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### Design of Lewis base functionalized ionic liquids for the

### *N*-formylation of amines with CO<sub>2</sub> and hydrosilane: The cation

### effects

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### **Graphical Abstract**



### Highlights

- [DBUC<sub>12</sub>]Br is developed as an efficient catalyst for the *N*-formylation of amines with CO<sub>2</sub>
- [DBUC<sub>12</sub>]Br can be reused over 5 times without significant loss of its activity.

- Control experiments indicate the active hydrogen on the IL's cation hinders the *N*-formylation
- DFT calculations show that amine activation is not the rate-determining step to this transformation.

### Abstract

A series of functionalized ionic liquids (ILs) were developed for the reductive functionalization of  $CO_2$  with amine and hydrosilane to afford formamides under mild conditions. It was found that 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)-based IL *i.e.* [DBUC<sub>12</sub>]Br showed high efficiency for the *N*-formylation reaction of amines without using any organic solvents or additives. Furthermore, control experiments suggested the cations with active hydrogen may weaken the nucleophilicity of anions through ion pairing interactions, thereby affecting the activation of hydrosilane. The reaction mechanism was then investigated by Density Functional Theory (DFT) calculations. This protocol represents a highly efficient and environmentally friendly example for catalytic conversion of  $CO_2$  into value-added chemicals such as formamide derivatives by employing DBU functionalized ILs.

#### **Keywords**

Carbon dioxide fixation, Formylation, Ionic liquid, Metal-free catalysis, Reduction

### **1. Introduction**

As carbon dioxide  $(CO_2)$  is a non-toxic, abundant, easily available, and environmentally benign feedstock, a series of thriving research fields have been built around its chemical modification and conversion [1-6]. In view of green and sustainable chemistry, designing recyclable catalysts for the transformation of  $CO_2$ into various value-added chemicals under mild conditions is interesting and significant both in academia and society [7-13]. Ionic liquids (ILs), consisting of

2

cations and anions, have attracted intense interest in the areas of chemistry and industry as efficient catalysts and solvents in the past few decades owing to their outstanding characters, such as thermal and chemical stability and non-volatility [14-17]. The property of ILs can be adjustable for a variety of desired reactions through designing the structures of cations and anions [18]. Particularly, task-specific ILs such as amino-, amino acid-, azolate-, phenolate-, pyridine-containing ILs and so on have been also reported as efficient catalysts in CO<sub>2</sub> capture or utilization by rational designing their structures [12, 19-22].

The reductive functionalization of  $CO_2$  combining both  $CO_2$  reduction and C-N, C-C or C-O bond formation in one pot has boomed recently, which significantly broadens the range of chemicals accessible from CO<sub>2</sub> [23-29]. In this context, selective 2-, 4-, 6-electron reduction of  $CO_2$  with a reducing reagent e.g. hydrogen, hydrosilane or hydroboron and different nucleophiles to give various products such as formamides [30-34], formamidine derivatives [35], formates [36], benzothiazoles [37-38], aryl aldehydes [39-41], aminals [42-45], methylene [46], homoallylic alcohols [47], dimethoxymethane (DMM) [48-50], dithioacetals [51], methylamine [52-55] and so on (Scheme 1). In recent years, intensive investigations focus on the 2-electron reductive functionalization of CO<sub>2</sub> especially the *N*-formylation reaction of amines into formamide derivatives, since formamides are a kind of versatile chemicals and important building blocks for the production of drug molecules and agrochemicals, for instance, fluoroquinolines, 1,2-dihydroquinolines, substituted aryl imidazoles, nitrogen-bridged heterocycles, etc [30-32, 56]. In this context, Cantat and co-workers firstly reported the novel diagonal transformation pathway for CO<sub>2</sub> recycling with 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD)-catalyzed system to produce formamides employing hydrosilane as reducing reagent in combination with amines as nucleophile in 2012 [23]. Following this initial work, diverse efficient transition-metal-free catalysis systems based on N-heterocyclic carbenes (NHCs) [30, 57-59], 1,3,2-diazaphospholene (NHP-H) [60], inorganic bases [61-63], organic bases [43, 45, 64-65], as well as catalyst-free [66-68] protocol have been developed for the N-formylation reaction.

