

# Tandem Amine and Ruthenium-Catalyzed Hydrogenation of CO<sub>2</sub> to Methanol

Nomaan M. Rezayee,<sup>†</sup> Chelsea A. Huff,<sup>†</sup> and Melanie S. Sanford\*

Department of Chemistry, University of Michigan, 930 North University Avenue, Ann Arbor, Michigan 48109, United States

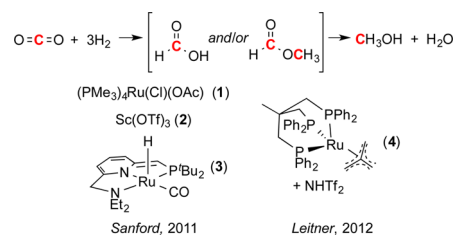
**S** Supporting Information

**ABSTRACT:** This Communication describes the hydrogenation of carbon dioxide to methanol via tandem catalysis with dimethylamine and a homogeneous ruthenium complex. Unlike previous examples with homogeneous catalysts, this CO<sub>2</sub>-to-CH<sub>3</sub>OH process proceeds under basic reaction conditions. The dimethylamine is proposed to play a dual role in this system. It reacts directly with CO<sub>2</sub> to produce dimethylammonium dimethylcarbamate, and it also intercepts the intermediate formic acid to generate dimethylformamide. With the appropriate selection of catalyst and reaction conditions, >95% conversion of CO<sub>2</sub> was achieved to form a mixture of CH<sub>3</sub>OH and dimethylformamide.

Rapidly increasing atmospheric carbon dioxide levels are projected to have detrimental consequences on the global climate.<sup>1</sup> One strategy to address this problem involves remediating CO<sub>2</sub> emissions via capture at a point source, with subsequent sequestration in underground geological formations. This approach, termed “carbon capture and sequestration” (CCS), has been the subject of extensive research and commercialization efforts.<sup>2</sup> However, CCS suffers from the fundamental limitation that it fails to productively utilize CO<sub>2</sub>.<sup>3,4</sup> An attractive and complementary approach would be to use captured CO<sub>2</sub> as a carbon source for the synthesis of fuels and/or chemicals such as methanol.<sup>5</sup> Over the past 40 years, there has been significant work on the development of CuZnO and other heterogeneous catalysts for the conversion of CO<sub>2</sub> to CH<sub>3</sub>OH;<sup>5,6</sup> however, these systems generally operate at high temperatures (>200 °C), which limits conversion in this entropically unfavorable reduction reaction.<sup>7</sup> Additionally, it remains challenging to rationally tune the reactivity and selectivity of such heterogeneous catalysts. Single-site homogeneous catalysts could offer an attractive alternative, since they generally operate at lower temperatures and contain readily tunable ligand environments.

Despite many years of effort,<sup>8,9</sup> homogeneous catalysts capable of selectively converting CO<sub>2</sub> and H<sub>2</sub> to CH<sub>3</sub>OH have been disclosed only recently.<sup>10–13</sup> In 2011, our group reported a combination of three homogeneous catalysts (1–3) that operate in tandem to sequentially convert CO<sub>2</sub> to formic acid, methyl formate, and ultimately CH<sub>3</sub>OH (Scheme 1).<sup>10</sup> More recently, several reports by Leitner have demonstrated that the combination of ruthenium complex 4 and NHTf<sub>2</sub> catalyzes the conversion of CO<sub>2</sub> to CH<sub>3</sub>OH via either a formic acid or methyl formate intermediate.<sup>13</sup> However, both of these systems operate

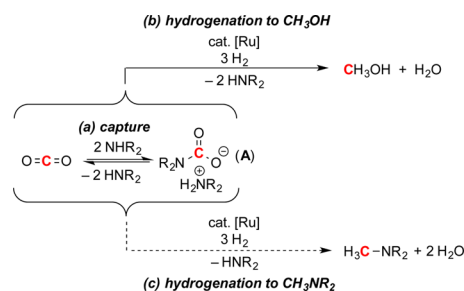
## Scheme 1. Homogeneous Catalysts for the Hydrogenation of CO<sub>2</sub> to CH<sub>3</sub>OH



under acidic conditions, and are thus incompatible with the bases typically utilized for CO<sub>2</sub> capture.<sup>2</sup>

