Selective synthesis of formamides, 1,2-bis(N-heterocyclic)ethanes and methylamines from cyclic amines and CO$_2$/H$_2$ catalyzed by an ionic liquid–Pd/C system†

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The reduction of CO$_2$ with amines and H$_2$ generally produces N-formylated or N-methylated compounds over different catalysts. Herein, we report the selective synthesis of formamides, 1,2-bis(N-heterocyclic)ethanes, and methylamines, which is achieved over an ionic liquid (IL, e.g., 1-butyl-3-methylimidazolium tetrafluoroborate, [BMIm][BF$_4$])–Pd/C catalytic system. By simply varying the reaction temperature, formamides and methylamines can be selectively produced, respectively, in high yields. Interestingly, 1,2-bis(N-heterocyclic)ethanes can also be obtained via the McMurry reaction of the formed formamide coupled with subsequent hydrogenation. It was found that [BMIm][BF$_4$] can react with formamide to form a [BMIm]$^+$–formamide adduct; thus combined with Pd/C it can catalyze McMurry coupling of formamide in the presence of H$_2$ to afford 1,2-bis(N-heterocyclic)ethane. Moreover, Pd/C–[BMIm][BF$_4$] can further catalyze the hydrogenolysis of 1,2-bis(N-heterocyclic)ethane to access methylamine. [BMIm][BF$_4$]–Pd/C was tolerant to a wide substrate scope, giving the corresponding formamides, 1,2-bis(N-heterocyclic)ethanes or methylamines in moderate to high yields. This work develops a new route to produce N-methylamine and opens the way to produce 1,2-bis(N-heterocyclic)ethane from cyclic amine as well.

Introduction

Carbon dioxide (CO$_2$) is an abundant, readily available, nontoxic and renewable C1 building block, and its transformation into value-added chemicals and fuels is of great significance for green and sustainable development.¹–⁶ The reactions of amines with CO$_2$ in the presence of reductants such as hydrosilanes and H$_2$ have been widely investigated, and they generally produce formamides or methylamines.⁷–¹¹ For the reaction of amines with CO$_2$/H$_2$, the production of methylamines is more difficult than that of formamides,¹²–¹⁷ and it requires harsh reaction conditions and catalysts with very high activity.¹⁸–²¹ 1,2-Bis(N-heterocyclic)ethanes (e.g., 1,2-bis(piperidine)ethane) are a kind of high value chemical and are generally synthesized via the reaction of cyclic amines with ethyl halides, suffering from production of a large amount of acid waste and complicated post-treatment.²²,²³ The synthesis of 1,2-bis(N-heterocyclic)ethanes from cyclic amines and CO$_2$/H$_2$ is a green and promising route, but this has not been realized yet.

Compared to molecular solvents (e.g., water and organic solvents), ionic liquids (ILs) that are completely composed of ions have unique properties, such as a wide liquid window, very low vapor pressure, specific H-bonding between anions and cations, and so on, which make them promising media for chemical processes.²⁴–²⁸ In particular, they can be designed with specific functions via selection of suitable cations and/or anions, and have been widely applied in catalysis, showing great potential. For example, as both the solvent and catalyst, 1-ethyl-3-methylimidazolium acetate worked well for the transformation of alcohols to esters using O$_2$ as an oxidant under metal-free conditions.²⁹ CO$_2$-philic ILs that can capture CO$_2$ via forming carbonates or carbamates have been reported to be excellent media and/or catalysts for CO$_2$ transformation into value-added chemicals.³⁰,³¹ 1-Butyl-3-methylimidazolium ([BMIm]$^+$) chloride combined with Rh nanoparticles and ZnCl$_2$ could realize the efficient reduction of heteroarenes.³² Carbanion-functionalized IL along with Pd(OAc)$_2$ was capable of catalyzing the alkyloxycarbonylation reactions of CO to benzoate products under ambient conditions.³³ In these

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reactions, ILs generate synergistic effects with other active species, promoting or catalyzing the reactions.