**Carbon reduction** 



Scheme 1. The examples of reductive functionalization of CO<sub>2</sub>.

Recently, imidazolium-based ILs [69], acetylcholine-carboxylate ILs [70], ILs-decorated COFs (Covalent Organic Frameworks) catalysts [71], and ILs-functionalized Zn(salen) catalysts [72] have showed good activity for the *N*-formylation of amines with CO<sub>2</sub> to form formamides under mild conditions. Notably, theses ILs exhibited outstanding catalytic performance in reusability, which can reduce cost and avoid pollution. Moreover, it is found that the ILs serve as bifunctional catalysts, anions play a significant role for the activation of hydrosilane and cations can help to activate substrate e.g. amine or CO<sub>2</sub> simultaneously. However, the role and effect of the cation of ILs in this *N*-formylation reaction has not been studied in detail. Therefore, we decided to design some functionalized ILs and further investigated the role of cation and the possible mechanism, which is essential to develop efficient IL-based catalysts for the *N*-formylation reaction as depicted in **Scheme 2**. We choosed moderate nucleophilic bromide or chloride as anions [73] and various cations with or without active hydrogen, for example, imidazolium, guanidinium, quaternary ammonium, DBU and DBN-based ILs. The DBU-based ILs *i.e.* [DBUC<sub>12</sub>]Br and

[DBUC<sub>4</sub>]Br showed excellent activity for catalyzing the *N*-formylation reaction to afford formamides at room temperature, and had excellent reusability through washing with hexane from the reaction mixture.



Scheme 2. Design of functionalized ILs for the *N*-formylation reaction from  $CO_2$  and the structures of ILs employed in this work.

### 2. Experimental section

#### 2.1 Materials and methods

The starting materials including amines and hydrosilanes were commercially available from Innochem, Energy Chemical or J&K Company and were used without further purification. Ionic liquids were prepared according to the methods of literatures. Products were isolated by column chromatography on silica gel (200-300

mesh) using petroleum ether (60-90 °C) and ethyl acetate. All compounds were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR and mass spectroscopy, which are consistent with those reported in literature. <sup>1</sup>H NMR spectra was recorded on 400 MHz spectrometers using CDCl<sub>3</sub> as solvent referenced to tetramethylsilane (TMS, 0 ppm). The <sup>13</sup>C NMR chemical shifts were reported in ppm relative to the carbon resonance of CDCl<sub>3</sub> (central peak is 77.0 ppm). GC-MS data were performed on Shimadzu GCMS-QP2010 with an ionization voltage of 70 ev and a capillary column model of RTX-5MS. High-resolution mass spectrometry (HRMS) was conducted using Agilent 6520 Q-TOF LC/MS Infrared. Melting points are measured on an X4 apparatus and uncorrected.

#### 2.2 General procedure for the N-formylation reaction of amines with CO2

The formylation reaction was conducted in a stainless steel autoclave (25 mL inner volumes). In a typical reaction, the reactor was charged with [DBUC<sub>12</sub>]Br (20.0 mg, 20 mol% relative to amine), *N*-methylaniline (27  $\mu$ L, 0.25 mmol) and phenylsilane (62  $\mu$ L, 0.5 mmol) successively at room temperature. Then, CO<sub>2</sub> was introduced into the reactor and the pressure was adjusted to 5 bar at room temperature for 6 h. After the reaction was completed, the excess of CO<sub>2</sub> was carefully vented and then 1,3,5-trimethyoxybenzene (21.0 mg) was added as an internal standard for <sup>1</sup>H NMR yield determination. The residue was purified by column chromatography with ethyl acetate–petroleum ether as the eluent to afford the desired formylated product. The characterization data of the products (**1b-15b**) can be found in supporting information.

#### 2.3 General procedure for the recovery of the IL catalyst

After the reaction was completed under the optimal conditions, the reaction mixture was washed with hexane five times to extract the formylated product remained in the organic phase. Nevertheless, the residual IL catalyst at the bottom of the bottle was separated with product due to its insoluble in hexane.

#### 2.4 Computational methods

Theoretical calculations were performed with the Gaussian 09 program [74].

