# Organocatalysis

# Fluoride-Catalyzed Methylation of Amines by Reductive Functionalization of CO<sub>2</sub> with Hydrosilanes

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**Abstract:** An effective and inexpensive organocatalyst tetrabutylammonium fluoride (TBAF) was developed for the reductive functionalization of  $CO_2$  with amines to selectively afford formamides or methylamines by employing hydrosilanes. Hydrosilanes with different substituents show discriminatory reducing activity. Thus, the formation of formamides and further reduction products, that is, methylamines could be controlled by elegantly tuning hydrosilane types. Formamides were obtained exclusively under an atmospheric pressure of  $CO_2$  with triethoxysilane. Using phenylsilane as a re-

With the increasing environmental and societal concerns about carbon emission, great efforts have been devoted to carbon dioxide fixation over the past two decades.<sup>[1]</sup> Indeed, CO<sub>2</sub> has been widely used as a sustainable C1 building block for the production of various chemical products, for example, cyclic carbonates,<sup>[2]</sup> oxazolidinones,<sup>[3]</sup> carboxylic acid,<sup>[4]</sup> and methanol,<sup>[5]</sup> since CO<sub>2</sub> is nontoxic, economical, and abundant. However, due to its thermodynamic stability and kinetic inertness, highly reactive nucleophiles or transition-metal catalysts for CO<sub>2</sub> activation, high-energy starting materials, or drastic reaction conditions are commonly required for performing the reactions involving CO<sub>2</sub> smoothly. To expand the scope of valueadded chemicals available from CO<sub>2</sub>, efficacious catalysts that are able to promote CO<sub>2</sub> functionalization (i.e. CO<sub>2</sub> conversion through the formation of the C–O, C–N, or C–C bond) under mild conditions especially atmospheric pressure and/or at room temperature are highly desirable. One promising methodology in this area is the reductive functionalization of CO<sub>2</sub> with amines and reductants to selectively produce formamides and methylamines, successively, as shown in Scheme 1.<sup>[6]</sup>

Formamides are versatile chemicals and building blocks in inorganic synthesis,<sup>[7]</sup> for example, *N*,*N*-dimethylformamide is widely utilized as a solvent and reagent for chemical reactions.<sup>[8]</sup> On the other hand, methylamines are important inter-

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ductant, methylamines were attained with up to 99% yield at 50 °C coupled to a complete deoxygenation of CO<sub>2</sub>. The crucial intermediate silyl formate in the formylation step was identified and thereby a tentative mechanism involving the fluoride-promoted hydride transfer from the hydrosilane to CO<sub>2</sub>/formamide was proposed. Striking features of this metal-free protocol are formylation and methylation of amines by reductive functionalization of CO<sub>2</sub> with hydrosilanes and mild reaction conditions.

$$\begin{array}{c} R\\ NH\\ R^{1} \end{array} + CO_{2} + H \xrightarrow{cat.} \qquad R^{N}_{1} + R^{N}_{0} - CH_{3} \\ R = H, alkyl, phenyl, benzyl \end{array}$$

 $R^1$  = alkyl, phenyl, benzyl  $H^-$  = H<sub>2</sub>, hydrosilane, hydroborane

**Scheme 1.** Reductive functionalization of CO<sub>2</sub> with amines.

mediates that find widespread applications in the preparation of dyes, natural products, fine chemicals, etc.<sup>[9]</sup> Conventionally, formamides are synthesized by formylation of amines with toxic CO as a C1 source,<sup>[10]</sup> and methylamines are often obtained by employing formaldehyde, methyl iodide, or dimethyl sulfates as methylating agents from amines.<sup>[11]</sup> In this regard, using CO<sub>2</sub> as a C1 building block becomes an alternative and promising route to formamides and methylamines from amines if a green and sustainable route is desired.

