



# Synthesis of Methanol and Diols from CO<sub>2</sub> via Cyclic Carbonates under Metal-Free, Ambient Pressure, and Solvent-Free Conditions

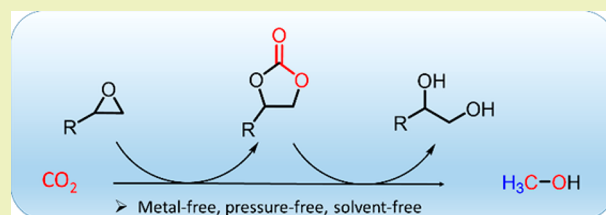
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**S** Supporting Information

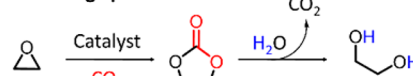
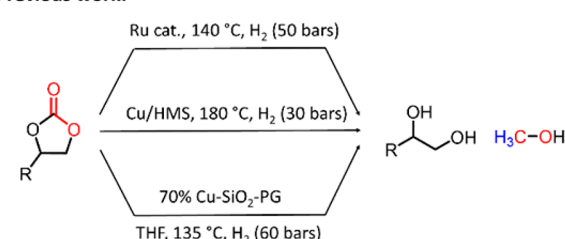
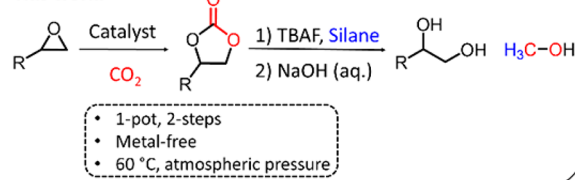
**ABSTRACT:** The synthesis of methanol and diols from cyclic carbonates using *N*-tetrabutylammonium fluoride (TBAF) as a simple metal-free catalyst, and hydrosilanes as the reducing agent, under solvent-free conditions, is described. Methanol was efficiently obtained in 93% yield (from propylene carbonate) and also from a range of other carbonates that were all derived from their corresponding epoxides and CO<sub>2</sub>. Concomitantly, the corresponding diol was formed in excellent yields (e.g., 93% of propylene glycol from propylene carbonate). Labeling experiments allowed the preparation of <sup>13</sup>CD<sub>3</sub>OD or <sup>13</sup>CH<sub>3</sub>OH in high yield at atmospheric pressure.

**KEYWORDS:** Cyclic carbonate, Indirect CO<sub>2</sub> reduction, Hydrosilanes, Solvent-free, Metal-free catalysis

**I** INTRODUCTION

The transformations of CO<sub>2</sub> into value-added chemical products is of considerable interest<sup>1</sup> as a way of utilizing this increasingly abundant greenhouse gas.<sup>2,3</sup> A particularly important product derived from CO<sub>2</sub> is methanol because it can be used as fuel,<sup>4</sup> as a solvent, or as reactive substrate, for example in transesterification reactions.<sup>5</sup> The importance of methanol has led to the concept of the so-called methanol economy.<sup>6</sup> Many different catalysts and routes have been used to convert CO<sub>2</sub> to methanol, including direct reduction with H<sub>2</sub> or hydrosilanes using homogeneous<sup>7–9</sup> and heterogeneous catalysts,<sup>10,11</sup> electrocatalytic processes,<sup>12</sup> and various indirect routes including CO<sub>2</sub> capture from air with subsequent reduction.<sup>13,14</sup> The reduction of CO<sub>2</sub> to methanol via cyclic carbonates and carbamates has attracted attention recently because the reaction proceeds under relatively mild conditions compared to direct routes.<sup>13</sup> However, the hydrogenation of carbonates to produce methanol relies on the use of metal catalysts and, even if the conditions are milder than those for direct CO<sub>2</sub> reduction, high temperatures and hydrogen pressures are still required (Figure 1).<sup>15–18</sup> The production of MeOH via the reduction of cyclic carbonates, and in particular ethylene and propylene carbonate, produces valuable diol compounds in addition to MeOH. Propylene glycol (PG) and ethylene glycol (EG) are important compounds finding applications in antifreeze formulations, as precursors to polyester fibers<sup>19</sup> and elsewhere.<sup>20</sup> Currently, EG is prepared via the Shell Omega process,<sup>21</sup> as depicted in Figure 1, which relies on the hydrolysis of EC by water. This process avoids unwanted polymerization reactions that occur during ethylene oxide hydrolysis and the CO<sub>2</sub> byproduct can be recycled and reused.

