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Catalyzed CO_2 Reduction

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Deoxygenative Reduction of Carbon Dioxide to Methane, Toluene, and Diphenylmethane with $[Et_2Al]^+$ as Catalyst**

*Manish Khandelwal and Rudolf J. Wehmschulte**

Dedicated to Professor Josef Grobe on the occasion of his 80th birthday

Although nature uses CO_2 as its main carbon source, the employment of CO_2 as a readily available inexpensive feedstock for commodity chemicals is still in its infancy.[1] Major industrial applications include the synthesis of urea, salicylic acid, and cyclic and polymeric carbonates.[2] The reduction of CO_2 to formic acid, methanol, or methane on an industrial scale is much less advanced. For example, there are only few pilot plants that are investigating and optimizing the heterogeneous catalytic reduction of CO_2 with H_2 to afford methanol.[3] Homogeneous catalysis continues to rely on expensive and rare late-transition-metal complexes,[2,4] as is illustrated by a recent report describing a very active homogeneous iridium-based system for the reduction of CO_2 with H_2 to give formic acid.[5] Hydrosilanes have also been applied as the reducing agent, mainly because the slightly polar and weaker Si–H bond (bond dissociation energy (BDE) 384 $kJ\,mol^{-1}$ in SiH_4)[6] is easier to activate than the strong non-polar H–H bond (BDE 436 $kJ\,mol^{-1}$).[7] Furthermore, the reaction products of the former are rather inert siloxanes, whereas hydrogen will be oxidized to water, which can be detrimental to certain catalysts. Some recent reports describe the ruthenium-catalyzed hydrosilylation of CO_2 to formoxysilanes,[8] and a cationic zirconium phenoxide complex catalyzed the reduction of CO_2 to methane with various hydrosilanes at room temperature.[9] Furthermore, metal-free, basic organocatalytic systems involving N-heterocyclic carbenes or amines were reported to catalyze the reduction of CO_2 to methoxysilanes[10] or formamides.[11] There are also several examples in which frustrated Lewis pairs (FLPs) have activated CO_2,[12] and its catalytic reduction to methane with Et_3SiH has been achieved using the FLP tetramethylpipiridine and $B(C_6F_5)_3$.[13] Surprisingly, there are no examples of CO_2 reductions catalyzed by Lewis acids to date. A few examples leading to aromatic and heteroaromatic carboxylic acids under Friedel Crafts conditions use the Lewis acid (usually an aluminum halide) as a stoichiometric reagent.[14] Very recently, the reaction of a stoichiometric amount of silylium ions with CO_2 led to the formation of benzoic acid, formic acid, and methanol after workup.[15]

Since we have observed during our investigations of the chemistry of cationic low-coordinate organoaluminum[16] and -zinc compounds[17] that these species catalyze the rapid reduction of benzophenone to diphenylmethane with Et_3SiH at room temperature, we wondered whether CO_2 (a “diketone”) could also be reduced under these conditions. Herein, we present the conversion of CO_2 into methane, toluene, and diphenylmethane with various hydrosilanes using $[Et_2Al][CH_6B_{11}I_6]$ (**1**)[18] as the Lewis acid catalyst.

A C_6D_6 solution of **1** and Et_3SiH in an approximately 1:10 ratio was treated with CO_2 (ca. 1.3 atm), and the progress of the reaction was monitored by ^1H and ^{13}C NMR spectroscopy. As no immediate reaction was observed at room temperature, the mixture was heated to 80 °C. After 14 h, approximately 50 % of the silane was consumed. Interestingly, not only the expected signal due to methane, but also signals due to $[D_5]$toluene, $C_6D_5CH_3$, and $[D_{10}]$diphenylmethane, $(C_6D_5)_2CH_2$, were observed (Figure 1). These signals increased in intensity until the hydrosilane was consumed (60 h). Furthermore, the major silane product was Et_4Si, not the expected siloxane $(Et_3Si)_2O$. Some low-intensity broad ^1H NMR signals indicate the formation of oligomeric or polymeric siloxanes, such as $(Et_2SiO)_n$. The same reaction with a catalyst loading of only 1 % resulted in 58 % Et_3SiH consumption after 216 h at 80 °C and the formation of methane (90 %), $[D_5]$toluene (8 %), and $[D_{10}]$diphenylmethane (2 %) with a turnover number (TON) of 14.

