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Heck reactions in a non-aqueous ionic liquid using silica supported palladium complex catalysts

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Abstract—The Heck reaction of iodobenzene and 4-methyl-iodobenzene with olefins using silica-supported palladium complex catalysts was conducted in 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF_6), exhibiting higher activities than in DMF in addition to easy product isolation and catalyst recycling. © 2002 Elsevier Science Ltd. All rights reserved.

Ionic liquids are attractive alternatives to conventional organic solvents because their non-volatile nature can reduce the emission of toxic organic compounds and facilitate the separation of products and/or catalysts from the reaction solvents.[1] Especially, ionic liquids consisting of dialkylimidazolium cations have several useful properties, such as keeping the liquid condition under a wide range of temperature and having good solubility for many substrates and molecular catalysts.[2] The range of applications of ionic liquids has been expanded into solvents for catalytic reactions over the past few years, because ionic liquids are capable of separation of products and reuse of the solvents with catalysts is possible.[3]

Palladium-catalysed carbon–carbon bond forming Heck reactions have contributed remarkably to synthetic organic chemistry.[4,5] Ionic liquids are a candidate for use as solvents for Heck reactions because of the facile separation of the products and recycling of the ionic liquids containing the palladium catalysts. Seddon et al.[6] first reported the Heck reaction of aryl halides and benzoic aldehydes with alkenes using homogeneous palladium complex catalysts and phosphine ligands in 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF_6). The hydrophobic ionic liquid [bmim]PF_6 could be separated from the products and salt byproducts by extraction through the simple decantation of the organic solvent and water, respectively. They also reported that the [bmim]PF_6 containing palladium complex catalysts could be recycled six times without loss of activity. Recently, Hagiwara et al.[7] reported that Heck reactions proceeded to give satisfactory yields with a charcoal-supported palladium catalyst (Pd/C) and without phosphine ligands in [bmim]PF_6 and under the system the ionic liquid could be easily recycled involving a heterogeneous palladium catalyst as well. However, the reaction conditions were time-consuming (>12 h) and required high temperature (>373 K) because of the high viscosity and low solubility of the ionic liquid [bmim]PF_6.

In this paper we report the highly active and re-usable supported palladium complex catalyst in [bmim]PF_6 for the Heck reaction with triethylamine and without phosphine.

The ionic liquid [bmim]PF_6 was prepared according to the procedures reported.[8] A silica-supported palladium complex catalyst (Pd^{II}/SiO_2) was prepared by an ion-exchange method.[9] Palladium was loaded by adding a weighed quantity of silica gel powder (Aldrich, Davisil™ 646) to the desired volume of tetraammine palladium dichloride ($Pd(NH_3)_4Cl_2$) solution of 20 mmol/l. The pH was adjusted to 11.5–12.0 by adding ammonium solution, and the support was kept immersed in this solution at room temperature for 3 days. Under the conditions used, almost all of the palladium precursors present in the solution were adsorbed by the support. After filtration, the powder was washed with distilled water and vacuum-dried at 393 K for 6 h. The quantity of palladium loaded was fixed at 5 wt%. The actual amounts of palladium loaded were examined by measuring the residual

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amounts of the metal remaining in the solution by atomic absorption spectroscopy. The actual weights loaded were in good agreement with the nominal value. The Pd^{II}/SiO_2 catalyst was reduced at 573 K for 3 h under flowing hydrogen to prepare a palladium metal catalyst (Pd^0/SiO_2). A mixture of $Pd(NH_3)_4Cl_2$ and silica (mix-Pd^{II}-SiO_2) was also prepared. The palladium loading of the catalyst was 5 wt%. The reaction was carried out in a test tube. Typical experimental procedure was as follows. To a stirred slurry of a 5 wt% silica-supported palladium catalyst (21.6 mg, 0.010 mmol) in $bmimPF_6$ (1.5 ml) was added iodobenzene (204 mg, 1.0 mmol), ethyl acrylate (163 μl, 1.5 mmol) and triethylamine (140 μl, 1.0 mmol). The resulting slurry was heated at 353 K under a nitrogen atmosphere. After cooling to room temperature, the product was extracted three times with *t*-butyl methyl ether by vigorous stirring, followed by decantation of the organic layer. The components in the organic solution were analyzed by a gas chromatograph with a FID detector (Shimazu GC-14A, ULBON HR-52 capillary column 25 m×0.32 mm).