The reaction between epoxides and CO<sub>2</sub> to afford cyclic carbonates represents a benchmark reaction in CO<sub>2</sub> chem-

**Shell Omega process:****Previous work:****This work:**

**Figure 1.** Shell Omega process for EG production, previous contributions to metal-catalyzed carbonate reduction, and the method reported here for the simultaneous synthesis of MeOH and diols.

istry.<sup>22,23</sup> In this respect, numerous catalytic systems have been reported, and simple organic salts, such as *n*-tetrabutylammo-

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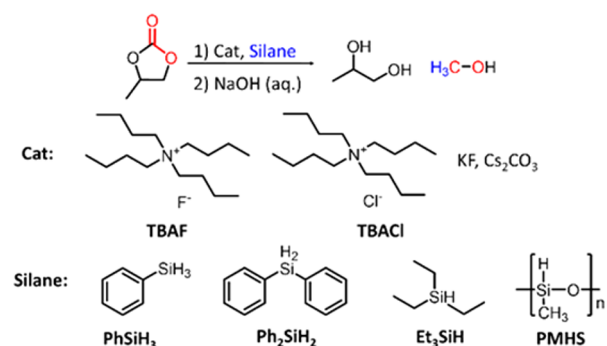
anium (TBA)<sup>24</sup> or imidazolium halides,<sup>25</sup> are potent catalysts for the reaction. Interestingly, the fluoride salt of TBA also catalyzes the deprotection of silylated-alcohols (silyl ethers),<sup>26</sup> and possesses a remarkable cooperativity with hydrosilanes. For example, TBAF-silane mixtures are potent catalysts for amide reductions to amines or nitriles<sup>27</sup> and for the formylation of amines using CO<sub>2</sub> as the C1 source.<sup>28</sup> On the basis of the ability of TBA salts to catalyze both epoxide-CO<sub>2</sub> coupling<sup>24</sup> and hydrosilylation/reduction reactions,<sup>29–31</sup> we set-out to develop a simple, metal-free route to simultaneously produce MeOH and PG from PC, which itself can be derived from propylene oxide and CO<sub>2</sub>, while employing a compatible catalytic system that is efficient for both steps of the process.

## RESULTS AND DISCUSSION

The hydrosilylation/hydrolysis reaction of propylene carbonate was optimized under solvent-free conditions (Table 1, see experimental details in the Supporting Information for full details). The initial reaction conditions were chosen according to results obtained for analogous TBAF-hydrosilane mixtures, that is, 10 mol % TBAF catalyst and PhSiH<sub>3</sub> (3 equiv) as the hydride source,<sup>28</sup> followed by addition of water to release the alcohol product. These conditions resulted in the full conversion of propylene carbonate (PC) to PG and MeOH (Table 1, entry 4, 100% conversion and 70% MeOH). In the absence of PhSiH<sub>3</sub>, hydrolysis of PC affords PG in 23% yield (Table 1, entry 1), indicating why the selectivity of the process toward MeOH is lower than that of PG in most cases. Increasing the hydrosilane concentration led to an increase in conversion, but to a decrease in the yield of MeOH (Table 1, entries 2, 3, and 4, see Figure S1 for representative example), with the optimized quantity of silane being 1 equiv, which led to 93% of PG and 93% of MeOH. One equivalent of PhSiH<sub>3</sub> was sufficient to produce a near-quantitative yield of MeOH, suggesting that all three hydrogens of the hydrosilane are transferred in the reaction. Furthermore, reducing the catalyst loading to 1 mol % resulted in a decrease in the yield (Table 1 entry 16). While this transformation is effective and does not require a solvent, pressure, high temperatures or a metal catalyst, we appreciate that the turnover number (TON) value of the catalyst is modest for the transformation (TON = 61 when 1 mol % catalyst is used). In comparison, the utilization of homogeneous or heterogeneous Ru catalyst led to TONs ranging from 4500 to 87 000, whereas cheaper Cu-based catalysts resulted in TONs that were comparable to those reported herein (TON = 5–10).<sup>13,15,18</sup>

The N-formylation of amines using CO<sub>2</sub> as the C1 source and hydrosilanes as the reductant is efficiently catalyzed by simple potassium salts or basic salts.<sup>28,32</sup> Consequently, a series of related salts were evaluated as catalysts in the conversion of PC to PG and MeOH, but the reaction proceeded in low yields (KF, 4% MeOH; Cs<sub>2</sub>CO<sub>3</sub>, 16% MeOH; and TBACl, 9% MeOH, Table 1, entries 5–7). In addition, other silanes were screened, but all of them resulted in a lower yields and selectivities (Table 1, entries 8–10), although the reaction proceeds to some extent (63% MeOH with Ph<sub>2</sub>SiH<sub>2</sub>, 11% MeOH with Et<sub>3</sub>SiH—commonly employed in hydrosilylation reactions including the hydrosilylation of CO<sub>2</sub><sup>33</sup> and 21% MeOH with polymethylhydrosiloxane, PMHS). PMHS is particularly interesting because it is a waste-product from the silicon industry.<sup>34,35</sup> Under the solvent-free reaction conditions the polymer rapidly solidifies, presumably due to cross-linking, and the product becomes trapped in the pores hindering

