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# Pd-TPPTS catalyzed Mizoroki–Heck coupling in halogen-free ionic liquids [Rmim][*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>]

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# A R T I C L E I N F O

# ABSTRACT

Article history: Received 2 November 2010 Received in revised form 20 December 2010 Accepted 9 January 2011 Available online 19 January 2011

Keywords: Heck coupling Palladium Ionic liquid Aryl halide

#### 1. Introduction

The transition metal palladium-catalyzed Heck coupling [1] is one of the most powerful reactions in the synthesis of natural products, pharmaceutical, and agrochemical derivatives [2,3]. Since the availability and the economic viability, aryl chlorides are the most attractive starting materials among aryl halids [4], but its reaction must be performed in the presence of electron-rich and sterically bulky tertiary phosphine ligands under harsh conditions [5]. In view of the increased demand for environmental benign reaction process, numerous efforts have been made to investigate this reaction in non-conventional reaction media [6], such as water [7], ionic liquids [8], and supercritical CO<sub>2</sub> [9], etc. Especially, the development of homogeneous/heterogeneous catalysts in ionic liquids leads to a variety of different catalyst systems for the Heck coupling [10], such as hybrid P,O-ligand [11], P,Nligand [12], palladacycles [13], N-heterocyclic carbenes (NHCs) [14,15], and electron-rich monodentate phosphine [16], polymeric system in water [17], ligand-free palladium nanoparticles [18]. Herein, subsequent experimental and theoretical trials suggest that Pd-catalyzed the Heck coupling in ionic liquids shows the stable and recycling advantages. However, the challenging problems are how to improve the solubility of complexes or ligands in the ionic liquid, to decrease the loading of transition metal, and to reduce the loss of transition metal complex caused by organic solvent extraction while workup, etc.

In this paper, our attention is focused on studying water-soluble Pd-TPPTS [TPPTS: trisodium salt of tri(*m*-sulphonylphenyl)phosphine]

A highly efficient system composed of Pd-TPPTS [TPPTS: trisodium salt of tri(*m*-sulphonylphenyl)phosphine] and halogen-free ionic liquid ([Rmim][*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>], R = methyl, ethyl, *n*-butyl, *n*-hexyl, *n*-octyl, *n*-dodecyl) has been established for Heck coupling of aryl halides with styrene. Most of the investigated substrates could give the complete conversions (>95%) with the catalyst of 1 mol% at 110 °C. The resulting products can be easily separated from the ionic liquids by simple liquid-liquid extraction, and the catalyst immobilized by ionic liquids can be consecutively run five times without significant loss in catalytic activity.

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catalyzed the Heck coupling to reduce effectively the loss of catalyst caused with organic solvent extraction. Furthermore, as the low solubility of TPPTS and its complexes in [bmim]PF<sub>6</sub> and [bmim]BF<sub>4</sub> would cause the slow reaction rate [19,20], anionic groups in [bmim] BF<sub>4</sub> and [bmim]PF<sub>6</sub> are exchanged with sulfonate aromatic group to increase the similarity of ionic liquid with TPPTS and to improve the solubility of TPPTS and Pd-TPPTS species. It is found that Pd-TPPTS in the resulting ionic liquids 1-alkyl-3-methylimidazolium *p*-toluenesulfonate ([Rmim][*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>], R = methyl, *n*-ethyl, *n*-butyl, *n*-hexyl, *n*- octyl, *n*-dodecyl) (see Fig. 1) is highly efficient system for the Heck coupling.

#### 2. Experimental

## 2.1. Materials and methods

1-Methylimidazole (Alfa, 99%), 1-butanol (Alfa, 99%), 1-octanol (Alfa, 99%) and the other reagents were commercially available and used as received. TPPTS, ionic liquids [Rmim][p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>] were synthesized according to known methods in our laboratory. The conventional ionic liquids [bmim]Br, [bmim]BF<sub>4</sub> and [bmim]PF<sub>6</sub> were prepared according to the literatures [21]. The transmission electron microscopy (TEM) observation was taken on a Tecnai G<sup>2</sup> F20 S-TWIN at an accelerating voltage of 200 kV. And the IR spectra were recorded on a NEXUS 670.