Fig. 1 shows the conversion profiles for the Heck reactions of iodobenzene with ethylacrylate (Scheme 1) catalyzed by supported palladium catalysts. (*E*)-Ethylcinnamate was the only product, and the reaction proceeded without phosphine ligands on all the catalysts used. The reaction proceeded with time on palladium metal catalysts (Pd/C and Pd^0/SiO_2). The induction periods were observed in the system with unreduced catalysts (Pd^{II}/SiO_2 and mix-Pd^{II}-SiO_2). In the case of the Pd^{II}/SiO_2 catalyst, the color of the catalyst gradually changed from pale yellow to black, and then the Heck reaction proceeded. The induction period would be the reductive process from the divalent to an active metal palladium (Pd^0) in the ionic liquid. The final conversion with the Pd^{II}/SiO_2 catalyst was higher than that of the mix-Pd^{II}-SiO_2 catalyst ($Pd(NH_3)_4Cl_2$ complex). Seddon et al.[6] reported that the Heck reaction of iodobenzene and ethyl acrylate proceeded in $[bmim]PF_6$ with $Pd(OAc)_2$ and triphenylphosphine at 373 K. Our results indicate that the supported complex catalyst proceeds the Heck reaction without phosphine ligands at 353 K, and the catalytic activity of the palladium complex supported on silica was higher than that of the palladium complex itself. Fig. 2 shows the palladium concentration profiles in $[bmim]PF_6$ solvent during the Heck reactions. The palladium species was dissolved from the silica support during the reactions. Half amounts of the palladium supported were eluted from the supports into $[bmim]PF_6$ after 1 h. The palladium concentrations in the ionic liquid were higher than those in organic solvent (Tables 1 and 2). Biffs et al.[10] proposed that the palladium species dissolved from the supported Pd catalysts into the solvents were the active sites in the heterogeneous Heck reaction. The Heck reaction of iodobenzene with ethylacrylate was conducted again with the ionic liquid $[bmim]PF_6$ recycled, from which the catalyst powder was separated after the reaction. The ionic liquid recycled showed the same conversion as that of the first run, indicating that the reaction proceeded by the palladium species dissolved in the ionic liquid. This re-usability without loss of catalytic activity is a major advantage of the present study. The palladium concentration was not proportional to the activity in our results. The Pd^{II}/SiO_2 catalyst showed higher yields than the mix-Pd^{II}-SiO_2 catalyst, though the amount of palladium dissolved from the Pd^{II}/SiO_2 catalyst into $[bmim]PF_6$ was lower than that from the mix-Pd^{II}-SiO_2 catalyst. It is probable that the number of the active palladium sites in the $[bmim]PF_6$ liquid with the Pd^{II}/SiO_2 catalyst was higher than that with the mix-Pd^{II}-SiO_2 catalyst.

The Heck reaction in organic solvents normally requires more than 1 equiv. of a base to remove halogen atoms and to reproduce the active metal palladium

