**$CO_2$ Reduction**

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# Silyl Cation Mediated Conversion of $CO_2$ into Benzoic Acid, Formic Acid, and Methanol**

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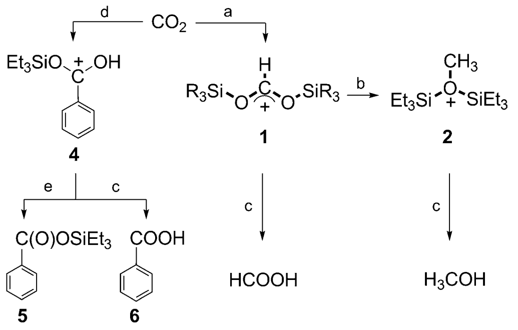
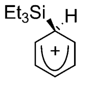
The use of $CO_2$ as a renewable and environmentally friendly $C_1$ source for the synthesis of carboxylic acids and fuels such as methanol and methane is a topic of current interest.[1–4] The high thermodynamic stability of $CO_2$ clearly calls for highly efficient activation which must be combined with a strong thermodynamic driving force to ensure irreversible fixation. While in the past transition-metal chemistry played a dominant role in $CO_2$ conversion chemistry,[5] recent years have seen the emergence of organocatalytic methods for $CO_2$ reduction.[6–14] For example N-heterocyclic carbenes have been applied for the nucleophilic activation of $CO_2$, and subsequent reduction of the resulting imidazolium carboxylates by silanes yielded methanol.[9] In addition stoichiometric and catalytic reductions of $CO_2$ have been reported which utilize frustrated Lewis pairs (FLPs)[10] for the activation, and dihydrogen, silanes, or ammonia borane as the hydrogen source.[11–14] In view of the high electrophilic activity of silyl cations[15] and their complexes with solvents and counteranions, we were intrigued by the possibility of exploiting this extreme reactivity in $CO_2$ activation. Silanes then would be the logical hydrogen source for the reduction and would provide the desired thermodynamic driving force through the formation of siloxanes.

Here we report on a metal-free reduction of $CO_2$ by trialkylsilanes, $R_3SiH$ (R = Et, *i*Pr), using stoichiometric amounts of trityl borate $[Ph_3C][B(C_6F_5)_4]$. The reduction is fast under ambient conditions, but different products—depending on the applied solvent—are formed. In chlorobenzene (PhCl) either disilylated formic acid **1** or the disilylmethyl oxonium ion **2** is formed, depending on the substituent R at the silane. Simple hydrolysis of these compounds yields formic acid and methanol (Scheme 1). In benzene (PhH), the reaction of $CO_2$ with the preformed silylbenzenium salt $[Et_3Si(C_6H_6)][B(C_6F_5)_4]$ (**3**$[B(C_6F_5)_4]$) leads to further functionalization of $CO_2$.[8b] In this case the benzylic cation **4** is formed, which can be easily transformed either by hydrolysis into benzoic acid ($PhCO_2H$, **6**), or, by careful deprotonation, into the silylester **5** (Scheme 1).



*Scheme 1.* Reduction of $CO_2$ by $[Ph_3C][B(C_6F_5)_4]/R_3SiH$ in different solvents (the $B(C_6F_5)_4^-$ anion is omitted, **1a**: R = Et, **1b**: R = *i*Pr). Conditions: a) 0.1013 MPa $CO_2$, 1 equiv $Ph_3C^+$, 2 equiv $R_3SiH$, PhCl, room temperature; b) 2 equiv $Et_3SiH$, RT; c) $H_2O$; d) 0.1013 MPa $CO_2$, 1 equiv $Ph_3C^+$, 1 equiv $Et_3SiH$, PhH, room temperature; e) *sym*-collidine, PhH, temperature.



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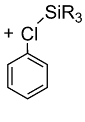

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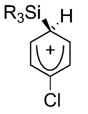

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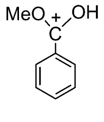

**9**

Reaction of triethylsilane with one equivalent of the trityl borate $[Ph_3C][B(C_6F_5)_4]$ in benzene yields benzenium ion **3**, identified by its characteristic $^{29}Si$ NMR resonance at $\delta(^{29}Si) = 97.4$ ppm[16] (Table 1). Also when PhCl is used as the solvent, cationic complexes $[R_3Si(PhCl)]^+$ (**7**) are formed, as indicated by the strongly deshielded $^{29}Si$ NMR resonances at $\delta(^{29}Si) = 99.9$ (R = Et, **7a**) and 103.3 ppm (R = *i*Pr, **7b**; Table 1). Based on the results of our quantum mechanical calculations, however, we assign to these complexes the chloronium ion structure **7** rather than the chloroarenium ion structure **8**.