Herein, we report the reduction of CO\textsubscript{2} with amine and H\textsubscript{2} over an IL–Pd/C catalytic system, which accomplished the selective synthesis of formamides, 1,2-bis(N-heterocyclic) ethanes and methylamines. Interestingly, the combination of Pd/C with [BMIm][BF\textsubscript{4}] could realize the selective production of formamides (at 120 °C or N-methylamines (at 160 °C) in high yields, respectively, as illustrated in Scheme 1. Moreover, 1,2-bis(N-heterocyclic)ethanes can also be obtained via the McMurry reaction of the formed formamide coupled with subsequent hydrogenation. It was found that [BMIm][BF\textsubscript{4}] could react with formamide to form a [BMIm]–formamide adduct; thus combined with Pd/C, it can catalyse McMurry coupling of formamide in the presence of H\textsubscript{2} to afford 1,2-bis(N-heterocyclic)ethane and further catalyse hydrogenolysis of 1,2-bis(N-heterocyclic)ethanes to access methylamine. In addition, detailed studies indicate that the IL played multiple roles in the reactions including modifying the electronic properties of the metallic Pd particles to enhance their catalytic activity and activating the amine and the intermediate via strong hydrogen bonding. [BMIm][BF\textsubscript{4}]-Pd/C was tolerant to a wide substrate scope, giving the corresponding formamides, 1,2-bis(N-heterocyclic)ethanes or methylamines in moderate to high yields. This work develops a new route to N-methylamine and opens the way to produce 1,2-bis(N-heterocyclic)ethane from cyclic amine and CO\textsubscript{2}/H\textsubscript{2}.

Results and discussion
Preparation and characterization of the Pd/C catalyst
To prepare the Pd/C catalyst with a loading of 5 wt%, a porous carbon support was first fabricated according to our previous report, on which Pd nanoparticles were immobilized via the equal volume impregnation method followed by hydrogen reduction. In the TEM images of the Pd/C catalyst (Fig. 1a and b), the dark dots were identified as Pd nanoparticles, which were uniformly distributed on the support with an average particle size around 1.7 nm. The N\textsubscript{2} adsorption/desorption isotherms (Fig. 1c) indicated that the carbon support exhibited microporous and mesoporous structures with a specific surface area of 950.6 m\textsuperscript{2} g\textsuperscript{-1}. The pore radius distribution curve (Fig. 1d) showed that the pore radii were centered at 15 nm according to the BJH model, a typical feature of mesoporous materials accompanied by some micropores.

| Table 1 | The reaction of piperidine with CO\textsubscript{2}/H\textsubscript{2} over various catalytic systems\textsuperscript{a} |
|---|---|---|---|
| Entry | Solvent | 2a (%) | 3a (%) | 4a (%) |
| 1 | Ethanol | 99 | 0 | 0 |
| 2 | THF | 99 | 0 | 0 |
| 3 | Octane | 99 | 0 | 0 |
| 4 | [BMIm][BF\textsubscript{4}] | 6 | 11 | 82 |
| 5 | [BMIm][BF\textsubscript{4}] | 3 | 6 | 90 |
| 6 | [HMIm][BF\textsubscript{4}] | 17 | 22 | 49 |
| 7 | [BMIm][Cl] | 81 | 14 | 1 |
| 8 | [BMIm][PF\textsubscript{6}] | 46 | Trace | 53 |
| 9 | [BMIm][NTf\textsubscript{2}] | 67 | 13 | 18 |
| 10 | [P\textsubscript{4444}][BF\textsubscript{4}] | 99 | 0 | 0 |
| 11 | [N\textsubscript{4444}][BF\textsubscript{4}] | 99 | 0 | 0 |
| 12 | [BMIm][BF\textsubscript{4}] + [BMIm][Cl] | 16 | 57 | 26 |
| 13 | [BMIm][BF\textsubscript{4}] + THF | 1 | 77 | 22 |

