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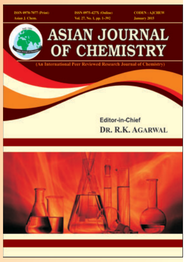

An Efficient and Recyclable Catalytic System: $PdCl_2$-$Dppc^+$-PF_6^--[bmim][PF_6] for Heck Coupling Reaction

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An efficient $PdCl_2$-$Dppc^+$-PF_6^--[bmim][PF_6] catalytic system has been developed for the Heck coupling reaction of various aryl iodides with olefins. The catalytic system allows the coupling reaction to proceed smoothly in excellent yields and can be recycled 5 times with minimal loss of activity.

Keywords: $Dppc^+$-PF_6^- , Heck coupling reaction, Recyclable.

INTRODUCTION

The Palladium-catalyzed Heck reaction is one of the most powerful tools for the formation of the C-C bonds in organic synthesis[1-5]. Because of its tolerance to different functional groups, the method has been widely used in the synthesis of natural products, optical materials, fine chemicals, macrocycles and polymers. Despite the high importance and excellent advances concerning the application of the Heck coupling reaction in organic synthesis, the methodology suffers from the recovery of the expensive Pd catalysts and the separation of the final products from the reaction mixture and need for organic solvents[6-8]. Recently, many efforts have been made to solve these problems by immobilization on zeolite or polymer, the use of aqueous media and the use of ionic liquid[9-12]. The use of ionic liquids as solvent for the Heck coupling reactions has attracted increasing attention[13-16]. Usually, the neutral catalyst system were used in ionic liquid and easily dissolve in organic solvents during the work-up, which resulting in difficulty in the recovery and reuse. $Dppc^+PF_6^-$ [1,1-*bis*-(diphenylphosphino)cobaltocenium hexafluorophosphate] (**1**), an ionic ligand, proved to be a most suitable ligand for biphasic hydroformylation in ionic liquids, with high solubility in [bmim][PF_6] (1-butyl-3-methyl imidazolium hexafluorophosphate) and insoluble in non-polar organic solvent. As part of our ongoing project on palladium catalyzed reactions[17-20], herein, we report that $PdCl_2$ -$Dppc^+PF_6^-$, in combination with [bmim][PF_6] as solvent, an efficient and recyclable catalysis system for the Heck coupling reaction (Fig. 1).

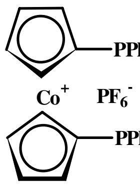


Fig. 1. Structure of $Dppc^+PF_6^-$

EXPERIMENTAL

All commercially available solvents and reagents were used as supplied unless otherwise stated. $Dppc^+PF_6^-$ (**1**)[21] and [bmim][PF_6][22] were prepared according to literature procedures. Product yields were calculated by GC, using a 6890N Network GC system (Agilent Technologies).

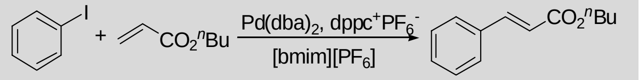
Typical procedure for Heck coupling reaction: A mixture of iodobenzene (**2a**) (212 µL, 2 mmol), *n*-butyl acrylate (dba) (**2b**) (314 µL, 0.6 mmol), Et_3N (580 µL, 4 mmol), $PdCl_2$ (0.71 mg, 0.004 mmol), $dppc^+PF_6^-$ (2.81 mg, 0.004 mmol) and [bmim][PF_6] (2 mL) under nitrogen in a sealed tube was heated to 120 °C and maintained for 1.5 h. Then it was cooled and extracted with diethyl ether (4 × 5 mL). After evaporation under reduced pressure, the residue was purified on silica gel (petroleum ether/ethyl acetate as eluent) to give the desired product **3a**.

Typical procedure for catalyst recycling of Heck coupling reaction: After the product was extracted with diethyl ether (4 × 5 mL), water (3 × 5 mL). Excess amount of diethyl ether and water was removed under reduced pressure. To the remaining ionic liquid containing Pd catalyst was added iodobenzene (**2a**) (212 μL, 2 mmol), *n*-butyl acrylate (**2b**) (314 μL, 0.6 mmol), Et_3N (580 μL, 4 mmol) and heated at the required temperature with stirring for the proper time.

