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General concerns regarding global warming, climate changes, and the need for renewable fuels have prompted researchers from around the world to target methodologies to utilize CO₂ as a C₁ source. Transition metal catalysts have been discovered that can hydrogenate, hydrosilylate, or hydroborate CO₂ to formic acid, methanol, methane, CO and methoxide derivatives. An alternative strategy for the reduction of CO₂ which is gaining attention is based on non-metal catalysts. While strong Lewis bases can reduce CO₂ to give methanol, the use of C₂-containing Lewis bases can generate formaldehyde as intermediates. The mechanism of CO₂ reduction is considered.

Although hydroboration and hydrosilylation of CO₂ to methanol are academically interesting, only the hydrogenation of CO₂ could be industrially viable. Ashley and O’Hare have reported the only metal-free system in which CO₂ is hydrogenated. Employing the FLP catalyst, the hydroboration of CO₂ was generated as a C1 free system.

In our hands, the proximity of the Lewis acid and base reduces the entropic barrier, catalyzing the hydrogenation of CO₂ affording mixtures of HCO₂(BC₆H₄), H₂OCOB(C₆H₄), and MeOB(C₆H₄).

Stephan and coworkers have also reported the catalytic reduction of CO₂ using phosphine/CH₃B to give formyl, acetal and methoxy-derivatives. Since then, various workers have employed FLPs for the capture and the reduction of CO₂. Since the original report by Stephan and co-workers on the capture of CO₂ by FLPs, a number of inter- or intramolecular FLP variants have been employed to sequester CO₂ and many of these has been reviewed. Beyond capture, FLP mediated CO₂ reductions have been probed. The reaction of Al/P FLPs with CO₂ and ammonia-borane was shown to give methanol, while an alternative reaction pathway affords CO. In a related study, Piers and coworkers used Et₃SiH as a reductant to catalytically generate CH₄ and (Et₃Si)₂O. While Stephan and coworkers have also reported the catalytic reduction of CO₂ using phosphate/CH₃B and ZnBr₂ to give CO and phosphate oxide, FLPs and coworkers described one of the most efficient systems to date for the reduction of CO₂ using ambiphilic FLP Ph₂PC(H)B(O₂C₆H₄)₄, generating methoxyboranes with TOF exceeding 900 h⁻¹ at 70 °C. In related work, Stephan and co-workers have also described the use of C₂H₂(NPR₂)₂BC₆H₄I₃ and phosphinates to catalyze the hydorboration of CO₂ affording mixtures of HCO₂(BC₆H₄), H₂OCOB(C₆H₄), and MeOB(C₆H₄).
The reactivity of these bright green compounds with both $H_2$ and $CO_2$ was investigated. When a benzene-$d_4$ solution of 1 was exposed to either 1 atm of $CO_2$ or 4 atm of $H_2$, no change was evidenced by $^1H$ NMR spectroscopy. However, heating for 24 h a solution of 1 at 80°C under 1 atm of HD led to isotopic scrambling as evidenced by the observation of $H_2$ and HD by $^1H$ NMR spectroscopy. In addition, new signals at 6.72 and 2.16 ppm were observed and assigned to free mesitylene, suggesting that protodeborylation occurred after the activation of $H_2$. Indeed, protodeborylation reactions have been shown to occur before in related systems. Monitoring of this protodeborylation with the use of cyclohexane as an internal standard, revealed that 1 releases both of its mesityl groups after 72 hours at 80 °C affording (1-BH$_2$-2-NMe$_2$-C$_6$H$_3$)$_2$ (3). The nature of the aryl group impacts the facility of protodeborylation as the species 2, with one less methyl in ortho position than 1, was converted to 3 after 72 hours at room temperature or after 6 hours at 80°C. Compound 3 was prepared on a larger scale from 1 at 80 °C under 4 atm of $H_2$ for 48 hours and was ultimately isolated in 54% yield. The broad signal at 3.55 ppm in the $^1H$ NMR spectrum was attributed to B-H protons, which became sharper with $^{11B}$ decoupling. The presence of the B-H bonds was further confirmed by the broad $^{11B}$ NMR signal at 2.5 ppm. The HRMS data suggest that compound 3 is dimeric (m/z: 265 = [M-H]), which is further supported by the observation of inequivalent methyl groups on nitrogen (see ESI). This view was further supported by computational studies, in which a number of isomeric forms of 3 were considered and where the dimeric form which adopts a “boat” shaped 8-membered ring was computed to be 9.2 kcal.mol$^{-1}$ more stable than the monomeric form (Scheme 2). It is noteworthy that Repo and coworkers have recently described 1-BH$_2$-2-TMP-C$_6$H$_3$, which is also a dimer; however in this case, structural characterization confirmed that the steric congestion favors dimerization via the B–H bonds.

