

**CO₂ Hydrogenation Catalysis** Hot Paper

Selective Catalytic Frustrated Lewis Pair Hydrogenation of CO₂ in the Presence of Silylhalides

Tongtong Wang⁺, Maotong Xu⁺, Andrew R. Jupp, Zheng-Wang Qu,^{*} Stefan Grimme, and Douglas W. Stephan^{*}

Abstract: The frustrated Lewis pair (FLP) derived from 2,6-lutidine and B(C₆F₅)₃ is shown to mediate the catalytic hydrogenation of CO₂ using H₂ as the reductant and a silylhalide as an oxophile. The nature of the products can be controlled with the judicious selection of the silylhalide and the solvent. In this fashion, this metal-free catalysis affords avenues to the selective formation of the disilylacetal (R₃SiOCH₂OSiR₃), methoxysilane (R₃SiOCH₃), methyl iodide (CH₃I) and methane (CH₄) under mild conditions. DFT studies illuminate the complexities of the mechanism and account for the observed selectivity.

The dramatic and continuous increase in the atmospheric CO₂ level since the industrial revolution results from the extensive use of fossil fuels and is the major contributor to climate change. This has prompted the scientific community to target a variety of new technologies to reduce emissions or provide alternative energy sources as these offer the most promising avenues to address climate change. Nonetheless, other efforts targeting the capture or use of atmospheric CO₂ have also garnered attention. One potential avenue to the use of atmospheric CO₂ involves reduction via hydrogenation.^[1] For example, recent reviews have described the conversion of CO₂ to methanol using homogeneous and heterogeneous transition metal-based catalysts^[2] while other reports have demonstrated the production of longer chain fuels^[3] or olefins or higher alcohols.^[4] In addition to the above metal-catalyzed processes, there have also been extensive efforts to employ

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main group reagents to mediate CO₂ reduction processes. A number of studies^[5] have explored catalytic processes including both base-mediated and frustrated Lewis pair (FLP) hydrosilylations^[6] and hydroborations^[7] of CO₂ while others have probed aminations.^[8]

Despite the seminal finding in 2009 in which Ashley and O'Hare^[9] reported the FLP-mediated reduction of CO₂ to methanol (Scheme 1), albeit in low yield and at 160 °C for 6 days, the direct hydrogenation of CO₂ mediated by a main group species has garnered limited attention. A collaborative effort with the Fontaine group^[10] described the stoichiometric reactions of the intramolecular FLP, 1-BMe₂-2-NMe₂-C₆H₄, with H₂ and CO₂ yielding formyl, acetal and methoxy-borane derivatives (Scheme 1). This study suggested that judicious selection of the combination of the Lewis acid and the base could plausibly lead to catalytic H₂/CO₂ chemistry. More recently, Zhao et al.^[11] described the hydrogenation of CO₂ in the presence of H₂ and K₂CO₃ using B(C₆F₅)₃ as the catalyst, affording effective turn-over to K[HCO₂] at comparatively high H₂/CO₂ pressures of 60 bar (Scheme 1). While the achievement of catalytic hydrogenation is impressive, the reduction was limited to the formation of formate product.

Pondering an FLP system that would effect reduction beyond formate, we recognized that in earlier studies methanol or methane were obtained exploited hydrosilanes or hydroboranes that provide both a reducing agent and an

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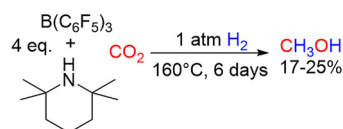
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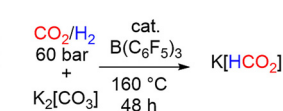
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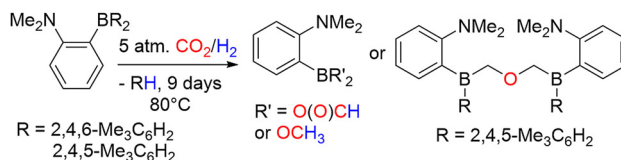
Ashley, O'Hare, 2009



