Catalysis Today 158 (2010) 279–285

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Experimental and theoretical investigation of reaction of aniline with dimethyl carbonate catalyzed by acid–base bifunctional ionic liquids

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ARTICLE INFO

Article history:
Available online 7 May 2010

Keywords:
Ionic liquid
Acid–base cooperativity
Simulation
Mechanism

ABSTRACT

Acid–base bifunctioanal ionic liquid, 1-(2-(1′-piperidinyl) ethyl)-3-methyl imidazolium trichlorolead ([PEmim]$PbCl_3$), is an efficient catalyst for the reaction of aniline and dimethyl carbonate (DMC). The [PEmim]$PbCl_3$ catalyzed reaction gives methyl-N-methyl-N-phenylcarbamate in the yield of 72%, while the basic ionic liquid, 1-(2-(1′-piperidinyl) ethyl)-3-methyl imidazolium chloride, and the acidic $PbCl_2$ give the yields of 47% and 6%, respectively. The high reactivity of [PEmim]$PbCl_3$ is accounted for its ability to activate both aniline and DMC by the acidic and basic sites cooperatively. Density functional theory (DFT) calculations simulate the structures and charge properties of [PEmim]$PbCl_3$, complex of [PEmim]$PbCl_3$ and aniline, and complex of [PEmim]$PbCl_3$ and DMC. The calculations show that [PEmim]$PbCl_3$ can increase the electrophilicity of DMC and the nucleophilicity of aniline by its acid and base sites.

1. Introduction

Organic carbamates are very important intermediates in drug synthesis [1], agrochemicals [2], and polyurethane based polymers [3]. Conventionally, carbamates were mostly synthesized using phosgene or its derivatives [4,5]. Obviously, these procedures are neither convenient nor environmentally benign. To avoid these drawbacks, numerous studies on the synthesis of carbamates have been investigated. Many efforts are currently being turned to the utilization of dimethyl carbonate (DMC) which is considered as a safe, nontoxic and green reagent [6–13]. Methyl-N-methyl-N-phenylcarbamate is an important carbamate and mostly synthesized from N-methyl aniline or methyl-N-phenyl carbamate [14,15]. Raucher and Jones [14] reported that secondary amines reacted with bis(trimethylsilyl)acetamide followed by addition of methyl chloroformate to produce the corresponding carbamates. Barany et al. [15] found that N-methyl aniline reacted with acid chlorides to give carbamates in nominally quantitative yields. Heaven reported the synthesis of methyl-N-methyl-N-phenylcarbamate by the reaction of N-methyl aniline with trimethylorthoformate under high pressure of CO in the autoclave [16]. On the other hand, Tundo found that two-step procedure was necessary in order to get high yield of methyl-N-methyl-N-phenylcarbamate. Methyl-N-phenyl carbamate was synthesized from aniline and DMC, and subsequently methylated with DMC at 230 °C to afford methyl-N-methyl-N-phenylcarbamate [17]. Although it was reported that methyl-N-methyl-N-phenylcarbamate was synthesized from aniline and DMC in the presence of potassium carbonate and tetrabutylammonium bromide (Bu_4NBr), it encountered the problems of large amount of catalysts and complicated work-up and separation [18].

Ionic liquids, as a new kind of solvents and catalysts, have been applied in the reactions of aliphatic amines and indole with DMC [19–21]. However, these ionic liquids did not show any activity for the reaction of aromatic amines with DMC. Moreover, the reaction mechanism, especially how the ionic liquid activates the reactants was not well studied. In this paper, we synthesized acid–base bifunctional ionic liquids which have basic sites to activate aniline and acidic sites to activate DMC, to catalyze the reaction of aniline and DMC for producing methyl-N-methyl-N-phenylcarbamate in one-pot. The acid–base cooperative effect of the ionic liquids was simulated by the density functional theory (DFT) [22].

2. Experimental

2.1. General

DMC was fractionally distilled and stored over molecular sieves (4 Å). The other reagents were commercial reagents of AR grade and used without further purification. NMR spectra were recorded on Bruker 500 MHz with tetramethylsilane as the internal standard.

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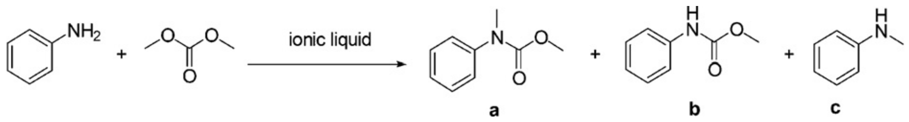
doi:10.1016/j.cattod.2010.03.060



Scheme 1. Reaction of aniline and DMC.

