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# Short Communication

# An ester appending multifunctional ionic liquid for Pd(II) catalyzed Heck reaction

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## 1. Introduction

The palladium-catalyzed Heck arylation of olefins is one of the most important carbon–carbon bond forming processes in synthetic organic chemistry [1–3]. The availability of a wide spectrum of functional groups in both the substrates makes this reaction more compatible for total synthesis. At present there are some concerns with respect to this reaction *viz*. activation of C–Cl bond, development of phosphine-free palladium catalyst, high reaction temperature (usually above 100 °C) and recyclability of the catalytic system. Even though the arylchlorides are easily available starting materials, they require drastic reaction conditions (>140 °C), use of phosphine ligands and hindered amines [4]. Phosphine ligands act as stabilizers for *in situ* generated catalytically active Pd(0) complexes. However, due to high cost, air sensitivity and environmental concerns related to phosphine containing systems, recently development of phosphine-free catalyst has received considerable attention.

Green and cost-effective catalyst systems with high efficiency and selectivity are the cornerstones of contemporary synthetic chemistry. In the last decade the field of ionic liquids (ILs) has emerged as a promising field to address concerns of organic chemists. These ILs being non-volatile and thermally stable became popular as substituents to conventional volatile organic solvents. Apart from this, their chemical and physical properties can be tuned by modifying cation or anion, which has further popularized them as a catalyst and as conducive reaction media. Our group has [5,6] explored the

## ABSTRACT

A basic, ester functionalized, imidazolium based ionic liquid (IL2), 3-Methyl-1-(ethoxycarbonylmethyl) imidazolium hydroxide was designed eyeing *in situ* generation and stabilization of palladium nanoparticles for palladium catalyzed Heck reaction of haloarenes and olefins. This phosphine-free Pd-IL catalyst demonstrated excellent activity and reusability at relatively low reaction temperature (80 °C) for a wide spectrum of haloarenes including chloroarenes. The relatively low reaction temperature could be attributed to *in situ* generation of uniform and spherical palladium nanoparticles (~5 nm).

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potential of ILs as reaction media and as catalyst for some organic transformations. In one of our recent findings, we have demonstrated [7] the importance of ionic liquid as superior reaction media for cycloaddition reaction catalyzed by copper nanoparticles. Since the first report [8], there are a number of reports on Heck reaction in ionic liquid with very recent reports [9,10] of use of palladium nanoparticles in ionic liquids. It is now well-versed that nanoparticles provide enhanced catalytic activity due to increased surface area and rotational degrees of freedom [11]. In general, the larger the surface area (i.e. smaller size), the greater the catalytic activity. Thus, smaller NPs are preferable, although they tend to be less stable and are prone to aggregation ultimately leading to less effective catalysts. Agglomeration of nanoparticles can be avoided by use of stabilizing agents. However, these stabilizing agents have substantial effects on their catalytic activity [12]. Ionic liquids have been shown to provide "electrostatic" stabilization for metal nanoparticles and also more surface area for the reaction to take place [13,14]. Multiphase systems of ionic liquid-nanoparticles facilitate easy recovery of nanoparticles. Recently, Wang et al. [15] reported a novel ethanolamine based quaternary ammonium salt for Heck reaction. The ionic liquid showed very high activity with reusability of palladium. Taking into account advantages of use of ionic liquids in synthesis of nanoparticles and as an attempt to circumvent the concerns of traditional Heck reaction, we decided to design and synthesize an ionic liquid (IL) that can act as base, ligand and reaction media and also provide stability to in situ generated palladium nanoparticles. Herein we report an ester appending imidazolium based basic ionic liquid (2) for Heck reaction of olefins and aryl halides. IL2 is designed, eyeing in situ generation and stabilization of the palladium nanoparticles. The IL2 showed excellent activity, reactivity and reusability for the Heck reaction.

