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Selective Synthesis of Formamides, 1,2-Bis(Nheterocyclic)ethanes and Methylamines from Cyclic Amines and CO₂/H₂ Catalyzed by Ionic Liquid-Pd/C system

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The reduction of CO₂ with amines and H₂ 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 methylamine, which is achieved over ionic liquid (IL, e.g., 1-butyl-3-methylmidazolium tetrafluoroborate, [BMIm][BF₄])-Pd/C catalytic system. By simply varying the reaction temperature, formamides and methylamine can be selectively produced, respectively, in high yields. Interestingly, 1,2-bis(N-heterocyclic)ethanes can also be obtained via McMurry reaction of the formed formamide coupled with subsequent hydrogenation. It was found that [BMIm][BF₄] can react with formamide to form [BMIm]⁺-formamide adduct, thus combined with Pd/C it can catalyze McMurry coupling of formamide in the presence of H₂ to afford 1,2-bis(N-heterocyclic)ethane to access methylamine. [BMIm][BF₄] can further catalyze the hydrogenolysis of 1,2-bis(N-heterocyclic)ethane to access methylamine. [BMIm][BF₄]-Pd/C was tolerant to a wide substrate scope, giving the corresponding formamides or 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

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Carbon dioxide (CO₂) is an abundant, readily available, nontoxic and renewable C1 building block, and its transformation into valueadded chemicals and fuels is of great significance for green and sustainable development.¹⁻⁶ The reactions of amines with CO₂ in the presence of reductants such as hydrosilanes and H₂ have been widely investigated, which 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 the formation of formamides,¹²⁻¹⁷ which requires harsh reaction conditions and the 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 chemicals, which are generally synthesized via the reaction of cyclic amines with ethyl halides, suffering from production of large amount of acid waste and complicated posttreatment.^{22,23} The synthesis of 1,2-bis(N-heterocyclic)ethanes from cyclic amines and CO₂/H₂ provides 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 wide liquid window, very low vapor pressure, specific H-bonding between anion and cation, and so on, which make them promising media for chemical processes.24-28 Particularly, they can be designed with specific functions via selection of suitable cations and/or anions, and have been widely applied in catalysis, showing great potentials. For example, as both solvent and catalyst 1-ethyl-3-methylimidazolium acetate worked well for the transformation of alcohols to esters using O₂ as an oxidant under metal-free conditions.²⁹ CO₂-philic ILs that can capture CO_2 via forming carbonates or carbamates have been reported to be excellent media and/or catalysts for CO₂ transformation into value-added chemicals.^{30,31} 1-Butvl-3methylimidazolium ([BMIm]⁺) chloride combined with Rh nanoparticles and ZnCl₂, could realize the efficient reduction of heteroarenes.³² Carbanion-functionalized IL along with Pd(OAc)₂ was capable of catalyzing the alkoxycarbonylation reactions of CO to benzoate products under ambient conditions.³³ In these reactions, ILs generate synergistic effects with other active species, promoting or catalyzing the reactions.

Herein, we report the reduction of CO₂ with amine and H₂ over 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][BF₄] could realize the selective production of formamides (at 120 °C) or N-methylamines (at 160 °C) in high yields, respectively, as illustrated

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in Scheme 1. Moreover, 1,2-bis(N-heterocyclic)ethanes can also be obtained via McMurry reaction of the formed formamide coupled with subsequent hydrogenation. It was found that [BMIm][BF₄] could react with formamide to form [BMIm]*-formamide adduct, thus combined with Pd/C, catalyse McMurry coupling of formamide in the presence of H₂ to afford 1,2-bis(N-heterocyclic)ethane, and further catalyse hydrogenolysis of 1,2-bis(N-heterocyclic)ethane to access methylamine. In addition, the detailed studies indicate that the IL played multiple roles in the reactions with modifying the electronic property of the metallic Pd particles to enhance their catalytic activity, activating the amine and the intermediate via strong hydrogen bonding. [BMIm][BF₄]-Pd/C was tolerant to a wide substrate scope, giving the corresponding formamides or 1,2-bis(Nheterocyclic)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 and CO₂/H₂.



