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Palladium-Catalyzed Heck Reaction in the Multi-Functionalized Ionic Liquid Compositions

**Qing-Xia Wan · Ye Liu · Yong Lu ·
Min Li · Hai-Hong Wu**

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Abstract In the multi-functionalized ionic liquid compositions (MFILC), composed of 1-n-butyl-2-diphenylphosphino-3-methylimidazolium hexafluorophosphate, [BDPPMIM]PF6), 1-(2-piperid-1-yl-ethyl)-3-methylimidazolium hexafluorophosphate, [PEMIM]PF6), and 1-n-butyl-3-methylimidazolium hexafluorophosphate ([BMIM] PF6), PdCl2 served as an efficient catalyst for Heck reactions of aryl iodides and bromides. The built-up PdCl2-MFILC, including stoichiometrically consumed base of [PEMIM]PF6, could be reused at least for seven cycles without activity loss.

Keywords Heck reaction · Functionalization · Ionic liquids · Palladium catalyst

1 Introduction

The palladium-catalyzed coupling of olefins with aryl or vinyl halides, known as Heck reaction, is one of the most important and reliable reactions for carbon–carbon bond formation in organic synthesis [1, 2]. However, the drawbacks of this reaction hampered its large-scale applications, due to the following problems [1, 2]. First, the palladium black often precipitates from reaction solution (i.e., deactivation) and Pd contamination of the products has to be controlled. Second, many expensive phosphines have to be widely used to stabilize palladium catalysts, but they are unpleasant to work with due to toxicity and sensitivity to air/moisture. Third, the universal uses of non-recoverable organic/inorganic bases as acid scavengers. Fourth, the volatile organic compounds (such as acetonitrile, DMF, DMA, or NMP) were required to act as the reaction media. Herein the selection of palladium precursor, phosphine ligand, base and even organic solvent obviously played important roles for the reaction rate and the catalyst lifetime deriving from the PdH neutralization [1, 2].

The recent developed procedures in Heck reactions are quite impressive, including uses of elegant Pd catalyst precursors (heterocyclic carbenes [3], carbene-palladacycles [4]) and non-(phosphine) ligand stabilized Pd catalysts [5, 6], or heterogenization of homogeneous Pd catalysts [7]. Ionic liquids (ILs), known for their nonvolatile, nonflammable and thermal stable properties, have been recently used in the Heck reaction under the catalysis of palladium with or without a phosphine ligand [8]. As alternatives to volatile organic solvents, ILs can serve as excellent media and mobile supports for metal catalysts [9, 10]. To avoid metal catalysts leaching out of IL system, the efforts have been made to enhance the solubility of the catalysts in ILs, such as grafting functional groups into ILs which can coordinate with metal centers [11–14], or introducing imidazolium/pyridinium tags into a metal complex [15, 16].

Since the typical requirements to fulfill Heck reaction includes a ligand-stabilized active Pd species, a base, and a reaction medium, although recently many ligand-free systems have been developed as the promising methods for C–C coupling reactions [6]. The mutual influences and limitations among Pd precursor, ligand, base and solvent are finally showing the comprehensive effects on the catalytic performance (activity, selectivity and stability) and

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Q.-X. Wan · Y. Liu (✉) · Y. Lu · M. Li · H.-H. Wu
Shanghai Key Laboratory of Green Chemistry and Chemical Processes, Chemistry Department of East China Normal University, Shanghai 200062, China
e-mail: yliu@chem.ecnu.edu.cn

