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Phosphine is shown to catalyse the reaction of CO$_2$ with 9-BBN to give mixtures of HCO$_2$(OBpin)$_2$, H$_2$C(OBpin)$_2$, MeOBpin, and MeOB(C$_8$H$_4$)$_2$ at 97% yield at 60 °C with TON of almost 5500 and a TOF of 170. Under stoichiometric conditions the species (R$_2$PCH$_2$O)(HC(O)O)B(C$_8$H$_4$)$_2$ (R = tBu, 4-MeC$_6$H$_4$$_2$) were isolated and characterized.

Prompted by concerns over global warming, climate changes and the need for renewable fuels, numerous research groups have undertaken efforts seeking to develop highly efficient methodologies to utilize CO$_2$ as a C1 source for organic synthesis. To this end, a number of transition metal catalysts have been developed which effect the reduction of CO$_2$ to formic acid and methanol, the hydroisilylation of CO$_2$ to formic acid, and methanol and methane, and the reduction of CO$_2$ with borane reagents into CO and methoxide. Sabo-Etienne and co-workers provided an interesting example of the reduction of CO$_2$ by [RuH$_2$(H)$_2$(PC$_3$)$_2$] and pinacolborane (HBpin) generating the formic acid ester, CH$_2$(OBpin)$_2$, and the methoxide MeOBpin. More recently, our group demonstrated a related CO$_2$ reduction with HBpin, catecholborane (HBCat) or 9-borabicyclo[3.3.1]nonane (9-BBN) to generate methoxyboranes using a Ru-tris(aminophosphine) catalyst. Shintani and Nazaki have reported the copper-catalyzed hydroboration of CO$_2$ with HBpin yielding formic acid ester.

While these strategies for CO$_2$ reduction exploit transition metal based catalysts, non-metal catalysts have also been developed. For example, N-Heterocyclic carbene (NHC) have also been exploited for reduction of CO$_2$. In addition, frustrated Lewis pairs (FLPs) have been utilized to activate and reduce CO$_2$. Piers and co-workers used B(C$_6$F$_5$)$_3$ and amines to transform CO$_2$ to methane with silanes. We have reported use of Zn(II) and in situ generated carbodiphosphines to reduce CO$_2$ to CO. The Berke group used Re-H and B(C$_6$F$_5$)$_3$ as FLPs in the hydrogenation of CO$_2$ into formate. In recent efforts, Fontaine and coworkers have demonstrated the catalytic activity of R$_2$PC$_6$H$_4$B(O$_2$C$_4$H$_4$)$_2$ in the hydrogenation of CO$_2$ to methoxyborane, ultimately generating methanol on hydrolysis. Recently, we reported the N,N'-diphosphanyl-imidazol-2-ylidene (NHC-P) ring expansion with 9-BBN to intramolecular FLPs which catalyze the hydroboration of CO$_2$ to methoxyborane. In the present report, we demonstrate that an intermolecular FLP approach is also effective as catalytic amounts of phosphines in the presence of 9-BBN effect the reduction of CO$_2$, in one case achieving TON of over 5500.

The combination of tBuP and 9-BBN in bromobenzene-d$_5$ under $^{13}$CO$_2$(5 atm) at 25°C for 6 hours, resulted in the formation of new products as evidenced by $^1$H NMR spectroscopy. Two doublets appeared at 8.74 ppm ($^1$J$_{C-H} = 208$ Hz), 5.46 ppm ($^1$J$_{C-H} = 165$ Hz) and one doublet of doublets appeared at 4.32 ppm ($^1$J$_{C-H} = 208$ Hz, $^3$J$_{C-C} = 145$ Hz) in the $^1$H NMR spectrum. In the case of Cy$_3$P and the methoxide MeOBpin$_n$. These assignments were further confirmed by the corresponding $^{13}$C NMR signals at 169.1 ppm (d, $^1$J$_{C-H} = 208$ Hz) and 85.44 ppm (t, $^1$J$_{C-H} = 165$ Hz). A peak at 52.45 ppm (t, $^1$J$_{C-P} = 145$ Hz) in the $^{13}$C NMR spectrum also gave rise to the corresponding doublet at 43.3 ppm on $^{13}$P ($^1$H) NMR spectrum were assigned to an tBuP$_n$CH$_2$OBr$_3$ fragment.

