,<sup>[20]</sup> etc. Moreover, the methods adopted are usually facile, cost-effective, but also employ harsh reaction conditions that are both economically and environmentally hazardous. Apart from these, the procedures employed are quite time-consuming and laborious. Herein, we report a simple as well as very quick and efficient novel protocol for the synthesis of biaryls using the salting-out agent LiCl-promoted in

-WILEY-Organometallic Chemistry situ-generated palladium nanoparticle catalyst. The in situ-generated catalyst showed significant applicability in Suzuki-Miyaura cross-coupling reactions with satisfactory yields of the desired coupled products. To the best of our knowledge, this method is one of the quickest methods that affords palladium nanoparticles within just a few seconds.

### 2 | EXPERIMENTAL

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### 2.1 | General reaction procedure for Suzuki-Miyaura cross-coupling reaction

The Suzuki-Miyaura cross-coupling reaction was performed using the in situ-prepared palladium nanocatalyst. A mixture of aryl bromide (1 mmol) and arylboronic acid (1.2 mmol) was stirred in a 100-ml round-bottom flask in isopropanol and water system (1 ml) with  $K_2CO_3(2 \text{ mmol})$ as base, PdCl<sub>2</sub> as catalyst and 1 ml of 3 M LiCl (aq.) as promoter. The reaction mixture was stirred for the indicated time at room temperature. After completion of the reaction (by thin-layer chromatography monitoring), the reaction mixture was extracted with diethyl ether  $(4 \times 10 \text{ ml})$  and after that the organic layer was washed with deionized water  $(3 \times 10 \text{ ml})$ . The organic layer was then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and the separated organic layer was evaporated in a rotary evaporator. The products were purified by column chromatography over silica gel using *n*-hexane and ethyl acetate (9:1  $\nu/v$ ) as eluents to obtain the purified cross-coupled product. The products were then characterized by <sup>1</sup>H NMR and <sup>13</sup>C NMR.

#### **RESULTS AND DISCUSSION** 3

To evaluate the efficiency of the catalytic system, the Suzuki-Miyaura cross-coupling reaction of 4-bromoanisole and phenyl boronic acid was examined in *i*-PrOH and water system using K<sub>2</sub>CO<sub>3</sub> as base at room temperature (Table 1, entries 1-6). To adopt a satisfactory optimized condition, the effect of the amount of PdCl<sub>2</sub> in the reaction was investigated. From Table 1, it has been observed that excellent yield of the desired biaryl was obtained within 30 min in the presence of 4 mol% of catalyst (Table 1, entry 1). Decreasing the catalyst loading to 3.5 mol% and 3 mol% afforded the coupled product in sufficient isolated yield (Table 1, entries 2 and 3). A further decrease in the catalyst loading to 2 mol% also furnished the desired product with excellent yield within a very short period of time (Table 1, entry 4). However, a slight decrease in the yield was observed along with a longer reaction time when the amount of catalyst was decreased to 1 mol% (Table 1, entry 5). A further decrease in the catalyst loading to 0.5 mol% resulted in good isolated yield of 89% (Table 1, entry 6). Further reactions were carried out using 2 mol% of the catalyst, which was established as the ideal optimized reaction condition for catalyst loading.

In order to investigate the role of solvent and base, the Suzuki reaction between 4-bromoanisole and phenyl boronic acid was performed. The choice of solvent and base is a very important factor in carrying out Suzuki-Miyaura cross-coupling reactions. The reaction was carried out in various organic and aqueous solvents, and a significant variation in the yield of the coupled product was noticed in each case. It was seen from Table 2 that excellent yields of the desired coupled products were obtained in water-i-PrOH system (Table 2, entry 3). This may be due to the greater solubility of the aryl halides in *i*-PrOH that increases the rate of reaction to a considerable extent. Literature reports indicate that base plays a crucial role in Suzuki-Miyaura cross-coupling reactions. Hence, a variety of bases were also investigated to study the reaction rate, and the best result was obtained using K<sub>2</sub>CO<sub>3</sub> as base and water-*i*-PrOH as the solvent system affording 96% of the desired product in just 30 min (Table 2, entry 3). Use of a strong base enhances sideproducts, which in return decreases the yield of the desired product, while a weak base fails to activate the boronic acid for coupling. Because of these reasons, bases such as KOH, Et<sub>3</sub>N, etc. do not give satisfactory results.