Geometry optimizations were carried out at the B3LYP [75-78]/6-31+G(d) level. Frequency calculations were carried out at the same level to conform that there was no imaginary frequency for ground state structures and only one imaginary frequency for transition state structures. The transition state was confirmed by examining the vibrational mode of the imaginary frequency. Some important transition states were further checked by intrinsic reaction coordinate (IRC) calculations. Single point energy calculations for optimized structures were performed at M06-2X [79-81]/cc-pvtz level with SMD [82] solvation model used to account for solvent (dichloroethane) effects, because dichloroethane had similar dielectric properties with ILs [83]. In addition, we utilized a correction of (n-m)\*5.4 kcal/mol for a process from m- to n-components [84].

#### 3. Results and discussion

#### 3.1 Catalyst screening for the N-formylation

In our initial investigation, the model reaction of *N*-formylation using *N*-methylaniline (**1a**), CO<sub>2</sub> and phenylsilane (PhSiH<sub>3</sub>) was established to evaluate the catalytic activity of ILs, and the results were summarized in **Table 1**. To our surprise, catalytic amount (20 mol%) of [MImC<sub>12</sub>]Br and [TMGC<sub>12</sub>]Br, which could be regarded as bifunctional catalysts, only obtained **1b** in 9% and 42% yields respectively in the presence of CO<sub>2</sub> at 0.5 MPa and room temperature without any solvent (entry 1 and 2). However, **1a** was almost completely converted when using [N<sub>222</sub>C<sub>12</sub>]Br, indicating it's catalytic activity is much higher than [MImC<sub>12</sub>]Br and [TMGC<sub>12</sub>]Br (entry 3). To our delight, [DBUC<sub>12</sub>]Br allowed the desired reaction to afford **1b** in 99% yield (entry 4). [DBNC<sub>12</sub>]Br (entry 5). With a shorter chain, [DBUC<sub>4</sub>]Br was also effective for this reaction, indicating the chain length had no effect on its activity (entry 6). We didn't choose [DBUC<sub>4</sub>]Br, though it is cheaper than [DBUC<sub>12</sub>]Br, when considering the toxicity of 1-bromobutane. However, [DBUC<sub>4</sub>]Cl exhibited lower catalytic activity comparing with [DBUC<sub>4</sub>]Br, maybe owing to the difference nucleophilicity of anions

(entry 7). According to those results, we found that cations have a great influence on this *N*-formylation reaction. The less steric hindrance of imidazolium than other ILs will lead to a stronger interaction between imidazolium and Br<sup>-</sup>. In addition, guanidinium with active hydrogen resulted in lower catalytic activities comparing with quaternary ammonium, DBU and DBN. It was also proposed that strong cation-anion interaction could lead to a weaker nucleophilic of ion pairs [73, 85].

Then being reduced the pressure of  $CO_2$  to 0.2 MPa, **1b** could be obtained with 90% yield (entry 8). Notably, as the amount of [DBUC<sub>12</sub>]Br was increased to 50 mol%, **1b** yield could attain to 89% at atmospheric pressure (entry 9). Moreover, the reaction did not occur without  $CO_2$  and IL, implying that  $CO_2$  acted as  $C_1$  source and IL acted as catalyst was indispensable for this reaction (entry 10 and 11). Subsequently, various hydrosilanes were also investigated and PhSiH<sub>3</sub> was the best reductant (see **Table S1**).

### Table 1.

*N*-formylation of amines to formamides with  $CO_2^a$ .

	CH <sub>3</sub> NH	ILs	$\sim$	CH <sub>3</sub> N C H	
	+ PhS				
1a				1b	
	Entry	ILs	$CO_2$	Conv. of	Yield of
			(MPa)	$\mathbf{1a}^{b}\left(\% ight)$	$\mathbf{1b}^{b}$ (%)
	1	[MImC <sub>12</sub> ]Br	0.5	11	9
	2	[TMGC <sub>12</sub> ]Br	0.5	42	42
	3	$[N_{222}C_{12}]Br$	0.5	99	77
	4	[DBUC <sub>12</sub> ]Br	0.5	99	99
	5	[DBNC <sub>12</sub> ]Br	0.5	99	95
	6	[DBUC <sub>4</sub> ]Br	0.5	99	99
	7	[DBUC <sub>4</sub> ]Cl	0.5	86	80
	8	[DBUC <sub>12</sub> ]Br	0.2	92	90
	9 <sup>c</sup>	[DBUC <sub>12</sub> ]Br	0.1	92	89
	$10^d$	[DBUC <sub>12</sub> ]Br	-	0	0
	11	-	0.5	0	0

