Organocatalytic Reductive Functionalization of Carbon Dioxide

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Abstract The catalytic transformation of carbon dioxide (CO_2) into value-added chemicals and high-value fuels is the most promising strategy to mitigate the concentration of CO_2 in the atmosphere. Among the various catalytic approaches used in the conversion of CO_2, its reductive functionalization is a very attractive way to access the array of interesting scaffolds such as formic acid, formates, formamides, methanol, and methane as key C1 building blocks for energy and synthetic chemistry. Several reports are available for the reductive functionalization of CO_2 with homogeneous and heterogeneous catalysts using molecular hydrogen and other soft reducing agents like hydrosilanes and hydroboranes. Although these catalysts demonstrated excellent activity and selectivity, they suffer from several drawbacks like use of precious, toxic metals, and air- and moisture-sensitive complexes and generally follow the lengthy synthetic process. However, the use of transition metal-free catalysts or organocatalysts has attracted much attention in recent years because it follows the green chemistry rules, is cost-effective, and avoids contamination of products that are common by using transition metal catalysts. In recent years, numerous reports are raised in the utilization of well-defined organocatalysts for the reductive functionalization of CO_2 due to its activity, selectivity, and sustainability. Here, we overview the use of organocatalysts for the reductive functionalization of CO_2 using hydrosilanes, hydroboranes, and hydrogen as a reducing agent for the synthesis of value-added chemicals and fuels in recent days. Homogeneous transition metal and heterogeneous and heterogenized organocatalysts are out of the scope of this chapter.

Keywords Catalytic reduction · Carbon dioxide · Organocatalysis · Hydrosilanes · Hydroboranes · CO_2 reduction

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Abbreviations

aNHC	Abnormal N-heterocyclic carbene
9-BBN	9-Borabicyclo[3.3.1]nonane
Ar	Aryl
atm	Atmosphere
Bu	Butyl
Cat	Catechol
Cat.	Catalyst
DABCO	1,4-Diazabicyclo[2.2.2]octane
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
DMAP	(4-Dimethylaminopyridine)
Et	Ethyl
FLPs	Frustrated Lewis pairs
h	Hour(s)
Me	Methyl
Mes	Mesityl; 2,4,6-trimethylphenyl
MIC	Meso-ionic carbene
NHC	N-heterocyclic carbene
NHO	N-heterocyclic olefin
Ph	Phenyl
Pin	Pinacol
Pr	Propyl
rt	Room temperature
TBD	1,5,7-Triazabicyclo [4.4.0] dec-5-ene
THF	Tetrahydrofuran

1 Introduction

Anthropogenic activity generated excess amounts of greenhouse gases, creating significant environmental threats to humankind and the ecosystem in terms of global warming, ocean acidification, rising sea level, etc. Among them, the generation of excess amount of CO_2 as a greenhouse gas by the burning of fossil fuel is highly responsible for global warming. Thus, the mitigation of CO_2 is the highest interest of research from academic, industry, and environmental points of view [1]. Various strategies have been developed to capture conversion and use of anthropogenic CO_2 to value-added chemicals and fuels [2]. Among them, the transformation of CO_2 to value-added chemicals and fuel would be a great alternative to the conversion of CO_2 [3]. However, the transformation of CO_2 is a challenging task due to the highest oxidized form of carbon and its inert nature [4]. In addition to this, its thermodynamic stability and kinetic inertness hamper its applications in the synthesis of chemicals and fuel. Due to this CO_2 is sluggish to react, it generally needs strong reagents, harsh

conditions, and potential catalysts [5]. In this regard, catalytic conversion of CO_2 is taking intense attention, and a range of well-defined homogeneous and heterogeneous catalysts has been developed. Although homogeneous organometallic catalysts are widely used, they utilize precious metals, are highly air- and moisture-sensitive, and require a lengthy ligand synthesis method [6]. In heterogeneous catalysis, there is a lack of well-defined active centers, and low yields and poor selectivity are the major issues. Recently, the use of well-defined organocatalysts for various transformations has been of high interest because they feature well-defined active centers, avoid the use of precious transition metals, are easy to synthesize, and can act as a replacement for transition metals [7].

Recently, a range of organocatalysts such as frustrated Lewis's acid–base pairs (FLP), NHC's, Lewis' acids such as $B(C_5F_5)_3$, bases, and functional ionic liquids (ILs) demonstrated potential applications in catalytic activation of CO_2. Especially, reductive functionalization of CO_2 with reducing agents like hydroboranes, hydrosilanes, and hydrogen is widely explored for various organic transformations (Scheme 1a). These reducing agents offer very exciting products from CO_2 (Scheme 1b) such as formic acid ($2e^-$), formaldehyde ($4e^-$), methanol ($6e^-$), and methane ($8e^-$) [8]. Along with these reactions and using suitable coupling partners like amines, various reactions like N-formylation, N-formylation/cyclization, and N-methylation were also achieved to synthesize the very important functional groups under mild reaction conditions. We sensed that no one has summarized this topic systematically, with mechanistic aspects toward the active centers of organocatalysts and its diverse substrate scope. Hence, in the present book chapter, we will review the recent progress by organocatalytic reductive functionalization of CO_2 with hydroboranes, hydrosilanes, and hydrogen concisely and mechanistically.
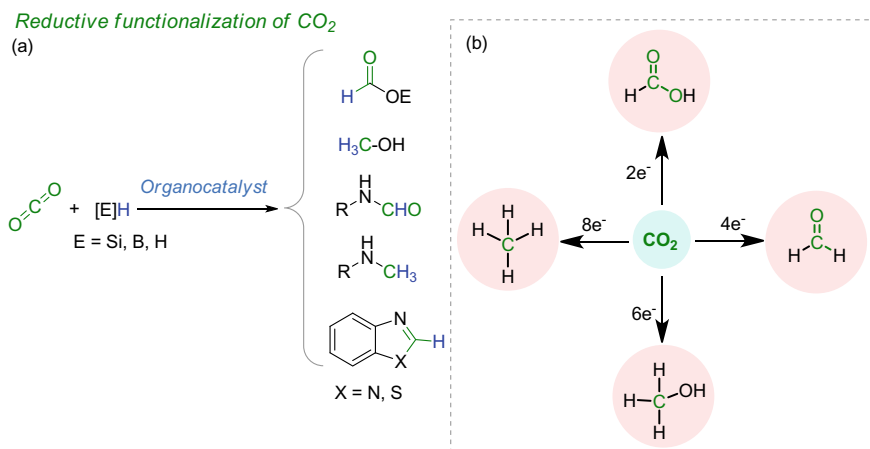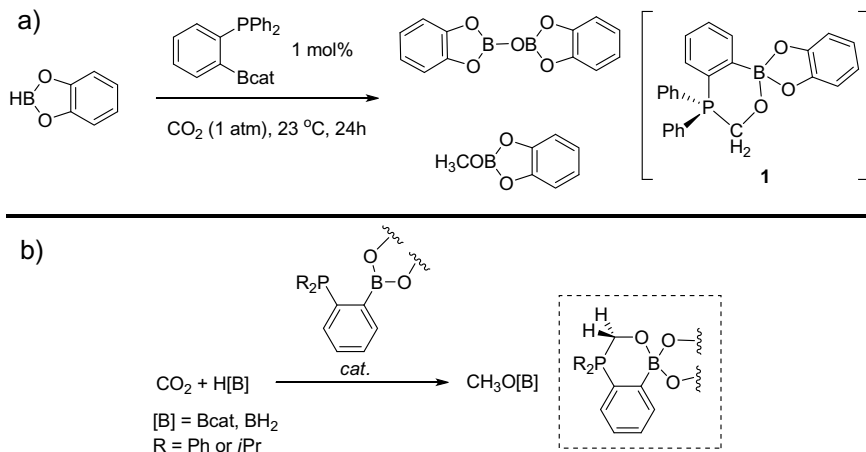

Scheme 1 **a** Reduction of CO_2 to different chemicals and **b** reduction level of CO_2 to various products
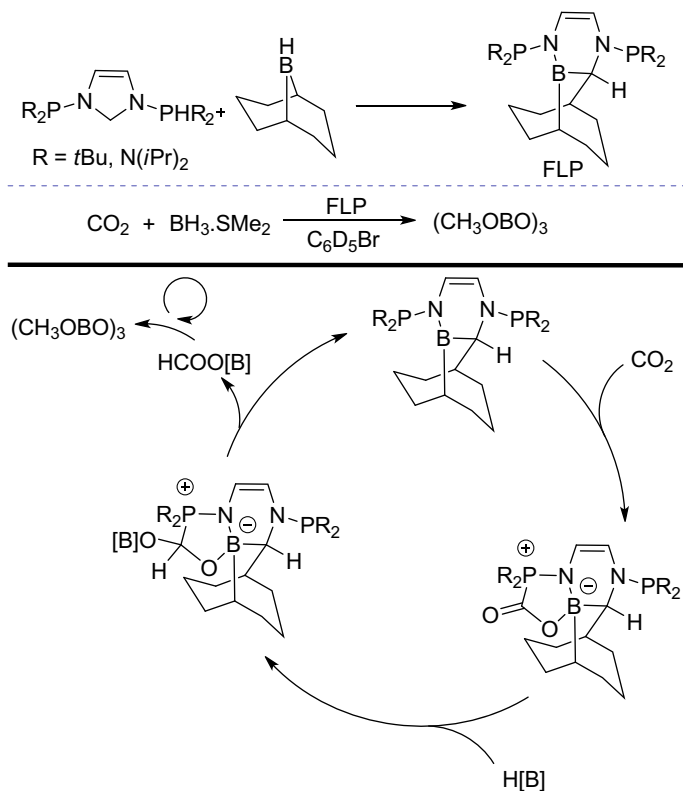
Organocatalytic hydroboration of CO_2

Hydroboranes are very important reducing agents and are considered as soft reducing agents for a broad spectrum of reductive transformations. In recent years, various boranes have been used to reduce the CO_2. In 2013, Fontaine et al. used 1-Bcat-2-PPh_2-C_6H_4 (cat = catechol) as an ambiphilic organocatalyst for the reductive functionalization of CO_2 using catechol boranes to synthesize CH_3OBR_2 or $(CH_3OBO)_3$. Their easy hydrolysis generates methanol (Scheme 2a) [9]. High TON and TOF up to > 2950 and 853 h^{-1} have been noted. A range of boranes like catecholborane (HBcat), pinacolborane (HBpin), 9-borabicyclo[3.3.1]nonane (9-BBN), $BH_3 \cdot SMe_2$, and $BH_3 \cdot THF$ has been screened. A reaction mechanism has been anticipated, as the presence of active centers of Lewis acid and base on the catalyst assists the catalysis by liberating the reduction products. In an isotope experiment study, it was found that when the adduct **1** formed, it remains as it is and acts as an active catalyst (Scheme 2b) [10]. Cascade activation of borane and CO_2 using an ambiphilic catalyst is the key for these transformations. This concept of CO_2 activation was inspired by the work of G. Erker, where they have used the base tBu_3P and $B(C_6F_5)_3$ as an acid pair and FLP-CO_2 as a solid product that was isolated [11].

Stephan and coworkers in 2014 applied stoichiometric tri-*tert*-butylphosphine (tBu_3P) for the reduction of CO_2 using 9-BBN as a reducing agent which yielded $(R_3PCH_2O)(HC-(O)O)B(C_8H_{14})$ [12]. The catalyst works like FLP pathway, and at the 60 ˚C, around 98% yields were observed with TON up to 5500 and a TOF of 170 h^{-1} (Scheme 3). Experimental evidence suggested that the reaction mechanism follows FLP to activate the CO_2 molecule and the subsequent transfer of hydride to the electrophilic carbon center.