To explore the substrate scope and wide applications of Suzuki-Miyaura cross-coupling reactions, a series of aryl bromides were allowed to react with aryl boronic acids under the experimentally adopted optimized reaction conditions (Table 3, entries 1-14). Both structurally as well as electronically diverse substrates were tested using our newly prepared palladium nanocatalysts in *i*-PrOH:H<sub>2</sub>O system at room temperature. It is noteworthy that the catalytic system so prepared tolerated a large number of functional groups, such as -CH<sub>3</sub>, -OCH<sub>3</sub>, -CN, -CHO, -NO<sub>2</sub>, etc., and also afforded a quite significant vield of the desired biaryls. Interestingly, heteroaryls such as 3-bromothiophene and 2-bromopyridine also provided us with good to excellent yield of the desired coupled product (Table 3, entries 12, 13). Moreover, an important observation is that the formation of homocoupling product of arylboronic acid, which sometimes lowers the expected yield of the desired product, is not observed during our experiment. Thus, this catalytic system affords a quite easy and efficient method for the preparation of biaryls at room temperature in a very short period of time.

The effect of salting-out agents such as LiCl on kinetics of organic transformations has been discussed in terms of several parameters, such as hydrophobic packing, solvent pressure, hydrogen bonding, hydrophobic hydration, **TABLE 1** Effect of the catalyst quantity in the coupling reaction of 4-bromoanisole and phenyl boronic acid in *i*-PrOH/H<sub>2</sub>O as solvent,  $K_2CO_3$  as base and 3 M LiCl as promoter at room temperature<sup>a</sup>

$H_{3}CO$					
Entry	Catalyst (mol%)	Time (min)	Yield <sup>b</sup> (%)		
1	4	30	99		
2	3.5	30	99		
3	3	30	99		
4	2	30	99		
5	1	50	92		
6	0.5	50	89		

<sup>a</sup>Reaction conditions: aryl bromide (1 mmol), phenyl boronic acid (1.2 mmol), K<sub>2</sub>CO<sub>3</sub> (2 mmol), 3 M LiCl (1 ml) in *i*-PrOH and water as solvent (1:1, 1 ml) at room temperature.

<sup>b</sup>Isolated yield.

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H <sub>3</sub> CO Br + Solvent, Base PdCl <sub>2</sub> , 3 M LiCl, RT H <sub>3</sub> CO							
Entry	Solvent	Base	Time (h)	Yield <sup>b</sup> (%)			
1	H <sub>2</sub> O	K <sub>2</sub> CO <sub>3</sub>	2	70			
2	ETOH/H <sub>2</sub> O (1:1)	K <sub>2</sub> CO <sub>3</sub>	4	60			
3	<i>i</i> -PrOH/H <sub>2</sub> O (1:1)	K <sub>2</sub> CO <sub>3</sub>	0.5	96			
4	<i>i</i> -PrOH/H <sub>2</sub> O (1:1)	Na <sub>2</sub> CO <sub>3</sub>	3	40			
5	_	Et <sub>3</sub> N	5	30			
6	<i>i</i> -PrOH/H <sub>2</sub> O (1:1)	Et <sub>3</sub> N	3	40			
7	EtOH	Et <sub>3</sub> N	3	30			
8	-	K <sub>2</sub> CO <sub>3</sub>	5	70			
9	<i>i</i> -PrOH	NaHCO <sub>3</sub>	4	65			
10	H <sub>2</sub> O	Cs <sub>2</sub> CO <sub>3</sub>	4	40			

**TABLE 2** Screening the efficiency of solvent and base for coupling of aryl bromides and phenyl boronic acid<sup>a</sup>

<sup>a</sup>Reaction conditions: aryl bromide (1 mmol), phenyl boronic acid (1.2 mmol), PdCl<sub>2</sub> (2 mol%), 3 M LiCl (1 ml) at room temperature. <sup>b</sup>Isolated yield.

