

Highly efficient ionic liquid-mediated palladium complex catalyst system for the oxidative carbonylation of amines

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Abstract

A highly efficient catalyst system, palladium complex–ionic liquid, was developed for the carbonylation of amines to give carbamate or urea. The desired products could be precipitated by adding water into the resulting mixture and the catalyst system could be reused with slight loss of catalytic activity.

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1. Introduction

Isocyanates, e.g., toluene diisocyanate and 4,4'-diphenylmethyl diisocyanate, are currently manufactured by phosgenation of the corresponding amines with toxic phosgene in industry, which may cause serious environmental pollution and equipment corrosion. Therefore, produced either by oxidative carbonylation of amines or by reductive carbonylation of nitro compounds in the presence of an alcohol, carbamates as intermediates for the synthesis of isocyanates with nonphosgene routes have been extensively studied for the past two decades. Pd, Ru, Rh, Au, and other transitional metal complexes were employed as the catalysts [1–7], in which complexes of Pd coordinated with N-containing compounds are the most effective catalyst systems [8]. The corresponding catalytic turnover frequency (TOF), however, is still not high enough for industrial application, and large amounts of volatile organic solvents were inevitably used in most of these processes. Furthermore, palladium complexes coordinated with N-containing compounds are usually insoluble in most conventional organic solvents, and it is well known that reaction media play an important role in homogeneous catalysis, although, so far, such mediation is still not very clear. Moreover, organic solvents, for establishing a suitable homogeneous catalyst system for the carbonylation of N-containing compounds, are very limited.

Recently, room temperature ionic liquids, a new kind of reaction media with very low vapor pressure and high dissolvability toward many organic and inorganic substances, have been attracting growing interests, and many catalytic reactions proceeded in ionic liquids as reaction media were reported with excellent performance [9–16]. It can be assumed that the diversity of ionic liquids may form an optimal homogeneous catalyst system with a specific organometallic complex toward a specific reaction.

In this work, the ionic liquid-mediated palladium (1,10-phenanthroline)²⁺ complex catalyst system for the oxidative carbonylation of amines to give corresponding carbamates or ureas was investigated without using any additional organic solvents. The aim is to establish an effective catalytic system for the carbonylation of amines through the selective dissolvability and special mediation of ionic liquid.

2. Experimental

The ionic liquids, BMImBF₄ (BMIm = 1-butyl-3-methylimidazolium), BMImPF₆, BMImFeCl₄, and BMImCl, and palladium (1,10-phenanthroline)²⁺ complexes were respectively synthesized according to previously published papers [17,18] with slight modifications. Pd(OAc)₂ and Pd(acac)₂ were of AR grade. Characterizations of ionic liquids and palladium complexes were conducted with FT Raman (Nicolet 910) and FTIR (Bruker H210).

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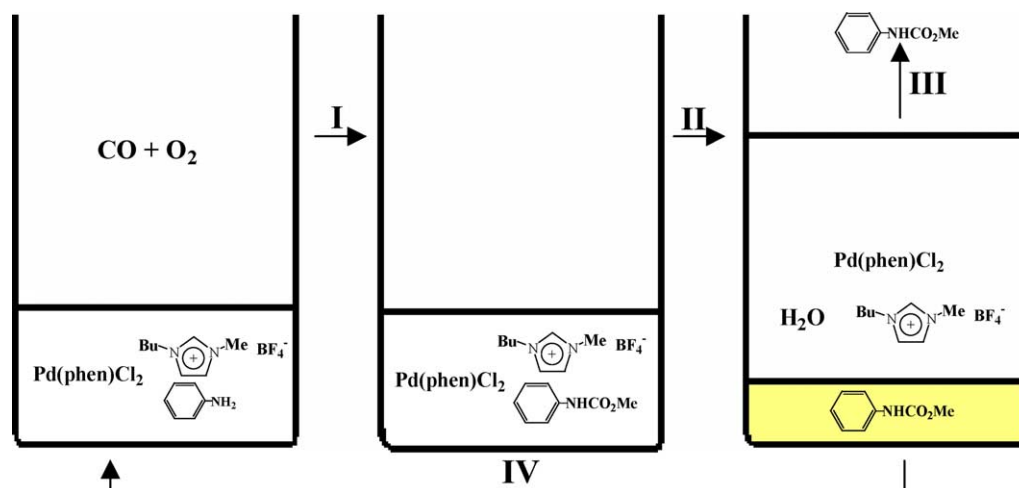


Fig. 1. Step I: Carbonylation of aniline with CO, O₂, and MeOH in the presence of Pd(phen)Cl₂/(BMImBF₄) and a liquid mixture containing the desired product were obtained after reaction. Step II: About 10 ml water was added into the resulting liquid mixture, the resulting product would precipitate. Step III: Desired solid product and corresponding yield could be recovered and obtained after filtration and dryness. Step IV: Ionic liquid containing Pd(phen)Cl₂ could also be recovered and reused after the percolate was distilled to remove water.

