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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: ChemSusChem 10.1002/cssc.201601490

Link to VoR: http://dx.doi.org/10.1002/cssc.201601490



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Cooperative Catalytic Activation of Si-H Bonds: CO₂-based Synthesis of Formamides from Amines and Hydrosilanes under Mild Conditions

Rongchang Luo, Xiaowei Lin, Yaju Chen, Wuying Zhang, Xiantai Zhou and Hongbing Ji*^[a]

Abstract: The simple cooperative catalytic system had been successfully developed for the solvent-free N-formylation of amines with CO2 and hydrosilanes at ambient conditions, which was composed of the Zn(salen) catalyst and quaternary ammonium salt. These commercially available binary components could activate the Si-H bonds effectively originated from the intermolecularly synergistic effect between Lewis base-transition metal center (LB-TM), and subsequently facilitate the insertion of CO₂ to form the active silvl formats, thereby leading to obtain the excellent catalytic performance at a low catalyst loading. Furthermore, the bifunctional Zn(salen) complexes owning two imidazolium-based ionic liquid (IL) units at the 3,3'-position of salen ligand were acted as intramolecularly cooperative catalysts and the feature of solvent-regulated separation resulted in the ease of catalyst recycle and reuse.

Introduction

Recently, carbon dioxide (CO₂) is widely used as an abundant, inexpensive and bio-renewable C1 building block for chemical synthesis.^[1] Converting waste CO₂ into useful products or fuels is usually considered as an attractive method, which is also known as "carbon capture and utilization" (CCU).^[2] The major challenge in this area may be the lack of effective catalysts to facilitate its activation and subsequent transformation due to its thermodynamic and kinetic stability.^[3] Among these, an interesting route for the synthesis of formamides is the Nformylation of amines with CO2 in the presence of various reducing agents (Scheme 1)^[4] because formamides are versatile chemicals with wide applications in industry as important solvents and platform compounds.^[5] Although hydrogen gas (H₂) is the cleanest and most atom economical reductant, hydrogenation of CO₂ in the presence of an amine often requires noble metal catalysts (Ru,^[6] Pd,^[7] Pt,^[8] Au,^[9] Ir,^[10] etc^[11]) working at harsh reaction conditions, such as high reaction temperature and pressure, thereby leading to obtain the low activity and prevent its broad application. Metal hydrides and hydroboranes are generally sensitive to air and moisture aroused from the limitation in the substrate scope.^[12] Hydrosilanes are used as a kind of cheap, nontoxic and easyto-handle reducing agent, even the polar Si-H bond as well as

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a mild reduction potential was kinetically more reactive.^[13] Therefore, the reduction of CO₂ to formamides using amines and hydrosilanes is an attractive method for incorporating CO₂ into valuable organic compounds because they often operate under mild conditions with remarkable chemoselectivity. However, the promising process has been investigated less compared to other CO₂ reductive emission.^[14]



Scheme 1. The chemoselective reduction of CO₂ to formamides with amines over various reductive agents

In 2012, Cantat et al first discovered an organocatalytic version of this reaction with organic bases (e.g. TBD) as catalysts, but the diagonal transformation only proceeds at high temperatures (>=100 °C) with solvent and presents the limited substrate scope.^[15] They also reported a highly active organocatalytic system based on N-heterocyclic carbenes (NHCs) that has been designed for the N-formylation of various ambient conditions.^[16] amines at Subsequently, the were comprehensively studied with mechanisms DFT calculations.^[17] Nevertheless, these catalytic systems with a high catalyst loading to achieve high efficiency were sensitive to air and moisture. Although a rhodium-based bis(NHC) complex could exhibit the high activity at a low catalyst loading and a wide substrate scope were compatible, the reported routes generally suffered from drawbacks such as requiring noble metal catalysts, inert gas atmosphere, and complicated route of catalyst synthesis.^[18] Some toxic organic phosphine ligands^{[5d,} ^{19]} or in combination with copper^[12, 20] or iron^[13] salts were also used to promote the reductive functionalization of CO2 at ambient conditions, which was inaccordance to the requirement of green chemistry. Recently, Liu et al reported the simple imidazolium-based ionic liquid (IL) can directly catalyze the Nformylation of amines using CO₂ and hydrosilane originated from the cooperative catalysis between anion and cation within IL moiety.^[21] Additionally, some strong polar solvents including DMSO^[22] and v-valerolactone^[23] might also promote this transformation. Alkaline metal carbonates (Cs₂CO₃) can facilitate the selective formylation and methylation of amines efficiently in line with "cesium effect", but the reaction required not green organic solvent (MeCN) to achieve the catalytic cycle.^[24] Likewise, a handful of heterogeneous catalysts had been successfully applied for preparing the formamide products on the basis of their characteristics of easy recycling. $^{\left[5b,\,25\right] }$

