Microwave-assisted ligand-free, base-free Heck reactions in a task-specific imidazolium ionic liquid

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DOI: http://dx.doi.org/10.3998/ark.5550190.0012.b17

Abstract

1-(2-cyanoethyl)-3-(2-hydroxyethyl)-1*H*-imidazol-3-ium tetrafluoroborate (**IL-2**) in presence of $PdCl_2$ was found to be an efficient and reusable, ligand-free, base-free catalytic system for Heck-coupling of activated and deactivated iodo- and bromoarenes with different olefins. Under microwave irradiation, it exhibited good efficiency in terms of activity, selectivity and recyclability for six consecutive runs without significant loss of activity.

Keywords: Task specific ionic liquid, ligand free, Heck reaction, palladium catalyst, microwave irradiation

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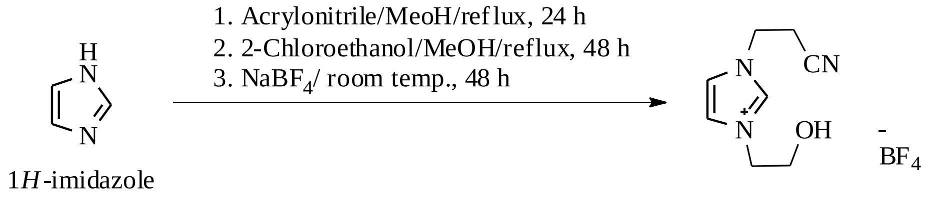
Introduction

Heck reaction, a powerful method for synthesizing diverse olefinic compounds, generally involves carbon-carbon coupling of aryl halides with olefins.[1] In the last few years, considerable development involving coupling of various pseudo-halides such as aryl triflates,[2] acid chlorides,[3] aryl anhydrides,[4] aryl sulfonyl chlorides,[5] and aromatic diazonium salts[6] has been reported. Many drugs and intermediates such as naproxen (Anti-inflammatory agent), prosulfuron (Herbicide) and 2-ethylhexyl-*p*-methoxy cinnamate (sunscreen agent) are synthesized using the Heck reaction.[7] The catalytic system for an efficient Heck reaction consists of a palladium source, a ligand, base and solvent. Usually, phosphine containing ligands are used in the Heck reaction, as they play an important role in stabilization and *in-situ* generation of Pd(0) species from Pd(II) complexes. Due to the high cost, toxicity and thermal instability of the phosphine containing ligands,[8] various phosphine free catalytic systems[9] have been developed. However, most of them showed poor efficiency and reusability in palladium catalyzed Heck reactions.[10] Hence, ligand free homogeneous catalytic systems[11] were of great interest for palladium catalyzed Heck reactions. However, in homogeneous systems, it is difficult to overcome the problems associated with catalyst/product separation and catalyst reusability. In this concern, various heterogeneous catalyst[12] systems have been developed by immobilization of palladium catalyst. However these systems are failed to show higher activity compared to homogeneous systems due to extensive palladium leaching.[13]

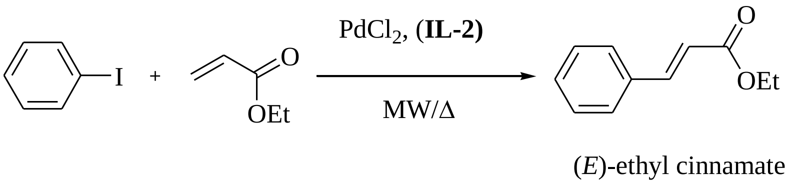
In the last few decades, ionic liquids have gained great interest in synthetic organic chemistry since they are eco-friendly, nonvolatile, recyclable, and possess good thermal properties.[14] Ionic liquids can not only serve as a good alternative to volatile toxic, organic solvents as a reaction medium but also can provide mobile support to palladium catalysts. Many ionic liquids are reported to be used as reaction media for the Heck reaction, but most of them are used along with expensive phosphine-ligands.[15] Hence, the synthesis of functionalized ionic liquids (FILs) through the additional incorporation of the specific pendent groups which could act as ligands and could enhance thermal stability, efficiency and recyclability of the catalyst, are areas of interest. Various reported functionalized imidazolium ionic liquids contain functional groups such as, amine, phosphonite, nitrile, hydroxyl and diols, phosphoryls. Some of the functionalized ionic liquids suffer from drawbacks like air and moisture sensitivity, high palladium loading, difficulties in product isolation, tedious recovery processes and low recyclability.[16] Diol-functionalized ionic liquids have shown good catalytic efficiency in terms of activity and reusability, when used as a kind of ligand for the palladium catalyzed Heck reaction in DMF.[17] Hence it would be still enviable to develop simpler, cost effective, reusable, phosphine free catalytic system for palladium catalyzed Heck reaction.