\textsuperscript{a} Conditions: 1a (0.5 mmol), Pd/C (20 mg), solvent (1 mL) or IL (5 mmol), H\textsubscript{2} (6 MPa), total pressure of 10 MPa, 160 °C, 6 h. \textsuperscript{b} H\textsubscript{2} (5 MPa), total pressure of 8 MPa, [BMIm][BF\textsubscript{4}] (1.7 mmol), [BMIm][Cl] (3.3 mol), 9 h. \textsuperscript{c} H\textsubscript{2} (5 MPa), total pressure of 8 MPa, [BMIm][BF\textsubscript{4}] (2.5 mmol), THF (2.5 mL), 9 h. \textsuperscript{d} Yield was determined by GC using trimethoxybenzene as the internal standard.
affected the product selectivity. Molecular solvents including ethanol, tetrahydrofuran (THF) and octane exclusively afforded 2a (Table 1, entries 1–3), while imidazolium-based ILs including [BMIm][BF₄], [BMIm][PF₆], [BMIm][NTf₂] and [BMIm][Cl] could offer 2a, 3a and 4a in different yields under the experimental conditions (Table 1, entries 4–9). Among these ILs, [BMIm][BF₄] showed the best performance for the production of 4a, achieving a yield of 90% within 9 h (Table 1, entry 5). However, only 2a was obtained in the ILs [P4444][BF₄] and [N4444][BF₄] (Table 1, entries 10 and 11). These results indicated that for the imidazolium-based ILs the cations played a key role in the formation of 4a, and the anions influenced the activity of the cations. Given that 3a is an important chemical and it has not been accessed from 1a and CO₂/H₂, we optimized the reaction conditions to obtain 3a as the main product (Table S1†). Combined with Pd/C the mixtures of [BMIm][BF₄] with THF or with [BMIm][Cl] could afford 3a in yields higher than 50% at 160 °C (Table 1, entries 12 and 13). Considering that using THF as the reaction medium only 2a was obtained, it can be deduced that [BMIm][BF₄] and Pd/C combine to catalyze the formation of 3a and 4a.

Since [BMIm][BF₄]–Pd/C showed the best performance for methylation of 1a with CO₂/H₂ to 4a, it was applied to explore the effects of temperature and reaction time on the reaction. As illustrated in Fig. 2a, the reaction temperature significantly influenced the product selectivity. At 120 °C, 2a was the sole product in an almost quantitative yield within 9 h, while both 3a and 4a were detected in the temperature range of 130–160 °C with the 4a yield increasing with temperature up to 90% at 160 °C. Notably, the yield of 3a was maintained around 20% in this temperature range, while at 160 °C it decreased significantly and 4a became the main product. From the dependence of the 2a and 3a yields on the reaction time at 160 °C (Fig. 2b), it was deduced that 2a and 3a were finally converted into 4a under the experimental conditions.

**Generality of the [BMIm][BF₄]–Pd/C catalytic system**

To explore the generality of the [BMIm][BF₄]–Pd/C catalytic system, it was applied in the reactions of various cyclic amines with CO₂/H₂. As shown in Scheme 2, this catalytic system was effective for catalyzing the reactions of the tested substrates with CO₂/H₂, and formylated and methylated products were selectively obtained at 120 and 160 °C, respectively. Pyrrolidine, piperidine, hexamethylenimine, and morpholine exhibited good reactivity, affording corresponding formylated and methylated products in 90–99% yields under the optimized conditions. By using substituted piperidines like 3-methylpiperidine, 4-methylpiperidine, 2-methylpiperidine, 3,5-dimethylpiperidine, 1,2,3,4-tetrahydrosquinozoline and 1,2,3,4-tetrahydroquinoline as substrates, the reaction also proceeded smoothly and selectively furnished the desired products in moderate to high yields. However, 2-methylpiperidine was converted into the corresponding formamide (2d) only in 10% yield at 120 °C and 1,2,3,4-tetrahydroquinoline led to the corresponding methylamine in low yield.

After detailed screening of the reaction conditions, 1,2-bis(N-heterocyclic)ethanes could be achieved in moderate yields in most cases. The highest yield of 1,2-bis(N-heterocyclic)ethane (e.g., 3e) reached up to 77%. Interestingly, using pyridine, 4-methylpyrididine, and 4-phenylpyridine as the substrates, they were first hydrogenated, and the corresponding formamides and methylamines were obtained in high yields. However, in these cases corresponding 1,2-bis(N-heterocyclic)ethanes were detected in small amounts, and the reason is unclear. In addition, [BMIm][BF₄]–Pd/C was also effective in the reaction of chain secondary amines (e.g., 1,2-diaminopropane) with CO₂/H₂, selectively producing formamide or methylamine in excellent yields, but it was difficult to access the corresponding 1,2-bis(aminoo)ethane (Scheme S1†).

