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Eco-friendly acetylcholine-carboxylate bio-ionic liquids for controllable *N*-methylation and *N*-formylation using ambient CO_2 at low temperatures†

Wenfeng Zhao,[a] Xiaoping Chi,[b] Hu Li, *[a] Jian He,[a] Jingxuan Long,[a] Yufei Xu[a] and Song Yang *[a]

Catalytic fixation of CO_2 to produce valuable fine chemicals is of great significance to develop a green and sustainable circulation of excessive carbon in the environment. Herein, a series of non-toxic, biodegradable and recyclable acetylcholine-carboxylate bio-ionic liquids with different cations and anions were simply synthesized for producing formamides and methylamines using atmospheric CO_2 as a carbon source, and phenylsilane as a hydrogen donor. The selectivity toward products was tuned by altering the reaction temperature under solvent or solvent-free conditions. *N*-Methylamines (*ca.* 96% yield) were obtained in acetonitrile at 50 °C, while *N*-formamides (*ca.* 99% yield) were attained without a solvent at 30 °C. The established bio-ionic liquid catalytic system found a wide range of applicability in substrates and possessed a high potentiality in scale-up to gram-grade production. The developed catalytic system was fairly stable, which could be easily reused without an apparent loss of reactivity, possibly due to the strong electrostatic interactions between the cation and anion. The combination of experimental and computational results explicitly elucidated the reaction mechanism: $PhSiH_3$ activated by a bio-IL was favorable for the formation of silyl formate from hydrosilylation of CO_2, followed by a reaction with an amine to give an *N*-formamide, while an *N*-methylamine was formed by further hydrosilylation of the *N*-formamide.

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Introduction

Carbon dioxide, known as the main reason for the "greenhouse effect", has stimulated much effort to develop technologies and methods for the decrease of the CO_2 level in the atmosphere. In view of sustainable development, employing CO_2 as an abundant, nontoxic and cheap C1 building block resource for the production of value-added chemicals has recently emerged as a meaningful way to mitigate the greenhouse effect.[1–3] Although the CO_2 molecule is fairly stable both in terms of thermodynamics and kinetics, many strategies involving the formation of C–C, C–O and C–N bonds for chemical fixation of CO_2 have been developed.[4] Most of the reported CO_2 valorization strategies for C–C and C–O bond construction, such as the conversion of CO_2 into carboxylic acids,[5] cyclic carbonates[6–8] and heteroarene acids,[9,10] usually require relatively hash reaction conditions. However, C–N bond construction, as a promising process for the utilization of CO_2, has attracted much attention considering that it can be realized under relatively mild conditions.[11] Recently, a series of formylation and methylation products, which are widely applied as superior solvents and medicinal chemicals, were able to be synthesized *via* reductive functionalization of CO_2 with amines.[12,13]

To obtain *N*-substituted compounds from CO_2 *via* *N*-formylation and *N*-methylation, CO_2 should be reduced first. Although various hydrogen donors such as hydrogen have been widely used in the C–N bond construction of amines with CO_2, the hydrosilane provided more advantages including easy handling, low energy dissipation and high selectivity, showing better application prospects.[14–18] In recent years, precious and transition metal complexes, such as Pd,[19] Zn[20] and Cu[21] with corresponding ligands, have been developed to acti-

[a]*State Key Laboratory Breeding Base of Green Pesticide & Agricultural Bioengineering, Key Laboratory of Green Pesticide & Agricultural Bioengineering, Ministry of Education, State-Local Joint Laboratory for Comprehensive Utilization of Biomass, Center for Research & Development of Fine Chemicals, Guizhou University, Guiyang, Guizhou 550025, China. E-mail: jhzx.msm@gmail.com, hli13@gzu.edu.cn; Fax: (+86)851 88292170; Tel: (+86)851 88292171*

[b]*Beijing National Laboratory of Molecular Science, State Key Laboratory of Molecular Reaction Dynamics, Institute of Chemistry, Chinese Academy of Sciences; University of Chinese Academy of Sciences, Beijing 100049, China*

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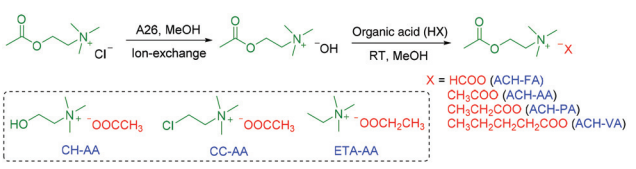
vate this reaction in the presence of hydrosilanes. As is well known, metal complex systems were efficient for C–N bond construction, but they were toxic for the environment and needed complicated preparation processes. Many basic metal salts such as Cs_2CO_3 and K_2WO_4 have also been utilized in the transformation of CO_2 to *N*-formamide and *N*-methylamine.[22,23] However, these catalytic systems suffered from relatively rigorous reaction conditions (long time ≥12 h, 2 MPa CO_2) and the used catalysts could not be reused. On the other hand, numerous metal-free catalysts such as NHCS,[24] TBAF[25] and thiazolium carbine[26] have been testified to be only capable of promoting *N*-formylation, and these catalysts were unstable which resulted in the difficulty of catalyst recycling as well. In order to enable the recyclability of the catalysts, heterogeneous polymeric materials such as functional ionic polymers, zwitterionic covalent organic frameworks, and poly-*N*-heterocyclic carbines have been developed for catalysing C–N construction,[27–29] while tedious catalyst preparation processes with rigorous reaction conditions were often required. In this regard, ionic liquids (ILs) exhibited unique properties such as good chemical stability, tuneable active sites and low vapour pressure, which have been applied in many catalytic systems.[30,31] Although a number of ionic liquids have been developed for CO_2 conversion into valuable chemicals,[32–36] only a few studies focused on C–N construction.[37,38] Moreover, the extensive application of those imidazolium-based or halide-containing ionic liquids was limited by issues of toxicity, ecology, and economy.

