

Short communication

Dimerization of styrene to 1,3-diphenyl-1-butene catalyzed by palladium–Lewis acid in ionic liquid

Jiajian Peng, Jiayun Li, Huayu Qiu, Jianxiong Jiang, Kezhi Jiang, Jianjiang Mao, Guoqiao Lai*

Key Laboratory of Organosilicon Chemistry and Material Technology of Ministry of Education, Hangzhou Teachers College, Hangzhou 310012, China

Received 6 March 2006; received in revised form 22 March 2006; accepted 23 March 2006
Available online 3 May 2006

Abstract

Dimerization of styrene was investigated in ionic liquids and organic solvents with the catalysis of several palladium–Lewis acids catalyst systems. Pd(OAc)₂/Cu(OTf)₂ and Pd(OAc)₂/In(OTf)₃ in 1-butyl-3-methylimidazolium hexafluorophosphate were found to be effective catalyst systems towards the dimerization of styrene to 1,3-diphenyl-1-butene at room temperature.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Dimerization of styrene; Room temperature ionic liquid; Pd(OAc)₂/Lewis acid catalyst

The selective dimerization of styrene is a great practical method for the production of 1,3-diphenyl-1-butene, and the initiators for this reaction are generally strong Brønsted acids, Lewis acids or zeolite catalysts. However, some byproducts such as indan derivative or higher oligomers are formed [1]. Recently, a number of cationic, electrophilic transition metal compounds have been demonstrated to be efficient catalysts for the dimerization of vinylic monomers. Among those transition metal compounds, palladium complexes, known as powerful and widely used catalysts for carbon–carbon bond formation, have been particularly studied because of their high selectivities in the dimerization of vinylbenzene, and the carbocationic mechanism has been demonstrated [2]. Very recently, asymmetric styrene dimerization using chiral palladium catalyst in the presence of indium(III) triflate in 1,4-dioxane was reported [3].

Room temperature ionic liquids, which are entirely constituted of ions, have attracted great interests as novel and environmentally friendly benign media and catalyst system. Many organic reactions have been performed in ionic liquids with excellent yields and chem- and/or enantio-selectivities (for reviews see Ref. [4]). On account of the carbocationic mechanism for the dimerization of styrene, we would like to believe that

this ionic pathway would be facilitated in an ionic environment provided by ionic liquids, and herein we report the dimerization of styrene with palladium–Lewis acid as catalyst systems in ionic liquids (Scheme 1).

We initially examined the catalytic activity and selectivity of Pd(OAc)₂/Cu(OTf)₂ for the dimerization of styrene, and the results are summarized in Table 1. Treatment of styrene (2.5 mmol) with 4 mol% of Pd(OAc)₂ and 1 mol% of Cu(OTf)₂ in 1-butyl-3-methylimidazolium hexafluorophosphate (BMImPF₆) (0.5 mL) at room temperature for 2.5 h obtained almost 100% 1,3-diphenyl-1-butene with complete conversion of styrene (entry 1). According to entries 1, 2, 5, 6 and 7, the increase in the amount of Pd(OAc)₂ as well as BMImPF₆ is favorable for the improvement of the activity and selectivity. However, some reduction of catalytic activity was observed at the second and third run (entries 3 and 4). No consumption of styrene was observed when either Pd(OAc)₂ or Cu(OTf)₂ or BMImPF₆ was solely used (entries 8, 9 and 10). The other palladium catalysts were examined next, however, the use of PdCl₂ instead of Pd(OAc)₂ lowered the activity, whereas Pd(PPh)₃Cl₂ failed to catalyze the dimerization of styrene (entries 11 and 12).

Effect of medium on the activity and selectivity was then examined and the results are summarized in Table 2. However, Pd(OAc)₂/Cu(OTf)₂ catalyst system was totally inactive when other ionic liquids such as 1-butyl-3-methylimidazolium tetrafluoroborate (BMImBF₄) or 1-ethyl-3-methylimidazolium

* Corresponding author. Tel.: +86 571 28865136; fax: +86 571 28865135.
E-mail address: gqlai@hztc.edu.cn (G. Lai).

Table 1
Dimerization of styrene catalyzed by Pd/Cu(II) Lewis acid in ionic liquid^a