Among the methods developed, metal catalytic systems including Ru,<sup>[12a,b,g-j]</sup> Fe,<sup>[12c,d]</sup> Cu,<sup>[12e,l]</sup> Zn,<sup>[12f]</sup> and Ni<sup>[12k]</sup> have been developed for reductive functionalization of CO<sub>2</sub> with amines in the presence of molecular hydrogen or hydrosilanes as reductants. Recently, a number of organocatalysts, such as TBD (1,5,7-triazabicyclo[7.4.0]dec-5-ene),<sup>[13]</sup> NHCs (N-heterocyclic carbenes),<sup>[14,18]</sup> NHP-H (1,3,2-diazaphospholene),<sup>[15]</sup> ILs (ionic liquids)<sup>[16]</sup> as well as proazaphosphatrane superbases,<sup>[17]</sup> CDCs (carbodicarbenes),<sup>[19]</sup> and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub><sup>[20]</sup> have also shown high activity in comparison with transition-metal catalysis under comparable reaction conditions. From a mechanistic standpoint, the amine is initially converted to its formamide, which is subsequently further reduced to the corresponding methylamine.<sup>[12f,g]</sup> The latter step is more difficult,<sup>[12c]</sup> providing an opportunity for selective reduction towards CO<sub>2</sub> or the formamide in-

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termediate. For example, the thiazolium carbenes have been developed for N-formylation with PMHS (polymethylhydrosiloxane) at 50 °C. Nevertheless, the N-methylation product, that is, methylated amine can be obtained in 81 % yield under slightly more forcing conditions (100 °C).<sup>[21]</sup> It is well known that hydrosilanes with different substituents show discriminatory reducing ability.<sup>[22]</sup> We envisioned that divergent reducing ability towards CO<sub>2</sub> or the formamide intermediate may be realized by choosing hydrosilanes with different substituents, and thus different products, that is, formamide or methylamine can be obtained with high selectivity.

Fluoride has been usually employed for the reduction of aldehydes and ketones with a hydrosilane as a reductant.<sup>[23]</sup> Fluoride anion interacts with the Si atom of hydrosilane to generate the penta- or hexa-coordinated silicon intermediate, thus elevating the hydrosilane reducibility. Baba et al. used CsF as catalyst for the hydrosilylation of CO<sub>2</sub> to silyl formate for the first time, resulting in successful synthesis of the formamides from piperidine and N-methylaniline with dimethylphenylsilane, though with relative high temperature and long time.<sup>[24a]</sup> Herein, we would like to report TBAF (tetrabutylammonium fluoride) as an excellent organocatalyst for fixing CO<sub>2</sub> with various amines using hydrosilanes as reductants. Excellently, formamides and further reduction products methylamines could be selectivity controlled by simply tuning hydrosilane types, thus realizing chemoselective two- and six-electron reduction of CO<sub>2</sub> coupled to C-N bond construction. A tentative mechanism involving the fluoride-promoted hydride transfer from the hydrosilane to CO<sub>2</sub> was proposed based on the identified intermediate silyl formate.

The reductive functionalization of  $CO_2$  in the presence of Nmethylaniline (1 a) with triethoxysilane as a reductant was investigated to find suitable catalysts as summarized in Table 1. No reaction occurred in the absence of any catalyst (entry 1, Table 1). CsF and KF were almost inactive (entries 2 and 3). Interestingly, combination of KF and [18]crown-6 gave an excellent result with 96% yield of N-methylformanilide (1b) (entry 4), although [18]crown-6 itself was ineffective (entry 5). This may be because [18]crown-6 is able to coordinate with potassium cation, thus enhancing the nucleophilicity of fluoride anion and the catalyst solubility. Inspired by this, we envisaged that a bulky group, that is, the tetrabutylammonium ion presumably works as the potassium fluoride/[18]crown-6 system, thus enhancing the nucleophilicity of the fluoride anion and improving the catalyst solubility in organic solvent compared with potassium or cesium cation.<sup>[25]</sup> As such, TBAF allowed the reaction to afford a quantitative yield of 1b successfully (entry 6). On the other hand, TBAB (tetrabutylammonium bromide) and TBAC (tetrabutylammonium chloride) exhibited barely any activity (entries 7 and 8 vs. 6), suggesting that the anion is crucial to the reaction. Accordingly, the tetrabutylammonium cation could improve the nucleophilicity of the fluoride anion and the catalyst solubility, thus improving the catalytic reactivity of TBAF by activating the Si-H bond of triethoxysilane.