**Table 1. Optimization of the Reaction Conditions for the Transformation of PC to PG and MeOH**



entry	cat.	silane (eqs)	solvent	conv. [%]	yield PG [%]	yield MeOH [%]
1	TBAF·3H <sub>2</sub> O	PhSiH <sub>3</sub> (0)	none	24	23	0
2	TBAF·3H <sub>2</sub> O	PhSiH <sub>3</sub> (1)	none	93	93	93
3	TBAF·3H <sub>2</sub> O	PhSiH <sub>3</sub> (2)	none	100	99	78
4	TBAF·3H <sub>2</sub> O	PhSiH <sub>3</sub> (3)	none	100	98	70
5	TBACl	PhSiH <sub>3</sub> (2)	none	44	11	9
6	KF	PhSiH <sub>3</sub> (2)	none	54	8	4
7	Cs <sub>2</sub> CO <sub>3</sub>	PhSiH <sub>3</sub> (2)	none	76	23	16
8	TBAF·3H <sub>2</sub> O	Ph <sub>2</sub> SiH <sub>2</sub> (2)	none	100	67	63
9	TBAF·3H <sub>2</sub> O	PMHS (2)	none	53	25	21
10	TBAF·3H <sub>2</sub> O	Et <sub>3</sub> SiH (2)	none	70	22	11
11	TBAF·3H <sub>2</sub> O	PhSiH <sub>3</sub> (2)	DMF- <i>d</i> <sub>7</sub> (1 mL)	87	87	73
12	TBAF·3H <sub>2</sub> O	PhSiH <sub>3</sub> (2)	DMSO- <i>d</i> <sub>6</sub> (1 mL)	72	72	67
13	TBAF·3H <sub>2</sub> O	PhSiH <sub>3</sub> (2)	CH <sub>3</sub> CN- <i>d</i> <sub>3</sub> (1 mL)	76	76	54
14 <sup>b</sup>	TBAF·3H <sub>2</sub> O	PhSiH <sub>3</sub> (1)	DMSO- <i>d</i> <sub>6</sub> (1 mL)	89	88 <sup>c</sup>	71
15 <sup>d</sup>	TBAF·3H <sub>2</sub> O <sup>d</sup>	PhSiH <sub>3</sub> (1)	none	90		89
16	TBAF·3H <sub>2</sub> O <sup>e</sup>	PhSiH <sub>3</sub> (1)	none	75	61	56

<sup>a</sup>Conditions: Cat (10 mol %), PC (1 mmol), hydrosilane (1–3 equiv), 60 °C, 3 h. Then NaOH<sub>aq</sub> (5%, 0.1 mL), r.t., 2 h. Yields determined by <sup>1</sup>H NMR spectroscopy using CH<sub>2</sub>Br<sub>2</sub> as a standard.

<sup>b</sup>Ethylene carbonate used as the substrate.

<sup>c</sup>Ethylene glycol yield.

<sup>d</sup>DMC used as substrate, reaction performed with 1 g of substrate.

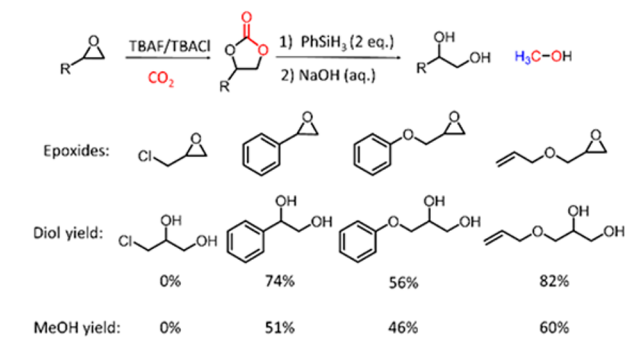
<sup>e</sup>1 mol %, 24 h reaction.

efficient extraction. For all the hydrosilanes used herein, the addition of water results in the formation of a white solid precipitate (mixture of siloxanes and silyl ethers). Polar aprotic solvents can be applied in the reaction mixture, but they lower the yield of MeOH (Table 1, entries 11–13). However, as the reaction is exothermic, for larger scale reactions a solvent such as DMSO or DMF helps to dissipate the heat. It is notable that a high selectivity is achieved only with the combination of PhSiH<sub>3</sub> and TBAF. When other combinations are used, the selectivity is lower (Table 1, entries 5–10). Presumably, other C1 products are formed such as formaldehyde, which have been observed in the reduction of CO<sub>2</sub> catalyzed by ruthenium complexes.<sup>36,37</sup> For example when Cs<sub>2</sub>CO<sub>3</sub> is used as the

catalyst (Table 1, entry 7), a peak at 8.5 ppm is present in the  $^1\text{H}$  NMR spectrum tentatively assigned to formaldehyde.<sup>37</sup> A peak at 8.5 ppm is also present when  $\text{Et}_3\text{SiH}$  is used as the reducing agent (Table 1, entry 10). In addition, ethylene carbonate is smoothly converted to ethylene glycol and methanol to afford 88% of the glycol and 71% of MeOH (Table 1, entry 14). Using dimethylcarbonate (DMC) as the starting material results in the formation of 3 equiv of MeOH, and the reaction proceeds smoothly (265% yield, noted as 89% yield in Table 1, entry 15). The reaction was conducted on a 1 g scale allowing the facile distillation of MeOH from the reaction mixture, since no other volatile components other than water are present in the final reaction mixture.