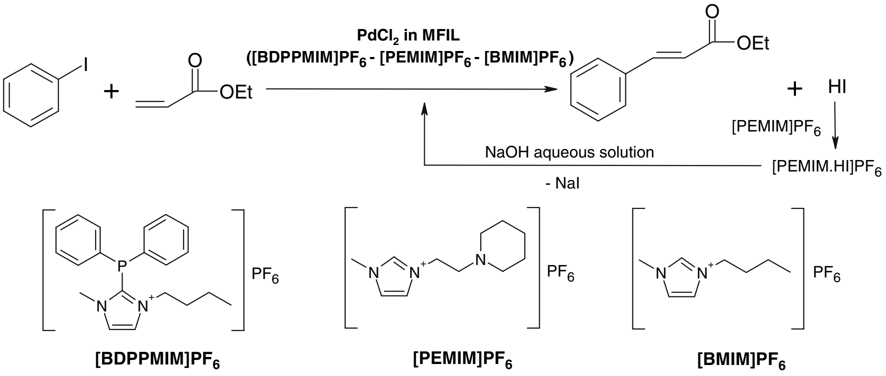
the resultant separation work-up. Especially it is well known that the role of base was fundamentally important as the acid scavenger, the co-ligand and the reducing agent for Pd(II) to Pd (0) [1, 2]. In this work we used the phosphino-functionalized IL (1-n-butyl-2-diphenylphosphino-3-methylimidazolium hexafluorophosphate, [BDPPMIM]PF_6 [17]) as a phosphine-ligand, the piperidyl-functionalized IL (1-(2-piperid-1-yl-ethyl)-3-methylimidazolium hexafluorophosphate, [PEMIM]PF6) as a base, and the non-functionalized IL (1-n-butyl-3-methylimidazolium hexafluorophosphate, [BMIM]PF6) as a solvent. In such case, the required phosphine ligand, base and solvent in Heck reactions got related by ILs with the similar imidazolium skeleton and the same hydrophobic anion of PF_6^-. Such built-up multi-functionalized ionic liquid compositions (MFILC) exert the functions of ligand, base and reaction medium as one unit.

2 Results and Discussion

The model Heck reactions of iodobenzene (PhI) with ethyl acrylate catalyzed by $PdCl_2$–MFILC, were summarized in Table 1. The reaction conditions were optimized in terms of temperature, reaction time and P/Pd ratio. Under the optimal conditions, iodobenzene and ethyl acrylate coupled efficiently with 100% yield of *E*-ethyl cinnamate (Entry 3). If TOF (turnover frequency per hour) was used to measure the activity of Pd catalyst, the highest activity was obtained when the reaction time was 1 h at 0.5 mol% Pd catalyst (Entry 1). The most attractive features of this $PdCl_2$–MFILC were as follows: (1) This system could be used 7 times without activity loss; (2) When the coupling reaction occurred at 130 °C, the reaction mixture was totally homogeneous, avoiding the mass transfer limitation. (3) The separation workup was facilitated by extracting organic products from IL phase directly; (4) Even the base of [PEMIM]PF_6 consumed stoichiometrically could be recovered and reused by neutralizing [PEMIM·HI]PF_6 salt with NaOH aqueous solution.

The comparison of the catalytic performance of $PdCl_2$–MFILC to that of conventional PPh_3-base-DMF system was presented in Table 2. If the conventional base of *N*-methyl piperidine or Et_3N was used to replace [PEMIM]PF_6, the catalytic activity of $PdCl_2$ decreased obviously (Entry 3, 4). In the conventional system, the

Table 1 Heck reaction of iodobenzene with ethyl acrylate catalyzed by $PdCl_2$–MFILC[a]



Entry	Time (h)	Temp (°C)	[BDPPMIM]PF_6/ Pd (molar ratio)	Pd concentration (mol %)[b]	Conv. (%)[c]	Sel. (%)[d]	TOF (h^{-1})
1	1	130	1	0.5	86	99	172
2	2	130	1	0.5	94	100	94
3	3	130	1	0.5	100	100	67
4	3	110	1	0.5	60	100	40
5	3	90	1	0.5	29	100	19
6	3	130	2	0.5	99	100	66
7	10	130	1	0.1	99	100	99
8	10	130	1	0.05	81	100	162