etc.<sup>[21a,21b,21c,21d]</sup> At present, we are not clear whether any one of these parameters or combination of all work for LiCl-promoted Suzuki–Miyaura cross-coupling reactions. Literature reports also suggest that the complexation of PdCl<sub>2</sub> and LiCl results in the *in situ* formation of a water-soluble complex, Li<sub>2</sub>PdCl<sub>4</sub>, which is believed to catalyse the Suzuki–Miyaura cross-coupling reaction. It was noteworthy that a longer reaction time for the completion of the reaction with a comparatively decreased yield of the product was observed when the reaction was performed in the absence of LiCl.

Reusability of a heterogeneous catalyst serves as an important factor in determining the efficiency of a catalyst both from an economic and a green chemistry point of view.<sup>[21e]</sup> The level of recyclability of the prepared nanocatalytic system was investigated by consecutive Suzuki–Miyaura cross-coupling of 4-bromoanisole and phenyl boronic acid. After the first reaction cycle, diethyl ether was added to the reaction mixture followed by centrifugation and the clear organic layer was separated, which was then evaporated to get the desired product. The recovered catalyst system consisting of Pd nanoparticles, LiCl (aq.)/*i*-PrOH was immediately used in the  $2^{nd}$  reaction cycle by adding fresh reactants. Almost identical results were obtained till the 5<sup>th</sup> cycle of consecutive reactions, which confirmed its efficiency as a reusable catalyst without significant loss of its catalytic activity at least up to five times (Table 4, entries 1–5).

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**TABLE 3** Pd (0) catalyzed Suzuki–Miyaura reactions using arylbromides and arylboronic acids<sup>a</sup>



<sup>a</sup>Reaction conditions: aryl bromide (1 mmol), arylboronic acid (1.2 mmol), PdCl<sub>2</sub> (2 mol%), K<sub>2</sub>CO<sub>3</sub> (2 mmol), 3 M LiCl (1 ml); *i*-PrOH:H<sub>2</sub>O (1:1, 1 ml) at room temperature.

<sup>b</sup>Isolated yield.

# 3.1 | Characterization of the isolated catalyst

Generally, salts of PdCl<sub>2</sub>, Na<sub>2</sub>PdCl<sub>2</sub>, etc. are used as precursors for the preparation of palladium nanoparticles. In our procedure, when PdCl<sub>2</sub> is added to a mixture of 3 M LiCl, phenyl boronic acid and base ( $K_2CO_3$ ), appearance of black colour of the solution results within just a few seconds (Figure 1). The reaction mixture was stirred for 10 min to ensure complete reduction of Pd (II) salts. The resulting mixture was completely black in colour, which was then centrifuged and washed several times with organic solvents, such as ether, hexane, ethyl acetate, acetone to obtain pure palladium nanoparticles. The washed catalyst was then oven-dried at 80 °C for 6 h in order to get the dried powdered form of the catalyst.

Morphology, sizes and characterization of the particles were determined by various techniques viz. transmission electron microscopy (TEM), scanning electron microscopy (SEM), dynamic light scattering (DLS), Xray diffraction (XRD), TGA and Zeta potential. Figure 2 depicts some of the images of the newly synthesized Pd nanoparticles from TEM. It has been seen that the average size of the particles ranges from 2 to 20 nm, and are mostly spherical in shape (Figure 2a-c). Some of the particles are found in agglomerated form (Figure 2c). From high-resolution (HR)-TEM, lattice spacing between two adjacent planes of the synthesized nanoparticle was found to be 0.22 nm (Figure 2b), which is characteristic for Pd metallic nanoparticles. SEM was performed to determine the morphology of the nanoparticles deposited on the surface, and most of the particles were found to be cuboidal in shape (Figure 1; Supporting Information). Some of the SEM images are shown in Figure 1a-d (Supporting Information). TEM results represent the nanosize of Pd nanoparticles, where in SEM images these nanoparticles have agglomerated in the sample and adopted well-engineered shapes, such as cuboidal along with hexagonal, after drying. Composition of Pd nanoparticles in the newly prepared powdered sample was determined by dispersive X-ray spectroscopy (EDX), which showed a strong signal in the palladium region indicating the formation of Pd nanoparticles (Figure 1; Supporting Information). The XRD pattern of the newly synthesized Pd nanoparticles is shown in Figure 2 (Supporting Information). Prominent Bragg's diffracted peaks were observed at 20 values of 40.63°, 46.32° and 66.43°, which are assigned to be from (111), (200), (220) crystal planes of Pd nanoparticles.

