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Development of an efficient solvent free one-pot Heck reaction catalyzed by novel palladium (II) complex-via green approach

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ABSTRACT

A novel 1-glycyl-3-methyl imidazolium chloride–palladium (II) complex [[Gmim]Cl–Pd (II)] was found to be a heterogeneous catalyst for an efficient Heck reaction with good to excellent yield under solvent free condition. Tetra-coordinated palladium complex was prepared by reacting PdCl$_2$ with 1-glycyl-3-methyl imidazolium chloride and its catalytic function invented for the C—C bond formation. Spectroscopic evidence of complex has been proved by powder XRD, SEM, FT-IR and AFM. This protocol provides a simple strategy for the generation of a variety of new C—C bonds under environmentally benign condition.

1. Introduction

In recent years, Ionic liquids have emerged as a set of green solvent with unique properties such as tunable polarity, high thermal stability and immiscibility with a number of organic solvents, negligible vapor pressure and recyclability. Their non-volatile character and thermal stability makes the metal complexes potentially attractive alternatives to environmentally unfavorable organic co-solvents, notably chlorinated hydrocarbons. They are particularly promising as solvents for the immobilization of transition metal catalysts, Lewis acids and enzymes [1–6]. As a result of their green credential and potential to enhance reaction rate and selectivities, ionic liquids are finding increasing application in organic synthesis.

The Mizoroki–Heck synthesis is an important task due to their valuable applications in both laboratory and industry. The significance of these compounds exist in the organic synthesis, polymerization processes, UV screens, preparation of hydrocarbons and in advanced enantioselective synthesis of natural products and pharmaceutically active heterocyclic compounds [7]. In general, palladium catalysts suffer the problems concerning extraction from the reaction mixture, waste production, high toxicity and price, air-sensitivity and leaching [8]. Hence, we felt it would be keen interest to eradicate these negative aspects of palladium complex. In this regard, we have developed stable, selective, suitable ligand that leads to efficient heterogeneous palladium complex with high turnover and reprocessibility.

In last two years, Petrovi et al. was described the synthesis of N, N-diethyl ethanolamine ionic liquid in green Heck reaction [9] and Liu et al. was reported efficient palladium-catalyzed Heck reaction by the diol-functionalized imidazolium ionic liquid [10]. Furthermore, Vaultier et al. have synthesized binary task specific ionic liquid and an efficiency of palladium nano particle catalyzed Heck cross-coupling [11]. However, Salunkhe et al. was illustrated multi-functional ionic liquid for Pd (II) catalyzed Heck reaction [12]. Li et al. was exemplified the Pd-TPPTS catalyzed Mizoroki–Heck coupling in halogen-free ionic liquid [13]. Above all the methods provide good yield, but some have drawbacks such as lengthy work-up procedure, harsh reaction conditions (organic co-solvents) and require absolutely dry and inert media. Herein, we report a protocol based on palladium functionalized 1-glycyl-3-methyl imidazolium chloride (Fig. 1), which proved to be highly efficient at ambient temperature for C—C bond formation under solvent free condition.

However, recovery and leaching can occur in the extractive work up leading to a loss of the catalyst in the reaction mixture on the one hand and requests additional effort to purify the extracted product. To overcome such problems, novel complex was developed [14] by covalent linking of organo catalytic unit with an ionic liquid moiety (often chloroglycine). This imparts a low solubility of catalyst in the solvents used for extraction of the product on the one hand and high solubility in the reaction medium on the other hand [15–19].

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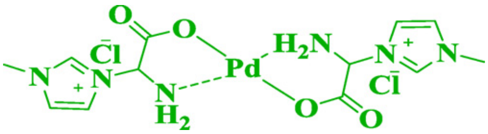


Fig. 1. 1-Glycyl-3-methyl imidazolium chloride–palladium (II) complex [Gmim]Cl–Pd (II).

This strategy was applied to Heck reaction providing high yield and good recyclability of the organocatalyst.

The objectives of the present study are to: (i) prepare tetra coordinated 1-glycyl-3-methyl imidazolium chloride–palladium (II) complex and to explore its application as catalyst, (ii) develop an efficient synthetic process for the facile conversion of Heck reaction. The present method developed for the Heck reaction offer many advantages including high conversion, short duration and the involvement of non-toxic reagents.

2. Experimental

2.1. Materials and methods

All solvents and chemicals were commercially available and used without further purification unless otherwise stated. [Gmim]Cl–Pd (II) complex was characterized by powder X-ray diffraction (P-XRD) diffractometer, a Bruker D8 (advance model); Germany and lynx eye detector operating with nickel filtered Cu-K radiation. The ^1H NMR spectra was record on a Bruker 500 MHz using $CDCl_3$/DMSO-d_6 as the solvent and mass spectra were recorded on JEOL GC MATE II HRMS (EI) spectrometer. FT-IR was recorded on AVATRA 330 Spectrometer with DTGS detector. Column chromatography was performed on silica gel (200–300 mesh). Analytical thin-layer chromatography (TLC) was carried out on precoated silica gel GF-254 plates. AFM and SEM was analyzed by (Nano Surf Easy Scan-2 Switzerland), (Carl Zeiss EVO MA 15(model)) respectively.

2.2. Preparation of [Gmim]Cl–Pd (II) complex

2.2.1. Protection of amino group using di. tert butyl pyrocarbonate (Boc)

A solution of the glycine (10 mmol) in a mixture of dioxane (10 mL), water (5 mL) and 0.5 N NaOH (5 mL) was stirred and cooled in an ice-water bath. Boc (8 mmol) was added and agitation continued at ambient temperature for 30–45 min. The resulting solution was concentrated in vacuo, cooled in an ice-water bath, covered with a layer of ethyl acetate (15 mL). Then, the reaction mixture was acidified to pH 2–3 using $KHSO_4$. The aqueous phase was extracted with ethyl acetate (3 × 10 mL). The ethyl acetate extract washed with water, dried over anhydrous Na_2SO_4 and evaporated in vacuo. The residue was recrystallized using ethanol [20,21].