Scheme 1. Selective reduction of CO₂ with amines and H₂.

Results and discussion

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Preparation and characterization of the Pd/C catalyst.



Fig. 1 TEM (a) and HRTEM (b) images, N_2 sorption isotherms (c) and pore size distribution (d) of the Pd/C catalyst used in this work.

To prepare the Pd/C catalyst with loading of 5 wt%, the porous carbon support was first fabricated according to our previous report³⁴, on which Pd nanoparticles were immobilized via equal volume impregnation method followed by hydrogen reduction. In the TEM images of the Pd/C catalyst (Fig. 1a and 1b), 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 N₂ adsorption/desorption isotherms (Fig. 1c), indicate that the carbon support exhibited microporous ¹(a)(P^{9})(mesoporous structures with specific surface area of 950.6 m²/g. The pore radius distribution curve (Fig. 1d) displayed that the pore diameters were centered at 15 nm according to the BJH model, a typical feature of mesoporous materials accompanied with some micropores.

Exploration on catalytic system for reaction of piperidine with CO_2/H_2 .

Table 1. The reaction of piperidine with CO_2/H_2 over various catalytic systems.^{*a*}

$ \underbrace{ \bigvee_{NH} + CO_2 + H_2 \xrightarrow{solvent} }_{Pd/BMC} \underbrace{ \bigvee_{N} & \bigvee_{N} + \underbrace{ \bigvee_{N} }_{N} + \underbrace{ \bigvee_{N} }_{N} $					
1 a	24	a	3a		4a
Fisher .	Calvant		Yield (%) ^e		
Entry	Solvent		2a	3a	4a
1	Ethanol		99	0	0
2	THF		99	0	0
3	Octane		99	0	0
4	[BMIm][BF ₄]		6	11	82
5 ^b	[BMIm][BF ₄]		3	6	90
6	[HMIm][BF ₄]		17	22	49
7	[BMIm][Cl]		81	14	1
8	[BMIm][PF ₆]		46	trace	53
9	[BMIm][NTf ₂]		67	13	18
10	[P ₄₄₄₄][BF ₄]		99	0	0
11	[N ₄₄₄₄][BF ₄]		99	0	0
12 ^c	[BMIm][BF ₄]+[BMIm]	[CI]	16	57	26
13 ^d	[BMIm][BF ₄]+THF		1	77	22

^{*a*} Conditions: **1a** (0.5 mmol), Pd/C (20 mg), solvent (1 mL) or IL (5 mmol), H₂ (6 MPa), total pressure of 10 MPa, 160 °C, 6 h. ^{*b*} 9 h. ^{*c*} H₂ (5 MPa), total pressure of 8 MPa, [BMIm][BF₄] (1.7 mmol), [BMIm][CI] (3.3 mol), 9 h. ^{*d*} H₂ (5 MPa), total pressure of 8 MPa, [BMIm][BF₄] (2.5 mmol), THF (2.5 mL), 9 h. ^{*e*} H₂ Vield was determined by GC using trimethoxybenzene as an internal standard.

In our initial experiments, the reaction of piperidine (1a) with CO_2/H_2 was performed using Pd/C as the catalyst to screen the catalytic system and reaction conditions for selective formation of formylpiperidine (2a) or 1,2-bis(piperidine)ethane (3a) or methylpiperidine (4a). In the absence of CO_2 and H_2 , no product was detected. As shown in Table 1, the solvents significantly affected the product selectivity. Molecular solvents including ethanol, tetrahydrogenfuran (THF) and octane exclusively afforded 2a (Table 1, entries 1-3), while the 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 involving $[P_{4444}][BF_4]$ and $[N_{4444}][BF_4]$ (Table 1, entries 10-11). These results indicated that for the imidazolium-based ILs the cations played 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 CO_2/H_2 , we optimized the reaction conditions to get 3a as the main product (Table S1). It was indicated that combined with Pd/C the mixtures of

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 $[BMIm][BF_4]$ with THF or with [BMIm][CI] could afford **3a** in yields higher than 50% at 160 °C (Table 1, entries 12-13). Considering that using THF as the reaction medium only **2a** was obtained, it can be deduced that $[BMIm][BF_4]$ and Pd/C cooperated to catalyze the formation of **3a** and **4a**.