Dynamic light scattering and Zeta potential measurements were performed to evaluate the hydrodynamic radii of nanoparticles and surface charge of Pd nanoparticles.

### **TABLE 4** Recyclability of the catalytic system<sup>a</sup>

	H <sub>3</sub> CO <sup>Br</sup> +	$\begin{array}{c} \begin{array}{c} & B(OH)_2 \\ & \xrightarrow{PdCl_2, \ 3 \ M \ LiCl, \ K_2CO_3 \\ \hline & & \xrightarrow{I}-PrOH:H_20, \ RT \end{array} \to \operatorname{H}_3CO  \begin{array}{c} & & \\ \end{array}$	
Entry	Run	Time (min)	Yield <sup>b</sup> (%)
1	$1^{st}$	30	98
2	2 <sup>nd</sup>	30	96
3	3 <sup>rd</sup>	30	96
4	4 <sup>th</sup>	50	84
5	5 <sup>th</sup>	90	78

<sup>a</sup>Reaction conditions: aryl bromide (1 mmol), phenyl boronic acid (1.2 mmol), PdCl<sub>2</sub> (1 mol%), 3 M LiCl (1 ml), K<sub>2</sub>CO<sub>3</sub> (2 mmol), *i*-PrOH:H<sub>2</sub>O (1:1, 1 ml) at room temperature.

<sup>b</sup>Isolated yield.



**FIGURE 1** Preparation of palladium nanocatalyst. (a) mixture of boronic acid,  $K_2CO_3$ , 3 M LiCl. (b) addition of PdCl<sub>2</sub> to (a). (c) instant change of colour after addition of PdCl<sub>2</sub> to (a). (d) reaction mixture before centrifugation. (e) reaction mixture after centrifugation. (f) dried powder form of prepared catalyst

Zetasizer Nano ZS light scattering apparatus (Malvern Instruments, UK) with a He – Ne laser (633 nm, 4 mW) at an angle of 90° where filtered solution through 0.22- $\mu$ m membrane filter was directly transferred into the cuvette. The intensity weighted size distribution (Figure 2 d) showed that nanoparticles have average hydrodynamic radii from 20 to 60 nm, with maximum intensity at 38 nm. The larger size was observed due to agglomeration of

Pd nanoparticles in solution. This size measurement validates the size measured from TEM. The Zeta potential value for Pd nanoparticles was also measured to check their colloidal stability, and the value of zeta potential was found to be near to  $\pm$  0.75 mV, which is far from the required value for stability. This indicates nil surface charge of the nanoparticles, and as a consequence they tend to agglomerate in the dispersion medium.

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FIGURE 2 TEM images of palladium nanoparticles (a-c) and intensity-weighted DLS of Pd nanoparticles (d) (yellow circle showing nanoparticle and arrow bars showing d-spacing)

### 4 | CONCLUSION

In summary, we have developed an efficient and very quick method for the synthesis of biaryls using rapid *in situ*-generated palladium nanoparticles. The newly generated *in situ* catalyst has been analyzed by several characterization techniques, such as TEM, SEM–EDX, XRD and TGA. Moreover, it plays an effective role in the Suzuki– Miyaura cross-coupling reactions of activated aryl halides and aryl boronic acids, providing a significant yield of the desired coupled products at room temperature.

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### ORCID

Diganta Sarma in http://orcid.org/0000-0001-5174-418X

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### SUPPORTING INFORMATION

Additional Supporting Information may be found online in the supporting information tab for this article.

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