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Tandem Frustrated Lewis Pair/Tris(pentafluorophenyl)borane-Catalyzed Deoxygenative Hydrosilylation of Carbon Dioxide

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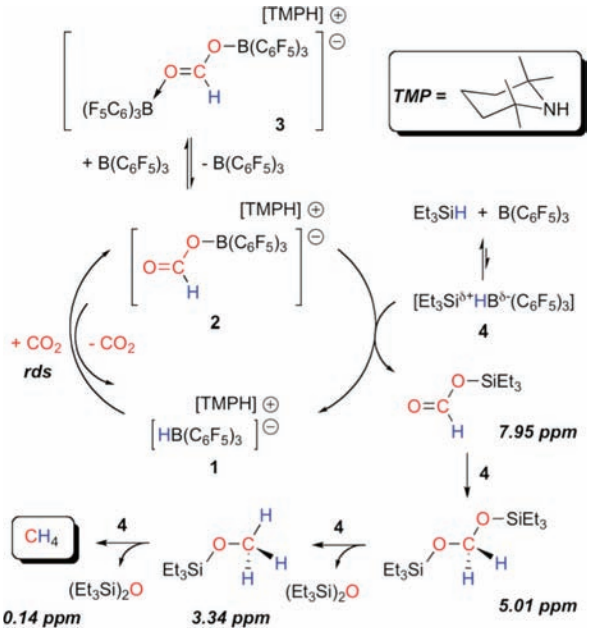
Abstract: The frustrated Lewis pair system consisting of 2 equiv of 2,2,6,6-tetramethylpiperidine (TMP) and tris(pentafluorophenyl)borane [$B(C_6F_5)_3$] activates carbon dioxide to form a boratocarbamate−TMPH ion pair. In the presence of triethylsilane, this species is converted to a silyl carbamate and the known ion pair $[TMPH]^+[HB(C_6F_5)_3]^-$, which recently was shown to react with CO_2 via transfer of the hydride from the hydridoborate to form the formatoborate $[TMPH]^+[HC(O)OB(C_6F_5)_3]^-$. In the presence of extra $B(C_6F_5)_3$ (0.1−1.0 equiv) and excess triethylsilane, the formatoborate is rapidly hydrosilated to form a formatosilane and regenerate $[TMPH]^+[HB(C_6F_5)_3]^-$. The formatosilane in turn is rapidly hydrosilated by the $B(C_6F_5)_3/Et_3SiH$ system to CH_4, with $(Et_3Si)_2O$ as the byproduct. At low [Et_3SiH], intermediate CO_2 reduction products are observed; addition of more CO_2/Et_3SiH results in resumed hydrosilylation, indicating that this is a robust, living tandem catalytic system for the deoxygenative reduction of CO_2 to CH_4.

The utilization of carbon dioxide as a sustainable and nontoxic C1 feedstock for the production of value-added chemical products such as carboxylic acids or fuels such as methanol and methane is of current interest.[1] The high thermodynamic stability of CO_2 necessitates its catalytic activation and coupling to a thermodynamic driver for efficient conversion. Transition-metal-based catalysts have played a dominant role in CO_2 conversion, but recently, an increasing number of organocatalytic CO_2 reduction schemes have emerged.[2] For example, N-heterocyclic carbenes (NHCs) reversibly form zwitterionic adducts $NHC \cdot CO_2$ that are considered key intermediates in the reductive deoxygenation of CO_2 using diphenylsilane as a sacrificial reducing agent, affording CH_3OH upon workup.[3]

In this context, activation of CO_2 by transition-metal-free "frustrated Lewis pairs" (FLPs)[4] has led to the development of stoichiometric reductions of CO_2 to CH_3OH. Here, the FLPs form bridging carboxylate species[5] that can accept hydrogen from ammonia borane[6] or via a thermally driven, multistep self-reduction in which the key step is a reversible B−H bond addition of hydridotris(pentafluorophenyl)borate to one C=O double bond of CO_2, affording the formatoborate anion $[HC(O)OB(C_6F_5)_3]^-$.[7] Ultimately, hydrolysis of $CH_3O{-}LA$ (LA = BX_3 or AlX_3) is required in order to obtain methanol.