<sup>&</sup>lt;sup>*a*</sup>Conditions: **1a** (0.25 mmol, 27  $\mu$ L), IL (20 mol%, relative to 1a), PhSiH<sub>3</sub> (0.5 mmol, 62 $\mu$ L). <sup>*b*</sup>Determined by <sup>1</sup>H NMR using 1,3,5-trimethyoxybenzene as an internal standard. <sup>*c*</sup> IL (20 mol%, relative to **1a**). <sup>*d*</sup>Argon instead of CO<sub>2</sub> atmosphere.

### 3.2 Catalytic activity towards other amine substrates

Using a catalytic amount of [DBUC<sub>12</sub>]Br (20 mol% relative to substrate), we then evaluated the scope of this *N*-formylation reaction with various amines in the presence of PhSiH<sub>3</sub> as reductant at room temperature without any solvent. As shown in **Scheme 3**, secondary aromatic amines with both electron-donating and electron-withdrawing substituents on the phenyl ring including 4-methyl, 4-chloro, 4-methoxyl were all suitable substrates, delivering *N*-methylformanilide derivatives in 89~99% yields

(2b-5b). However, *N*-methyl-4-nitroaniline (6a) was inactive, possibly due to the strong electron-withdrawing effect. *N*-ethyl-, *N*-isopropyl-, *N*-benzyl- and *N*-allylanilines proceeded efficiently to furnish the corresponding formylated products in 52~94% yields (7b-10b). Due to steric hindrance, bulk substrates gave relatively low product yields (9b-10b). Secondary aliphatic amines, such as morpholine, pyrrolidine and diethylamine, showed good reactivity and afforded the desired products in 64~94% yields (11b-13b). Notably, this *N*-formylation reaction was also applicable to cyclic amines such as 1,2,3,4-tetrahydroquinoline and indoline (14a and 15a).



**Scheme 3**. *N*-formylation of various amines with CO<sub>2</sub>. <sup>*a*</sup> Reaction were performed with amine (0.25 mmol), [DBUC<sub>12</sub>]Br (20 mol%, 20.0 mg), PhSiH<sub>3</sub> (2 mmol, 62  $\mu$ L), CO<sub>2</sub> (0.5 MPa) at room temperature for 12 h. Yields were determined by <sup>1</sup>H NMR using 1,3,5-trimethyoxybenzene as internal standard and the isolated yields were given in parentheses. <sup>*b*</sup> Reaction time is 6 h.

#### 3.3 Catalyst Recyclability

Reusability was also a significant criteria for IL catalysis. To investigate the recyclability of [DBUC<sub>12</sub>]Br, the reaction was performed under the optimal reaction conditions (**Fig. 1**). [DBUC<sub>12</sub>]Br was recovered from the reaction mixture through washing with hexane. It was shown that the yield of **1b** almost stayed constant during five successive recycles, indicating that its activity could maintain under this conditions.



Fig. 1. The recyclability of [DBUC<sub>12</sub>]Br.

#### 3.4 Possible mechanism

Clearly, DBU functionalized ILs in this study was found to be a better catalyst than others, particularly [MImC<sub>12</sub>]Br (entry 4 vs entry 1, **Table 1**), and this superiority drives us to find out the reason. At first, DFT calculations were conducted to investigate the mechanism as shown in **Fig. 2**. Firstly, Br<sup>-</sup> nucleophilic attacks PhSiH<sub>3</sub> and then CO<sub>2</sub> inserts into the Si–H bond to form silyl formate **IM2**, which has to overcome 17.8 kcal/mol barrier. To our surprise, the barrier for nucleophilic attacking from **1a** to **IM3** is only 10.4 kcal/mol, indicating that the amine activation is not a rate-determining step (RDS) to this transformation. Subsequently, with the assistance of H<sub>2</sub>O, **IM3** undergoes a 6-membered ring transition state **TS3** and then realize

hydrogen transformation step between N and O to form **IM4**, which is the RDS for this reaction (19.4 kcal/mol). After that, a new Si–O bond is formed accompanying with the obtaining of **1b**.