**Scheme 2** Reducing CO_2 to methanol using frustrated Lewis pairs

Scheme 3 FLP-catalyzed reduction of CO_2 to methanol

As established by Stephan, FLP for CO_2 activation, phosphine-bearing NHC (XX) adduct was synthesized and used as an intramolecular FLP by NHC ring expansion and 9-BBN (Scheme 4) [13]. This FLP comprises a strong basic site (P) and weak Lewis acidic site (B), which act as suitable FLP reagent for the hydroboration of CO_2 with boron hydride and resulted in methoxyborane as a product with a TON of 240.

In 2014, Fountain screened various base catalysts for the hydroboration of CO_2 using the borane-dimethylsulfide ($BH_3.SMe_2$) as hydroborating agent, among the various bases like MeONa, TBD, terpyridine, etc., and non-nucleophilic proton sponge demonstrated the highest activity with TOF up to 64 h^{-1} at 80 °C (Scheme 5) [14]. Hydroboration of CO_2 was slow at room temperature, while at 80 °C, proton sponge and $BH_3.SMe_2$ react rapidly and exothermically and accelerate the rate of reaction very efficiently. This observation also suggests that the generation of **2b** from **2a** is the rate-limiting state of this catalytic cycle.

Then Cantat and coworkers used 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) as a base for stabilizing the silylium species as FLP organocatalysts in the hydroboration of CO_2 to afford methoxide using 9-BBN, catBH, and pinBH as reducing agents (Scheme 6) [15]. The reaction of CO_2 and catalyst afforded the N/Si$^+$ FLP-CO_2 as an active adduct which is responsible for the catalytic cycle. In the reaction mechanism, initially, FLP activates the CO_2 molecule in the electrophilic carbon by the nitrogen Lewis base, while silicon acts as Lewis's acid.

Again, they have synthesized an ambiphilic phosphinoborane complex supported by the ferrocene backbone for the hydoboration of CO_2 [16]. With phosphine

Scheme 4 FLP-catalyzed reduction of CO_2 to methanol

(PPh_2), boranes such as 3-Bpin and 3-BMes$_2$ were installed on the ferrocene scaffold (Scheme 7). The 3-BMes$_2$ as a Lewis acid demonstrated excellent catalytic activity for this reaction, and TON up to 1980 and TOF up to 250 h^{-1} were noted. The presence of phosphines and boranes functional groups on ferrocene presented synergistic catalysis for the hydroboration of CO_2. However, when individually tested, no catalytic reduction in CO_2 was observed. In the reaction mechanism, both active centers participate in the activation of borane and CO_2 to furnish CH_3O–BBN.

Song et al. used organic ligands based on N-methyl-4,5-diazafluorenide, a molecule containing three as well as two rings for the reductive hydroboration of CO_2 to methyl boryl ether, which can be further hydrolyzed to methanol (Scheme 8) [17]. Carbon-centered reversible binding of CO_2 from these organocatalysts demonstrated excellent catalytic activity with wide boranes.

In 2018, Garca-Vivo used carbodiimides as organocatalyst for CO_2 reduction with hydroboranes such as 9-BBN or BH$_3$SMe$_2$ at 1 atm CO_2 to lead CH$_2$(OBBN)$_2$ and CH$_3$OBBN or (MeOBO)$_3$ and B(OMe)$_3$ at 25–60 °C (Scheme 9) [18]. Experimental and computational studies demonstrated that the formation of formaldehyde and
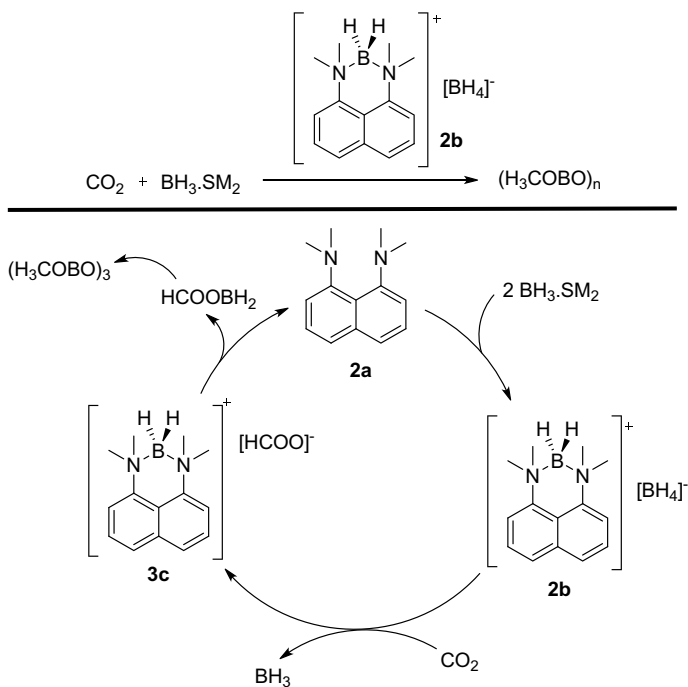
Scheme 5 Non-nucleophilic proton sponge-catalyzed reduction of CO_2 to methanol
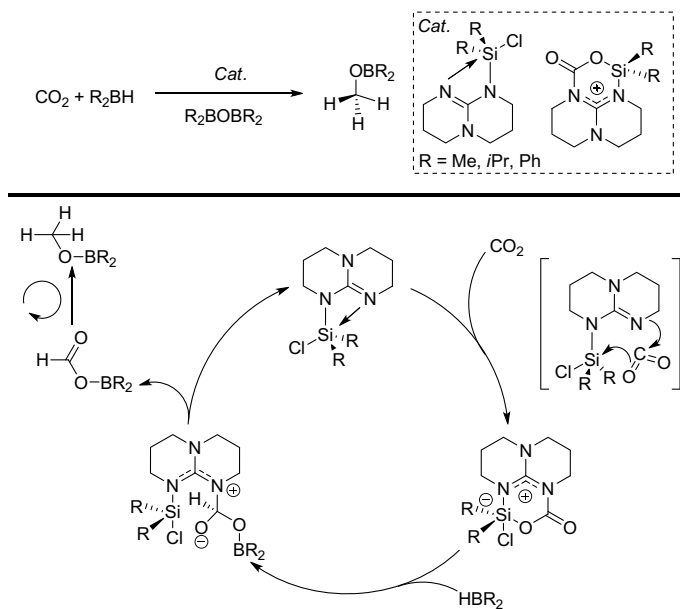
Scheme 6 N/Si$^+$ FLP for reductive activation of CO_2
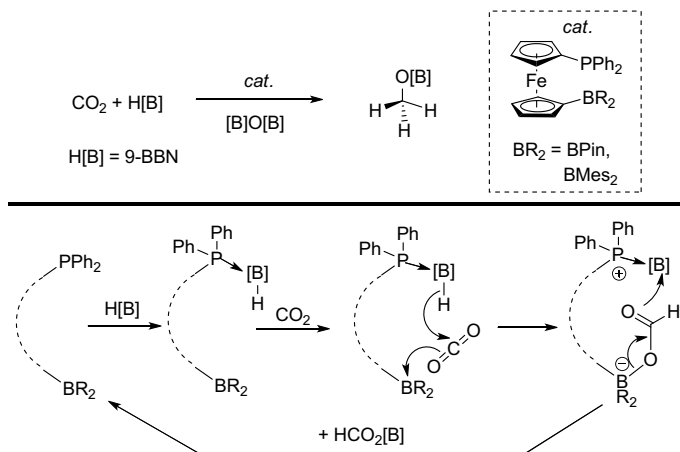
**Scheme 7** Phosphine-borane FLP for reductive activation of CO_2 with boranes
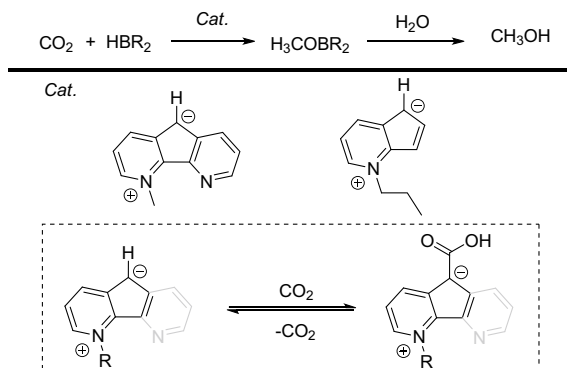
**Scheme 8** Organocatalyzed activation of CO_2 and reduction with boranes

triazaborinaneimine-BH_3 adducts (**4a** and **4b**) was responsible for CO_2 activation and subsequent reduction.

Recently, Ramos and coworkers synthesized phosphinoborane $Ph_2P(CH_2)_2BBN$ by reacting diphenyl(vinyl)phosphine and 9-BBN and used for the hydroboration of CO_2 to CH_3OBBN (MeOH), and TON up to 764 is noted (Scheme 10) [19]. It was found that this catalyst reacts with CO_2 and boranes to generate the formaldehyde adduct (**5**) $Ph_2P(CH_2)_2BBN(CH_2O)$ as in previous reports and is responsible for hydroboration reactions.

Cantat et al. used nitrogen bases like TBD, Me-TBD (MTBD), and DBU for the hydroboration of CO_2 with 9-BBN or CatBH and achieved a TON of up to 648 at room temperature (Scheme 11) [20]. The basic sites of TBD activate CO_2 and generate a TBD-CO_2 adduct which is the key step in the reduction of CO_2. Based on
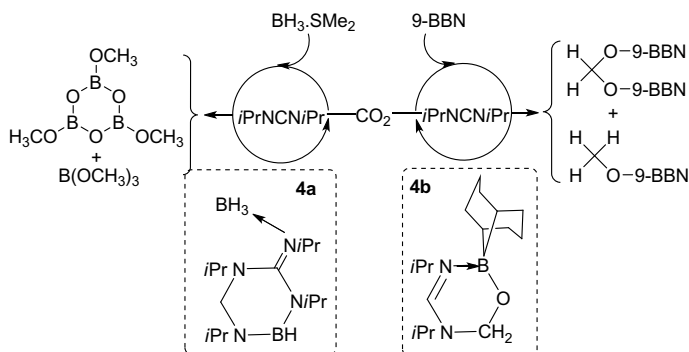
**Scheme 9** Carbodiimides as catalysts for the reduction of CO_2 with boranes
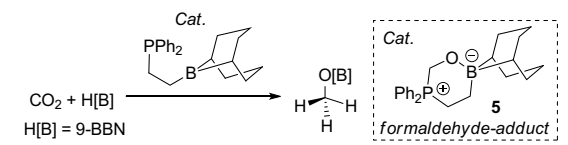
Scheme 10 Phosphinoborane as catalysts for the reduction of CO_2 with boranes

the experimental study, a reaction mechanism has been proposed, and TBD catalyst acts as Lewis's base to activate CO_2 and coordinates with hydroborane to generate an adduct **6b**, which facilitates the hydride transfer from borane to carbon, to give adduct **6c** with generation of boron formate intermediate which will further go reduction reaction to methoxyborane.

Mandal and coworkers used an abnormal N-heterocyclic carbene (aNHC) borane adduct formed by the reaction of aNHC with 9-BBN to capture CO_2 from the atmosphere and its integrated reduction into formic acid and methanol under mild conditions (Scheme 12) [21]. Reaction of 9-BBN and CO_2 in presence of aNHC afforded a TON of 6000 to methanol in C_6D_6 at the room temperature for 12 h. Initially, it is assumed that a reaction of CO_2 and aNHC afforded aNHC-CO_2 which is the key catalyst for the reduction of CO_2. This adduct activates the B–H bond of borane which further undergoes an insertion with another CO_2 molecule to lead to four-coordinated boron species. Then, the insertion of two molecules of 9-BBN to adduct gives a zwitterionic borondiformate with the releasing of a dimer B–O–B. Afterward, reaction of other 9-BBN results in the regeneration of catalyst with methoxide derivative.