Herein we report on 1-(2-cyanoethyl)-3-(2-hydroxyethyl)-1*H*-imidazol-3-ium tetrafluoroborate[18] (**IL-2**) (Scheme 1), as a simplest phosphine free catalytic system which acts not only as a solvent but also as a ligand and base and offers good activity and recyclability for six consecutive runs without significant loss of activity in the air. In this work, initially the Heck reaction was carried out using iodobenzene and ethyl acrylate with $PdCl_2$ (2.0 mol %) in ionic liquid (**IL-2)** at 100°C for 24 h, which resulted in (*E*)-ethyl cinnamate in low isolated yield 25%. This was significantly improved on application of microwave heating at 100°C for 10 min (Scheme 2). Microwave heating is reported to accelerate the reaction rate in organic synthesis.[19] A few microwave-assisted Heck reactions are reported in the ionic liquids; however, some of them used phoshine containing ligands.[20-21]



(IL-2)

Scheme 1. Synthesis of ionic liquid (IL-2).



Scheme 2. Heck reaction of iodobenzene with ethyl acrylate in ionic liquid (IL-2).

Results and Discussion

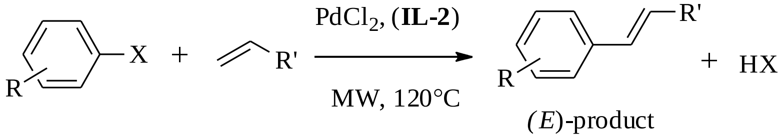
The reaction conditions were further optimized in terms of palladium loading, reaction temperature and time. 1.0 mol% $PdCl_2$ loading resulted in identical yield 69% as compared to 2.0 mol% $PdCl_2$. The rise in temperature from 100 °C to 120 °C showed significant increase in isolated yield 81% (Table 1), however, further increase in temperature to 140 °C, resulted in low yield 64%. Maximum yield 84% was achieved, when the reaction was carried out for 5 min. The optimal condition for Heck reaction in ionic liquid (**IL-2**) was obtained with the following conditions $PdCl_2$ (0.01 mmol), iodobenzene (1 mmol), ethyl acrylate (2 mmol), microwave power 200 W, reaction temperature 120 °C, reaction time 5 min.

Table 1. Effect of different temperature on the yield of Heck reaction

Sr. no.	Temperature (ºC)	Isolated yield (%)
1	80	37
2	100	69
3	120	81
4	140	64

The versatility of the optimized catalytic system for Heck reaction was evaluated with variety of substrates with different electronic and steric effects. The results are summarized in Table 2. Cross-coupling products of different iodoarenes (Table 2, runs 1-7) and bromoarenes (Table 2, runs 8-11) with ethyl acrylate and styrene were obtained in good yields under mild reaction condition (120 °C, 5-10 min); attributed to high reactivity of iodo- and bromoarenes. However, due to the steric hindrance, the coupling of 2-bromo methyl benzoate with different olefins (Table 2, runs 12-13) resulted in moderate yield. Good isolated yield were obtained when the effect of the alkyl chain length of terminal vinyl acrylates were studied (Table 2, runs 14-18). However, activated aryl chlorides were unsuccessful to give desired product, when tried to couple with ethyl acrylate under the same reaction condition (Table 2, runs 19-20).