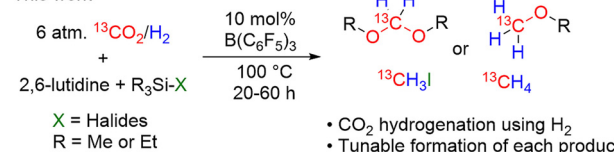
Hu, Wu, 2019



Stephan, Fontaine, 2015



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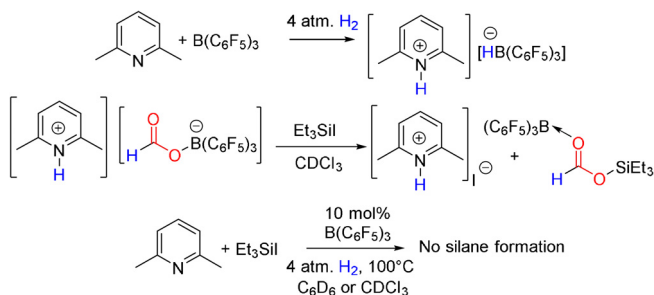
Scheme 1. Direct reactions of CO₂/H₂ mediated by main group reagents.

oxophile.^[6,7] In contrast, use of H₂ as the reducing agent in direct FLP hydrogenations of CO₂ does not provide such an oxygen-atom scavenger. Thus, we speculated that further hydrogenation of CO₂ could be effected in the presence of a silylhalide. Herein, we report the FLP-mediated catalytic hydrogenation of CO₂ using H₂ as the reducing agent performed in the presence of a silylhalide which acts as an oxophile. Judicious choices of the silylhalide and reaction solvent are shown to provide fine control over the nature of the products of catalysis.

The activation of H₂ by 2,6-lutidine/B(C₆F₅)₃ (Scheme 2)^[12] and subsequent reaction with CO₂ is known to afford the salt [C₅H₃Me₂NH][HCO₂B(C₆F₅)₃].^[13] This species was allowed to react with 1 equivalent of Et₃SiI in CDCl₃ resulting in the upfield shift of the formyl proton in the ¹H NMR from 8.31 ppm to 8.17 ppm and the appearance of a ¹¹B{¹H} NMR signal at -0.1 ppm. These data affirm the formation of B(C₆F₅)₃ adduct of silyl formate Et₃SiOC(O)H^[6c] and are consistent with the cleavage of the B–O bond in the formyl-borate salt (Scheme 2). Recognizing that the silyl formate-borane adduct will exist in an equilibrium with free borane, this implies that it should be accessible for further reaction.

We also queried the possibility of reduction of Et₃SiI in the presence of excess base. To this end, Et₃SiI and 2,6-lutidine were combined under H₂ (4 atm) in the presence of 10 mol % B(C₆F₅)₃ in either CDCl₃ or C₆D₆ and heated at 100 °C for 40 h (Scheme 2). In both cases no reduction of the silylhalide was observed. This suggested that the silylhalide could act as an oxophile in the presence of H₂, for the hydrogenation of CO₂, without the possibility of invoking a hydrosilylation mechanism.

Thus, targeting FLP hydrogenations of CO₂, reactions of 10 equivalents of Lewis base and silylhalide were performed in C₆D₆ or CDCl₃ solution of 10 mol % of B(C₆F₅)₃. In these reactions the substituted pyridines, 2,4,6-collidine and less basic 2,6-lutidine were employed and the systems were pressurized with H₂ (4 atm.) and ¹³CO₂ (2 atm.) and heated to 100 °C for up to 60 h. The reactions were monitored by ¹H NMR and ¹³C NMR spectroscopy. Initial reactions using Me₃SiCl and 2,6-lutidine in C₆D₆ or CDCl₃ (Table 1, entry 1, 2) as the solvent, afforded [C₅H₃Me₂NH][HCO₂B(C₆F₅)₃]^[13] as the major product as evidenced by the doublet resonance (¹J_{C-H} = 209 Hz) at 8.37 ppm in the ¹H NMR spectrum and the doublet resonance in the ¹H-coupled ¹³C NMR at 169.5 ppm. The generally poor reactivity in the presence of Me₃SiCl was attributed to the relatively strong Si–Cl bond and prompted



Scheme 2. Control reactions.