Entry	Pd cat. (mol%)	Cu co-cat. (mol%)	Ionic liquid (ml)	<i>t</i> (h)	Conversion ^b (%)	Selectivity ^c (%)
1	Pd(OAc) ₂ (4)	Cu(OTf) ₂ (1)	BMImPF ₆ (0.5)	2.5	100	100
2	Pd(OAc) ₂ (3)	Cu(OTf) ₂ (1)	BMImPF ₆ (0.5)	3	98.1	100
3 ^d	Pd(OAc) ₂ (3)	Cu(OTf) ₂ (1)	BMImPF ₆ (0.5)	3	80.4	98.6
4 ^e	Pd(OAc) ₂ (3)	Cu(OTf) ₂ (1)	BMImPF ₆ (0.5)	3	76.0	98.5
5	Pd(OAc) ₂ (2)	Cu(OTf) ₂ (1)	BMImPF ₆ (0.5)	4.5	99.6	99.5
6	Pd(OAc) ₂ (1)	Cu(OTf) ₂ (1)	BMImPF ₆ (0.5)	3	35.6	99.9
7	Pd(OAc) ₂ (3)	Cu(OTf) ₂ (1)	BMImPF ₆ (1.0)	2.5	100	100
8	None	Cu(OTf) ₂ (1)	BMImPF ₆ (0.5)			No reaction
9	Pd(OAc) ₂ (3)	None	BMImPF ₆ (0.5)			No reaction
10	Pd(OAc) ₂ (3)	Cu(OTf) ₂ (1)	None			No reaction
11	PdCl ₂ (2)	Cu(OTf) ₂ (1)	BMImPF ₆ (0.5)	3.5	14.3	100
12	Pd(PPh) ₃ Cl ₂ (2)	Cu(OTf) ₂ (1)	BMImPF ₆ (0.5)	3.5		No reaction

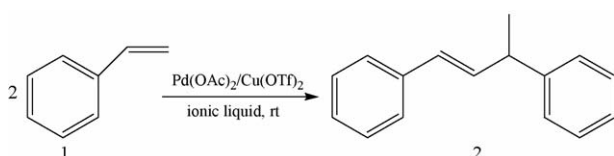
^a The reaction was performed at room temperature.

^b Conversion of styrene determined by GC–MS.

^c Selectivity of 1,3-diphenyl-1-butene determined by GC–MS, and byproduct is trimer.

^d The second run.

^e The third run.



Scheme 1.

tetrafluoroborate (EMImBF₄) were used (entries 13 and 14). In contrast to Pd(OAc)₂/In(OTf)₃, [2c] no product was detected for Pd(OAc)₂/Cu(OTf)₂ catalyst system in 1,4-dioxane and DMSO (entries 15 and 16), whereas 31.2% conversion was obtained using nitromethane as solvent (entry 17). The results presented in Table 2 also showed that catalytic activity of Pd(OAc)₂/Cu(CF₃CO₂)₂ was much lower than that of Pd(OAc)₂/Cu(OTf)₂ in BMImPF₆ (entry 18). As other triflates were concerned, indium triflate as well as copper triflate provided higher conversion compared with zinc triflate (entries 19 and 20). From the results presented in Tables 1 and 2, it could be concluded that the reactivity depended on the interaction among palladium complexes, Lewis acid and medium.

IR analysis of mixtures of styrene, ionic liquid and copper(II) Lewis acid reveals the disappearance of peaks of 1630 and 1600 cm⁻¹ of styrene (Fig. 1). It demonstrated that there is some

Table 2
Effect of medium and Lewis acid co-catalyst

Entry	Lewis acid	Solvent (ml)	<i>t</i> (h)	Conversion (%)	Selectivity (%)
13	Cu(OTf) ₂	BMImBF ₄	2.5	No reaction	
14	Cu(OTf) ₂	EMImBF ₄	2.5	No reaction	
15	Cu(OTf) ₂	1,4-Dioxane	3	No reaction	
16	Cu(OTf) ₂	DMSO	3	No reaction	
17	Cu(OTf) ₂	CH ₃ NO ₂	3	31.2	100
18	Cu(CF ₃ CO ₂) ₂	BMImPF ₆	3.5	<1	100
19	Zn(OTf) ₂	BMImPF ₆	3	62.3	100
20	In(OTf) ₃	BMImPF ₆	3	100	100

Conditions: Pd(OAc)₂ 3.0 mol%, Lewis acid 1.0 mol%, styrene 2.5 mmol, solvent 0.5 ml, rt.

interaction between copper(II) Lewis acid and styrene in ionic liquid. Although we have not carried out detailed mechanistic studies of the dimerization of styrene with Pd(OAc)₂/Cu(OTf)₂ in BMImPF₆ catalyst system, a pathway that involves styrene activated with copper(II) triflate to accept nucleophilic attack of palladium(0) complexes generated by reduction of Pd(OAc)₂ with 1,3-dialkylimidazolium salt at room temperature was supposed (Scheme 2) [2c,5].