Choline-based ILs, known as "Bio-ILs" composed wholly of biomaterials, have superior features of low toxicity, relatively high stability and fewer negative effects on the environment.[39–42] Not surprisingly, choline-based ILs have attracted substantial attention in organic synthesis because they are biodegradable and cheap. These ILs are conjugate bases of weak acids; therefore these "Bio-ILs" might possess strong basicity, which could enable efficient catalysis of the production of formamides and methylamines from CO_2 and amines in the presence of organosilanes. To the best of our knowledge, the choline-based ILs as catalysts for reductive fixation of CO_2 have rarely been reported.

Herein, we prepared a series of new acetylcholine-based ILs, as shown in Scheme 1, which could be used as non-toxic, cheap and efficient bio-catalysts for producing *N*-substituted compounds from CO_2 employing a hydrosilane as the reductant under benign conditions. A variety of amines were able to be converted into corresponding methylamines in considerable yields (up to 96%) in acetonitrile. On the other hand, the corresponding formamides were smoothly achieved (up to 99%) under solvent-free conditions. Remarkable electrostatic interactions between the cation and anion in an acetylcholine-based IL have been verified by a computational study, illustrating that the IL has good stability. Notably, this readily available acetylcholine-based IL can be reused at least five times with little loss of activity. A relatively reasonable mechanism was affirmed and elucidated by using DFT calculations and NMR study.



Scheme 1 Schematic illustration of the preparation of ionic liquid catalysts.

Experimental

Materials

Acetylcholine chloride (98%), chlormequat (98%), ethyltrimethylammonium iodide (98%), choline hydroxide, formic acid (98%), acetic acid (99%), propionic acid (99%), valeric acid (98%), and Amberlyst A26 (OH-form) were purchased from TCI Inc. (Shanghai). *N*-Methylaniline (98%), *N*-methylformanilide (99%), *N*,*N*-dimethylaniline (99%), *N*-methylcyclohexylamine (99%), *N*-butylaniline (99%), *N*-ethylpropylamine (98%), 2-methoxy-*N*-methylaniline (99%), *N*-methylbenzylamine (97%), *N*-methyl-1-(thiophen-2-yl) methanamine (95%), *N*-methyl-4-ethylbenzylamine (97%), *N*-benzylaniline (99%), *N*-methyl-*o*-toluidine (95%), *N*-methyl-*p*-toluidine (97%), *N*-ethylaniline (98%), *N*-benzylmethylamine (97%), *N*-cyclohexylaniline (98%), *N*-allylaniline (97%), 4-chloro-*N*-methylaniline (97%), 4-methoxy-*N*-methylaniline (97%), 4-bromo-*N*-methylaniline (97%), *N*-methyl-4-nitroaniline (97%), diethylamine (99%), *N*-benzyl-*p*-anisidine (99%), *N*-methyl-4-(4-morpholinyl) benzylamine (97%), naphthalene (99%), and pyrrolidine (99%) were bought from Aladdin Industrial Inc. (Shanghai). Phenylsilane (98%), morpholine (99%), acetonitrile-d_3 (99 atom% D), poly(methylhydrosiloxane) (PMHS), *n*-hexane (99%), ethanol (EtOH, 99%), acetonitrile (CH_3CN, 99%), tetrahydrofuran (THF, 99%), ethyl acetate (EA, AR), triethoxysilane (98%), diphenylsilane (>98%), triethylsilane (99%), sodium acetate (99%), and potassium acetate (99%) were bought from Beijing Innochem Sci. & Tech. Co. Ltd. Diphenyl (silane-d_2, 97 atom% D) was purchased from Sigma-Aldrich Co. LLC.

Catalyst preparation

Acetylcholine-based ionic liquids (ACH-ILs) with carboxylate anions with variable carbon-chain lengths, including acetylcholine formate (ACH-FA), acetylcholine acetate (ACH-AA), acetylcholine propionate (ACH-PA), and acetylcholine valerate (ACH-VA), were synthesized by a two-step ion exchange method at room temperature (Scheme 1). In a typical procedure, to a solution of 4 mmol acetylcholine chloride dissolved in 5 mL methanol in a 25 mL flask, solid Amberlyst A26 (2.5 g) was added to exchange a chloridion with an hydroxide. After stirring at room temperature for 12 h, the used Amberlyst A26 was removed by filtration. The ion-exchange process was repeated by adding fresh Amberlyst A26 (2.5 g) into the filtrate under

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identical reaction conditions to give acetylcholine hydroxide. After the removal of Amberlyst A26, acetic acid (4 mmol) was added into the resulting solution to enable neutralization with acetylcholine hydroxide. After stirring vigorously for 12 h, the target IL acetylcholine acetate was obtained by removing methanol and water under reduced pressure. To evaluate the effect of cations, other acetate ILs containing different cations, including choline acetate (CH-AA), ethyltrimethylammonium acetate (ETA-AA), and chlormequat acetate (CC-AA), were also synthesized using the same method.

Catalyst characterization

FT-IR spectra were recorded on a Thermo Fisher Scientific Nicolet iS50 equipped with a Smart Diamond ATR Accessory under ambient conditions in KBr disks. Structures of ILs were also identified by ^{1}H NMR and ^{13}C NMR using an Avance III HD-400 spectrometer at room temperature operating at 400 MHz.

Computational method

All structure optimization and energy calculations were performed using density functional theory (DFT) employing the B3LYP functional implemented in the Gaussian 09 program package. Pople's all-electron basis set 6-311G (d,p) was used for all atoms.[43–45] CC-AA was chosen as a model catalyst for transient state calculation.

Reaction procedures

***N*-Methylation of amines with ambient CO_2.** The *N*-methylation reaction of secondary and primary amines with CO_2 in the presence of a hydrosilane was conducted in a 15 mL reaction tube with an inner joint and a 2 mm glass stopcock equipped with a magnetic stirrer. In a typical experiment, the reaction tube was vacuumized by using a mechanical pump at first. Then, the amine (0.25 mmol), ACH-AA (6% mmol), 1 bar CO_2, 2.0 mL CH_3CN and phenylsilane (0.75 mmol) were successively added into the tube. This reaction mixture was stirred at 50 °C for 6 h. Upon completion of the reaction, the conversion and yield were determined by GC (Agilent 7890B) using naphthalene as an internal standard.