All reactions were conducted in a 90-ml autoclave with a glass tube inside equipped with magnetic stirring. In each reaction, 1 mg Pd complex catalyst, 1 ml ionic liquid, 1 ml amines, 10 ml methanol, and 5.0 MPa of mixture gases (CO purity 99.99% 4.5 MPa and O₂ 99.99% 0.5 MPa) were successively introduced without any additional organic solvent. The reaction proceeded at 175 °C for 1 h since low conversion was obtained at lower temperatures. When the conversion and selectivity were high enough, the resulting product “precipitated” when ca. 10 ml water was added into the resulting liquid mixture after reaction because carbamate is insoluble in water, while the Pd(phen)Cl₂ was still “dissolved” into the ionic liquid. Therefore, the desired solid product and corresponding yield could be recovered and obtained after filtration and dryness. Ionic liquid containing Pd(phen)Cl₂ could also be recovered and reused after the percolate was distilled to remove water and residual methanol. A schematic diagram of such reaction and separation processes is given in Fig. 1. Qualitative analyses were conducted with a HP 6890/5793 GC-MS. Quantitative analysis was conducted over a HP 1790 GC and the conversions and selectivities were determined by external standard, and were calculated according the chromatographic peak areas of the resulting products given by the GC chemstation.

3. Results and discussion

First, the solubility of Pd(phen)Cl₂ in water, methanol, and a series of ionic liquids was examined at room temperature (Table 1). Pd(phen)Cl₂ is completely insoluble in water or methanol, while ca. 0.11–0.12 g/100 ml of Pd(phen)Cl₂ solubility was observed in BMImBF₄ and BMImPF₆, which is high enough to establish a homogeneous Pd(phen)Cl₂ + ionic liquid catalyst system. About 6 g/100 ml of Pd(phen)Cl₂ solubility was achieved in

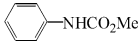
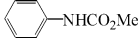
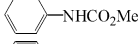
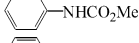
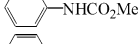
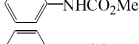
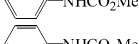
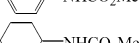
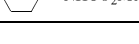
Table 1
Solubility of Pd(phen)Cl₂ in various liquid media (25 °C)

Solvent	Solubility (mg/100 ml)
BMImBF ₄	110
BMImPF ₆	120
BMImCl	6000
H ₂ O	< 2.5
MeOH	< 2.5
Chlorobenzene	< 2.5

BMImCl, indicating that the Pd(phen)Cl₂ solubility in ionic liquid can be adjusted through the tuning of cation or anion of ionic liquids. It is noteworthy that no Pd(phen)Cl₂ precipitate could be observed when ionic liquid containing Pd(phen)Cl₂ with soluble amounts was further mixed with a large amount of methanol or water, suggesting that some interaction between Pd(phen)Cl₂ and ionic liquid was formed, which modified the Pd(phen)Cl₂ solubility in methanol or water.

With BMIm⁺ as cation and in the presence of Pd(phen)Cl₂, the effect of anions, e.g., BF₄⁻, PF₆⁻, Cl⁻, and FeCl₄⁻ on the aniline carbonylation was examined (Table 2, entries 1–4). Moderate and high conversions with excellent selectivities were achieved in BMImBF₄ and BMImFeCl₄. The corresponding TOF reached to ca. 4540 mol mol⁻¹ h⁻¹, which is much higher than that reported in previous literatures [1]. BF₄⁻ was slightly better than FeCl₄⁻, although FeCl₃ was one of the most effective cocatalysts in the carbonylation reactions of N-containing compounds. Poor catalytic performances were observed for PF₆⁻. This may be related to the instability of BMImPF₆ ionic liquids under the reaction conditions employed in this work, because remarkable degradation of this ionic liquid was observed after reaction. Such degradation, however, was not observed with BMImBF₄. On the other hand, poor catalytic activity was