Reactions with amines

The first metal-free catalytic methylation of amines using CO_2 as a C1 source with boranes was reported by Cantat et al. in 2014 using proazaphosphatrane superbases as catalysts (Scheme 13) [22]. Boranes such as 9-BBN, HBcat, and HBpin were
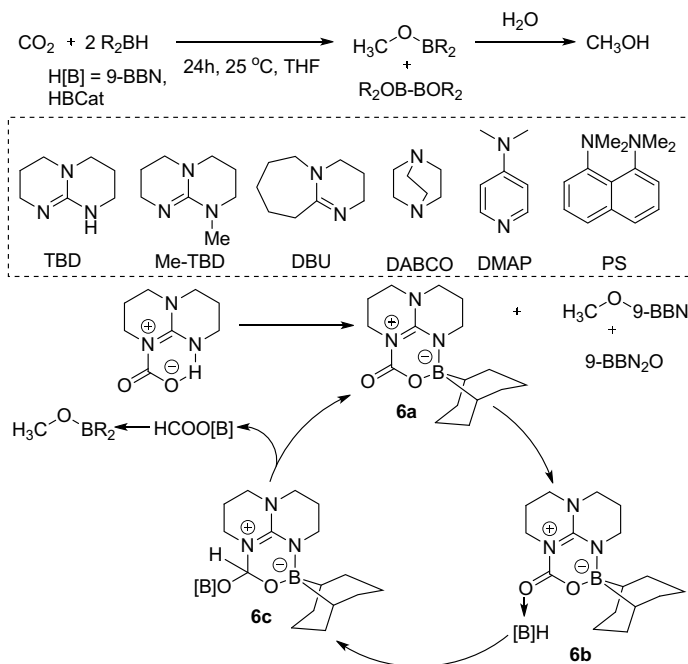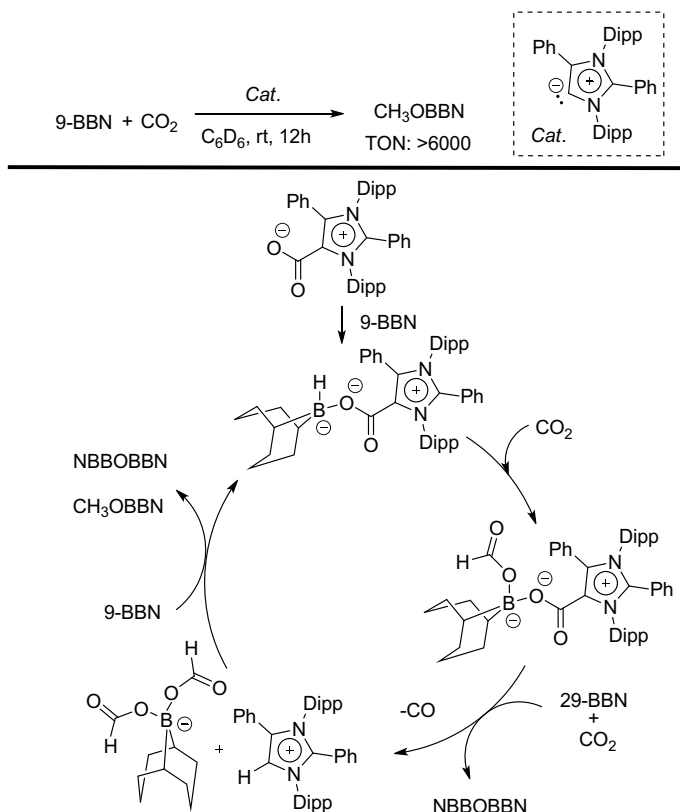
Scheme 11 TBD base-catalyzed reduction of CO_2 with boranes

screened, but the use of 9-BBN gave excellent yields. For monomethylation 4 equivalent and for dimethylation of amines 8 equivalent of the reducing agents were required. Various other organocatalysts were also screened such as TBD, NHCs, and other phosphine ligands, but the only substituted proazaphosphatrane afforded excellent yields and selectivity. Using this protocol, a large number of substrates tolerated excellent yields for the mono- as well as dimethylation of amines. Basic phosphine acts as a key catalyst for this transformation and tolerates the reaction effectively.

Ong and coworkers in 2015 synthesized novel carbodicarbenes (CDCs) as strong σ-donating ligands analogues to the NHC and used for the reductive N-methylation of amines using 9-BBN as reducing agent (Scheme 14) [23]. Wide range of functional amines that undergoes N-methylation efficiently afforded good to excellent yields of the products. Upon reaction, the CDC reagent ligand with borane adduct is generated which was assumed to be key catalytic active species for the reductive functionalization of CO_2. A reaction mechanism is also proposed similar to the previous scheme promoted by CDC catalyst. The CDC catalyst activates both the borane and CO_2 by a nucleophilic attack to generate formate intermediate, which subsequently reacts with amine molecule.

Bhanage and coworkers in 2016 synthesized a series of N-heterocyclic olefin (NHO) ligand systems and used them as catalysts for the reductive N-formylation of amines with CO_2 (Scheme 15) [24]. The presence of an ylidic exocyclic carbon atom of NHO ligand is a very powerful nucleophile and acts as a scavenger for CO_2 by

Scheme 12 aNHC-catalyzed reduction of CO_2 with boranes

forming an NHO-CO_2 adduct. This adduct is the key active catalyst for the reductive functionalization of CO_2 at mild conditions. 9-BBN and polymethylahydrosiloxane (PMHS) from silicon industry waste as a reducing agent were used for the various amines.

Bhanage et al. in 2018 used $B(C_6F_5)_3$ as a Lewis acid catalyst for CO_2 reduction with amines and dimethylamine borane as a reducing agent for N-formylation and N-cyclization of diamines to benzimidazoles [25]. High TONs up to 1237 and TOFs up to 309 h^{-1} were observed (Scheme 16). The catalyst $B(C_6F_5)_3$ is highly responsible for the activation of CO_2 with the amine molecule by acting as a FLP pair. Also, the activation of B–H bond is processed by the catalyst. Various amines including aliphatic and aromatic and diamines were tolerated effectively.

Recently, Gao and coworkers used a borane-trimethylamine complex as a reducing agent for the methylation and formylation of amines in presence of 6-amino-2-picoline as an organocatalyst with 1 atm of CO_2 (Scheme 17) [26]. A wide range of primary, secondary, and aliphatic amines tolerated under the optimized reaction condition for the methylation as well as formylation reaction. Synthetically important
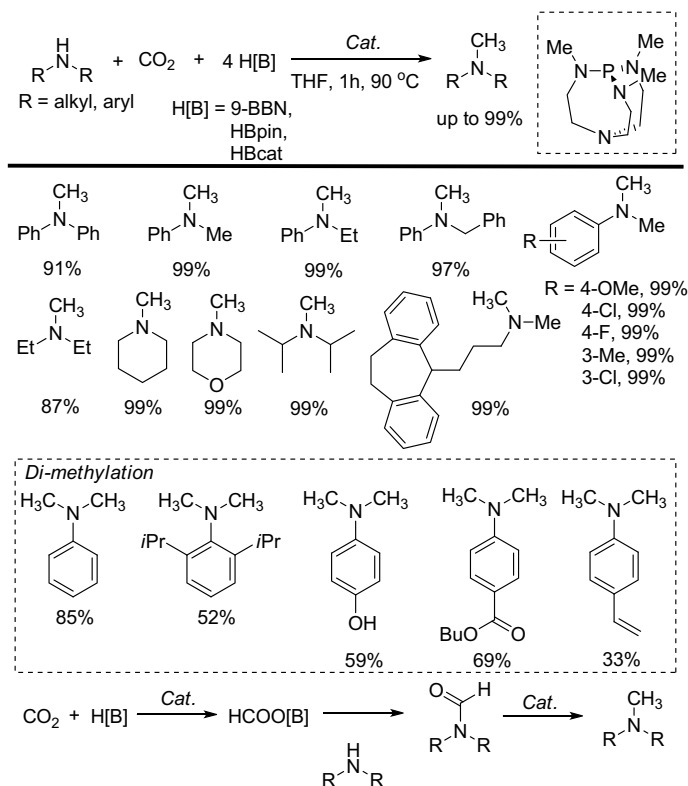
Scheme 13 Proazaphosphatrane superbases-catalyzed hydroboration of CO_2

molecules such as chlorcyclizine derivatives have also been formylated and methylated using this method. Organocatalyst 6-amino-2-picoline acts as intramolecular FLP to activate the CO_2 molecule. In the absence of the catalyst, the only formylated product was observed. An experimental and mechanistic study suggested that borane plays a dual role, acting as Lewis' acid for the generation of intramolecular FLP and reducing agent for CO_2.

Very recently, So et al. synthesized N-phosphinoamidinato NHC-diborene as an active catalyst for the hydroboration of CO_2 with HBpin to synthesize the MeOBpin and for the N-formylation of amines (Scheme 18) [27]. In the mechanistic study, it was found that the presence of double-bonded boron centers is the key catalytic center for the activation of CO_2 and further hydroboration reaction.