The analogous stoichiometric reactions of other phosphines with CO$_2$ and 9-BBN afforded similar products (see supplementary data) as evidenced by $^1$H, $^{31}$P and $^{13}$C NMR spectra. In the case of Ph$_3$P, the product proved difficult to isolate. In the case of the corresponding mixture of Cy$_3$P, 9-BBN and $^{13}$CO$_2$, the phosphine-borane adduct (Cy$_3$P)$_9$-BBN was observed as the predominant species in solution as evidenced by the $^{31}$P and $^{13}$B NMR spectra, although trace amount of [Cy$_3$P($^{13}$CH$_2$OBr)$_3$] and HCOOB Br$_2$ were observed (see supplementary data). This is consistent with the lesser steric demands and stronger basicity. The corresponding reaction of (4-MeC$_6$H$_4$)$_3$P with 9-BBN and $^{13}$CO$_2$ afforded isolation.
of ((4-MeC₆H₄)₃PCH₂O)(HC(O)O)B(C₆H₄)₂, 2 (Scheme 1, Figure 1 (b)), which was spectroscopically similar to 1.

Crystals of a product 1 and 2 were obtained from stoichiometric reaction of phosphine and 9-BBN (HBC₆H₄) under ¹³CO₂ in bromobenzene-d₄ layered with hexanes. X-ray study of these crystals confirmed the formulations as (Rᵥ₃PCH₂O)(HC(O)O)B(C₆H₄)₂ (R = tBu 1, 4-MeC₆H₄ 2) (Figure 1), in which CO₂ is incorporated both as a formate and in the phosphonium methoxy-fragment. These zwitterions incorporate phosphonium fragments linked via a CH₂ linker to the borate center. The four coordinate B atoms in each case are also coordinated to a formate anion. The B-O bond distances ranging from 1.499 (2) to 1.568 (3) Å. The remaining metric parameters are unexceptional.

![POV-ray depiction of (a) 1, (b) 2](image)

**Scheme 1. Isolation of 1 and 2.**

As the formation of these products illustrates the stoichiometric reduction of CO₂, we probed the reactions under catalytic conditions. Thus, 4 mol% of tBu₃P and 9-BBN (0.094 mmol) were combined with excess ¹³CO₂ at room temperature (Table 1, entry 2). After 16 h, the CO₂-reduction products include boron-bound formate species, HCO₂(B(C₆H₄)₂) 3, the diolate-linked compound H₂C(OB(C₆H₄)₂)₄ 4 and methoxide product MeOB(C₆H₄)₃ 5 fragments in the ratio of 3: 4: 5 of 36: 15: 49 (Table 1, entry 2). The formate product 3 was evident from the ¹H NMR doublet at 8.91 ppm (Jₐ, H = 199.7 Hz) and the ¹³C NMR doublet at 166.9 ppm (J₁₃C H = 200 Hz). The diolate derivative spectrum and a triplet at 85.44 ppm (J₁₃C H = 165 Hz) in ¹³C NMR spectrum. The boron-methoxide exhibited a doublet at 3.57 ppm (J₁₃C H = 143 Hz) in ¹H NMR spectrum and a quartet at 52.69 ppm (J₁₃C H = 143 Hz) in ¹³C NMR spectrum consistent with the formulation as 5. The electron deficient or sterically encumbered phosphines (C₆F₃)₃P, (2,4,6-Me₃C₆H₂)₂P and (2-MeC₆H₃)₂P showed no reactivity even at 60 °C. Employing 4 mol% Ph₃P, (4-MeC₆H₄)₂P and (3,5-Me₂C₆H₃)₂P were also effective in reduction of CO₂ producing mixtures of 3-5 (Table 1, Entry 3-5). Lowering the concentration of catalysts to 1-2 mol% increases the proportion of 5 in the products (Table 1, entry 6-8). In the case of tBu₃P lowering the concentration of tBu₃P to 0.2 and 0.02 mol% results in even higher production of 5 (Table 1, entry 9, 10); in the latter case 98% of the borane was converted to 5 with a minor amount of 4 (2%) after 31.5 h at 60 °C. This corresponds to a TON of 5556 and a TOF of 176.