2.2.2. Protection of acid group using methyl ester

Boc-glycine (10 mmol) was suspended in 2, 2-di methoxypropane (DMP) (50 mL) and concentrated HCl (5 mL) was added. The mixture was allowed to stand at ambient temperature over night. The volatile reactants were removed in vacuo at 60 °C, the residue dissolved in a minimum amount of dry methanol and the solution diluted with dry ether (50 mL). The crystalline methyl ester hydrochloride was collected on a filter, washed with ether and dried in vacuo over NaOH. Recrystallization from methanol–ether (9:1 mL) affords the analytically pure ester [22].

2.2.3. Chlorination of protected glycine

In 100 mL RB, thionyl chloride (6 mmol) was added and cooled in an ice-water bath. The protected glycine (4 mmol) was dissolved in ethanol and added to RB drop wise at (0 °C) and stirred at ambient temperature for 48 h. The resulting solution was concentrated under vacuo, cooled in an ice-water bath to get the desired precipitate. Recrystallization of the product using ethanol–ether affords the analytically pure chloroglycine.

2.2.4. Removal of protecting groups

An about 33% (10 mL) solution of HBr in acetic acid is placed in a 100 mL RB flask and protected chloroglycine (4 mmol) was added with stirring. The flask was closed with a cotton filled drying tube and swirled to effect complete dissolution of the protected chloroglycine. The deprotection occurred with evolution of CO_2 and heat. When the gas evolution ceases, dry ether (50 mL) was added with swirling and the reaction mixture was stored in an ice-bath. The precipitated chloroglycine ester was collected on a filter, washed with ether and dried over NaOH in vacuo.

Furthermore, a solution chloroglycine ester (4 mmol) in methanol (10 mL) was surrounded by water bath at ambient temperature and NaOH (20 mL) was added with stirring. The mixture was stored at ambient temperature for overnight. Dilute HCl (10 mL) was added and methanol removed in vacuo. The aqueous solution was cooled in ice-water for 2 h. Chloroglycine was collected on a filter, washed with ether and dried in air [23–25].

2.2.5. Synthesis of 1-glycyl-3-methyl imidazolium chloride [Gmim]Cl

First, chloroglycine (0.01 mol) reacted with N-methylimidazole (0.11 mol) in 50 mL acetonitrile at 70 °C for 24 h to generate chloroglycine ligand modified by imidazole salt (3-(amino(carboxy)methyl)-1-methyl-1H-imidazol-3-ium chloride) [Gmim]Cl. The solvent (acetonitrile) was removed under reduced pressure at 80 °C (water bath temperature). Then the residue was mixed with 50 mL water and extracted with ethyl acetate (3 × 5 mL). Further, the water phase was evaporated under reduced pressure at 80 °C until the mass of the residue did not change. ^1H NMR (500 MHz, DMSO-d_6): δ 2.2 (s, 1H), 3.3 (s, 3H), 5.0 (s, 2H), 6.92 (d, 1H), 7.0 (d, 1H), 7.6 (s, 1H), 9.1 (s, 1H). HRMS (EI): $C_6H_{10}ClN_3O_2$ (found: 191.10), cal (191.05). FT-IR (KBr, cm^{-1}): 3429, 3372, 2933, 2855, 1628, 1526 and 1382.

2.2.6. Synthesis of 1-glycyl-3-methyl imidazolium chloride–palladium (II) complex [Gmim]Cl–Pd (II)

In RB, [Gmim]Cl (0.02 mmol) was stirred with $PdCl_2$ (0.01 mol) in 100 mL methanol at 50 °C for 12 h to deliver the [Gmim]Cl modified by palladium complex [Gmim]Cl–Pd (II). The solvent (methanol) was removed under reduced pressure at 80 °C (water bath temperature). Finally, white [Gmim]Cl–Pd (II) complex was obtained with 95% [26].

2.3. Procedure for Heck reaction

In a conical flask (50 mL), a mixture of 1-bromo-4-methoxybenzene (1 mmol), styrene (1.2 mmol), triethylamine (1 mmol) and [Gmim]Cl–Pd (II) (0.1 mmol) was added and stirred at ambient temperature for a period as indicated in Tables 5 and 6 (The reaction was monitored by HPLC and TLC). The resulting heterogeneous mixture was extracted with ethyl acetate or diethyl ether (3 × 5 mL). The organic phase was separated and dried over anhydrous Na_2SO_4 and evaporated. The resulting crude was purified by flash chromatography to give the desired pure product with excellent yield.