Fig. 2 Effects of temperature (a) and reaction time (b) on the conversion of **1a** and the yields of **2a**, **3a** and **4a**. (a) 9 h. (b) 160 °C.

Since $[BMIm][BF_4]$ -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** yields 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** 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 CO_2/H_2 , and formylated and methylated products were selectively obtained at 120 and 160 °C, respectively. Pyrrolidine, piperidine, hexamethyleneimine, 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, 2-3,5-dimethylpiperidine, methylpiperidine. 1.2.3.4tetrahydroisoquinoline and 1,2,3,4-tetrahydroquinoline as substrates, the reaction also proceeded smoothly and selectively furnished the desired products in moderate to high yields. Whereas, 2-methylpiperidine was converted into corresponding formamide (2d) only in 10% yield at 120 °C, and 1,2,3,4-tetrahydroguinoline led to corresponding methylamine in low yield.

After detailed screening of 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-methylpyridine, 4-phenylpyridine as the substrates, they were first hydrogenated, and 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 for chain secondary amine (e.g., 1,2-diaminopropane) reacting with CO_2/H_2 , selectively producing formamide or methylamine in

excellent yields, but difficult to access corresponding 12bis(amino)ethane (Scheme S1). DOI: 10.1039/C9SC03242H





For N-formylation: substrate (0.5 mmol), Pd/C (20 mg), [BMIm][BF₄] (5 mmol), H₂ (3 MPa), total pressure of 5 MPa, 120 °C, 6 h, isolated yield was in the bracket. For methylation: H₂ (6 MPa), total pressure of 10 MPa, 160 °C, 6 h, the others are same as those for N-formylation. For accessing 1,2-bis(N-heterocyclic)ethanes: substrate (0.5 mmol), Pd/C (20 mg), [BMIm][BF₄] (1.7 mmol), [BMIm][Cl] (3.3 mmol), H₂ (5 MPa), total pressure of 8 MPa, 6 h. *a* 12 h. *b* 10 h. ^c 140 °C, 9 h. *d* 140 °C, 12 h,^e 160 °C, 24 h.

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 absorbing 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 decomposed 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.



Fig. 3 Pd 3d XPS spectra of (a) Pd/C and (b) IL-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 $3d_{3/2}$) and 335.5 eV (Pd $3d_{5/2}$) attributing to Pd⁰ 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 IL to the metallic Pd particles. This was also verified by the upshift of N 1s peak of IL-Pd/C as compared to that of IL-C (Fig. S2, IL-C refers to the IL-adsorbed on carbon support). The IR analysis (Fig. S3) indicates that the adsorbed IL on Pd/C showed red-shifted C-N stretching band of IL cation from 1580 to 1575 cm⁻¹, which is consistent with electron donation from N atom in [BMIm]⁺ to the Pd particles. FT-EXAFS spectra also gave the evidence that the IL complexed with Pd (Fig. S4). It is reasonable that the lone electron pair of N can affect the

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electronic state of the Pd particles attached to them because one N atom in $[BMIm]^+$ cation is essentially in the sp^2 hybridization state.



Fig. 4 ¹H NMR (a), FT-IR spectra (b) of [Bmim][BF₄], **2a** and their mixture, and ¹H NMR (c) of the mixture of IL and **2a** together with K_2CO_3 .