To demonstrate the versatility of the system for glycol production, several epoxides (epichlorohydrin, allyl glycidyl ether, phenyl glycidyl ether, and styrene oxide) were converted to their corresponding carbonates via insertion of  $\text{CO}_2$ , catalyzed by a TBAF–TBACl mixture (10 mol % of each cat, 100 mg of epoxide, 80 °C,  $\text{CO}_2$  balloon (1 atm.), 18 h, see Figures S2–S4 for representative examples). After reaction the mixture was allowed to cool to room temperature and the atmosphere was purged with  $\text{N}_2$ .  $\text{PhSiH}_3$  (2 equiv) was introduced and the reaction was performed according to the optimized procedure (60 °C, 3 h, then hydrolysis at r.t. for 2 h). The first step (cycloaddition of  $\text{CO}_2$  into the epoxide) proceeds in a near-quantitative yield for all the epoxides (determined by  $^1\text{H}$  NMR spectroscopy). The yields of the diols and MeOH are summarized in Scheme 1.

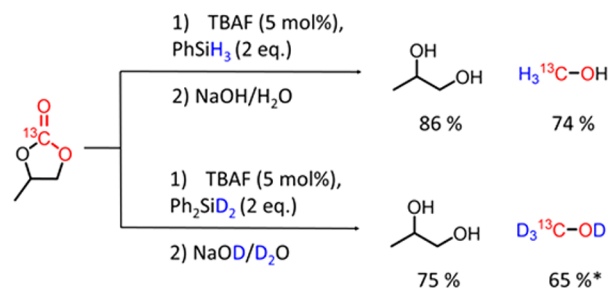
### Scheme 1. Epoxides Used in the Synthesis of Glycols and MeOH from Epoxides in a Single-Pot Reaction



Styrene oxide resulted in a yield of 51% of MeOH and 74% of glycol and phenyl glycidyl ether gave 46% of MeOH and 56% of corresponding diol. The use of allyl glycidyl ether resulted in a yield of 60% of MeOH and 82% of the corresponding diol. Notably, the double bond of allyl glycidyl ether remained intact under the hydrosilylation conditions. Epichlorohydrin did not react to form MeOH under the conditions employed despite the carbonate being formed quantitatively after the first step, presumably because of the electron-withdrawing chlorine atom in the substrate. In all the cases, the sequential reaction of epoxide to carbonate to MeOH (3-steps including hydrolysis, performed in a single pot) was less efficient than the reaction starting with the pure carbonate (results in Table 1), as the TBAF salt slowly decomposes at 80 °C under the reaction conditions (the mixtures turns yellow to brown).<sup>38</sup>

Labeling experiments showed that  $^{13}\text{CH}_3\text{OH}$  and  $^{13}\text{CD}_3\text{OD}$  were accessible using this method (Scheme 2). Labeled propylene carbonate was prepared from propylene oxide and

### Scheme 2. Labeling Experiments for the Hydrosilylation/Hydrolysis of Propylene Carbonate to Produce Labeled MeOH<sup>a</sup>

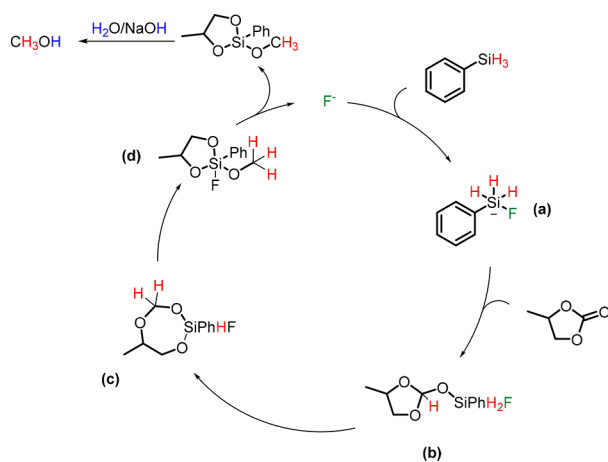


<sup>a</sup>Asterisk (\*) indicates yield estimated based on PG.