Table 1: CO₂ hydrogenation in the presence of silylhalides.

$$\begin{array}{c}
 {}^{13}\text{CO}_2 \text{ (2 atm)} \\
 + \text{H}_2 \text{ (4 atm)} \\
 \xrightarrow[\text{C}_6\text{D}_6 \text{ or CDCl}_3, 100^\circ\text{C}]{10 \text{ mol\% B(C}_6\text{F}_5)_3, \text{ base / R}_3\text{Si-X (1:1)}} \\
 \text{R}_3\text{Si-O-CH}_2\text{-O-SiR}_3 \quad \text{H-O-SiR}_3 \\
 \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\
 {}^{13}\text{CH}_3\text{I} \quad {}^{13}\text{CH}_4 \\
 \text{R = Me or Et; X = Br or I} \\
 + \text{base}\cdot\text{HX} + \text{R}_3\text{SiO-SiR}_3
 \end{array}$$

Ent	Solv.	Silylhalide ^[a]	base ^[a]	t [h]	Major product	Yield ^[b]
1	C ₆ D ₆	Me ₃ SiCl	Lut	20	-	< 1%
2	CDCl ₃	Me ₃ SiCl	Lut	20	-	< 1%
3	C ₆ D ₆	Me ₃ SiBr	Lut	40	MeOSiMe ₃	83%
4	CDCl ₃	Me ₃ SiBr	Lut	60	MeOSiMe ₃	73%
5	C ₆ D ₆	Me ₃ SiI	Lut	60	¹³ CH ₄	76%
6	CDCl ₃	Me ₃ SiI	Lut	20	¹³ CH ₄	85%
7	C ₆ D ₆	Et ₃ SiI	Lut	60	(Et ₃ SiO) ₂ ¹³ CH ₂	72%
8	CDCl ₃	Et ₃ SiI	Lut	40	¹³ CH ₃ I	82%
9	C ₆ D ₆	Et ₃ SiI	Col	40	(Et ₃ SiO) ₂ ¹³ CH ₂	8%
10	CDCl ₃	Et ₃ SiI	Col	40	MeOSiEt ₃	9%

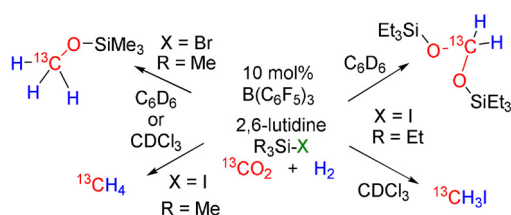
[a] 0.05 mmol silylhalide and Lewis base were added; Lut = 2,6-lutidine; Col = 2,4,6-collidine. [b] Yields are determined by ¹H NMR spectroscopy using 10 μL toluene as internal standard.

the use of 2,6-lutidine and Me₃SiBr. This led to an 83% yield of methoxysilane Me₃SiO¹³CH₃, after 40 h of heating in C₆D₆ (entry 3). In this case, the major product was identified by a ¹H NMR resonance at 3.25 ppm as a doublet (¹J_{C-H} = 141 Hz), the corresponding ¹³C{¹H} NMR signal is found at 49.9 ppm.^[6b] Repetition of the experiment in CDCl₃ also led to the selective production of Me₃SiO¹³CH₃ in 73% yield after 60 h heating (entry 4). The combination of 2,6-lutidine and Me₃SiI generated ¹³CH₄ in 76% yield after 60 h (entry 5). As these reactions were done in a sealed J-Young NMR tube, the methane was identified by ¹³C NMR spectroscopy as a pentet at -4.3 ppm (¹J_{C-H} = 126 Hz) and further confirmed by an HSQC experiment, revealing a correlation with the ¹H signal at 0.19 ppm.^[14] Further improvement in the reactivity was seen with use of CDCl₃ as the solvent as ¹³CH₄ was produced in 85% yield after 20 h at 100 °C (entry 6). Reactions with the more sterically hindered halosilane Et₃SiI afforded the acetal (Et₃SiO)₂¹³CH₂ as the dominant product in 72% yield after heating at 100 °C for 60 h (entry 7). This product exhibited a doublet at 5.06 ppm in the ¹H NMR with a ¹J_{C-H} of 162 Hz and a ¹³C{¹H} NMR signal at 84.5 ppm. Interestingly, performance of the reaction in the more polar solvent CDCl₃ (entry 8) afforded ¹³CH₃I in 82% yield as evidenced by the quartet resonance in the ¹³C NMR at -23.5 ppm with ¹J_{C-H} = 151 Hz, while the HSQC experiment revealed a correlation with the ¹H signal at 2.16 ppm.^[15] Use of the more basic 2,4,6-collidine resulted in a significant reduction in reactivity affording low yields of the acetal and methoxysilane in C₆D₆ and CDCl₃, respectively (entry 9, 10), likely due to slightly reduced reactivity for CO₂ reduction though better H₂-activation reactivity is expected.