Table 2. Heck reaction of various aryl halides in ionic liquid (IL-2)



Entry	R	X	R’	Time (min)	Isolated yield (%)[a]
1	*p*-$COCH_3$	I	-$CO_2C_2H_5$	5	86
2	H	I	-$CO_2C_2H_5$	5	84
3	*p*-$CO_2C_2H_5$	I	-$CO_2C_2H_5$	5	88
4	*p*-OCH_3	I	-$CO_2C_2H_5$	5	81
5	*p*-$COCH_3$	I	-C_6H_5	5	82
6	*p*-$CO_2C_2H_5$	I	-C_6H_5	5	85
7	*p*-OCH_3	I	-C_6H_5	5	80
8	*p*-$COCH_3$	Br	-$CO_2C_2H_5$	10	74
9	*p*-OCH_3	Br	-$CO_2C_2H_5$	10	72
10	*p*-$COCH_3$	Br	-C_6H_5	10	72
11	*p*-OCH_3	Br	-C_6H_5	10	70
12	*o*-CO_2CH_3	Br	-$CO_2C_2H_5$	10	57
13	*o*-CO_2CH_3	Br	-C_6H_5	10	53
14	H	Br	-$CO_2C_2H_5$	5	68
15	H	Br	-C_6H_5	5	65
16	H	Br	-CN	5	69
17	H	Br	-$CO_2(CH_2)_3CH_3$	10	65
18	H	Br	-$CO_2CH_2CH(C_2H_5)(CH_2)_3CH_3$	10	62
19	*p*-$CO_2C_2H_5$	Cl	-$CO_2C_2H_5$	20	NR
20	*p*-$COCH_3$	Cl	-$CO_2C_2H_5$	20	NR

$PdCl_2$ (0.01 mmol), ionic liquid (**IL-2**) 2.0 mL, haloarene (1 mmol), olefin (2 mmol), Microwave power 200W, reaction temperature 120°C. [a] The isolated (*E*)-products are confirmed by ^1H NMR

Recyclability of ionic liquid (**IL-2**) was investigated using iodobenzene (1 mmol), ethyl acrylate (2 mmol) in ionic liquid (**IL-2**) and its results are listed in Table 3. Ionic liquid (**IL-2**) has showed good isolated yields in the range of 80% - 84% for six consecutive runs without significant loss of activity.

Table 3. Recyclability of the ionic liquid (IL-2) for palladium catalyzed Heck reaction

Entry	Isolated Yield (%)					
	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6
1	84	84	83	83	82	80
2	83	82	82	82	80	80

$PdCl_2$ (0.01 mmol), ionic liquid (**IL-2**) 2.0 mL, iodoarene (1.0 mmol), ethyl acrylate (2.0 mmol), Microwave power 200W, reaction temperature 120°C, reaction time 5.0 min.

Conclusions

In conclusion, we have successfully developed an efficient, air stable and phosphine free catalytic system for Heck reaction using ionic liquid (**IL-2**) as solvent, ligand and base and palladium chloride as a catalyst. The *in-situ* formed palladium complex proved to be an excellent catalyst for olefination of activated and deactivated iodo- and bromoarenes including sterically hindered, methyl-2-bromo-benzoate. It also exhibited significant efficiency for less reactive vinyl acrylates such as n-butyl acrylate and 2-ethylhexyl acrylate. Due to the advantageous features of the ionic liquid (**IL-2**) like multiple coordinating sites, the palladium catalyst showed good stability and could be recycled for six consecutive runs without loss of activity. The mechanism for the Heck reaction in ionic liquid (**IL-2**) in presence of $PdCl_2$ is being experimentally validated. Further investigation of the developed catalytic system for various palladium-catalyzed coupling reactions is under investigation.