$^{13}\text{CO}_2$  using a heterogeneous polymeric salt catalyst<sup>39</sup> affording  $^{13}\text{C}$ -PC in high yield. Employing  $^{13}\text{C}$ -PC as the starting material in combination with  $\text{PhSiH}_3$  or  $\text{Ph}_2\text{SiD}_2$ ,  $^{13}\text{C}$  NMR spectra of the crude reaction mixture demonstrate that the carbon atom of the propylene carbonate is transformed into  $^{13}\text{CH}_3\text{OH}$  or  $^{13}\text{CD}_3\text{OD}$ , respectively (see Figures S5 and S6). Further spectroscopic studies show that the protons of the methanol are derived from the hydrosilane, whereas the methanol OH and diol protons of PG are derived from water. Note, prior to the hydrolysis step, MeOH is detected by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy due to the presence of water in the hygroscopic catalyst. Currently,  $^{13}\text{CH}_3\text{OH}$  and  $^{13}\text{CD}_3\text{OD}$  are produced from appropriately labeled syngas mixtures under pressure in the presence of metal catalysts, and our procedure is advantageous as it avoids toxic  $^{13}\text{CO}$  (and  $\text{D}_2$ ). Moreover, the methanol product can conveniently be extracted from the reaction mixture by distillation.

The hydrosilylation/hydrolysis of carbonates presumably occurs via a mechanism similar to that for ketones, which has been proposed for different types of catalysts, usually proceeding by the same pathway. In the first step, the hydrosilane is activated by the catalyst, enabling a hydride to react with the electropositive C atom of the carbonate with simultaneous binding of the oxygen atom to the silicon center,<sup>40,41</sup> as depicted in Scheme 3 (intermediate b). All the hydrogen atoms from the hydrosilane can be donated to the C atom, since 1 equiv of  $\text{PhSiH}_3$  is sufficient (see Table 1, entry

### Scheme 3. Proposed Mechanism for the Transformation of Propylene Carbonate into MeOH and PG



3). Moreover, labeling experiments with  $\text{Ph}_2\text{SiD}_2$  demonstrate that the deuterium atoms are incorporated into the methanol, rather than the diol. Since silicon is oxophilic, a 7-membered ring (c) can be formed upon hydride transfer. An example of a similar scaffold has been isolated from the silylation of ribose with a source of bis(tertbutyl)silyl.<sup>42</sup> Moreover, pentacoordinated species analogous to that of (d) have been proposed in the past, albeit with a N-donor group to stabilize the silicon center.<sup>43,44</sup> In the final step, the hydrolysis of intermediate (d) generates MeOH and PG and various siloxanes, explaining the broad peaks observed in the aromatic region in the  $^1\text{H}$  NMR spectrum of the crude reaction mixture prior to product purification (see SI).  $^{29}\text{Si}$  NMR and  $^{19}\text{F}$  NMR spectra were recorded in DMSO- $d_6$  for the typical reaction prior to the hydrolysis step (Table 1, entry 12) in an attempt to identify possible intermediates in the catalytic cycle. The  $^{29}\text{Si}$  NMR spectrum (see Figure S7 for a representative  $^{29}\text{Si}$  NMR spectrum) contains three singlets at  $-56$ ,  $-57$ , and  $-58$  ppm, which are in the same region as  $\text{PhSiH}_3$  (singlet at  $-59$  ppm). These peaks may be tentatively attributed to  $\text{PhSi}(\text{OMe})_2\text{F}$ -type species related to intermediate (d) in Scheme 3.<sup>45,46</sup> A triplet was also observed at  $-109.16$  ppm, with a J-coupling of 206 Hz—this value is typical of a  $\text{SiF}_2$  species,<sup>47</sup> indicating that a catalytic intermediate with two F atoms is also present. The corresponding  $^{19}\text{F}$  NMR spectrum (see Figure S8) possesses a peak at approximately  $-140$  ppm, which has previously been attributed to a  $\text{SiF}_2$ -type compound.<sup>47</sup> Finally, a singlet peak is observed at  $-35$  ppm in the  $^{29}\text{Si}$  NMR spectrum which is close in value to  $\text{PhSiH}(\text{OEt})_2$ <sup>48</sup> and a related species could possibly form following elimination of the F atom in structure (c). The GC-MS trace of the reaction mixture prior to hydrolysis shows the presence of tris(methoxy)phenylsilane, indicating that some MeOH is formed prior to hydrolysis due to the moisture content in the catalyst (see above) and that the MeOH can exchange with the substituents attached to the Si-center. As a control, TBAF and  $\text{PhSiH}_3$  were reacted in the absence of PC, and the resulting NMR spectra are completely different to those described above (see Figure S8 for a comparison). Moreover, the TBAF- $\text{PhSiH}_3$  mixture was markedly less stable in DMSO- $d_6$  in comparison with the TBAF- $\text{PhSiH}_3$ -PC mixture, and a white suspension is observed in the TBAF- $\text{PhSiH}_3$  system, whereas the reaction of PC-TBAF- $\text{PhSiH}_3$  remains clear, suggesting that the substrate helps to stabilize the catalytic system. Together, these experiment indicate that a more complex reaction mechanism to that presented in Scheme 3 is plausible. We were unable to recover and reuse the catalyst, which presumably undergoes decomposition during workup.