RESULTS AND DISCUSSION

We initially chose the cross-coupling of iodobenzene with *n*-butyl acrylate as the model reaction to examine the catalyst and optimize the reaction conditions. First, the effect of base was tested in the presence of 0.1 mol % $Pd(dba)_2$ at 120 °C for 1.5 h in [bmim][PF_6]. As shown in Table-1, Et_3N was the best choice, NaOAc was less effective, other bases afforded < 5 % yield in this reaction. We then examined the activities of Pd source using Et_3N as base, as shown in Table-2. Among the Pd sources tested, $PdCl_2$ displayed most excellent catalytic activity, afforded the product **3a** in 85 % yield (entry 2 in Table-2). Increasing the amount of the $PdCl_2$ and ligand dppc$^+PF_6^-$ to 0.2 mol %, the yield improved sharply to 99 % (entry 4 in Table-2).

TABLE-1
EFFECT OF BASE ON THE HECK COUPLING REACTION[a]



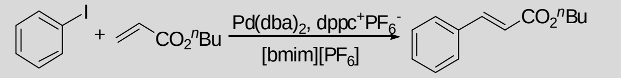
Entry	Base	Yield (%)[b]
1	K_3PO_4	< 5
2	NaOAc	21
3	K_2CO_3	< 5
4	NaOH	< 5
5	Et_3N	40

[a]Reaction conditions: Iodobenzene (2 mmol), *n*-butyl acrylate (2.2 mmol), base (2 equiv), $Pd(dba)_2$ (0.002 mmol), dppc$^+PF_6^-$ (0.002 mmol), and [bmim][PF_6] (2 mL) at 120 °C for 1.5 h in a pressure tube. [b]GC yields

Thus, Heck reaction of a variety of aryl iodides with olefins were investigated under the optimum conditions. As shown in Table-3, all the electron with drawing and electron-donating aryl iodides react with various olefins smoothly in excellent yields to give the corresponding products. For methyl-substituted iodobenzene, 2-iodotoluene and 4-iodotoluene reacted with *n*-butyl acrylate can afford the desired product in 94 and 92 % yield, respectively (entries 2 and 3, Table-3). For strongly electron-donating methoxyl substitute, 3-iodoanisole reacted with *n*-butyl acrylate (**2b**) can afford the coupling product in excellent yield (entry 5, Table-3), meanwhile, 4-iodoanisole can also give the satisfactory yield by increasing the amount of catalyst to 0.4 mol % and extending the reaction time to 3 h (entry 4, Table-3). The reaction of 4-chloroiodobenzene and 4-iodoacetophenone with *n*-butyl acrylate (**2b**) gave the desired product in 94 and 93 % yield, respectively (entries 6 and 7, Table-3). The coupling reaction of nitroiodobenzene with *n*-butyl acrylate (**2b**) gave the desired products in poor yields, probably because of the poor solubility of the nitroiodobenzene in the [bmim][PF_6]. Excellent yields were just obtained by increasing the catalyst loading and prolonging the reaction time (entries 8, 9 and 10, Table-3). Heteroaromatic compound 2-iodothiophene also reacted with *n*-butyl acrylate (**2b**) to give the desired product in 93 % yield using 0.4 % catalyst loading and extending the reaction time to 3 h. In addition, the reaction of iodobenzene (**2a**) with other olefins can also give the desired products in excellent yields (entries 12-15, Table-3).

After carrying out the reaction, the products could be easily separated from the reaction mixture by extraction with

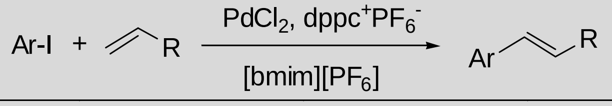
TABLE-2
EFFECT OF CATALYST ON THE HECK COUPLING REACTION[a]



Entry	Catalyst	Yield (%)[b]
1	$Pd(dba)_2$ (0.1 mol %), dppc$^+PF_6^-$ (0.1 mol %)	40
2	$PdCl_2$ (0.1 mol %), dppc$^+PF_6^-$ (0.1 mol %)	85
3	$Pd(OAc)_2$ (0.1 mol %), dppc$^+PF_6^-$ (0.1 mol %)	7
4	$PdCl_2$ (0.2 mol %), dppc$^+PF_6^-$ (0.2 mol %)	99