In view of the fact that the common intermediate in metalcatalyzed hydrosilylation reactions of CO_2 is the metal hydride complex (M–H form),^[26] as well as our previous works on the metal-catalyzed cycloaddition reaction of CO_2 /epoxides,^[27] we envisioned that the strong electron-donating ability of

macrocyclic salen ligand may increase the nucleophilicity of the metal hydride species and facilitate the reduction of the weakly electrophilic CO2. In addition, the Lewis base-transition metal center (LB-TM) catalytic system could activate hydrogen molecular (H₂) effectively inspired by the activation mechanism of hydrogenase in nature.^[28] Herein, the efficient binary catalytic system, i.e. simple Zn(salen) complex together with quaternary ammonium salts, were successfully developed for N-formylation reaction of amines using CO2 and hydrosilanes under solventfree conditions. Moreover, several IL-functionalized Zn(salen) catalysts were also synthesized for promoting the transformation on account of the mechanism of the synergistic catalysis as described in Scheme 2. To the best of knowledge, this is the first example for the metallosalen-catalyzed selective reduction of CO₂ in a homogenous medium, leading to the production of formamides with excellent yield and unprecedented chemoselectivity under mild conditions. Thus, inter- or intramolecularly cooperative catalysis could activate Si-H bonds of hydrosilane leading CO₂ inserting and thereby implementing the activation of this molecule.



Scheme 2. The N-formylation of amines using CO_2 and hydrosilanes catalyzed by the binary or bifunctional catalysts in this paper

Results and Discussion

Intermolecularly cooperative catalysis

In our preliminary experiments, the reductive N-formylation of N-methylaniline (**1a**) with CO₂ and phenylsilane (PhSiH₃) as a representative reaction to produce the corresponding N-methyl formanilide (**2a**) was carried out without solvent at 40 °C and 1.5 MPa CO₂ pressure. As shown in Figure 1(A), when using 1.0 mol% tetrabutylammonium bromide (denoted as TBAB) as an one-component catalyst, the yield of 80 % was achieved after 24 h. The experimental results were in consistence with that reported by Liu *et al* in their recent works related to the imidazolium-based ILs used in stoichiometric amount.^[21] It was believed that the cooperative catalysis between the cation and anion of IL might lead to activate the Si–H bond of phenylsilane. Additionally, it was also found that the catalyst Zn(salen) could

directly catalyze the N-formylation reaction owing to the formation of the highly active Zn-H species. The consequences were accessible that both can make it more favorable for the insertion of CO₂. Because the high reaction temperature might result in the formation of methylamines from the N-methylation of amines, it was necessary to perform the N-formylation reaction under mild conditions in order to control the chemoselectivity. When the CO₂ pressure (from 1.5 MPa to 0.5 MPa) and the reaction temperature (from 40 °C to 25 °C) were decreased, only a negligible yields could be obtained using Zn(salen) or TBAB as a sole catalyst (Table 1, entries 1-3). However, it was also found that the reaction catalyzed by both one-component catalysts required the longer reaction time (24-48 h) to obtain the excellent yields at 40 °C and 1.5 MPa. Therefore, on the basis of the promising results, we observed these simple one-component catalytic systems required high catalyst loading or higher reaction temperature/pressure or longer reaction time to obtain a better catalytic performance. Thus, we hypothesized to use a new catalytic system constituted by Zn(salen) and TBAB that would take advantage of both the catalysts properties. As expected, only 0.5 mol% Zn(salen) in combination with 1.0 mol% TBAB represented an efficient binary catalytic system for the production of formamides and an excellent yield of 99 % was obtained for 7 h at 25 °C and 0.5 MPa without adding any solvent (Table 1, entry 4). Furthermore repeating the reaction at 40°C and at 1.5 MPa it was possible to obtain the product in 99 % yield after only 3 hours as shown in Figure 1(B). The by-product N,N'dimethylaniline (2b) could not be detected, and the 100 % chemo-selectively was obtained. On the basis of the promising results of the kinetic investigation, it was believed that the synergistic effect between Lewis base and transition metal promotes the reaction with low catalyst loading and consequently it was possible to operate under low CO2 pressure and room temperature. Decreasing the TBAB loading from 1.0 mol% to 0.5 mol%, a longer reaction time (15 h) was required (Table 1, entry 5). Moreover, when reducing the CO₂ pressure to 0.1 MPa, the efficiency of the N-formylation decreased (88 % yield) in spite of the prolongation of reaction time (Table 1, entry 6).



Figure 1 Kinetic curves of the N-formylation reaction from N-methylaniline, CO_2 and PhSiH₃ catalyzed by the one-component (A) or Zn(salen)/TBAB bicomponent catalysts (B). Reaction conditions: 10 mL stainless-steel autoclave, N-methylaniline (1.0 mmol), PhSiH₃ (1.0 mmol), Zn(salen) (0.5 mol%), TBAB (1.0 mol%), CO₂ pressure (0.5 MPa or 1.5 MPa), reaction temperature (25 °C or 40 °C).