Experimental Section

General. The ionic liquid was characterized by FTIR, ^{1}HNMR, Mass spectroscopy and CHN analysis. FTIR spectra were obtained on a Shimadzu FTIR-8400S spectrometer using neat samples and ^{1}H NMR (300 MHz) and ^{13}C NMR (75MHz) data were recorded on a Varian Mercury VXR-300 NMR spectrometer using DMSO and $CDCl_3$ as a solvent with an internal standard. ESI-MS was obtained with micromass - Q – Tof (YA105) spectrometer and elemental analysis (C,H,N elements) were carried out using ThermoFinnigan EA112 Elemental analyser. All reactions were carried out in CEM Discover Benchmate^{TM} microwave appratus (CEM Corp.). All chemicals were purchased from Sigma Aldrich, S.D. Fine chemicals and Spectrochem private Ltd, India and were used without further purification.

1-(2-Cyanoethyl)-3-(2-hydroxyethyl)-1*H*-imidazol-3-ium tetrafluoroborate (IL-2). In this procedure, 1H-imidazole (25 mmol) was dissolved in anhydrous methanol and acrylonitrile (25 mmol) was added to the resultant solution. The reaction mixture was heated to 70 °C for 24 h, and then 2-chloroethanol (25 mmol) was added to the reaction mixture and stirred at 70 °C for another 48 h. The reaction was cooled to room temperature and $NaBF_4$ (30 mmol) was added to the reaction mixture, stirred at room temperature for 48 h, then filter and solution was concentrated under vacuum to get brown red viscous liquid (Yield = 82%). IR (neat, cm^{-1}): 3559 (OH), 2252 (CN). ^{1}H NMR (300 MHz, DMSO-d_6, ppm): δ_H 9.15 (s, 1H, NC(H)N$^+$), 7.75 (dd, 2H, *J* = 9.3 Hz, NC(H)C(H)N$^+$), 5.21 (s, 1H, OH), 4.50 (t, 2H, *J* = 13.1 Hz, CH_2N), 4.24 (t, 2H, *J* = 9.6 Hz, CH_2N^+), 3.73 (t, 2H, *J* = 9.9 Hz, OH-CH_2), 3.17 (t, 2H, *J* = 12.9 Hz, CH_2-CN). ^{13}C NMR (75 MHz DMSO-d_6): δ = 137. 41 (N*C*$_{Ar}$N), 123.81 (N*C*H$_{Ar}$CH$_{Ar}$), 122.81 (NCH$_{Ar}$*C*H$_{Ar}$), 118.32 (CH*C*N), 59.87 (*C*HOH), 52.54 (N$_{Ar}$*C*HCHOH), 45.04 (N$_{Ar}$*C*HCHCN), 19.32 (*C*HCN) ppm. ESI-MS: M^+/z 166, M^-/z 87. Elemental Analysis: $C_8H_{12}BF_4N_3O$, calcd (%): C 37.98, H 4.78, N 16.61; found: C 37.939, H 4.771, N 16.677.

General procedure for palladium catalyzed Heck reaction. (*E*)-Acetyl stilbene (5)