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# 2. Experimental

## 2.1. Materials

Palladium acetate, aryl halides, olefins, ethyl bromoacetate and 1methyl imidazole were obtained from Aldrich and used as received. All other reagents were AR grade and used as received. Ionic liquid (2) was prepared as indicated in Scheme 1. Progress of reaction was monitored by TLC (Silica gel 60  $F_{254}$ ). The formed IL2 was characterized with ESI-MS, <sup>1</sup>H, <sup>13</sup>C and <sup>1</sup>H <sup>13</sup>C HETCOR NMR and HRMS. Products of Heck reaction were characterized by <sup>1</sup>H and <sup>13</sup>C NMR analysis. The isolated palladium nanoparticles were characterized by TEM analysis.

# 2.2. General procedure for preparation of IL 2

lonic liquid 1 was prepared by the following reported method [16]. To a stirred solution of 1-methylimidazole (8.0 mL, 100 mmol) in THF (50 mL) at -5 °C under a nitrogen atmosphere was added dropwise ethyl bromoacetate (13.4 mL, 120 mmol). The reaction mixture was stirred vigorously at -5 °C for 1 h, then at r.t. for 3 h. The THF top phase was decanted and the IL washed with diethyl ether (3×15 mL), then residual solvent removed *in vacuo*. The product was dried at 60 °C under vacuum for 72 h to give a clear viscous hygroscopic oil as ionic liquid 1 (IL1).

Solid potassium hydroxide (2.3 g, 40 mmol) was then added to ionic liquid 1 (10.4 g, 40 mmol) in dry dichloro methane and stirred vigorously for 5 h. The precipitated salt (KBr) was filtered off, and the filtrate was evaporated to leave the crude ionic liquid 2 (IL2) as a viscous liquid. It was washed with ether ( $2 \times 20$  mL) and dried ( $80 \,^{\circ}$ C) under inert atmosphere for 5 h to get the pale yellow coloured viscous liquid for use. This ionic liquid 2 was characterized by <sup>1</sup>H, <sup>13</sup>C, <sup>1</sup>H <sup>13</sup>C HETCOR NMR, ESI-MS and HRMS analysis.

# 2.3. General procedure for Heck reaction

To IL 2 (0.2 g) in a 50 ml round bottom flask was added the palladium acetate (2.3 mg) and stirred at 80 °C for 10 min. After that aryl halide and olefin (1 mmol each) were introduced in the flask and stirred for 8 h at 80 °C. After completion of reaction, ethyl ether was added and the organic layer was washed with water and dried over sodium sulfate. The organic layer was evaporated under reduced pressure and the crude product was purified by column chromatography.



X = CI, Br, I  $R = Ar, CO_2R_1$ 

Scheme 1. Synthesis and application of IL 2 for Heck reaction.

# 3. Results and discussion

#### 3.1. Synthesis and application of IL to Heck reaction

With the aim to improve the catalytic activity by in situ generation and stabilization of palladium nanoparticles, we designed and synthesized IL 2 for Heck reaction. In our earlier work on ionic liquid mediated synthesis of copper nanoparticles and their use in 1-3 dipolar cycloaddition reaction, it was observed that only imidazole containing ILs could not provide sufficient stability to nanoparticles making the use of stabilizing agents mandatory. These stabilizing agents may have profound effect on course of reaction, further jeopardizing the whole procedure. It is now a well established fact that mechanism of Heck reaction involving palladium nanoparticles proceeds via the formation of soluble palladium complexes. Taking into account these aspects we decided to design a carbonyl functionalized ionic liquid. In one of the earlier reports [16], the ester functionalized ILs were found to have advantages of biodegradability and analogous behavior to their alkyl side chain analogues (like [bmim]PF<sub>6</sub>, [bmim]OH etc.). However, from some recent reports [17– 22], we came to the conclusion that an ionic liquid with ester function can best fit for the stabilization of nanoparticles. Keeping these points in mind an IL was prepared starting with ethyl bromoacetate and 1methyl imidazole. Addition of ethyl bromoacetate was carried out slowly at lower temperature and the reaction mixture was then stirred at room temperature for 3 h to get the ionic liquid 1. IL 1 was then subjected to metathesis with potassium hydroxide to get the desired IL 2. Post-reaction analysis (ESI-MS) of ionic liquid wards off the possibility of hydrolysis of appending ester function (at elevated reaction temperature). The stability of IL after reaction was confirmed by NMR analysis of the recovered IL (after reaction).