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although both Cu(OAc)₂/dppe^[12] Moreover, and Fe(acac)₂/PP₃^[13] binary catalytic systems enable the conversion of CO₂ to formamide derivatives under mild reaction conditions (Table 1, entries 7-8), there are some significant drawbacks such as the instability of iron(II) salts, difficult preparation of phosphine donors, environmental unfriendliness and even using the poisonous organic solvent or raw materials. In addition, Fe-catalyzed formylation with CO2 and hydrosilanes often requires high catalyst loading (5.0 mol%) and longer reaction time (18 h) to obtain the excellent catalytic performance.^[13] Han et al have reported Cu-dppe complex could efficiently catalyze this transformation at ambient condition with only a 0.1 mol% catalyst loading.^[12] However, the binary catalytic system does not meet the criteria of green chemistry and could not be recovered and reused in the reductive conditions via a simple separation method, and the recyclability of these bifunctional catalysts is discussed later in detail in the article.

 $\begin{array}{l} \textbf{Table 1. The results of N-formylation reaction of N-methylaniline with CO_2 \\ and PhSiH_3 \ catalyzed \ by \ various \ catalytic \ systems^{[a]} \end{array}$

		H PO						
		1	SiH ₃	Catals solvent-	free	NN.	+	N
	1a				2	a	2b	
Fata	Loading	Cocatalyst	Т	CO_2	Time	Conv.	Yield (2	a)
Entry	/mol%	/mol%	/⁰C	/MPa	/h	/% ^[b]	/% ^[b]	Rei.
1	-		40	1.5	12	n.d.	n.d.	Our work
2	-	TBAB (1.0)	25	0.5	12	<3	2	Our work
3	SZ (1.0)		25	0.5	12	<1	n.d.	Our work
4	SZ (0.5)	TBAB (1.0)	25	0.5	7	>99	99 (96)	Our work
5	SZ (0.5)	TBAB (0.5)	25	0.5	15	99	99 (95)	Our work
6 ^[c]	SZ (0.5)	TBAB (0.5)	25	0.1	30	92	92 (88)	Our work
7 ^[c]	Cu(OAc) ₂	dppe	25	0.1	2	99	99	[12]
8 ^[c]	Fe(acac) ₂	PP_3	25	0.1	18	95	95	[13]

^[a] Reaction conditions: N-methylaniline (1.0 mmol), catalyst (0.5 or 1.0 mol%), cocatalsyt (0.5 or 1.0 mol%), PhSiH₃ (1.0 mmol), reaction temperature (25 °C), CO₂ pressure (0.5 MPa), Zn(salen) was abbreviated to **SZ**; ^[b] Determined by GC and the values in parentheses were the isolated yields of products; ^[c] The reaction was performed at ambient conditions (25 °C, balloon).

In order to further understand the synergistic effect between Zn(salen) and TBAB, we investigated the influence factors for the catalytic performance, including the type of ligand, metal center, and the type of cocatalysts, which was elaborated in Figure 2. It was found that the conversion of N-methylaniline was negligible in the case of salen ligand or ZnBr₂ salt as the alternative catalyst under identical conditions. Additionally, the completely negligible yields was acquired by the Zn-based catalysts containing N₄-chelating ligand. such as tetraphenylporphyrin (ZnTPP) and tris(2-pyridylmethyl)amine (ZnTPA). The promising observations suggested that the ligand owning the appropriate structure was crucial for obtaining the excellent catalytic activity. Surely, the catalytic activity of metallosalen catalysts was closely related with the type of a metal active center since the activation of Si-H bond within the

hydrosilane required the participation of the metal center to form the highly active metal hydride complex, which was well known to be one of the key steps in the metal-catalyzed hydrosilylation reaction of CO_2 .^[29] As a result, if using aluminium, copper or cobalt instead of zinc as metal active center, the low-to-moderate yields were obtained with Cu(salen) and Co(salen) catalyst, whereas Al(salen) complex could not catalyze the reaction effectively at the same conditions. The interesting phenomenon signified the nucleophilicity and stability of the metal hydride intermediate had significant influence on the catalytic performance in the reduction N-formylation of amines.



Figure 2 The N-formylation reaction from N-methylaniline, CO_2 and $PhSiH_3$ promoted by various catalysts using TBAB as cocatalyst. Reaction conditions 10 mL stainless-steel autoclave, N-methylaniline (1.0 mmol), $PhSiH_3$ (1.0 mmol), CO_2 pressure (1.5 MPa), reaction temperature (25 °C), Catalyst (0.5 mol%), TBAB (1.0 mol%).