*Table 1:* NMR parameters of cations **1**–**4** and **7** (at 305 K).[a]

| Compound | $\delta(^{29}Si)$ | $\delta(^{13}C)$[b] | $\delta(^{1}H)$[c] | $^{1}J(CH)$ |
|---|---|---|---|---|
| **7a** (R = Et)[d] | 99.9 | -- | – | – |
| **7b** (R = *i*Pr)[d] | 103.3 | -- | – | – |
| **3**[e] | 97.4 | -- | – | – |
| **1a** (R = Et)[d,f] | 55.7 | 172.8 | 7.03 | 234 |
| **1b** (R = *i*Pr)[d] | 50.2 | 172.5 | 7.43 | 231 |
| **2**[d,f] | 64.4 | 60.9 | 3.09 | 154 |
| **4**[e] | 49.4 | 178.0 | – | – |

[a] $\delta$ in ppm, $^{1}J$ in Hz. [b] Signal of the original $CO_2$ C atom. [c] Signals for the H atoms attached to the original $CO_2$ C atom. [d] In [D$_5$]chlorobenzene. [e] In [D$_6$]benzene. [f] **1a** and **2a** detected in the same sample.

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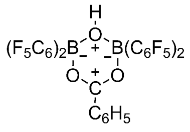
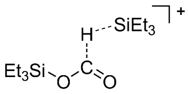
When chloronium ion **7b** and a second equivalent of triisopropylsilane in PhCl were treated with $CO_2$ under ambient conditions, disilylated formic acid **1b** was detected by NMR spectroscopy as the only product. Addition of excess triisopropylsilane did not lead to further reduction of the cation **1b**. Simple hydrolysis of the reaction mixture with $D_2O$ yielded deuterated formic acid, HCOOD, in 89–95% yield[17] [$\delta(^1H) = 8.19$ ppm, $\delta(^{13}C) = 167.4$ ppm; $^1J(CH) = 220$ Hz] and hexaisopropyldisiloxane (major product) and triisopropylsilanol (minor product). When the less bulky triethylsilane was applied in the reaction with $CO_2$, a mixture of cations **1a** and **2** was obtained. Hydrolysis of this mixture yields formic acid, methanol [$\delta(^1H) = 3.11$ ppm, $\delta(^{13}C) = 49.0$ ppm; $^1J(CH) = 143$ Hz], and hexaethyldisiloxane. When a large excess (more than 4 equiv) of triethylsilane was applied at room temperature, methanol (87–98% yield)[17] and hexaethyldisiloxane were the sole products after hydrolysis.

Cations **1** and **2** were identified by $^1H$, $^{13}C$, $^{29}Si$, and two-dimensional $^1H,^{29}Si$ and $^1H,^{13}C$ NMR spectroscopy. Characteristic for disiloxycarbenium ions **1** are the doublets in the proton-coupled $^{13}C$ NMR spectra at relatively low field [$\delta(^{13}C) = 172.8$, 172.5 ppm; $^1J(CH) = 234$, 231 Hz] and the correlated signals for the methine protons at $\delta(^1H) = 7.03$ and 7.43 ppm. These values can be favorably compared with those reported for dimethoxycarbenium tetrafluoroborate, $[(MeO)_2CH][BF_4]$ [$\delta(^{13}C) = 181.4$ ppm, $\delta(^1H) = 8.9$ ppm].[18] The $^{29}Si$ resonances of cations **1** and **2** [$\delta(^{29}Si) = 50.2$–64.4 ppm] are found in the typical region for silylated oxonium ions [i.e. $\delta(^{29}Si) = 46.7$ ($tBu_3SiOH_2^+$), 59.0 ($(Me_3Si)_2OEt^+$), 66.9 ppm ($Me_3SiOEt_2^+$)].[19,20]


**10**


**14**

The reaction of triethylsilyl benzenium borate $\mathbf{3}[B(C_6F_5)_4]$ with $CO_2$ in benzene at room temperature yielded the perfluorinated tetraphenyl borate of protonated benzoic ester **4** in almost quantitative yield, as judged from NMR spectroscopy (Scheme 1). The reaction was complete in minutes even at room temperature under ambient $CO_2$ pressure. In contrast, when the reaction was conducted in a Young NMR tube without stirring, the reaction was slow and could be monitored conveniently by $^{29}Si$ NMR spectroscopy over hours (see Figure 1a). The protonated silylester **4** was identified by its characteristic NMR chemical shifts (see Table 1). In particular, the $^{29}Si$ NMR resonance at $\delta(^{29}Si) = 49.4$ ppm is of high diagnostic value as it is shifted to lower field by $\Delta\delta^{29}Si = 23.0$ ppm compared to the neutral silylester **5**. The benzylic carbon atom gives rise to a signal in the $^{13}C$ NMR spectrum at $\delta(^{13}C) = 178.0$ ppm, which is close to the NMR chemical shift value reported for the protonated benzoic methyl ester **9** in $SO_2ClF$ [$\delta(^{13}C) = 181.9$ ppm for $C^+$ in **9**].[20] When $^{13}C$-labeled $CO_2$ was applied in the reaction with $\mathbf{3}[B(C_6F_5)_4]$, the $^{13}C$ atom was found exclusively in the benzylic position as indicated by the strong increase of the intensity of the $^{13}C$ NMR signal at $\delta(^{13}C) = 178.0$ ppm (Figure 1b). Further evidence for the formation of cation **4** in the reaction of $CO_2$ with silylarenium ion **3** came from its independent synthesis by protonation of the silylester **5** and by silylation of benzoic acid **6**.[22] Finally, deprotonation of **4** with collidine allows the isolation of silylester **5**, although only in poor yield (11%). Alternatively, hydrolysis of **4** afforded benzoic acid **6** in 51% yield.