Scheme 2: DFT study of isomers 3. Level of theory (ωB97XD/6-31++G**, solvent=benzene, SMD). ΔG (ΔH) are reported in kcal.mol$^{-1}$.

DFT calculations were also employed to shed light on the mechanism of this transformation (Scheme 3). The activation of $H_2$ by 1 or 2 proceeds through TS1 to generate $A'$ and $A''$, respectively, in a slightly endothermic process. Subsequent protodeborylation can occur through TS2, eliminating the B-bound aryl substituent to give the ambiphilic hydroboranes $B'$ and $B''$, respectively. Further activation of $H_2$ via TS3 to give $C'$ and $C''$, prompts a second protodeborylation reaction pathway via TS4 affording the primary amino-borane product 3. While the computed energies for these reactions of 1 and 2 follow the same trends, the reduced steric demands of 2 leads to significant lowering of the activation barriers.

Scheme 3: DFT study of $H_2$ activation and protodeborylation at the (ωB97XD/6-31++G**, solvent=benzene, SMD) level of theory. ΔG (ΔH) are reported in kcal.mol$^{-1}$, X’ refers to R = 2,4,6-Me$_3$C$_6$H$_2$, X” refers to 2,4,5-Me$_2$C$_6$H$_3$.

Table 1: Hydrogenation of carbon dioxide by 1 and 2.

<table>
<thead>
<tr>
<th>FLP $CO_2$ (atm)</th>
<th>T (h)</th>
<th>$H_2$ (atm)</th>
<th>COO</th>
<th>HCOO</th>
<th>CH$_3$</th>
<th>H$_2$ consumed</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 $^1$</td>
<td>1</td>
<td>216</td>
<td>80</td>
<td>0.89</td>
<td>0.31</td>
<td>0</td>
</tr>
<tr>
<td>2 $^1$</td>
<td>0.5</td>
<td>216</td>
<td>80</td>
<td>0.84</td>
<td>0.34</td>
<td>0.1</td>
</tr>
<tr>
<td>3 $^1$</td>
<td>0.1</td>
<td>216</td>
<td>80</td>
<td>0</td>
<td>0.08</td>
<td>0.25</td>
</tr>
<tr>
<td>4 $^1$</td>
<td>1</td>
<td>24</td>
<td>130</td>
<td>0.75</td>
<td>0.21</td>
<td>0.07</td>
</tr>
<tr>
<td>5 $^2$</td>
<td>1</td>
<td>72</td>
<td>23</td>
<td>0</td>
<td>0.37</td>
<td>0.03</td>
</tr>
<tr>
<td>6 $^2$</td>
<td>1</td>
<td>3</td>
<td>80</td>
<td>0.21</td>
<td>0.30</td>
<td>0</td>
</tr>
</tbody>
</table>

Conditions: 0.014 mmol 1 or 2, 0.4 mL C$_6$D$_6$, 4 atm $H_2$. Yields were determined by NMR integration with respect to an internal standard (cyclohexane). a. Equivalents of the indicated hydrogenation moiety relative to the amount of starting aminoborane. b. A white precipitate crashed out of the solution so 0.1 mL of CD$_3$CN was added before taking the spectra. c. Reaction was carried out in bromobenzene-$d_4$. d. Reaction was carried out under 1 atm of $H_2$. Compound 4 was exclusively formed. The hydrogenation of $CO_2$ with 1 and 2 was investigated and in general was found to produce several boron bound formates, acetals and methoxides (Table 1). Heating a benzene-$d_4$ solution of 1 to 80 °C for 24 hours under 4 atm of $H_2$ and 1 atm of $^{13}CO_2$, resulted in the appearance of doublets arising from the coupling with the $^{13}C$ atom of the formate (HCOO at ca. 8.5 ppm ($J_{CO}$ ~ 210 Hz)) and acetals (ca. 5.2 ppm ($J_{CO}$ ~ 165 Hz)). It was
found that CO₂ was transformed into 0.89 equivalents of boron bound formates relative to the amount of 1 at the start of the reaction, and 0.31 equivalents of boron bound acetals. Repeating the experiment with a reduced CO₂ pressure (0.5 atm) led to similar conversions to formates and acetals, but in addition 0.1 equivalent boron bound methoxides were formed (ca. 3.5 ppm, J_HH ≈ 140 Hz). Further reduction of the CO₂ pressure to 0.1 atm resulted in the formation of methoxides and traces of ¹⁵H₂C≡CH. An experiment under 1 atm of CO₂ and 4 atm H₂ in bromobenzene δ₁ fitted 0.75, 0.21 and 0.07 equivalents of formate, acetel and methoxide species respectively after only 24 hours at 130°C. In contrast, 3 did not react in the presence of H₂ and CO₂, even after prolonged heating at 80°C. This lack of reactivity is consistent with its dimeric nature that provides a stabilization of 13.4 kcal mol⁻¹.