Very recently, Mandal et al. used mesoionic N-heterocyclic olefin (NHO) as an active catalyst for the N-methylation of amines with CO_2 using 9-BBN as reducing agent using THF as solvent at 40 °C (Scheme 19) [28]. As a NHC ligand, the NHO ligands have more electron density at the olefinic carbon, which unveiled the activation of borane and CO_2. A wide range of secondary and primary amines undergoes mono- and dimethylation reactions under mild reaction conditions. Additionally, the
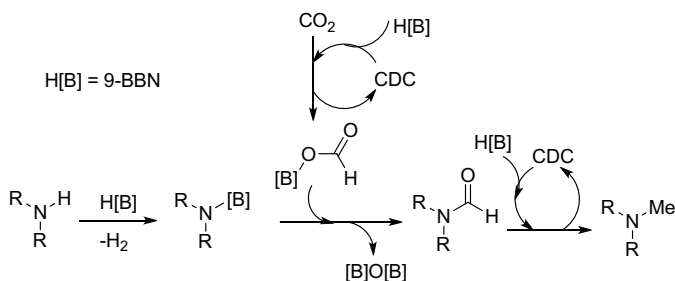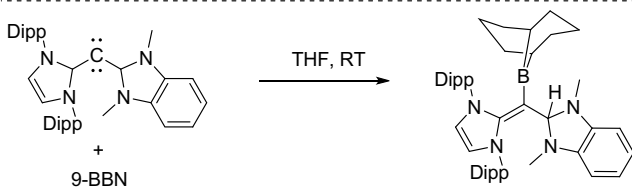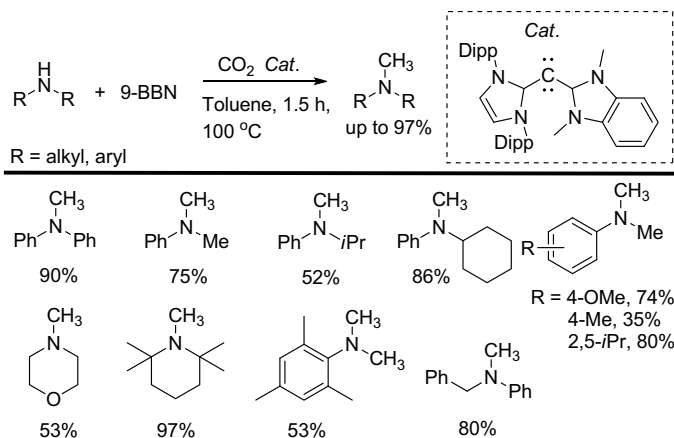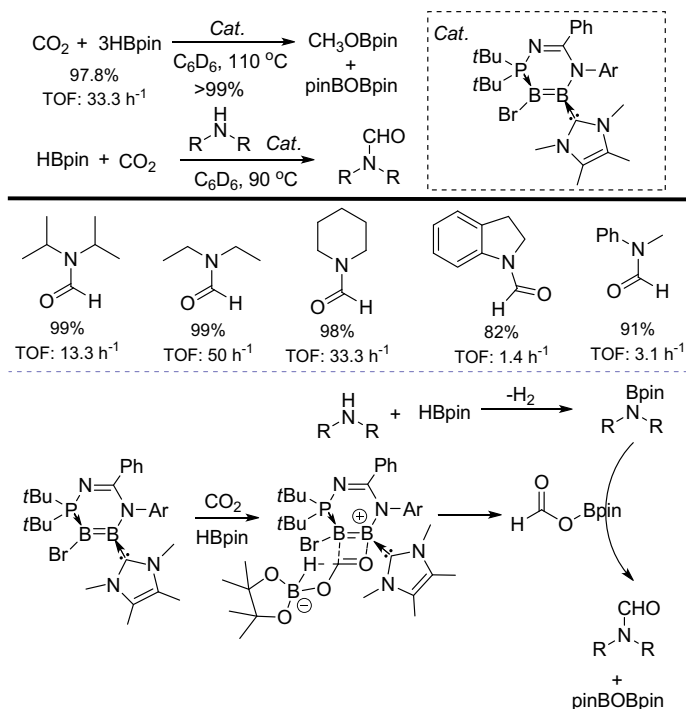
Scheme 14 CDC-catalyzed hydroboration of CO_2
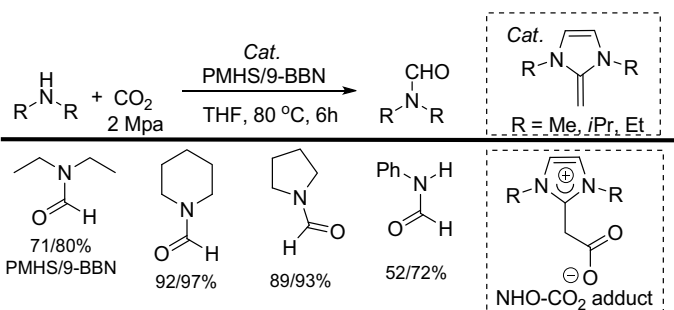
Scheme 15 NHO-catalyzed hydroboration and hydrosilyation of CO_2
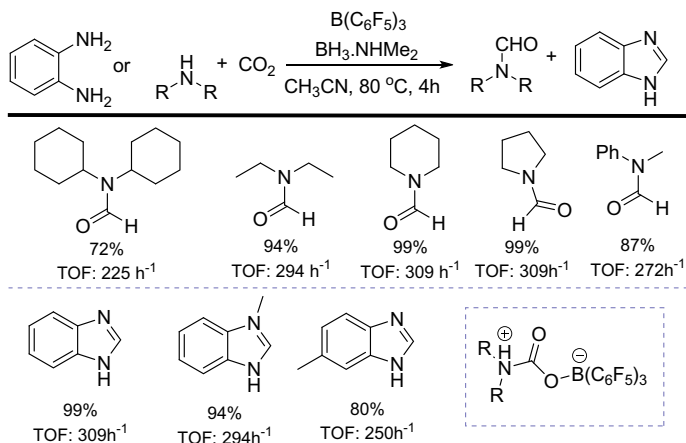
Scheme 16 Lewis's acid-catalyzed hydroboration of CO_2
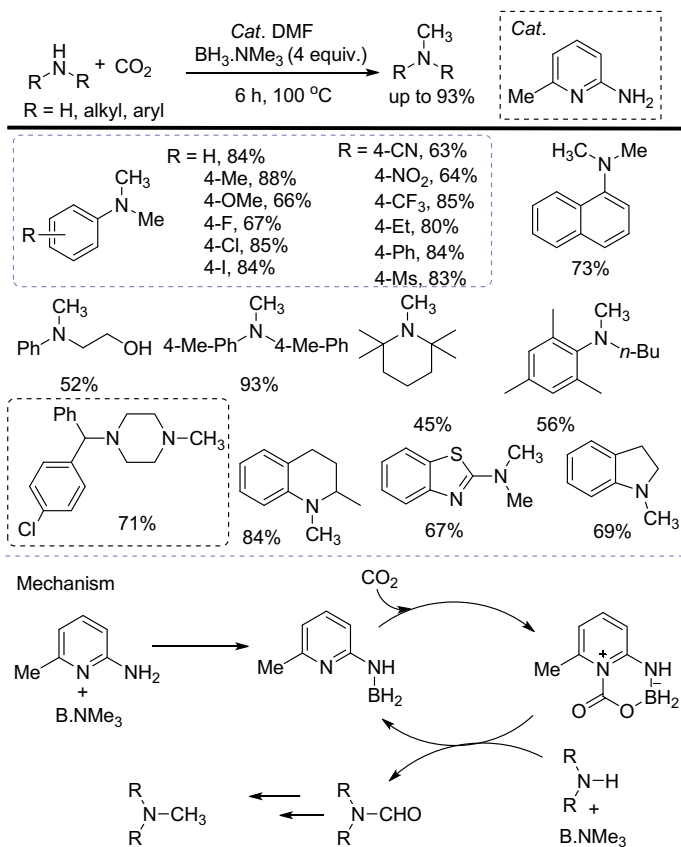
**Scheme 17** 6-amino-2-picoline-catalyzed hydroboration of CO_2

Scheme 18 N-phosphinoamidinato NHC-diborene-catalyzed hydroboration of CO_2

protocol demonstrated the synthesis of pharmaceutically important drugs such as angustureine as an antimalarial drug and pempidine as a ganglion-blocking drug. Mechanistic assumptions were made based on the various computational and experimental studies, and it is assumed that the nucleophilic mesoionic NHO attack on the boron center of the 9-BBN makes hydrogen more hydridic to transfer to the CO_2 effectively.

## Organocatalytic hydrosilylation of CO_2

Among all hydroelements, silanes are important and versatile reducing reagents. Reduction of CO_2 with silane soft reducing agent with homogeneous catalysts is well established. Cantat and coworker demonstrated the reactivity of amines and alcohols with CO_2 in the presence of a base to yield carbamate and carbonate salts, respectively (Scheme 20) [29]. The reaction of the CO_2-amine/alcohol-silane tricomponent systems was elucidated for the reductive functionalization of CO_2. With various bases as catalysts such as TBD, Methyl-TBD, DBU, DABCO, and DMAP, the results obtained showed that stronger bases such as Me-TBD, DBU, and DMAP proved to be efficient catalysts for the formylation product. Organosilanes can also be used as a reducing agent without additional energy expenditure. This is particularly attractive to be used as a reducing agent with added benefits of low to non-toxicity
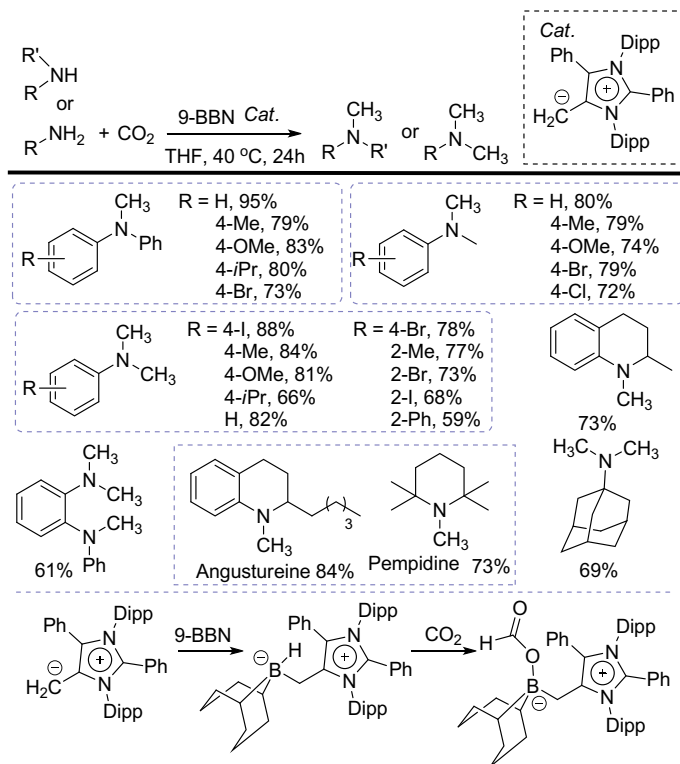
Scheme 19 mNHO-catalyzed hydroboration of CO_2

and cost-effectiveness. Furthermore, dialkylamines such as piperidine, morpholine, Me_2NH, and Et_2NH were used as carbonate substitutes that were converted to their corresponding formamide derivatives with good yield. The yield ranged between 47 and 65% with minimum catalyst loading, that is, 5 mol%.

Following this work, Cantat et al. have further demonstrated the use of a TBD catalyst for the selective reduction of CO_2 with silane and amines in aminals (Scheme 21) [30]. In this case, interesting results were found for the 'four-electron reduction of CO_2' in the presence of secondary aromatic amines. In the reaction describing the metal-free hydrosilylation conditions, the CO_2 bonds were cleaved, and the organocatalysts attack on CO_2 to balance with the reactivity and to endorse the selective development of two C–OH and two C-N bonds. The methodology allows the formation of various unsymmetrical as well as symmetrical aminals efficiently. Potential reaction paths are suggested in the scheme, and the reductive functionalization of CO_2 to formamides is demonstrated, specifically TBD's role in catalysis of this process. Interestingly though, reactivity is absent when N-methylformanilide is combined with $PhSiH_3$ in the presence of 5 mol% TBD at 80 °C, even when N-methylaniline is present (or absent; under Ar or CO_2). It therefore appears that
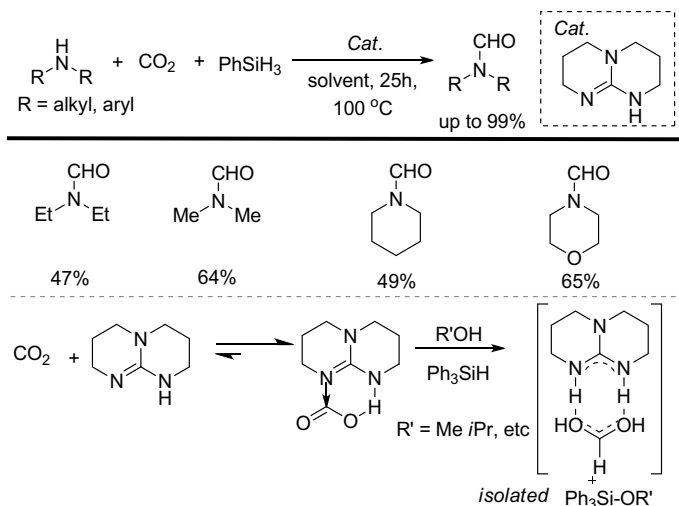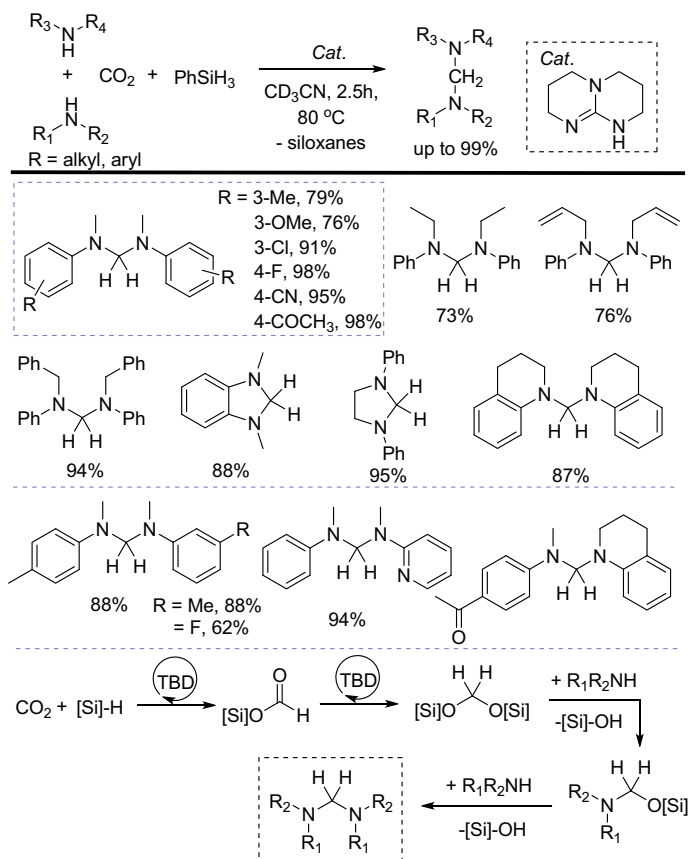
Scheme 20 TBD-catalyzed reduction of CO_2 to formamides using amines and $PhSiH_3$

formamides manifest as competition products in the conversion of CO_2 to aminals. The activation of CO_2 to aminals proceeds via reduction of CO_2 to a silyl acetal species which undergoes two successive nucleophilic attacks by the amine group.