***N*-Formylation of amines with ambient CO_2.** In a typical process to synthesize a formamide from an amine and CO_2, the reaction tube was initially vacuumized by using a mechanical pump. Then, the amine (0.25 mmol), ACH-AA (6% mmol), 1 bar CO_2 and phenylsilane (0.75 mmol) were successively added into the reaction tube. The solvent-free reaction mixture was stirred at 30 °C for 6 h. After the reaction completed, the resulting mixture was diluted with CH_2Cl_2, and the liquid products were quantitatively analyzed by GC using naphthalene as an internal standard.

Deuterium-labeling study. ^{1}H NMR, ^{13}C NMR, and GC-MS spectra were recorded for the reaction mixtures of *N*-methylaniline and CO_2 after being reacted in CD_3CN-d_3 with D-labeled silicon: diphenyl (silane-d_2). In a typical reaction process, the reaction tube (15 mL) was vacuumized by using a mechanical pump at first, into which the amine (0.25 mmol), ACH-AA (6% mmol), 1 bar CO_2, 2.0 mL CD_3CN-d_3 and diphenyl (silane-d_2) (0.75 mmol) were successively added, and kept stirring at 50 °C for 6 h.

Scale-up reaction study. 12.5 mmol *N*-methylaniline (1.35 g), 6% mmol ACH-AA (0.3 g), 10 mL CH_3CN and 37.5 mmol $PhSiH_3$ were added into a 25 mL magnetic Harrington reactor. The reaction mixture was stirred at 500 rpm using 1 bar CO_2 at 50 °C for 48 h. This reaction was also conducted with identical feeding using 2.0 MPa CO_2 at 50 °C for 20 h. The conversion and yield were determined by GC using naphthalene as an internal standard.

Catalyst recycling study

The catalyst recyclability of ACH-AA was examined under the optimal reaction conditions for the synthesis of *N*,*N*-dimethylaniline: 0.25 mmol *N*-methylaniline, 6% mol ACH-AA, 0.75 mmol $PhSiH_3$, 2 mL CH_3CN, 1.0 bar CO_2, 50 °C and 6 h. After each cycle of the reaction, 2 mL water was added into the reaction mixture, and then the aqueous phase was disengaged by the addition of 2 mL diethyl ether, and repeatedly extracted for three times. Then, 10 mg activated carbon was added to the resulting water phase and stirred (200 rpm) at room temperature for 24 h to thoroughly remove siloxane products and impurities. After the removal of the solid residue by filtration, the recovered ACH-AA was obtained by removing water under reduced pressure at 80 °C, which was then directly employed for the next run.

Sample analysis

The concentrations of *N*-methylaniline, *N*,*N*-dimethylaniline and *N*-methylformanilide were determined using a GC instrument equipped with an HP-5 chromatographic column (30 m × 0.320 mm × 0.25 μm) and an FID, using naphthalene as an internal standard referring to the standard curves (R^2 > 0.999) obtained with commercial specimens. Other substrates and corresponding products were quantified by ^{1}H NMR spectroscopy of the crude reaction mixture using 1,3,5-trimethoxybenzene as the internal standard.

Results and discussion

Catalyst synthesis and characterization

All acetylcholine-ILs were synthesized mainly from non-toxic biomass derivatives through a two-step ion-exchange method under ambient conditions. This newly developed preparation approach was benign and much easier to operate, as compared with previous ones used for the preparation of (DBU)-based ionic liquids (N_2 atmosphere and 50 °C),[46] phosphonium-based ionic liquids (100 °C, 24 h),[47] *N*-methyl-*N*-propylpyrrolidinium acetate (multi-steps),[48] and so on. Importantly, the fairly strong hydrogen-bond interaction between the anion and cation of the bio-ILs was observed by computational calculations (Fig. S1†), which possibly resulted in better catalyst solubility. It was reported that the catalyst basicity of the hydrogen-bond estimated from the Kamlet–Taft parameters[49]

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was dominated by the properties of the anion.[50] Here, the basicity of the ILs mapped with hydrogen-bond basicity was generally inversely proportional to the acidities of the conjugate acid radicals (*i.e.*, the anions of the ILs), typically in the order of formate (FA) > acetate (AA) > propionate (PA) > valerate (VA).

The FT-IR spectra of various IL catalysts prepared from different precursors are displayed in Fig. 1. The band at 1760 cm^{-1} was observed for all ACH-ILs, contained the anhydride group, illustrating the existence of acetylcholine. It was evident that weak absorption was detected for C–O vibrations of the anhydride in all ACH-ILs, which is consistent with the effect of strong electrostatic interactions. In addition, the band at 1470 cm^{-1} corresponding to the C–N vibrations of ACH in all prepared ACH-ILs was strong and broad (Fig. 1A). The bands at 1560 and 1360 cm^{-1} were the characteristic peaks of the carboxylate that was derived from the neutralization of an organic acid with acetylcholine hydroxide. The structures of other acetate ILs (ETA-AA, CH-AA, and CC-AA) containing different cations of ethyltrimethylammonium, choline and chlormequat were also confirmed, respectively (Fig. 1B). The characteristic peaks of C–Cl (CC-AA) at 711 cm^{-1} and –OH (CH-AA) at 3360 cm^{-1}, along with the characteristic peaks of the carboxylate similar to ACH-ILs, could be observed (Fig. 1B).

To further identify the structures of all as-prepared bio-ILs, ^{1}H and ^{13}C NMR analyses were also conducted. All of the ACH-IL catalysts with the carboxylate as the anion with variable carbon-chain lengths (Fig. S2 & S3†) were confirmed to be successfully prepared. The carboxylate hydrogen atom was found to be sensitive to the concatenation of the positive charge of the trimethylethanium salt which moved to the high frequency along with the increased carbon-chain length except ACH-FA. For example, the NMR ^{1}H signal of $-CH_2$ of the carboxylate anion in ACH-AA gradually moved from 1.7 ppm to 2.01 ppm as compared with that in ACH-VA. Likewise, the ^{13}C NMR spectra displayed similar chemical shift rhythmicity for the carboxylate carbon atoms. In addition, the structures of other three acetate ILs containing different cations were also identified by ^{1}H and ^{13}C NMR (Fig. S4 and S5†).

