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From Carbon Dioxide to Methane: Homogeneous Reduction of Carbon Dioxide with Hydrosilanes Catalyzed by Zirconium−Borane Complexes

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Carbon dioxide is the stable carbon end product of metabolism and other combustions, and it is an abundant yet low-value carbon source. This molecule would be very valuable as a renewable source if it were to be effectively transformed into reduced organic compounds under mild conditions.[1] However, thermodynamic stability of CO_2 has prevented its utilization in industrial chemical processes, and thus this represents a continuing scientific challenge. Here we show that CO_2 is catalytically converted into methane (CH_4) and siloxanes via bis(silyl)acetals with a mixture of a zirconium benzyl phenoxide complex and tris(pentafluorophenyl)-borane ($B(C_6F_5)_3$). In addition, an appropriate choice of hydrosilane may lead to selective formation of the initial acetal product and isolation of polysiloxane materials.

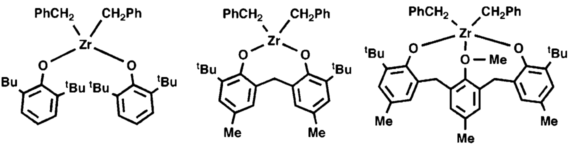
$$CO_2 + 4Si{-}H \rightarrow CH_4 + 4Si{-}O \qquad (1)$$

The overall reaction stoichiometry described here proceeds as illustrated in eq 1. We have studied early transition metal complexes having phenoxide-based multidentate ligands to understand their reactivity toward small molecules such as dinitrogen and carbon monoxide.[2] As part of these investigations, we have begun to study activation of carbon dioxide. Synthetic systems capable of reducing CO_2 to CH_4 have been elusive, despite the wealth for precedent of metal complexes that undergo the conversion of CO_2 into a variety of organic products.[3−5] Hydrosilation of the carbon−oxygen double bond is a mild method for reduction of carbonyl functions of organic compounds.[6] Since the reaction is exothermic, the use of hydrosilanes in the reduction of CO_2 is very attractive. For example, the reactions of CO_2 with hydrosilanes mediated by late transition metal complexes have produced silyl formate and methoxide.[7,8]

In a first set of experiments, we studied the catalytic activity of cationic zirconium benzyl complexes bearing phenoxide ligands (Chart 1) in the course of reducing CO_2 with $PhMe_2SiH$ as the test substrate. The catalysts used in this study were synthesized by treatment of the dibenzyl complexes with $B(C_6F_5)_3$ in toluene.[2,9] Reaction of $(\mathbf{L}^3)Zr(CH_2Ph)_2$ with $[Ph_3C][B(C_6F_5)_4]$ in toluene solution produced Ph_3CCH_2Ph and $[(\mathbf{L}^3)Zr(CH_2Ph)][B(C_6F_5)_4]$. Since improved reactivity and yield were achieved through in situ generation of cationic species, subsequent experiments were performed by premixing the dibenzyl complexes and boranes prior to the addition of hydrosilanes and CO_2.

The results of the catalytic CO_2 reduction with $PhMe_2SiH$ are depicted in Table 1. The reaction proceeded exothermically to form $(PhMe_2Si)_2O$. Performing the analogous reaction in benzene-d_6 in a NMR tube revealed the release of CH_4 as the byproduct. The resonance due to CH_4 was observed as singlet at 0.15 ppm in the ^1H NMR spectrum. Mono- and bisphenoxide ligands $\mathbf{L}^1$ and $\mathbf{L}^2$ gave zirconium complexes that preformed with low activity (entries 1 and 2) relative to the tridentate ligand $\mathbf{L}^3$. It is obvious from entries 4 and 5 that the combination of a zirconium complex with $B(C_6F_5)_3$ is responsible for this result. Thus, neither zirconium cationic species nor $B(C_6F_5)_3$ alone provided an active catalyst. The enhanced reactivity associated with the tridentate−phenoxide ligand made $(\mathbf{L}^3)Zr(CH_2Ph)_2$ attractive for further study.