Figure 1: ORTEP depiction of 4, 50% thermal ellipsoids are shown, N: blue, C: carbon, O: red, B: orange. H-atoms are omitted for clarity.

Interestingly, the analogous reactions of 2 gave a single acetal species after 72 hours at room temperature in the presence of 1 atm H₂ and 1 atm CO₂ as evidenced by ¹H NMR spectroscopy. On the other hand, higher temperature gave some additional formate species. When carried out on a larger scale, product 4 was isolated in 60% yield. The NMR data and the crystallographic structure (Figure 1) supported the formulation of 4 as (C₆H₅(NMe₂)(B(2,4,6-Me₃C₆H₃))O)₂CH₃. Based on these observations, the first protodeborylation step is believed to be required prior to CO₂ reduction while complete protodeborylation inhibits the reduction processes due to dimerization of 3.

The initial steps in reaction of 1 and 2 with H₂/CO₂ were probed using DFT computations. The reactions of the products of H₂ activation A-C (Scheme 3) with CO₂ were considered. The barriers to reduce CO₂ with A and B were computed to range between 27.2 and 34.7 kcal mol⁻¹ whereas the transition state with C was found to be only 24.4 kcal mol⁻¹ for R = 2,4,6-Me₃C₆H₂ and 22.1 kcal mol⁻¹ for R = 2,4,5-Me₂C₆H₁. The transition state of interest (Figure 2) illustrates a concerted interaction of the proton on N with one of the O of CO₂ with the simultaneous interaction of the boron-bound hydride with the C atom, thus directing the hydride delivery to the carbon atom. This TS is reminiscent of that proposed for the bifunctional Noyori-type catalysts for metal-based ketone reduction and a similar transition state was proposed by Musgrave, Zhang and Zimmerman²¹ for CO₂ reduction using ammonia borane as a model reductant.²² Subsequent reductions of formic acid are thought to proceed either via similar hydride delivery to formate or by simple hydroboration, generating acetal derivatives. It is also interesting that the minor variation in the steric demands of the substituent on B provide a mixture of reduction products in the case of reactions of 1 yet allow the isolation of 4 at room temperature in the reaction of 2.

Figure 2: Geometry of TS for reaction of C with CO₂ as calculated by ωB97X-D/6-31+G** level of theory; (solvent = benzene, SMD).

While previous reports have described conceptually important metal-free catalytic hydrosilylation or hydroboronation of CO₂, the present report is a rare example of direct FLP hydrogenation of CO₂ as only the earlier report by O'Hare and Ashley³⁰ described the use of H₂ in the metal-free reduction of CO₂. Nonetheless, the present intramolecular FLPs effect this reduction under much milder conditions (ambient temperature).

Conclusions

The reactions of the present N/B intramolecular FLPs with H₂ demonstrate a rare case where weakly Lewis acidic boron centres participate in H₂ activation. Such systems offer an increased facility for hydride delivery and thus provide an avenue to CO₂ reduction. Moreover, the reaction with CO₂ was facilitated by the concurrent interaction of NH and BH₄⁻ fragments with CO₂ affording formate, acetel and methoxide derivatives. While the present systems are generated by protodeborylation, the reactivity suggests that judicious substituent selection could provide an avenue to the design of intramolecular FLPs catalysts for H₂/CO₂ chemistry. Efforts towards such metal-free catalysts for CO₂ hydrogenation are the subject of current work in our laboratories.

Acknowledgements

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Notes and references

Crystallographic data have been deposited in the CCDC; CCDC #: 1059372. Spectral and computational data have been deposited in the supplementary data.


20. B could not be isolated as the second H2 activation/protodeborylation events are faster than the first. Nonetheless, B was intercepted by reacting 1 with H2 and benzaldehyde to give a borinic ester.