The N-methylation and N-formylation strategies of amines were further studied by Li et al. by using the DBU as a base catalyst [31]. In DBU catalysis, it was found that a temperature switch (30–100 °C) with a corresponding change in reaction time from 72–48 h controls the reaction mechanism from N-formylation to N-methylation. Ying and coworker in 2009 for the first time used NHC as an organocatalyst for the CO_2 reduction with hydrosilanes [32]. The reaction conditions used were 1,3-bis(2,4,6-trimethylphenyl)imidazolium carboxylate (IMes-CO_2) in N,N-dimethylformamide (DMF) through H_2SiPh_2 at 1 bar of CO_2 pressure carried out at room temperature. After 24 h, the yield observed was the methoxide species $(CH_3O)_2SiPh_2$ and $[(CH_3O)SiPh_2O]$. The TON and the TOF using the NHC catalyst at the mentioned reaction conditions reached 1840 and 25.5 h^{-1}, respectively. From the obtained results, nucleophilic NHC turns as an excellent CO_2 activator. In the reaction mechanism, they proposed that imidazolium carboxylate was formed which reacts with silanes even if a free carbene might also trigger the Si–H bond.

Followed by this work, Cantat et al. used very active organocatalysts based on NHCs for the N-formylation of NH bonds [33]. Various forms of nitrogen molecules and heterocyclic groups were applied using CO_2 and polymethylhydrosiloxane (PMHS), which are the two chemical wastes from the industries. IPr NHC was unveiled high activity in the formylation of morpholine with CO_2 and $PhSiH_3$, which showed in that TOF was 160 h^{-1} and also on further investigation of the scope of reaction for formylation with various types of N–H bonds, like $PhSiH_3$ as reductant and IPr as organocatalyst. Aliphatic secondary amines, such as piperidine, morpholine,

Scheme 21 TBD-catalyzed reduction of CO_2 to formamides using amines and $PhSiH_3$

and diethylamine, were transformed to corresponding formamides quantitatively after 24 h at r.t., under 1 bar of CO_2 pressure (Scheme 22). Dimethylformamide (DMF) was obtained as the only product when dimethylammonium dimethylcarbamate was employed as a substrate. Primary aliphatic amines showed particular reluctant substrates using nitrogen bases as catalysts (e.g., TBD). Various simple aliphatic, bulky, and aromatic substrates were also tolerated under the optimized reaction condition. Electron-donating groups have a constructive impact on the translations observed for aniline derivatives. The scope of catalyst extended by using less expensive and active organosilanes like polymethylhydrosiloxane (PMHS) is one of the by-products as a waste produced from silicon industries. PMHS is more advantageous over other silanes because of its non-toxicity, moisture stability, and cost effectivity. PMHS was an active reducing reagent for the formylation of N–H bonds in primary and secondary amines, hydrazines, imines, anilines, and N-heterocycles as showed with the decent to outstanding yields found in the synthesis of DMF.
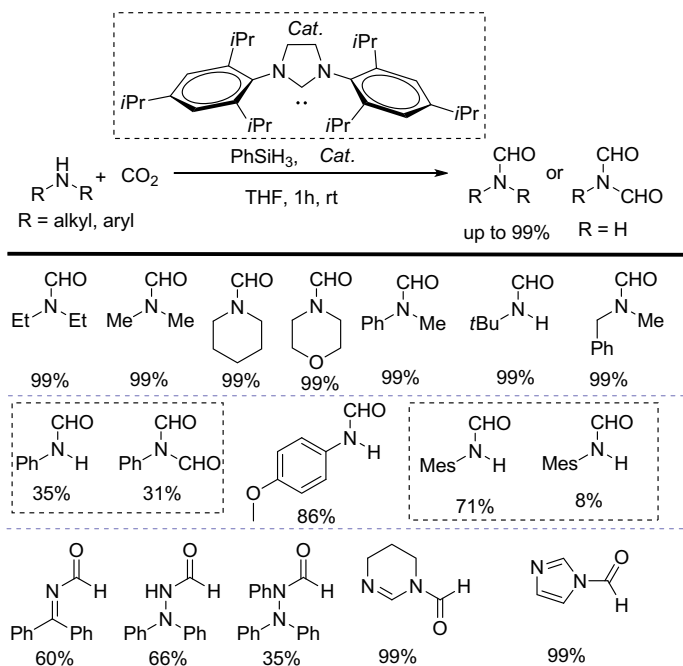
Scheme 22 NHC-catalyzed reduction of CO_2 to formamides using silanes

Dyson et al. describe the green and practically scalable route for the hydrosilylative N-formylation and N-methylation of various primary and secondary amines using carbon dioxide CO_2, by applying relatively cheap thiazolium carbene-type NHC ligand as a catalyst [34]. The catalyst is air-sensitive and must be generated fresh just before the use; consequently, the techniques used to prepare and manipulate the catalyst are described. The synthetic approach described in this protocol does not use any toxic reagents. The appropriate catalyst furnished N-formylated or N-methylated products with high selectivity.
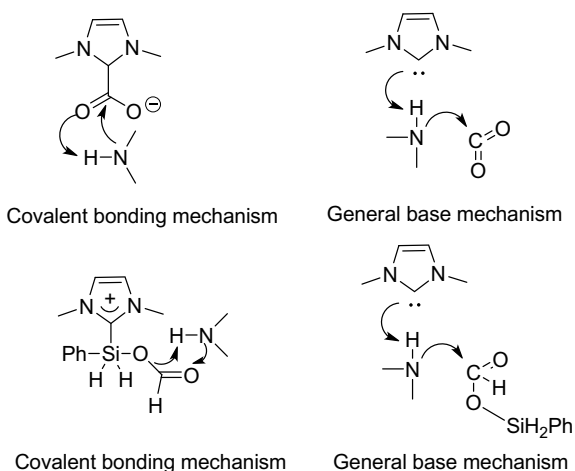
Cantat's group presents advancement in metal-free organocatalysis of CO_2 utilization, as discussed earlier, and subsequent in-depth mechanistic analysis of the same is reported by several groups working on efficacy of carbenes and formates as catalysts. For instance, phenyl substitution on amine-N atom providing high reaction, the efficacy with good conversion and yields, while a biphenyl substitution preventing activity, has been discussed by Cao et al [35]. A theoretical approach was involved to demonstrate the reaction mechanism of amide formation from amine substrates using CO_2 (Scheme 23). The reaction mechanism was categorized in four key steps, (a) silane activation, (b) CO_2 incorporation in an intermediate, (c) NHC driven amine-intermediate conjugation, and (d) C–O bond cleavage to get amide product. Two mechanisms are revealed through DFT analysis, sequential covalent bonding and general base catalysis, with different Gibbs free energy profiles. DFT reveals the
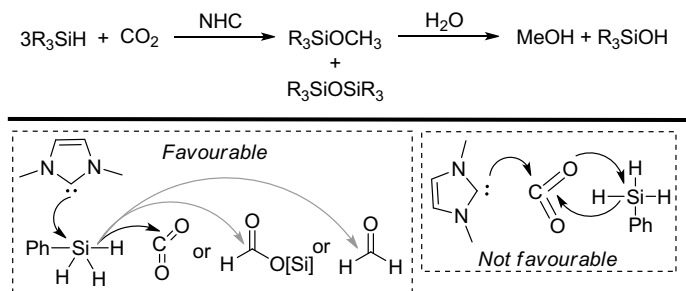
most favorable mechanism being general base catalysis with a lower overall Gibbs barrier driven by NHC. However, the duality of the reaction mechanism will generate by-products such as carbamate anion. The reaction mechanism and predicted product formation are closely aligned with Cantat's findings. This DFT study also provides an explanation for the differential reactivity of substrates conjugated on the amine nitrogen. While methyl and phenyl conjugates are highly active, biphenyl substitution results in complete loss of activity, shown earlier by Cantat. Wang and Cao show how biphenyl substitution presents a greater thermodynamic barrier resulting in selective reaction preference. The phenomenon is explained by the nucleophilic enhancement of the substitution atom due to the aromatic substitution. Dual-phenyl substitution renders the substitution atom (N) highly nucleophilic leading to reaction arrest.

Further, based on the conversion of CO_2 to methanol [32], Huang et al. demonstrated detailed DFT calculations to study the reaction mechanism catalyzed by NHC [36]. They reveal the presence of formaldehyde as a productive intermediate in a reaction scheme examined earlier by other groups. While previously unreported, the formaldehyde along with other intermediates such as formoxysilane (FOS) and bis(silyl)acetal forms a compelling reaction complex to lead to the formation of methanol which is a desirable output for CO_2 utilization. NHC plays a crucial role here by activating the Si–H bond in silanes and promoting the formation of electron-dense hydridic H atoms which can couple with the electrophilic C center of the appropriate substrate, in this case, CO_2, CH_2O, and FOS (Scheme 24). Interestingly, Huang et al. also highlighted the phenomenon first described by Cantat wherein biphenyl substitution is counterproductive compared to phenyl or methyl substitution in performing the conversion, as discussed earlier.

Further, Cantat and coworker studied complete catalytic deoxygenation of CO_2 into formamidine derivatives [37]. In this study, they found application for the synthesis of derivatives of benzimidazole by the reductive functionalization of CO_2 in

Scheme 23 NHC promoted activation of CO_2 and silanes in various pathways

Covalent bonding mechanism

General base mechanism

Covalent bonding mechanism

General base mechanism

$$3R_3SiH + CO_2 \xrightarrow{\text{NHC}} R_3SiOCH_3 \xrightarrow{\text{H}_2\text{O}} MeOH + R_3SiOH$$
$$+$$
$$R_3SiOSiR_3$$

Scheme 24 Possible pathways for NHC-catalyzed activation of CO_2 and silanes

the existence of hydrosilanes such as H_3SiPh or poly(methylhydrosiloxane) (PMHS) replacing TBD with IPr (NHC) as catalysts and ortho-diamines as coupling partners. Very recently, Yang and coworkers synthesized NHC-CO_2 adduct as a catalyst for the N-formylation and cyclization reactions of CO_2 (1 atm.) with amines using silane as a reducing agent [38]. At the specific temperature, this NHC adduct decarboxylates and removes the CO_2, and hence, it acts as not only the nucleophilic center but also the C1 source.

As stated by Huang et al., aldehydes may be underreported in their role and presence in the system of formylation reactions. Murata et al. report a study detailing utilization of CO_2 in the downstream synthesis of important aldehydes [39]. As a two-part process, solvent-free preparation of silyl formats is elucidated driven by tetra-butylammonium acetate (TBAA) as a catalyst (Scheme 25). The subsequent process while driven by Grignard's reagent is easily substituted for metal-free catalysts. Various aldehydes have been tolerated efficiently using the developed system. Based on the DFT calculations, a reaction mechanism has been described, where an OAc anion of catalyst attacks on electrophilic Si center of hydrosilane which led a penta-coordinate silicate intermediate. Further transfer of hydride ion to CO_2 from intermediate affords silyl acetate and $Bu_4N^+HCO_2^-$. Generated HCO_2^- acts as a nucleophile to form another pentacoordinate silicate intermediate. Finally, hydride transfer on carbon dioxide generated HCO_2SiR_3 which subsequently undergoes nucleophilic attach by Grignard's reagent to form the corresponding aldehyde.