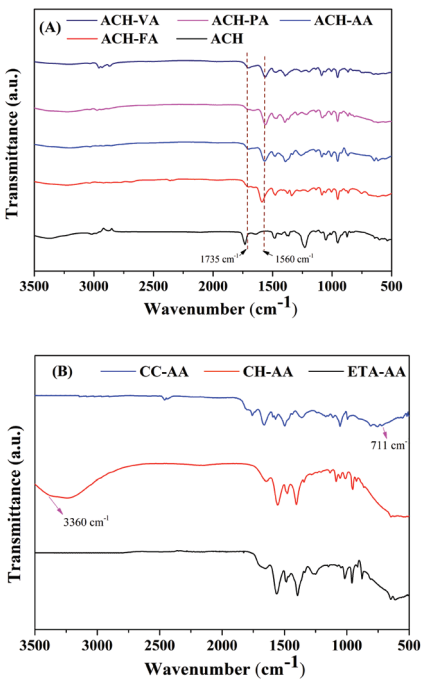
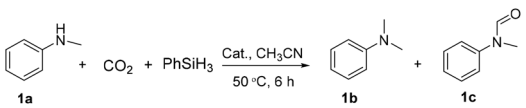


Fig. 1 FT-IR spectra of ACH-based ILs with a carboxylate with variable alkyl chain lengths (A); FT-IR spectra of CH-AA, CC-AA and ETA-AA (B).

Catalyst screening for methylation of *N*-methylaniline with CO_2

To start the catalytic activity investigation, the effect of different catalysts on the methylation of *N*-methylaniline with CO_2 was initially investigated. The reactions were accomplished at 50 °C within 6 h under ambient CO_2 pressure in CH_3CN using phenylsilane ($PhSiH_3$) as the hydrogen-donor in the presence or absence of a catalyst, and the obtained results are shown in Table 1. The reaction could not occur without adding any catalyst or with ACH (Table 1, entries 1 and 2). In contrast, ACH-AA displayed highly efficient catalytic performance in the *N*-methylation of CO_2 to *N*-substituted compound **1b** with a yield of up to 96% (entry 3). However, the activity of ACH ILs bearing formate (FA), propionate (PA), and valerate (VA) groups were inferior to that with the acetate group (entries 4–6), possibly due to their relatively low permeability and diffusivity of CO_2. It was reported that the viscosity of ILs increased with the increase of the carbon-chain length of carboxylic acids,[51] accordingly increasing the CO_2 permeability and diffusivity.[52] On the other hand, carboxylic anions can serve as a strong base because carboxylic acids are weak acids, with basicity in the order of $HCOO^-$ (FA) < CH_3COO^- (AA) < $CH_3CH_2COO^-$ (PA) < $CH_3(CH_2)_3COO^-$ (VA). However, as the

Table 1 Catalyst screening for selective methylation of *N*-methylaniline with CO_2 in the presence of $PhSiH_3$[a]



Entry	Cat.	Conv. (**1a**, %)	Yield (**1b**, %)	Yield (**1c**, %)
1	No	0	0	0
2	ACH	0	0	0
3	ACH-AA	100	96	4
4	ACH-FA	68	12	28
5	ACH-PA	99	77	22
6	ACH-VA	69	42	15
7[b]	ACH-AA	64	54	6
8	CC-AA	100	92	0
9[b]	CC-AA	47	34	12
10	ETA-AA	99	88	11
11	CH-AA	94	61	21
12	CH_3COOK	98	57	39
13	CH_3COONa	1	0	1

[a] Reaction conditions: 0.25 mmol **1a**, 0.75 mmol $PhSiH_3$, 6 mol% catalyst, 2.0 mL CH_3CN, 1 bar CO_2, 50 °C and 6 h. Conversion of **1a**, and the yield of **1b** and **1c** were determined by GC using naphthalene as an internal standard. [b] Reaction time is 2 h.

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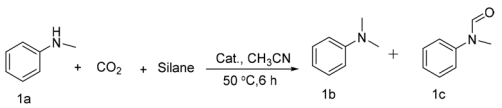
optimal catalyst used for this system, ACH-AA possessed appropriate viscosity and higher nucleophilicity than ACH-PA and ACH-VA, as well as higher basicity than ACH-FA. For ILs with different cations, the electron withdrawing order of the substituent groups in cations is ester (ACH) > chlorine (CC) > ethyl (ETA) group, which was proportional to the nucleophilicity of the acetate anion in ILs. Those properties were consistent with the activity order of the catalysts (entries 3 and 7–10). Nevertheless, the electron-withdrawing ability of the hydroxyl group (CH) is higher than that of the ethyl (ETA) group but it would be able to consume the silane during the reaction process, resulting in lower efficiency of CH-AA (entry 11) than that of ETA-AA (entry 10).[53] The possible synergistic role of both anion and cation of ACH-AA could be supported by the relatively lower activity of two inorganic acetates (entries 12 and 13) employed for the methylation of **1a**. It is worth noting that a much lower conversion of **1a** was achieved over CH_3COONa, which could be ascribed to its relatively lower solubility (46 g/100 g, 20 °C) than CH_3COOK (256 g/100 g, 20 °C).[54] Based on the above results and discussions, it could be inferred that both carboxylate anion and the type of quaternary ammonium cation influenced the catalytic activity of ILs, where the anion as a nucleophilic reagent interacted with the Si atom on $PhSiH_3$, while the cation collaboratively adjusted the nucleophilicity of the anion to cooperatively promote the reaction. In addition, the appropriate viscosity and superior solubility of ACH-AA also contribute to its pronounced reactivity.