2.2. Synthesis of ionic liquids

1-(2-(1′-Piperidinyl) ethyl)-3-methyl imidazolium chloride ([PEmim]Cl): in a 100 mL round-bottomed flask equipped with reflux condenser and magnetic stirrer, N-methylimidazole (2.05 g, 25 mmol), 1-(2-chloroethyl)piperidine hydrochloride (3.68 g, 20 mmol) and absolute ethanol (10 mL) were added. The mixture was refluxed for 24 h. After the reaction, the solvent was removed under vacuum, the residue was washed with dichloromethane and dried at 70 °C under vacuum. The white solid was dissolved in the mixture of ethanol (5 mL) and water (5 mL), and neutralized by NaOH (0.8 g, 20 mmol). After removal of solvents, the product was extracted with dichloromethane, dried at 70 °C under vacuum for 10 h. Pale yellow oily liquid was obtained (4.12 g, yield: 90%).

Synthesis of 1-(2-(1′-piperidinyl) ethyl)-3-methyl imidazolium trichlorolead ([PEmim]$PbCl_3$): under a dry nitrogen atmosphere, [PEmim]Cl (2.29 g, 10 mmol) and $PbCl_2$ (2.78 g, 10 mmol) were stirred at 120 °C for 2 h. After cooled to room temperature, the pale brown sticky oil was obtained in the quantitative yield.

^1H NMR (500 MHz, DMSO-d_6) δ 1.35–1.47 (m, 6H, piperidin–H), 2.36–2.50 (m, 4H, piperidin–H), 2.62 (t, J = 5.9 Hz, 2H, –CH_2–piperidinyl), 3.88 (s, 3H, N–CH_3), 4.27 (t, J = 5.9 Hz, 2H, N–CH_2–), 7.68(s, 1H, imidazole–H), 7.73(s, 1H, imidazole–H), 9.12 (s, 1H, imidazole–H). $[PEmim]^+$, m/z = 194.2.

1-((2-diethylamino) ethyl)-3-methyl imidazolium trichlorolead ([DEAEmim]$PbCl_3$) was synthesized by the similar procedure.

^1H NMR (500 MHz, DMSO-d_6) δ 0.85 (t, J = 7.0 Hz, 6H, ethly–CH_3), 2.43–2.50 (m, 4H, ethyl–CH_2–), 2.70 (t, J = 5.8 Hz, 2H, diethylamino–CH_2), 3.86 (s, 3H, N–CH_3), 4.18 (t, J = 5.8 Hz, 2H, N–CH_2–), 7.67(s, 1H, imidazole–H), 7.73(s, 1H, imidazole–H), 9.04 (s, 1H, imidazole–H). $[DEAEmim]^+$, m/z = 182.2.

2.3. Typical procedure for the reaction of aniline and DMC catalyzed by ionic liquid

The reaction of aniline and DMC was carried out in a 40 mL stainless autoclave with a polytetrafluoroethylene tube inside and a magnetic stirring bar. Aniline (2.0 mmol, 186 mg), [PEmim]$PbCl_3$ (0.2 mmol) and DMC (10 mL) were stirred at 160 °C for 4 h. The reaction mixture was analyzed with a gas chromatograph (Shimadzu GC-14B, equipped with a capillary column CBP1-M25-025) using n-dodecane as the internal standard. The structure of products was characterized by GC–MS (Agilent 6890 series GC system, Agilent 5973 network Mass selective detector). The pure product was obtained by chromatography on silica gel.

Methyl-N-methyl-N-phenylcarbamate:

^1H NMR (500 MHz, $CDCl_3$) δ 3.31 (s, 3H, N–CH_3), 3.71 (s, 3H, –OCH_3), 7.21–7.26 (m, 3H, Ar–H), 7.34–7.37 (m, 2H, Ar–H). GC–MS: m/z = 165[M^{+1}].

Methyl-N-phenyl carbamate:

^1H NMR (500 MHz, $CDCl_3$) δ 3.78 (s, 3H, –OCH_3), 6.61 (s, 1H, N–H), 7.06–7.09 (m, 1H, Ar–H), 7.26–7.31 (m, 2H, Ar–H), 7.32–7.39 (m, 2H, Ar–H). GC–MS: m/z = 151[M^{+1}].

N-methyl aniline:

GC–MS: m/z = 107[M^{+1}].

3. Computational methods

The simulations of structures and natural bond orbital (NBO) charge of ionic liquids were performed by the density functional theory (DFT) with Becke's three-parameter exchange functional in combination with the Lee, Yang, and Parr correlation functional (B3LYP) using the 6-31G** basis set for C, H, N, O, Cl and Lanl2dz for Pb with Gaussian 03 [23].

4. Results and discussion

4.1. Reaction of aniline and DMC catalyzed by various ionic liquids

Conventionally, the reaction of aniline and DMC was considered as a base catalyzed reaction [10,24]. Base can increase the nucleophilicity of aniline through the abstraction of proton. On the other hand, the reaction also can be accelerated by Lewis acid catalysts through activation of DMC [12]. [PEmim]$PbCl_3$, as a model of bifunctional ionic liquid, has both the Lewis basic site of piperidine and the Lewis acidic site of Pb^{2+}. Considering the ability to activate both aniline and DMC, [PEmim]$PbCl_3$ was applied to catalyze the reaction of aniline and DMC. The reaction of aniline and DMC gave three products, methyl-N-methyl-N-phenylcarbamate (**a**), methyl-N-phenyl carbamate (**b**) and N-methyl aniline (**c**) (Scheme 1). The results were listed in Table 1.