2.2. Typical procedure for the Heck coupling of bromobenzene with styrene

Catalyst precursor  $PdCl_2$  (0.02 mmol, 3.5 mg), ionic liquid [bmim] [p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>] (1.1 g) and TPPTS (0.08 mmol, 45.4 mg) were placed

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R = methyl, ethyl, n-butyl, n-hexyl, n-octyl, n-dodecyl

Fig. 1. The structure of ionic liquid [Rmim][p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>].

in a dried flask. The flask was placed in preheated oil bath at 110 °C and stirred for 5 min under inert atmosphere to give a pale yellow solution as the catalyst. Subsequently, bromobenzene (2 mmol, 0.21 mL), styrene (2.4 mmol, 0.28 mL), Et<sub>3</sub>N (2.8 mmol, 0.39 mL) and H<sub>2</sub>O (0.2 mL) were added into the pre-formed catalyst, and then reacted at 110 °C for 2 h. At the end of reaction, the solution was cooled and extracted with ethyl ether (3×10 mL). The product was concentrated under vacuum. The conversion and selectivity were analyzed by GC Agilent-6890 N equipped with a capillary column SE-30 (30 m  $\times$  0.25 mm). The isolated products were further determined by <sup>1</sup>H and <sup>13</sup>C NMR (Bruker Avance II-400, 400 MHz for <sup>1</sup>H NMR, and 100 MHz for <sup>13</sup>C NMR).

## 2.3. Catalyst recycles

Successive runs were carried out as following procedures. At the end of reaction, the solution was cooled and extracted with ethyl ether (3×10 mL). And then the residual organic solvent in ionic liquid immobilized catalyst was evaporated under vacuum at 70 °C for 1 h. The remaining liquid phase was added with fresh bromobenzene (2 mmol, 0.21 mL), styrene (2.4 mmol, 0.28 mL), Et<sub>3</sub>N (2.8 mmol, 0.39 mL), and  $H_2O$  (0.2 mL) for the next run.

#### 3. Results and discussion

Firstly, the performance of different palladium precursors was tested in ionic liquid [bmim][p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>]. The results shown in Table 1 indicated that PdCl<sub>2</sub> was the most effect precursor at the same conditions. Besides, when the reaction time was prolonged, [Pd(C<sub>3</sub>H<sub>5</sub>)Cl]<sub>2</sub> and Pd(OAc)<sub>2</sub> precursors also gave the satisfying yields (Scheme 1, Table 1, entries 3 and 6). These results revealed that  $[bmim][p-CH_3C_6H_4SO_3]$  is a good solvent for Heck coupling and the investigated palladium precursors could show the good catalytic performance in it.

According to the results in Table 2, if PdCl<sub>2</sub> was used as a precursor and no TPPTS was introduced in this system, lots of palladium black was guickly generated and a low yield of 27.6% was given (Table 2, entry 1). The low yield demonstrated that PdCl<sub>2</sub> could be transformed into the active species without TPPTS and catalyzed this reaction in the water-soluble ionic liquid [bmim][p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>]. Dupont et al. reported that active Pd nanoparticles could be formed in ionic liquid

#### Table 1

The catalytic performance of different palladium precursors for Heck coupling of bromobenzene with styrene <sup>a</sup>.

Entry	Catalyst precursor	Yield <sup>b</sup> (%)
1	PdCl <sub>2</sub>	99.6
2	$[Pd(C_3H_5)Cl]_2$	15.6
3 <sup>c</sup>	$[Pd(C_3H_5)Cl]_2$	81.5
4	$Pd(OAc)_2$	15.3
5 <sup>d</sup>	PdCl <sub>2</sub>	63.8
6 <sup>e</sup>	$Pd(OAc)_2$	88.0

<sup>a</sup> bromobenzene 2 mmol, styrene 1.2 equiv., NEt<sub>3</sub> 1.4 equiv., H<sub>2</sub>O 0.2 mL, catalyst 1 mol%, P/Pd = 4 (molar ratio), [bmim][p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>] 1.1 g, temperature 110 °C, time 2 h.