**The roles of the IL**

To explore the roles of the IL in the reactions, the interactions of the IL with Pd/C and with 1a, 2a, and 3a were investigated. Thermogravimetric analysis on the Pd/C catalysts after adsorption of IL at 120 °C and 160 °C (Fig. S1†) indicates that the amounts of the IL adsorbed on Pd/C reached 1.28 and 0.69 wt%, respectively, and its decomposition temperature (500 °C) was much higher than that of the free IL (380 °C). These results indicate that the IL had strong interaction with Pd/C.
The Pd/C adsorbing 1.28 wt% [BMIm][BF4] (denoted as IL–Pd/C) was examined by XPS. In the XPS spectrum of IL–Pd/C, the peaks at 340.8 (Pd 3d3/2) and 335.5 eV (Pd 3d5/2) attributed to Pd in Pd/C–IL exhibited a downshift of 0.3 eV compared with those of Pd/C (Fig. 3), indicating a possible electron transfer from the IL to the metallic Pd particles. This was also verified by the upshift of the N 1s peak of IL–Pd/C as compared to that of IL–C (Fig. S2†). IL–C refers to the IL adsorbed on a carbon support. The IR analysis (Fig. S3†) indicates that the adsorbed IL on Pd/C showed a red-shifted C–N stretching band of the IL cation from 1580 to 1575 cm⁻¹, which is consistent with electron donation from N atoms in [BMIm]+ to the Pd particles. FT-EXAFS spectra also gave evidence that the IL was complexed it because one N atom in the [BMIm]+ shifted greatly, suggesting the strong C–H...O interaction between the acidic H(2) of [BMIm]+ and the O atom of the formyl group in IL, also supporting the NMR results (Fig. 4b). As reported, the above results indicate that the IL can activate CO2 noticeably.

Furthermore, the interactions of [BMIm][BF4] with CO2, 1a, 2a and 3a were investigated via NMR analysis. No new signals or obvious chemical shifts were observed in the 1H, 13C, 19F and 11B NMR spectra of the mixture of [BMIm][BF4] and CO2 (Fig. S5†), indicating that this IL cannot activate CO2 noticeably. Given that 1a is easily converted to a white solid, dihydropyridine-monocarboxylic acid, once exposed to CO2, it is supposed that CO2 is activated by 1a via forming an adduct. 1H, 13N, 11B NMR (Fig. S6, S7A and B†) and FTIR (Fig. S8†) analyses on the [BMIm][BF4]–1a mixture indicate that 1a was activated by the IL via hydrogen bonding and electrostatic interaction. In the 1H NMR spectrum of the [BMIm][BF4]–2a mixture (Fig. 4a), the 1H signal of the formyl group in 2a and that of the H atoms in [BMIm]⁺ shifted greatly, suggesting the strong C–H...O interaction between the acidic H(2) of [BMIm]⁺ and the O atom of the formyl group in 2a. Specifically, the 13C NMR signals of the formyl group also shifted accordingly (Fig. S9†), further revealing the activation of the formyl group by the IL. In the FTIR spectrum, the absorption band at 1669 cm⁻¹ attributed to the stretching vibration of C==O of 1a shifted to 1664 cm⁻¹ upon 1a interacting with [BMIm][BF4], and the peaks at 3162 and 3122 cm⁻¹ belonging to the stretching vibration of C–H from the imidazole ring of [BMIm]⁺ shifted accordingly. The FTIR analysis gave evidence of the interaction between 1a and the IL, also supporting the NMR results (Fig. 4b). As reported, reactive carbenes can be generated at the C(2) position of [BMIm]⁺ under mild basic conditions. In this work, the basic reaction environment provided by 1a or 4a may be favorable for the formation of carbenes from [BMIm]⁺, which may further react with 2a to form an intermediate. To confirm this hypothesis, a mixture of IL and 2a together with K2CO₃ was examined. Based on 1H NMR and 1H–1H correlation spectroscopy (COSY) analysis (Fig. 4c and S10†), an intermediate from [BMIm][BF4] and 2a (denoted as [BMIm–OH–2a][BF4]) was detected (Fig. 4e), which was also confirmed by the detection of [BMIm–OH–2a][BF4][BMIm][BF4][2a]⁺ (m/z = 591.4) by electrospray-ionization mass spectrometry (ESI-MS) (Fig. S1†). The above results indicate that the IL can activate 2a to form a [BMIm]⁺–formamide adduct, which may be favorable for the formation of 3a and 4a. In addition, 3a can also be activated by the IL, as supported by NMR analysis with the obvious changes of chemical shifts as it mixed with the IL in the presence of 2a (Fig. S12†), which can explain why the IL promotes the hydrogenolysis of 3a.