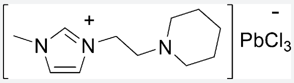
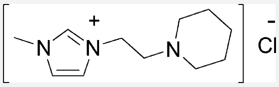
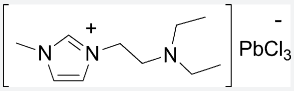
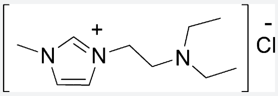
As shown in Table 1, [PEmim]$PbCl_3$ gave methyl-N-methyl-N-phenylcarbamate in the yield of 72% (entry 1). However, the corresponding basic ionic liquid [PEmim]Cl gave methyl-N-methyl-N-phenylcarbamate in the yield of 47% (entry 2). In the meanwhile, $PbCl_2$ afforded methyl-N-methyl-N-phenylcarbamate in the yield of 6% and the main product was methyl-N-phenylcarbamate (35%) (entry 3) which was similar with the reaction catalyzed by other lead salts [7,12,25]. The higher activity of [PEmim]$PbCl_3$ is probably due to its acid–base cooperative effect. The similar observation was also found in the reaction catalyzed by [DEAEmim]$PbCl_3$ (entries 4 and 5). The relative low activity and selectivity of [DEAEmim]$PbCl_3$ is probably owing to its high steric hindrance (entries 1 and 4).

4.2. Reaction of aniline and DMC catalyzed by [PEmim]$PbCl_3$

4.2.1. Effect of reaction time

The effect of reaction time on the conversion of aniline and the yields of methyl-N-methyl-N-phenylcarbamate, methyl-N-phenyl carbamate and N-methyl aniline was shown in Fig. 1. The conversion of aniline increased fast in the first 3 h and almost did not change after 3 h. The yield of methyl-N-methyl-N-phenylcarbamate increased parallel with the conversion in the first 3 h and reached the highest (72%) in 4 h. In the meanwhile, the yield of methyl-N-phenyl carbamate increased in the first 2 h and reached to the maximum of *ca.* 20%. Then the yield decreased about 10% from 2 to 4 h. It was interesting to note that the increase of the yield of methyl-N-methyl-N-phenylcarbamate was consistent with the decrease of the yield of methyl-N-phenyl carbamate. Presumably, methyl-N-methyl-N-phenylcarbamate was formed from the reaction of methyl-N-phenyl carbamate with DMC. The details of the reaction mechanism will be discussed in Section 4.4.

Table 1
Reaction of aniline and DMC catalyzed by various ionic liquids.

Entry[a]	Ionic liquid	Conversion (%)	Yield (%)[b]		
			a	**b**	**c**
1		87	72	8	4
2		70	47	5	7
3	$PbCl_2$	51	6	35	5
4		60	30	20	7
5		30	13	9	3

[a] Reaction conditions: aniline: 2 mmol, DMC: 10 mL, ionic liquid: 0.2 mmol, 160 °C, 4 h.
[b] GC yield.

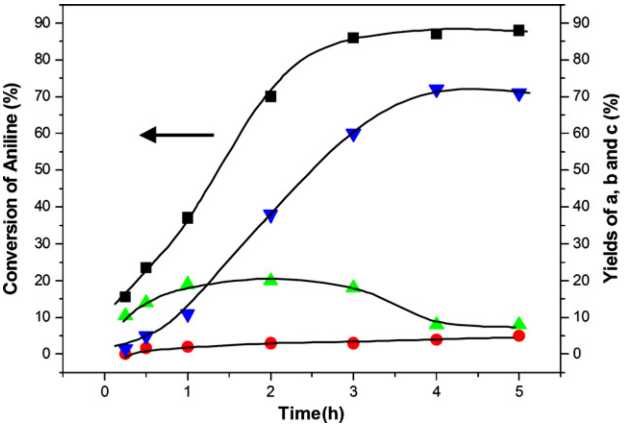


Fig. 1. Effect of reaction time. Reaction conditions: aniline: 2 mmol, DMC: 10 mL, [PEmim]$PbCl_3$: 0.2 mmol, reaction temperature: 160 °C. (■) Conversion of aniline; (▼) yield of methyl-N-methyl-N-phenylcarbamate (**a**); (▲) yield of methyl-N-phenyl carbamate (**b**); (●) yield of N-methyl aniline (**c**).