Table 2
Carbonylation of amines catalyzed with a palladium complex in ionic liquids

Entry	Ionic liquid	Conversion (%)	Selectivity (%)	TOF	Desired product
1 ^a	BMImBF ₄	99	98	4540	
2	BMImPF ₆	5	99	228	
3	BMImCl	58	99	2680	
4	BMImFeCl ₄	96	> 99	4420	
5	–	2.1	99	104	
6 ^b	BMImBF ₄	71.4	99	3250	
7 ^c	BMImBF ₄	99	98	4540	
8 ^d	BMImBF ₄	41	> 99	980	
9 ^e	BMImBF ₄	96	< 1	3560	

^a Isolated yield, 91%.

^b The catalyst system reused for the second time.

^c 0.3 mg of additional Pd(phen)Cl₂ was added.

^d Pd(OAc)₂ was used as catalyst.

^e Cyclohexyl amine was used as substrate and dicyclohexyl urea with 90% selectivity was obtained.

observed if reaction proceeded in the absence of ionic liquid (entry 5).

The recycling of the BMImBF₄ + Pd(phen)Cl₂ catalyst system was also examined. Since carbamate is insoluble with water, the resulting product “precipitated” when ca. 10 ml water was added into the resulting liquid mixture after reaction, while the Pd(phen)Cl₂ could be still “dissolved” into the ionic liquid (Fig. 1). Therefore, the desired solid product could be recovered after filtration to separate the liquid mixture containing BMImBF₄, Pd(phen)Cl₂, residual methanol, and water, and 91% of yield was achieved after dryness (entry 1). Ionic liquid containing Pd(phen)Cl₂ could also be recovered and reused after the percolate was distilled to remove residual methanol and water, and 70% of conversion was observed (entry 6). However, 98% of conversion was regained if 0.2–0.3 mg of extra Pd(phen)Cl₂ was added into the recovered BMImBF₄ ionic liquid containing Pd(phen)Cl₂ (entry 7), indicating that part of Pd(phen)Cl₂ may leach during the separation and recovery.

The experimental results also confirmed that Pd(phen)Cl₂ was the most effective catalyst for the reaction since Pd(OAc)₂ or Pd(acac)₂ (though not shown here) showed poor catalytic performance under similar conditions (entry 8), indicating that phenanthroline is also indispensable and it was unlikely that in situ formation of the Pd–carbene complex was the catalytic species for the carbonylation. The synergism among palladium, phenanthroline, and ionic liquids resulted in high catalytic activity.

The main by-product detected was *N*-phenylamide for the oxidative carbonylation of aniline. Since no species resulting from the oxidized imidazole was detected with GC-MS, the imidazolium cations could be stable enough under the reaction conditions employed in this work. Using the

most effective Pd(phen)Cl₂/BMImBF₄ catalyst system, the oxidative carbonylation of aliphatic amines, i.e., cyclohexyl, was also tested (entry 9). High conversion of cyclohexyl amine was achieved, but the selectivity for carbamate was less than 1% while dicyclohexyl urea was the main product with > 90% selectivity. At the same time, since the solubility of dicyclohexyl urea in such reaction medium was very low, crystallized product could be obtained by simple filtration. These results showed that BMImBF₄ ionic liquid + Pd(phen)Cl₂ is an effective catalytic system not only for the oxidative carbonylation of aniline to give corresponding carbamate but also for the cyclohexyl amine to give urea.

In order to gain insight into the ionic liquid-mediated Pd(phen)Cl₂ catalyst system, characterizations of FT Raman (Fig. 2) and FTIR (Fig. 3) were conducted. BMImCl was selected because it possessed higher solubility for Pd(phen)Cl₂ (ca. wt 6%) but < 0.2 wt% toward other ionic liquids. In comparison with FT Raman spectra of pure Pd(phen)Cl₂ and BMImCl, strong or new peaks at 704 cm⁻¹ (ν_{C-H} of imidazolium), 1399 cm⁻¹ (imidazolium ring stretching), and 1588 cm⁻¹ (imidazolium ring stretching) [19–21] appeared, while strong adsorption between 700 and 900 cm⁻¹ (δ_{C-H} of *o*-phenanthroline) [22,23] of pure Pd(phen)Cl₂ disappeared when Pd(phen)Cl₂ was added into BMImCl. A strong and new peak was also observed at 1517 cm⁻¹ (imidazolium ring stretching) [19–21] in FTIR spectra. These changes suggested that there exist strong interactions between imidazole cations and Pd(phen)²⁺.

