CO_2 Reduction

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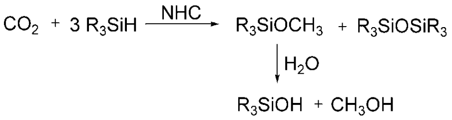
Conversion of Carbon Dioxide into Methanol with Silanes over N-Heterocyclic Carbene Catalysts**

Siti Nurhanna Riduan, Yugen Zhang, and Jackie Y. Ying**

Carbon dioxide is attractive as a renewable carbon source and an environmentally friendly chemical reagent.[1–4] Significant efforts have been devoted towards exploring technologies for CO_2 transformation, whereby metal catalysts play a key role.[5–10] N-heterocyclic carbenes (NHCs) are well established as organocatalysts and ligands in organic synthesis.[11–14] With their lone pair of carbene electrons, NHCs behave as nucleophiles. It has been known that nucleophilic NHCs can activate CO_2 to form imidazolium carboxylates.[15,16] However, the application of such carboxylates has been limited to the preparation of precursors to NHC–metal complexes and halogen-free ionic liquids, and some stoichiometric transcarboxylation reactions.[17–20] The release of CO_2 from the imidazolium carboxylates and the completion of a catalytic cycle with NHCs may lead to a new and exciting metal-free protocol for CO_2 transformation. In this work, we envision the use of a hydrosilane in the reaction as a hydride donor to the activated carbon dioxide, reducing CO_2 ultimately to methoxide (Scheme 1).



$$\begin{tikzcd} CO_2 + 3\,R_3SiH \arrow[r, "NHC"] & R_3SiOCH_3 + R_3SiOSiR_3 \arrow[d, "H_2O"] \\ & R_3SiOH + CH_3OH \end{tikzcd}$$

Scheme 1. Overall stoichiometric reaction.

Catalytic reduction of CO_2 with hydrosilane would proceed exothermically and could facilitate utilization of CO_2. The development of highly active and robust catalysts for such a reaction remains a major scientific challenge. In previous reports of the addition of hydrosilane to CO_2, active transition-metal complexes served as catalysts. Ruthenium and iridium complexes were first reported in the early 1980s as catalysts for the hydrosilylation of CO_2.[21,22] More recently, Pitter and co-workers described the hydrosilylation of CO_2 catalyzed by ruthenium–acetonitrile complexes, yielding formoxysilanes.[23–25] Matsuo and Kawaguchi reported the homogeneous reduction of CO_2 with hydrosilanes catalyzed by zirconium–borane complexes, yielding methane.[26] The practicality of applications of these different systems was limited by their sensitivity to air and moisture, as well as the low activities of the organometallic catalysts. Herein we describe the first hydrosilylation of CO_2 using an organocatalyst. Stable NHC catalysts mediated the effective conversion of CO_2 to methanol under very mild conditions and allowed the use of air as a feedstock.

In a typical reaction 1,3-bis(2,4,6-trimethylphenyl)imidazolium carboxylate (Imes-CO_2, **1**; 0.1 mmol)[15] was dissolved in *N*,*N*-dimethylformamide (DMF, 2 mL) in a vial, and CO_2 was introduced with a balloon. Diphenylsilane (1 mmol) was introduced to the vial, and the reaction mixture was stirred at room temperature. The reaction was monitored by gas chromatography/mass spectrometry (GC–MS). It was found that diphenylsilane was fully consumed in 6 h. The expected formoxysilane product occurred as a minor product in the early stages of the reaction and disappeared as the reaction progressed. Further studies showed that the reaction intermediates, diphenyldiformoxysilane ($Ph_2Si(OCHO)_2$, **2**) and diphenylformoxysilane ($Ph_2SiH(OCHO)$, **3**), were not stable. They underwent further reduction to bis(silyl)acetal ($Ph_2HSiOCH_2OSiHPh_2$, **4**) and silylmethoxide ($Ph_2HSiOMe$, **5**). In the ^1H NMR spectrum of the reaction mixture in $[D_7]$DMF solvent, a major group of peaks was observed at $\delta \approx 3.5$ ppm, corresponding to methoxide products. Some minor peaks at $\delta = 4.5–5.0$ ppm and 8.5 ppm were also identified, corresponding to silylacetal and formoxysilane intermediates. These intermediates were further confirmed by GC–MS (see the Supporting Information).