[a] [PEMIM]PF_6 15 mmol, iodobenzene 10 mmol, ethyl acrylate 10 mmol, [BMIM]PF_6 2 mL

[b] Based on the ratio of $PdCl_2$ to iodobenzene

[c] Of iodobenzene

[d] To *E*-ethyl cinnamate

Table 2 Comparison of the catalytic performance of PdCl$_2$ in the MFILC and in the conventional PPh$_3$-base-DMF system for the Heck reaction[a]

Entry	Ligand	Base	Solvent	Conv. (%)[b]	Sel. (%)[c]
1	[BDPPMIM]PF$_6$	[PEMIM]PF$_6$	[BMIM][PF$_6$]	99	100
2	[BDPPMIM]PF$_6$	[PEMIM]PF$_6$	–	99	100
3	[BDPPMIM]PF$_6$	N-methy piperidine	[BMIM][PF$_6$]	61	99
4	[BDPPMIM]PF$_6$	Et$_3$N	[BMIM][PF$_6$]	42	99
5[d]	PPh$_3$	N-methy piperidine	DMF	72	98
6[d]	PPh$_3$	Et$_3$N	DMF	24	99
7[d]	PPh$_3$	N-methy piperidine	[BMIM][PF$_6$]	83	98
8[d]	PPh$_3$	Et$_3$N	[BMIM][PF$_6$]	100	99

[a] PdCl$_2$ 0.05 mmol, phosphine ligand 0.05 mmol, base 15 mmol, iodobenzene 10 mmol, ethyl acrylate 10 mmol, solvent 2 mL; reaction temperature 130 °C, reaction time 3 h

[b] Of iodobenzene

[c] To *E*-ethyl cinnamate

[d] Large amount of palladium black precipitated

palladium catalyst deactivated rapidly along with precipitation of Pd black (Entry 5, 6). Even when DMF was replaced by [BMIM]PF$_6$, which was considered to be able to stabilize active Pd(0) species [4(c), 8], the formation of large amount of Pd black still could be observed, although the activity was improved (Entry 7, 8). These results indicated that PdCl$_2$–MFILC was superior to the conventional PPh$_3$-base-DMF systems in terms of activity and stability.

Apparently, the MFILC gave rise to good activity and stability of PdCl$_2$ catalyst as one unit, in which [BDPPMIM]PF$_6$ acted as a ligand, [PEMIM]PF$_6$ as a base, and [BMIM]PF$_6$ as a reaction medium individually. Meanwhile, the synergistic effects in the MFILC also contributed to the improved activity and stability of the Pd catalyst. As shown in Table 3, if PPh$_3$ was used to replace [BDPPMIM]PF$_6$ (System I), the conversion of PhI decreased gradually to 54% after five cycles while the Pd black precipitated gradually. The ^{31}P NMR analysis of the used IL solution after five cycles indicated that, besides a signal at δ 23.9 ppm ascribed to the fresh PdCl$_2$–PPh$_3$–[PEMIM]PF$_6$ system, a small signal appeared at δ 29.7 ppm is contributed to the formed O=PPh$_3$ oxide. This result is in consistent with the viewpoint that the deactivation of the Pd catalyst can derive from degradation of phosphine ligand due to weak oxidation tolerance [1, 2]. Similarly, if DMF was used to replace [BMIM]PF$_6$ (System II) as a solvent, the Pd black also precipitated from reaction solution during the recycling uses along with the decreased PhI conversion to 51%. The obtained results suggested that the imidazolium-based IL of [BMIM]PF$_6$, besides acting as a solvent, additionally play the role of stabilizing Pd(0) species with no formation of Pd black by forming *N*-heterocyclic palladium carbene complex (NH*C*N) in-situ as reported before [4(c), 15, 18].