Optimizing reaction conditions for methylation of *N*-methylaniline with CO_2

The influence of reaction parameters, such as the reaction temperature, reaction time, hydrosilane type, and catalyst dosage, on the fixation of CO_2 with **1a** was further investigated (Table 2). A considerable yield of **1b** with a small quantity of **1c** was obtained using $PhSiH_3$ as the H-donor under relatively mild reaction conditions of 50 °C and 6 h (Table 2, entry 1). At room temperature, the dominant product was found to be **1c** (entry 2), while a higher temperature of 70 °C resulted in unpleasant reaction activity (entry 3), mainly due to the lower solubility of CO_2 at a relatively high reaction temperature.[55] The yield of **1b** gradually increased on prolonging the reaction time from 2 to 12 h at 50 °C (entries 1, 4–6). However, only 63% conversion of **1a** was attained using Ph_2SiH_2 (entry 7) instead of $PhSiH_3$, possibly due to its high steric hindrance. Moreover, $PhSiH_3$ was testified as the priority of the hydrosilane for this reaction. In contrast, the main product was **1c** by using PMHS and EtO_3SiH as hydrogen donors, respectively (entries 8 and 9). It seemed that these hydrosilanes were inactive and unable to accomplish the reduction process. Even worse, the reaction did not take place using Et_3SiH due to its poor hydride-donating ability, which was typically activated by a noble metal such as Pt nanoparticles.[56] The results further indicated the significant effect of the type of hydrosilane. On the other hand, the reaction activity was unsatisfactory when the dosage of $PhSiH_3$ was insufficient, and 3 equiv. of the hydride relative to the substrate were found to be optimum for *N*-methylation of **1a** (entries 4, 10–13).

Table 2 Parameter optimization for the reaction of CO_2 with *N*-methylaniline using ACH-AA as a catalyst[a]



Entry	Reaction conditions	Silane	Silane dosage/mmol	Conv. (**1a**, %)	Yield (**1b**, %)	Yield (**1c**, %)
1	50 °C, 6 h	$PhSiH_3$	0.75	100	96	3
2	RT, 6 h	$PhSiH_3$	0.75	94	23	66
3	70 °C, 6 h	$PhSiH_3$	0.75	74	51	10
4	50 °C, 2 h	$PhSiH_3$	0.75	64	54	6
5	50 °C, 4 h	$PhSiH_3$	0.75	89	78	7
6	50 °C, 12 h	$PhSiH_3$	0.75	99	98	1
7	50 °C, 6 h	Ph_2SiH_2	0.75	63	54	8
8	50 °C, 6 h	EtO_3SiH	0.75	58	0	56
9	50 °C, 6 h	PMHS	0.75	23	4	16
10	50 °C, 6 h	Et_3SiH	0.75	0	0	0
11	50 °C, 6 h	$PhSiH_3$	0.25	26	8	7
12	50 °C, 6 h	$PhSiH_3$	0.5	48	18	10
13	50 °C, 6 h	$PhSiH_3$	1.25	100	98	2

[a] Reaction conditions: 0.25 mmol **1a**, 1 bar CO_2, 6 mol% ACH-AA and 2.0 mL CH_3CN. Conversion of **1a** and the yield of **1b** and **1c** were determined by GC using naphthalene as an internal standard.

Effect of the solvent type on the *N*-methylation of *N*-methylaniline with CO_2

The reaction activity and selectivity were examined to be also affected by the type of solvent used (Fig. 2). The reactivity in different solvents obeyed the following order of DMF ≈ CH_3CN > THF > EA > EtOH > *n*-hexane,[57] which was roughly in

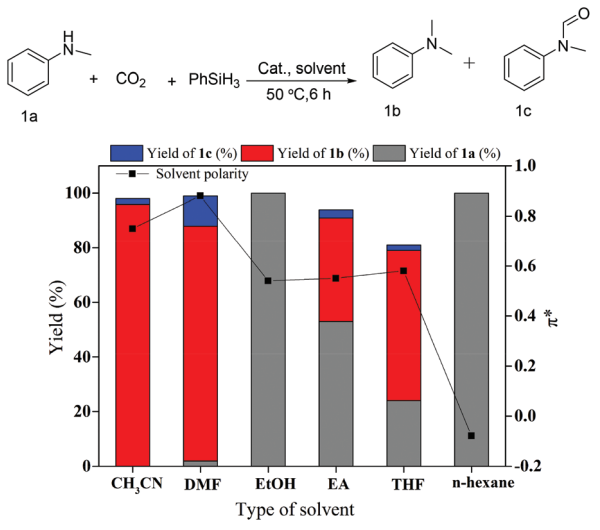


Fig. 2 Effect of solvent polarity on catalytic methylation of *N*-methylaniline with CO_2. Reaction conditions: 0.25 mmol **1a**, 0.75 mmol $PhSiH_3$, 6 mol% ACH-AA, 2.0 mL solvent, 1 bar CO_2, 50 °C and 6 h.

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line with their polarity. The solvent with high polarity was beneficial for *N*-methylation of an amine with CO_2, which could be attributed to the increased homogenization and nucleophilicity of the catalytic system, thus the bio-IL being dissolvable into the above solvent.[58] This result is in agreement with previous reports, where the amine could be activated by a strong polar solvent like DMF or DMSO.[59] Although EtOH had polarity comparable to EA, the reaction did not proceed at all, since $PhSiH_3$ was consumed rapidly by its reaction with an alcoholic solvent to form siloxane and hydrogen was released out quickly.[60] Under solvent-free conditions, the dominant product was observed to be **1c** at 50 °C (Table S1,† entry 7). Typically, the solvent plays a promotional role in facilitating the mass transfer and enhancing the nucleophilicity of the catalyst. In the absence of a solvent, the use of a viscous IL would reduce the reaction rate accordingly. This speculation can be rationalized by tuning the rate of silyl formate formation in solvents with variable polarity, thereby promoting the generation of **1c** other than **1b**.[38,61,62] Inspired by these data, we tried to perform reductive functionalization of CO_2 at a lower reaction temperature of 30 °C under solvent-free conditions. Surprisingly, **1c** was smoothly formed in 90% yield after the reaction for 6 h, which supports the speculation that the reaction rate was reduced in the absence of a solvent at relatively lower temperatures.