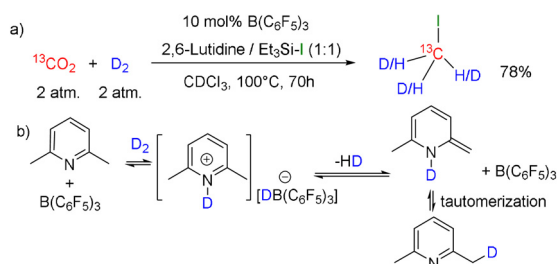
The above reactions demonstrate that simple tuning of the reaction conditions for FLP hydrogenation of CO₂ provided variation of the major products. While lutidine was identified as the preferred base in the presence of the Lewis acid catalyst B(C₆F₅)₃, the use of Me₃SiBr produced Me₃SiO¹³CH₃, whereas Me₃SiI afforded primarily ¹³CH₄ as the CO₂ reduc-

tion product. The acetal, $(\text{Et}_3\text{SiO})_2^{13}\text{CH}_2$, was formed preferentially when Et_3SiI was employed in C_6D_6 solution. Perhaps most remarkably, however was the impact of the use of Et_3SiI in CDCl_3 which resulted in the formation of $^{13}\text{CH}_3\text{I}$ as the major product (Scheme 3).^[16]

Efforts to probe the reaction affording isotopically enriched methyl iodide prompted us to monitor the reaction of $^{13}\text{CO}_2$ (2 atm) and D_2 (2 atm) in the presence of 2,6-lutidine, Et_3SiI and 10 mol% $\text{B}(\text{C}_6\text{F}_5)_3$ in CDCl_3 at 100°C . At this lower pressure and with the shorter reaction time of 24 h, the reaction was not complete. However, the NMR spectra revealed the formation of isotopologues of the acetal and methoxy species in 33% yield and 21% yield, respectively. The three isotopologues of the acetal, $(\text{Et}_3\text{SiO})_2^{13}\text{CH}_2$ and $(\text{Et}_3\text{SiO})_2^{13}\text{CHD}$ and $(\text{Et}_3\text{SiO})_2^{13}\text{CD}_2$ were formed in an approximately 1:4:1 ratio. The isotopologue $(\text{Et}_3\text{SiO})_2^{13}\text{CHD}$ exhibited a triplet in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum at 84.0 ppm ($^1J_{\text{C-D}}=25$ Hz) as well as a doublet at 5.03 ppm ($^1J_{\text{C-H}}=161$ Hz) in the ^1H NMR spectrum; while the $(\text{Et}_3\text{SiO})_2^{13}\text{CD}_2$ was found as a pentet in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum at 83.6 ppm ($^1J_{\text{C-D}}=25$ Hz). The four isotopologues of methoxy, $\text{Et}_3\text{SiO}^{13}\text{CH}_3$, $\text{Et}_3\text{SiO}^{13}\text{CH}_2\text{D}$, $\text{Et}_3\text{SiO}^{13}\text{CHD}_2$ and $\text{Et}_3\text{SiO}^{13}\text{CD}_3$ were generated in a 1:5:8:4 ratio, each of them was found in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum at 50.8 ppm, 50.5 ppm, 50.2 ppm and 49.7 ppm as singlet, triplet, pentet and septet resonance with $^1J_{\text{C-D}}=22$ Hz, respectively. In addition, the NMR data showed the formation of H_2 as a singlet at 4.63 ppm and HD as a triplet at 4.59 ppm ($J_{\text{H-D}}=43$ Hz) and a triplet at 2.39 ppm ($^2J_{\text{H-D}}=2$ Hz) adjacent the methyl resonance of 2,6-lutidine, which is corresponding to the mono-methyl-deuterated 2,6-lutidine. These data suggest that competitive to reaction with CO_2 , the product of initial activation of D_2 , $[\text{C}_5\text{H}_3\text{Me}_2\text{ND}][\text{DB}(\text{C}_6\text{F}_5)_3]$, can evolve HD, generating a transient enamine, while tautomerization regenerates lutidine leading to H/D scrambling into the methyl groups of lutidine, the generation of HD and H_2 , and the generation of the isotopologues of the CO_2 reduction products (Scheme 4). It is