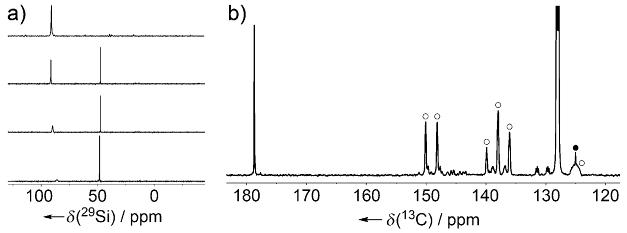


***Figure 1.*** a) $^{29}Si$ NMR spectra of $\mathbf{3}[B(C_6F_5)_4]$ in $C_6D_6$ at 305 K under argon atmosphere (top) and of a mixture of $\mathbf{3}[B(C_6F_5)_4]$ and $\mathbf{4}[B(C_6F_5)_4]$ resulting from the reaction with $CO_2$ after 4, 24, 36 h (lower spectra). b) $^{13}C$ NMR spectrum of $[^{13}C_1]$-**4** obtained by reaction of **3** with $^{13}CO_2$ in $C_6D_6$ (● $^{13}CO_2$, ○ $[B(C_6F_5)_4]^-$ anion).

Carbocation **4** is only marginally stable at room temperature and decomposes slowly also at temperatures around 5 °C. This instability is one reason for the low yields of isolated benzoic acid **6** and silylester **5** and it severely hampers all crystallization attempts. For example, from a $C_6F_6$ solution of $\mathbf{4}[B(C_6F_5)_4]$ heterocycle **10** was isolated in low yield (17%). Compound **10** was formed by degradation of the anion. In its molecular structure the original $CO_2$ unit is preserved and this provides pictorial evidence for the $CO_2$ fixation (Figure 2).[22]

A mechanistic proposal for the $CO_2$ fixation by silylarenium ions, outlined in Scheme 2 for **3**, starts with a pre-equilibrium between benzenium ion **3** and the silyl–$CO_2$ complex **11a**. As a result of the activation by the Lewis acid $Et_3Si^+$, the electrophilicity of the central carbon atom in complex **11a** is enhanced and in a subsequent step it

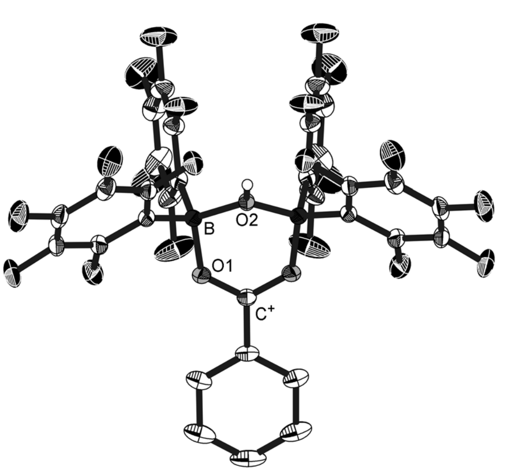
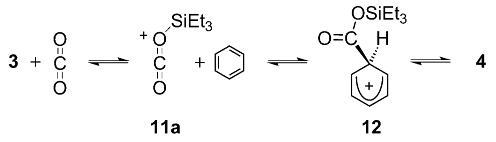
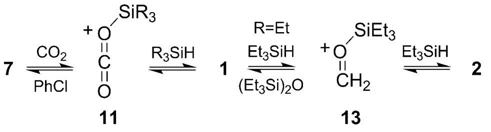


***Figure 2.*** Ellipsoid presentation of the molecular structure of the heterocyclic compound **10** in the crystal (50% probability, only the H atom attached to $O^2$ is shown). Pertinent bond lengths [pm]: $C^+$–$C^{ipso}$ 146.12(25), $C^+$–O1 127.63(12), B–O1 150.42(17), B–O2 152.13(14).