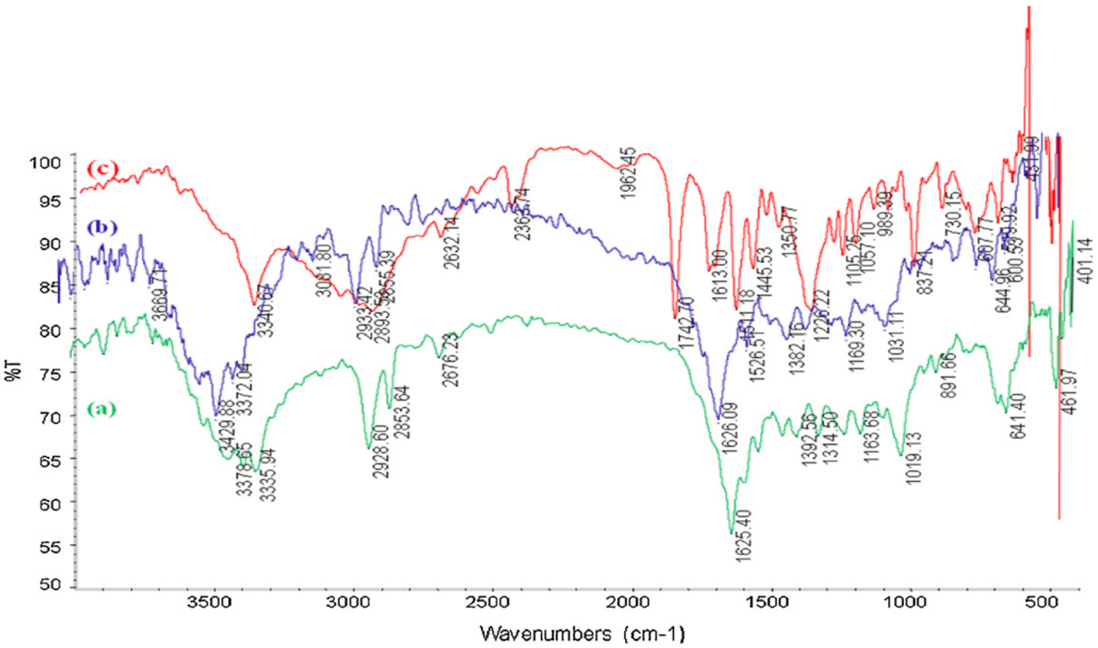


Fig. 2. FT-IR of (a) chloroglycine, (b) 1-glycyl-3-methyl imidazolium chloride [Gmim]Cl, and (c) 1-glycyl-3-methyl imidazolium chloride–palladium (II) complex [Gmim]Cl–Pd (II).

2.4. Recycling of the catalyst for the model reaction of 1-bromo-4-methoxybenzene with styrene using [Gmim]Cl–Pd (II) under solvent free condition

1-Bromo-4-methoxybenzene (1 mmol) was reacted with styrene (1.2 mmol) in the presence of [Gmim]Cl–Pd (II) (0.1 mmol) and triethylamine (1 mmol) at ambient temperature. After completion of the reaction (TLC/HPLC), the product was extracted as stated in the preceding general method. The white solid [Gmim]Cl–Pd (II) was isolated by centrifugation. Furthermore, the recovered complex was washed with diethyl ether and dried in air. The resulting catalyst was charged to another batch of the similar reaction. This was repeated for 8 runs to complete the reaction in 6 h to give the desired product with 96–88% yield (Table 7).

3. Results and discussion

3.1. Characterization of complex

[Gmim]Cl–Pd (II) catalyst has been characterized by FT-IR, XRD, SEM and AFM.

3.1.1. FT-IR analysis

Compounds	C—H	C—N	C=O	Pd—O	Pd—N	O—H	N—H
[Gmim]Cl–Pd (II)	2933s	1350s	1742s	639m	431m	–	3340m
Chloroglycine	2928s	1392s	1625s	–	–	3378s	3335m
[Gmim]Cl	2893s	1382s	1626s	–	–	3429s	3372m

FT-IR spectra of [Gmim]Cl–Pd (II) at different dissociation degrees are shown in Fig. 2. For carboxylate ion, the broad peak at 1742 cm^{-1} corresponds to carbonyl symmetric stretching. The asymmetric stretching of carboxylate was shifted to 1626 cm^{-1} [Gmim]Cl in contrast with the shift to 1625 cm^{-1} in chloroglycine, which appeared when [Gmim]Cl was treated with $PdCl_2$ and thus the carbonyl stretching was decreased. However, the plane of C—OH at 3378, 3429 cm^{-1} was present in chloroglycine, [Gmim]Cl respectively, but when the networks were treated with $PdCl_2$ no signal was noticed for the —OH group, indicates the formation of Pd—O (639 cm^{-1}) bond. Although, the NH_2 signal in chloroglycine, [Gmim]Cl was detected at 3340, 3335 cm^{-1} with doublet, but in the case of [Gmim]Cl–Pd (II), we also found the doublet at 3372 cm^{-1}, this also shows the formation of Pd—NH (431 cm^{-1}) bond in the catalyst [27]. In all spectra, stretching of C—H and C—N was observed at 2933 and 1350 cm^{-1}, respectively. Notably, the FT-IR spectra revealed that a series of new palladium complex with ionizable groups had been synthesized.

3.1.2. Powder XRD analysis

The formation of the Pd (II) catalyst was also supported by the XRD patterns with those of glycine, chloroglycine, Pd (II) complex. In comparison with glycine, chloroglycine, Pd (II) complex which showed major peaks respectively at 32.50, 38.81, 44.98 and 64.07 (confirming palladium peak with JCPDS data care no: 99-200-3904 for Pd (II)), the [Gmim]Cl–Pd (II) pattern was in good agreement with peak at 38.81 and 44.98 (Fig. 3).

3.1.3. SEM analysis

The SEM image of the catalyst is shown in Fig. 4. From this image it is clear that [Gmim]Cl–Pd (II) has nano sphere like

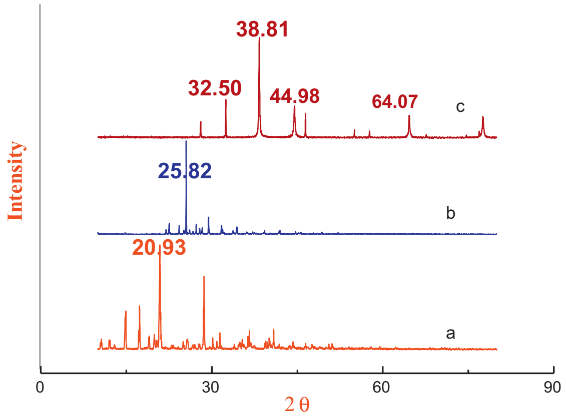


Fig. 3. Powder X-ray diffraction patterns of (a) glycine, (b) chloroglycine, and (c) 1-glycyl-3-methyl imidazolium chloride–palladium (II) complex [Gmim]Cl–Pd (II).