GC-MS analysis.

<sup>c</sup> 4 h.

<sup>d</sup> TPPDS was added.

e 3.5 h.

[bmim][p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>]



Scheme 1. The Heck coupling of bromobenzene with styrene in [bmim]  $[p-CH_3C_6H_4SO_3].$ 

under reaction conditions and promoted the catalytic reaction [22]. Many chemists have proved that Pd nanoparticles are highly active to C-C coupling [23-25], but they must be effectively protected with the suitable reagent, such as PEG [26]. It is also found that the imidazole ring of ionic liquid could form the carbene complex with Pd species and stabilize the active Pd species. Our result, a lot amount of Pd black precipitated quickly without TPPTS, did not support the formation of the carbene complex in this system. When 2 equiv. of TPPTS added into the reaction media, the catalytic system not only gave a high vield of 93.5%, but also the formation of Pd black was obviously inhibited (Table 2, entry 2). The result indicated that the watersoluble catalytic species of Pd-TPPTS were formed by reacting PdCl<sub>2</sub> with TPPTS in situ or the active Pd species could be efficiently stabilized with TPPTS in [bmim][p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>]. A small amount of the reacted sample was transferred to a carbon-coated copper grid and analyzed with TEM (see Fig. 2). The size of TPPTS-stabilized Pd particles is about 5-10 nm with irregular shape. In order to prove whichever the true active species was nanoparticles or molecule species. Mercury poisoning experiment, which is an effective method to distinguish nanoparticles and molecule species [27], revealed a typical character of nanoparticles catalysis in this system because the activity of this system was completely lost as soon as mercury was added into the system. An induction period of 40 min in the kinetic curve (Fig. 3) further supported that Pd nanoparticles acted as the catalytically active specie. Interestingly, a complete conversion was obtained at 110 °C for 2 h. Using the highly reactive iodobenzene as the substrate and palladium of 2 mol% as the catalyst, Earle et al. got a yield of near 100% in [C<sub>6</sub>py]Cl at 100 °C for 24 h [28]. Iranpoor et al. used an imidazolium-based phosphinite ionic liquid (IL-OPPh<sub>2</sub>) as a ligand for the Heck coupling of bromobenzene with styrene, but it needed a high Pd loading of 3 mol% [11]. Shreeve et al. investigated the catalytic performance of Pd complex bearing pyrazolylfunctionalized N-heterocyclic carbene ligand for the Heck coupling of bromobenzene with *n*-butyl acrylate. Although the amount of palladium complex was up to 2 mol%, the system only gave a yield of 49% at 120 °C for 12 h [14]. This simple and efficient system compares well with previously reported catalysts in ionic liquid. If the amount of TPPTS continually increased, the active site of Pd could be occupied by TPPTS and the reaction rate decreased a little (Table 2, entries 3 and 4).

According to the reported results, the solubility of ligand in ionic liquid and the change of the cation or anion ions in ionic liquids

Effect of molar ra	tio of Pd to P on the Heck coupling of bromobe	nzene with styrene
Entry	Pd/P (molar ratio)	Yield <sup>b</sup> (%)

Entry	Pd/P (molar ratio)	Yield <sup>b</sup> (%)		
1	-	27.6		
2 <sup>c</sup>	1:2	93.5		
3 <sup>d</sup>	1:3	83.0		
4 <sup>e</sup>	1:4	78.7		
5 <sup>f</sup>	1:4	99.6		

<sup>a</sup> bromobenzene 2 mmol, styrene 1.2 equiv., NEt<sub>3</sub> 1.4 equiv., H<sub>2</sub>O 0.2 mL, PdCl<sub>2</sub> 1 mol%, [bmim][p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>] 1.1 g, temperature 110 °C, time 1.5 h.

GC analysis.

Table 2

Pd black precipitated largely.

<sup>d</sup> Pd black precipitated slightly.