Scheme 3. Summary of major products of CO_2 reduction using the FLP catalyst $\text{B}(\text{C}_6\text{F}_5)_3/2,6$ -lutidine.



Scheme 4. a) Deuteration of CO_2 b) deuteration of lutidine, mediated by $\text{B}(\text{C}_6\text{F}_5)_3$ under D_2 .

noteworthy that on prolonged reaction for 70 h, the above reaction gave 78% yield of the expected isotopologues of methyl iodide, CH_3I , CH_2DI , CD_2HI and CD_3I in a 1:5:5:4 ratio. These species are observed in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum at -23.39 ppm, -23.41 ppm, -23.44 ppm and -23.47 ppm as singlet, triplet, pentet and septet resonances, respectively. The deuterated species exhibited $^1J_{\text{C-D}}$ values of 23 Hz.

Mechanistically, the above reactivity indicates that the present hydrogenation of CO_2 begins with the known FLP activation of H_2 followed by the reaction with CO_2 affording a formyl borate anion. Reaction with the silylhalide affords the silyl-formate and frees the borane for further activation of H_2 . Hydrido-borate attack of the silyl-formate and reactions with the silylhalide affords the acetal and subsequently the methoxy-silane, although the dominance of these reactions depends on the nature of the silyl-substituent, the halide and the solvent. In a non-polar solvent, reaction of the methoxy-silane with the hydrido-borate in the presence of the silylhalide affords methane and the disilylether. In contrast, a polar solvent favors attack by iodide, affording methyl iodide as the dominant product.

This view of the reactivity was further probed by extensive DFT calculations at the dispersion-corrected PW6B95-D3/def2-QZVP + COSMO-RS// TPSS-D3/def2-TZVP + COSMO level of theory in chloroform solution,^[17] using the typical substrates of 2,6-lutidine (Lut), H_2 , CO_2 and Me_3SiI along with the Lewis-acid $\text{B}(\text{C}_6\text{F}_5)_3$ as the catalyst. The final PW6B95-D3 free energies (in kcal mol^{-1} , at 298 K and 1 M concentration) are discussed.