## CONCLUSIONS

We have developed a simple and user-friendly approach to produce methanol and diols in high yield from  $\text{CO}_2$  and epoxides. The remarkable cooperativity between a simple fluoride salt (TBAF) and a hydrosilane ( $\text{PhSiH}_3$ ), allows the reaction to take place under mild conditions. To the best of our knowledge this reaction represents the first hydrosilylation/reduction process of cyclic carbonate products. As a caveat, we appreciate that hydrosilanes are employed as the reducing agent and hence the reaction generates large quantities of waste, nonetheless, waste silane can be used in the reaction, for example, PMHS. Notably, fully labeled  $^{13}\text{CD}_3\text{OD}$  can be obtained from the reaction of  $^{13}\text{CO}_2$  and  $\text{Ph}_2\text{SiD}_2$  at atmospheric pressure, avoiding  $^{13}\text{CO}$  and high

pressures. On the basis of the available experimental/spectroscopic evidence a tentative catalytic cycle for the reaction has been proposed

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.8b02453.

Experimental details and  $^1\text{H}$  NMR spectra (PDF)

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### Notes

The authors declare no competing financial interest.

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## REFERENCES

- (1) Liu, Q.; Wu, L.; Jackstell, R.; Beller, M. Using carbon dioxide as a building block in organic synthesis. *Nat. Commun.* **2015**, *6*, 5933–5948.
- (2) Anderson, K.; Peters, G. The trouble with negative emissions. *Science* **2016**, *354*, 182–183.
- (3) Buck, H. J. Rapid scale-up of negative emissions technologies: social barriers and social implications. *Clim. Change* **2016**, *139*, 155–167.
- (4) Liu, H.; Song, C.; Zhang, L.; Zhang, J.; Wang, H.; Wilkinson, D. P. J. A review of anode catalysis in the direct methanol fuel cell. *J. Power Sources* **2006**, *155*, 95–110.
- (5) Helwani, Z.; Othman, M. R.; Aziz, N.; Kim, J.; Fernando, W. J. N. Solid heterogeneous catalysts for transesterification of triglycerides with methanol: A review. *Appl. Catal., A* **2009**, *363*, 1–10.
- (6) Olah, G. A. Beyond Oil Gas: The Methanol Economy. *Angew. Chem., Int. Ed.* **2005**, *44*, 2636–2639.
- (7) Riduan, S. N.; Zhang, Y.; Ying, J. Y. Conversion of Carbon Dioxide into Methanol with Silanes over N-Heterocyclic Carbene Catalysts. *Angew. Chem.* **2009**, *121*, 3372–3375.
- (8) Huff, C. A.; Sanford, M. S. Cascade Catalysis for the Homogeneous Hydrogenation of  $\text{CO}_2$  to Methanol. *J. Am. Chem. Soc.* **2011**, *133*, 18122–18125.
- (9) Sordakis, K.; Tang, C.; Vogt, L. K.; Junge, H.; Dyson, P. J.; Beller, M.; Laurenczy, G. Homogeneous Catalysis for Sustainable Hydrogen Storage in Formic Acid and Alcohols. *Chem. Rev.* **2018**, *118*, 372–433.
- (10) Cai, W.; de la Piscina, P. R.; Toyir, J.; Homs, N.  $\text{CO}_2$  hydrogenation to methanol over CuZnGa catalysts prepared using microwave-assisted methods. *Catal. Today* **2015**, *242*, 193–199.
- (11) Studt, F.; Sharafutdinov, I.; Abild-Pedersen, F.; Elkjær, C. F.; Hummelshøj, J. S.; Dahl, S.; Chorkendorff, I.; Nørskov, J. K. Discovery of a Ni-Ga catalyst for carbon dioxide reduction to methanol. *Nat. Chem.* **2014**, *6*, 320–324.
- (12) Kuhl, K. P.; Hatsukade, T.; Cave, E. R.; Abram, D. N.; Kibsgaard, J.; Jaramillo, T. F. Electrocatalytic conversion of carbon dioxide to methane and methanol on transition metal surfaces. *J. Am. Chem. Soc.* **2014**, *136*, 14107–14113.
- (13) Balaraman, E.; Gunanathan, C.; Zhang, J.; Shimon, L. J. W.; Milstein, D. Efficient hydrogenation of organic carbonates, carbamates

and formates indicates alternative routes to methanol based on CO<sub>2</sub> and CO. *Nat. Chem.* **2011**, *3*, 609–614.