**Table 1 Product Ratios for Reduction of CO₂ with 9-BBN catalyzed by Phosphines**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Phosphines</th>
<th>Conc mol%</th>
<th>t/T h°C</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>No catalyst</td>
<td>-</td>
<td>19/25</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>tBu₃P</td>
<td>4</td>
<td>16/25</td>
<td>36</td>
<td>15</td>
<td>49</td>
</tr>
<tr>
<td>3</td>
<td>Ph₃P</td>
<td>4</td>
<td>19/25</td>
<td>60</td>
<td>36</td>
<td>4</td>
</tr>
<tr>
<td>4</td>
<td>(4-MeC₆H₄)₂P</td>
<td>4</td>
<td>15/25</td>
<td>28</td>
<td>34</td>
<td>38</td>
</tr>
<tr>
<td>5</td>
<td>(3,5-Me₂C₆H₃)₂P</td>
<td>4</td>
<td>30/25</td>
<td>7</td>
<td>30</td>
<td>63</td>
</tr>
<tr>
<td>6</td>
<td>(4-MeC₆H₄)₂P&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1</td>
<td>20/25</td>
<td>8</td>
<td>41</td>
<td>51</td>
</tr>
<tr>
<td>7</td>
<td>Ph₃P&lt;sup&gt;b&lt;/sup&gt;</td>
<td>2</td>
<td>13/25</td>
<td>19</td>
<td>24</td>
<td>57</td>
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<tr>
<td>8</td>
<td>tBu₃P&lt;sup&gt;b&lt;/sup&gt;</td>
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<td>16/25</td>
<td>3</td>
<td>29</td>
<td>68</td>
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<tr>
<td>9</td>
<td>tBu₃P&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.02</td>
<td>32/60</td>
<td>0</td>
<td>2</td>
<td>98</td>
</tr>
</tbody>
</table>

<sup>a</sup> bromobenzene; ¹³CO₂: 5 atm; all 9-BBN dimer (0.094 mmol) was consumed; ratios based on integration of resonances in H NMR spectra using the protonated solvent as the internal standard; <sup>b</sup> 9-BBN dimer (0.410 mmol) was consumed.

The consumption of borane in these reactions was monitored in the reactions using 1.0 mol% tBu₃P, 1.0 mol% Ph₃P and 1.0 mol% (p-MeC₆H₄)₂P as the catalyst. These reactions were complete in 13, 20 and 30 h, respectively (Figure 2).

In the latter two cases, an induction period was observed. In these cases, doubling the phosphine concentration halved the observed induction period. This is consistent with the slow formation of a phosphine derivative which is subsequently and sequentially reduced to give 3, 4 and 5. In addition it suggests that as the concentration of the reduction product increase the reaction accelerates. This view is consistent with the observation of only traces of 3 during these induction periods. These data support a mechanism in which initial FLP-like binding of CO₂ takes place and is subsequently reduced (Scheme 2). The slow binding of CO₂ by the arylyphosphines is consistent with the reduced steric demands.
prompting an equilibrium involving the classical Lewis P/B adduct. In the case of bBu3P, steric demands preclude such adduct formation. In addition, the weaker basicity of the aryl-phosphines presumably slows nucleophilic attack of CO2. The species 1 or 2 are generated in the reaction under stoichiometric conditions inferring that further reaction with borane effects the conversion to 4 and 5. Indeed reaction of isolated 1 with 9-BBN at room temperature gave 4 and 5 in 10 min.

Further monitoring of these reductions revealed the presence of two transient species with phosphine adjacent a methylene fragment. In the case of the bBu3P reaction, this was evidenced by signals at 42.4 ppm (d, 1JCP = 54 Hz) and 41.6 ppm (d, 1JCP = 51 Hz) in 31P NMR spectrum and 54.9 ppm (d, 1JCP = 54 Hz) and 55.0 ppm (d, 1JCP = 51 Hz) in 13C{1H} NMR spectrum. These species are attributed to the intermediate reductions species (Scheme 2).

**Scheme 2.** Proposed mechanism for phosphine catalysed CO2-reduction with 9-BBN.

**Conclusions**

In conclusion, herein we have described a facile approach to the metal-free catalytic reductions of CO2 in the presence of 9-BBN. These reactions proceed via an FLP-type CO2 activation intermediate. Subsequent reaction with borane effects sequential reduction ultimately yielding the boron-methoxide. In the best case described herein, the catalyst bBu3P gives rise to 5500 turnovers of hydride transfers to CO2. Further studies of FLP systems for CO2 reductions are the subject of continuing study in our laboratories.

**Notes and references**

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