The activation of H_2 by the separated FLP Lut/ $\text{B}(\text{C}_6\text{F}_5)_3$ (Figure 1 A) is -10.0 kcal mol^{-1} exergonic over a low free energy barrier of 15.9 kcal mol^{-1} (via **TS1**) giving the ion pair $[\text{LutH}]^+[\text{HB}(\text{C}_6\text{F}_5)_3]^-$ (**A**). In CHCl_3 solution, the separated ions are 1.1 kcal mol^{-1} less stable at room temperature but are easily accessible and even more stable upon heating due to favorable entropic effects. In contrast, both CO_2 and Me_3SiI cannot be activated by the FLP, as the adduct $\text{LutCOOB}(\text{C}_6\text{F}_5)_3$ and the separated ions of $[\text{LutSiMe}_3]^+$ and I^- , are 11.5 and 5.1 kcal mol^{-1} endergonic, respectively (see Supporting Information). However, CO_2 is easily reduced by **A** via hydride transfer from $[\text{HB}(\text{C}_6\text{F}_5)_3]^-$ to the carbon with H-bonding of $[\text{LutH}]^+$ to oxygen and the formation of $[\text{LutH}]^+[\text{HCOOB}(\text{C}_6\text{F}_5)_3]^-$ (**B**) is -5.3 kcal mol^{-1} exergonic over a free energy barrier of only 18.9 kcal mol^{-1} (via **TS2**). Consistent with experiment, the reduction of Me_3SiI with **A** to form Me_3SiH , $[\text{LutH}]\text{I}$ and regenerated $\text{B}(\text{C}_6\text{F}_5)_3$ catalyst is 10.1 kcal mol^{-1} endergonic and thus thermodynamically prevented (see Supporting Information). On the other hand, the reaction between Me_3SiI and **B** is -1.6 kcal mol^{-1} exergonic and proceeds easily over a low barrier of 14.3 kcal mol^{-1} (via **TS3**). This affords the neutral adduct $\text{Me}_3\text{SiOCHOB}(\text{C}_6\text{F}_5)_3$ (**C**) that still requires 3.9 kcal mol^{-1} to eliminate $\text{B}(\text{C}_6\text{F}_5)_3$ and give Me_3SiOCHO (**D**). Such trapping of $\text{B}(\text{C}_6\text{F}_5)_3$ with **D** effectively increases the free energy barrier to the initial H_2 -activation to 19.8 kcal mol^{-1} (via **TS1**), which is thus the rate-limiting step for the formation of **D**. For comparison, the Lewis bases Lut, Col, Cl^- and Br^- also form stable $\text{B}(\text{C}_6\text{F}_5)_3$ adducts that are -2.0 , -4.7 , -5.7 and -1.3 kcal mol^{-1}

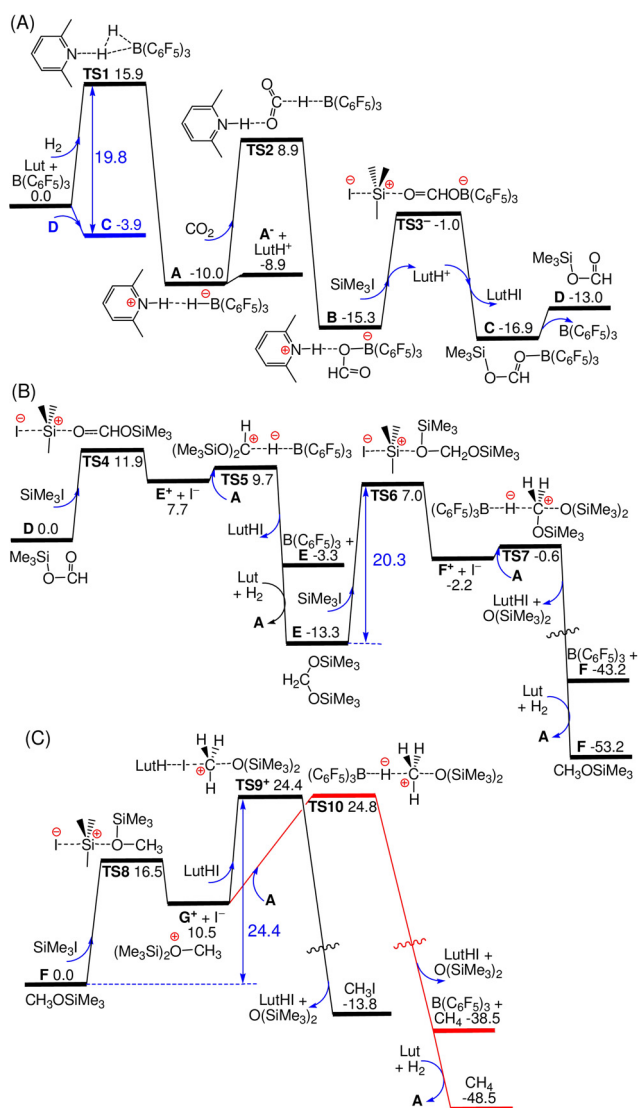


Figure 1. DFT-computed free energy paths for: A) the lutidine/ $\text{B(C}_6\text{F}_5)_3$ FLP-mediated H_2 activation and further reduction of CO_2 into HCOOSiMe_3 ; B) further reduction into $\text{H}_2\text{C(OSiMe}_3)_2$ and even $\text{H}_3\text{COSiMe}_3$; C) slower and kinetically competitive formation of CH_3I and CH_4 .

exergonic in CHCl_3 solution (see Supporting Information), respectively. The higher affinity for CoI and Cl^- may further inhibit H_2 -activation reactivity.