Following these promising results, we screened two phenylsilanes, $PhSiH_3$ and Ph_2SiH_2, and the more bulky tBuMe$_2$SiH for their reducing/hydrosilylation capability (Table 1). The two alkylsilanes are significantly more reactive than the phenylsilanes. Application of tBuMe$_2$SiH led to a higher yield of $[D_{10}]$diphenylmethane and thus a lower yield of methane compared to Et_3SiH. A possible reason for the lower reactivity of the phenylsilanes is their tendency of ligand scrambling in the presence of Lewis acids.[19] Within 15 minutes after addition of the phenylsilanes to a solution of **1** in C_6D_6, signals due to Ph_4Si, Ph_3SiH, Ph_2SiH_2, $PhSiH_3$, and SiH_4 are observed. In an further experiment involving Ph_2SiH_2 and a catalytic amount of **1**, crystalline Ph_4Si was obtained after 24 h at room temperature, along with the other silanes (Supporting Information, Figure S1).

The lower activity of phenylsilanes with respect to alkylsilanes is different from transition-metal- and amine-

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[*] Dr. M. Khandelwal, Prof. Dr. R. J. Wehmschulte
Department of Chemistry, Florida Institute of Technology
150 West University Boulevard, Melbourne, FL 32901 (USA)
E-mail: rwehmsch@fit.edu
Homepage: http://cos.fit.edu/chemistry/faculty/wehmschulte/

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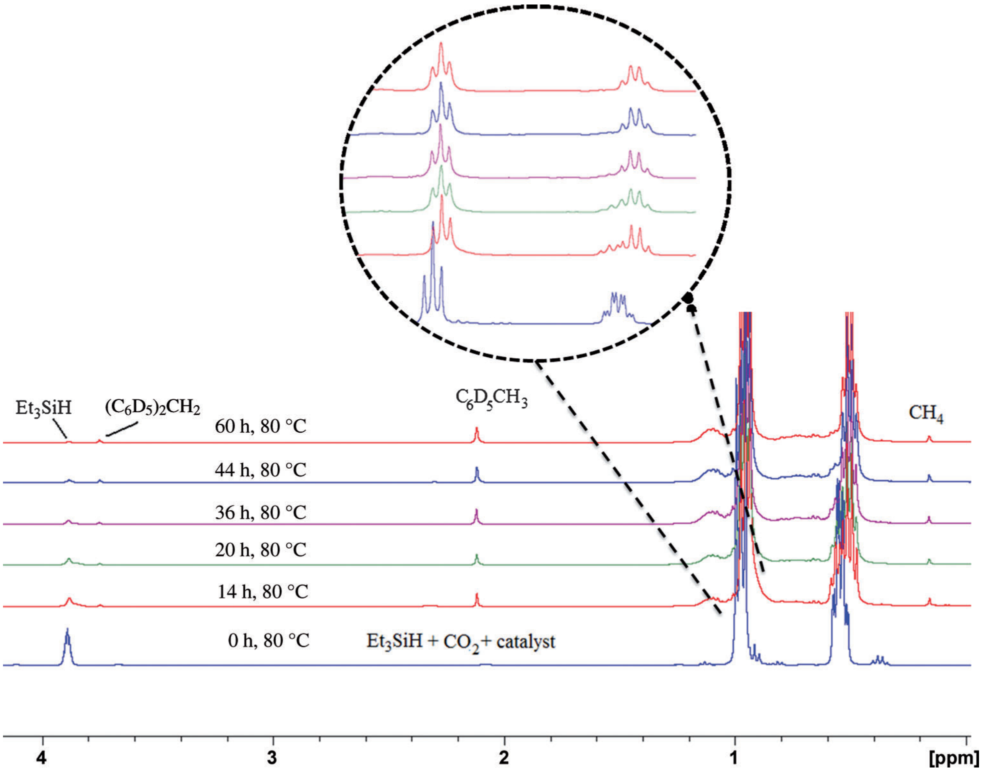


Figure 1. Reduction of CO_2 with Et_3SiH catalyzed by 10% **1** at 80 °C. The expansion of the aliphatic region shows the formation of Et_4Si.

Table 1: Reaction of hydrosilanes with CO_2 at 80 °C catalyzed by **1** with 10% loading.

Silane	*t* [h]	Products [%][a]		
		$C_6D_5CH_3$	$(C_6D_5)_2CH_2$	CH_4
Et_3SiH	60	26	4	70[b]
tBuMe$_2$SiH	60	32	28	40[b]
Ph_2SiH_2	148[c]	19	25	–
$PhSiH_3$	172[c]	9	12	–

[a] The yields were determined by integration of ^1H NMR signals of reactants and products versus an internal reference, and they are based on the amount of hydrosilane used. [b] Estimated assuming that the reactions were quantitative and that the remaining product is methane. [c] The reaction was halted.

catalyzed CO_2 reductions,[9,10] and is most likely a reflection of the strong Lewis acidity of $[AlEt_2]^+$.

