

Communication

Immobilization of Pd(II) Catalysts for Cyclopropanation in Ionic Liquid

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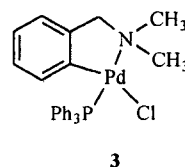
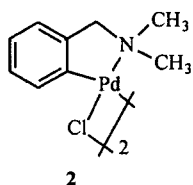
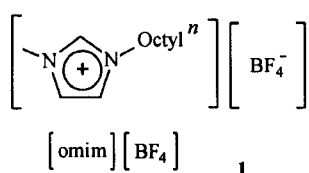
Cyclopropanation of styrene with ethyl diazoacetate catalyzed by Pd(II) in ionic liquid [omim][BF₄] was investigated. Palladium catalysts can be effectively immobilized in ionic liquid. The catalysts PdCl₂ and cyclopalladated complex **2** contained in ionic liquid could be recycled for 6 and 7 times, respectively, without losing the efficiency.

Keywords ionic liquid, cyclopropanation, palladium catalysts

Homogeneous catalysis offers many advantages over heterogeneous catalysis with respect to activity, selectivity, flexibility of operation. However, the continuous catalyst consumption, catalyst removal from the products and catalyst disposal have still to be improved. An attractive approach to overcome the problem is biphasic catalysis, a method to heterogenize a catalyst and product into two separate and immiscible phases without losing the efficiency and selectivity inherent in homogeneous catalysis. This method also provides an elegant solution to the catalyst/product separation and catalyst recycling associated with homogeneous catalysis. Among different strategies to realize biphasic catalysis, non-aqueous ionic liquids, *i. e.* a salt mixture with a melting point below or at ambient temperature, constitute a unique class of

versatile solvents with a great potential. This concept has been receiving increased attentions in the last few years. Recent applications include Friedel-Crafts reactions, Diels-Alder reactions, alkylations, olefin dimerisation and oligomerisation, Heck reaction, hydroformylation, palladium catalyzed allylation reaction,¹ epoxidation² and asymmetric ring opening reaction of epoxides.³

It is well known that palladium acetate/diazo esters is an efficient reagent for the cyclopropanation of terminal olefins.^{4,5} As a homogeneous catalysis, it is usually difficult to reuse it after the reaction. Herein, a practical recycling procedure of palladium catalyst involving the use of air- and moisture-stable ionic liquid, [omim]⁻ [BF₄] (**1**), ([omim]⁺ = 1-octyl-3-methylimidazolium cation) is reported. The ionic liquid **1** is conveniently prepared by literature method and has a limited miscibility with low polar organic solvents.⁶ Cyclopropanation of styrene with ethyl diazoacetate, a reaction which has been widely used for assessing the efficiency and selectivity in cyclopropane formation,⁷ was used to examine the biphasic catalysis. Palladium acetate, palladium chloride and cyclopalladated complexes **2**, **3** were employed as palladium catalysts in our study.



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Cyclopropanation reactions were carried out at ambient temperature, and the catalyst/product separation is easily achieved by simple phase decantation. The organic phase was analyzed, and the ionic liquid which con-

tained palladium catalyst was reused for further reactions. The results using palladium acetate and palladium chloride were summarized in Table 1.

Table 1 Cyclopropanation of styrene using Pd(OAc)₂ and PdCl₂ in [omim][BF₄]^a

Run	Time (h)	Yield (%) ^b		<i>trans/cis</i> Ratio ^c	
		Pd(OAc) ₂	PdCl ₂	Pd(OAc) ₂	PdCl ₂
1	10	98	95	1.7	1.6
2	10	98	94	1.7	1.6
3	10	96	93	1.7	1.7
4	10	73	93	1.6	1.6
5	20	34	95	1.6	1.6
6	20	8	95	1.6	1.6

^aReaction conditions: styrene, 7 mL (6×10^{-2} mol); catalyst, 4×10^{-5} mol; ethyl diazoacetate, 4×10^{-3} mol; [omim][BF₄], 1.5 mL. ^bDetermined by GC. ^cRatio of area in the GC peaks, *trans/cis* products were identified by comparison with authentic samples.

Usually palladium chloride is a less efficient catalyst than palladium acetate due to its poor solubility in organic media. However, its catalytic activity was greatly enhanced by the use of ionic liquid **1**. This was attributed to its higher solubility in ionic liquid. As shown in Table 1, in the case of palladium chloride, the recovery and reuse of the catalyst were more successful compared with the case of palladium acetate. For example, the above procedure was repeated for 6 times with a satisfactory yield when palladium chloride was used (Run 1–6, Table 1), while this procedure was repeated satisfactorily for only 3 times with a satisfactory yield using palladium acetate (Run 1–3, Table 1). During the reaction, the color of ionic liquid containing palladium acetate turned black after one run indicating the formation of palladium(0) species, which probably resulted from the reducing ability of ethyl diazoacetate. The catalytic activity was decreased greatly as the palladium(0) species was formed. In contrast, for palladium chloride, the color of ionic liquid remained pale yellow in the most of the time and only a trace of palladium deposit was observed. The catalytic activity still remained unchanged after PdCl₂ was recycled for 6 times. The reason of the decrease of the catalytic activity for Pd(OAc)₂ along with the increase of recycling times maybe is that the formation of palladium(0) is easier for Pd(OAc)₂ than that for PdCl₂.