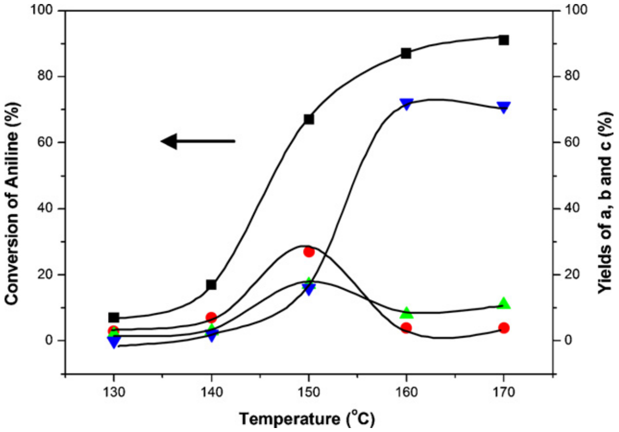


Fig. 2. Effect of reaction temperature. Reaction conditions: aniline: 2 mmol, DMC: 10 mL, [PEmim] $PbCl_3$: 0.2 mmol, reaction time: 4 h. (■) Conversion of aniline; (▼) yield of methyl-N-methyl-N-phenylcarbamate (**a**); (▲) yield of methyl-N-phenyl carbamate (**b**); (●) yield of N-methyl aniline (**c**).

4.2.2. Effect of reaction temperature

The reaction of aniline and DMC was carried out in the temperature range of 130–170 °C. The effect of reaction temperature on the conversion of aniline and the yields of methyl-N-methyl-N-phenylcarbamate, methyl-N-phenyl carbamate and N-methyl aniline were shown in Fig. 2. The conversion of aniline increased slightly below 140 °C and increased dramatically with further increase in the temperature from 140 to 160 °C. However, the conversion almost leveled off with the further increase of the temperature. Similarly, the yield of methyl-N-methyl-N-phenylcarbamate increased with the increase of temperature and reached the highest of 72% at 160 °C. This indicates that the reaction is highly sensitive to the temperature.

4.2.3. Effect of the [PEmim]Cl/$PbCl_2$ molar ratio

Ionic liquids with variety of chemical composition were prepared by varying the ratio of [PEmim]Cl and $PbCl_2$. When the molar ratio of [PEmim]Cl/$PbCl_2$ was 2:1, $[PEmim]_2PbCl_4$ was formed, as such, when the molar ratio of [PEmim]Cl/$PbCl_2$ was 1:2, [PEmim]Pb_2Cl_5 was formed, which is similar to the chloroaluminate(III) ionic liquids [26,27]. These ionic liquids were applied to catalyze the reaction of aniline with DMC. The conversion of aniline and yields of products was listed in Fig. 3. As shown in Fig. 3, the yield of methyl-N-methyl-N-phenylcarbamate slowly increased with increasing molar ratio of [PEmim]Cl/$PbCl_2$, and reached the maximum at the molar ratio of 1:1. However, the yield decreased dramatically with the further increasing of the molar ratio. Since [PEmim]Cl has the basic site of piperidine and $PbCl_2$ has the acidic

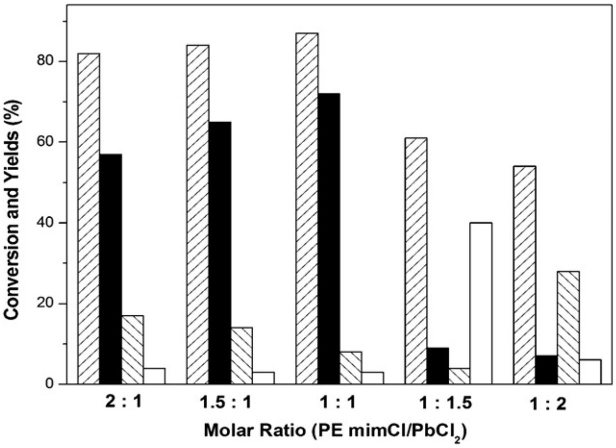
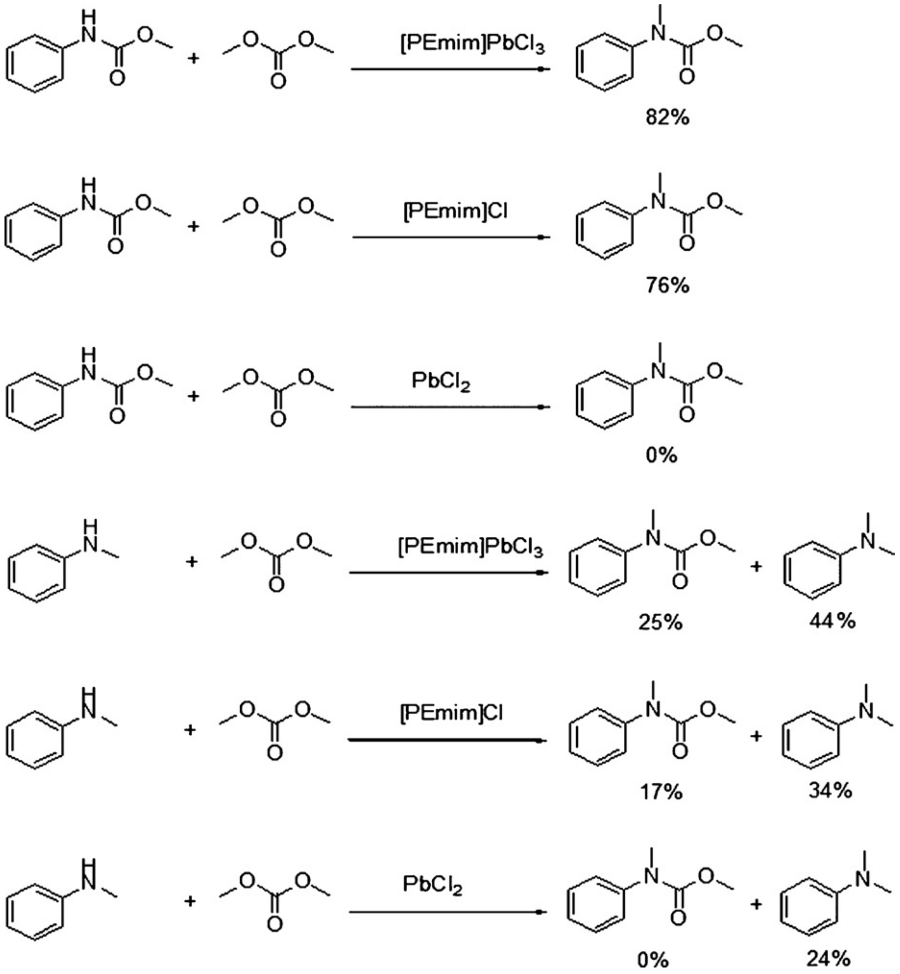