4. Conclusion

In summary, this is the first demonstration that ionic liquid-mediated palladium complexes could be a very effec-

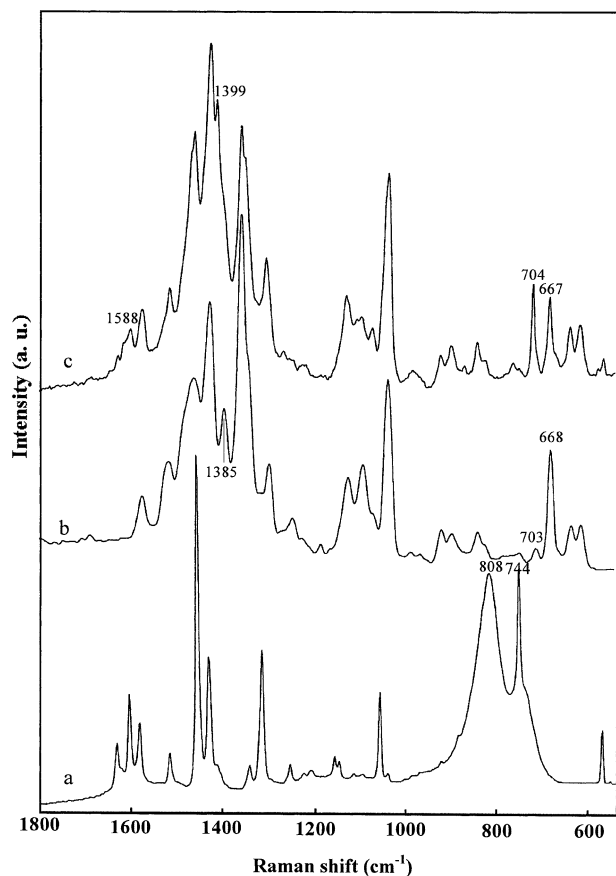


Fig. 2. Raman spectra of pure Pd(phen)Cl₂ (a), pure BMImCl (b), and Pd(phen)Cl₂ (0.6 wt%) in BMImCl (c).

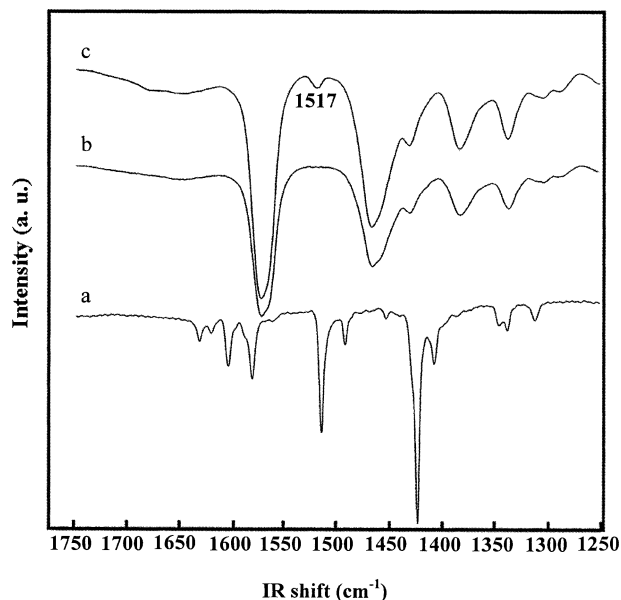


Fig. 3. IR spectra of pure Pd(phen)Cl₂ (a), pure BMImCl (b), and Pd(phen)Cl₂ (6 wt%) in BMImCl (c).

tive catalyst system for oxidative carbonylation of amines to give either carbamate or urea. This work also demonstrated that the diversity of the ionic liquids could form an optimal homogeneous catalyst system with a specific organometallic toward specific reactions. There exist strong interactions between the ionic liquid and the palladium complex, which may not only enhance but also stabilize the palladium complex catalyst. The nonvolatility of ionic liquid, interaction between the ionic liquid and the palladium complex, and the insolubility of carbamate or urea in water make such a catalyst system recyclable.

Acknowledgment

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