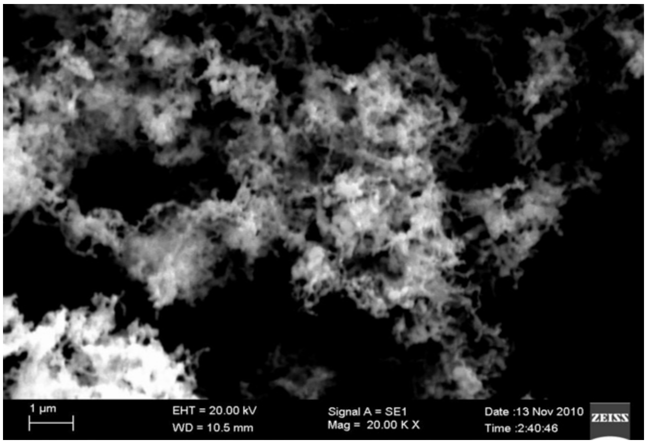


Fig. 4. SEM image of [Gmim]Cl–Pd (II).

Table 1
Effect of the base on Heck coupling reaction.[a]

Entry	Base	Time (h)	Yield[b] (%)
1	–	48	Trace
2	Py	48	–
3	Imidazole	48	–
4	K_2CO_3	48	40
5	KOH	48	53
6	NaOH	48	58
7	Et_3N	48	96
8	Et_3N	24	96
9	Et_3N	18	96
10	Et_3N	12	96
11	Et_3N	6	96
12	Et_3N	3	90
13	Et_3N	1	83

[a] *Reaction condition*: 1-bromo-4-methoxybenzene (1 mmol), styrene (1.2 mmol), different base (1 mmol), and [Gmim]Cl–Pd (II) (0.1 mmol) stirring at ambient temperature for 6 h.

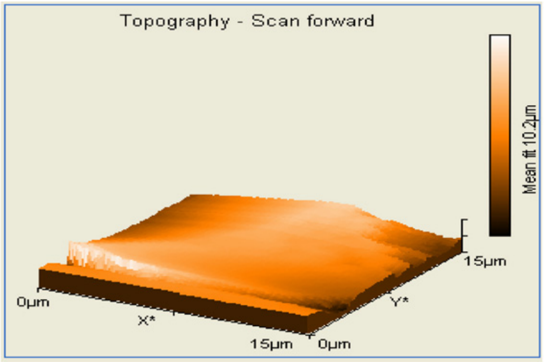
[b] Yield determined by HPLC.

morphology with particles of dimensions ca. 75–100 nm and these are distributed uniformly throughout the material.

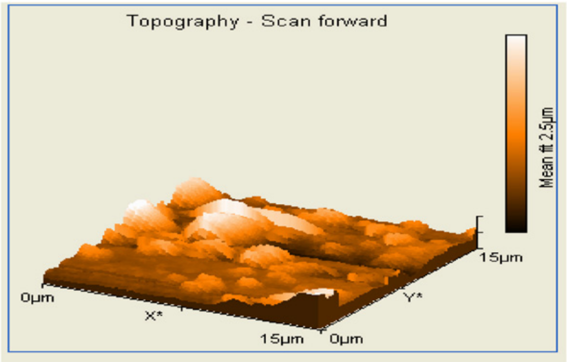
3.1.4. AFM analysis

The 3D AFM images of the 1-glycyl-3-methyl imidazolium chloride and [Gmim]Cl–Pd (II) complex is shown in Fig. 5. The 3D image for 1-glycyl-3-methyl imidazolium chloride was present 10.2 μm^2 size of the particles. It can be seen that the surface was very smooth, crystalline ligand are notably different, the grain size and the shape vary significantly (Fig. 5(a)). After doping the $PdCl_2$ to the [Gmim]Cl, Fig. 5(b), 3D AFM image was obtained. From this image, the larger scan size also emphasizes the differences between the [Gmim]Cl and [Gmim]Cl–Pd (II). The surface of palladium doped ionic liquid, showed in the rough topography that confirmed the formation of film with palladium complex in the size of 2.5 μm^2.

The palladium complex catalyzed Heck reaction was carried out using styrene and 1-bromo-4-methoxybenzene as a model reaction to investigate different parameters, such as effect of solvent, diverse bases, catalysts and its concentration of the catalyst. Initially, the influence of different bases to the model reaction was studied; these results are summarized in Table 1. It was observed that, organic bases showed maximum conversion over the inorganic bases. Moreover, this reaction was unsuccessful in the absence of base (Table 1, entry 1). However, there was no product formation between 1-bromo-4-methoxybenzene and styrene in the presence of pyridine and imidazole (Table 1, entries 2 and 3). Furthermore,



(a) AFM image of 1-glycyl-3-methyl imidazolium chloride



(b) AFM image of 3-(amino (carboxy) methyl)-1-methyl-1H-imidazol-3-ium chloride

Fig. 5. (a) AFM image of 1-glycyl-3-methyl imidazolium chloride, and (b) AFM image of 3-(amino (carboxy) methyl)-1-methyl-1H-imidazol-3-ium chloride supported palladium complex.

Table 2
Effect of the solvent on the Heck coupling reaction.[a]

Entry	Solvent	Temp (°C)	Time (h)	Yield[b] (%)
1	DCM	35	48	Trace
2	$CHCl_3$	50	48	Trace
3	THF	50	48	Trace
4	Methanol	50	48	Trace
5	Ethanol	65	48	Trace
6	CH_3CN	60	48	51
7	DMF	130	48	67
8	Solvent free	Rt	6	96
9	Solvent free	20	6	90
10	Solvent free	35	6	96
11	Water (5 mL)	90	48	43

[a] *Reaction condition*: 1-bromo-4-methoxybenzene (1 mmol), styrene (1.2 mmol), triethylamine (1 mmol) solvent (5 mL), and [Gmim]Cl–Pd (II) (0.1 mmol) stirring at ambient temperature for 6 h.
[b] Yield determined by HPLC.