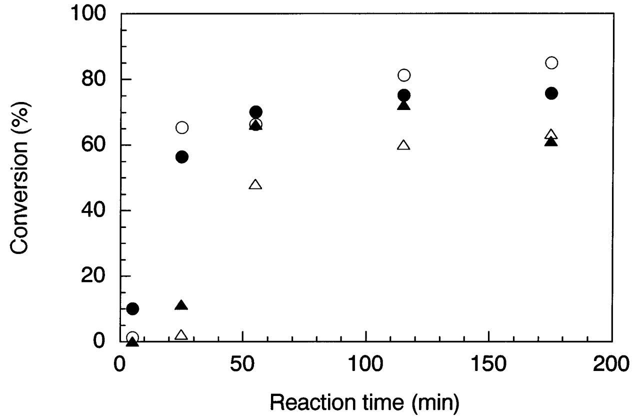
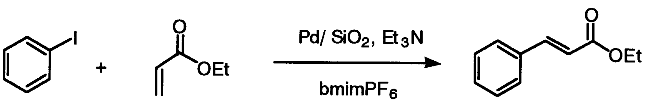


Figure 1. The conversion profiles for Heck reactions of iodobenzene with ethylacrylate with several catalysts (○: Pd^{II}/SiO_2, ●: Pd^0/SiO_2, △: mix-Pd^{II}-SiO_2, ▲: Pd/C) and Et_3N 1 mmol (1 equiv.) in $[bmim]PF_6$. The reaction temperature was 353 K.



Scheme 1.

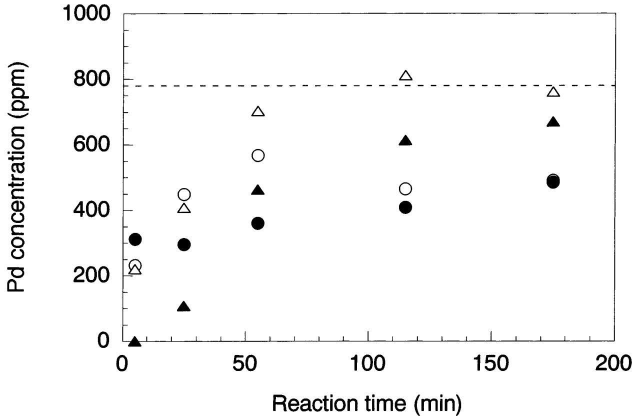


Figure 2. The palladium concentration in $[bmim]PF_6$ during the Heck reactions of iodobenzene and ethylacrylate (○: Pd^{II}/SiO_2, ●: Pd^0/SiO_2, △: mix-Pd^{II}-SiO_2, ▲: Pd/C). The broken line is the total amount of the palladium in the system. The reaction temperature was 353 K. One equivalent of Et_3N (1 mmol) was added.

Table 1. Heck reaction of iodobenzene with ethylacrylate using supported palladium catalysts

Entry[a]	Catalyst	Solvent	Et_3N (mmol)	Conversion (%)[c]	Pd concentration (ppm)[d]
1	Pd^{II}/SiO_2	$bmimPF_6$	1	66	382
2[b]	Pd^{II}/SiO_2	$bmimPF_6$	1	71	395
3	Pd^{II}/SiO_2	$bmimPF_6$	2	99	311
4	Pd^0/SiO_2	$bmimPF_6$	1	57	261
5	Pd^0/SiO_2	$bmimPF_6$	2	59	246
6	Pd/C	$bmimPF_6$	1	66	555
7	Pd/C	$bmimPF_6$	2	66	638
8	$Pd(NH_3)_4Cl_2$	$bmimPF_6$	1	49	871
9	$Pd(NH_3)_4Cl_2$	$bmimPF_6$	2	82	743
10	Pd^{II}/SiO_2	DMF	1	85	145
11	Pd^{II}/SiO_2	DMF	2	88	72
12	Pd^0/SiO_2	DMF	1	81	57
13	Pd^0/SiO_2	DMF	2	83	65

[a] All reactions were carried out at 353 K for 1 h except for entry 2.

[b] Reaction was carried out at 353 K for 24 h.

[c] Yields were determined by GLC analysis. Only *E*-isomers were obtained.

[d] The Pd concentrations in solvents were analyzed by an atomic absorption spectroscopy.