In the last decades, cyclopalladated complexes have attracted people's interests increasingly.^{8–11} The com-

plexes, with palladium center stabilized by a five-member ring, are thermally stable and not sensitive to oxygen and moisture. They have shown super catalytic activity for some palladium-mediated reactions.^{12–14} The previous study by our group demonstrated that complexes **2** and **3** are good homogeneous catalysts for Heck reaction and cyclopropanation.¹⁵ Their applications in biphasic catalysis for cyclopropanation were also conducted here. The results were summarized in Table 2.

The results showed that complex **2** is more efficient and recyclable than complex **3**. This was also indicated by respective color of ionic liquid layer. The color of ionic liquid layer containing complex **2** remained pale yellow for all runs. However, for complex **3**, the color turned black after one run indicating formation of palladium(0) species. We suppose that the differences of catalytic activities result from the triphenylphosphine ligand which is the substantial difference between structures **3** and **2**. It is assumed then that the triphenylphosphine ligand promotes the formation of palladium(0).¹⁶ So the Palladium(0) was more readily formed from complex **3** as compared with complex **2**, which leads to the decrease of the catalytic activity of complex **3**. Moreover, the results in Table 2 also showed that biphasic catalysis using cyclopalladated complex **2** was more efficient than that using palladium chloride.

In summary, we have developed a practical recycling procedure of palladium catalysts for cyclopropanation by use of ionic liquid **1**. Our results showed that palladium chloride, which was not an efficient catalyst

Table 2 Cyclopropanation of styrene using complexes **2** and **3** in [omim][BF₄]^a

Run	Time / (h)	Yield (%) ^b		<i>trans/cis</i> Ratio ^c	
		2	3	2	3
1	10	99	98	1.8	1.7
2	10	98	97	1.7	1.7
3	10	98	93	1.7	1.6
4	10	98	62	1.6	1.6
5	10	98	21	1.6	1.6
6	10	97	8	1.6	1.6
7	20	96	7	1.6	1.6
8	20	83	4	1.6	1.6

^aReaction conditions: styrene, 7 mL (6×10^{-2} mol); catalyst, 2×10^{-5} mol for complex **2** and 4×10^{-5} mol for complex **3**; ethyl diazoacetate, 4×10^{-3} mol; [omim][BF₄], 1.5 mL. ^bDetermined by GC. ^cRatio of area in the GC peaks.

for cyclopropanation in ordinary cases, became more active in biphasic catalysis mediated by ionic liquid. Meanwhile, biphasic catalysis using cyclopalladated complex **2** turned out to be successful in our study. At the end of the reaction, the catalyst contained in ionic liquid could be easily recycled for several times. The use of ionic liquid provides not only a simple recycling of palladium catalyst, but also the additional advantage of enhancing the catalytic activity of a catalyst. A further study concerning the detailed interaction between the palladium salts and the ionic liquid and the application of this methodology to other homogeneous catalysis is currently in progress.

References

- 1 Welton, T. *Chem. Rev.* **1999**, *99*, 2071.
- 2 Song, C. E.; Roh, E. J. *Chem. Commun.* **2000**, 837.
- 3 Song, C. E.; Oh, C. R.; Roh, E. J.; Choo, D. J. *Chem. Commun.* **2000**, 1743.
- 4 Anciaux, A. J.; Hubert, A. J.; Noels, A. F.; Petiniot, N.; Teyssié, P. *J. Org. Chem.* **1980**, *40*, 695.
- 5 Anciaux, A. J.; Demonceau, A.; Noels, A. F.; Warin, R.; Hubert, A. J.; Teyssié, P. *Tetrahedron* **1983**, *39*, 2169.
- 6 Holbrey, J. D.; Seddon, K. R. *J. Chem. Soc.* **1999**, 2133.
- 7 Fritschi, H.; Leutenegger, U.; Pfaltz, A. *Helv. Chem. Acta* **1988**, *71*, 1553.
- 8 Ryabov, A. D. *Synthesis* **1985**, 233.
- 9 Newkome, G. R.; Puckett, W. E.; Gupta, V. K.; Kiefer, G. E. *Chem. Rev.* **1986**, *86*, 451.
- 10 Ryabov, A. D. *Chem. Rev.* **1990**, *90*, 403.
- 11 Wang, H. X.; Ding, L.; Wu, Y. J. *Chin. J. Org. Chem.* **2000**, *20*, 44 (in Chinese).
- 12 Bose, A.; Saha, C. R. *J. Mol. Catal.* **1989**, *49*, 271.
- 13 Herrmann, W. A.; Böhm, V. P. W.; Reisinger, C. P. *J. Organomet. Chem.* **1999**, *576*, 23.
- 14 Gai, X.; Grigg, R.; Ramzan, M. I.; Sridharan, V.; Collard, S.; Muir, J. E. *Chem. Commun.* **2000**, 2053.
- 15 Zhang, Y. M.; Yang, F.; Zheng, R.; Tang, J. *Chin. J. Org. Chem.* **2001**, *21*, 533 (in Chinese).
- 16 Ozawa, F.; Kubo, A.; Hayashi, T. *Chem. Lett.* **1992**, 2177.

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