In addition, polar solvents were more favorable for this formylation, probably due to the coordination capability with the

Table 1. Catalyst and solvent screening for the formylation of $1a$ with $\text{CO}_2$ and triethoxysilane.^{(a)}							
-	$ \begin{array}{c} H \\ CH_3 + CO \\ 1 ba \end{array} $	9 <sub>2</sub> +(EtO) <sub>3</sub> SiH ar30	cat. °C, CH <sub>3</sub> 0		°CH <sub>3</sub>		
Entry		Solvent	t [n]	Conv. [%]	field [%] <sup>(8)</sup>		
1	-	CH₃CN	12	0	0		
2	CsF	CH₃CN	12	6	5		
3	KF	CH₃CN	12	trace	trace		
4	KF/[18]crown-6	CH₃CN	12	98	96		
5	[18]crown-6	CH₃CN	12	0	0		
6	TBAF	CH₃CN	12	99	99		
7	TBAB	CH₃CN	12	trace	trace		
8	TBAC	CH₃CN	12	8	5		
9	TBAF	DMF	12	99	98		
10	TBAF	toluene	12	trace	trace		
11	TBAF	THF	12	trace	trace		
12	TBAF	1,4-dioxane	12	8	6		
13 <sup>[c]</sup>	TBAF	CH₃CN	12	85	84		
14 <sup>[d]</sup>	TBAF	CH₃CN	12	76	74		
15	TBAF	CH₃CN	8	99	99		
16	TBAF	CH₃CN	4	92	90		
[a] Conditions: <b>1a</b> (108 $\mu$ L, 1 mmol), catalyst (5 mol%, relative to <b>1a</b> ), (EtO) <sub>3</sub> SiH (0.74 mL, 4 mmol), 1 bar CO <sub>2</sub> , 30 °C, solvent (2 mL). [b] Determined by GC using 1,3,5-trimethyoxybenzene as an internal standard. [c] (EtO) <sub>3</sub> SiH (0.56 mL, 3 mmol). [d] TBAF (3 mol%).							

hypervalent silicon intermediate (entry 6 vs. 9–12, Table 1). Less polar solvents such as toluene, THF, and 1,4-dioxane were incompatible with the catalytic system, leading to poor results (entries 10–12), presumably due to the decreased stability of the hypervalent silicon intermediate  $[HSiF(OEt)_3(solvent)]^-$  in those solvents.<sup>[23b]</sup> Lowering the amount of triethoxysilane or TBAF led to a decrease in the yield of **1b** to some extent (entries 13 and 14 vs. 6). Four hours was enough to complete the reaction (entry 16).

Various hydrosilanes were investigated for the N-formylation of **1a** with CO<sub>2</sub> (Table 2). PMHS (polymethylhydrosiloxane), TMDS (1,1,3,3-tetramethyldisiloxane), triethylsilane, and triphenylsilane were found to be inactive (entries 1–4, Table 2). Dimethylphenylsilane, diethoxymethylsilane, and triethoxysilane were effective for the N-formylation (entries 5–7), and triethoxysilane showed the highest reactivity among the monohydrosilanes in this study (entry 7 vs. 1–6). The discriminatory activity of various hydrosilanes is presumably due to electronic and steric effects of the substituted groups.<sup>[20]</sup>