In the current study, we sought an alternative strategy that would combine CO<sub>2</sub> capture to form a carbamate salt (A in Scheme 2a) with hydrogenation to generate CH<sub>3</sub>OH (Scheme

## Scheme 2. Proposed Tandem CO<sub>2</sub> Capture/Hydrogenation Sequence



2b).<sup>14</sup> Conceptually, this approach is very different than those in Scheme 1, as it involves catalysis under basic, rather than acidic conditions. Thus, it should be compatible with CO<sub>2</sub> capture processes. We report herein the successful implementation of this strategy by employing the combination of NHMe<sub>2</sub> and a homogeneous ruthenium hydrogenation catalyst ([Ru]). Under our developed reaction conditions, NHMe<sub>2</sub> and [Ru] catalyze the hydrogenation of CO<sub>2</sub> to a mixture of DMF and CH<sub>3</sub>OH with up to 96% conversion of CO<sub>2</sub> in a single batch reactor.

Dimethylammonium dimethylcarbamate (DMC), which is formed upon the reaction of CO<sub>2</sub> with NHMe<sub>2</sub>, was selected as a representative example of the CO<sub>2</sub> capture intermediate A. Our initial studies focused on identifying homogeneous catalysts capable of converting DMC to CH<sub>3</sub>OH. We anticipated several

Received: November 4, 2014

Published: January 16, 2015

key challenges associated with this transformation. First, the carbonyl functionality in DMC is very weakly electrophilic; thus, the ideal catalyst should be highly reactive toward C=O hydrogenation. Second,  $\text{NHMe}_2$ , a Brønsted base and potential ligand, will be released over the course of the reaction; thus, the catalyst must be stable under basic conditions and must not be inhibited by  $\text{NHMe}_2$ . Third, the formation of trimethylamine is a possible competing side reaction (Scheme 2c);<sup>15</sup> thus, the catalyst must be selective for hydrogenation with C–N cleavage (to produce  $\text{CH}_3\text{OH}$ ) over hydrogenation with C–O cleavage (to yield  $\text{NMe}_3$ ).<sup>16</sup> These requirements led us to examine Ru complexes **3**, **5**, and **6** as catalysts for this reaction. These complexes are known to catalyze the hydrogenation of related ester,<sup>12,17</sup> amide,<sup>18</sup> and/or neutral carbonate<sup>12</sup> substrates. Additionally, catalysts **3**, **5**, and **6** have all been demonstrated to be compatible with amines.<sup>12,18</sup> Finally, **5** has been shown to catalyze the hydrogenation of *N*-formylmorpholine to selectively generate  $\text{CH}_3\text{OH}$  rather than the tertiary amine, *N*-methylmorpholine.<sup>18a</sup> The latter result suggests that selective hydrogenation with C–N cleavage to generate  $\text{CH}_3\text{OH}$  is feasible with this class of pincer catalysts.

We first examined the reaction of DMC with 1 mol % of catalysts **3**, **5**, or **6** at 155 °C in THF under 50 bar of  $\text{H}_2$ . As shown in Table 1, entries 1–3, very low turnover numbers (TON

**Table 1. Hydrogenation of DMC to  $\text{CH}_3\text{OH}$ <sup>a</sup>**

entry	catalyst	base	TON		
			$\text{CH}_3\text{OH}$	DMF	$\text{NMe}_3$
1	<b>3</b>	none	0	0	<1
2	<b>5</b>	none	3	0	<1
3	<b>6</b>	none	3	2	<1
4	<b>3</b>	$\text{K}_3\text{PO}_4$	0	3	<1
5	<b>5</b>	$\text{K}_3\text{PO}_4$	4	3	<1
6	<b>6</b>	$\text{K}_3\text{PO}_4$	19	3	<1
7 <sup>b</sup>	<b>6</b>	$\text{K}_3\text{PO}_4$	20	0	<1

