

# Carbonylation of iodobenzene catalyzed by water-soluble palladium–phosphine complexes in ionic liquid

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## Abstract

The carbonylation of iodobenzene catalyzed by water-soluble palladium–TPPTS complex (TPPTS: trisodium salt of tri(*m*-sulphonylphenyl)phosphine) has been investigated in ionic liquid 1-*n*-butyl-3-methylimidazolium *p*-toluenesulfonate ([bmim][*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>]) in the presence of alcohol. The ionic liquid [bmim][*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>] used as the reaction media brings some definitive advantages over the halogen-containing analogue [bmim]BF<sub>4</sub>, [bmim]PF<sub>6</sub> and conventional organic solvents. The combination of palladium–TPPTS complex and [bmim][*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>] exhibits excellent catalytic activity and selectivity, and simplifies the separation of the products from catalyst. In the carbonylation of iodobenzene, TOF (turnover frequency) of up to 1938 h<sup>-1</sup> was observed and the selectivity for ethyl benzoate was over 99%. The catalyst can be easily separated from the organic products and reused for 10 times without the significant decrease of activity and selectivity. © 2006 Elsevier B.V. All rights reserved.

**Keywords:** Ionic liquid; Palladium; TPPTS; Carbonylation; Iodobenzene

## 1. Introduction

Palladium-catalyzed carbonylation of aryl halides and their derivatives is a powerful method of C–C coupling reactions for the synthesis of many aromatic compounds; especially, carboxylic acids and their derivatives (Scheme 1) [1], but the difficult separation of the products from catalyst in the traditional homogeneous catalysis hinders its application in industrial process. This problem can be overcome by means of water-soluble metal complexes as catalysts in aqueous–organic biphasic systems [2]. However, the reaction rate in the aqueous–organic biphasic system is very slow due to the poor solubility of aryl halides in water.

In recent years, the room temperature ionic liquids (ILs), as novel environmentally friendly solvents, have been received increasing recognition and acceptance in the organic synthesis and catalysis [3]. They exhibit great potential advantages in the development of novel catalytic technologies of organic synthesis with better yield and selectivity [4–10]. While the most of

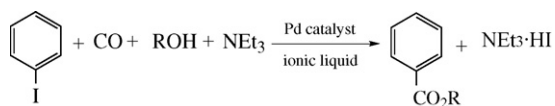
ionic liquids investigated up to date are the compounds containing halogen, the application of halogen-free ionic liquids has been only described in a few papers [11]. Mizushima [12] and Calò [13] groups have reported the palladium-catalyzed carbonylation and hydroxycarbonylation of aryl halides in ionic liquids media, but the catalyst recycling is still difficult in the reports. We have prepared a series of halogen-free ionic liquids [Rmim][*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>] (R = *n*-butyl, *n*-octyl, *n*-dodecyl, *n*-cetyl), which have been successfully applied as reaction medium in the asymmetric hydrogenation of aromatic ketones [14] and the hydroformylation of higher olefins [15]. This paper reports some results of our studies on the carbonylation of iodobenzene catalyzed by water-soluble palladium complexes and the role exerted by halogen-free ionic liquid [bmim][*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>] (1-*n*-butyl-3-methylimidazolium *p*-toluenesulfonate) on the catalyst activity and stability.

## 2. Experimental

### 2.1. Chemicals and instruments

1-Methylimidazole (Aldrich, >99%), palladium acetate (Aldrich, 98%), palladium chloride (Fluka, >99%) were

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Scheme 1. The carbonylation of iodobenzene.

used as received without further treatment. The other reagents are analytically pure. The ionic liquids [bmim][*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>][15], [bmim]PF<sub>6</sub> [16] and [bmim]BF<sub>4</sub> [17] were prepared by the methods described in literatures. TPPTS [TPPTS: P(*m*-C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>Na)<sub>3</sub>], TPPDS [TPPDS: (C<sub>6</sub>H<sub>5</sub>)P(*m*-C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>Na)<sub>2</sub>], TPPMS [TPPMS: (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>P(*m*-C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>Na)] and bidentate ligand BISBIS (BISBIS: sodium salt of sulfonated 2,2'-bis(diphenylphosphinomethyl)-1,1'-biphenyl) and PdCl<sub>2</sub>(TPPTS)<sub>2</sub> were prepared by the methods reported in literatures [18–20]. The compositions of carbonylation products were determined by 6890/5973N GC–MS (HP-5MS, 0.25 mm × 0.25 μm × 30 m) and GC on HP1890 with a capillary column SE-30 (0.25 mm × 0.25 μm × 30 m). The palladium content in the product was measured by inductively coupled plasma–atomic emission spectrometry (ICP–AES) on an IRIS Advantage instrument.

