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

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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), methyliodide (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. For example, recent reviews have described the conversion of CO₂ to methanol using homogeneous and heterogeneous transition metal-based catalysts while other reports have demonstrated the production of longer chain fuels or olefins or higher alcohols. In addition to the above metal-catalyzed processes, there have also been extensive efforts to employ main group reagents to mediate CO₂ reduction processes. A number of studies have explored catalytic processes including both base-mediated and frustrated Lewis pair (FLP) hydroisylations and hydroborations of CO₂ while others have probed aminations.

Despite the seminal finding in 2009 in which Ashley and O'Hare 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 described the stoichiometric reactions of the intramolecular FLP, 1-BMes₂-2-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. 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 from silylhalides or hydroboranes that provide both a reducing agent and an oxophile. In this work, we describe the hydrogenation of CO₂ using a metal-free FLP to afford a variety of products under mild conditions.

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

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oxophile. 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) and subsequent reaction with CO₂ is known to afford the salt [C₂H₆NMe₂][HCO₂B(C₆F₅)₃]. 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 doublet resonance in the ¹H-coupled ¹³C NMR at 169.5 ppm. Interestingly, the presence of excess base. To this end, Et₃SiI and 2,6-lutidine were combined under H₂ (4 atm) in the presence of 100 mol% of B(C₆F₅)₃, the use of Me₃SiBr produced 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 3). In this case, the major product was identified by ¹H NMR spectroscopy as a pentet J=126 Hz) and further confirmed by an HSQC experiment, revealing a correlation with the ¹H signal at 0.19 ppm. 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 acetel (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 ¹³C{¹H} NMR signal at 84.5 ppm. The generally poor reactivity in the presence of Me₃SiCl was attributed to the relatively strong Si–Cl bond and prompted

**Table 1: CO₂ hydrogenation in the presence of silylhalides.**

| Ent. | Solv. | Silylhalide[a] | base[b] | t [h] | Major product | Yield[0] |
|------|-------|---------------|--------|-------|---------------|--------|
| 1    | C₂D₆ | Me₃SiCl      | Lut    | 20    | -             | <1%    |
| 2    | CDCl₃| Me₃SiCl      | Lut    | 20    | -             | <1%    |
| 3    | C₂D₆ | Me₃SiBr      | Lut    | 40    | MeOSiMe₃     | 83%    |
| 4    | CDCl₃| Me₃SiBr      | Lut    | 60    | MeOSiMe₃     | 73%    |
| 5    | C₂D₆ | Me₃SiI       | Lut    | 60    | ¹³CH₃        | 76%    |
| 6    | CDCl₃| Me₃SiI       | Lut    | 20    | ¹³CH₄        | 85%    |
| 7    | C₂D₆ | Et₃SiL       | Lut    | 60    | (Et₃SiO)₂¹³CH₂| 72%    |
| 8    | CDCl₃| Et₃SiL       | Lut    | 40    | ¹³CH₃J       | 82%    |
| 9    | C₂D₆ | Et₃SiL       | Col    | 40    | (Et₃SiO)₂¹³CH₂| 8%     |
| 10   | CDCl₃| Et₃SiL       | Col    | 40    | MeOSiEt₃     | 9%     |

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-

![Scheme 2. Control reactions.](image-url)
tion product. The acetal, \(\text{Et}_3\text{SiO})_2\text{CH}_3\), was formed preferentially when \(\text{Et}_3\text{SiI}\) was employed in CDCl₃ solution. Perhaps most remarkably, however, was the impact of the use of \(\text{Et}_3\text{SiI}\) in CDCl₃ which resulted in the formation of \(^{13}\text{CH}_1\) as the major product (Scheme 3).[10]

Efforts to probe the reaction affording isotopically enriched methyl iodide prompted us to monitor the reaction of \(^{13}\text{CO}_2\) (2 atm) and \(\text{D}_2\) (2 atm) in the presence of 2.6-lutidine, \(\text{Et}_3\text{SiI}\) and 10 mol % \(\text{B(C}_6\text{F}_5)_3\) in CDCl₃ 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, \((\text{Et}_3\text{SiO})_2^{13}\text{CH}_3\) and \((\text{Et}_3\text{SiO})_2^{13}\text{CHD}\) and \((\text{Et}_3\text{SiO})_2^{13}\text{CD}_3\) 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, 50.8 ppm, 50.5 ppm, 50.2 ppm and 49.7 ppm as singlet, triplet, pentet and septet resonances, respectively. The deuterated species exhibited \(J_{\text{C–D}}\) values of 23 Hz.