To further investigate the intervening processes of the reaction, we performed the reaction with isotopically enriched $^{13}CO_2$ (99 atom % ^{13}C). $^{13}CO_2$ was introduced into an NMR tube, fitted with a J. Young valve, that contained 0.1 mmol of silane and 0.01 mmol of Imes-CO_2 **1** in $[D_7]$DMF solvent. The reaction was monitored with ^{13}C ^1H-decoupled NMR spectroscopy. Within 90 min, three groups of new peaks appeared: at $\delta \approx 160$ ppm, corresponding to the formation of formoxysilanes **2** and **3**; at $\delta \approx 85$ ppm, indicating the formation of silylacetal ($SiOCH_2OSi$) intermediates, and at $\delta \approx 50$ ppm, associated with methoxide (SiOMe) products. As the reaction progressed, the relative intensity of the peaks at $\delta = 85$ ppm decreased while those at $\delta = 50$ ppm increased, confirming that the silylacetal intermediates further reacted to form methoxide products (see Figure 1). We also performed ^{13}C-coupled ^1H (gated decoupling) NMR experiments. The peak corresponding to $\delta = 85$ ppm split into a

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[*] S. N. Riduan, Dr. Y. Zhang, Prof. J. Y. Ying
Institute of Bioengineering and Nanotechnology
31 Biopolis Way, The Nanos, Singapore 138669
Fax: (+65) 6478-9020
E-mail: ygzhang@ibn.a-star.edu.sg
jyying@ibn.a-star.edu.sg

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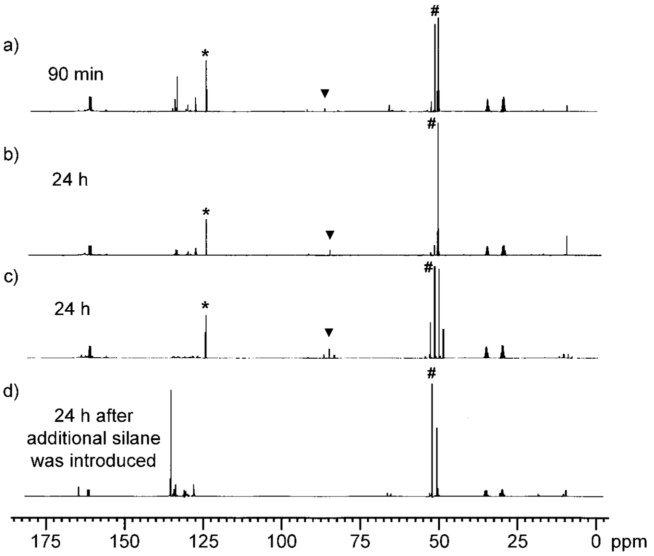
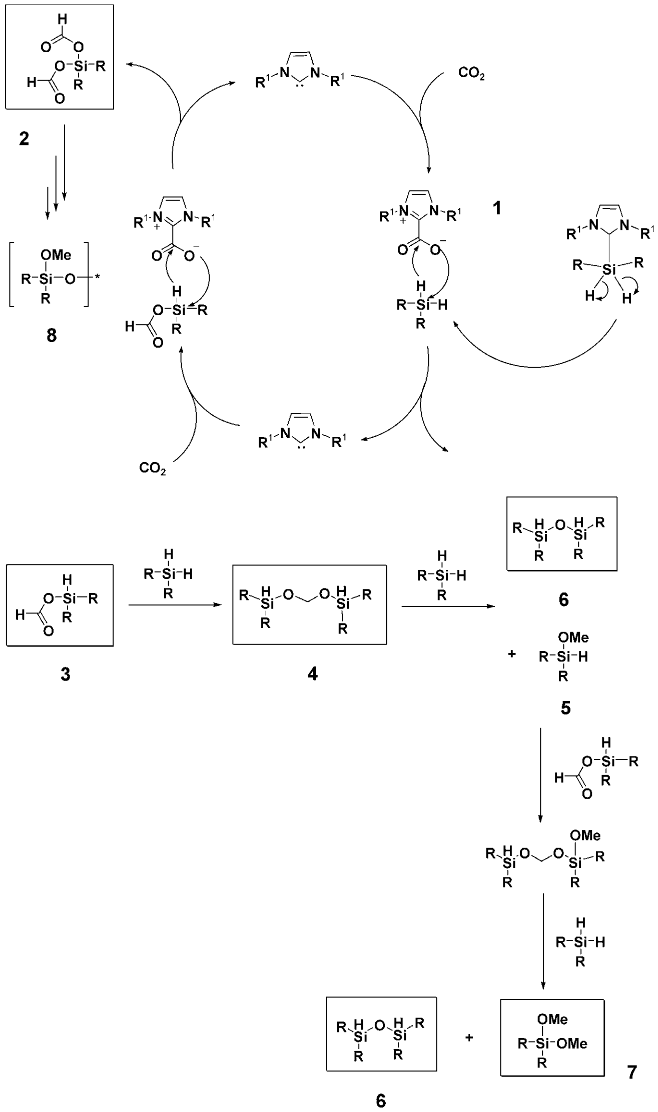