Fig. 3. Effect of the [PEmim] Cl/$PbCl_2$ molar ratio. (▨) Conversion of aniline; (■) yield of methyl-N-methyl-N-phenylcarbamate (**a**); (▧) yield of methyl-N-phenyl carbamate (**b**); (□) yield of N-methyl aniline (**c**).



Scheme 2. Reactions of methyl-N-phenyl carbamate, N-methyl aniline and DMC.

site of Pb^{2+}, the molar ratio of [PEmim]Cl/$PbCl_2$ represents the ratio of basic and acidic sites. Therefore, an appropriate ratio of acidic and basic site in the ionic liquids was necessary in order to get the high yield of methyl-N-methyl-N-phenylcarbamate.

4.3. Reactions of substituted phenylamines and DMC catalyzed by [PEmim]$PbCl_3$

In order to investigate the generalities of this procedure, the reactions of various substituted phenylamines with DMC were carried out in the presence of [PEmim]$PbCl_3$. The results were summarized in Table 2. Tolylamine gave methyl-N-methyl-N-tolylcarbamate, methyl-N-tolylcarbamate and methyl-tolylamine in the yield of 23, 18, 6%, respectively (entry 1). In the meanwhile, 4-methoxy-phenylamine and 4-nitro-phenylamine afforded the corresponding carbamates in relative higher yields (entries 2 and 3). The steric hindered amine, such as 4-bromo-2, 6-dimethyl-phenylamine also furnished the corresponding carbamate in the yield of 50% (entry 4). These results indicate that the acid–base bifunctional ionic liquid [PEmim]$PbCl_3$ is also an efficient catalyst for reactions of substituted phenylamines and DMC.

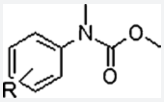
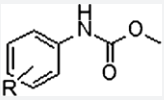
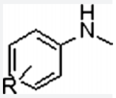
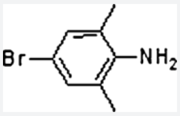
4.4. Reaction mechanism

In order to investigate the reaction path of formation of methyl-N-methyl-N-phenylcarbamate, methyl-N-phenyl carbamate and N-methyl aniline were used as starting materials, respectively, to react with DMC (Scheme 2). Interestingly, the reactions of methyl-N-phenyl carbamate and DMC gave methyl-N-methyl-N-phenylcarbamate as a sole product in the yield of 82%, 76% and 0% in the presence of [PEmim]$PbCl_3$, [PEmim]Cl and $PbCl_2$, respectively. The basic site of ionic liquid was accounted for the conversion of methyl-N-phenyl carbamate to methyl-N-methyl-N-phenylcarbamate. However, the reactions of N-methyl aniline and DMC afforded N,N-dimethyl aniline as a main product in the yield of 24–44% in the presence of different catalysts. Considering the fact that the yield of N-methyl aniline was lower than 5% and N,N-dimethyl aniline was not observed in the reaction of aniline and DMC (Section 4.2.1), the reaction path of formation of methyl-N-methyl-N-phenylcarbamate was reasonably assumed to be through methyl-N-phenyl carbamate.