In a typical example, 4-iodo-acetophenone (1 mmol), styrene (2 mmol) and $PdCl_2$ (0.01 mmol) were added to 2 mL of ionic liquid (**IL-2**) in a microwave vessel. Vessel was then sealed and kept in the microwave cavity (CEM Discover Benchmate™, CEM Corp). Initially microwave irradiation of 200 Watt was applied to reach the target temperature of 120°C (measured using built-in IR temperature device); the reaction mixture was stirred at this temperature for 5 min. During this time, the microwave power was varied automatically to retain the target temperature at 120 °C. The reaction mixture was allowed to cool to room temperature. The product was extracted with diethyl ether and ether layer was concentrated under reduced pressure. The residue was purified by column chromatography using hexane: ethyl acetate (9:1) as a solvent, to obtain (*E*)-acetyl stilbene as white solid (Yield = 82%). mp 149–150 °C (Lit.[23] 150-151 °C); ^{1}H-NMR (300 MHz, $CDCl_3$, Me_4Si, ppm): δ 7.91 (2H, d, *J* 12Hz), 7.64 (4H, m, *J* 21.0Hz), 7.42 (2H, dd, *J* 9.0Hz), 7.35 (1H, dd, *J* 11.0Hz), 7.23 (2H, dd, *J* 15.0Hz), 2.66 (3H, s). ^{13}C NMR (75 MHz $CDCl_3$): δ = 197.68 (CH*C*OCH), 142.25 (CH*C*$_{Ar}$CH), 136.93 (CH*C*$_{Ar}$CH), 136.20 (CH*C*$_{Ar}$CH), 131.70 (*C*H$_{Ar}$), 129.10 (*C*H$_{Ar}$), 129.02 (*C*H$_{Ar}$), 128.54 (*C*H$_{Ar}$), 127.68 (*C*H$_{Ar}$), 127.04 (*C*H$_{Ar}$), 126.73 (*C*H$_{Ar}$), 26.79 (CO*C*H) ppm. Elemental Analysis: $C_{16}H_{14}O$, calcd (%): C 86.45, H 6.35; found: C 86.459, H 6.354.

(*E*)-Ethyl cinnamate (2). Colorless oil[23] ^{1}H-NMR (300 MHz, $CDCl_3$, Me_4Si, ppm): δ 7.71 (1H, d, *J* 16.0Hz), 7.53-7.56 (2H, m), 7.39-7.41 (3H, m), 6.46 (1H, d, *J* 16.0Hz), 4.29 (2H, q, *J* 7.1Hz), 1.36 (3H, t, *J* 7.1Hz).

(*E*)-Ethyl 3-(4-acetylphenyl) acrylate (1). White crystals; mp 41-42 °C (Lit.[19(a)] 42-43 °C); ^{1}H-NMR (300 MHz, $CDCl_3$, Me_4Si, ppm): δ 7.91 (2H, d, *J* 8.0Hz), 7.73 (1H, d, *J* 16Hz), 7.62 (2H, d, *J* 1.5Hz), 6.52 (1H, d, *J* 16.0Hz), 4.35 (2H, q, *J* 21.0Hz), 2.67 (3H, s), 1.35 (3H, t, *J* 14.0Hz).

(*E*)-Ethyl 4-(3-ethoxy-3-oxoprop-1-enyl) benzoate (3). White solid; mp 51–52 °C (Lit.[22] 51-52 °C); ^{1}H-NMR (300 MHz, $CDCl_3$, Me_4Si, ppm): δ 8.05 (2H, d, *J* 8.6Hz), 7.70 (1H, d, *J* 16.0Hz), 7.58 (2H, d, *J* 8.6Hz), 6.52 (1H, d, *J* 16.0Hz), 4.39 (2H, q, *J* 7.0Hz), 4.28 (2H, q, *J* 7.2Hz), 1.40 (3H, t, *J* 7.0Hz), 1.35 (3H, t, *J* 7.2Hz).

(*E*)-Ethyl 4-methoxy cinnamate (4). White crystals; mp 49-50 °C (Lit.[19(a)] 50-51 °C); ^{1}H-NMR (300 MHz, CDCl$_3$, Me$_4$Si, ppm): δ 7.64 (1H, d, *J* 15.9Hz), 7.46 (2H, d, *J* 9.0Hz), 6.88 (2H, d, *J* 9.0Hz), 6.30 (1H, d, *J* 15.9Hz), 4.24 (2H, q, *J* 7.2Hz), 3.81 (3H, s), 1.32 (3H, t, *J* 7.2Hz).

(*E*)-Ethyl-4-styrylbenzoate (6). White solid; mp 107–108 °C (Lit.[23] 107-108 °C); ^{1}H-NMR (300 MHz, CDCl$_3$, Me$_4$Si, ppm): δ 8.04 (2H, d, *J* 8.4Hz), 7.55 (4H, m), 7.41 (2H, m), 7.32 (1H, m), 7.22 (1H, d, *J* 16.3Hz), 7.12 (1H, d, *J* 16.3Hz), 4.39 (2H, q, *J* 7.1Hz), 1.41 (3H, t, *J* 7.1Hz).

