

Communication

Heck Reaction of Iodoarenes with Methyl Acrylate Catalyzed by Cyclopalladated Complexes of Tertiary Arylamines Immobilized in Ionic Liquid [Bmim]⁺BF₄⁻

ZHENG, Ru(郑瑞) YANG, Fan(杨帆) ZOU, Gang(邹刚) TANG, Jie*(汤杰)
HE, Ming-Yuan(何鸣元)

Center for the Chemistry of Ionic Liquids, Department of Chemistry, East China Normal University, Shanghai 200062, China

Heck reaction of iodoarenes with methyl acrylate, catalyzed by cyclopalladated complexes of tertiary arylamines, was investigated in ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim]⁺BF₄⁻). The products can be isolated conveniently from the ionic liquid-catalyst system. The catalysts could be reused for more than 10 times still with satisfactory catalytic activity.

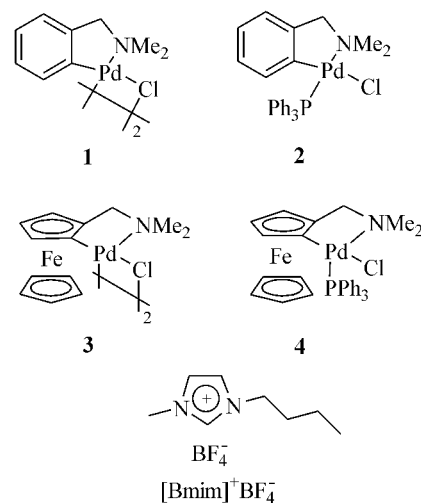
Keywords cyclopalladated complexes of tertiary arylamines, ionic liquid, Heck reaction

Introduction

As one of the most important C—C formation reactions and one-step method for the arylation of olefins, Heck reaction has attracted much interest.¹ However, the reaction usually needs a relatively large amount of palladium catalyst (> 1 mol%) for satisfactory conversions. Recently, a variety of palladacycles incorporating cyclometallated phosphine,² phosphite,³ carbene,⁴ imine⁵ and oxime⁶ have been reported. The use of catalysts with nitrogen-based ligands was demonstrated to possess very high activity. We have reported the cyclopalladated complexes of tertiary arylamines as highly efficient catalysts in the Heck reaction,⁷ but the catalyst is often lost at the end of the reaction, and the polar solvent DMF or DMA was required, which leads to tedious work-up for the product separation.

Ionic liquids are attracting a great deal of attention as possible replacement of traditional solvents for catalytic and organic reactions. Features that make ionic liquids attractive include their lack of vapor pressure and the great versatility of their chemical and physical properties.⁸ For example, [Bmim]⁺BF₄⁻ is insoluble in non-polar organics but it readily dissolves many transition metal catalysts. Such biphasic organo-ionic liquid systems make the products separation and catalysts recycling convenient. However,

Heck reaction catalyzed by palladacycles immobilized in ionic liquid has rarely been reported.⁹ In this paper, a study on the Heck reaction catalyzed by the cyclopalladated complexes of tertiary arylamines in ionic liquid [Bmim]⁺BF₄⁻ is reported.



Results and discussion

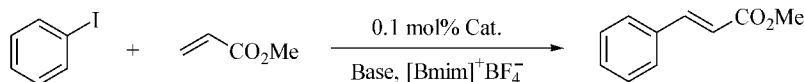
The complexes 1—4 were investigated as catalysts for the Heck reaction of iodobenzene with methyl acrylate in [Bmim]⁺BF₄⁻. These complexes are not only thermally stable but also not sensitive to oxygen and moisture. They were conveniently prepared by treatment of Na₂[PdCl₄] with the corresponding amines, and the monomeric complexes were obtained immediately by treatment of PPh₃ with the respective dimmers in benzene.¹⁰

Various bases such as sodium acetate, triethylamine, potassium carbonate, sodium bicarbonate and sodium car-

* E-mail: jtang@chem.ecnu.edu.cn; Fax: 021-62232100

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Table 1 Heck reaction of iodobenzene with methyl acrylate in [Bmim]⁺BF₄⁻^a

Run	Cat. (0.1 mol %)	Base	Time (h)	Temp. (°C)	Yield ^b (%)	TON/TOF
1	3	NaOAc	3.5	130	52	520/149
2	3	K ₂ CO ₃	3.5	130	< 10	< 100/ < 29
3	3	NEt ₃	3.5	130	95	950/271
4	3	Na ₂ CO ₃	3.5	130	14	140/40
5	3	NaHCO ₃	3.5	130	6	60/17
6	1	NEt ₃	3.5	130	93	930/266
7	2	NEt ₃	3.5	130	< 5	< 50/ < 13
8	4	NEt ₃	3.5	130	88	880/251
9	3	NEt ₃	2.5	150	98 ^c	980/392

^a 5 mmol of PhI, 6 mmol of methyl acrylate, 7 mmol of NEt₃ and 0.1 mol% of catalyst in 10 mL of ionic liquid. ^b Determined by GC-MS, based on PhI. ^c Benzene as by-product.