In a parallel study with a counter-point focus, Motokura et al. investigated the effect of various formate salts on the hydrosilylation of CO_2, and it was found that the tetrabutylammonium (TBA)formate demonstrated excellent catalytic activity [40]. Experimental study like in-situ FT-IR and ^{1}H NMR spectrometry suggested that along with the formate anion, Lewis basic solvents like NMP and DMSO enhance the rate of reaction by donating electrons to the Si center. Motokura et al. demonstrate a mechanism aligned instead, with that elaborated by Murata et al., which emphasizes the role of formates in aiding hydrosilylation of CO_2 (Scheme 26). Based on reaction acceleration by in-situ-formed formate in a typical organometal/transition metal-catalyzed silylation reaction, the application of formates, using the class-typical
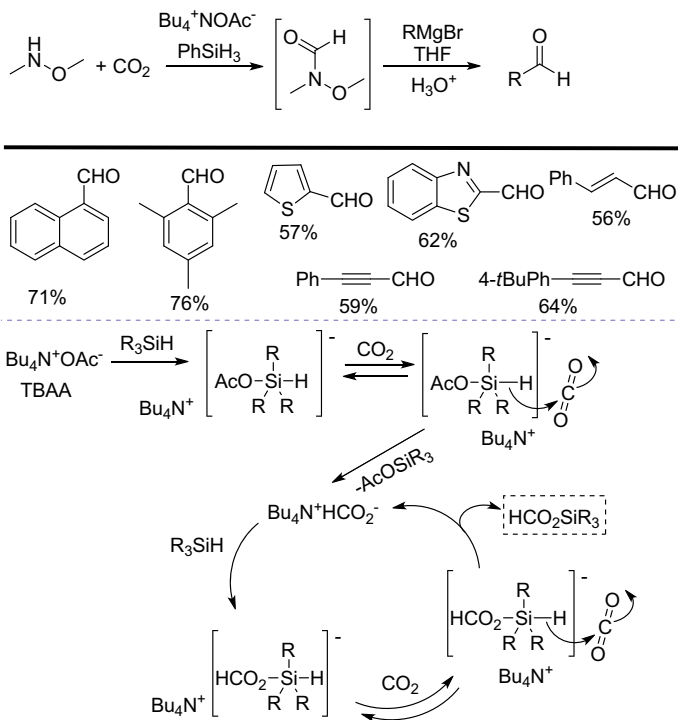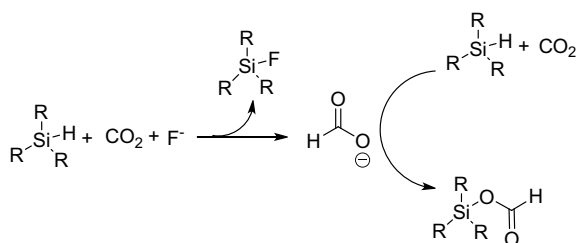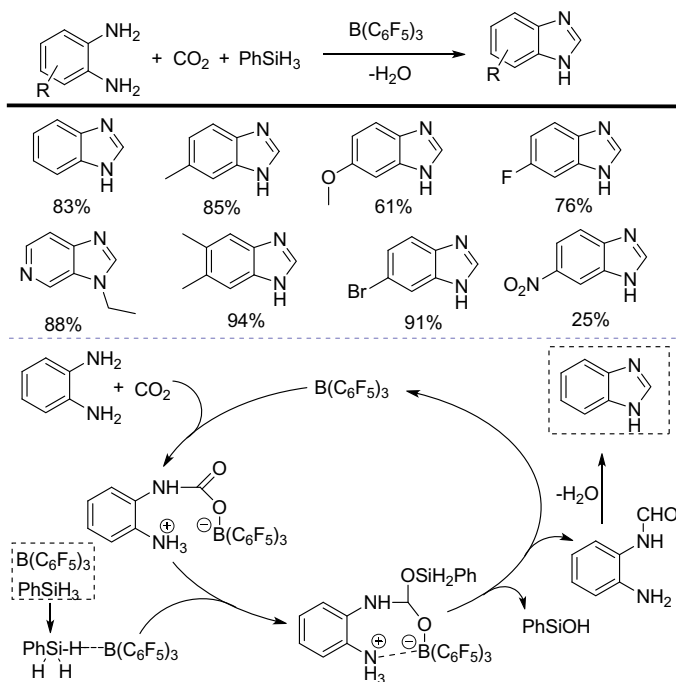
Scheme 25 ILs-catalyzed activation of CO_2 and silanes for the formation of various bonds

example of TBA formate, derived from TBAA is shown in the hydrosilylation of CO_2 [41].

Importantly, a CO_2 can be used as the very efficient C1 source for the synthesis of heterocycles like benzimidazoles. In 2016, Sun used $B(C_6F_5)_3$ as Lewis's acid catalyst for the synthesis of benzimidazoles from *o*-phenylenediamine as an amine source and $PhSiH_3$ as a reducing agent at 120 °C for 24 h in THF as a solvent (Scheme 27) [42]. A wide range of derivatives of *o*-phenylenediamine was tolerated using this catalytic system and afforded moderate to good yields. To elucidate the reaction mechanism, experimental studies such as ^{13}C NMR were carried out, which

Scheme 26 Reaction mechanism for the formate-catalyzed activation silane

Scheme 27 Lewis's acid-catalyzed synthesis of benzimidazoles using amine, CO_2, and silane

suggested that the reaction mechanism follows the FLP pathway for the activation of amine, silane, and CO_2.

In an exploration of additional catalysts used in the formylation of amines applying the metal-free green route, studies published by Liu and coworkers demonstrated the use of ionic liquids (ILs) as potential catalysts (Scheme 28) [43]. 1-Alkyl-3-methylimidazolium [BMim]Cl was used as a catalyst for the N-formylation of amines with CO_2 and $PhSiH_3$ as reducing agent. 1-Butyl-3-methylimidazolium acetate, [Bmim][OAc] catalyzes the N-formylative cyclization of CO_2 using EtO_3SiH as a reducing agent. The derivatives of benzothiazoles and benzimidazoles were afforded [44], while, equally functional as NHCs, ILs are the advantages in terms of physical state, reactivity, and freedom from the use of precious metals. ILs have been studied extensively for multiple catalytical roles such as those in the formation of carbamates or carbonates. ILs demonstrate a fundamental difference in mechanism of CO_2 uptake, compared to NHC. IL, embodied here as imidazolium ion and counter-ion system, directly activate silane Si–H bond to accept CO_2, leading to direct formation of formoxysilanes, whereas NHC itself connects with CO_2 to form an adduct which is passed onto the silane. Further, they also evaluated the role of various cations and anions in ILs. Ions comprising Cl^-, NO_3^-, and Br^- exerted a positive effect on the activation of Si–H, whereas the cation with complex anions such as BF_4^- and PF_6^- reacted poorly. The reaction is effective at room temperature which makes it

valuable for commercialization, relying on relatively low CO_2 pressure. Employed ILs shown reusability of the catalyst which can be employed in cost-effectiveness for large-scale conversions.

Further, in 2017 Liu and his group investigated metal-free and versatile route for synthesis of unsymmetrically N,N-disubstituted formamides (NNFAs) using CO_2 [45]. For the reaction, primary amines and aldehyde were used with ionic liquid (1-butyl-3-methylimidazolium chloride) at room temperature. IL was recycled five times without loss in its catalytic activity. This was the novel approach, based on metal-free system, which was applied in simple and versatile route for the synthesis of unsymmetrical N,N-disubstituted formamides (NNFAs) by using three-component reductive coupling of primary aldehyde, amine, and CO_2 with phenylsilane in the presence of [BMIm]Cl at room temperature. The substrate scope was screened providing various unsymmetrical NNFAs in good to excellent yields.

Following the classic route of CO_2 hydrosilylation, the efficiency of which rides on the choice of catalyst, and reaction conditions, most groups working on the area attempt to optimize high-functioning catalysts with the highest potential for conversion and yield. Fluorides have been demonstrated earlier, in the form of CsF in the
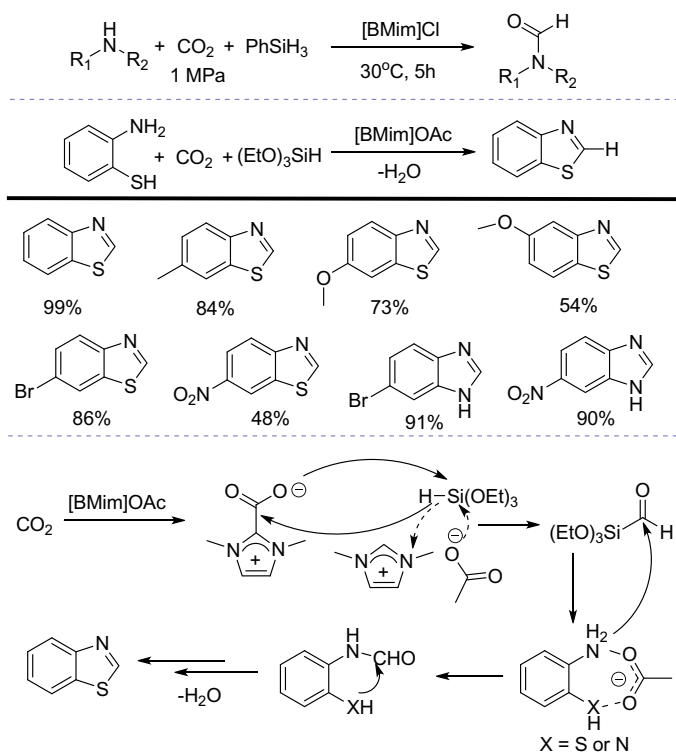

Scheme 28 ILs-catalyzed synthesis formylation and cyclization reactions using amine, CO_2, and silane

effective hydrosilylation of CO_2. The chemistry of fluorine allows potent interaction with Si reaction center of silanes due to high electronegativity to form penta- or hexa-coordinated silicon intermediates, thereby enhancing the reduction potential of silanes. He et al. used tetrabutylammonium fluoride (TBAF) as a potent metal-free organocatalyst with a wide selectivity spectrum for amines [46]. The TBAF and acetonitrile offered high conversion and yields (92–99% and 90–99%, respectively), compared to other catalysts. It was observed that polar solvents are more suited for catalyst coordination chemistry. The silane choice itself allows tunability for reaction selectivity. For instance, triethoxysilane allows N-formylation more readily, while phenylsilane promotes N-methylation.

Hu et al. reported the use of lecithin, a commonly occurring natural product in eggs, soy beans, etc., in the hydrosilylation of CO_2 [47]. The common trait that enables the two unusual catalysts is their zwitterionic nature. They report very high conversion rates and yields (~99 and 99%, respectively) with lecithin using aniline, p-Br-aniline, and morpholino substrates and further describe lecithin as being selective toward the formation of mono-formylated products due to steric restriction of the catalyst. N-methylation as catalyzed by lecithin is also highly efficient with conversion rate and yield reported up to 99% each, using substrates such as aniline, *p*-methyl, and *p*-chloroaniline. The reaction conditions and molar ratios of components can be modulated to switch between formylation and methylation; e.g., formylation is carried out at room temperature, 0.5 MPa CO_2 pressure, 1 mmol phenylsilane, and 5 mol% of lecithin. Methylation is proceeded under lower CO_2 pressure (0.2 MPa), 2 mmol phenylsilane, and at 100 °C.