(*E*)-4-Methoxystilbene (7). White solid, mp 136-137 °C (Lit.[23] 138-139 °C); ^{1}H-NMR (300 MHz, CDCl$_3$, Me$_4$Si, ppm): δ 7.51 (4H, m), 7.38 (2H, m), 7.24 (1H, m), 7.08 (1H, d, *J* 16.3Hz), 6.94 (1H, d, *J* 16.3Hz), 6.90 (2H, d, *J* 7.5Hz), 3.84 (3H, s).

(*E*)-Methyl 2-(3-ethoxy-3-oxoprop-1-enyl) benzoate (12). Colorless oil;[24] ^{1}H-NMR (300 MHz, CDCl$_3$, Me$_4$Si, ppm): δ 8.05 (2H, d, *J* 8.7Hz), 7.70 (1H, d, *J* 15.9Hz), 7.59 (2H, d, *J* 8.7Hz), 6.52 (1H, d, *J* 15.9Hz), 4.29 (2H, q, *J* 7.2Hz), 3.94 (3H, s), 1.35 (3H, t, *J* 7.2Hz).

(*E*)-Methyl 2-styrylbenzoate (13). Yellow oil;[25] ^{1}H-NMR (300 MHz, CDCl$_3$, Me$_4$Si, ppm): δ 7.97 (10H, m), 7.21 (1H, d, *J* 16.0Hz), 6.90 (1H, d, *J* 16.0Hz), 4.30 (3H, s).

(*E*)-Stilbene (15). White solid; mp 121–122 °C (Lit.[23] 122-123 °C); ^{1}H-NMR (300 MHz, CDCl$_3$, Me$_4$Si, ppm): δ 7.15 (2H, s), 7.30 (2H, m), 7.39 (4H, m), 7.56 (4H, m).

(*E*)-Cinnamonitrile (16). Colorless liquid;[26] ^{1}H-NMR (300 MHz, CDCl$_3$, Me$_4$Si, ppm): δ 5.87 (1H, d, *J* 16.7Hz), 7.41 (1H, d, *J* 16.7Hz), 7.46 (5H, m).

(*E*)-n-Butyl cinnamate (17). Yellow liquid;[27] ^{1}H-NMR (300 MHz, CDCl$_3$, Me$_4$Si, ppm): δ 7.68 (1H, d, *J* 15.9Hz), 7.53 (2H, m), 7.50 (2H, m) 7.38 (3H, m), 6.44 (1H, d, *J* 15.9Hz), 4.21 (2H, t, *J* 7.2Hz), 1.74 (2H, m), 1.37 (2H, m), 0.96 (3H, t, *J* 7.2 Hz).

(*E*)-2-Ethylhexyl cinnamate (18). Colorless liquid;[28] ^{1}H-NMR (300 MHz, CDCl$_3$, Me$_4$Si, ppm): δ 7.68 (1H, d, *J* 16.0 Hz), 7.54 (2H, m), 7.39 (3H, m), 6.45 (1H, d, *J* 16.0 Hz), 4.16 (2H, m), 1.66 (1H, m), 1.44 (8H, m), 0.89–0.95 (6H, m).

General procedure for recyclability of catalytic system

After extracting the mixture from diethyl ether, Ionic liquid (**IL-2**) was dissolved in acetone (5 mL). Then, neutralization of the acid generated during the reaction was done by addition of the potassium carbonate. The salt precipitated out was filtered off and acetone layer was concentrated under reduced pressure at room temperature. Without any further purification; the resultant residue was used for the next run, after addition of iodobenzene (1 mmol), ethyl acrylate (2 mmol) again, for six consecutive runs.

Acknowledgements

I am thankful to University Grant Commission, Delhi for financial support for project and fellowship and also Omkar Chemicals, Mumbai for providing useful chemicals.

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