Pale yellow solution.

f Reaction time, 2 h.



Fig. 2. TEM micrographs of Pd nanoparticles dispersed in [bmim][p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>].



Fig. 3. The kinetic test for the Heck coupling of bromobenzene with styrene.

would greatly influence the catalytic performance. Therefore, the effect of the structure of ionic liquid on the Heck coupling was also investigated. The results listed in Table 3 showed that the catalytic activity was highly sensitive to the structure of the ionic liquids. Since the hydrophobicity of ionic liquid and the solubility of organic substrates would be improved simultaneously with increasing the chain-length of alkyl in imidazolium ring, the reaction conversions

#### Table 3

Effect of different ionic liquid cation and anion on the Heck coupling of bromobenzene with styrene <sup>a</sup>.

Entry	Ionic liquids	Yield <sup>b</sup> (%)
1	$[mmim][p-CH_3C_6H_4SO_3]$	14.8
2	[emim][ p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> ]	29.0
3	$[bmim][ p-CH_3C_6H_4SO_3]$	99.6
4	$[hmim][p-CH_3C_6H_4SO_3]$	94.7
5	$[omim][p-CH_3C_6H_4SO_3]$	83.1
6	$[dmim][p-CH_3C_6H_4SO_3]$	15.3
7	[bmim]Br	5.9
8	[bmim]BF <sub>4</sub>	<5.0
9	[bmim]PF <sub>6</sub>	55.2

 $^{\rm a}$  bromobenzene 2 mmol, styrene 1.2 equiv., NEt\_3 1.4 equiv., H<sub>2</sub>O 0.2 mL, PdCl<sub>2</sub> 1 mol%, P/Pd = 4 (molar ratio), ionic liquids 1.1 g or 1 mL, temperature 110 °C, time 2 h.  $^{\rm b}$  GC analysis.

also enhanced from 14.8% to 99.6% with increasing the chain-length of alkyl from C1 to C4 (Table 3, entries 1, 2 and 3). Obviously, the low solubility of substrates in ionic liquids led to the mass transfer of substrates becoming the determining step of the reaction rate. In addition, the chain-length of alkyl in imidazolium ring increased too much, it would lead to the solubility decrease of water-soluble palladium-phosphine species in ionic liquid, so that the reaction conversion decreased from 99.6% to 15.3% (Table 3, entry 6). The similar phenomenon was also observed in the asymmetric hydrogenation of aromatic ketones [29]. Compared with the traditional ionic liquids, the novel system, especially in [bmim][p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>], gave much higher catalytic activity (Table 3, entries 7, 8 and 9). It is reasonably suggested that there is a matched relationship between the chain-length of alkyl in imidazolium and the solubility of Pd-TPPTS or substrates. The matched relationship is to maintain the solubility of substrates as well as the reasonable solubility of Pd-TPPTS species in the ionic liquid.

It is reported that water deeply affects the reaction when RTILs are used as a solvent [30–32]. If we used a dry ionic liquid as solvent, we obtained a low conversion (Table 4, entry 1). Added a small amount of water, the catalytic system showed a high activity due to the improvement of the solubility of water-soluble catalyst (Table 4, entries 2 and 3). When the amount of water was added too much, the activity of this system was inhibited due to the hydrophobicity of substrates (Table 4, entries 4, 5 and 6). Similarly, the effect of water on this reaction was also observed in other ionic liquids.

To extend the scope of the protocol, we applied these optimum conditions to screen a wide array of substrates (Scheme 2, Table 5). It was found that the catalytic system is suitable to all kinds of aryl

Effect of different water volume on the Heck coupling of bromobenzene with styrene <sup>a</sup> .			
Entry	Water volume (mL)	Yield <sup>b</sup> (%)	
1	No water	5.0	
2	0.1	87.2	
3	0.2	99.6	
4	0.3	53.7	
5 <sup>c</sup>	0.4	7.0	
6 <sup>d</sup>	0.6	8.8	
7	No IL	5.2	

<sup>a</sup> bromobenzene 2 mmol, styrene 1.2 equiv., NEt<sub>3</sub> 1.4 equiv., PdCl<sub>2</sub> 1 mol%, P/Pd = 4 (molar ratio), [bmim][p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>] 1.1 g, temperature 110 °C, time 2 h.