Table 3 The recycling uses of PdCl$_2$ catalyst in MFILC, System I and System II respectively for Heck reaction[a,b]

Runs	MFILC[BDPPMIM]PF$_6$ + [PEMIM]PF$_6$ + [BMIM]PF$_6$		System I PPh$_3$ + [PEMIM]PF$_6$ + [BMIM]PF$_6$		System II [BDPPMIM]PF$_6$ + [PEMIM]PF$_6$ + DMF	
	[PEMIM]PF$_6$ (mmol)[c]	Conv. of PhI (%)	[PEMIM]PF$_6$ (mmol)[c]	Conv. of PhI (%)	[PEMIM]PF$_6$ (mmol)[c]	Conv. of PhI (%)
1	15	100	15	100	15	100
2	0	99	0	99[d]	10	96[d]
3	0	100	0	82[d]	10	88[d]
5	0	99	10	54[d]	10	51[d]
6	0	97	–	–	–	–
7	0	94	–	–	–	–

[a] PdCl$_2$ 0.05 mmol, iodobenzene 10 mmol, ethyl acrylate 10 mmol; [BDPPMIM]PF$_6$ or PPh$_3$ 0.05 mmol, [BMIM]PF$_6$ or DMF 2 mL, reaction temperature 130 °C, reaction time per cycle 3 h

[b] The selectivity to E-ethyl cinnamate was always ≥99% during the recycling uses for all systems, and was not indicated in this table

[c] Base added per cycle

[d] The slight palladium black precipitated gradually

Although the basic IL of [PEMIM]PF$_6$ could be regarded as a *N*-containing ligand for Pd catalyst [5], the complete replacement of [BDPPMIM]PF$_6$ by [PEMIM]PF$_6$ was not acceptable (System III in Table 4). Without the presence of [BDPPMIM]PF$_6$, the conversion of PhI decreased to 61% after six cycles along with the slight precipitation of Pd black.

If the ambient IL of [PEMIM]PF$_6$ was used as an acid scavenger, a reaction medium and a source of carbene sites simultaneously without the involvement of [BMIM]PF$_6$, the conversions of PhI also decreased gradually during the recycling uses though the precipitation of Pd black was not observed (System IV in Table 4). It was found that [PEMIM]PF$_6$ with slight solubility in water (2.4 g/100 mL H_2O), due to the hydrophilic nature of piperidyl group, could carry $PdCl_2$ and [BDPPMIM]PF$_6$ (which are miscible in [PEMIM]PF$_6$) into the aqueous phase during the treatment of [PEMIM·HI]PF$_6$ by NaOH aqueous solution. Resultantly, the cumulative loss of Pd in aqueous phase was more than 15 μg/g (0.014 mmol, the total amount of $PdCl_2$ catalyst was 0.05 mmol), leading to ca. 28% loss of Pd catalyst totally. Comparatively, in the MFILC, the cumulative loss of Pd in aqueous phase was only ca. 2.0 μg/g (0.002 mmol) after seven reuses. Therefore, the more hydrophobic [BMIM]PF$_6$ was used as the solvent together, the loss of Pd from MFILC into aqueous phase could be suppressed greatly. And due to good solubility/coordination of the palladium complex in the IL phase, the total loss of Pd in the combined organic phase was below the limit of ICP detection (<0.1 μg/g).

Since [PEMIM]PF$_6$ was slightly soluble in water, the additional [PEMIM]PF$_6$ was added in several runs in Table 3 and 4 (Systems I–IV) to offset the loss of [PEMIM]PF$_6$ into the aqueous phase as the scavenger, which could influence the reaction rate greatly. The results in Table 3 (System I, System II) and Table 4 (System III and System IV) indicated that the activity and stability of $PdCl_2$ catalyst decreased dramatically, only due to the replacements of [BDPPMIM]PF$_6$ and [BMIM]PF$_6$ in the MFILC by the others, or the leaching of the Pd catalyst into the aqueous phase, but not coming from the loss of ability to scavenge acids (HI) by [PEMIM]PF$_6$.

