

## Unexpected CO<sub>2</sub> Splitting Reactions To Form CO with *N*-Heterocyclic Carbenes as Organocatalysts and Aromatic Aldehydes as Oxygen Acceptors

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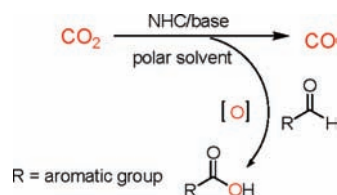
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Carbon dioxide, as the main cause of global warming, attracts much attention around the world. The anthropogenic source of atmospheric carbon dioxide is mainly from the burning of fossil fuel (>60%).<sup>1</sup> An important pathway to cut global carbon dioxide emission is its reduction to carbon monoxide.<sup>2</sup> Carbon monoxide could easily convert water to hydrogen via the industrial well-established “water gas shift reaction”.<sup>3</sup> Carbon dioxide may thus be utilized as a “green” renewable source for making fuel and chemically reduced to carbon monoxide in an economical way.<sup>4</sup>

Due to the high stability of carbon dioxide, to split the O=C(O) bond and generate carbon monoxide requires large energy input.<sup>5</sup> The current carbon dioxide splitting methods could be classified into four categories: (1) Enzyme carbon monoxide dehydrogenase/acetyl-CoA synthase (CODH/ACS);<sup>6</sup> (2) Photoreduction;<sup>7</sup> (3) Electrochemical reduction;<sup>8</sup> (4) Use of metal complexes or metal oxides to abstract the oxygen from carbon dioxide to form carbon monoxide in low turnover.<sup>9</sup> Recently, Sadighi group developed organocopper(I) complexes supported by *N*-heterocyclic carbene (NHC) ligands in the reduction of carbon dioxide to carbon monoxide with diboron reagent.<sup>10</sup> Metals play an important role in all of these catalytic systems. But reduction of carbon dioxide with organocatalysts remained widely undeveloped until our group reported the first hydrosilylation of carbon dioxide using NHC catalyst<sup>11–13</sup> under mild conditions recently.<sup>14</sup> In our efforts to look for cheaper and more accessible reductants for CO<sub>2</sub> reduction, the new reaction for carbon dioxide splitting into carbon monoxide with aromatic aldehydes as oxygen acceptors was successfully developed (Scheme 1). To our best knowledge, this is the first case in the reduction of carbon dioxide to form carbon monoxide using organocatalysts.

Initially, the reaction between cinnamaldehyde and imidazolium-carboxylate (Imes-CO<sub>2</sub>) was investigated, and carbonate and/or anhydrate were expected as products. Carbon dioxide (1 atm, in balloon) was firstly introduced into 1,3-dimesitylimidazol-2-ylidene (IMes) (0.05 mmol in 1 mL of DMF) to generate carboxylate (IMes-CO<sub>2</sub>)<sup>12</sup> and followed by the addition of cinnamaldehyde (0.5 mmol) at room temperature. However, the expected products were not obtained, and instead, four different products were observed. Saturated acid and lactone dimer were generated respectively from the internal redox reaction,<sup>15</sup> and dimerization<sup>16</sup> of cinnamaldehyde occurred as reported in literatures. The presence of novel oxidized product **2a** revealed the existence of oxidant, and carbon dioxide seemed the only possible oxidant in the reaction mixture.<sup>17,18</sup> To prove the role of NHC and carbon dioxide, several control reactions were performed. Without carbon dioxide, strong bases (1 equiv) could lead to self-redox reactions in the absence/presence of NHC, and cinnamaldehyde disappeared within 2 h (Table 1). However, no reaction happened in the presence of both strong bases and carbon dioxide without NHC catalyst. **2a** was obtained as major product only in the system with NHC as catalyst and in the presence of base and carbon dioxide. The reaction conditions were further

**Scheme 1.** CO<sub>2</sub> Splitting Reaction with Aldehyde Catalyzed by NHC



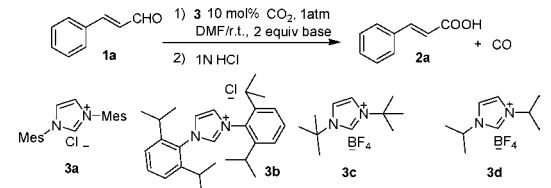
**Table 1.** Background Investigation<sup>a</sup>

entries	conditions	time (h)	yield ( <b>2a</b> %) <sup>b</sup>
1	<b>3a</b> 10 mol %, 10 mol % KOt-Bu, 1 atm CO <sub>2</sub>	72	32 <sup>c</sup>
2	20 mol % KOt-Bu, 80 mol % NaH	2	37 <sup>d</sup>
3	20 mol % KOt-Bu, 80 mol % NaH, 1 atm CO <sub>2</sub>	48	N.R. or trace <sup>e</sup>
4	<b>3a</b> 10 mol %, 20 mol % KOt-Bu, 80 mol % NaH	2	18 <sup>d</sup>
5	<b>3a</b> 10 mol %, 20 mol % KOt-Bu, 80 mol % NaH, 1 atm CO <sub>2</sub>	72	90 <sup>d</sup>

<sup>a</sup> The reactions were conducted at 0.5 mmol scale in 1 mL of anhydrous DMF. <sup>b</sup> Determined by crude <sup>1</sup>H NMR. <sup>c</sup> ~50% cinnamaldehyde was recovered. <sup>d</sup> 100% conversion yield of **1a**. <sup>e</sup> Cinnamaldehyde was recovered.