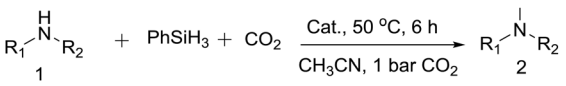
Selective *N*-methylation of CO_2 with various amines

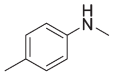
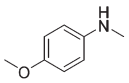
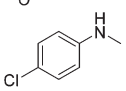
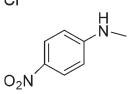
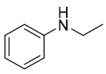
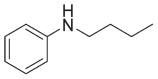
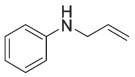
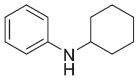
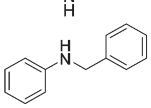
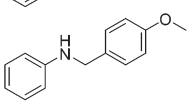
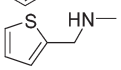
To examine the generality of the developed catalytic system, selective *N*-methylation of various aromatic amines was conducted under the optimized reaction conditions discussed above using 6 mol% ACH-AA, 0.25 mmol substrate and 0.75 mmol $PhSiH_3$ in acetonitrile under 1 bar of CO_2 at 50 °C (Table 3). It was found that most amines could be successfully transformed into corresponding *N*-methylated products with excellent yields after reacting for 6 or 8 h. Among the tested substrates, the compounds with electron-donating *ortho*-substituents (Table 3, entries 1 & 3) showed lower activity than those with *para*-substituents (Table 3, entries 2 & 4), which could be ascribed to the relatively higher steric hindrance effect of the substituent groups. On the other hand, substrates bearing electron-donating groups at the *para*-position (Table 3, entries 2 & 4) displayed activity superior to those containing electron-withdrawing groups (Table 3, entries 5 & 6). In addition, chlorine, nitro, and olefinic species were well tolerated during the reaction process (Table 3, entries 5, 6 & 10). Notably, the carbon-chain length of the substituent groups attached to the nitrogen of the substrates showed no obvious effect on activity (Table 3, entries 7–9 & 11). Moderate yields of *N*-methylated products were obtained when benzyl aniline with larger steric hindrance (Table 3, entries 12 & 13) and a heterocyclic amine that is typically inert to react (Table 3, entry 14) were used as starting materials.

Selective *N*-formylation of various amines

Besides *N*-methylation discussed above, *N*-formylation of amines with CO_2 could also exclusively take place at 30 °C under solvent-free conditions in the present study. As shown in Table 4, a variety of secondary aromatic compounds were examined in this established reaction system, and corresponding formylated products were observed with excellent yields (Table 4, entries 1–9). Due to steric hindrance, bulk substrates afforded relatively low product yields (Table 4, entries 8 and 9). Notably, a series of secondary aliphatic amines could be successfully formylated as well, giving products with

Table 3 Examples of ACH-AA catalyzing the reaction of CO_2 with amines to yield *N*-methylamines[a]



Entry	Substrate	Conversion (**1**, %)	Yield (**2**, %)	Selectivity (**2**, %)
1		99	85	87
2		100	93	93
3		93	81	87
4		100	99	99
5		99	91	92
6		15	8	53
7		100	96	96
8		99	92	93
9		98	96	97
10		99	80	81
11		90	89	99
12[b]		98	87	89
13[b]		96	80	83
14[b]		99	88	89

[a] Reaction conditions: 0.25 mmol, 1 bar CO_2, 6 mol% ACH-AA, 0.75 mmol $PhSiH_3$, 2.0 mL CH_3CN, 50 °C and 6 h. [b] Reaction time is 8 h.

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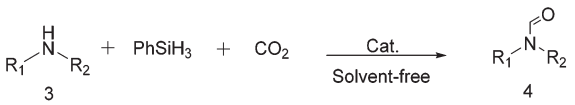
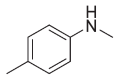
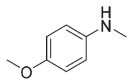
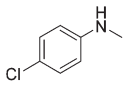
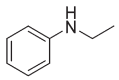
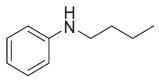
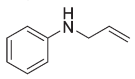
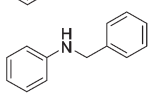
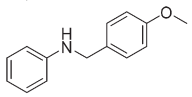
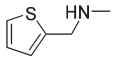
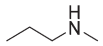
Table 4 Catalytic results for the reaction of various amines with CO_2 to give formamides over ACH-AA[a]



Entry	Substrate	Conversion (**3**, %)	Yield (**4**, %)	Selectivity (**4**, %)
1		100	90	90
2		93	88	95
3		99	91	92
4		100	90	90
5		100	90	90
6		98	90	92
7		90	86	96
8		89	81	91
9		63	60	95
10		100	90	90
11		98	96	98
12		99	90	91
13		100	100	100
14		100	96	96
15		96	93	97

[a] Reaction conditions: 0.25 mmol 3, 1 bar CO_2, 6 mol% ACH-AA, 0.75 mmol $PhSiH_3$, solvent-free, 30 °C and 6 h.

superior yields under mild reaction conditions (Table 4, entries 10–15).

Scaled-up production and catalyst recyclability

From a viewpoint of practical applications, the scaled-up production of **1b** was fairly necessary. This gram-grade production experiment was conducted by amplifying 50 times based on the substrate feed (see the Experimental section for details). However, due to the substrate being unable to make sufficient contact with CO_2 under ambient atmosphere (1 atm), the scale-up reaction system could not afford comparable efficiency (83% **1a** conversion) at 50 °C even after 48 h, and **1c** (75% yield) was found to be the dominant product instead of **1b** (7% yield). In this regard, a relatively higher CO_2 pressure would be helpful to increase the selectivity toward **1b**. Gratifyingly, 94% conversion of **1a** with 87% yield of **1b** was obtained at 2.0 MPa CO_2 pressure at 50 °C in 20 h. These results show the great potential of the developed catalytic systems for scale-up upgrading of CO_2.

In addition, the IL ACH-AA could be readily separated from the reaction mixture by extraction with diethyl ether after adding water (Fig. S6†). The recovered bio-IL (ACH-AA) was able to be reused at least five times with a slight loss of activity in the synthesis of **1b** under optimal reaction conditions (Fig. S7†). The minor decline in the catalytic performance of the IL during consecutive cycles was mostly due to a part of the IL catalyst being adsorbed by the precipitated silane after adding water, as demonstrated by FT-IR (Fig. S8†). In addition, the incorporation of the partial IL into degradation compounds might result in the sealing of active sites to somehow deactivate the catalyst as well.[63] The sealed and adsorbed IL could be released after adding water and stirring the obtained reaction mixture for 24 h under ambient conditions, while the impurities with the catalyst were able to be eliminated with activated carbon.[64] This post-treatment process can significantly maintain the IL activity in the consecutive reaction cycles.