The effect of source of palladium on the Heck reaction was tested for reaction of p-iodoanisole and styrene. Among the screened palladium salts as illustrated in Table 1, Pd(OAc)<sub>2</sub> was found effective for Heck reaction in IL 2. A temperature of 80 °C was found to be optimum for an 8 h reaction time. The applicability and generality of this Pd-IL 2 catalytic system for Heck reaction of olefins and aryl halides were studied with a wide array of substrates. Representative results of the coupling reaction are summarized in Table 2. In order to investigate the effect of substituent group on arylhalide, various substituted arylhalides were used. The coupling reaction for arylhalides with both electron deficient and electron rich substituents, underwent smoothly as indicated in Table 2. There was no any substantial effect of substituent on reaction. Even though iodoarenes and bromoarenes gave excellent yields in stipulated time of 8 h, the arylchlorides showed some reluctance and gave moderate yields (Entries 16–19 Table 2). Though the general experimental procedure was based on 1 mmol scale, 50 mmol reactions produced similar results. Initially when the ionic liquid was stirred with palladium acetate at 80 °C, within 10 min the reaction mixture turned black. This blackening of the reaction mixture at the beginning prompted us to isolate the palladium. The isolated palladium was characterized by transmission electron microscopy (TEM). From TEM images, generation of palladium nanoparticles with average size of 5 nm and

 Table 1

 Palladium salts for Heck reaction.

No	Catalyst	Yield <sup>a</sup> (%)
1	Palladium powder (<1 µ)	40
2	Pd/C	56
3	$Pd(PPh_3)_2Cl_2$	71
4	PdCl <sub>2</sub>	88
5	$Pd(OAc)_2$	95

 $^{\rm a}\,$  Isolated yields. Reaction conditions:  $p\mbox{-lodoanisole}$  (1 mmol), styrene (1 mmol), Pd source (0.01 mmol), IL 2 (0.2 g), 80  $^\circ$ C, 8 h.

Table 2				
Palladium-catalyzed	Heck	reaction	in	IL2

Entry	Ar	Х	R	Yield %
1	C <sub>6</sub> H <sub>5</sub>	Ι	C <sub>6</sub> H <sub>5</sub>	94
2	p-NO <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	Ι	C <sub>6</sub> H <sub>5</sub>	98
3	p-CH <sub>3</sub> OC <sub>6</sub> H <sub>5</sub>	Ι	C <sub>6</sub> H <sub>5</sub>	96
4	C <sub>6</sub> H <sub>5</sub>	Ι	COOBu	94
5	p-CH <sub>3</sub> OC <sub>6</sub> H <sub>5</sub>	Ι	COOBu	98
6	p-CH <sub>3</sub> OC <sub>6</sub> H <sub>5</sub>	Ι	COOMe	95
7	C <sub>6</sub> H <sub>5</sub>	Ι	COOMe	95
8	p-CH <sub>3</sub> C <sub>6</sub> H <sub>5</sub>	Ι	COOMe	96
9	2-C <sub>10</sub> H <sub>7</sub>	Ι	COOBu	98
10	p-CNC <sub>6</sub> H <sub>5</sub>	Br	COOBu	94
11	p-CH <sub>3</sub> COC <sub>6</sub> H <sub>5</sub>	Br	COOBu	93
12	p-CH <sub>3</sub> COC <sub>6</sub> H <sub>5</sub>	Br	C <sub>6</sub> H <sub>5</sub>	93
13	p-CH <sub>3</sub> COC <sub>6</sub> H <sub>5</sub>	Br	COOMe	95
14	p-C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub>	Br	COOBu	92
15	C <sub>6</sub> H <sub>5</sub>	Cl	C <sub>6</sub> H <sub>5</sub>	85
16	p-CH <sub>3</sub> OC <sub>6</sub> H <sub>5</sub>	Cl	COOBu	89
17	p-CNC <sub>6</sub> H <sub>5</sub>	Cl	COOBu	86
18	p-C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub>	Cl	COOBu	83