Mechanistically, the above reactivity indicates that the current hydrogenation of \(\text{CO}_2\) begins with the known FLP activation of \(\text{H}_2\) followed by the reaction with \(\text{CO}_2\) affording a formyl borane anion. Reaction with the silylhalide affords the silyl-formate and frees the borane for further activation of \(\text{H}_2\). Hydroid-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 methyloxysilane with the hydroxido-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), \(\text{H}_2\), \(\text{CO}_2\) and \(\text{Me}_3\text{SiI}\) along with the Lewis-acid \(\text{B(C}_6\text{F}_5)_3\) as the catalyst. The final PWB6B95-D3 free energies (in kcal/mol), at 298 K and 1 M concentration) are discussed.

The activation of \(\text{H}_2\) by the separated FLP \(\text{Lut}/\text{B(C}_6\text{F}_5)_3\) (Figure 1A) is −10.0 kcal/mol exergonic over a low free energy barrier of 15.9 kcal/mol (via TS1) giving the ion pair \([\text{LutH}]^+\text{[HB(C}_6\text{F}_5)_3]^-\) (A). In CHCl₃ solution, the separated ions are 1.1 kcal/mol less stable at room temperature but are easily accessible and even more stable upon heating due to favorable entropic effects. In contrast, both \(\text{CO}_2\) and \(\text{Me}_3\text{SiI}\) cannot be activated by the FLP, as the adduct \(\text{LutCOOB-(C}_6\text{F}_5)_3\) and the separated ions of \([\text{LutSiMe}_3]^+\) and \(\Gamma^-\), are 11.5 and 5.1 kcal/mol endergonic, respectively (see Supporting Information). However, \(\text{CO}_2\) is easily reduced by A via hydride transfer from \([\text{HB(C}_6\text{F}_5)_3]^-\) to the carbon with H-bonding of \([\text{LutH}]^-\) to oxygen and the formation of \([\text{LutH}]^-\cdot[\text{HCOOB(C}_6\text{F}_5)_3]^-\) (B) is −5.3 kcal/mol exergonic over a free energy barrier of only 18.9 kcal/mol (via TS2). Consistent with experiment, the reduction of \(\text{Me}_3\text{SiI}\) with A form \(\text{Me}_3\text{SiH}, \text{[LutH]}\) and regenerated \(\text{B(C}_6\text{F}_5)_3\) catalyst is 10.1 kcal/mol endergonic and thus thermodynamically prevented (see Supporting Information). On the other hand, the reaction between \(\text{Me}_3\text{SiI}\) and B is −1.6 kcal/mol exergonic and proceeds easily over a low barrier of 14.3 kcal/mol (via TS3). This affords the neutral adduct \(\text{Me}_3\text{SiOCHO(B(C}_6\text{F}_5)_3\text{)}\) (C) that still requires 3.9 kcal/mol to eliminate \(\text{B(C}_6\text{F}_5)_3\) and give \(\text{Me}_3\text{SiOCHO(B(C}_6\text{F}_5)_3\text{)}\). Such trapping of \(\text{B(C}_6\text{F}_5)_3\) with D effectively increases the free energy barrier to the initial \(\text{H}_2\)-activation to 19.8 kcal/mol (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 \(\text{B(C}_6\text{F}_5)_3\) adducts that are −2.0, −4.7, −5.7 and −1.3 kcal/mol.
Silylium transfer from MeSiI to F to give the cation H$_3$CO(SiMe$_3$)$_2^+$ (G$^+$) and the I$^-$ anion (via TS8, Figure 1 C), is 10.5 kJ mol$^{-1}$ endergonic over a low barrier of 16.5 kJ mol$^{-1}$ and thus is kinetically feasible. Further nucleophilic iodide transfers from [LutH]I to G$^+$ to give the experimentally observed CH$_3$I and O(SiMe$_3$)$_2$ is $-$24.3 kJ mol$^{-1}$ exergonic over a low barrier of 13.9 kJ mol$^{-1}$ (via TS9$^+$. The overall formation of CH$_3$I from F is thus $-$13.8 kJ mol$^{-1}$ exergonic over a sizable barrier of 24.4 kJ mol$^{-1}$, consistent with the moderate heating required experimentally. On the other hand, nucleophilic hydride transfer from A to G$^+$ to give CH$_4$, O(SiMe$_3$)$_2$ and [LutH]I is still possible over a slightly higher barrier of 20.3 kJ mol$^{-1}$ (via TS6$^+$), but is $-$39.9 kJ mol$^{-1}$ exergonic. Under moderate heating, both formation of E and F should be kinetically facile. The use of bulkier silanes such as Et$_3$SiI 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).

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 B(C$_6$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, Me$_3$SiOCH$_3$, the acetal (Et$_3$SiO)$_2$CH$_2$, CH$_4$ and CH$_3$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.

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