Figure 1. ^{13}C NMR spectra from the reaction of $^{13}CO_2$, diphenylsilane, and Imes-CO_2 catalyst **1** (5 mol%) in [D_7]DMF. Proton-decoupled spectra are shown in (a), (b), and (d); the spectrum in (c) was recorded without proton decoupling. The spectra in (a) and (b) show the conversion of $^{13}CO_2$ (*) to $^{13}CH_2(OSiR_3)_2$ (▼) to $^{13}CH_3OSiR_3$ (**#**). The spectrum in (d) shows that all $^{13}CO_2$ was converted to $^{13}CH_3OSiR_3$ 24 h after additional silane was introduced to the mixture in (b).

triplet, and the peak at $\delta = 50$ ppm split into a quartet, with coupling constants of 168.1 and 142.9 Hz, respectively. This observation clearly confirmed that CO_2 was catalytically reduced to methoxide products with hydrosilane as the hydrogen source. The reaction proceeded rapidly at room temperature. After 90 min, about 50% of the hydrogen atoms from the hydrosilane were converted to methoxide as shown by ^1H NMR analysis. This conversion increased up to 90% after a reaction time of 24 h. These results indicated that NHCs were more highly efficient catalysts for this reaction than transition-metal catalysts, which required weeks to provide the final reduction products.[26] We also found that an excess amount of the silane led to a much faster rate with the same final methoxide products; intermediate products were not detected.

The detailed mechanism for the overall catalytic system remained unclear, but herein we propose a possible reaction pathway based on spectrometrically and spectroscopically observed intermediates (Scheme 2). The nucleophilic carbene would activate CO_2 to form an imidazolium carboxylate. This adduct would then be more reactive towards silanes, although the Si–H bond might also be activated by a free carbene.[27,28] The carboxyl moiety of imidazolium carboxylate would attack the electropositive silane center and promote hydride transfer to form formoxysilanes **2** and **3**. Formoxysilane **3**, a key intermediate in the catalytic cycle, would react with other free hydrosilanes in the presence of the NHC catalyst to provide intermediates **4**–**6** and the final methoxide products $Ph_2Si(OMe)_2$ **7** and $(Ph_2(MeO)SiO\text{-})_n$ **8**. This catalytic cycle would continue until the supply of hydrosilane as a hydride donor is exhausted. Intermediates **2**–**4**, **6**, and **7** suggested in Scheme 2 have been detected by GC–MS.



Scheme 2. Proposed catalytic cycle and reaction pathway. R^1 = mesityl, R = Ph.

Efforts to isolate the formoxysilane intermediates from the reaction mixture were not successful as they are unstable. The introduction of bulky alcohols to stabilize the formoxysilane intermediates was assessed as a strategy. When the reaction mixture was spiked with phenol, a stable intermediate—substituted formoxysilane ($Ph_2Si(OCHO)(OC(O)OPh)$) **9**—was isolated as a mixture with the $Ph_2Si(OPh)_2$ by-product (see the Supporting Information).

Reactions were performed with a carbene catalyst generated in situ by treatment of imidazolium salts with a strong base. The subsequent introduction of CO_2 to the reaction vessel gave a catalyst with the same activity as the imidazolium carboxylate. The reaction worked well if a non-nucleophilic base was used for the in situ generation of the carbene moiety. The counter anions from nucleophilic bases, such as potassium *tert*-butoxide, might react with the electropositive silane to form *tert*-butoxide–silane adducts as undesired by-products. Sodium hydride and potassium hexadimethylsilazane were found to be excellent bases for the reaction, while the use of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) did not result in any reaction. A control reaction with only base present did not give any CO_2-reduction products. Reaction with isolated pure Imes-CO_2 **1** also indicated the catalytic role of the NHC in this reaction. The reaction generally worked well in polar aprotic solvents; DMF, THF, and acetonitrile were found to be good solvents for this reaction. However, the reactions were slower in THF and acetonitrile. This is because DMF, as a Lewis base, will also activate silane and speed up the reaction. The use of methanol as a solvent resulted in nucleophilic addition of methoxide to the hydrosilane. No reaction was observed in CH_2Cl_2 (see Table 1).