Heck reaction was carried out using K_2CO_3, KOH and NaOH, the formation of (E)-1-methoxy-4-styrylbenzene increases from 40 to 58% (Table 1, entries 4–6). After inventing the best catalyst systems, we further optimized the reaction conditions in presence of Et_3N. The experiments showed that on decreasing the time from 24 to 6 h gave the same results with full conversion and 96% yield of (E)-1-methoxy-4-styrylbenzene (Table 1, entries 7–11). However, the yields were dropped appreciably on decreasing the time from 6 to 1 h (Table 1, entries 12 and 13). By all these experimental results and discussions it was concluded that 1 mmol Et_3N is sufficient to brought out the complete Heck reaction in 6 h at 25 °C.

Subsequently, in order to find a suitable solvent for the reactions, the coupling of 1-bromo-4-methoxybenzene and styrene was carried out with different solvents and Et_3N. According to publications from Hartwig and co-workers [28], Zapf and Beller [29], Bohm and Herrmann [30] and Rafiee [1] polar, aprotic solvents tend to give the best results for the Heck reaction, while Fu [31] obtained high-activity of catalysts in dioxane solvent. Among the previous reports, catalysis in absence of solvent was the most productive, as compared with the polar and non-polar solvents (Table 2). This may be due to the easy coordination of complex with organic co-solvents. It has also been reported that H_2O molecule sometimes is required to activate the Pd (II) catalyst. In our case, carrying out the reaction in H_2O (5 mL) 90 °C gave a negative effect on the product yield in comparison with solvent free condition. This lower yield could be due to complex delocalization under aqueous condition.

Next, in order to optimize the reaction conditions for a particular catalyst the coupling reaction of 1-bromo-4-methoxybenzene and styrene was executed in presence of Et_3N by using different catalysts and the results are given in Table 3. When the reaction was carried out using various catalysts such as L-glycine, chloroglycine, [Cemim] Br, [Aemim] Br, $PdCl_2$/[Cemim] Br, $PdCl_2$/[Aemim] Br and $PdCl_2$/[Gmim]Cl with Et_3N, it gave trace to 78% of product respectively (Table 3, entries 1–7). However, when the same reaction was conducted with [Gmim]Cl–Pd (II) as a catalyst it gave remarkable yield of product in short duration (Table 3, entry 8). Almost similar yield was obtained when increasing the duration of reaction (Table 3, entry 9).

Table 3
Effect of the various catalysts on Heck coupling reaction.[a]

Entry	Catalyst	Time (h)	Yield[b]
1	L-Glycine	48	Trace
2	Chloroglycine [Cl-gly]	48	Trace
3	[Cemim] Br	48	Trace
4	[Aemim] Br	48	Trace
5	$PdCl_2$/[Cemim] Br	48	65
6	$PdCl_2$/[Aemim] Br	48	70
7	$PdCl_2$/[Gmim]Cl	48	78
8	[Gmim]Cl–Pd (II)	6	96
9	[Gmim]Cl–Pd (II)[c]	7	97

[a] *Reaction condition*: 1-bromo-4-methoxybenzene (1 mmol), styrene (1.2 mmol), triethylamine (1 mmol), and catalyst (0.1 mmol) stirring at ambient temperature for 6 h.
[b] Yield determined by HPLC.
[c] Reaction duration 7 h.

Table 4
Effect of the catalyst loading on Heck coupling reaction.[a]

Entry	[Gmim]Cl–Pd (II) mmol	Time (h)	Yield[b]
1	–	48	–
2	0.025	24	58
3	0.05	24	64
4	0.075	24	79
5	0.1	6	96
6	0.125	6	97
7	0.15	6	97

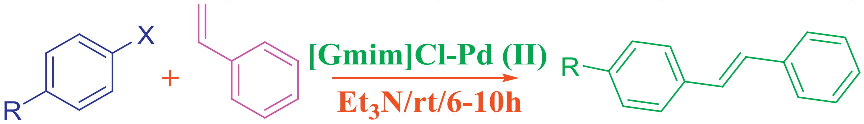
[a] *Reaction condition*: 1-bromo-4-methoxybenzene (1 mmol), styrene (1.2 mmol), triethylamine (1 mmol), and [Gmim]Cl–Pd (II) (0.1 mmol) stirring at ambient temperature for 6 h.
[b] Yield determined by HPLC.