A proposed reaction mechanism for the formation of methyl-N-methyl-N-phenylcarbamate is expressed as follows (Scheme 3):

[PEmim]$PbCl_3$ (i) has both acidic site and basic site. The acidic site of Pb^{2+} interacts with DMC to form $Pb^{2+}OC(OCH_3)_2$ species. In the meanwhile, the basic site of piperidinyl group activates aniline through the formation of hydrogen bond (N–H···N) (ii). The activated aniline undergoes the nucleophilic attack on the carbonyl group of $Pb^{2+}OC(OCH_3)_2$ species to form methyl-N-phenyl carbamate species (iii). Methyl-N-phenyl carbamate species undergoes the nucleophilic attack on the methyl group of another molecular DMC to give methyl-N-methyl-N-phenylcarbamate and the species (iv). [PEmim]$PbCl_3$ (i) is recycled from species (iv) with the release of methanol and carbon dioxide [10,17].

Table 2
Reactions of substituted phenylamines and DMC catalyzed by [PEmim]$PbCl_3$.

Entry[a]	Substrates	Yield (%)[b]		
				
1		23	18	6
2		55	10	6
3		76	0	20
4		50	0	0

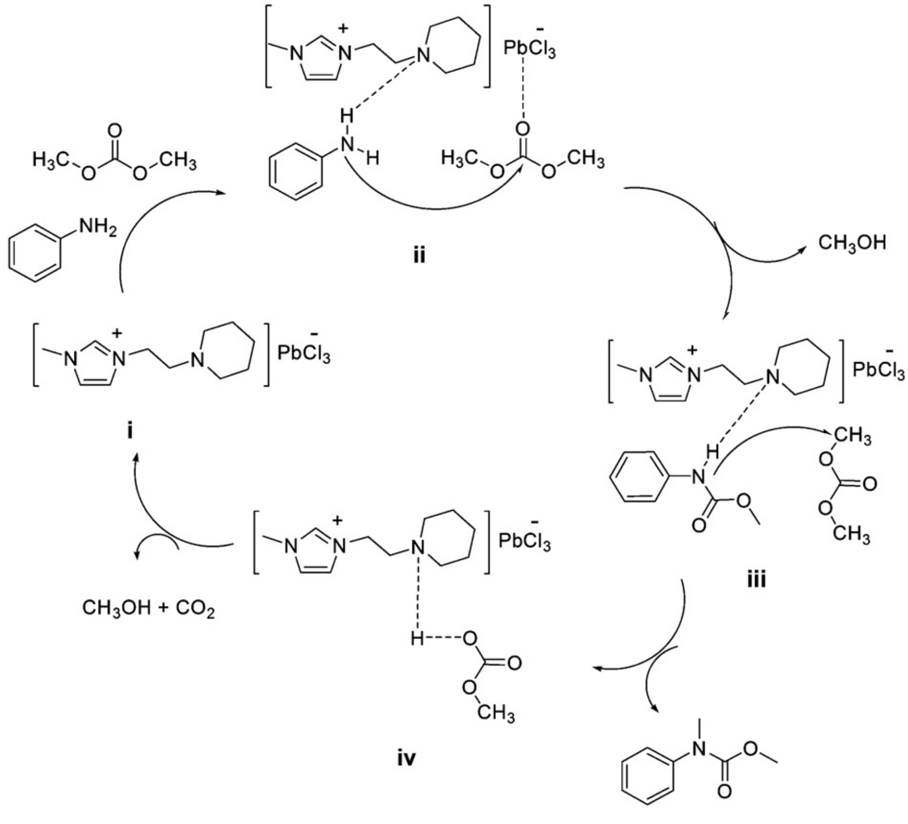
[a] Reaction conditions: aromatic amine: 2 mmol, DMC: 10 mL, [PEmim]$PbCl_3$: 0.2 mmol, 160 °C, 4 h.
[b] GC yield.

4.5. *Quantum chemical calculation*

4.5.1. *Calculated geometry and charge property of [PEmim]$PbCl_3$*

Optimized structure of [PEmim]$PbCl_3$ was calculated at the B3LYP/6-31G** level. As shown in Fig. 4, anion ($[PbCl_3]^-$) is above the plane of imidazolium ring in the ionic liquid. The $[PbCl_3]^-$ has close contact with C_2–H (H2), hydrogen of methyl (H1) and hydrogen of methylene (H3). The bond lengths between Cl and H are 2.6776 Å (Cl(1)–H(1)), 2.8330 Å (Cl(2)–H(2)), 2.6476 Å (Cl(3)–H(3)), respectively. The NBO analysis was applied to evaluate the NBO charge of the optimized structure [28,29]. The positive charge is localized not only H atom of the imidazolium ring, but also the methyl, methylene in the side chains of the imidazolium ring.

The electrostatic potential surfaces for [PEmim]$PbCl_3$ have been constructed to qualitatively gain the possible interaction modes between $[PbCl_3]^-$ and $[PEmim]^+$. As shown in Fig. 5, more negative charges are concentrated on the regions around the Cl atoms, whereas more positive charges can be observed in the imidazolium ring and the methyl, methylene in the side chains of the imidazolium ring. This indicates electrostatic effect is the main source of the anion ($[PbCl_3]^-$) and cation ($[EPmim]^+$) attraction, and piperidine in the cation does not coordinate with Pb^{2+} in the anion.