Mechanism study

To explicitly disclose the reaction mechanism of the bio-IL-catalysed reaction of CO_2 with an amine to yield a methylated or formylated product, a series of control experiments were conducted. The role of the IL in the reaction was confirmed by ^{1}H NMR analysis, through testing the interaction of the IL (ACH-AA) with $PhSiH_3$, **1a**, and CO_2 under the designated reaction conditions. As shown in Fig. S9,† the proton signal intensity of Si–H (4.20 ppm) in $PhSiH_3$ disappeared after mixing with ACH-AA, implying that this catalyst was capable of activating the hydrosilane to release the hydride, which could further promote the production of the key intermediate silyl formate (Fig. S10†). Subsequently, it was noticed that there was no variation in the proton signal of the *N*-CH_3 proton (2.72 ppm) between **1a** and its mixture with ACH-AA, indicating that there was no distinct interaction between them (Fig. S11†). Moreover, no new proton signal was observed in the mixture of **1a** and $PhSiH_3$, demonstrating that **1a** cannot be activated by the hydrosilane (Fig. S12†). In order to affirm the carbon sources of *N*-CH_3 on **1b** originating from CO_2 rather than ACH-AA, a control experiment was performed for methylation in the absence of CO_2 under the optimized reaction conditions, while no **1a** conversion was found (Fig. S13†). The isotopic study using diphenylsilane-d_2 instead of $PhSiH_3$ as the H-donor was carried out in deuterated acetonitrile; **1b** with 122–125 amu *m*/*z* and **1c** with 136–137 amu *m*/*z* were formed

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in a much higher proportion to the corresponding normal products with 121 and 135 amu *m*/*z*, respectively (Fig. 3 & S14†), further elucidating that the proton of *N*-CH_3 and *N*-CHO originated from the hydrosilane.

In addition, the reaction of **1a** with CO_2 and $PhSiH_3$ was conducted in deuterated acetonitrile at 50 °C, and analyzed by ^1H NMR (Fig. 4). A new proton signal intensity at 2.93 ppm, belonging to N-CH_3 on **1b**, gradually increased with the extension of the reaction time from 0 to 6 h, and the proton signal intensity at 2.77 ppm assigned to *N*-CH_3 of **1a** completely disappeared after 4 h. The proton signal intensity at 3.32 ppm and 8.42 ppm, attributed to the proton of the formyl and methyl groups in **1c**, respectively, presented in 2–6 h but it decreased on prolonging the reaction time. It was interesting that a new signal intensity of 8.18 ppm appeared after 6 h, which was assigned to the proton of silyl formate formed from the interaction of residual phenylsilane and CO_2 when the substrate **1a** was completely consumed. A possible reaction mechanism for generation of the formylated product from the amine with CO_2 as the carbon source was proposed on the basis of the above discussions and previous reports (Scheme 2). The IL catalyst (CC-AA) with a succinct structure and comparable activity was chosen to further study the reaction mechanism. First, the bio-IL (CC-AA) interacts with $PhSiH_3$ to form an active intermediate CC-HS, which promotes the hydrosilylation of CO_2 resulting in silyl formate. Second, the formamide was formed by the formylation of amines with the formate.

However, there is ambiguity about the mechanism of formation of the methylated product in previous reports.[22,39,50,51] The focus was thus concentrated on determining whether the generation of N-CH_3 occurred through direct hydrogenation of formamide (Path B) or methylation with bis(silyl)acetal(III) (Path A). From the above NMR experiments (Fig. 3), it was found that the intensity of **1b** gradually increased within 2–6 h, but the intensity of **1c** weakened accordingly. Moreover, no bis(silyl)acetal(III) intensity signal was observed in the reaction. It could be inferred that the reaction pathway for the formation of N-CH_3 is Path B. In order to further prove this inference, DFT calculations were conducted to demonstrate that

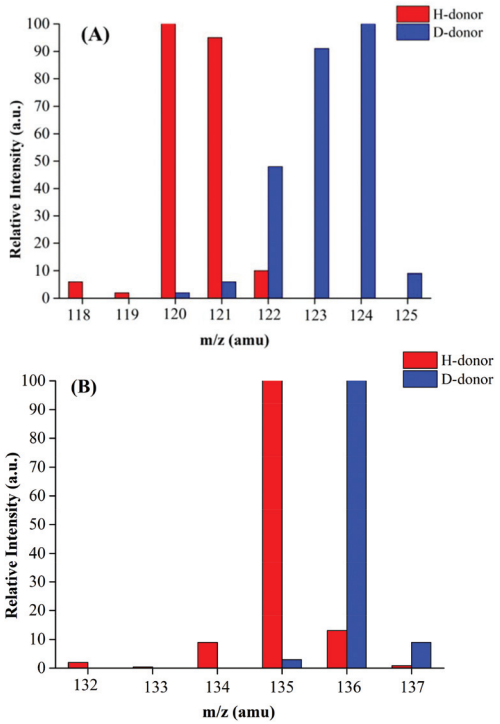


Fig. 3 Mass fragmentation analyses (all intensities scaled to 100%) of **1a** (A) and **1c** (B) from **1a** by using $PhSiH_3$ as the H-donor and diphenyl (silane-d_2) as the D-donor.