Obviously, the experimental findings also indicated that the catalytic activity of the binary catalytic system strongly depended on the kind of cocatalyst as reported in Figure 3. Replacing TBAB with organic nitrogen base such as DMAP, Et₃N, DBU, or Ph₃P as cocatalyst, the poor results were observed due to the lack of bifunctionality between cation and anion.^[21] However, all of the familiar quaternary ammonium salts (TBA⁺BF₄⁻, TBA⁺Br⁻, TBA⁺I⁻) achieved the moderate-to-excellent yields, and bromide anion (Br⁻) having the moderate nucleophilicity was the best choice. The phenomenon was also demonstrated by Liu group using NMR as an analytical tool.^[21] In fact, the presence of both Zn(salen) and quaternary ammonium salts was necessary to obtain excellent catalytic activity in the selective reduction of CO₂.



Figure 3 The N-formylation reaction from N-methylaniline, CO_2 and $PhSiH_3$ promoted by Zn(salen) catalyst and various cocatalysts. Reaction conditions: 10 mL stainless-steel autoclave, N-methylaniline (1.0 mmol), $PhSiH_3$ (1.0 mmol), CO_2 pressure (1.5 MPa), reaction temperature (25 °C), Zn(salen) (0.5 mol%), cocatalyst (1.0 mol%).

Intramolecularly cooperative catalysis

On the basis of the mechanism of the intermolecularly cooperative catalysis, the binary Zn(salen)/TBAB catalytic system could obtain the excellent catalytic performance on the reductive N-formylation reaction of N-methylaniline at ambient conditions. However, there were some disadvantages such as the difficulty for catalyst recycle and the complexity of product separation. Recently, the IL-based metallocatalysts might present the special characterization on the catalyst reuse in view of the concept of "one-phase catalysis and two-phase separation". Our groups reported the metallosalen complexes^[27a] or 2,2'-bipyridine metallocatalysts^[27b] having two IL moieties with built-in nucleophilicity could effectively catalyze the cycloaddition reaction of CO2/epoxides under mild conditions, and these catalysts should also be capable of recycling from the reaction system. In the initial experiments, the imidazolium-based IL [BMIm]Br exhibited the similar catalytic properties with respect to the cocatalyst TBAB under identical conditions, which was described in Figure 3. Since bifunctional catalysts might show high catalytic activity, the imidazolium-based ILs were successfully introduced into salen zinc complexes by covalent attachment (Scheme 3), and this kind of catalyst design encouraged us to perform the Nformylation reaction of amines under mild conditions and make the recycling of catalyst much easily. In addition, the introduction of the long alkyl chain (n-octyl) was beneficial to improving the moisture resistance of these bifunctional catalysts. Therefore, the catalytic performances of the novel catalysts were measured in the reduction N-formylation reaction of N-methylaniline with CO₂ and PhSiH₃, which was conducted in a batch operation under mild conditions (see Table 2). The synthetic route of these bifunctional catalysts was reported by our previous work.^[27a] At first, N-octylimidazole was directly reacted with benzyl halides (CH₂X) modified salicyclaldehyde to afford IL-substituted salicyclaldehyde. The successive Schiffbase condensation between the aldehyde (-CHO) group and the amino (-NH₂) groups was used to form the corresponding salen ligand, and subsequently the IL-functionalized metallosalen complexes were obtained with high yields via the metallization process under nitrogen protection (Scheme 3).



Scheme 3. Synthetic route of various bifunctional Zn(salen) catalyst

Table 2. The results of N-formylation reaction of N-methylaniline with CO₂ and PhSiH₃ over various bifunctional catalysts.^[a]

		I_3 over v	anous bilund	lional	catalysis.	
Entry	Catalyst	T /⁰C	CO ₂ /MPa	t /h	Conv. ^[b] /%	Yield ^[b] /%
1	-	40	1.5	12	-	-
2	Zn(salen) (1.0)	40	1.5	3	n.d.	n.d.
3	IL (2.0)	40	1.5	3	5	<3
4	Zn(salen)/IL	40	1.5	3	90	90
5	ILSA1 (1.0)	40	1.5	3	<1	n.d.
6	ILST1 (1.0)	40	1.5	3	<2	1
7	ILSC1 (1.0)	40	1.5	3	21	20
8	ILSZ1 (1.0)	40	1.5	3	>99	99 (95)
9	ILSZ2 (1.0)	40	1.5	3	>99	99 (95)
10	ILSZ3 (1.0)	40	1.5	3	20	19
11	ILSZ4 (1.0)	40	1.5	3	35	35
12	ILSZ5 (1.0)	40	1.5	3	12	10
13	ILSZ1 (1.0)	40	0.5	6	88	88
14	ILSZ1 (1.0)	25	1.5	9	94	94 (90)
15	ILSZ1 (1.0)	25	0.5	12	90	90
16	ILSZ1 (0.5)	25	0.5	12	63	63
17	ILSZ1 (2.0)	25	0.1	12	99	98(95)

^[a] Reaction conditions: N-methylaniline (1.0 mmol), catalyst (0.5–2.0 mol%), PhSiH₃ (1.0 mmol), CO₂ pressure (0.1–1.5 MPa), temperature (25–40 °C), solventless; ^[b] Determined by GC or GC-MS, the values in parentheses are the isolated yields.