## 2.2. Carbonylation of iodobenzene in ionic liquids

The carbonylation was conducted in 60 ml stainless steel autoclave with magnetic stirrer. After the desired amounts of palladium catalyst, ligand and ionic liquid were introduced into autoclave and the mixture was stirred for 10 min. Subsequently, iodobenzene, triethylamine and alcohol were added. The autoclave was purged with carbon monoxide for three times. The reaction was carried out under the designed conditions for a desired time. After the reaction, the autoclave was cooled in an ice-water bath. The organic products were separated by extraction with cyclohexane (3 × 1 ml) and analyzed by GC–MS and GC. The triethylammonium iodide formed in the reaction was separated from ionic liquid by centrifugation. The ionic liquid layer containing palladium catalysts was reused in the next run.

## 3. Results and discussion

### 3.1. Effect of catalyst precursor

The effect of catalyst precursor on the carbonylation of iodobenzene is investigated, and the results are summarized in Table 1. In all the runs, the conversion of iodobenzene is higher than 85% and the selectivity for ethyl benzoate in the products is over 99%, only trace amounts of by-products PhCO<sub>2</sub>H and PhCO<sub>2</sub>NEt<sub>2</sub> are detected by GC–MS. The data in Table 1 indicate that the catalyst precursors exhibit the comparative activities and selectivity for ethyl benzoate. It suggests that the catalytic active species could be similar to Pd–TPPTS complexes and could form through a fast reaction between Pd(OAc)<sub>2</sub> or PdCl<sub>2</sub> and TPPTS [21,22].

Table 1  
Effect of catalyst precursors on the carbonylation of iodobenzene

Catalyst precursor	Conversion (%) <sup>a</sup>	TOF (h <sup>-1</sup> ) <sup>b</sup>
Pd(OAc) <sub>2</sub>	89.3	797
PdCl <sub>2</sub>	88.6	791
PdCl <sub>2</sub> (TPPTS) <sub>2</sub>	85.3	762

Reaction conditions—[Pd]=0.01 mol l<sup>-1</sup>; [TPPTS]/[Pd]=4 (molar ratio); [bmim][*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>]: 1 ml; PhI: 8.93 mmol; NEt<sub>3</sub>: 8.93 mmol; EtOH: 8.93 mmol; P<sub>CO</sub>=3.0 MPa; 150 °C; 1 h.

<sup>a</sup> The conversion of iodobenzene was determined by GC (the selectivity for ethyl benzoate was kept over 99%).

<sup>b</sup> TOF: mole of ethyl benzoate per mole of palladium per hour (h<sup>-1</sup>).

### 3.2. Effect of temperature and pressure

Although optimization was not carried out, several trends are apparent. The effect of temperature and CO pressure on the reaction is shown as in Table 2. The conversion of iodobenzene increases from 72.2% to 89.3% as the temperature increases from 130 to 150 °C (Table 2, entries 1 and 3). In all runs (unless otherwise stated), the selectivity for ethyl benzoate in the products is over 99%. As CO pressure increases from 1 to 2 MPa (Table 2, entries 8 and 9), the conversion of iodobenzene and TOF rise from 92.8% and 829 h<sup>-1</sup> to 100% and 893 h<sup>-1</sup>, respectively. All of these suggest the high temperature and pressure are advantageous for the carbonylation of iodobenzene.

### 3.3. Effect of PhI/EtOH and PhI/NEt<sub>3</sub> (molar ratio)

The molar ratios of PhI/EtOH and PhI/NEt<sub>3</sub> have great influence on the reaction. When the molar ratio of PhI/EtOH or PhI/NEt<sub>3</sub> increases from 1 to 1.2, iodobenzene completely converts into ethyl benzoate (Table 2, entries 3, 6 and 7). When both the molar ratios of PhI/EtOH and PhI/NEt<sub>3</sub> are kept at 1.2, the values of TOF increase with the increase of molar ratio of substrate to catalyst (PhI/Pd) (Table 2, entries 10–12). A high TOF of 5268 h<sup>-1</sup> with good conversion of iodobenzene can be obtained when the molar ratio of PhI/Pd increases to 6000:1.