To better understand the role of $[AlEt_2]^+$ as catalyst or precatalyst in the CO_2 activation, the activity of silylium ions $[R_3Si]^+$ toward CO_2 activation was probed. Silylium ions are known as potent catalysts in the reduction of ketones,[20] and a small amount of silylium ions could be present in the $[AlEt_2]^+$-catalyzed reaction mixtures, according to Equation (1). The existence of a weak adduct between $B(C_6F_5)_3$ and Et_3SiH has been demonstrated,[20] although NMR spectra of mixtures of $[AlEt_2]^+$ and Et_3SiH do not show any evidence for the adduct formation.

$$[Et_2Al]^+ + HSiEt_3 \rightleftharpoons [Et_2Al{\cdots}H{\cdots}SiEt_3]^+ \qquad (1)$$

The silylium ions investigated herein were synthesized in situ through the addition of 10% $[Ph_3C][CH_6B_{11}I_6]$ to the hydrosilane solutions. The results show that silylium ions catalyze the CO_2 reduction, but their activity is significantly lower than that of $[AlEt_2]^+$ (Table 2). Interestingly, $[Et_3Si]^+$ showed the lowest activity, followed by the phenylsilanes and tBuMe$_2$SiH. The phenysilanes underwent ligand scrambling as before.

No methane was detected, indicating that the putative intermediates R_3SiOCH_3 and $(R_3SiO)_2CH_2$ (see below) alkylate the solvent faster than being further reduced to methane. Contrary to these results, a very recent report showed that silylium ions $[Et_3Si(arene)][B(C_6F_5)_3]$ can activate CO_2 in a stoichiometric reaction.[15] The lower reactivity observed in our systems involving catalytic amounts may be explained by the formation of less reactive hydride bridged species, such as $[Et_3Si{\cdots}H{\cdots}SiEt_3]^+$, in the presence of excess hydrosilane.[21]

The CO_2 reduction with Et_3SiH catalyzed by **1** was investigated in more detail, beginning with the solvent influence. CO_2 was added to solutions of **1** and Et_3SiH in C_6D_6 and C_6D_5Br. After 40 h at room temperature, approximately 10% of Et_3SiH was consumed for the reaction in C_6D_6 and 25% for the reaction in C_6D_5Br. Small amounts of Et_4Si were detected in both reactions as initial products, along with a trace of the formate ester $HCOOSiEt_3$. Subsequent heating at 80 °C for 24 h led to the consumption of the hydrosilane, and the formation of $[D_{10}]$diphenylmethane, $[D_5]$toluene, and methane for the reaction in C_6D_6 and mostly methane (> 95%) and minor amounts of bromotoluene (< 1%) for the reaction in C_6D_5Br. The significantly lower amount of

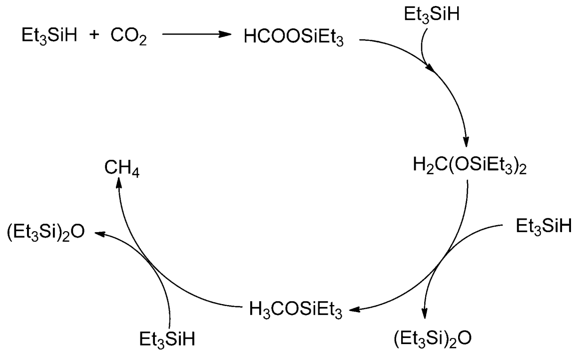
Table 2: Reaction of hydrosilanes with CO_2 at 80 °C catalyzed by 10% silylium ion.

Silane	*t* [h]	Products [%][a]	
		$C_6D_5CH_3$	$(C_6D_5)_2CH_2$
Et_3SiH	187	0.2	0
tBuMe$_2$SiH	187	15	66
Ph_2SiH_2	187	9	20
$PhSiH_3$	187	10	39

[a] The yields were determined by integration of ^1H NMR signals of reactants and products versus Ph_3CH as internal reference, and they are based on the amount of hydrosilane used.

alkylation products in C_6D_5Br is most likely due to the deactivation property of the bromine susbtituent in this aromatic compound. This also means that the product distribution can be controlled by the choice of the solvent. After the addition of a second charge of hydrosilane and CO_2, 48 h of heating were required for the consumption of the Et_3SiH. The activity of the catalytic system slowly declined as is indicated by the even slower conversion of the third charge: After 55 h at 80 °C, 89 % of the silane was consumed for the reaction in C_6D_6 and only 35 % for the reaction in C_6D_5Br. Whereas the C_6D_5Br reaction mixture remained homogeneous, a small amount of a colorless oil separated from the C_6D_6 reaction mixture. This oil possessed some catalytic activity, as shown by the consumption of 86 % Et_3SiH during 104 h at 80 °C. The nature of this oil is subject to ongoing investigations.