[a]Reaction conditions: Iodobenzene (2 mmol), *n*-butyl acrylate (2.2 mmol), Et_3N (2 equiv), and [bmim][PF_6] (2 mL) at 120 °C for 1.5 h in a pressure tube. [b]GC yields

TABLE-3
HECK COUPLING REACTION OF ARYL IODIDES WITH TERMINAL ALKYNES CATALYZED BY $PdCl_2$-Dppc$^+PF_6^-$ in [bmim][PF_6][a]

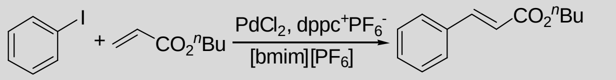


Entry	Aryl halide	Olefin	Cat. (mol %)	Time (h)	Yield (%)[b]
1	C_6H_5I	$CH_2 = CHCO_2{}^nBu$	0.2	1.5	92
2	4-MeC_6H_4I	$CH_2 = CHCO_2{}^nBu$	0.2	1.5	94
3	2-MeC_6H_4I	$CH_2 = CHCO_2{}^nBu$	0.2	1.5	90
4	4-$MeOC_6H_4I$	$CH_2 = CHCO_2{}^nBu$	0.4	3	87
5	3-$MeOC_6H_4I$	$CH_2 = CHCO_2{}^nBu$	0.2	1.5	94
6	3-ClC_6H_4I	$CH_2 = CHCO_2{}^nBu$	0.2	1.5	94
7	4-$MeCOC_6H_4I$	$CH_2 = CHCO_2{}^nBu$	0.2	1.5	93
8	4-$NO_2C_6H_4I$	$CH_2 = CHCO_2{}^nBu$	1	3	95
9	3-$NO_2C_6H_4I$	$CH_2 = CHCO_2{}^nBu$	0.4	3	94
10	2- $NO_2C_6H_4I$	$CH_2 = CHCO_2{}^nBu$	0.4	4	90
11	2-Iodothiophene	$CH_2 = CHCO_2{}^nBu$	0.4	3	93
12	C_6H_5I	$CH_2 = CHCO_2Et$	0.2	1.5	92
13	C_6H_5I	$CH_2 = CHCO_2Me$	0.2	1.5	93
14	C_6H_5I	$CH_2 = CHCN$	0.2	1.5	94
15	C_6H_5I	$PhCH = CH_2$	0.2	1.5	88

[a]Reaction conditions: Ayl iodide (2 mmol), olefin (2.2 mmol), Et_3N (2 equiv), and [bmim][PF_6] (2 mL) at 120° in a pressure tube, [b]Isolated yields

diethyl ether and no apparent leaching of PdCl$_2$ and dppc$^+$PF$_6^-$ was found in the organic extraction. The inorganic by-products can be removed by washing with water. The resulting ionic liquid containing PdCl$_2$ and dppc$^+$PF$_6^-$ catalyst could be recovered and reused. The reusability of the present catalysis system was examined in the coupling reaction of iodobenzene with *n*-butyl acrylate. The catalysis system could be reused four times without significant loss in its activity and only a slight loss after the five times (Table-4). The decrease was probably due to the loss of the ionic liquid during the work-up.

TABLE-4
RECYCLING EXPERIMENTS FOR THE PdCl$_2$ –Dppc$^+$PF$_6^-$ -[bmim][PF$_6$]-CATALYZED HECK COUPLING REACTION^A



Run	Time (h)	Yield (%)^b
1	1.5	99
2	1.5	99
3	1.5	99
4	1.5	98
5	1.5	85

^{a}Reaction conditions: Iodobenzene (2 mmol), *n*-butyl acrylate (2.2 mmol), Et$_3$N (2e quiv), PdCl$_2$ (0.2 mol %), dppc$^+$PF$_6^-$ (0.2 mol %), and [bmim][PF$_6$] (2 mL) at 120 °C for 1.5 h in a pressure tube. ^{b} GC yields

Conclusion

Heck coupling reaction of aryl iodides with olefins, irrespective of their being electron-rich or electron-poor substitute, proceeded smoothly in ionic liquid [bmim][PF$_6$], using PdCl$_2$ -dppc$^+$PF$_6^-$ as catalyst. The use of this system permitted the product to be easily separated from the reaction mixture and the recovered catalyst could be reused at least five times without significant loss in activity. Further studies of the catalyst on other coupling reaction and the better catalyst design are being investigated.

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