Further, So and coworkers have investigated the use of silicon (II) complex of the NHC-silyliumylidene cation [(IMe)$_2$SiH]I (1, IMe = :C{N(Me)C(Me)}$_2$) as a catalyst for the N-formylation using CO_2 and PhSiH$_3$ under mild reaction conditions furnishing the relevant formamides (Scheme 29) [48]. For primary amines, the reaction time was 4.5 h; a typical yield obtained was up to 95%, and the average TOF was 8 h^{-1}. While in the case of secondary amines, average yield obtained was 98%, and the typical TOF was 17 h^{-1}. The catalytic activity of silicon(II)complex and product yields were found to be more superior to the currently available non-transition metal catalysts used for this reaction. Mechanistic studies suggested that the silicon(II) center in complex catalyzed the C−N bond formation through a different pathway in comparison with non-transition metal catalysts. The trail of activation was CO_2, PhSiH$_3$, and amines, which proceeded through a dihydrogen elimination mechanism, to synthesize formamides, dihydrogen gas, and siloxanes. They have explained the mechanistic pathway for the formylation of amine. Silyene compound has the presence of lone pair of electrons and a P vacant orbital on the silicon(II). Due to the unique properties of the silyene complex, it comprises both nucleophilic and electrophilic characters, leading to Lewis ambiphilicity. It was shown for the first time that catalytically or stoichiometrically activating both N−H bond and CO_2 bond simultaneously, resulting in the formation of the C−N bond. Catalyst activates both amines and CO_2 simultaneously for formation of C−N bond. It has been proven that NHC-silyliumylidene cation complex selectively catalyzed N-formylation of CO_2
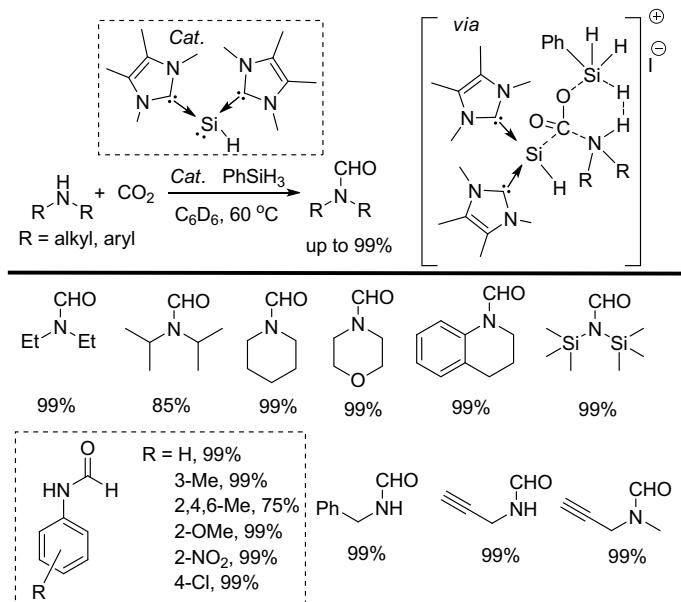
Scheme 29 NHC-silyliumylidene cation catalyzed formylation of amines

and amines to formamides. The activity of catalyst was because of transition metal-like catalysis, where the silicon(II) center sequentially activates CO_2, amines, and $PhSiH_3$ and further proceeds via a dihydrogen elimination mechanism, leading to form siloxanes, formamides, and dihydrogen gas.

Lu and coworkers in 2015 synthesized a series of phosphorus ylide (P-ylide) CO_2 adducts and used them as catalysts for the various organic transformations, including reductive formylation and methylation of amines with CO_2 and amines (Scheme 30) [49]. Phosphorus ylide reacts with the CO_2 molecule and generates the P-ylide-CO_2 adduct, which is a key catalytic center for the activation of silane for the reductive functionalization.

Mandal et al., in 2018, used abnormal N-heterocyclic carbene (aNHC) as a catalyst for the N-formylation of challenging substrate like amides with CO_2 using hydrosilane at mild reaction conditions (Scheme 31) [50]. Various NHC-based ligands were tested for this transformation which represented a good to moderate activity at the atmospheric pressure of CO_2 and room temperature. A range of amides
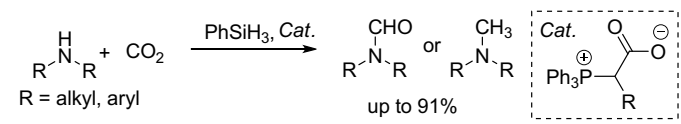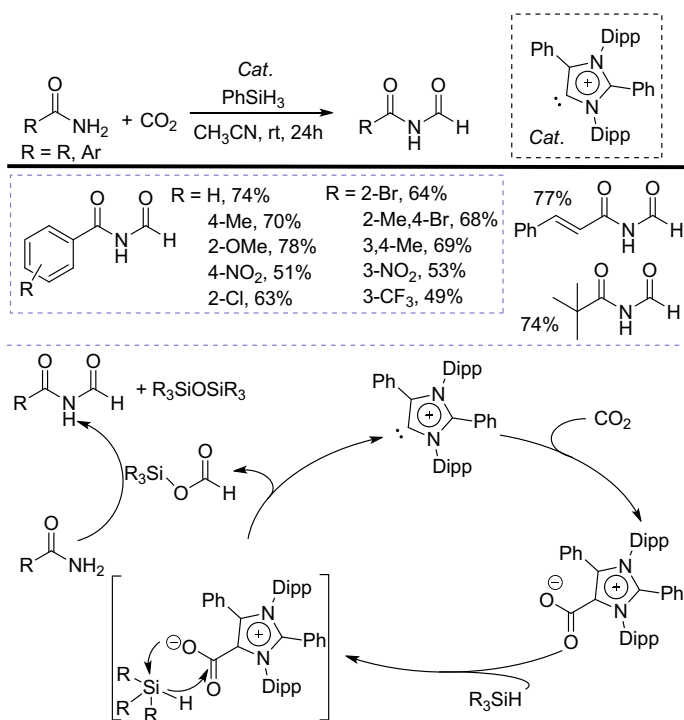

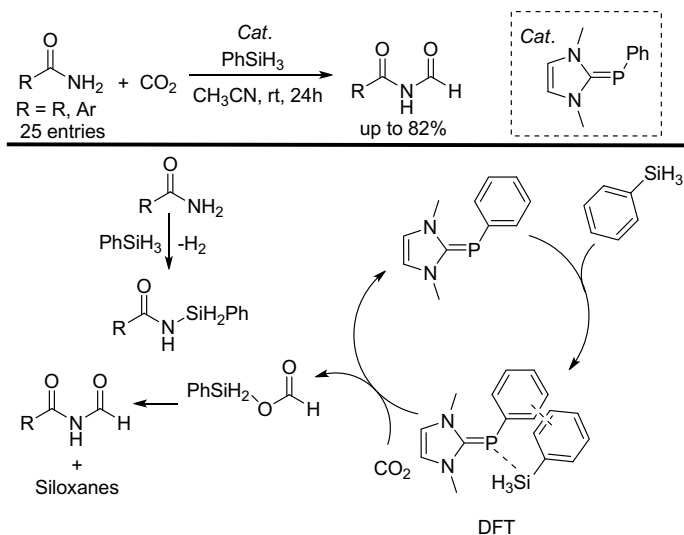**Scheme 30** Phosphine ylide-catalyzed activation of CO_2 and silane

undergoes formylation reaction at room temperature and represented good yields. A reaction mechanism is proposed, where the aNHC ligand initially reacts with CO_2 molecule and forms the aNHC-CO_2 adduct which subsequently attacks the silane molecule to afford the formoxysilanes intermediate. This intermediate then undergoes nucleophilic attack by amide to furnish final product.

Following this work, again very recently, they have used another organocatalytic approach of NHC stabilized phosphinidene 1,3-dimethyl-2-(phenylphosphanylidene)-2,3-dihydro1H-imidazole for the N-formylation of amides using silane as reducing agent at atmospheric pressure of CO_2 (Scheme 32) [51]. Based on the experimental findings and DFT studies, a reaction mechanism has been developed. Phosphinidene catalyst assists the dehydrogenation reaction of phenylsilane and amide to form N-silylated amide with the liberation of H_2 (identified by ^{1}H NMR and GCMS spectrometry). After this, N-silylated amide reacts with the phenylsilyl formate generated by another catalytic cycle of catalyst and formyl transfer occurred to furnish the final product with siloxanes as a by-product.

Complex chemistry to expand the depth of CO_2 application is a major challenge. In 2017, Zhu et al. took an innovative green route to access the high-value products using stepwise C–C and C-N bond formation using CO_2 and silylation chemistry for the synthesis of spiro-indolepyrolidine (SIP), catalyzed by TBD (Scheme 33)
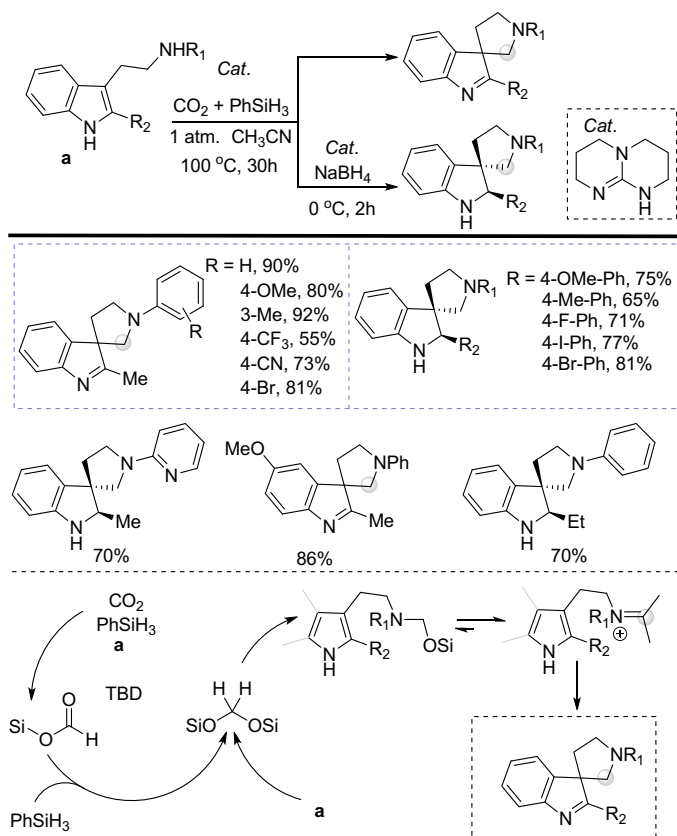

Scheme 31 aNHC-catalyzed activation of CO_2 and silane for the formylation of amides

Scheme 32 Phosphine-catalyzed activation of CO_2 and silane for the formylation of amides

[52]. Here, CO_2 as a green and cost-effective C1 feedstock was used to reform tryptophan into the SIP products. The innovative approach emphasizes the versatility of silane reagents in hydrosilylation permitting effective utilization of CO_2 into value-added processes. The general reaction scheme is illustrated showing the primary that gives the integrated product with CO_2-derived C–C and C-N bonds. Subsequent reductive reaction with sodium borohydride gives a saturated product with a chiral arm which is instrumental in the formation of SIP-based chiral compounds. The reported yields are typically very good, depending on the solvent system used and the catalyst loading (0.2–0.5 mmol). In acetonitrile yields, 93–95% were obtained. Catalyst substitution with pyridine or solvent switching with THF resulted in very poor reactivity (~15% yield). Although Zhu et al. present a viable route of value-added utilization of CO_2, process requirements of high temperature over a significant period of time along with relatively high catalyst loading in some cases may require optimization before commercial impact. The proposed mechanism based around the use of TBD as the best-suited catalyst implies the formation of formate silane and subsequently bis(silyl) acetate. This generated acetate that reacts with the tryptophan in acetonitrile at relatively high temperature to form reactive intermediates which are further converted to the final product by nucleophilic addition at the carbon center.