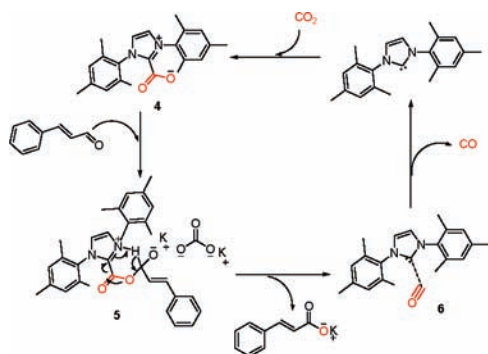
optimized, and we were pleased to find that the reaction gave the best results (yield up to 95%) when it was performed in DMSO with potassium carbonate as additive and 1,3-dimesitylimidazol-2-ylidene (IMes) as catalyst (Table 2).

It was proposed that carbon dioxide was reduced to carbon monoxide, if the overall reaction equation is considered (see Scheme 2). NHC reacts with carbon dioxide resulting in imidazolium carboxylate **4**, which attacks the 2-position of cinnamaldehyde, generating the possible intermediate **5**. The nitrogen on imidazolium carboxylate then traps the hydrogen from the 2-position carbon on cinnamaldehyde, and the electron pair moves to the newly formed carbon–oxygen bond, forming transition state **5** ([1,5] H shift). The possible intermolecular hydrogen interaction (N–H...C) in **5** may help to stabilize the intermediate structure. Subsequently the base traps the H<sup>+</sup> on the nitrogen of the imidazolium ring and results in carbon dioxide splitting from the oxygen–carbon bond and formation of cinnamic salt. Meanwhile, carbon monoxide is released from NHC–CO complex **6**, and in the presence of CO<sub>2</sub>, the imidazolium carboxylate is regenerated very quickly. It should be noted that there is no stable structure associated with the combination of NHC and CO, other than “a non-bonded weakly interacting (van der Waals) complex” intermediate **6**.<sup>19</sup> The production of

**Table 2.** Optimization of the Reactions<sup>a</sup>


entries	base	catalyst	time (d)	yield (2a %) <sup>b</sup>
1	Cs <sub>2</sub> CO <sub>3</sub>	3a	3	92
2	K <sub>2</sub> CO <sub>3</sub>	3a	4	70
3	K <sub>3</sub> PO <sub>4</sub>	3a	4	81
4	Na <sub>2</sub> CO <sub>3</sub> <sup>c</sup>	3a	5	50
5	Cs <sub>2</sub> CO <sub>3</sub> <sup>c</sup>	3a	4	95
6	K <sub>2</sub> CO <sub>3</sub> <sup>c</sup>	3a	4	95
7	K <sub>2</sub> CO <sub>3</sub> <sup>c</sup>	3b	4	40 (1a, 50%)
8	K <sub>2</sub> CO <sub>3</sub> <sup>c</sup>	3c	4	25 (1a, 75%)
9	K <sub>2</sub> CO <sub>3</sub> <sup>c</sup>	3d	4	32 (1a, 66%)

<sup>a</sup> The reactions were conducted at 0.5 mmol scale in 1 mL of anhydrous DMF. <sup>b</sup> Determined by crude <sup>1</sup>H NMR. <sup>c</sup> DMSO as solvent.

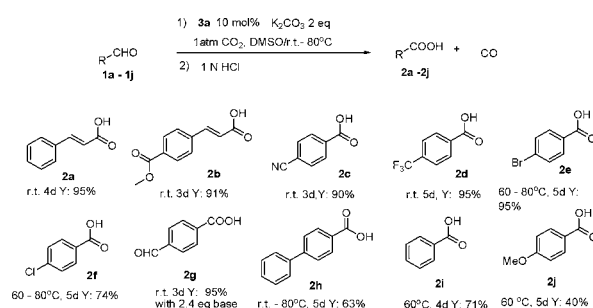
**Scheme 2.** Catalytic Cycle in the Reduction of CO<sub>2</sub> To Form CO

carbon monoxide was confirmed by GC analysis and by the reduction of PdCl<sub>2</sub> solution (see Supporting Information).<sup>20</sup>

The calculated free energy profile (DFT, B3LYP/6-31G level) showed that the overall reaction is an exothermic process with a small negative energy difference of  $\Delta E = -7.0$  kcal/mol.<sup>21</sup> The structure of the identified stationary point related to **5** in Scheme 2 is depicted in SFigure 2 (SI).

With the optimized conditions in hand, various aldehydes as reductants were examined with 10 mol % IMes as organocatalyst. Cinnamaldehyde with a methyl carboxylate group (**2b**) and benzaldehydes with strong electron-withdrawing groups (**2c** and **2d**) could split carbon dioxide efficiently in shorter reaction times. Halogen-substituted benzaldehydes and benzaldehyde with electron-donating groups (**2e**, **2f**, **2i**, **2j**) are also tolerated to reduce carbon dioxide by increasing the temperature (60 or 80 °C). And terephthalaldehyde was selectively oxidized to 4-formylbenzoic acid with excellent yield at room temperature (**3g**).

In summary, we have achieved the catalytic reduction of carbon dioxide to carbon monoxide under mild conditions using aromatic aldehydes as reductants and NHCs as organocatalysts. This carbon dioxide splitting reaction provides a new method for carbon dioxide reduction and steps forward in utilizing carbon dioxide as renewable

**Scheme 3.** Reaction Using Other Aldehydes

“green” source. On the other hand, this reaction also shows a new economical way to oxidize aromatic aldehydes under mild conditions using carbon dioxide.

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**Supporting Information Available:** Experimental procedures, NMR of products, and DFT calculation. This material is available free of charge via Internet at <http://pubs.acs.org>.

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