Figure 4 (A) Increase in N-methylformanilide formation amount with time using **ILSZ1** as catalyst at the different CO₂ pressure. Reaction conditions: N-methylaniline (1.0 mmol, if use), PhSiH₃ (1.0 mmol), **ILSZ1** (1.0 mol%), CO₂ (0.5-1.5 MPa), Temperature (40 °C); (B) Decrease in PhSiH₃ remaining amount with time using **ILSZ1** as catalyst without N-methylaniline (a) or adding N-methylaniline as substrate (b). Reaction conditions: N-methylaniline (1.0 mmol, if use), PhSiH₃ (1.0 mmol), **ILSZ1** (1.0 mol%), CO₂ (1.0 MPa), Temperature (40 °C).

As expected, the Zn-based catalyst ILSZ1 exhibited the excellent catalytic performance with a catalyst loading of 1.0 mol% for 3 h at 40 °C and 1.5 MPa, which was superior to the binary Zn(salen)/IL catalytic system (Table 2, entry 8 vs entry 3) The satisfying results might be due to the intramolecularly cooperative catalysis between metal center and the IL moieties within one molecule, which was similar to the binary catalytic system. Surely, if employed the other IL-based metallocatalysts owing the same structure and the different metal centers such as aluminum (ILSA1), tin (ILST1), cobalt (ILSC1), the low vields were also obtained under identical conditions (Table 2. entries 5-7). In order to further understand the reaction process from the kinetic perspective, the kinetic curves were conducted to discuss the proposed reaction pathway. Notably, the hydrosilylation of CO₂ were converted smoothly to the corresponding silvl formats in the absence of amine at the different CO₂ pressure as well as the amount of PhSiH₃ decreased quickly, which was elaborated in Figure 4. When adding N-methylaniline into the above reaction mixture, the FULL PAPER

yield of N-methylformanilide increased obviously. This finding demonstrated that the reaction might involve the two-steps reaction process and the formation of silyl formates intermediate was very fast. Additionally, if adding all of the reactants (including CO₂, amine, PhSiH₃) at the beginning of N-formylation reaction, the consumption rate of PhSiH₃ reduced to a certain extent compared to the previous results. Thus, the rate limiting step might be the amine N-formylation step for the active formoxysilane, which was consistent with the proposed reaction mechanism.

Next, a series of bifunctional Zn-based catalysts were also synthesized for comparison via covalent linkage following the similar methods, such as ILSZ2-ILSZ5. Based on the investigation to the catalytic performance of these catalysts, we discovered the structure of these bifunctional Zn(salen) catalysts had a huge influence on the catalytic activity. As expected, the bifunctional Zn(salophen) catalyst ILSZ4 was inferior to the Zn(salen) catalyst ILSZ1 on the catalytic activity (Table 2, entry 11 vs entry 8). Moreover, the Zn(salen) catalyst ILSZ3 functionalized by ILs at the 5,5'-position of salen ligand also exhibited the lower catalytic performance compared to that at 3,3'-position (Table 2, entry 10 vs entry 8). The interesting experimental results implied the Zn(salen) complexes having the proper space structure might require the excellent catalytic activity in the reduction of CO₂. More surprisingly, the CI-based catalyst ILSZ2 showed the considerable activity than that of Brbased catalyst ILSZ1 (Table 2, entry 9 vs entry 8). In order to further investigate the difference between the two, i.e. ILSZ1 and ILSZ2, both of the kinetic curves were conducted to demonstrate the catalyst ILSZ2 owing the highest catalytic activity. We speculated the phenomenon was due to the nucleophilic ability of halogen anion (Cl->Br) because the Nformylation reaction might proceed via nucleophilic attack on the hydrosilane to promote the formation of a hypervalent silicon species.^[30] Recently, He et al also reported TBAF (tetrabutylammonium fluoride) as an excellent organocatalyst for the formation of formamides from amines, CO2 and hydrosilanes, and the mechanism involving the fluoride effect was proposed because the fluoride could promote hydride transfer from the hydrosilane to CO2, which was originated from its strong nucleophilicity.^[31] From another angle, the catalyst ILSZ2 presented the higher activity relative to catalyst ILSZ3 even though both of them contained chloride anion within ILs (Table 2, entry 9 vs entry 10). It followed that the structure of catalyst was a key factor for the catalytic performance. Finally, it was understandable for us the Zn(salen) complex having additional quaternary ammonium salts ILSZ5 presented the bad catalytic activity probably due to the poor solubility (Table 2, entry 12). It was well-known that a significant drawback of using CO₂ as a raw material may be the potential dangers associated with high-temperature and high-pressure operations. Then, we investigated the catalytic performance of the bifunctional catalyst ILSZ1 at selected different conditions (Table 2, entries 13-17). More specifically, the N-formylation of amine using CO₂ and PhSiH₃ proceeded efficiently even at atmospheric CO₂ pressure (0.1 MPa) and at room temperature (25 °C). Therefore, the bifunctional catalytic system was capable of catalyzing the

reduction of CO₂ to formanilide at room temperature and atmospheric pressure ascribed to the excellent intramolecularly synergistic effect. In addition, it was noting that the reduction of CO₂ might also depend on the nature of the reductant and less reactive hydrosilanes, such as Ph₂SiH₂, PhMe₂SiH, Et₃SiH, (EtO)₃SiH, TMDS and PMHS, were unreactive under the same conditions owning to the steric and electronic effect (see Figure 5).^[21]