Interestingly, when a stronger reductant diphenylsilane in comparison with triethoxysilane<sup>[26]</sup> was used as a reductant, further reduction of the formamide **1b**, namely, methylation product *N*,*N*-dimethylaniline (**1c**) was detected (entry 8 vs. 7, Table 2).<sup>[12h]</sup> The N-methylation reaction involves two steps, that is, formylation and the further reduction of the formamide intermediate. The latter step is more difficult than the former,<sup>[12c]</sup> thus providing an opportunity for selective reduction by tuning the reducing ability of hydrosilanes. Phenylsilane, which has a stronger reducing ability,<sup>[27]</sup> was found to be more favorable for the methylation step than diphenylsilane (entry 9 vs. 8). At last, the methylation product **1c** was successfully ach-

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<b>Table 2.</b> Hydrosilane effect on the reductive functionalization of $CO_2$ with <b>1</b> a. <sup>[a]</sup>						
$\begin{array}{c} \begin{array}{c} \begin{array}{c} H\\ \\ \end{array}\\ \end{array} \\ \begin{array}{c} \\ \\ \end{array} \\ \begin{array}{c} \\ \\ \end{array} \\ \begin{array}{c} \\ \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \\ \end{array} \\ \begin{array}{c} \\ \\ \\ \end{array} \\ \begin{array}{c} \\ \\ \end{array} \\ \begin{array}{c} \\ \\ \end{array} \\ \begin{array}{c} \\ \\ \\ \end{array} \\ \begin{array}{c} \\ \\ \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \begin{array}{c} \\ \\ \end{array} \\ \begin{array}{c} \\ \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \begin{array}{c} \\ \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ $						
1a		1b	1c			
Entry	Hydrosilane (equiv.)	Yield <b>1 b</b> [%] <sup>[b]</sup>	Yield <b>1 c</b> [%] <sup>[b]</sup>			
1	PMHS (4)	-	-			
2	TMDS (2)	-	-			
3	Et₃SiH (4)	-	-			
4	Ph₃SiH (4)	trace	-			
5	Me <sub>2</sub> PhSiH (4)	27	-			
6	(EtO) <sub>2</sub> MeSiH (4)	60	-			
7	(EtO) <sub>3</sub> SiH (4)	99	-			
8	$Ph_2SiH_2$ (2)	45	21			
9	PhSiH <sub>3</sub> (2)	41	57			
10	PhSiH <sub>3</sub> (3)	26	74			
11 <sup>[c]</sup>	PhSiH <sub>3</sub> (3)	4	95			
[a] Unless otherwise specified, all the reactions were performed with <b>1a</b> (108 $\mu$ L, 1 mmol), TBAF (50 $\mu$ L in 1 $\mu$ THF solution, 0.05 mmol), 30 °C, CO <sub>2</sub> balloon, CH <sub>3</sub> CN (2 mL), 12 h. [b] Determined by GC using 1,3,5-trime-thyoyubenzene as an internal standard [c] 50 °C						

ieved in almost quantitative yield under an atmospheric pressure of  $CO_2$  at relative higher temperature (entry 11 vs. 10). As a consequence, simply changing hydrosilane types can enable this methodology with TBAF catalysis in 2- or 6-electron reduction of  $CO_2$ , offering the formamide and *N*-methylamine product, respectively.

After having established the TBAF-catalyzed N-formylation and N-methylation protocol, we first examined the generality of the formylation process through triethoxysilane-controlled reductive functionalization of  $CO_2$  as listed in Scheme 2. Secondary aromatic amines gave the corresponding formamides in good yields at 30 °C and an atmospheric pressure of  $CO_2$  (**1 b**– **4 b**). However, *N*-methyl-4-nitroaniline was unreactive, maybe



**Scheme 2.** Formylation of various amines with CO<sub>2</sub> by using (EtO)<sub>3</sub>SiH as a reductant. Unless otherwise stated, the reactions were conducted on a 1 mmol scale of the amine with TBAF (50  $\mu$ L in 1  $\mu$  THF solution, 0.05 mmol), (EtO)<sub>3</sub>SiH (0.74 mL, 4 mmol), and CH<sub>3</sub>CN (2 mL), 30 °C, 1 bar CO<sub>2</sub> for 4 h. Yields were determined by <sup>1</sup>H NMR spectroscopy using 1,3,5-trime-thyoxybenzene as an internal standard. \*: Isolated yield.