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 white solid, dihydropyridine-monocarboxylic acid, once exposing to CO₂, it is supposed that CO₂ is activated by 1a via forming adduct. The ¹H, ¹⁵N, ¹¹B NMR (Fig. S6, S7A and S7B) and FTIR (Fig. S8) analysis 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 [BMIm][BF₄]-2a mixture (Fig. 4a), the ¹H signal to the formyl group in **2a** and those to 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 formyl group in 2a. Specifically, the ¹³C NMR signals to formyl group also shifted accordingly (Fig. S9), further revealing the activation of formyl group by the IL. In the FTIR spectrum, the absorption band at 1669 cm⁻¹ attributing to 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 imidazole ring of [BMIm]⁺ shifted accordingly. The FTIR analysis gave the evidence of 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.³⁵ In this work, the basic reaction environment provided by 1a or 4a may be favorable to the formation of carbenes from [BMIm]⁺, which may further react with 2a to form intermediate. To confirm this hypothesis, the mixture of

IL and **2a** together with K_2CO_3 was examined. Based on the 14 MMB and ¹H-¹H correlation spectroscopy (COSY) analysis (FB). Ac and Fig. S10), an intermediate from [BMIm][BF₄] and **2a** (denoted as [BMIm-OH-**2a**][BF₄]) was detected (Fig. 4c), which was also confirmed by the detection of {[BMIm-OH-**2a**][BF₄][BMIm](**2a**)}⁺ (m/z=591.4) in the electrospray-ionization mass spectrometry (ESI-MS) (Fig. S11). The above results indicate that the IL can activate **2a** to form [BMIm]⁺-formamide adduct, which may be favorable to the formation of **3a** and **4a**. In addition, **3a** can also be activated by the IL, supported by the 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 to form **3a** and **4a**, control experiments were performed. Previous reports revealed that **2a** could catalytically convert to **4a** via hydrogenation under appropriate conditions.³⁶ However, in this work taking **2a** as the substrate to react with CO_2/H_2 or only with H_2 over Pd/C in [BMIm][BF₄], no **4a** was detectable (Scheme S2A and S2B). 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 H_2 , and implies that **2a** undergoes **3a** to form **4a**.





As known, McMurry coupling is a reductive reaction, in which two ketone or aldehyde groups are coupled to form an alkene using titanium chloride compound (e.g., titanium (IV) chloride) and a reducing agent (e.g, Zinc) in the presence of a base.³⁷ In the process of **1a** reacting with CO_2/H_2 , the reaction system always kept basic environment due to the presence of the amine feedstock or the formed methylamine, which might facilitate McMurry reaction of the formed formamide to occur. To verify this, we treated **2a** in the presence of **1a** or **4a** over Pd/C in [BMIm][BF₄], respectively (Scheme 3a, 3b), and **3a** was excitingly obtained in appreciate yields This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.

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in both cases, different from the results as shown in Scheme S2A and S2B. This suggests that 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, prolonging reaction time to 12 h, both 2a and 3a disappeared, and 4a became the sole product (Scheme 3b). This indicates that 3a 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][BF₄] containing t-BuOK to produce 4a (Scheme 3d). Generally, C-N bond breaks more easily than C-C bond. However, in this work the C-C bond rather than C-N bond in 3a was broken. To give the reasonable explanation on this, Gaussian calculation was performed, which showed that the acidic hydrogen atom H(2) of [BMIm]⁺ could interact with N atom of 3a, inducing the length of C-C bond in 3a to become longer (Fig. S13). This may be responsible for the cleavage of C-C bond in **3a** to give **4a**. [BMIm][BF₄] played the 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 base *t*-BuOK (Scheme S2C).



Scheme 4. Plausible pathways for formation of 2a, 3a and 4a.