Figure 5 The N-formylation reaction from N-methylaniline and CO_2 over catalyst **ILSZ1** using various hydrosilanes as a reductive agent. Reaction conditions: 10 mL stainless-steel autoclave, N-methylaniline (1.0 mmol), hydrosilane (3 eq. Si-H), **ILSZ1** (1.0 mol%), reaction temperature (40 °C), CO_2 pressure (1.5 MPa).

Finally, the recyclability and reusability of catalyst ILSZ1 was further investigated as well at 40 °C and 1.5 MPa, as described in Figure 6, In a typical catalytic cycle, the catalyst was separated as a solid by centrifugation after adding organic solvent (e.g. ether or ester), and the yield of Nmethylformanilide remained basically unchanged after reused for five times, indicating that the bifunctional catalyst was quite stable in this catalytic system and ILSZ1 should be denoted as an easily recyclable catalyst by the solvent-regulated separation techniques. The FT-IR analysis of the recovered **ILSZ1** was indirectly confirmed the stability of catalyst under mild conditions. The reason was that the FT-IR spectra show characteristic vibration bands at around 1635 cm⁻¹ and 1547 cm⁻¹, which were associated with the stretching vibration modes of C=N and C-O at the salen ligand, respectively. Thus, it was proved that the imine group of salen backbone might be tolerated at the reductive conditions.



Figure 6. (A) Recyclability and reusability of the catalyst **ILSZ1** in the N-formylation reaction of N-methylaniline from CO₂ and PhSiH₃; Reaction conditions: 10 mL stainless-steel autoclave, N-methylaniline (1.0 mmol), PhSiH₃ (1.0 mmol), **ILSZ1** (1.0 mol%), CO₂ pressure (1.5 MPa), reaction temperature (40 °C), reaction time: 3 h.

Substrate scope

As listed in Table 3, it was further demonstrated that different kinds of amines including aliphatic, alicyclic and aromatic amines with CO₂ (0.5 MPa) and PhSiH₃ were N-formylated to the corresponding formamides in moderate to excellent yields at 25 °C within 15 h with 0.5 mol% Zn(salen) catalyst and equivalent TBAB cocatalyst (or at 40 °C for 6 h with 0.5 mol% ILZ1), reflecting excellent substrate generality and tolerance to various functionalities.^[32] As expected, for each secondary amine, sole N-formylated product was obtained with a negligible yield of methylamine products. Notably, both steric and electronic effects play an important role in the Nformylation reaction of amines. For N-alkyl phenylamine derivatives, the decreased catalytic activity was observed as the alkyl length of N-substituted substrate increased in the following order. *i.e.*, methyl>ethyl>isopropyl (2a>2b>2c). Similarly, N.N'-dibenzylamine present the low activity compared to N-methylbenzylamine due to the steric hindrance (2e<2d). Dibenzvlamine exhibited good reactivity. producing dibenzylformamide in a yield of 93 % after doubling the catalyst loading to 1.0 mol%. Undoubtably, the enhanced catalytic activity of aliphatic secondary amines was observed following the increased alkyl chains and the order was: ethyl>n-butyl>nhexyl (2f>2g>2h). Especially, diallylamine furnished selectively the N-formylation product 2i in a moderate yield without reduction of the double bond, reflecting the tolerance to alkenyl group. Moreover, the yields obtained from N-methylaniline derivatives with electron-donating groups at the para-position of phenyl group were generally lower than those with electrongroups withdrawing under identical conditions, i.e. methoxyl>methyl>bromide>chloride>nitro (2j>2k>2l>2m>2n). It had been verified indirectly the N-formylation of amine from the second step of mechansim might be the rate limiting step. Unfortunately, strongly electron-withdrawing substituent (-NO₂) on benzene ring was not well tolerated, and *p*-nitroaniline (2n) was unreactive under the identical conditions. It is worthwhile to mention that the substrate with reducible functional groups (i.e. bromo, chloro, carbonyl, nitro) could be tolerated quantitatively without reductive by-products. For example, the 4-acetyl-Nmethylaniline was converted to the corresponding formamide (20) without the reduction of carbonyl group. Additionally, methoxyl substituted N-methylaniline at the ortho-position presented the lower catalytic activity compared to that at the para-position of phenyl group due to the steric hindrance (2p<2j).