Matsuo[9] and Piers[13] have shown that the reduction of CO_2 with silanes is a stepwise process (Scheme 1). As we have not observed any intermediates during the 80 °C reactions, we suspected that those will be reduced much faster than CO_2.



Scheme 1. Proposed pathway of the CO_2 reduction.

We have prepared the silyl ester $HCOOSiEt_3$ and the silyl ethers $H_3COSiEt_3$ and $BnOSiEt_3$ (Bn = $PhCH_2$) and monitored their reduction with Et_3SiH in C_6D_6 solution catalyzed by compound **1.** As expected, the silyl ester was reduced rapidly at 80 °C, and the silyl ethers alkylated the solvent at room temperature even in the absence of Et_3SiH. The reaction of $HCOOSiEt_3$ with 5 % catalyst loading and 3 equiv of Et_3SiH per ester was complete within 1 h at 80 °C. The intermediate CH_3OSiEt_3 was observed during the reaction, whereas $CH_2(OSiEt_3)_2$ was not detected. The ultimate products were CH_4, $C_6D_5CH_3$, and $(Et_3Si)_2O$ (Supporting Information, Table S1). This result is also consistent with the CO_2 reduction by Et_3SiH where only 4 % diphenylmethane was formed [Equation (2)].

$$\mathrm{HCOOSiEt_3} \xrightarrow[\substack{2\,\mathrm{Et_3SiH} \\ -\,(\mathrm{Et_3Si})_2\mathrm{O}}]{\text{cat. }\mathbf{1}} \mathrm{CH_3OSiEt_3} \xrightarrow[\substack{\mathrm{Et_3SiH} \\ -\,(\mathrm{Et_3Si})_2\mathrm{O}}]{\text{cat. }\mathbf{1}} \mathrm{CH_4} \tag{2}$$

An additional charge of $HCOOSiEt_3$ was reduced within 45 min at 80 °C and a third charge within 1 h, thus indicating that the catalytic system remains active.

Next, the catalytic reduction of the silylethers CH_3OSiEt_3 and $BnOSiEt_3$ (Bn = $PhCH_2$) was investigated. The latter is the assumed intermediate for the formation of diphenylmethane from $CH_2(OSiEt_3)_2$ via electrophilic aromatic substitution according to Equation (3).

$$\mathrm{CH_2(OSiEt_3)_2} \xrightarrow[\substack{\mathrm{C_6D_6} \\ -\,\mathrm{Et_3SiOD}}]{[\mathrm{AlEt_2}]^+} \mathrm{C_6D_5CH_2OSiEt_3} \xrightarrow[\substack{\mathrm{C_6D_6} \\ -\,\mathrm{Et_3SiOD}}]{[\mathrm{AlEt_2}]^+} \mathrm{(C_6D_5)_2CH_2} \tag{3}$$

As expected, the reduction of CH_3OSiEt_3 with Et_3SiH is fast with 1 h at room temperature and 15 min at 80 °C. The mixture remained active for at least one additional loading with substrate. The products are mostly methane accompanied by 12–14 % [D_5]toluene. The benzyl ether is even more reactive, and the electrophilic alkylation of the solvent competed successfully with the silane reduction. The benzyl ether was consumed within 10–15 min at room temperature (the time it takes to take the sample out of the dry box, go to the NMR spectrometer, and collect a spectrum), and the products are $(C_6D_5)_2CH_2$ (96 %), $C_6D_5CH_3$ (4 %), unreacted Et_3SiH (73 %), and $(Et_3Si)_2O$ (72 %).

The interaction of the silyl ethers in the absence of Et_3SiH with **1** in benzene solution was also probed. The benzyl ether was consumed within 15 min at room temperature to give exclusively the [D_5]diphenylmethane $Ph(C_6D_5)CH_2$ and $(Et_3Si)_2O$. The nature of the colorless solid that precipitated immediately after silyl ether addition is likely a hydrated cationic aluminum oxide/hydroxide/silyloxide based on the idealized balanced reaction in Equation (4).

$$\begin{aligned} &\mathrm{PhCH_2OSiEt_3} + \mathrm{C_6D_6} \xrightarrow[\mathrm{C_6D_6}]{[\mathrm{AlEt_2}]^+} \mathrm{PhCH_2C_6D_5} + \mathrm{Et_3SiOD} \\ &\xrightarrow[\mathrm{C_6D_6}]{[\mathrm{AlEt_2}]^+} \mathrm{PhCH_2C_6D_5} + 0.5\,(\mathrm{Et_3SiO})_2 + 0.5\,\mathrm{D_2O} \end{aligned} \tag{4}$$