Yields are isolated yields; olefin (1 mmol), aryl halide (1 mmol) and Pd (OAc)<sub>2</sub> (2.3 mg) in IL 2 (0.2 g) at 80  $^{\circ}$ C for 8 h.

uniform spherical shape was observed (Fig. 1). This *in situ* generation of palladium nanoparticles can be attributed to the dual role of IL 2 as a reductant and a stabilizing agent. TEM analysis of palladium after second and third reuses confirmed the regeneration of palladium nanoparticles.

Reusability of catalyst is an important aspect from a commercial point of view. The reusability of catalyst was tested using *p*-iodoanisole and styrene as substrates. After completion of reaction, the reaction mixture was extracted with diethyl ether  $(3 \times 30 \text{ ml})$  to obtain the desired product. The catalyst left in the reaction vessel was dried under vacuum (3 h). This dried catalyst-IL system was reused for the next run. It was observed that there was no any substantial loss of catalytic activity even after the fifth run as indicated by TON (Table 3). Although kinetic measurements or TOF50 values should be a better way of assessing the true reusability of the catalyst, [24] the current results clearly indicate that our system has a significant potential in this regard. The catalyst leaching was tested after each run and from ICP analysis it was found that palladium leaching was not more than 1% after the fifth run.



Fig. 1. TEM image of palladium nanoparticles.

**Table 3**Reusability of the catalyst.

5	
Cycle	TON
1	96.19
2	95.23
3	93.80
4	92.85
5	90.47

Reaction conditions : 10 mmol of each 4-lodoanisole and styrene, 0.1 mmol (23 mg) of Pd(OAc)\_2, 2 g of IL, 80  $^\circ$ C, 8 h.

TON (turn over number) [23] = mmol of product/ mmol of catalyst.

# 3.2. Characterization

The IL 2 was characterized by ESI-MS (+ve mode), <sup>1</sup>H, <sup>13</sup>C, <sup>1</sup>H <sup>13</sup>C HETCOR NMR and HRMS. ESI-MS analysis was done on Bruker Daltonics ESI-MS with ion trap detector. The ESI-MS analysis was carried out by dissolving the IL2 in methanol. Peak in positive mode at 169.0 confirmed the presence of desired cation. The <sup>1</sup>H and <sup>13</sup>C NMR were recorded in CDCl<sub>3</sub> (Aldrich 225789, 99.8 atom% D) on Bruker Avance II spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at 300 MHz and 75.4 MHz respectively. In <sup>1</sup>H NMR of the IL2 there was an ambiguity about peak of OH at  $\delta$  3.61. However from the <sup>1</sup>H <sup>13</sup>C HETCOR NMR (Fig. 2), as there was no correlation for this proton, this peak could be assigned for OH anion. Analysis of palladium nanoparticles with transmission electron microscopy (TEM) was performed on a JEOL JEM 2010 transmission electron microscope operating at 200 kV with nominal resolution of 0.25 nm. From TEM images and SEAD pattern it is clear that uniformly distributed spherical nanoparticles were formed at an average size of 5 nm.

#### 4. Conclusion

We have described a meticulously designed multifunctional IL 2 as base, ligand and reaction media for palladium-catalyzed Heck reaction. The present IL2-Pd catalyst system showed excellent activity for a wide range of haloarenes, including chloroarenes. No use of phosphine ligand, no need of inert atmosphere, use of environmentally benign reaction media of IL, relatively low reaction temperature and reusability are the advantages of this IL2-Pd catalyst system. *In situ* generation of uniform and spherical nanoparticles (5 nm) of palladium may be responsible for reactions at relatively low temperature (80 °C). Further investigation on preparation of some



new ILs for synthesis of metal nanoparticles and study on their applications is currently underway in our laboratory.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.catcom.2010.10.004.

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