due to a strong electron-withdrawing effect largely weakening the nucleophilicity of the amine (5 b). Aromatic amines with alkenyl (6b) and carbonyl groups (7b) afforded the corresponding formamides without the reduction of the oxidizing groups. Secondary aliphatic amines, such as piperidine, morpholine, and diethylamine could also be converted to the corresponding formamides in quantitative yields (8b-10b), whereas the amine with steric hindrance produced a sluggish reaction (11 b). Additionally, primary amines behaved in a similar fashion to secondary amines, forming the monoformylated products without further methylation (12b-17b). Anilines with electron-donating groups were more active than those with electron-withdrawing groups, which is consistent with the nucleophilicity of amines (13b, 14b vs. 15b, 16b). Cyclohexylamine also showed excellent reactivity towards formylation (17b).

Furthermore, we explored the utility of the phenylsilaneswitched methylation of amines with  $CO_2$  by using TBAF as a catalyst. As listed in Scheme 3, *para*-substituted *N*-methylanilines performed smoothly to give the corresponding products in excellent yields (1 c-4c). Comparatively, *p*-Cl-substituted *N*-



**Scheme 3.** N-methylation of various amines with CO<sub>2</sub> by using PhSiH<sub>3</sub> as a reductant. Reaction conditions: amine (0.25 mmol), TBAF (13  $\mu$ L in 1  $\mu$  THF solution, 0.0125 mmol, 5 mol%), PhSiH<sub>3</sub> (93  $\mu$ L, 0.75 mmol), 50 °C, 1 bar CO<sub>2</sub>, 12 h; yields were determined by <sup>1</sup>H NMR using 1,3,5-trimethyoxybenzene as an internal standard. \*: Isolated yield. \*\*: PhSiH<sub>3</sub> (186  $\mu$ L, 1.5 mmol), 24 h.

methylaniline exhibited a relatively higher reactivity than *N*methylanilines substituted with electron-donating groups, such as methyl or methoxyl (**4c** vs. **2c** and **3c**). *N*-allylaniline was transformed into the corresponding methylated products without the reduction of the unsaturated bond (**7c**). Secondary aliphatic amines showed low activity for the methylation, while they were favorable for the formylation reaction (**8c** and **9c** in Scheme 3 vs. **8b** and **9b** in Scheme 2). In the formylation step, the amine reactivity is consistent with its nucleophilicity. Yet, the further reduction of the formamide intermediate is facilitated by the eletrophilicity of the formamide. The two steps follow opposite electronic demands.<sup>[12f]</sup> As a whole, for the Nmethylation reaction, both opposite factors consisting of the amine nucleophilicity and the formamide eletrophilicity influ-

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ence the amine reactivity. On the other hand, for the N-formylation reaction, the nucleophilicity of the amine determines the amine reactivity. Primary amines including aromatic and aliphatic ones were then examined, and dimethylated products were obtained dominantly by increasing the hydrosilane amount and extending the reaction time (12c-19c).

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To gain insight into the reaction mechanism, several control experiments were performed as depicted in Scheme 4. Firstly, the possible intermediate silvl formate was prepared through the reaction of CO<sub>2</sub> with triethoxysilane catalyzed by TBAF within four hours (Eq. (1), Scheme 4, see the Supporting Infor-



Scheme 4. Control experiments.

mation for details). Then, the silyl formate was subjected to Nmethylaniline (1 a) in the presence of TBAF, giving N-methylformanilide (1 b) in quantitative yield. Interestingly, the reaction between the silyl formate and 1a proceeded smoothly even in the absence of TBAF (Eq. (2), Scheme 4), thus suggesting that the amine activation is not a prerequisite for the formylation. When 1b reacted with triethoxysilane at 30 or 50 °C, methylation product 1 c was not observed. While using phenylsilane as a reductant, a 95% yield of 1c was obtained (Eq. (3), Scheme 4). These control experiments indicated that the formamide reduction to methylamine is more difficult than the formylation step,<sup>[12c]</sup> which requires a highly active reducing agent such as phenylsilane. By tuning the reducing ability of the hydrosilane, selectivity towards different reduction products could be tuned elegantly.