### 3.4. Effect of TPPTS/Pd (molar ratio)

As showed in Table 2, the molar ratio of TPPTS/Pd exhibits also significant effect on the carbonylation of iodobenzene. The highest conversion of iodobenzene is obtained at TPPTS/Pd=4. When the molar ratio of TPPTS/Pd is lower or higher than that value, the catalytic activity drops markedly (Table 2, entries 2–5). When the molar ratio of TPPTS/Pd is 2, the lower concentration of TPPTS in ionic liquid is unfavorable for the stability of palladium complexes, and the palladium complexes are readily reduced by carbon monoxide to the inactive palladium black under the reaction conditions [2a], which may be responsible for the low conversion of iodobenzene. The increase of TPPTS concentration in ionic liquid can effectively prevent the reduction of palladium complexes to palladium black. So an excess of TPPTS is often required in order to avoid the catalyst deactivation. However, when the molar ratio of TPPTS/Pd is higher than 4, TPPTS could coordinate with palladium to form a stable

Table 2  
Effect of reaction parameters on the carbonylation of iodobenzene

Entry	PhI/Pd (mol/mol)	PhI/EtOH (mol/mol)	PhI/NEt <sub>3</sub> (mol/mol)	TPPTS/Pd (mol/mol)	Temperature (°C)	P <sub>CO</sub> (MPa)	Conversion (%)	TOF (h <sup>-1</sup> )
1	893	1	1	4	130	3.0	72.2	645
2	893	1	1	2	150	3.0	51.9	463
3	893	1	1	4	150	3.0	89.3	797
4	893	1	1	6	150	3.0	61.9	553
5	893	1	1	8	150	3.0	50.9	435
6	893	1.2	1	4	150	3.0	100	893
7	893	1	1.2	4	150	3.0	100	893
8	893	1.2	1.2	4	150	1.0	92.8	829
9	893	1.2	1.2	4	150	2.0	100	893
10 <sup>a</sup>	2000	1.2	1.2	4	150	3.0	96.9	1938
11 <sup>a</sup>	4000	1.2	1.2	4	150	3.0	95.8	3833
12 <sup>a</sup>	6000	1.2	1.2	4	150	3.0	87.8	5268

Reaction conditions—Pd(OAc)<sub>2</sub>: 0.01 mmol; [bmim][*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>]: 1 ml; 1 h.

<sup>a</sup> Pd(OAc)<sub>2</sub>: 4.3 × 10<sup>-3</sup> mmol.

complex, and thereby cause the decrease of the catalytic activity (Table 2, entries 4 and 5).

### 3.5. Effect of different phosphine ligands

The carbonylation of iodobenzene was performed using palladium catalyst modified with different water-soluble phosphine ligands, such as TPPTS, TPPDS, TPPMS and BISBIS. The results (in Table 3) indicate that the activity of Pd–TPPTS catalyst is higher than Pd–TPPDS or Pd–TPPMS under the same reaction conditions. Because the basicity of TPPDS or TPPMS is stronger than that of TPPTS, the palladium complexes modified by TPPMS or TPPDS are more stable than that modified by TPPTS, resulting in the decrease of the catalytic activity of Pd–TPPMS or Pd–TPPDS in comparison to that of Pd–TPPTS. Similarly, the palladium complex modified by bidentate ligand BISBIS is more stable; therefore, the catalyst exhibits very low catalytic activity (Table 3). In good agreement with this experimental result, the palladium complex modified by the chelate ligand BINAS (BINAS: sodium salt of sulfonated 2,2′-bis(diphenylphosphinomethyl)-1,1′-binaphthalene) also showed lower catalytic activity than that modified by monophosphine ligand TPPTS in Pd-catalyzed biphasic carbonylation of benzyl chloride [23].

Table 3  
Effect of ligand on the carbonylation of iodobenzene

Phosphine ligand	Conversion (%)	TOF (h <sup>-1</sup> )
TPPTS	96.9	1938
TPPDS	73.5	1470
TPPMS	57.8	1156
BISBIS	3.2	64

Reaction conditions—[Pd] = 4.3 × 10<sup>-3</sup> mol l<sup>-1</sup>; P/Pd = 4; [bmim][*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>]: 1 ml; PhI: 8.93 mmol; NEt<sub>3</sub>: 10.7 mmol; EtOH: 10.7 mmol; P<sub>CO</sub> = 3.0 MPa; 150 °C; 1 h.