Chart 1



$(\mathbf{L}^1)_2Zr(CH_2Ph)_2$ (**1**) $(\mathbf{L}^2)Zr(CH_2Ph)_2$ (**2**) $(\mathbf{L}^3)Zr(CH_2Ph)_2$ (**3**)

Table 1. Reduction of CO_2 with $PhMe_2SiH$ at Room Temperature

entry	catalyst (mol %)[a]	TOF (h^{-1})	TON[b]	yield (%)[c]	time (h)
1	**1**/$B(C_6F_5)_3$ (0.45)	23	34	15	1.5
2	**2**/$B(C_6F_5)_3$ (0.42)	31	46	19	1.5
3	**3**/$B(C_6F_5)_3$ (0.44)	150	225	98	1.5
4[d]	**3**/$[Ph_3C][B(C_6F_5)_4]$ (1.8)			0	1.5
5	$B(C_6F_5)_3$ (1.9)			0	*e*

[a] The Zr/B ratio = ca. 1. [b] TON and TOF are based on the zirconium complex per Si−H bond. [c] Isolated yields of $(PhMe_2Si)_2O$. [d] Conversion of $PhMe_2SiH$ into Ph_2Me_2Si and Me_2SiH_2 was observed. [e] 3 days.

To obtain insight into the intervening processes in the reaction, isotopically enriched $^{13}CO_2$ (99 atom % ^{13}C) was admitted into a resealable NMR tube containing a solution of $(\mathbf{L}^3)Zr(CH_2Ph)_2$, $B(C_6F_5)$, and Et_3SiH in benzene-d_6 at room temperature. When Et_3SiH is used as a hydrosilane, the reaction requires approximately one week for completion and is easily monitored by NMR spectroscopy (Figure 1). The reaction proceeded cleanly, during which time $^{13}CO_2$ and Et_3SiH were fully consumed. Monitoring the reaction by $^{13}C\{^1H\}$ NMR spectroscopy indicates the presence of bis(silyl)acetal$^{13}CH_2(OSiEt_3)_2$ as a detectable intermediate. The resonance at 84.5 ppm due to $^{13}CH_2(OSiEt_3)_2$ grew to a maximum relative intensity over a period of about 7 h and then decreased as that at −4.4 ppm due to $^{13}CH_4$. It then continued to grow until, after about 1 week, it was the only resonance attributable to a ^{13}C-labeled product. Additionally, in the absence of proton decoupling, the resonances due to $^{13}CH_2(OSiEt_3)_2$ and $^{13}CH_4$ split into a triplet and a quintet with a coupling constant of 161.5 and 125.6 Hz, respectively. This observation unambiguously confirms that the carbon atom of CH_4 originates from CO_2, and the source of its hydrogen atoms is added Et_3SiH.

The scope of reduction of CO_2 by various hydrosilanes was examined with **3**/$B(C_6F_5)_3$ as the catalyst (Table 2). The six hydrosilanes examined were shown to be effective for reduction of CO_2 to CH_4, and the **3**/$B(C_6F_5)_3$ catalyst is sensitive to steric hindrance around the substrate Si−H bond. For example, triethylsilane reacted more slowly than diethylmethylsilane (entries 1 and 2), while bulkier triphenylsilane did react but required more catalyst and prolonged reaction time to give a mixture of $(Ph_3SiO)_2CH_2$ and $(Ph_3Si)_2O$ (entry 4). Primary and secondary silanes can also be employed. The reaction with diethylsilane produced a mixture

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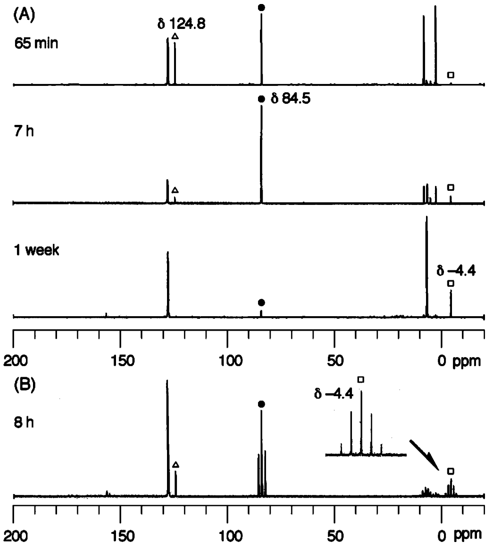


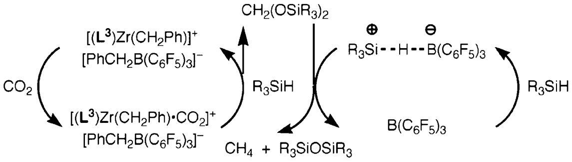
Figure 1. (A) $^{13}C\{^1H\}$ NMR spectra showing conversion of $^{13}CO_2$ (△) to $^{13}CH_2(OSiEt_3)_2$ (●) to $^{13}CH_4$ (□) using 1.5 mol % catalyst ($\mathbf{L}^3$)Zr(CH_2-Ph)$_2$/ $B(C_6F_5)_3$ at room temperature; (B) ^{13}C NMR spectrum of the reaction mixture after 8 h at room temperature.