On the basis of the above experimental results and previous reports on the fluoride-catalyzed carbonyl reduction,<sup>[23]</sup> a possible mechanism for the present fluoride-catalyzed reductive functionalization of CO<sub>2</sub> in the presence of amine with hydrosilane as a reductant was proposed (Scheme 5). At first, the fluoride anion reacts with the hydrosilane to afford the hypervalent silicon intermediate I, thus allowing the CO<sub>2</sub> insertion to readily form the crucial intermediate silvl formate II. Then, the nitrogen atom of the amine nucleophilically attacks the carbon



Scheme 5. Proposed mechanism for the TBAF-catalyzed reductive functionalization of CO<sub>2</sub>.

atom of intermediate II to give the formamide product III along with the silanol as a byproduct. When employing triethoxysilane as a reductant, the formamide is exclusively obtained as the final product. Whereas when using a stronger reducing agent, phenylsilane, as a reductant, the formamide could go through further reduction to afford N-methylated product IV through a similar fluoride-catalyzed hydride transfer. Thus, this organocatalytic procedure represents a perfect example for chemoselective two- or six-electron reduction of CO<sub>2</sub> coupled with C–N bond construction.

In conclusion, a TBAF-promoted metal-free protocol for the reductive functionalization of CO<sub>2</sub> in the presence of amines has been developed with high yield as well as tunable chemoselectivity. The formamide and methylamine product could be accessed by tuning the hydrosilane type. When using triethoxysilane as a reductant, this protocol enabled the formylation of a variety of amines with TBAF under an atmospheric pressure of CO<sub>2</sub>. With the stronger reducing agent phenylsilane, the catalytic system was active in the methylation at 50 °C. A tentative mechanism involving the fluoride-promoted hydride transfer from hydrosilanes to CO<sub>2</sub>/formamide was proposed. Such control allows chemoselective 2- or 6-electron reduction of CO<sub>2</sub> in combination with C-N bond construction. Further studies on the reaction mechanism and to expand the utility of this organocatalytic system are in progress in our laboratory.

### **Experimental Section**

#### General procedure

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Under an inert atmosphere (Ar), a 10 mL Schlenk flask was charged successively with amine (1.0 mmol), hydrosilane, and  $CH_3CN$  (2 mL). After the mixture had been stirred for 5 min, 50 µL TBAF in THF solution (1 M) was added and bubbles of gas were observed. The reaction mixture was stirred at a typical temperature for the desired time under an atmosphere of CO<sub>2</sub> (99.999%, balloon). After the reaction was complete, 1,3,5-trimethyoxybenzene (42.0 mg) was added as an internal standard and then a sample was taken to be

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injected into the GC to determine the conversion and yield. All catalytic reactions were performed at least twice to ensure reproducibility. To identify the structure of the formylated/methylated product, the reaction mixture was concentrated and purified by silica gel column chromatography (petroleum ether-EtOAc) to afford the corresponding formamide/methylamine.

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**Keywords:** carbon dioxide fixation • chemoselectivity hydrosilanes • organocatalysis • reductive functionalization

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# FULL PAPER

# Organocatalysis

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Fluoride-Catalyzed Methylation of Amines by Reductive Functionalization of CO<sub>2</sub> with Hydrosilanes



**Highly efficient organocatalysis**: Reductive functionalization of CO<sub>2</sub> with amines employing tetrabutylammonium fluoride affords formamides and methylamines, respectively. Such a protocol allows selective two- or six-electron reduction of  $CO_2$  coupled to C–N bond construction (see scheme).

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