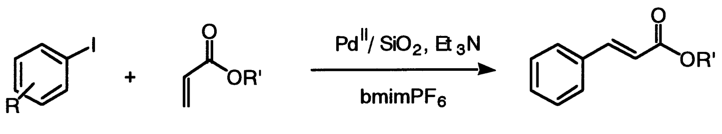
Table 2. Heck reactions with Pd^{II}/SiO_2 catalysts in several solvents

Entry[a]	Aryl iodide (R =)	Olefin	Et_3N (mmol)	Solvent	Time (h)	Conversion (%)[b]	Pd concentration (ppm)[c]
1	H	Me	1	$bmimPF_6$	1	52	545
2	H	Me	2	$bmimPF_6$	1	98	468
3	H	Me	1	DMF	1	90	122
4	H	Me	2	DMF	1	88	85
5	H	Bu	1	$bmimPF_6$	1	57	497
6	H	Bu	2	$bmimPF_6$	1	70	413
7	H	Bu	1	DMF	1	72	127
8	H	Bu	2	DMF	1	67	156
9	4-Me	Et	1	$bmimPF_6$	2	64	514
10	4-Me	Et	2	$bmimPF_6$	2	99	268
11	4-Me	Et	2	DMF	2	78	61
12	4-OMe	Et	1	$bmimPF_6$	6	16	442
13	4-OMe	Et	2	$bmimPF_6$	6	79	421
14	4-OMe	Et	2	DMF	6	85	30
15	4-COMe	Et	1	$bmimPF_6$	6	1	517
16	4-COMe	Et	2	$bmimPF_6$	6	33	496
17	4-COMe	Et	2	DMF	6	99	30

[a] All reactions were carried out at 353 K.

[b] Yields were determined by GLC analysis.

[c] The Pd concentrations in solvents were analyzed by an atomic absorption spectroscopy.



Scheme 2.

(0) sites.[11] We examined the effect of the quantity of the base for the Heck reactions in $[bmim]PF_6$. The conversions were increased with increasing the quantity of triethylamine added from 0 to 1 equiv. for iodobenzene on all the catalysts used. Adding more than 1 equiv. of the base in the reaction with such organic solvents as DMF and acetonitrile did not enhance the conversion. The conversions were increased with increasing the amount of the base added to more than 1 equiv. and became maxima on adding 2 equiv. of triethylamine to the $[bmim]PF_6$ solvent with non-reduced palladium catalysts, though the palladium concentrations were decreased (entries 3, 5 and 9 in Table 1).

The base effects for the Heck reaction using the Pd^{II}/SiO_2 catalyst in $[bmim]PF_6$ were studied with a combination of other iodobenzene derivatives and olefins (Scheme 2, Table 2). The enhancement of conversion with the Pd^{II}/SiO_2 catalyst was observed for all of the experiments by adding 2 equiv. of the base to $[bmim]PF_6$.

The conversion of 66% after 1 h was slightly improved after 24 h with the Pd^{II}/SiO_2 catalyst and 1 equiv. of the base (entry 2 in Table 1); however, the Heck reaction was almost completed by adding 1 further equiv. (total 2 equiv.) of triethylamine after the reaction of entry 2, indicating that 2 equiv. of the base were needed to proceed the Heck reactions in $[bmim]PF_6$. Supported metal palladium catalysts showed high activities for Heck reactions in organic solvents;[12] however, we showed that the unreduced Pd^{II}/SiO_2 catalyst with 2 equiv. of base in $[bmim]PF_6$ were more active than supported palladium catalysts in DMF in this study.

We observed that $[bmim]PF_6$ was decomposed by heating at 403 K; however, the decomposition temperature was increased above 433 K by adding a small amount of triethylamine, suggesting that triethylamine molecules interact with the ionic solvent and more than 1 equiv. of the base was needed to proceed the reaction in the ionic liquid.

In summary, high conversions of the Heck reactions were obtained in ionic liquid $[bmim]PF_6$ with a non-reduced Pd^{II}/SiO_2 catalyst and 2 equiv. of triethylamine and without phosphine ligands at 375 K.

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