Scheme 3. Reaction mechanism of aniline and DMC catalyzed by [PEmim]$PbCl_3$.

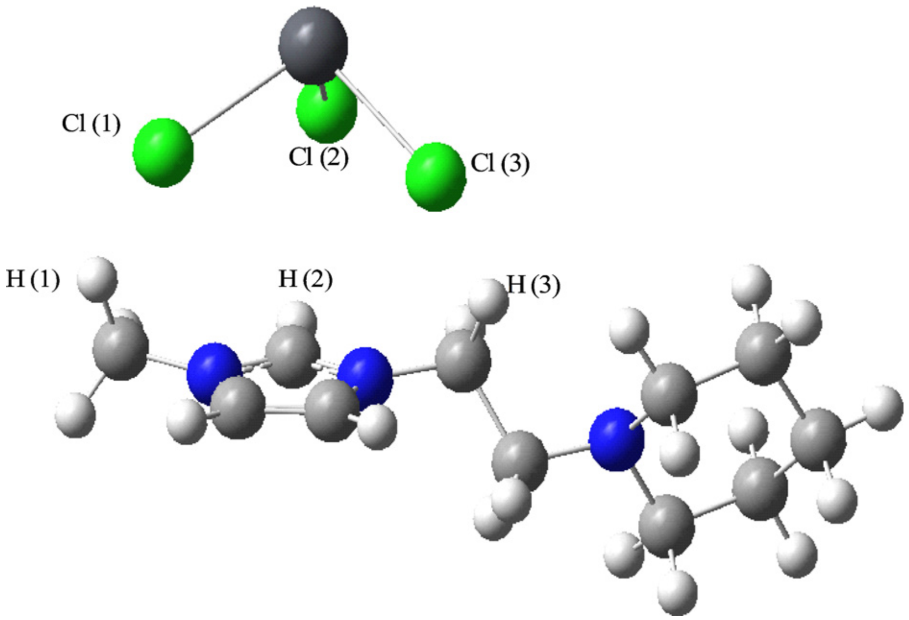


Fig. 4. Calculated geometry and NBO analysis of [PEmim]$PbCl_3$. Bond lengths: Cl(1)–H(1): 2.6776 Å, Cl(2)–H(2) 2.8330 Å, Cl(3)–H(3): 2.6476 Å. NBO charge: H(1): 0.285, H(2): 0.276, H(3): 0.283, Cl(1): −0.701, Cl(2): −0.707, Cl(3): −0.699, N(2): −0.518. Pb^{2+}: 1.161.

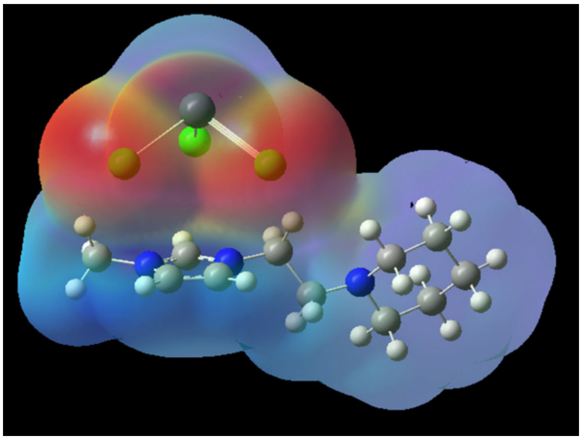


Fig. 5. The electrostatic potential surfaces for [PEmim]$PbCl_3$. The regions of more negative and positive charges are represented by red and blue color, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

4.5.2. Calculated geometry and charge property of complexes of [PEmim]$PbCl_3$ and aniline

The geometry of complexes of [PEmim]$PbCl_3$ and aniline was optimized at the B3LYP/6-31G** level. For comparison, the geometry of aniline was also calculated at the same level (Fig. 6). NBO analysis was applied to evaluate the NBO charge of the optimized structures. As shown in Fig. 6, bond length of N–H is elongated from 1.0047 Å in aniline to 1.0189 Å in the complex. The short distance (2.2646 Å) between H of amino and the N of piperidine indicates the formation of N–H···N hydrogen bond between aniline and piperidine. NBO charge of N in aniline increases from −0.846 to −0.853 in the complex. The increase of the negative charge is accounted for the interaction between aniline and the basic site of [PEmim]$PbCl_3$. Obviously, the nucleophilic ability of anilline increases *via* the interaction with [PEmim]$PbCl_3$.