In summary, dimerization of styrene with palladium–Lewis acids as catalyst in ionic liquid was investigated. This experimental results showed that both Pd(OAc)₂/Cu(OTf)₂ and Pd(OAc)₂/In(OTf)₃ in 1-butyl-3-methylimidazolium hexafluorophosphate were quite effective catalyst systems for the

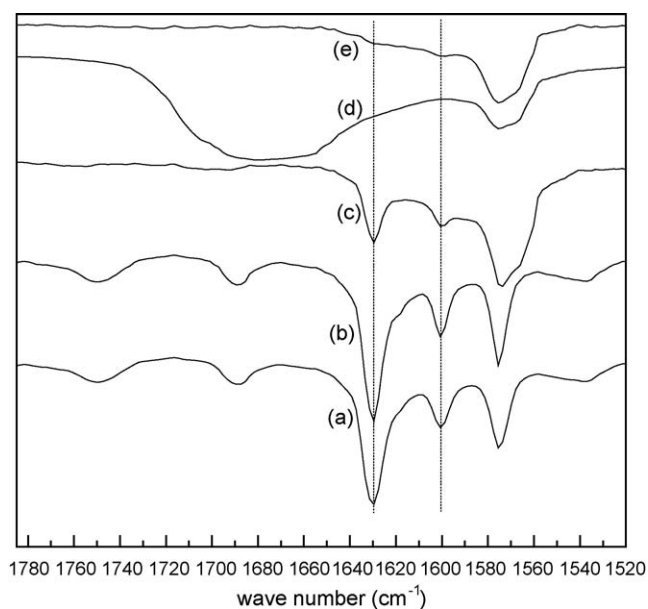
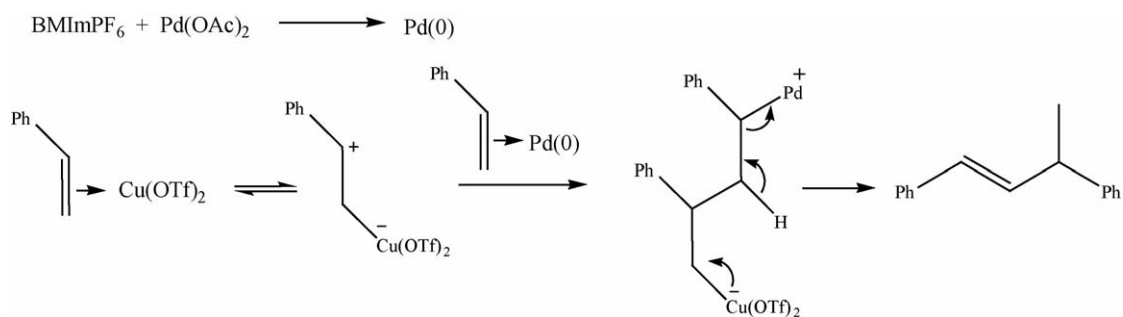


Fig. 1. IR analysis of mixtures of styrene and copper(II) Lewis acid: (a) styrene; (b) styrene:Cu(OTf)₂ = 1:1 (mole ratio); (c) styrene:BMImPF₆ = 1:5 (mole ratio); (d) styrene:Cu(CF₃COO)₂:BMImPF₆ = 1:1:5 (mole ratio); (e) styrene:Cu(OTf)₂:BMImPF₆ = 1:1:5 (mole ratio).



Scheme 2.

dimerization of styrene, whereas Lewis acid $\text{Cu}(\text{CF}_3\text{CO}_2)_2$ was demonstrated to be poor catalytic activity. Exploring the details of reaction mechanism and the role of ionic liquids are in progress.

Acknowledgment

We are grateful to Zhejiang Natural Science Foundation (R203154) for financial support.

References

- [1] T. Higashimura, M. Hiza, H. Hasegawa, *Macromolecules* 12 (1979) 217; A. Benito, A. Corma, H. Garcia, J. Primo, *Appl. Catal. A: Gen.* 116 (1994) 127.
- [2] (a) Z. Jiang, A. Sen, *J. Am. Chem. Soc.* 112 (1990) 9655; (b) Z. Jiang, A. Sen, *Organometallics* 12 (1993) 1406; (c) T. Tsuchimoto, S. Kamiyama, R. Negoro, E. Shirakawa, Y. Kawakami, *Chem. Commun.* (2003) 852; (d) G.W. Kabalka, G. Dong, B. Venkataiah, *Tetrahedron Lett.* 45 (2004) 2775; (e) G. Myagmarsuren, V.S. Tkach, F.K. Schmidt, M. Mohamad, D. Suslov, *J. Mol. Catal. A: Chem.* 235 (2005) 154.
- [3] R.B. Bedford, M. Betham, M.E. Blake, A. Garcés, S.L. Millar, S. Prashar, *Tetrahedron* 61 (2005) 9799.
- [4] T. Welton, *Chem. Rev.* 99 (1999) 2071; P. Wasserscheid, W. Keim, *Angew. Chem. Int. Ed.* 39 (2000) 3772; J. Dupont, R.F. de Souza, P.A.Z. Suarez, *Chem. Rev.* 102 (2002) 3667.
- [5] R.R. Deshmukh, R. Rajagopal, K.V. Srinivasan, *Chem. Commun.* (2001) 1544.