Furthermore, cyclic secondary amine including five- and sixmembered ring converted to the corresponding formamides in excellent yields (**2q**, **2r**, **2s**). Thereinto, the activity of 1,2,3,4tetrahydroquinoline was superior to indoline owing to the ring tension (**2s**>**2q**). Nevertheless, it was also better than 4phenylpiperidine due to the result of comprehensive action from the steric hindrance and electronic effect (**2s**>**2r**). Unfortunately, the reactivity of piperidine derivatives with four methyl groups at the 2-position the reaction is negligible ascribed to the steric bulkiness (**2t**). This catalytic reaction was also found to be robust in the N-formylation of complicated N-heterocyclic compounds. For example, morpholine with ether functional group achieved the best yield of 99 % (2u) in a relatively short period of time, and N-substituted piperazine derivatives also exhibited the high activity under the optimized conditions (2v and 2w). However, a second N-formylation of 2,6dimethylpiperazine did not occur at the hindered site, with only mono-formylation product 2x being obtained in a moderate yield. Similarly, using 1,2-diphenylhydrazine as a selected substrate, the mono-formylation product 2y was also acquired under identical conditions. Additionally, the reaction did not proceed in the case of DL-proline following the recovered substrate presumably because of the sterically hindered and deactivating COOH group on the adjacent carbon atom of the amine (2z). Likewise, the by-product with carboxyl group being reduced could not be afforded under mild conditions. Thus, not only linear and cyclic secondary amines, but also aliphatic (2A), alicyclic (2B) and aromatic primary amines (2C) were found to be reactive substrates. For most of primary amines, both N-H bonds of the amines were reactive for N-formylation, and monoand diformylated products were obtained under identical conditions.^[21] Delightfully, 4- ester or carbonyl group substituted phenylamine (2D and 2E) were suitable for this transformation and these substituents could be tolerated, which were obtained only mono-formylation products. Then, we chose two substrates containing the C=N bond (2F and 2G) to investigate the stability of imine group in this reductive conditions. As expected, benzophenone imine (2F) and benzophenone hydrazine (2G) were converted to their corresponding formamides without the reduction of the unsaturated bond. The similar phenomenon was also reported by Prof. Paul J. Dyson's group using the TBAF•3H₂O as a sole catalyst.^[30] Additionally, Gao et al had recently reported a series of ionic mesoporous pyrene COFs ([Et₄NBr]-Py-COFs) imine-linked were successfully applied for this transformation.^[25b] Moreover, the N-H bonds in heteroaromatic compounds as a less basic substrate such as 1H-pyrrole (2H) or imidazole (2J) were resistant to N-formylation, which was ascribed to the ratedetermining step of amine formylation. In a word, both the binary and bifunctional catalytic system exhibited the excellent substrate compatibility with oxidizing groups such as alkenes, halides, ethers, aldehydes, ketones, esters, nitro compounds, amides and imines. Finally, it was demonstrated that our methodology could be used for the synthesis of various fine chemicals.

Table 3. The results of chemoselective reduction of CO_2 to formamides using various amines and PhSiH₃ catalyzed by the binary and bifunctional catalytic systems without solvent.^[a]

Entry	Substrate	Product	Number	Cat.1 ^[b]	Cat.2 ^[c]
1	н	н _{ур} о	2a: R ₁ =Me	95	88
2	() ^{N.} R ₁	N.R1	2b : R ₁ =Et	74	87
3	×	\checkmark	2c : R ₁ = <i>i</i> -Pr	56	38
4	П н		2d: R ₂ =Me	54	73
5	₩ ^N . _{R2}	N. _{R2}	2e : R ₂ =Bz	20	19
6			2f : R ₃ =Et	>99	99
7	H	H_O	2g : R₃= <i>n</i> -Bu	48	70
8	R ₃ ⁽¹)R ₃	R ₃ ^Ń R ₃	2h : R ₃ = <i>n</i> -Oct	22	10
9			2i: R ₃ =allyl	53	43



^[a] Reaction conditions: 10 mL autoclave, amine (1.0 mmol), PhSiH₃ (1.0 mmol), CO₂ pressure (0.5 MPa); ^[b] Zn[salen] (0.5 mol%), TBAB (0.5 mol%), 25 °C, 15 h; ^[c] **ILSZ1** (1.0 mol%), 40 °C, 6 h.