<sup>b</sup> GC analysis.

Table 4

<sup>c</sup> Pd black precipitated.

<sup>d</sup> Pd black precipitated largely.

Scheme 2. The Heck coupling of halides with styrene in [Rmim][p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>].

bromides. Not only did the activated bromides with electronwithdrawing substituents convert efficiently into the desired products, but the inactive bromides with electron-donating substituents also exhibited high reactivity in this reaction system. In addition, chlorobenzene and activated aryl chlorides with acetyl and trifluoromethyl groups and N-heterocycle substrates could convert into desired products in low to high yields under the relatively mild conditions. These results are better than that in many conventional and functioned ionic liquids. Such that, Hagiwara et al. obtained a low product yield of 29% by reacting *p*-acetylbromobenzene with styrene over Pd/C of 3 mol% in [bmim]PF<sub>6</sub> [33], and T. Liu et al. got only stilbene of 41% in functioned ionic liquid [bmim][TPPTMS] under the

 Table 5

 Heck coupling of halides with styrene in ionic liquid <sup>a</sup>.

Substrates	Time (h)	Yield <sup>b</sup> (%)	Substrates	Time (h)	Yield <sup>b</sup> (%)
MeO	18	>99.9	Br	24	94.4 <sup>c</sup>
F <sub>3</sub> C	18	>99.9	Br	24	>99.0 <sup>c</sup>
F <sub>3</sub> C Br	18	>99.9	I	15 min	>99.9 <sup>d</sup>
ĊF <sub>3</sub>	24	>99.9	H <sub>3</sub> COC	22	45.0 <sup>e</sup>
H <sub>3</sub> COC	24	98.0	F <sub>3</sub> C	22.5	25.8 <sup>e</sup>
NC	24	86.3	Cl	24	15.6 <sup>e</sup>
H <sub>3</sub> COC	24	91.2	O <sub>2</sub> N Br	24	>99.5 <sup>f</sup>
OHC Br	24	95.0	Br	24	88.7
OHC Br	24	97.5	Br	24	83.2
H <sub>3</sub> CO Br	24	>99.5			

<sup>a</sup> aryl halide 2 mmol, styrene 1.2 equiv., NEt<sub>3</sub> 1.4 equiv.,  $H_2O 0.2 \text{ mL}$ , PdCl<sub>2</sub> 1 mol%, P/Pd = 4 (molar ratio), [bmim][*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>] 1.1 g, temperature 110 °C.

<sup>b</sup> GC analysis and determined by <sup>1</sup>H NMR.

<sup>c</sup> 0.1 mL DMF added.

<sup>d</sup> 100 °C.

<sup>e</sup> Pd black precipitated largely.

<sup>f</sup> 0.2 mL DMF added.



Fig. 4. Recycling results for the Heck coupling of bromobenzene with styrene.

conditions of S/C = 100 and 140 °C [34]. It was noteworthy that a small amount of DMF was introduced to improve the solubility and mass transfer of *o*-bromotoluene and *p*-bromotoluene in this hydrophilic system. We also demonstrated that the catalyst immobilized in [bmim][*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>] was stable and could be recycled (see Fig. 4). After this system was run five times, its activity had no significant loss and the product was separated from the ionic liquid by means of a simple liquid–liquid extraction with ethyl ether at the end of each run. Considering the salt produced in the reaction, each recycling need to extend reaction time for one more hour [35].

#### 4. Conclusion

In summary, we successfully applied Pd-TPPTS as the catalyst and water-soluble ionic liquid [Rmim][p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>] as solvent for the Mizoroki–Heck coupling and obtained the high conversion and good selectivity. The resulting products can be easily separated from the catalyst system by extraction with ethyl ether. The catalyst immobilized in ionic liquid can be recoverable and reused five times without significant loss of the conversion and selectivity.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.catcom.2011.01.008.

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