(14) Kothandaraman, J.; Goepfert, A.; Czaun, M.; Olah, G. A.; Prakash, G. K. S. Conversion of CO<sub>2</sub> from Air into Methanol Using a Polyamine and a Homogeneous Ruthenium Catalyst. *J. Am. Chem. Soc.* **2016**, *138*, 778–781.

(15) Han, Z.; Rong, L.; Wu, J.; Zhang, L.; Wang, Z.; Ding, K. Catalytic hydrogenation of cyclic carbonates: a practical approach from CO<sub>2</sub> and epoxides to methanol and diols. *Angew. Chem., Int. Ed.* **2012**, *51*, 13041–13045.

(16) Lian, C.; Ren, F.; Liu, Y.; Zhao, G.; Ji, Y.; Rong, H.; Jia, W.; Ma, L.; Lu, H.; Wang, D.; Li, Y. Heterogeneous selective hydrogenation of ethylene carbonate to methanol and ethylene glycol over a copper chromite nanocatalyst. *Chem. Commun.* **2015**, *51*, 1252–1254.

(17) Chen, X.; Cui, Y.; Wen, C.; Wang, B.; Dai, W.-L. Continuous synthesis of methanol: heterogeneous hydrogenation of ethylene carbonate over Cu/HMS catalysts in a fixed bed reactor system. *Chem. Commun.* **2015**, *51*, 13776–13778.

(18) Liu, H.; Huang, Z.; Han, Z.; Ding, K.; Liu, H.; Xia, C.; Chen, J. Efficient production of methanol and diols via the hydrogenation of cyclic carbonates using copper–silica nanocomposite catalysts. *Green Chem.* **2015**, *17*, 4281–4290.

(19) Nanda, M. R.; Yuan, Z.; Qin, W.; Xu, C. Recent advancements in catalytic conversion of glycerol into propylene glycol: A review. *Catal. Rev.: Sci. Eng.* **2016**, *58*, 309–336.

(20) Yue, H.; Zhao, Y.; Ma, X.; Gong, J. Ethylene glycol: properties, synthesis, and applications. *Chem. Soc. Rev.* **2012**, *41*, 4218–4244.

(21) Sun, J.; Yao, X.; Cheng, W.; Zhang, S. 1,3-Dimethylimidazolium-2-carboxylate: a zwitterionic salt for the efficient synthesis of vicinal diols from cyclic carbonates. *Green Chem.* **2014**, *16*, 3297–3304.

(22) Rintjema, J.; Kleij, A. W. Aluminum-Mediated Formation of Cyclic Carbonates: Benchmarking Catalytic Performance Metrics. *ChemSusChem* **2017**, *10*, 1274–1282.

(23) Bobbink, F. D.; Dyson, P. J. Synthesis of carbonates and related compounds incorporating CO<sub>2</sub> using ionic liquid-type catalysts: State-of-the-art and beyond. *J. Catal.* **2016**, *343*, 52–61.

(24) Caló, V.; Nacci, A.; Monopoli, A.; Fanizzi, A. Cyclic Carbonate Formation from Carbon Dioxide and Oxiranes in Tetrabutylammonium Halides as Solvents and Catalysts. *Org. Lett.* **2002**, *4*, 2561–2563.

(25) Peng, J.; Deng, Y. Cycloaddition of carbon dioxide to propylene oxide catalyzed by ionic liquids. *New J. Chem.* **2001**, *25*, 639–641.

(26) Nelson, T. D.; Crouch, R. D. Selective Deprotection of Silyl Ethers. *Synthesis* **1996**, *1996*, 1031–1069.

(27) Zhou, S.; Junge, K.; Addis, D.; Das, S.; Beller, M. A general and convenient catalytic synthesis of nitriles from amides and silanes. *Org. Lett.* **2009**, *11*, 2461–2464.

(28) Hulla, M.; Bobbink, F. D.; Das, S.; Dyson, P. J. Carbon Dioxide Based N-Formylation of Amines Catalyzed by Fluoride and Hydroxide Anions. *ChemCatChem* **2016**, *8*, 3338–3342.

(29) Zhang, Y. Q.; Funken, N.; Winterscheid, P.; Gansäuer, A. Hydroxy-directed, fluoride-catalyzed epoxide hydrosilylation for the synthesis of 1,4-diols. *Angew. Chem., Int. Ed.* **2015**, *54*, 6931–6934.

(30) Bornschein, C.; Werkmeister, S.; Junge, K.; Beller, M. TBAF-catalyzed hydrosilylation for the reduction of aromatic nitriles. *New J. Chem.* **2013**, *37*, 2061–2065.

(31) Das, S.; Addis, D.; Knöpke, L. R.; Bentrup, U.; Junge, K.; Brückner, A.; Beller, M. Selective catalytic monoreduction of phthalimides and imidazolidine-2,4-diones. *Angew. Chem., Int. Ed.* **2011**, *50*, 9180–9184.