Boron−hydrogen bond addition to CO_2 mediated by phosphonium or ammonium borate ion pairs formed via FLP hydrogen splitting thus offers a potential entry point into catalytic CO_2 fixation in the presence of a suitable reducing agent (oxygen acceptor). We have shown that perfluoroarylboranes are excellent catalysts for the reductive hydrosilylation of carbonyl functions[8] and C−O bonds,[9] a potentially useful reaction for subsequent steps in the reductive deoxygenation of CO_2 to CH_4.

Scheme 1



The ammonium hydridoborate ion pair **1** formed by treatment of the FLP $B(C_6F_5)_3$/2,2,6,6-tetramethylpiperidine (TMP) and hydrogen[10] (32 mM, C_6D_5Br) reacted with CO_2 (2−4 atm) in the presence of Et_3SiH (18 equiv) at 56 °C to afford the previously reported[7] formatoborate **2** exclusively (see Scheme 1).[11] The reaction was monitored by ^1H and ^{19}F NMR spectroscopy, and integration versus an internal standard ($C_6H_5CF_3$, 9 mM) revealed that no Et_3SiH was consumed. Thus, although the formation of **2** is reversible,[7] there does not appear to be sufficient free $B(C_6F_5)_3$ present under these conditions to activate silane for further reduction of **2**.

Accordingly, we carried out a reaction under identical conditions with an additional 1.0 equiv of $B(C_6F_5)_3$ (relative to **1**) present. This resulted in the immediate and complete conversion of **2** back into **1** at room temperature and the appearance of the products of CO_2 hydrosilylation. Further monitoring of the reaction by ^1H and ^{19}F NMR spectroscopy at 56 °C showed that silane was gradually consumed and that CH_4 along with 2 equiv of $(Et_3Si)_2O$ were formed as the ultimate reaction products. Minor amounts of bis(triethylsilyl)acetal, $(Et_3SiO)_2CH_2$, (∼10%) were also present. Interestingly, **1** and $B(C_6F_5)_3$ were the only boron-containing compounds detectable during the reaction but diminished in favor of a new species, **3**, upon complete silane consumption. At the same time, the characteristic signals of HCO_2SiEt_3, $\{Et_3SiO\}_2CH_2$, and Et_3SiOCH_3 in C_6D_5Br became evident in the ^1H NMR spectra. Upon addition of further silane equivalents and pressurization with fresh CO_2, these partially reduced intermediates were depleted and methane formation resumed, indicating a "living" catalytic system.

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Collectively, these observations suggest that the chemistry depicted in Scheme 1 is operative. Analysis of the ^{19}F NMR spectra indicated that the coordinated $B(C_6F_5)_3$ in compound **3** is labile in solution.[12] Thus, the equilibrium between **3** and **2**/$B(C_6F_5)_3$ is rapid and provides a source of free borane to activate the Et_3SiH present via **4**, as previously reported.[8] The fact that neither **3** nor **2** was detected in the reaction mixture in the presence of silane implies that B−H bond addition of **1** to CO_2 is the rate-limiting step. Consequently, the overall rate of silane consumption showed a zeroth-order concentration dependence over four half-lives (~240 min) when the reaction was monitored at 56 °C by ^{1}H NMR spectroscopy (see Figure S2 in the Supporting Information). As the silane concentration decreased, the concentration of CH_4 increased at a rate one-quarter that of silane consumption while [**1**] remained constant, as expected. Once **2** was generated, the reaction with $B(C_6F_5)_3$-activated silane **4** was rapid and eventually produced CH_4 and $(Et_3Si)_2O$ (as shown in Scheme 1) via well-documented $B(C_6F_5)_3$-mediated transformations.[13]