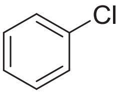
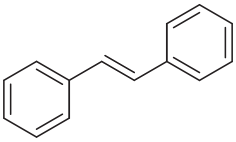
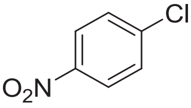
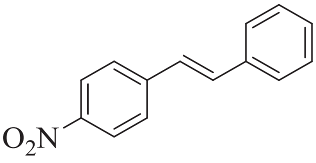
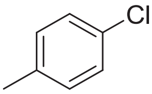
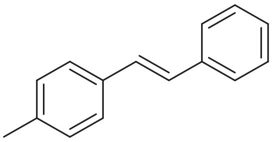
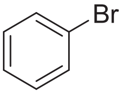
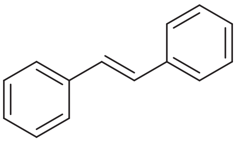
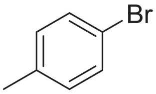
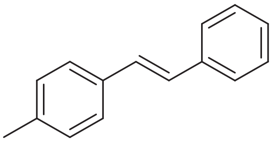
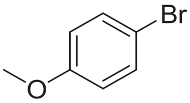
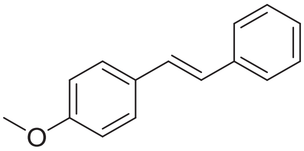
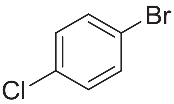
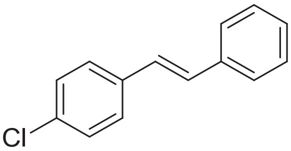
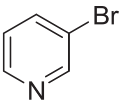
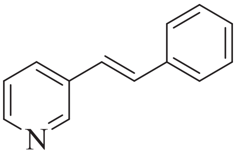
The catalytic reactions which can be carried out with a small amount of expensive complexes is the most useful feature of synthetic reaction involving palladium complex. According to literature, Petrovic et al. obtained good yield in the green Heck reaction of aryl halide with olefin using $PdCl_2$ (1.5 mol %) stirred at 100 °C for 12–18 h [9]. Using biphenyl-based phosphine in the range between 0.025 and 0.05 mmol, Joshaghani et al. observed acceptable rate in the Heck reaction [7]. Among the previous reports, increasing the quantity of the catalyst can improve the reaction yield and shorten reaction time. Initially, C—C formation was carried out in absence of catalyst at ambient temperature; it was found that no product formed even after 48 h (Table 4, entry 1). Further when the amount of the catalyst was increased from 0.025 to 0.075 mmol, albeit the yield was increased 58–79% (Table 4, entries 2–4). However using 0.1 mmol of [Gmim]Cl Pd (II), (E)-1-methoxy-4-styrylbenzene was obtained with 96% in 6 h (Table 4, entry 5). Almost similar yield was achieved when escalating the catalyst amount from 0.1 to 0.15 mmol (Table 4, entry 6 and 7). Moreover, temperature also plays an important role in the time and amount of catalyst. When we conducted the Heck reaction of 1-bromo-4-methoxybenzene and styrene as the model substrate at various temperatures from 25 °C to 100 °C, there was a decrease in the amount of catalyst required and time. Therefore, the Heck reaction was carried out at the molar radio of 1-bromo-4-methoxybenzene, styrene, triethylamine and [Gmim]Cl–Pd (II) 1:1.2:1:0.1 mmol at ambient temperature in absence of solvent.

In order to test the substrate generality of [Gmim]Cl–Pd (II) complex catalyzed Heck–Mizoroki reaction of substituted aryl halides with styrene were performed at ambient temperature to give their corresponding trans-stilbenes in the appropriate reaction times with excellent yields (Table 5). It can be noticed that a wide range of aromatic halides can efficiently contribute in the Heck reactions. However, both electron-rich and electron-poor aryl halides could be successfully converted to the desired products in (6–10 h) at room temperature. On the other hand, the reaction of aryl chlorides with styrene is usually very slow with low yields (Table 5, entries 1–3).

Finally, the reaction of methyl acrylate with different aromatic halides was investigated. In these reactions, variety of aryl halides were stirred with methyl acrylate in the presence of [Gmim]Cl–Pd (II) at room temperature in absence of solvent. The reaction proceeded smoothly with the formation of trans-isomers with 80–95% yields. In addition, it was found that, aromatic halides with

Table 5
Heck–Mizoroki coupling of different aryl halides with styrene in the presence [Gmim]Cl–Pd (II) and Et_3N as base.[a].



Entry	Aryl halides	Product	Time (h)	Yield[b] (%)
1			8	83
2			9	80
3			9	76
4			6	94
5			8	83
6			5	96
7			7	83
8			10	80

[a] *Reaction condition*: Aryl halide (1 mmol), Olefin (1.2 mmol), triethylamine (1 mmol), and [Gmim]Cl–Pd (II) (0.1 mmol) stirring at ambient temperature for 6 h.
[b] Yield determined by HPLC. All the products were characterized by spectroscopic analysis (IR, ^{1}H NMR) known compounds were compared with authentic data [32–34].

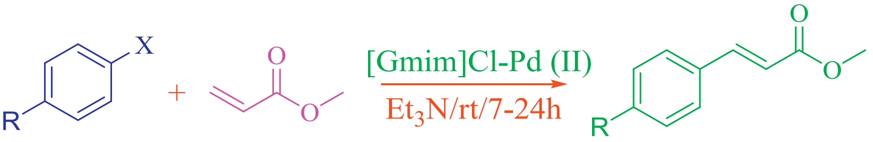
withdrawing group were more imprudent than that of electron donating group (Table 6, entries 1–8).

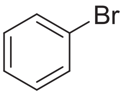
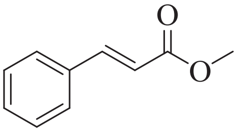
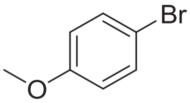
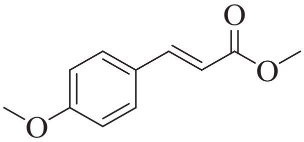
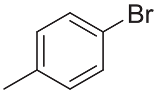
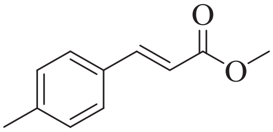
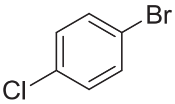
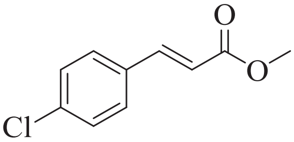
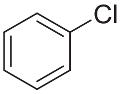
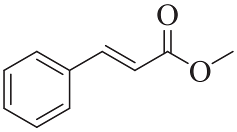
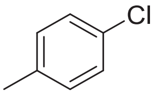
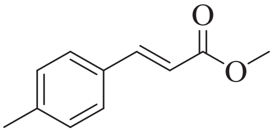
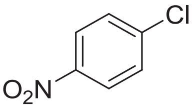
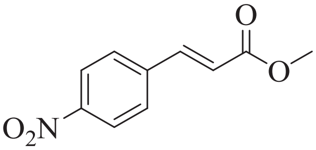
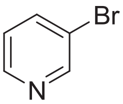
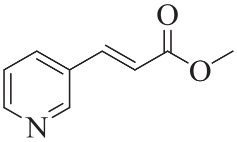
Isolation of the heterogeneous catalyst was easily performed by extraction or centrifugation. The isolated catalyst was washed with diethyl ether and dried in air. The regenerated catalyst was used for the reaction of 4-bromoanisole with styrene for eight runs to afford trans-stilbene with 96–88% isolated yields (Table 7).