Table 1: Hydrosilylation of CO_2 with diphenylsilane catalyzed by Imes-CO_2 (**1**).[a]

Entry	Catalyst loading [mol% Si–H]	Solvent	*t* [h][b]
1	1.25	DMF	24
2	1.25	THF	30
3	1.25	MeCN	88
4	1.25	CH_2Cl_2	–[c]
5	5.00	DMF	6
6	0.50	DMF	30
7	0.25	DMF	40
8	0.05	DMF	72

[a] Reaction conditions: 1 mmol of diphenylsilane, CO_2 balloon, 2 mL of solvent, room temperature. [b] Time required for the full consumption of diphenylsilane. [c] No reaction.

For the reduction of CO_2, the NHC catalyst was active even at a very low concentration. Diphenylsilane was fully consumed and converted with a catalyst loading as low as 0.05 mol%. A typical drawback for organocatalysis has been that the catalytic efficiency is relatively low compared to organometallic catalysis. However, in this work, the activity of the NHC organocatalysts for the CO_2 hydrosilylation reaction was much better than that of the organometallic catalysts. The turnover number (TON) and turnover frequency (TOF) for the NHC catalyst in this reaction at ambient conditions reached 1840 and $25.5\,h^{-1}$, respectively. In contrast, a zirconium catalyst[26] was reported to have TON and TOF values of only 92 and $0.54\,h^{-1}$, respectively, and ruthenium catalysts achieved values of 78–400 and $2.8–17\,h^{-1}$, respectively, at elevated temperatures and high CO_2 pressures (40 atm).[23–25] The reaction with the [Ir(CN)(CO)(dppe)] catalyst (dppe = (1,2-bis(diphenylphosphanyl)ethane)) produced a similar SiOMe end product with very low efficiency (TON = 2.28, TOF = $0.007\,h^{-1}$).[22] These results demonstrate that nucleophilic NHC acts as an excellent CO_2 activator. NHC catalysts hold great potential for future CO_2-fixation protocols.

A variety of NHC ligands were investigated for CO_2 reduction with diphenylsilane (Table S1 in the Supporting Information). In general, all NHCs examined were effective for CO_2 reduction. The NHCs with bulky substituents offered higher efficiencies. Various hydrosilanes were also studied for CO_2 reduction with mesitylimidazolylidene as the catalyst. The reaction was sensitive to steric hindrance around the substrate Si–H bond. Reactions with trisubstituted silanes were sluggish or inactive.

To convert CO_2 to methanol, the CO_2-reduction product was subjected to hydrolysis. Two equivalents of NaOH/H_2O were added to a typical CO_2-reduction mixture obtained from CO_2, diphenylsilane, and the mesitylimidazolylidene catalyst after a reaction period of 24 h. Methanol was typically produced in over 90% yield (based on silane), as characterized by GC against an external standard.

Conventional transition-metal catalysts for CO_2 reduction with silanes are usually highly oxygen-sensitive, which limits their practical application. In contrast, our NHC catalysts are tolerant to oxygen. When dry air was used as a feedstock in CO_2 reduction with diphenylsilane over the mesitylimidazolylidene catalyst, the reaction proceeded smoothly to form intermediates and the methoxide product. Owing to the low concentration of CO_2 in air, the reaction was very slow. Reaction with mixed CO_2/O_2 (1:1) feedstock offered the same results as that with pure CO_2. This demonstrates the practicality of our system in the transformation of CO_2 in dry air to methanol, which would be highly attractive for further development.

In conclusion, this study reports the first N-heterocyclic carbene catalyzed reduction of CO_2 with silane under ambient conditions. Compared to transition-metal catalysts, NHCs present superior efficiency and are amenable to milder, less stringent reaction conditions. The catalytic reduction of CO_2 by NHCs also produces the methoxide product selectively in excess of 90% hydrogen-transfer yield with gaseous CO_2 or dry air as the feedstock. This approach offers a very promising protocol for chemical CO_2 activation and fixation. Further studies aimed at replacing the expensive hydrosilane with alternative hydrogen sources are in progress.

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