Apparently, [BDPPMIM]PF$_6$, [PEMIM]PF$_6$ and [BMIM]PF$_6$ synergistically contributed to the beneficial effects on stability and activity of the palladium catalyst, leading to the advantages over each individual. As to [BDPPMIM]PF$_6$, its primary role as a phosphine ligand was to stabilize palladium in the form of stable Pd(0)L_4 or Pd(0)L_3 species and therefore help prevent the formation of inactive palladium black. Compared to PPh_3 ligand, The oxidation tolerance of [BDPPMIM]PF$_6$ could be improved due to strong electron-withdrawing effect on P atom from imidazolium cation. In fact, [BDPPMIM]PF$_6$, heating at 130 °C for 21 h (cumulative time for seven recycling uses) without N_2 protection, retained completely intact (^{31}P NMR analysis, $\delta = -26.1$ ppm). As to [PEMIM]PF$_6$ endowed with basicity corresponding to piperidyl group, it could behave as a N-containing co-ligand, besides the primary roles of scavenging proton of PdH species to allow restoration of Pd(0) catalyst and reducing Pd(II) to Pd(0) species [1, 2, 5]. However, due to the relatively hard coordinating nature compared to a phosphine ligand, the activating and protecting role of [PEMIM]PF$_6$ for Pd catalyst was supposedly not as efficient as that of [BDPPMIM]PF$_6$. As to [BMIM]PF$_6$, besides its primary role as a reaction medium, it could be a source to offer

Table 4 The recycling uses of $PdCl_2$ catalyst in MFILC, System III, and System IV respectively for Heck reaction[a,b]

Runs	MFILC [BDPPMIM]PF$_6$ + [PEMIM]PF$_6$ + [BMIM]PF$_6$		System III [PEMIM]PF$_6$ + [BMIM]PF$_6$		System IV[e] [BDPPMIM]PF$_6$ + [PEMIM]PF$_6$	
	[PEMIM]PF$_6$ (mmol)[c]	Conv. of PhI (%)	[PEMIM]PF$_6$ (mmol)[c]	Conv. of PhI (%)	[PEMIM]PF$_6$ (mmol)[c]	Conv. of PhI (%)
1	15	100	15	99	15	100
2	0	99	0	99	0	99
3	0	100	10	90 [d]	0	99
4	0	100	0	82 [d]	10	98
5	0	99	10	68 [d]	0	89
6	0	97	10	61 [d]	0	80
7	0	94	–	–	10	75

[a] $PdCl_2$ 0.05 mmol, iodobenzene 10 mmol, ethyl acrylate 10 mmol; [BDPPMIM]PF$_6$ 0.05 mmol, [BMIM]PF$_6$ 2 mL, reaction temperature 130 °C, reaction time per cycle 3 h

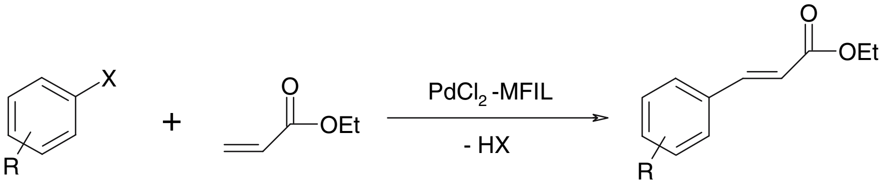
[b] The selectivity to *E*-ethyl cinnamate was always ≥99% during the recycling uses for all systems, and was not indicated in this table

[c] Base added per cycle

[d] The slight palladium black precipitated gradually

[e] The total loss of Pd in aqueous phase after seven runs was ca. 15 μg/g (0.014 mmol)

Table 5 Heck reaction with the different substrates in $PdCl_2$–MFILC[a]