For practical application in the Heck reaction, the lifetime of the heterogeneous catalysts and their reusability are very important factors. For the comparative study, Heck reaction was carried out with model reaction at the optimized conditions in presence of Pd/C catalyst. However, a significant difference in Pd leaching was observed. Without exclusion of air about 32% of the total palladium amount were lost from the Pd/C and found in solution (AAS) compared to [Gmim]Cl–Pd (II) where no leaching detected.

For those conformation, [Gmim]Cl–Pd (II) catalyst was collected after the completion of the reaction and analyzed by powder X-ray

Table 6
Heck reaction of methyl acrylate with some represented aryl bromides/chlorides.[a].



Entry	Aryl halides	Product	Time (h)	Yield[b] (%)
1			8	93
2			7	95
3			9	90
4			9	85
5			15	86
6			18	80
7			19	84
8			24	84

[a] *Reaction condition*: Aryl halide (1 mmol), Olefin (1.2 mmol), triethylamine (1 mmol), and [Gmim]Cl–Pd (II) (0.1 mmol) stirring at ambient temperature for 6 h.

[b] Yield determined by HPLC. All the products were characterized by spectroscopic analysis (IR, ^{1}H NMR) known compounds were compared with authentic data [32–34].

diffraction method and the diffraction patterns are given in Fig. 6. The analysis specifies that the [Gmim]Cl–Pd (II) do not undergo any chemical and structural changes, thus proving its surface catalytic activity towards the coupling reaction of 1-bromo-4-methoxybenzene with styrene. On the other hand, presence of peaks due to metallic palladium is noted in the powder XRD pattern of the complex in the case of 'Pd (II)' (Fig. 6(a and b)). Moreover, surface and size of that reused catalyst was captured by AFM. The surface of reused palladium complex showed in the rough topography evidence and reduced size of the particle 755 nm (Fig. 7). However, the extracted product was analyzed by P-XRD, which indicates the absence of peak at 38.81 that gave an evidence for 'no leaching' of the complex. Furthermore, Pd leaching was also studied by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis, indicating that the product mixture contained zero ppm of palladium accounting for 0.1 mmol of the initially added amount of Pd. From those three experimental results, we believe that no Pd leaching observed in Heck reactions, it is due to immobilized palladium in amino acid functionalized ionic liquid binding site located on the surface, which acts as a ligand through metal–ligand interaction. The anchoring of Pd species by amino acid sites supported on ionic liquid minimizes catalyst

Table 7
Recycling of the catalyst for the reaction of 4-bromoanisole with styrene.[a]

	Run							
	1	2	3	4	5	6	7	8
Yield[b] (%)	96	96	94	94	92	90	90	88

[a] *Reaction condition*: 1-bromo-4-methoxybenzene (1 mmol), styrene (1.2 mmol), triethylamine (1 mmol), and [Gmim]Cl–Pd (II) (0.1 mmol) stirring at ambient temperature for 6 h.
[b] Yield determined by HPLC.

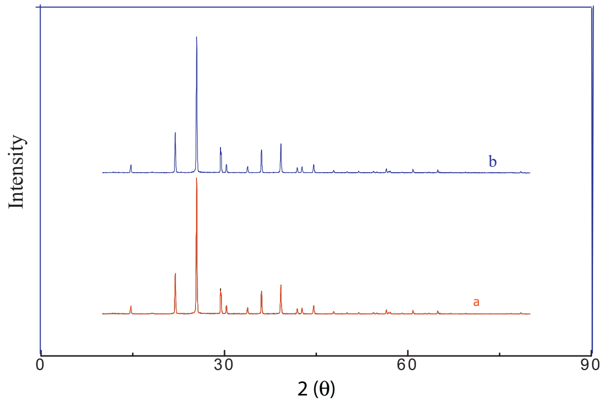
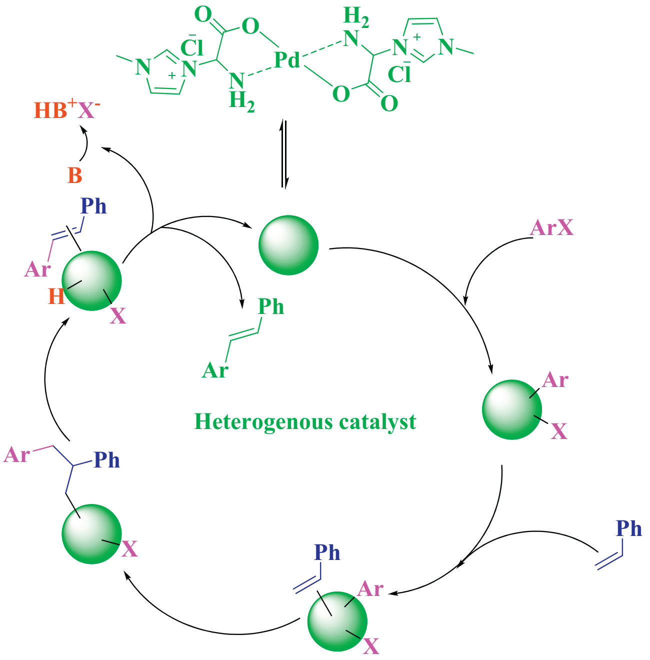


Fig. 6. Powder X-ray diffraction patterns of the [Gmim]Cl–Pd (II) complex (a) before reaction and (b) after reaction (8th run).