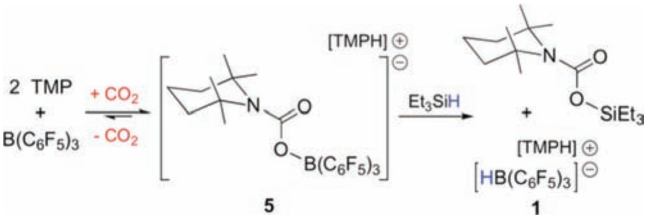
In accord with this postulate, the reaction of a 2:1 mixture of **2** and $B(C_6F_5)_3$ (in equilibrium with **3**) with Et_3SiH (1.2 equiv vs **2**) at room temperature instantly afforded $(Et_3SiO)_2CH_2$ (57%) along with starting material (42%) and trace amounts of Et_3SiOCH_3 and CH_4, suggesting that the triethylsilylformate intermediate is highly reactive toward **4**. Therefore, its production from **2** is critical. Here, the involvement of a silylium cation to react with anionic **2** greatly enhances its conversion rate in comparison with that for the reduction of **2** with further equivalents of anionic **1**.[7] In other words, silylium ion transfer to the formate moiety of **2** from **4** is Coulombically favored over hydride transfer from **1** and occurs under much milder conditions.[7] The reaction of **4** with **2** gives highly reactive HCO_2SiEt_3 but also regenerates **1** for rate-limiting activation of CO_2.

Compound **3** was generated separately by treatment of solutions of **2** with $B(C_6F_5)_3$ and was isolated by slow hexane diffusion into the reaction mixture at −30 °C. Its solid-state structure was elucidated by single-crystal X-ray diffraction, and an ORTEP diagram is shown in Figure 1 along with selected metrical data implying that the negative charge is delocalized over the bridging formate and flanking borane fragments. This compound was proposed by Ashley et al.[7] as an intermediate in the conversion of **2** to $[H_3COB(C_6F_5)_3]^-[TMPH]^+$ that accepts hydride from **1**; here it serves as a reservoir of borane catalyst for hydrosilylation of **2** and subsequent intermediates.

Figure 1. ORTEP plot for **3** (50% thermal displacement ellipsoids). Selected bond lengths (Å) and angles (deg): C1−O1, 1.256(3); C1−O2, 1.268(3); O1−B1, 1.587(3); O2−B2, 1.584(3); O1−C1−O2, 120.2(2); O1/2−C1−H, 119.9. The largest deviation from the least-squares plane through atoms B1, O1, C1, O2, and B2 is 0.015 Å for O1.

The above experiments were performed with isolated **1**, but this can be bypassed simply through the use of a 2:1 mixture of TMP/$B(C_6F_5)_3$ with CO_2 in the presence of silane (Scheme 2). In the absence of Et_3SiH, ion pair **5** was generated and could be characterized by X-ray crystallography.[11] As with other complexes of this type,[5,6] CO_2 activation is reversible, and small quantities of free borane are accessible to added silane, which rapidly converts **5** into the triethylsilyl carbamate and **1**, which in turn becomes available for catalytic reduction of CO_2 to CH_4 as in Scheme 1.

Scheme 2



In summary, ammonium borate **1** and $B(C_6F_5)_3$ act in tandem to catalytically convert CO_2 to CH_4 using triethylsilane as the reductant. The rate-limiting step involves transfer of hydride from **1** to CO_2, suggesting that a more nucleophilic hydridoborate might improve the rate of conversion. However, use of the less Lewis acidic borane $B(4\text{-}C_6F_4H)_3$[14] resulted in a kinetic profile essentially identical to that obtained for $B(C_6F_5)_3$ (Figure S3). Ongoing work will explore a range of boranes, amines, and sacrificial reductants aimed at increasing the turnover frequencies on the basis of the mechanistic details uncovered through these detailed spectroscopic studies.

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Supporting Information Available: Crystallographic data for **3** and **5** (CIF), additional experimental and spectroscopic details, and complete ref 1a. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) See the Supporting Information for experimental details.
(12) ^{19}F NMR spectra of mixtures of **2** and various amounts of $B(C_6F_5)_3$ in C_6D_5Br exhibited broad resonances consistent with the presence of **2**, **3**, and free $B(C_6F_5)_3$ in rapid equilibrium.
(13) This mechanistic scheme is similar in form to that proposed for a $Zr/B(C_6F_5)_3$-based catalytic system for the slow hydrosilation of CO_2. See: Matsuo, T.; Kawaguchi, H. *J. Am. Chem. Soc.* **2006**, *128*, 12362–12363.
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