*Scheme 2.* Proposed reaction course for the formation of cation **4** from $CO_2$.

undergoes an electrophilic addition to the benzene forming the Wheland intermediate **12**. The terminating step consists of a deprotonation–protonation sequence to give the protonated silylester **4** (Scheme 2). Silyl–$CO_2$ complexes **11** are also central for the $CO_2$ reduction in chlorobenzene (Scheme 3).



*Scheme 3.* Proposed reaction course for the formation of cations **1** and **2** from $CO_2$ (**a**: R = Et, **b**: *i*Pr).

In this case the electrophilic activation of $CO_2$ is not sufficient for its addition to the relatively electron-poor chlorobenzene. However, the reduction of $CO_2$ is facilitated by additional silane to give the bissilylated formic acids **1**. Clearly, this step shows parallels to the known hydrosilylation of carbonyl compounds.[23–25] When $i\mathrm{Pr}_3\mathrm{SiH}$ is applied in this reaction, no further conversion of cation **1** is observed. In contrast, with an excess of the less bulky $Et_3SiH$ further hydrosilylation of the partial CO double bond in cation **1** occurs to give the silylated formaldehyde **13**. It seems reasonable to assume that the highly activated cation **13** adds another equivalent of triethylsilane to yield the ultimately observed oxonium ion **2**.

The results of computations at the hybrid DFT B3LYP/6-311+G(d,p) level of theory support these mechanistic proposals.[22,26] In detail, they show that the reaction of silylarenium ion **3** with $CO_2$ to give the benzylic cation **4** is exergonic by 52.5 kJ mol$^{-1}$ (see Figure 3a). Although the formation of silylated $CO_2$, **11**, from silylarenium ion **3** is thermodynamically disfavored by 16.5 kJ mol$^{-1}$, the barrier for the nucleophilic attack to give arenium ion **12** is small enough for the reaction to proceed at room temperature at reasonable rates. Finally, it is the high exothermicity of the terminating formal 1,3-H shift to give the benzylic cation **4** which guarantees the quasi irreversibility of the complete reaction sequence (Figure 3a).

For the reaction in chlorobenzene the calculations predict a similar reaction profile. While the computational results indicate that the chloronium ion **7a** is more stable than the isomeric arenium ion **8a** by 24.1 kJ mol$^{-1}$, the formation of the silylated $CO_2$ **11a** is even less favored than in the case of the reaction of arenium ion **3** with $CO_2$ (Figure 3b). The barrier for the nucleophilic attack by the second $Et_3SiH$ molecule is, however, significantly smaller and on the $G^{298}$ surface the disilylated formic acid **1a** is produced in practically one extremely exergonic step ($\Delta G^{298} = -179.8$ kJ mol$^{-1}$). A high-lying hydrogen-bridged intermediate **14** for this step was located. It is, however, separated from the product **1a** only by a small activation barrier of 6.3 kJ mol$^{-1}$ which suggests that this intermediate cannot be detected under the applied experimental conditions. The calculation further shows that the following step (Scheme 3), the formation of silylated formaldehyde **13**, is slightly endergonic but this is overruled by the thermodynamically extremely favored formation of oxonium ion **2** (($\Delta G^{298}$(**13**) = +8.9 kJ mol$^{-1}$ and $\Delta G^{298}$ (**2**) = $-131.5$ kJ mol$^{-1}$ for the formation of compounds **13** and **2** from cation **1a** according to Scheme 3).

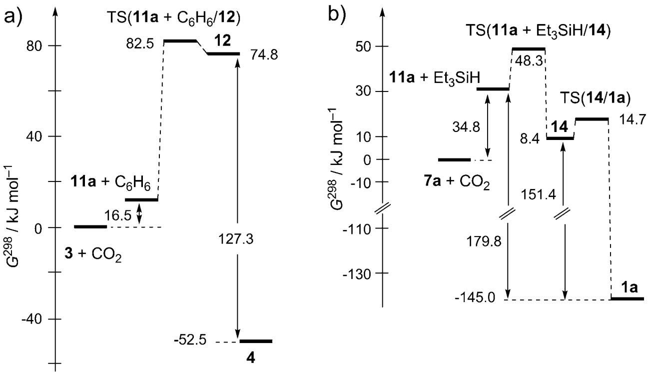


*Figure 3.* Calculated reaction coordinates for the reaction of $CO_2$ with silylarenium ion **3** (a) and chloronium ion **7a** (b). The labeling of the reaction coordinate for (b) is incomplete for a clearer presentation. The reaction coordinate is computed for $[C_{19}H_{36}ClO_2Si_2]^+$ starting from **7a** + $CO_2$ + $Et_3SiH$ and ending at **1a** + PhCl. (at B3LYP/6-311+G(d,p)). Free enthalpies at 298 K ($G^{298}$) are given relative to the starting materials.

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