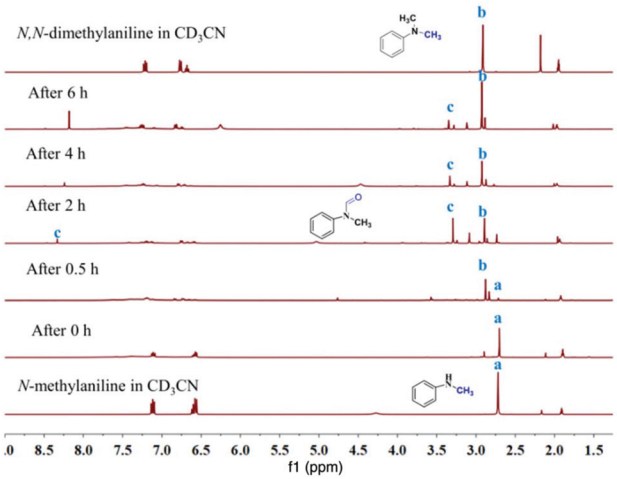
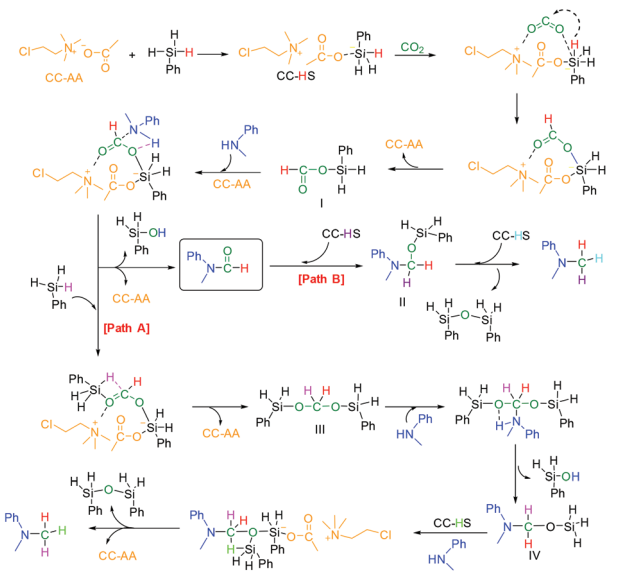


Fig. 4 ^1H NMR spectra for the *N*-methylation of **1a** (0.026 g, 0.25 mmol) with CO_2 (1 atm) in CD_3CN using $PhSiH_3$ (0.75 mmol) as the H-donor.



Scheme 2 The possible reaction pathways for producing methylated and formylated amines using CO_2 as the carbon source.

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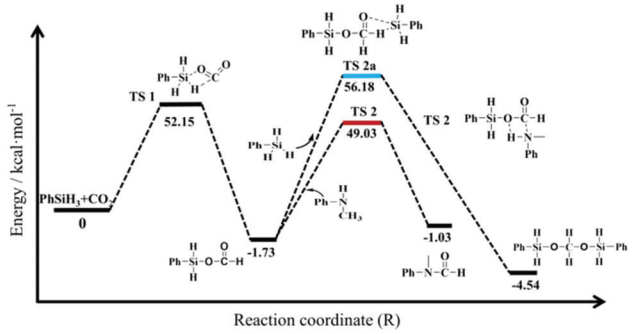

Fig. 5 The reaction energy profiles (in kcal mol^{-1}) for the computationally favorable pathway to synthesize methylation product *N*,*N*-dimethylaniline in the absence of a catalyst.

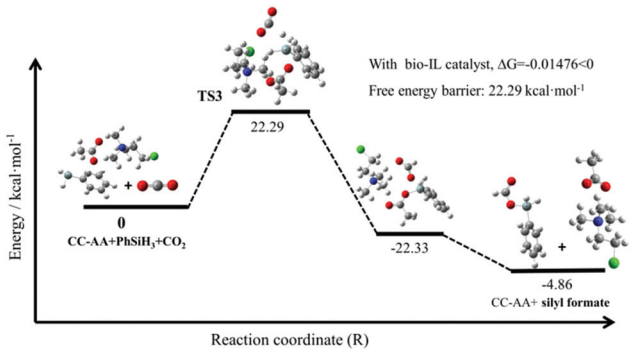

Fig. 6 The reaction energy profiles (in kcal mol^{-1}) for the synthesis of a silyl formate in the presence of a catalyst.

the formation of the formamide with silyl formate *via* transient state **TS2** (49.03 kcal mol^{-1}, Fig. 5) is easier than the formation of bis(silyl)acetal through transient state **TS2a** (56.18 kcal mol^{-1}, Fig. 5), which further illustrates that the reaction pathway for production of **1b** is Path B in Scheme 2. It is clearly seen that the activation energy barrier using CC-AA as a catalyst was reduced by as much as 29.86 kcal mol^{-1} through transition state **TS3** with a lower energy barrier (ΔG = 22.29 kcal mol^{-1}, Fig. 6), as compared with the catalytic system without a catalyst (ΔG = 52.15 kcal mol^{-1}, **TS1** in Fig. 5) in the formation of silyl formate, demonstrating the indispensable role of the bio-IL catalyst in the promotion of the reaction efficiency. Similarly, the generation of **1b** from hydrosilylation of **1c** with the IL catalyst also needed a lower energy barrier than that without a catalyst, further illustrating that the use of a catalyst is highly necessary for all these reaction processes (Fig. S15†).

Conclusions

In summary, a series of non-toxic, sustainable and natural bio-ILs were prepared by using a simple room-temperature approach. Among these prepared ILs, ACH-AA was demonstrated to be efficient for the catalytic transformation of CO_2 with amines into high-value *N*-substituted compounds in the presence of $PhSiH_3$. The product selectivity toward a formamide or a methylamine could be readily tuned by altering the reaction temperature together with or without using a solvent. This bio-IL catalyst exhibited good universality in substrate scope, and could be recycled without any evident loss of activity. Furthermore, NMR study and DFT calculations demonstrated that the bio-IL played a crucial role in both activating the hydrosilane and reducing the reaction activation energy in both *N*-methylation and *N*-formylation processes of CO_2 upgrading. By comparing the energy profiles of two controversial reaction pathways, a more reasonable catalytic mechanism was illustrated, where *N*-formamide was formed through the reaction of a silyl formate with an amine, followed by hydrosilylation to give *N*-methylamine. In addition, a satisfactory result could be obtained by amplifying the reaction to gram grade, which provides a promising strategy for large-scale production of *N*-substituted compounds from amines and CO_2.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

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