The reaction with the methyl ether $MeOSiEt_3$ in the absence of Et_3SiH requires three days for completion at room temperature. The products are $C_6D_5CH_3$ and $(Et_3Si)_2O$. Intermittently, methanol is also formed, but is consumed during the reaction. The Lewis acid mediated alkylation of aromatics with silyl ethers has been observed previously, but compound **1** is significantly more reactive.[22]

In many of the reactions discussed above, especially those involving long reaction times or heating, Et_4Si was the ultimate product rather than $(Et_3Si)_2O$. As it is known that siloxanes and silyl ethers can undergo ligand exchange in the presence of a Lewis acid,[23] we have reacted $(Et_3Si)_2O$ with **1**. Et_4Si formation was observed after 30 min at 80 °C, and the siloxane was consumed after 38 h. Broad signals in the ^{1}H NMR spectrum (Supporting Information, Figure S6) indicated the formation of oligo- and polysiloxanes similar to the side products in the CO_2 reductions. An idealized balanced reaction is given in Equation (5).

$$\mathrm{(Et_3Si)_2O} \xrightarrow[\substack{38\text{ h} \\ 80\text{ °C}}]{[\mathrm{AlEt_2}]^+} \mathrm{Et_4Si} + 1/n\,(\mathrm{Et_2SiO})_n \tag{5}$$

Mass spectrometric analyses of those compounds identified $(Et_2SiO)_4$ and various larger linear fragments possibly deriving from $Et_3Si(OSiEt_2)_nOSiEt_3$.

It should also be mentioned that CO_2 did not react with **1**, even after 30 h at 80 °C. This is contrary to the facile insertion of CO_2 into the Al–Et bond in $AlEt_3$,[24] but it is consistent with the observed lower activity of Al–C bonds in cationic aluminum species.[25]

For comparison, we have also tested the catalytic activity of $AlBr_3$ for the CO_2 reduction. After 20 h at room temperature, approximately 24 % of Et_3SiH was consumed, and the ^1H NMR spectrum showed peaks around $\delta = 8$ ppm, indicative of coordinated $HCOOSiEt_3$, and small amounts of Et_3SiOCH_3 were also detected. Additional Et_3SiH was consumed during heating at 80 °C for two days, after which time no significant changes were observed. The silyl ester and silyl ether signals disappeared, and the formation of methane and Et_3SiBr was detected. Overall, approximately 1.7 moles of Et_3SiH were consumed per $AlBr_3$, leading at best to 0.4 equiv of methane. An idealized equation for a stoichiometric reaction is given below [Equation (6)], but the lower amount of actually consumed hydrosilane suggests other pathways, including the formation of aluminum formates.

$$2\,AlBr_3 + CO_2 + 4\,Et_3SiH \xrightarrow[\substack{40\ h \\ 80\ ^\circ C}]{C_6D_6} 2\,Br_2AlOSiEt_3 + 2\,Et_3SiBr + CH_4 \qquad (6)$$

The formation of Et_3SiBr can be explained by the reaction of $AlBr_3$ with $(Et_3Si)_2O$. These types of reactions have been known for a long time[26] and have even been utilized for the formation of aluminum oxides at elevated temperatures.[27] A control reaction of $HCOOSiEt_3$ with $AlBr_3$, which afforded a benzene-insoluble precipitate and only Et_3SiBr as a soluble species, suggests another route for the formation of Et_3SiBr.

These results show that a strong Lewis acid, such as $[Et_2Al]^+$ and even $[R_3Si]^+$, catalyzes the CO_2 reduction by hydrosilanes. Based on the faster catalytic reduction of the intermediates $HCOOSiEt_3$ and $MeOSiEt_3$, the rate-limiting step is most likely the reduction of CO_2 to $HCOOSiEt_3$. The strong Lewis acidity of $[Et_2Al]^+$ manifests itself in solvent alkylation reactions and the conversion of the primary siloxane product into Et_4Si and polysiloxanes $(Et_2SiO)_n$. These side reactions may contribute to the observed activity decrease after three cycles. Current activities focus on the development of more reactive catalytic systems based on the potentially more robust $[(RO)_2Al]^+$ platform. Finally, preliminary results have shown that $[EtZn][CHB_{11}Cl_{11}]$ also catalyzes the CO_2 reduction with Et_3SiH, albeit a slightly more slowly than $[Et_2Al][CH_6B_{11}I_6]$.

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