Mechanism consideration

It was also indicated that it is necessary to promote the nucleophilic addition of the H atom to the C=O bond of CO₂.^[4] The binary or bifunctional catalytic system could activate the Si-H bond of hydrosilanes to form the formoxysilane intermediate, reflecting their respective characterization of

metal catalysts and organocatalysts. Moreover, it was found that the cation, the anion and metal center also showed an excellent synergistic effect on promoting the formation of formamides.^[21] To gain deep insight into the reaction pathway, the control experiment was conducted with isotopically labeled ¹³CO₂ as a C1 resource and the results examined by high resolution mass spectrometry (HRMS) and ¹³C NMR spectra demonstrated that the CO₂-reductive process can occur smoothly, as elaborated in Figure 6.^[33]



Figure 6. (i) The N-formylation of N-methylaniline from PhSiH3 and ¹³CO₂ under standard conditions; (ii) The possible mechanism for the N-formylation of amine over our catalytic systems

On the basis of the above experimental results and previous reports,^[13, 20a] a possible mechanism for the N-formylation of amines using CO2 and PhSiH3 to produce formamides catalyzed by the cooperative catalytic system was proposed.^[34] It was widely accepted that the metal hydride complexes (such as Co-H, Cu-H, Zn-H bonds) might exist in the metal-catalyzed hydrosilylation of CO2.^[14] Because of the different coordinated form of zinc cation (tetrahedron, octahedron ...), the Zn-H bond within the Zn(salen) catalyst could be formed in spite of the stable four-coordinated structure. The ¹H NMR analysis in DMSO-d₆ was conducted to gain deep insight into the role of these Zn(salen) catalysts. From the ¹H NMR spectra of PhSiH₃ without any catalysts and its mixture with [BMIm]Br or TBAB or ILSZ1 in the absence of CO₂, it was found that the signal assigning to Si-H of PhSiH₃ was shifted slightly, and the bifunctional catalyst ILSZ1 has the lower chemical shift values, suggesting there was the weak interaction between PhSiH₃ and ILSZ1 (see ESI). Understandably, it was the indirect evidence for the existence of the newly-formed intermediate species containing Zn-H bond. Thus, we suspected the Si-H bond of PhSiH₃ was activated by catalyst **ILSZ1**, which might make it more favorable for the insertion of CO₂ to yield formoxysilane. In order to further explain the cooperative effect between the metal, cation and anion and the effect the substrate, the ¹H NMR analysis of N-methylaniline without any catalysts and its mixture with [BMIm]Br or ILSZ1 or Zn(salen)/TBAB in DMSO-d₆ was also performed. As expected, the chemical shift of N-H in amine was observed in the ¹H NMR spectra of N-methylaniline with these catalysts, probably caused by the hydrogen bond between amine and the bromide anion of ILs (see ESI). In addition, the Lewis acid-base interaction might be originated from nitrogen lone pair electron within amine (nucleophilic) and metal center (electrophilic). In a word, all these results suggested that the catalyst could activate PhSiH₃ to react with CO₂ yielding formoxysilane, and simultaneously activated the amine to obtain the desired product. Additionally, the major differences between the Cu-based system and our Zn(salen) system were listed as follows: The copper catalyst activated the Si-H bond of PhSiH₃ to form the active intermediate (Cu-H bond), which made it more favorable for the insertion of CO₂. Subsequently, the formoxysilane can react with the amine to produce the final product. However, the Zn(salen) catalyst and ionic liquid (IL) could activate the Si-H bond of PhSiH₃ via synergistic effect between Lewis base-transition metal center (LB-TM). Subsequently, the active intermediate (Zn-H bond) facilitated the insertion of CO₂ to form the active silyl formats. In particular, the reaction might proceed via nucleophilic attack of halogen anion with ILs on the hydrosilane and the formation of the hypervalent silicon intermediate. Thus, considering the excellent fluoride effect originated from the strong nucleophilic ability, the synergistic effect between metal center and fluorine anion was underway in our laboratory.

Conclusions

In summary, the binary and bifunctional Zn(salen) catalytic system catalyzed the solvent-free N-formylation reactions of amines using CO₂ and hydrosilanes to produce formamide derivatives for the first time. The reactions can proceed under mild conditions due to the excellent synergistic effects, which could activate the Si-H bond of hydrosilane to form the silyl formats in situ-generated by metal-catalyzed hydrosilylation. Additionally, the IL-based catalysts can be easily recyclable and reused for five times without significant loss of activity and selectivity. In order to understand the reaction mechanism, further studies are underway in our laboratory.

Acknowledgements

This work was supported by the National Science for Distinguished Young Scholars of China (No. 21425627), the National Natural Science Foundation of China (No. 21676306), the Natural Science Foundation of Guangdong Province (Nos. 2016A030310211 and 2015A030313104), and the Fundamental Research Funds for the Central Universities of Sun Yat-sen University. The authors also thank Guangdong Technology Research Center for Synthesis and Separation of Thermosensitive Chemicals and Huizhou Research Institute of Sun Yat-sen University.

Keywords: CO₂ Reduction • Salen Zinc • N-formylation • Cooperative Catalysis • Ionic Liquid

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Text for Table of Contents

The reductive N-formylation of amines to produce formamides with CO_2 and hydrosilanes at ambient conditions catalyzed by the Zn(salen) complexes with inter- or intramolecular ionic liquid moieties.



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Cooperative Catalytic Activation of Si-H Bonds: CO₂-based Synthesis of Formamides from Amines and Hydrosilanes under Mild Conditions