### 3.6. Effect of reaction media

The catalytic activities are compared in different ionic liquids and organic solvents. The results are summarized in Table 4. The data in Table 4 showed that hydrophilic ionic liquids, e.g. [bmim][*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>] and [bmim]BF<sub>4</sub>, have the definitive advantage over hydrophobic media, e.g. [bmim]PF<sub>6</sub>. The rate enhancement effect of hydrophilic ionic liquids in palladium-catalyzed carbonylation can be attributed to the higher solubility of palladium catalytic species in [bmim][*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>] and [bmim]BF<sub>4</sub> than that in hydrophobic [bmim]PF<sub>6</sub>. The reaction rates in dioxane and THF are almost the same as in [bmim][*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>] and [bmim]BF<sub>4</sub>, but the separation of palladium catalyst from products is difficult in both the organic solvents.

### 3.7. Effect of different alcohols

The rate of ester formation is dependent on the structure of the alcohol used in the carbonylation of iodobenzene. The results listed in Table 5 suggest that the conversions of iodobenzene decrease gradually with increasing alkyl chain-length of alcohol from methyl to *n*-butyl. This is possible attributed to the increase of steric hindrance of alcohols. Consistent with the conclusion are our data showing the low reaction activities as *iso*-propanol and benzyl alcohol are used as reactants.

Table 4  
Effect of reaction medium on the carbonylation of iodobenzene

Entry	Medium	Conversion (%)	TOF (h <sup>-1</sup> )
1	[bmim][ <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> ]	96.9	1938
2	[bmim]BF <sub>4</sub>	83.0	1660
3	[bmim]PF <sub>6</sub>	74.5	1490
4	Dioxane	96.5	1930
5	THF	84.6	1692

Reaction conditions are the same as in Table 3.

Table 5  
Effect of alcohol on the carbonylation of iodobenzene

	Alcohol					
	MeOH	EtOH	PrOH	<i>i</i> -PrOH	<i>n</i> -BuOH	PhCH <sub>2</sub> OH
Conversion (%)	99.4	96.9	85.0	81.7	82.5	64.5
TOF (h <sup>-1</sup> )	2000	1938	1700	1634	1650	1290

Reaction conditions are the same as in Table 3.

Table 6  
Recycling of experiment

	Entry							
	1	2	3	4	5 <sup>a</sup>	6	9	10
Conversion (%)	96.9	99.5	99.1	98.8	95.1	95.0	92.1	88.9
TOF (h <sup>-1</sup> )	1938	1990	1982	1976	1902	1900	1842	1778

Reaction conditions are the same as in Table 3.

<sup>a</sup> One milliliter of additional ionic liquid was added.

### 3.8. Recycling of palladium catalyst

The reuse of Pd–TPPTS catalyst is investigated. The organic compounds are extracted with cyclohexane from the ionic liquid media after reaction. The ionic liquid layer containing palladium complex is directly reused in the successive recycling runs. The experimental results (Table 6) indicate that the catalyst immobilized in ionic liquid is reused for 10 runs without significant decrease in the activity and selectivity. Two experiments are designed to prove that palladium catalyst is immobilized in ionic liquid after the extraction. First, the extraction is directly transferred into autoclave and used as catalyst in the next run with addition of raw materials; the experimental result shows that only 2.3% iodobenzene is converted. Second, the extraction is detected by ICP–AES, the content of palladium in the extraction is only 0.15% of total amount of palladium. All of these demonstrate that the leaching of palladium catalyst to the extraction solution is rarely occurred. The gradual decrease in the activities could be due to the loss of the catalyst during handling and transferring of the solution. Although the triethylammonium iodide formed in the reaction does not influence the catalytic activity, its accumulation in the solution causes the reaction media become more viscous and increases the difficulty of further handling and transferring of materials. Triethylammonium iodide is separated by centrifugation. It is precipitated as solid after centrifugation. The upper ionic liquid containing catalyst can be conveniently transferred to autoclave and reused for next run.

## 4. Conclusion

The carbonylation of iodobenzene catalyzed by the water-soluble Pd–TPPTS complexes in the ionic liquid [bmim][*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>] can be realized with high rate and high selectivity. Compared with halogen-containing ionic liquids such as [bmim]BF<sub>4</sub> and [bmim]PF<sub>6</sub>, the halogen-free ionic liquid [bmim][*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>] as media greatly enhances the rate of iodobenzene carbonylation. Furthermore, the catalyst

can easily be separated from products by simple extraction and can be reused for 10 times without significant decrease of the activity and selectivity. This is advantageous to develop the novel green organic synthesis process.