Organocatalyzed CO_2 reactions are mainly divided into three main paths: (a) direct functionalization (i.e., carbonates, carbamates); (b) reduction into formaldehyde, formic acid, and methanol; and (c) reductive functionalization. The reductive functionalization of CO_2 with an amine gives formamides, N-methylamines, or aminals, which are very important value-added products. This class of processes has been investigated exhaustively with myriad catalysts, including carbenes, Lewis's acids, formates, ionic liquids, ylides, hydroxyl compounds, and to some extent guanidines.
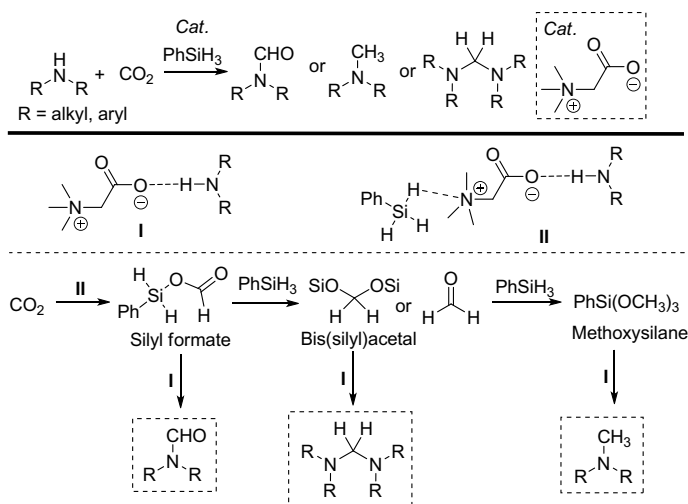
Scheme 33 TBD-catalyzed activation of CO_2 and silane to the synthesis of spiro-indolepyrrolidines

Given the exhaustive work done to unravel the mechanisms of typical reductive processes described above, Nicholls et al. explored the various steps of the reductive amination of CO_2 using a morpholine base [53].

At the same time, He et al. [54] and Han and coworkers [55] have reported naturally occurring glycine betaine as an efficient, active, and renewable catalyst for C-N bond formation using CO_2 and amines with $PhSiH_3$ as the reducing agent. A broad range of amines was screened for this reaction, which gave a significant yield. Also, they studied, by controlling reaction parameters, that selectivity of products can be tuned. Glycine betaine is a quaternary ammonium alkaloid having a zwitterionic structure. It is basic in nature, so it can be used in various chemical syntheses. The Han group proposed a plausible reaction mechanism on the basis of NMR results and literature. First, glycine betaine interacts with amines and $PhSiH_3$ to create Intermediates **I** and **II** (Scheme 34). Further, the Si–H bond in $PhSiH_3$ gets activated by Intermediate **II**, which further on insertion of CO_2 forms silyl active species. This was dependent on

the molar ratio of the reactants and the reaction temperature. Also, simultaneously N–H bond in glycine betaine gets activated by the formation of Intermediate **I**. At the end, nucleophilic amine attacks the silyl active species for the formation of C-N bonds to make products.

Similar to silanes, phosphines have been used to attempt hydrophosphination of CO_2. Due to the nucleophilic nature of phosphines, successful hydrophosphination of CO_2 has been rarely reported. To overcome this barrier, Chong and Kinjo adapted the principle of hydrophosphination to diazophospholene resulting in a successful reaction and formation of phospholene formate, which upon further CO_2 exposure transfers the formate to silyl group (Scheme 35) [56]. They proposed the role of formate species in catalytic activity driving the formylation of amines. The use of diazophospholene enables the route of one-pot synthesis of formamides in milder conditions.

Scheme 34 Betaine-catalyzed activation of CO_2 and silane for formylation and methylation reaction
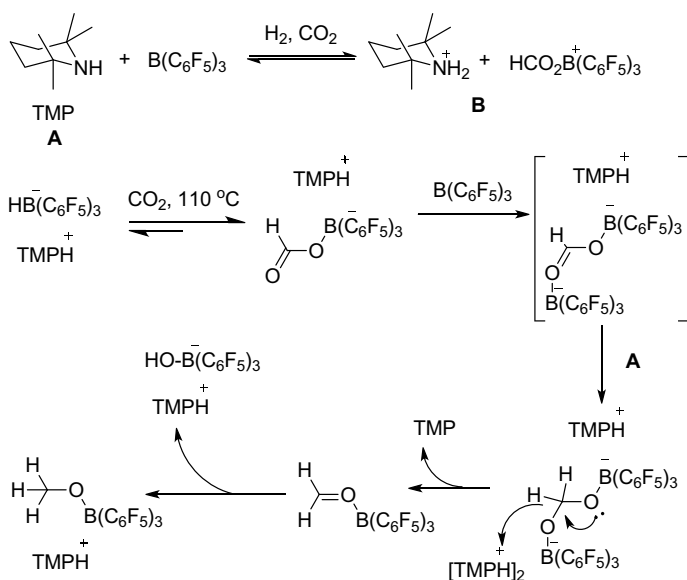

Scheme 35 Phosphine-catalyzed activation of CO_2 and silane for formylation and methylation of amines
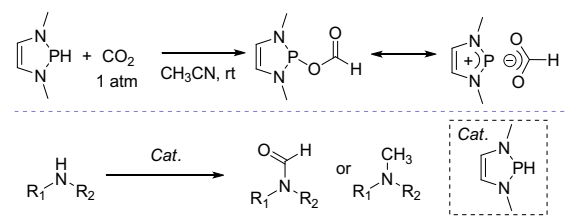
Organocatalytic hydrogenation of CO_2

Among other reducing agents, hydrogen is always considered superior in terms of atom economy, cost, and so on. However, the activation of dihydrogen is quite challenging through organocatalysts, and very few reports are available. In 2009 Stephen, Erker and coworkers pioneered the activation of CO_2 using a phosphino-borane FLP system [57]. From this discovery, reductive functionalization of CO_2 has taken intense attention over the last decade. In 2009, Ashley and O'Hare developed the first FLP-mediated activation of CO_2 and subsequent hydrogenation into methanol using hydrogen gas (Scheme 36) [58]. This work was inspired by the concept of FLP which split the H_2 heterolytically and then consecutive CO_2 activation to achieve the thermodynamically difficult task by organocatalysts. Under thermal conditions, $B(C_6F_5)_3$ and TMP (TMP = 2,2,6,6-tetramethylpiperidine) reacted with CO_2 and H_2 afforded formatoborate complex, [TMPH]-[$HCO_2B(C_6F_5)_3$]. Stepwise activation of H_2 and CO_2 occurred, where heterolytical cleavage of H_2 was promoted by an equimolar amount of $B(C_6F_5)_3$ and TMP to give [TMPH][$HB(C_6F_5)_3$]. Afterward, CO_2 (1 atm) in toluene at higher temperature (>110 °C) directed to the generation of a formatoborate complex [TMPH] [$HCO_2B(C_6F_5)_3$]. Finally, a quantitative amount of [$CH_3OB(C_6F_5)_3$][TMPH] was obtained by purging of CO_2 in a mixture of TMP/$B(C_6F_5)_3$ under an H_2 atmosphere.

Then, in 2015 Fountain used an intramolecular FLP system of N/B for the hydrogenation of CO_2 with H_2 to obtain the reduced derivatives of formate, acetal, and methoxy (Scheme 37) [59]. In FLP, weakly Lewis acidic boron activates the H_2
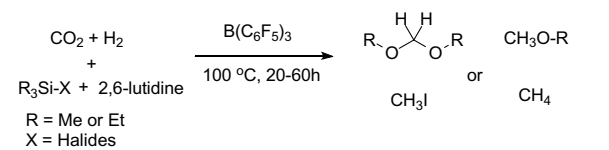

Scheme 36 FLP-catalyzed activation of CO_2 and H_2 to methanol

molecule and generates the NH and BH species, which are responsible for the concurrent reduction of CO_2. The NMR investigation study demonstrated that upon exposure of H_2 gas with ambiphilic FLP catalyst resulted in the synthesis of **7** at 80 ˚C by removing of mesitylene on boron by photodeborylation reaction.

Stephan and coworkers recently used FLP obtained from the 2,6-lutidine and B(C6F5)3 for the hydrogenation of CO_2 with H_2 and silylhalide used as an oxophile to remove the oxygen atom (Scheme 38) [60]. Due to well-established steric characteristics and suitable nature of silylhalide and solvent selection like C_6D_6 and $CDCl_3$, different types of hydrogenated products such as methoxysilane, Me_3SiOCH_3, the acetal $(Et_3SiO)_2CH_2$, CH_4, and CH_3I were obtained at 100˚C using CO_2 (2 atm) and H_2 (4 atm). The reaction mechanism was also determined on the basis of the experimental and DFT calculations. This begins with the known activation of H_2 by FLP, followed by the reaction of CO_2 to the formyl borate anion.
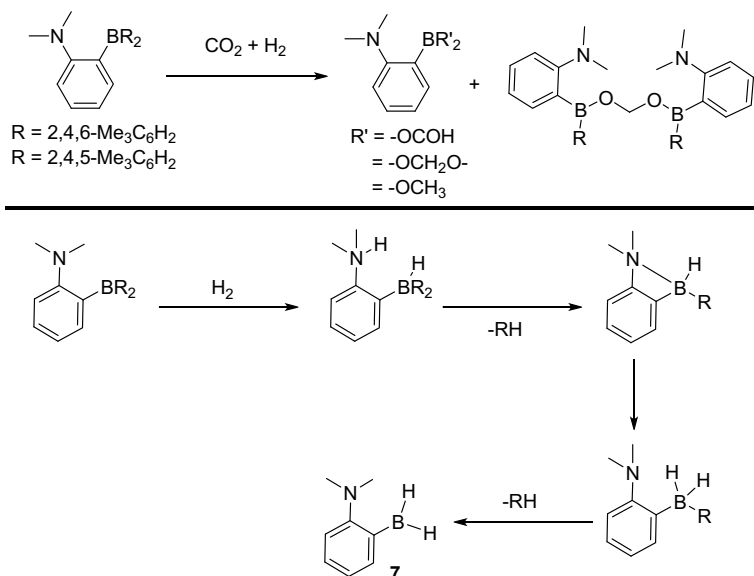
Scheme 37 Intramolecular FLP system of N/B for the hydrogenation of CO_2

Scheme 38 FLP-catalyzed activation of CO_2 and H_2

2 Summary and Outlook

Capture and conversion of CO_2 to value-added chemicals and fuels is taking enormous attention not only due to its environmental impacts but also to maintain the carbon neutral cycle by reducing CO_2 concentration. Furthermore, due to current concerns about environmental degradation, urgency is required in the development of efficient capture processes and the design of highly active catalysts for CO_2 reduction reactions. Here, we have summarized recent advancements in the utilization of organocatalysts for the reductive functionalization of CO_2 to possible structures using borane, silane, and dihydrogen molecules. This transformation results in fundamental C1 building blocks such as HCOOH, HCOH, CH_3OH, CH_4, and C_2H_5OH. Along with these and by depending on coupling partners, other bonds such as C–N, C–C, C–O, and C–S are also formed in reductive functionalization process.

Generally, CO_2 transformation reactions are mainly catalyzed by transition metal catalysts, which are expensive, toxic, and sensitive to handle under normal conditions. Furthermore, the hydrogenation process demands harsh reaction conditions such as high pressure and temperature, and catalyst deactivation by leaching is always associated with this process. On the other hand, organocatalysts perform the CO_2 reduction chemistry at the very mild reaction condition with high efficiency. Soft reducing agents like boranes and silanes with organocatalysts ultimately demonstrate the sustainability of processes. It is noteworthy that these reductive transformations of CO_2 can generate both fuel-type structures and also pharmaceutically necessary scaffolds. Active centers of organocatalysts such as Lewis' acids, basic amines, FLP, carbenes, ylides, cations, and anions demonstrated excellent efficiency in activating CO_2, reducing agents (boranes, silanes, and H_2), and coupling reagents. Various active intermediates such as formates, acetals, and activated hydride species are generated with various hydroelements (B, Si), which subsequently endow the generation of exciting functional groups such as N-formyls, N-methyls, methanol, methane, aminals, and heterocycles. In organocatalysis, silyl formate is generated as an initial reaction product or as an intermediate, which has its own importance in the formation of CH_3OH, CH_4, formic acid, formamides, etc. Various active organocatalysts with well-defined active centers such as FLP, NHC, IL, amine superbases, carbene, and phosphine ylides demonstrated excellent catalytic activity for the reductive transformation of CO_2. Along with this, we have tried to give mechanistic insights on organocatalytic active centers for the activation of CO_2 and reducing agents.

Notes

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