**Possible reaction pathway**

To gain deep insight into the reaction pathway of the formation of 3a and 4a, control experiments were performed. Previous reports revealed that 2a could be catalytically converted to 4a via hydrogenation under appropriate conditions. However, in this work taking 2a as the substrate to react with CO2/H2 or only with H2 over Pd/C in [BMIm][BF4], no 4a was detectable (Scheme S2A and B†). This indicates that Pd/C could not catalyze the direct hydrogenation of 2a to 4a in [BMIm][BF4], which excludes the pathway of 2a reduction with H2, and implies that 2a undergoes transformation to 3a to form 4a.

![Fig. 3 Pd 3d XPS spectra of (a) Pd/C and (b) IL–Pd/C.](image-url)

![Fig. 4 1H NMR (a) and FT-IR spectra (b) of [BMIm][BF4], 2a and their mixture, and 1H NMR (c) of the mixture of IL and 2a together with K2CO3.](image-url)
As is known, McMurry coupling is a reductive reaction, in which two ketone or aldehyde groups are coupled to form an alkene using a titanium chloride compound (e.g., titanium(IV) chloride) and a reducing agent (e.g., zinc) in the presence of a base.\(^7\) In the process of 1a reacting with CO\(_2\)/H\(_2\), the reaction system is always kept in a basic environment due to the presence of the amine feedstock or the formed methylamine, which might facilitate the occurrence of the McMurry reaction of the formed formamide. To verify this, we treated 2a in the presence of 1a or 4a over Pd/C in [BMIm][BF\(_4\)] (Scheme 3a and b), and 3a was excitedly obtained in appreciable yields in both cases, different from the results shown in Scheme S2A and B.\(^*\) This suggests that the McMurry reaction of 2a may occur to produce 1,2-bis(piperidine)ethylene although it was not detected in the reaction process, because it can be rapidly hydrogenated to 3a catalyzed by Pd/C (Scheme 3c). Notably, on prolonging the reaction time to 12 h, both 2a and 3a disappeared, and 4a became the sole product (Scheme 3b). This indicates that 3a was further converted into 4a via hydrogenolysis under the experimental conditions, which was confirmed by the reaction of 3a with H\(_2\) over Pd/C in [BMIm][BF\(_4\)] containing t-BuOK to produce 4a (Scheme 3d). Generally, the C–N bond breaks more easily than the C–C bond. However, in this work the C–C bond rather than the C–N bond in 3a was broken. To give a reasonable explanation for this, Gaussian calculation was performed, which showed that the acidic hydrogen atom H(2) of [BMIm]\(^+\) could interact with an N atom of 3a, causing the length of the C–C bond in 3a to become longer (Fig. S13†). This may be responsible for the cleavage of the C–C bond in 3a to give 4a. [BMIm][BF\(_4\)] played a crucial role in the hydrogenolysis of 3a to 4a, deduced from the fact that without the IL, the hydrogenolysis of 3a did not occur even in the presence of the base t-BuOK (Scheme S2C†).