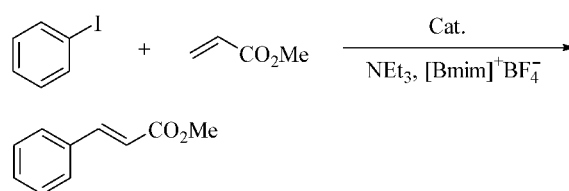
bonate were tested respectively with complex **3** as catalyst in the ionic liquid [Bmim]⁺BF₄⁻. The results are summarized in Table 1. Only triethylamine performed satisfactory.

Using triethylamine as base the Heck reaction of iodobenzene with methyl acrylate catalyzed by different palladacycles was carried out in [Bmim]⁺BF₄⁻ (Table 1). Satisfactory results were achieved when the reaction was catalyzed by 0.1 mol% of complexes **1**, **3** or **4** (Runs 6, 3 and 8). The catalytic activities of complexes **1**, **3** and **4** in [Bmim]⁺BF₄⁻ (TON: 930, 950, 880) were decreased compared with that in DMA,⁷ but the catalyst, which was immobilized in the ionic liquid [Bmim]⁺BF₄⁻, could be reused. Meanwhile, the product could be isolated conveniently by decantation instead of tedious work-up in DMA.

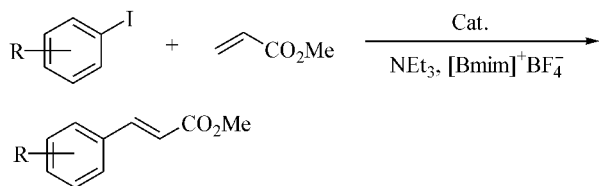
In order to investigate the electron and steric effect, the reaction of substituted iodobenzene with methyl acrylate was primarily tested under the optimized condition. The results are listed in Table 2. The conversion for the elec-

tron-donating substitution of iodobenzene, 4-methoxyiodobenzene, slightly decreased (Run 2 in Table 2). In contrast, the electron withdrawing substitution made the conversion improved (Run 3 in Table 2). Steric hindrance also influenced the reaction. Compared to methyl 2-iodobenzoate, the para substituted substrate, methyl 4-iodobenzoate, gave the higher yield under the same reaction condition (Runs 3 and 4 in Table 2).

The ionic liquid-catalyst system could be reused after the isolation of the product by decantation. It can be seen from the Table 3 that the catalytic activity of **1** or **3** was

Table 3 Recycle of the [Bmim]⁺BF₄⁻-cyclopalladated complexes in Heck reaction^a

Recycling times	Time (h)	Yield ^b (%)	
		Cat. 1	Cat. 3
1	3	95	> 99
2	3	95	95
3	3.5	97	98
4	3	94	91
5	3.5	95	89
6	4	96	92
7	4	94	89
8	4	94	91
9	4.5	92	89
10	4	91	91

Table 2 Substitution effects on Heck reactions of iodoarenes in [Bmim]⁺BF₄⁻^a

Run	R	Yield ^b (%)		
		Cat. 1	Cat. 3	Cat. 4
1	H	74	76	69
2	4-OCH ₃	70	63	66
3	4-COOCH ₃	98	87	71
4	2-COOCH ₃	43	68	trace

^a 5 mmol of aryl halide, 6 mmol of methyl acrylate, 7 mmol of NEt₃ and 0.1 mol% catalyst in 10 mL of ionic liquid, temperature: 130 °C, time of the reaction: 3 h. ^b Determined by GC-MS, based on aryl halide.

^a 5 mmol of PhI, 6 mmol of methyl acrylate, 7 mmol of NEt₃ and 0.1 mol% catalyst in 10 mL of ionic liquid, temperature: 140 °C. ^b Determined by GC-MS, based on PhI.

almost unchanged after ten times of recycling in [Bmim]⁺BF₄⁻. Only Et₃N·HI as by-product was left in the ionic liquid-catalyst system. It precipitated after the fourth run at room temperature, but resolved in the ionic liquid at elevated temperature.

Conclusions

This study indicated that cyclopalladated complexes of tertiary arylamines **1**, **3** and **4** are efficient catalysts for Heck reaction in ionic liquid [Bmim]⁺BF₄⁻. The catalyst can be immobilized in the ionic liquid [Bmim]⁺BF₄⁻ and the ionic liquid-catalyst system could be reused for ten times without losing the efficiency.

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