To identify possible intermediate in the reaction process, the reaction solution was analyzed by means of electrospray ionization mass spectrometry (ESI-MS.) As shown in the Fig. S14, {H[BMIm][BF₄](1a)]}* (m/z=312.2), {H[BMIm][BF₄](3a)]}* {[BMIm][N-(N-piperidinoglycolyl)piperidine](4a)}* (m/z=423.3), (m/z=464.4),{[BMIm-[N-(N-piperidinoglycolyl)piperidine](2a)}+ (m/z=476.4), {[BMIm-OH-2a][BF₄][BMIm](2a)}⁺ (m/z=591.4) and {([BMIm][BF₄])₂[BF₄][N-(N-piperidinoglycolyl)piperidine]} (m/z=765.4) were detected, suggesting that under the experimental conditions, [BMIm-OH-2a][BF₄], N-(Nand piperidinoglycolyl)piperidine were the key intermediates and [BMIm][BF₄] played a vital role in activating and stabilizing them.

Based on the experimental results, a possible is pathway units proposed, as shown in Scheme 4. Initially, $\mathbf{12}^{-1}$ is activated by the lt via hydrogen bond and electrostatic interaction, and undergoes formylation with CO₂/H₂ to yield **2a** over Pd/C. Subsequently, an intermediate [BMIm-OH-**2a**][BF₄] is formed from **2a** and [BMIm]⁺ in the presence of **1a**, and McMurry reaction proceeds through coupling of [BMIm-OH-**2a**][BF₄] 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, it is for the first time to realize McMurry reaction of formamide over Pd/C using H₂ as a reductant, 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][BF₄]-Pd/C catalytic system, and 1,2-bis(N-heterocyclic)ethanes were obtained via McMurry reaction of formamide coupled with subsequent hydrogenation. [BMIm][BF₄] displayed multiple functions with 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 or 1,2-bis(N-heterocyclic)ethanes or methylamines in moderate to high yields. We believe that these findings provide insights into achieving cooperativity between 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 to 10 MPa at room temperature. The autoclave was moved to a heating furnace of 433 K. After 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 to analyse.

Product analysis. Liquid sample was analysed by gas chromatography (Agilent 4890D) equipped with an ultra-inert capillary column (19091S-433UI HP-5ms). NMR spectra were collected in a coaxial insert NMR tube with d⁶-DMSO in the internal tube as a reference, recorded by Bruker 400 HD (¹H NMR, ¹¹B NMR and ¹³C NMR spectra) and Bruker 600 instruments (¹⁵N NMR, ¹⁹F NMR spectra and ¹H-¹H correlation spectrum (¹H-¹H COSY)). ¹¹B NMR and ¹⁹F NMR spectra were operated in the same equipment in succession. ¹H NMR data recorded in d⁶-DMSO was listed as the residual of DMSO as 2.50 ppm, while ¹³C NMR as 39.51 ppm, ¹H NMR data in d-CDCl₃ was listed as the residual of CHCl₃ as 7.26 ppm, while ¹³C NMR as 77.17 ppm. FT-IR spectra were recorded by Bruker

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Tensor-27 instrument, scanning from 400 to 4000 cm⁻¹. The transmission electron microscopy (TEM) images were obtained by JEOL-2100F. X-ray photoelectron spectroscopy (XPS) were collected on an ESCALab220i-XL electron spectrometer from VG Scientific at a pressure of 3×10^{-9} mbar using 300 W Al-K α radiation. The binding energies (BEs) were referenced to the C 1s line at 284.8 eV from adventitious carbon. The X-ray absorption data at the Pd K-edge of the samples were recorded at room temperature in fluorescence mode with silicon drift fluorescence detector at beam line BL14W1 of the Shanghai Synchrotron Radiation Facility (SSRF), China. The electron storage ring was operated at 3.5 GeV. Data processing was performed using the program ATHENA. The electrospray ionization mass spectrometry (ESI-MS) data (in both the negative and positive modes) was collected by Bruker 9.4T Solarix instrument model.

Conflicts of interest

There are no conflicts to declare.

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Selective Synthesis of Formamides, 1,2-Bis(N-heterocyclic)ethanes and Methylamines from Cyclic Amines and CO2/H2 Catalyzed by Ionic Liquid-Pd/C system

80x40mm (300 x 300 DPI)