To identify possible intermediates in the reaction process, the reaction solution was analyzed by means of electrospray ionization mass spectrometry (ESI-MS). As shown in Fig. S14,† {H[BMIm][BF\(_4\)](1a)}\(^+\) (m/z = 312.2), {H[BMIm][BF\(_4\)](3a)}\(^+\) (m/z = 423.3), {[BMIm][N-(N-piperidinoglycolyl)piperidine](3a)}\(^+\) (m/z = 464.4), {[BMIm-[N-(N-piperidinoglycolyl)piperidine](2a)}\(^+\) (m/z = 476.4), {[BMIm–OH–2a][BF\(_4\)][BMIm](2a)}\(^+\) (m/z = 591.4) and {[BMIm][BF\(_4\)]/[BF\(_4\)][N-(N-piperidinoglycolyl)piperidine]} (m/z = 765.4) were detected, suggesting that under the experimental conditions, [BMIm–OH–2a][BF\(_4\)] and N-(N-piperidinoglycolyl)piperidine were the key intermediates and [BMIm][BF\(_4\)] played a vital role in activating and stabilizing them.

Based on the experimental results, a possible pathway is proposed, as shown in Scheme 4. Initially, 1a is activated by the IL via hydrogen bonding and electrostatic interaction and undergoes formylation with CO\(_2\)/H\(_2\) to yield 2a over Pd/C. Subsequently, an intermediate [BMIm–OH–2a][BF\(_4\)] is formed from 2a and [BMIm]\(^+\) in the presence of 1a, and the McMurry reaction proceeds through coupling of [BMIm–OH–2a][BF\(_4\)] with 2a to produce N-(N-piperidinoglycolyl)piperidine, followed by hydrogenation to form 3a. Finally, hydrogenolysis of 3a results in the formation of 4a. Notably, this is the first time that the McMurry reaction of formamide over Pd/C using H\(_2\) as a reductant has been realized, very different from the traditional routes.

### Conclusions

In summary, selective reduction of CO\(_2\) with cyclic amines and H\(_2\) was realized over the [BMIm][BF\(_4\)]–Pd/C catalytic system, and 1,2-bis(N-heterocyclic)ethanes were obtained via the McMurry reaction of formamide coupled with subsequent hydrogenation. [BMIm][BF\(_4\)] displayed multiple functions including improving...
the catalytic activity of Pd particles and activating the amine substrate and the formed formamide intermediate. [BMIm][BF₄]·Pd/C was tolerant to a wide substrate scope, giving the corresponding formamides, 1,2-bis(N-heterocyclic)ethanes or methylamines in moderate to high yields. We believe that these findings provide insights into achieving cooperativity between the IL and metal catalysts.

**Experimental**

**General procedures for the reaction of N-containing compounds with CO₂/H₂**

All reactions were performed in a stainless steel autoclave equipped with a Teflon tube (16 mL inner volume) and a magnetic stirrer. In a typical experiment, piperidine (0.5 mmol), [BMIm][BF₄] (5 mmol) and Pd/C (20 mg) were successively loaded into the autoclave under an N₂ atmosphere, and then the autoclave was sealed. H₂ (6 MPa) and CO₂ were charged successively into the reactor until the total pressure reached 10 MPa at room temperature. The autoclave was moved to a heating furnace at 433 K. After the desired reaction time, the reactor was cooled down in ice water and the gas inside was vented slowly. Trimethoxybenzene (internal standard) and diethyl ether were added to the reaction solution, stirred vigorously and centrifuged. The upper liquid was extracted for analysis.

**Product analysis**

Liquid samples were analysed using a gas chromatograph (Agilent 4890D) equipped with an ultra-inert capillary column (19091S-433UI HP-5 ms). NMR spectra were collected using (Agilent 4890D) equipped with an ultra-inert capillary column. Liquid samples were analysed using a gas chromatograph. Product analysis was performed using the same equipment in succession. 1H NMR data recorded in d-CDCl₃ were listed with the residual CHCl₃ at 77.17 ppm. FT-IR spectra were obtained using a Bruker IFS 37 spectrometer. Electron storage ring was operated at 3.5 GeV. Data processing was performed using the program ATHENA. The electrospay ionization mass spectrometry (ESI-MS) data (in both negative and positive modes) were collected using a Bruker 9.4T Solarix instrument.

**Conflicts of interest**

There are no conflicts to declare.

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**Notes and references**