(32) Fang, C.; Lu, C.; Liu, M.; Zhu, Y.; Fu, Y.; Lin, B.-L. Selective Formylation and Methylation of Amines using Carbon Dioxide and Hydrosilane Catalyzed by Alkali-Metal Carbonates. *ACS Catal.* **2016**, *6*, 7876–7881.

(33) Berkefeld, A.; Piers, W. E.; Parvez, M. Tandem Frustrated Lewis Pair/Tris(pentafluorophenyl)borane-Catalyzed Deoxygenative Hydrosilylation of Carbon Dioxide. *J. Am. Chem. Soc.* **2010**, *132*, 10660–10661.

(34) Jacquet, O.; Das Neves Gomes, C.; Ephritikhine, M.; Cantat, T. Recycling of carbon and silicon wastes: Room temperature formylation of N-H bonds using carbon dioxide and polymethylhydrosiloxane. *J. Am. Chem. Soc.* **2012**, *134*, 2934–2937.

(35) Das, S.; Bobbink, F. D.; Bulut, S.; Soudani, M.; Dyson, P. J. Thiazolium carbene catalysts for the fixation of CO<sub>2</sub> onto amines. *Chem. Commun.* **2016**, *52*, 2497–2500.

(36) Bontemps, S.; Sabo-Etienne, S. Trapping formaldehyde in the homogeneous catalytic reduction of carbon dioxide. *Angew. Chem., Int. Ed.* **2013**, *52*, 10253–10255.

(37) Bontemps, S.; Vendier, L.; Sabo-Etienne, S. Ruthenium-catalyzed reduction of carbon dioxide to formaldehyde. *J. Am. Chem. Soc.* **2014**, *136*, 4419–4425.

(38) Sun, H.; DiMugno, S. G. Anhydrous tetrabutylammonium fluoride. *J. Am. Chem. Soc.* **2005**, *127*, 2050–2051.

(39) Zhong, W.; Bobbink, F. D.; Fei, Z.; Dyson, P. J. Polyimidazolium Salts: Robust Catalysts for the Cycloaddition of Carbon Dioxide into Carbonates in Solvent-Free Conditions. *ChemSusChem* **2017**, *10*, 2728–2735.

(40) Revunova, K.; Nikonov, G. I. Base-catalyzed hydrosilylation of ketones and esters and insight into the mechanism. *Chem. - Eur. J.* **2014**, *20*, 839–845.

(41) Parks, D. J.; Blackwell, J. M.; Piers, W. E. Studies on the mechanism of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>-catalyzed hydrosilylation of carbonyl functions. *J. Org. Chem.* **2000**, *65*, 3090–3098.

(42) Schulten, J.; Klüfers, P. Dibutylsilylene-pentose bis-chelates: On the glycoses' binding sites for strongly Lewis-acidic centres. *Carbohydr. Res.* **2011**, *346*, 1767–1775.

(43) Arya, P.; Corriu, R. J. P.; Gupta, K.; Lanneau, G. F.; Yu, Z. J. Organosilanes cycliques fonctionnels pentacoordonnés O,O disubstitués. *J. Organomet. Chem.* **1990**, *399*, 11–33.

(44) Carré, F. H.; Corriu, R. J. P.; Lanneau, G. F.; Yu, Z. Intramolecular Coordination at Silicon. The Small Effect of Equatorial Ligands upon the Stability of Pentacoordinated Organosilanes. *Organometallics* **1991**, *10*, 1236–1243.

(45) Lee, A. S.; Choi, S.-S.; Lee, H. S.; Baek, K.-Y.; Hwang, S. S. A new, higher yielding synthetic route towards dodecaphenyl cage silsesquioxanes: synthesis and mechanistic insights. *Dalt. Trans.* **2012**, *41*, 10585–10588.

(46) Wakabayashi, R.; Sugiura, Y.; Shibue, T.; Kuroda, K. Practical conversion of chlorosilanes into alkoxy silanes without generating HCl. *Angew. Chem., Int. Ed.* **2011**, *50*, 10708–10711.

(47) Voronkov, M. G.; Boyarkina, E. V.; Gebel, I. A.; Albanov, A. I.; Basenko, S. V. Cleavage of the C-Si bond in trifluoro(phenyl)silane with aliphatic alcohols. *Russ. J. Gen. Chem.* **2005**, *75*, 1927–1929.

(48) Khalimon, A. Y.; Simionescu, R.; Nikonov, G. I. Catalytic and stoichiometric reactivity of  $\beta$ -silylamido agostic complex of Mo: Intermediacy of a silanimine complex and applications to multi-component coupling. *J. Am. Chem. Soc.* **2011**, *133*, 7033–7053.