4.5.3. Calculated geometry and charge property of complexes of [PEmim]$PbCl_3$ and DMC

Geometry of [PEmim]$PbCl_3$ and DMC was optimized at the B3LYP/6-31G** level. For comparison, the geometry of DMC was

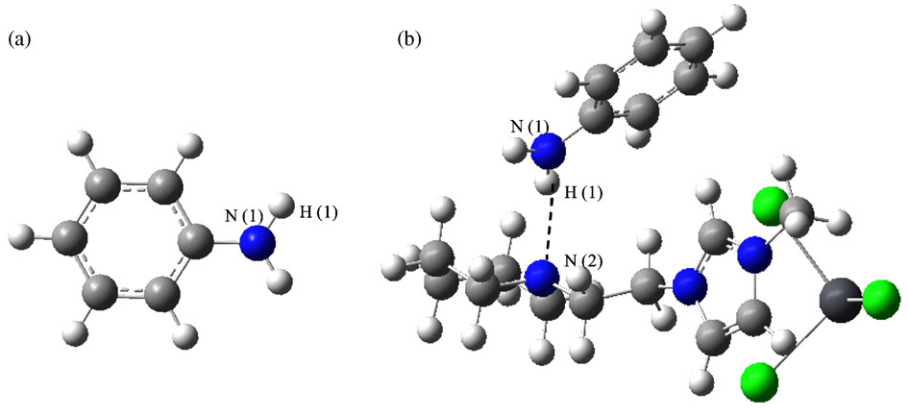


Fig. 6. The optimized geometrical structures and NBO analysis of aniline (**a**) and complexes of [PEmim]$PbCl_3$ and aniline (**b**). **a**: N(1)–H(1): 1.0047 Å, NBO charge: N(1): −0.846. **b**: N(1)–H(1): 1.0189 Å, N(2)–H(1): 2.2646 Å, NBO charge: N(1): −0.853 N(2): −0.533.

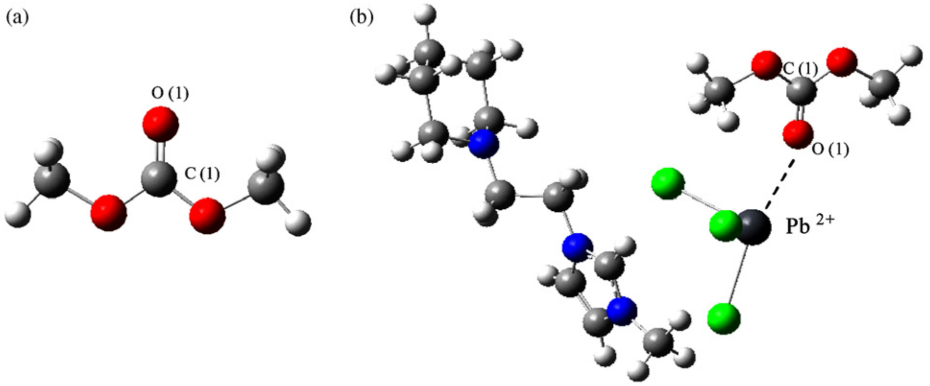


Fig. 7. The optimized geometrical structures and NBO analysis of DMC (**a**) and complexes of [PEmim]$PbCl_3$ and DMC (**b**). **a**: C(1)═O(1): 1.2119 Å, NBO charge: C(1): 1.046, O(1): −0.648. **b**: C(1)═O(1): 1.2192 Å, O(1)···Pb^{2+}: 2.9827 Å, NBO charge: C(1): 1.090, O(1): −0.684, Pb^{2+}: 1.191.

also calculated at the same level (Fig. 7). As shown in Fig. 7, the bond length of C═O of DMC is elongated from 1.2119 Å in DMC to 1.2192 Å in the complex. In the meanwhile, the distance between Pb^{2+} and O of carbonyl is 2.9827 Å, which is enough to induce the lone-pairs electrons of carbonyl to occupy an empty coordination obit of the Pb^{2+}. NBO positive charge of carbonyl C of DMC increases from 1.046 in DMC to 1.090 in the complex. Obviously, the electrophilic ability of DMC increases via the interaction with [PEmim]$PbCl_3$.

5. Conclusion

Acid–base bifunctional ionic liquid, [PEmim]$PbCl_3$, is efficient catalyst for the reaction of aniline and DMC. The reaction gives methyl-N-methyl-N-phenylcarbamate in the yield of 72% which is much higher than that of catalyzed by the corresponding basic ionic liquid ([PEmim]Cl) and acidic salt ($PbCl_2$). DFT calculations show that bond length of N–H in aniline and C═O of DMC increases 0.0142 Å and 0.0073 Å, respectively. NBO charge of N in aniline and carbonyl C of DMC increases 0.007 negative charge and 0.044 positive charge, respectively, when the interaction between reactants and ionic liquid was formed. Therefore, the acid–base cooperative effect of [PEmim]$PbCl_3$ is accounted for its ability to activate both aniline and DMC.

Acknowledgements

This work was supported by National Natural Science Foundation of China (20533010 and 20873041) and Shanghai Leading Academic Discipline Project (B409).

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