Scheme 1. Proposed catalytic mechanism.

deterioration and no metal leaching and therefore allows efficient catalyst recycling. The precise mechanism of the catalytic reaction needs to be elucidated, but it is noticeable that the mechanism is strongly modified depending of the halobenzene employed, obtaining *trans*-stilbene as the main product (Scheme 1).

The [Gmim]Cl–Pd (II) complex stumble on superiority over most of the reported catalysts [9,10] with many advantages: facile synthesis, thermal stability and structural versatility, easy handling, catalytic performance in air at 25 °C, without any additives, no inert atmosphere required without leaching of catalyst.

trans-1,2-Diphenylethene (Table 5, entry 1) ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 7.03 (s, 2H), 7.15–7.20 (m, 2H), 7.32 (t, *J* 7.6 Hz, 4H), 7.46 (d, *J* 7.5 Hz, 4H); ^{13}C NMR: δ 125.7, 127.2, 129.4, 138.3; IR (KBr, cm^{-1}) 3027, 2930, 1600, 1450, 970, 680.

trans-4-Nitrostilbene (Table 5, entry 2) ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 7.17 (d, *J* 18 Hz, 1H), 7.42–7.33 (m, 4H), 7.56 (d, *J* 6 Hz, 2H), 7.65 (d, *J* 9 Hz, 2H), 8.22 (d, *J* 6.0 Hz, 2H); ^{13}C NMR: δ 126.2, 128.3, 130.9, 132.1, 133.9, 133.9, 137.4, 137.9, 145.6, 148.8.

4-Methyl-*trans*-stilbene (Table 5, entry 3) ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 2.32 (s, 3H), 7.04 (s, 2H), 7.15 (d, *J* 8.4 Hz, 2H), 7.16–7.22 (m,1H), 7.30 (t, *J* 7.5 Hz, 2H), 7.35 (d, *J* 8.3 Hz, 2H), 7.44 (d, *J* 7.5 Hz, 2H); ^{13}C NMR: δ 26.2, 130.3, 130.4, 132.3, 132.7, 135.6, 138.3, 144.5, 147.4, 147.5; IR (KBr, cm^{-1}) 3021, 2917, 2855, 1589, 1506, 967, 804, 527.

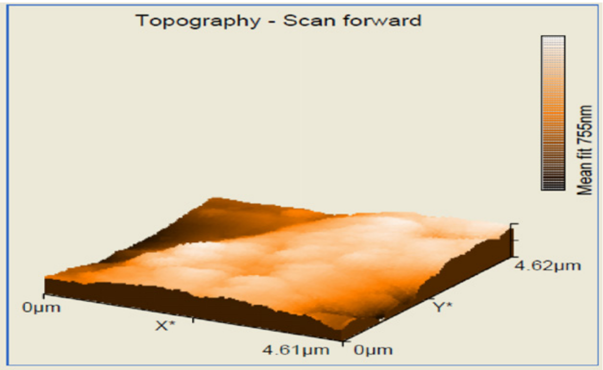


Fig. 7. AFM image of 3-(amino (carboxy) methyl)-1-methyl-1H-imidazol-3-ium chloride supported palladium complex after 8th run.

4-Methoxy-*trans*-stilbene (Table 5, entry 6) ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 3.83 (s, 3H), 6.82 (d, *J* 8.3 Hz, 2H), 6.90 (d, *J* 15.9 Hz, 1H), 7.01 (d, *J* 16.6 Hz, 1H), 7.15–7.31 (m, 4H), 7.38–7.44 (m, 3H); ^{13}C NMR: δ 60.8, 110.1, 123.3, 127.7, 129.2, 129.7, 130.2, 130.7, 136.2, 140.7, 160.3; IR (KBr, cm^{-1}) 3020, 2915, 2850, 1602, 1517, 1243, 1039, 824, 540.

3-Styrylpyridine (Table 5, entry 8) ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 7.06 (d, *J* 16.4 Hz, 1H), 8.70 (s, 1H), 7.16 (d, *J* 16.4 Hz, 1H), 7.31–7.25 (m, 2H), 7.39–7.35 (m, 2H), 7.55 (d, *J* 7.5 Hz, 2H), 7.83 (d, *J* 8.0 Hz, 1H), 8.45 (d, *J* 4.0 Hz, 1H); ^{13}C NMR: δ 123.5, 125.9, 128.7, 129.2, 129.8, 131.8, 133.6, 134.0, 136.6, 150.6.

4. Conclusions

In this study, for the first time, we have introduced [Gmim]Cl–Pd (II) as a catalyst for Heck–Mizoroki reaction with Et_3N in the absence of an organic co-solvent. Aryl bromides were reacted efficiently with styrene and methyl acrylate at ambient temperature in the presence of the catalyst. The procedure is easy and does not require special precautions. All the reactions were conducted in the air without the use of an organic co-solvent. In addition, it was found that, aromatic halides with withdrawing group were more reactive than that of electron donating group. Noteworthy features of this catalyst system are (1) synthesized a novel green 1-glycyl-3-methyl imidazolium chloride–palladium (II) complex; (2) its catalytic activity was tested in Heck reaction; (3) 0.1 mmol of catalyst was sufficient to furnish the *trans*-stilbenes with excellent yields (up to 96%). (4) The catalyst can be readily recovered and reused without significant loss of its activity.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2012.03.004.

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