Entry	R	X	Conversion (%)[b]	Isolated yield (%)[c]
1	H	I	100	98
2	*p*-Me	I	100	97
3	*m*-Me	I	98	96
4	*o*-Me	I	87	82
5	*p*-Ome	I	100	97
6	*m*-Ome	I	100	96
7	*o*-Ome	I	82	75
8	*p*-NO_2	I	100	96
9	*m*-NO_2	I	100	98
10	*o*-NO_2	I	100	96
11	*p*-CF_3	I	100	98
12	*m*-CF_3	I	88	83
13	*o*-CF_3	I	86	83
14[d]	H	Br	56	51
15[d]	*p*-NO_2	Br	86	82
16[d]	*p*-Me	Br	42	35
17[d]	*p*-Ome	Br	16	10
18[d]	H	Cl	<5	–

[a] $PdCl_2$ 0.05 mmol (0.5 mol%), [BDPPMIM]PF_6 0.05 mmol, [PEMIM]PF_6 15 mmol, [BMIM]PF_6 2 mL, aryl halide 10 mmol, ethyl acrylate 10 mmol, reaction temperature 130 °C, reaction time 3 h

[b] Of aryl halide

[c] The isolated *E*-cross-coupling product was characterized by ^1H NMR

[d] $PdCl_2$ 0.20 mmol (2.0 mol%), [BDPPMIM]PF6 0.20 mmol, reaction time 15 h. The other conditions were the same as those in [a]

carbene site at 2-C of imidazolium ring [11–15, 18], giving rise to form Pd-carbene complex.

Conclusively, the MFILC composed of [BDPPMIM]PF_6, [PEMIM]PF_6 and [BMIM]PF_6 not only exerted the functions of ligand, base and solvent respectively, but also embodied the synergistic effect as one unit. Due to more available coordinating sites in such MFILC, the palladium catalyst immobilized in the MFILC combined the advantageous activity and stability of N,P-containing ligand coordinated Pd complexes and Pd-carbene complexes [19]. Due to the strong hydrophobicity of the MFILC, the recovery of [PEMIM]PF_6 and the recycling uses of the palladium catalyst could be guaranteed. The replacement/omission of any individual in the MFILC could result in the deteriorated activity or stability/recyclability.

The generality of $PdCl_2$ immobilized in the MFILC for Heck reaction was demonstrated in Table 5, in which the substrates with different electronic and steric effects were selected. The results showed that the catalytic system of $PdCl_2$–MFILC was generally efficient to the conversion of aryl iodides. As to the activation of aryl bromides, the satisfactory conversions were obtained in cases of bromobenzene and *p*-bromonitrobenzene applied when reaction time extended to 15 h at 2 mol% $PdCl_2$ concentration. But the coupling of chlorobenzene with ethyl acrylate could not occur under such conditions.

3 Conclusions

We have developed an efficient and recyclable $PdCl_2$–MFILC catalytic system, by which an array of substrates including sterically hindered and electron-rich aryl iodides and activated aryl bromides, could successfully fulfill Heck reaction with high activity and stability. The most attractive feature of the $PdCl_2$–MFILC was its recyclability, in which even the acid scavenger of [PEMIM]PF_6 could be recoverably used at least seven cycles without reactivity loss. In the MFILC, composed of [BDPPMIM]PF_6, [PEMIM]PF_6 and [BMIM]PF_6, the improved oxidation tolerance of [BDPPMIM]PF_6 and the synergistic effect between [BDPPMIM]PF_6, [PEMIM]PF_6 and [BMIM]PF_6 did contribute to the activity and stability of the palladium catalyst. The MFILC ([BDPPMIM]PF_6–[PEMIM]PF_6–[BMIM]PF_6) could construct a P,N,carbene-containing ligand network for Pd center, facilitating the formation and lifetime of the active palladium (Pd (0)) species. At present it is as yet unclear whether the metal Pd is coordinated via the phosphine ([BDPPMIM]PF_6) and/or amine ([PEMIMI]PF_6), or forms Pd-carbene species. The work for clarifying this point is in progress.

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