Once intermediate **D** is formed (Figure 1B), further reduction via silylium transfer from Me_3SiI (via **TS4**) and subsequent hydride transfer from **A** (via **TS5**) to give the acetal $\text{H}_2\text{C(OSiMe}_3)_2$ (**E**) proceeds quickly and is $-13.3 \text{ kcal mol}^{-1}$ exergonic. Further silylium transfer from Me_3SiI to **E** (via **TS6**) and subsequent hydride transfer from **A** (via **TS7**) to give $\text{H}_3\text{COSiMe}_3$ (**F**), $\text{O(SiMe}_3)_2$ and $[\text{LutH}]\text{I}$ is still possible over a slightly higher barrier of $20.3 \text{ kcal mol}^{-1}$ (via **TS6**), but is $-39.9 \text{ kcal mol}^{-1}$ exergonic. Under moderate heating, both formation of **E** and **F** should be kinetically facile. The use of bulkier silanes such as Et_3SiI may enhance the barrier to silylium transfer and thus slow formation of **F**, making selective acetal formation possible in less polar benzene solution (Table 1, entry 7).

Silylium transfer from Me_3SiI to **F** to give the cation $\text{H}_3\text{CO(SiMe}_3)_2^+$ (**G**⁺) and the I^- anion (via **TS8**, Figure 1C), is $10.5 \text{ kcal mol}^{-1}$ endergonic over a low barrier of $16.5 \text{ kcal mol}^{-1}$ and thus is kinetically feasible. Further nucleophilic iodide transfers from $[\text{LutH}]\text{I}$ to **G**⁺ to give the experimentally observed CH_3I and $\text{O(SiMe}_3)_2$ is $-24.3 \text{ kcal mol}^{-1}$ exergonic over a low barrier of $13.9 \text{ kcal mol}^{-1}$ (via **TS9**⁺). The overall formation of CH_3I from **F** is thus $-13.8 \text{ kcal mol}^{-1}$ exergonic over a sizable barrier of $24.4 \text{ kcal mol}^{-1}$, consistent with the moderate heating required experimentally. On the other hand, nucleophilic hydride transfer from **A** to **G**⁺ to give CH_4 , $\text{O(SiMe}_3)_2$ and regenerate $\text{B(C}_6\text{F}_5)_3$ is $-49.0 \text{ kcal mol}^{-1}$ exergonic over a low barrier of $14.3 \text{ kcal mol}^{-1}$ (via **TS10**). Coupled with the facile H_2 activation, the overall formation of CH_4 from **F** is thus $-53.2 \text{ kcal mol}^{-1}$ exergonic over a barrier of $24.8 \text{ kcal mol}^{-1}$. This is thermodynamically more favorable but kinetically comparable with the formation of CH_3I . Indeed, the use of Et_3SiI and Me_3SiI are found to favor iodide and hydride transfer affording CH_3I and CH_4 , respectively.

In conclusion, we have achieved metal-free catalytic hydrogenation of CO_2 using H_2 and a silylhalide as an oxophile in the presence of a FLP derived from lutidine and $\text{B(C}_6\text{F}_5)_3$. The judicious selection of the steric demands and nature of the silylhalide and the solvent provides control of these catalytic reductions affording avenues to the selective formation of the methoxysilane, $\text{Me}_3\text{SiO}^{13}\text{CH}_3$, the acetal $(\text{Et}_3\text{SiO})_2^{13}\text{CH}_2$, $^{13}\text{CH}_4$ and $^{13}\text{CH}_3\text{I}$. The complexities of the mechanisms involved have been detailed using DFT studies. We are continuing to explore the use of FLPs in reactions of interest.

Supporting Information available: Synthetic and spectral data, computational details and DFT-computed energies and Cartesian coordinates are deposited.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: acetal · CO_2 hydrogenation catalysis · frustrated Lewis pair · methane · methyl iodide

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