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## References

- [1] (a) M. Beller, in: B. Cornils, W.A. Herrmann (Eds.), Applied Homogeneous Catalysis with Organometallic Compounds, VCH, Weinheim, 1996, pp. 148–159; (b) J. Tsuji, Palladium Reagents and Catalysts, John-Wiley & Sons, Chichester, 1995, p. 188; (c) H.M. Colquhoun, D.J. Thompson, M.V. Twigg, Direct Synthesis of Carbonyl Compounds, Plenum Press, New York, 1991.
- [2] (a) F. Bertoux, E. Monflier, Y. Castanet, A. Mortreux, J. Mol. Catal. A: Chem. 143 (1999) 11; (b) I.P. Beletskaya, A.L. Lapidus, K.B. Petronskii, Russ. J. Org. Chem. 34 (1998) 1464; (c) F. Monteil, P. Kalck, J. Organomet. Chem. 482 (1994) 45; (d) F. Monteil, L. Miquel, R. Queau, P. Kalck, in: I.T. Horvath, F. Joo (Eds.), Aqueous Organometallic Chemistry and Catalysis, Kluwer, Dordrecht, 1995, p. 131.
- [3] P. Wasserscheid, T. Welton (Eds.), Ionic Liquids in Synthesis, Wiley-VCH Verlag GmbH & Co. KGaA, 2002.
- [4] N. Karodia, S. Guise, C. Newlands, J. Andersen, Chem. Commun. (1998) 2341.
- [5] M.H. Valkenberg, C. de Castro, W.F. Hölderich, Appl. Catal. A: Gen. 215 (2001) 185.
- [6] P.J. Dyson, Appl. Organomet. Chem. 16 (2002) 495.
- [7] J. Fraga-Dubreuil, K. Bourahla, M. Rahmouni, J.P. Bazureau, J. Hamelin, Catal. Commun. 3 (2002) 185.
- [8] P. Ludley, N. Karodia, Tetrahedron Lett. 42 (2001) 2011.
- [9] O. Bortolini, A.E. Visser, W.M. Reichert, H.D. Willauer, G.A. Broker, R.D. Rogers, Green Chem. 3 (2001) 156.
- [10] M.V. Alexander, A.C. Khandekar, S.D. Samant, J. Mol. Catal. A: Chem. 223 (2004) 75.
- [11] (a) N. Karodia, S. Guise, C. Newlands, J. Andersen, Chem. Commun. (1998) 2341;

- (b) A. Riisager, P. Wasserscheid, R. Hal, R. Fehrmann, *J. Catal.* 219 (2003) 452;
- (c) J. Golding, S. Forsyth, D.R. Macfarlane, M. Forsyth, G.B. Deacon, *Green Chem.* 4 (2002) 223.
- [12] (a) E. Mizushima, T. Hayashi, M. Tanaka, *Green Chem.* 3 (2001) 76;  
(b) E. Mizushima, T. Hayashi, M. Tanaka, *Top. Catal.* 29 (2004) 163.
- [13] V. Calò, P. Giannoccaro, A. Nacci, A. Monopoli, *J. Organomet. Chem.* 645 (2002) 152.
- [14] W. Xiong, Q. Lin, H. Ma, H. Zheng, H. Chen, X. Li, *Tetrahedron Asymm.* 16 (2005) 1959.
- [15] Q. Lin, H. Fu, X. Fang, M. Yuan, H. Chen, X. Li, *Acta Phys. Chim. Sin.* 22 (2006) 465.
- [16] J.G. Huddleston, H.D. Willauer, R.P. Swatloski, A.E. Visser, R.D. Rogers, *Chem. Commun.* (1998) 1765.
- [17] (a) P.A.Z. Suarez, J.E.L. Dullius, S. Einloft, R.F. de Souza, J. Dupont, *Polyhedron* 15 (1996) 1217;  
(b) J.D. Holbrey, K.R. Seddon, *J. Chem. Soc., Dalton Trans.* (1999) 2133.
- [18] H. Chen, X. Li, Y. Li, H. Liu, *ZL* 96 1 20055.3 (1996).
- [19] V.V. Grushin, H. Alper, *Organometallics* 12 (1993) 1890.
- [20] W. Wojtków, A.M. Trzeciak, R. Choukroum, J.L. Pellegatta, *J. Mol. Catal. A: Chem.* 224 (2004) 81.
- [21] C. Amatore, E. Blart, J.P. Genêt, A. Jutand, S. Lemaire-Audoire, M. Savignac, *J. Org. Chem.* 60 (1995) 6829.
- [22] W.A. Hermann, J. Kellner, H. Riepel, *J. Organomet. Chem.* 389 (1990) 103.
- [23] C.W. Kohlpaintner, M. Beller, *J. Mol. Catal. A: Chem.* 116 (1997) 259.