Fig. 2. Potential energy surface for the formation of 1b.

According to previous reports [44] and our DFT calculations, the activation of PhSiH<sub>3</sub> is crucial to initiate the reaction. Therefore, we wanted to find out the difference between [DBUC<sub>12</sub>]Br and [MImC<sub>12</sub>]Br in the ability to activate PhSiH<sub>3</sub>. It was disappointing that only a tiny shift for the hydrogen on PhSiH<sub>3</sub> was found in <sup>1</sup>H NMR, after mixing [DBUC<sub>12</sub>]Br with PhSiH<sub>3</sub> (see **Fig. S1**). Inspired by previous reports [86] that CO<sub>2</sub> could facilitate the hydrogen activation, we performed these control experiments under 0.5 MPa CO<sub>2</sub>. With [DBUC<sub>12</sub>]Br as catalyst, the reaction between PhSiH<sub>3</sub> and CO<sub>2</sub> afforded the key intermediate **IM2** in 18% yield, but it did

not occur by using [MImC<sub>12</sub>]Br as catalyst or in the absence of catalyst (**Scheme 4**). In other words, the poor ability to activate  $PhSiH_3$  is the reason for the poor activity of [MImC<sub>12</sub>]Br. The consequence could also support our hypothesis that cations with active hydrogen may weaken the nucleophilicity of anions through ion pairing interactions, thereby affecting the activation of hydrosilane.

H Ph-Si- H 0.5 mr	−H <mark>+ CO</mark> 2 —— mol 0.5 MPa	cat. H r.t., 6h Ph <sup>∽ I</sup> H Silyl for	OH U mate IM2
-	cat.	yield of <b>IM2</b> (%	)
	no cat.	0	
[	[MImC <sub>12</sub> ]Br (20 mo	1%) 0	
	[DBUC <sub>12</sub> ]Br (20 mo	1%) 18	

**Scheme 4**. Control experiments to explore the role of the ILs in activating phenysilane.

On the basis of our experimental results and previous reports [44, 69, 73, 87], a tentative reaction mechanism for the [DBUC<sub>12</sub>]Br-catalyzed *N*-formylation of amines with CO<sub>2</sub> was proposed in **Scheme 5**. Initially, Br<sup>-</sup> of [DBUC<sub>12</sub>]Br nucleophilic attacks PhSiH<sub>3</sub> forming the active hypervalent silicon intermediate **IM1**. Then CO<sub>2</sub> inserts into the Si–H bond to form silyl formate **IM2**. Next, **IM2** is nucleophilically attacked by **1a** generating **IM3** under the activation of Br<sup>-</sup>. Subsequently, with the assistance of H<sub>2</sub>O, **IM3** undergoes a 6-membered ring transition state **TS3** to realize hydrogen transformation step between N and O to form **IM4**. Finally, C–O bond on **IM4** cleavages providing the target product **1b**.



**Scheme 5.** Possible reaction mechanism for the [DBUC<sub>12</sub>]Br-catalyzed *N*-formylation of amines with CO<sub>2</sub>.

### 4. Conclusions

In summary, DBU-based ILs, [DBUC<sub>12</sub>]Br, was proven to be a highly efficient and recoverable catalyst for efficient CO<sub>2</sub> conversion into formamides under mild conditions. The poor activity for [MImC<sub>12</sub>]Br should be ascribed to its ion pairing interactions weakening the nucleophilic of Br<sup>-</sup> for the activation of hydrosilane, as identified by control experiments. The protocol was found to be applicable to different kinds of secondary amines giving the corresponding formamide products in moderate to excellent yields. Moreover, the catalyst was easy recovery and could be reused over 5 times without significant loss of its activity. This work will undoubtedly shed light on the direction for designing catalyst on reductive functionalization of CO<sub>2</sub>.

#### **Declaration of interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### **Credit Author Statement**

X.-Y. Li, H.-C. Fu and S.-H. Yang performed the catalyst preparation, CO<sub>2</sub> reduction experiments. X.-Y. Li, X.-F. Liu, K.-H. Chen, and L.-N He provided helpful discussion. K.-H. Chen perform the DFT calculation. X.-Y. Li, K.-H. Chen, and L.-N He analyzed the data, and wrote the paper. K.-H. Chen, and L.-N He designed the study.

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