Table 2. Reduction of CO_2 with Hydrosilanes by 3/$B(C_6F_5)_3$ at Room Temperature[a]

entry	substrate	product	TOF (h^{-1})	TON[b]	yield (%)[c]	time (h)
1	Et_2MeSiH	$(Et_2MeSi)_2O$	7.3	211	93	29
2	Et_3SiH	$(Et_3Si)_2O$	1.1	180	93	162
3	Et_3SiH	$(Et_3SiO)_2CH_2$ $(Et_3Si)_2O$	1.2	203	82 11	165
4	Ph_3SiH	$(Ph_3SiO)_2CH_2$ $(Ph_3Si)_2O$	0.13	50	64 28	384
5	Et_2SiH_2	$(Et_2SiO)_n$	0.57	108	45	189
6	Ph_2SiH_2	$(Ph_2HSi)_2O$	0.29	49	46	168
7	$PhSiH_3$	$(PhSiO_{1.5})_n$	1.1	162	74	145

[a] The Zr/B ratio = ca. 1, except for entries 2 (0.69) and 3 (1.96) (0.41 to ~0.52 mol % ($\mathbf{L}^3$)Zr($CH_2Ph)_2/B(C_6F_5)_3$ except for entry 4 (1.8 mol %)). [b] TON and TOF are based on the zirconium complex per Si−H bond. [c] Isolated yields of siloxane.

Scheme 1



of cyclic and linear siolxane oligomers $(Et_2SiO)_n$ ($n = 3-11$, entry 5), and phenylsilane was transformed into a silsequioxane polymer $(PhSiO_{1.5})_n$ ($M_w = 4220$, $M_w/M_n = 2.72$, entry 7). This result implies the possibility to prepare polysiloxane materials from hydrosilanes and CO_2. However, when diphenylsilane was used, the formation of $(Ph_2HSi)_2O$ remarkably reduced the reactivity of its remaining Si−H bonds (entry 6).

A detailed mechanism for the overall catalytic process cannot yet be deduced, but an outline of a potential mechanism is provided in Scheme 1. First, the zirconium cationic complex forms the adduct with CO_2, because of the highly electrophilic character of the phenoxide-supported zirconium(IV) cationic species.[10] In the absence of zirconium complexes, reduction of CO_2 is not observed, suggesting coordination of CO_2 to the Zr center prior to the actual reduction. This coordination might render the CO_2 reactive toward hydrosilation to yield the initial product $CH_2(OSiR_3)_2$. The nature of the counteranion is critical, because replacing $[PhCH_2B(C_6F_5)_3]^-$ with $[B(C_6F_5)_4]^-$ resulted in disproportionation of hydrosilane (entry 4 in Table 1). The $[PhCH_2B(C_6F_5)_3]^-$ counterion seems to play important roles in the course of transformation of CO_2 and R_3SiH into $CH_2(OSiR_3)$. The resulting bis(silyl)acetal is subsequently reduced by R_3SiH to CH_4 and $(R_3Si)_2O$. This final step was found to be facilitated by a catalytic amount of $B(C_6F_5)_3$ alone, and $B(C_6F_5)_3$ is known to act as an effective catalyst for hydrosilane reduction of a variety of aldehydes, ketones, esters, ethers, and alcohols.[11] The $[PhCH_2B(C_6F_5)_3]^-$ counterion slowly decomposed during the reaction to generate $B(C_6F_5)_3$, as monitored by ^{19}F NMR spectroscopy. It is noteworthy that the yield of bis(silyl)actal was increased with a ($\mathbf{L}^3$)Zr($CH_2Ph)_2/B(C_6F_5)_3$ ratio equal to 1.96 to prevent the release of free $B(C_6F_5)_3$, whereas the use of excess $B(C_6F_5)_3$ promoted conversion of $CH_2(OSiEt_3)_2$ into CH_4 and $(Et_3Si)_2O$ (entries 2 and 3 in Table 2).

The method for catalytic reduction of CO_2 presented here offers some significant advantages, since it proceeds under mild conditions and permits complete reduction of CO_2 to CH_4. Another curious aspect of this system is the formation of polysiloxane from CO_2 and hydrosilane in chemical CO_2 fixation. The present results are promising, but we note that catalytic activity will need to be improved and the long-term stability and performance of the catalyst demonstrated.

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Supporting Information Available: Experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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