<sup>a</sup>Conditions: 50 bar  $\text{H}_2$ , 0.5 mmol of DMC (0.32 M in THF), 5  $\mu\text{mol}$  of  $[\text{Ru}]$ , 0.25 mmol of  $\text{K}_3\text{PO}_4$ , 18 h. TONs determined by  $^1\text{H}$  NMR spectroscopic analysis.<sup>19</sup> <sup>b</sup>Reaction time of 30 h.

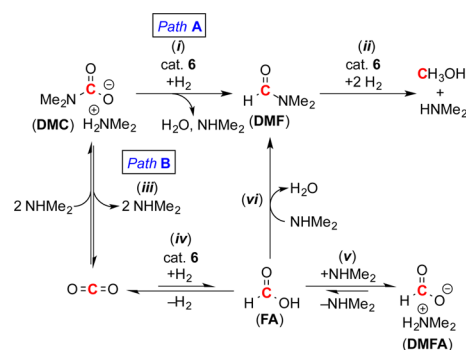
between 0 and 3) were observed in all cases. We noted that exogenous bases can enhance the reactivity of ruthenium carbonyl hydrogenation catalysts.<sup>20</sup> An evaluation of different base/catalyst combinations revealed that the use of commercially available catalyst **6** and  $\text{K}_3\text{PO}_4$  was particularly effective for our system. The addition of 50 equiv of  $\text{K}_3\text{PO}_4$  relative to **6** resulted in up to 19 turnovers of  $\text{CH}_3\text{OH}$  at 155 °C (TON determined relative to the loading of **6**, entry 6). Importantly, this reaction was highly selective for  $\text{CH}_3\text{OH}$  over  $\text{NMe}_3$  (<1 turnover of  $\text{NMe}_3$  was detected). Small quantities of dimethylformamide (DMF, 3 turnovers) were also formed under these conditions.

The **6**-catalyzed conversion of DMC to  $\text{CH}_3\text{OH}$  (Table 1, entry 6) provides exciting proof-of-principle for our approach.

However, there is still major room for improvement, as this result represents just 22% conversion of DMC to hydrogenated products over 18 h. Notably, increasing the reaction time to 30 h had minimal impact on conversion (entry 7). This result suggests that catalyst decomposition is competitive with DMC hydrogenation at 155 °C.

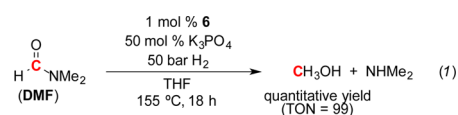
To develop a rational strategy to improve this reaction, we analyzed possible pathways from DMC to  $\text{CH}_3\text{OH}$ . Literature precedent suggests that there are at least two possible routes for the conversion of DMC to  $\text{CH}_3\text{OH}$  in this system. The most direct is shown in Scheme 3, Path A, and involves initial

**Scheme 3. Possible Paths for the Hydrogenation of DMC to  $\text{CH}_3\text{OH}$ <sup>22</sup>**

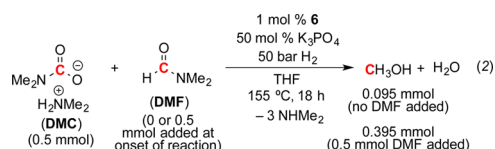


hydrogenation of DMC to DMF (step i) followed by hydrogenation of DMF with C–N bond cleavage to produce  $\text{CH}_3\text{OH}$  (step ii). Notably, Milstein has demonstrated the Ru-catalyzed hydrogenation of carbonates,<sup>12</sup> carbamates,<sup>12</sup> and amides<sup>18a</sup> related to DMF and DMC. Alternatively, DMC could reversibly release  $\text{CO}_2$  and 2 equiv of  $\text{NHMe}_2$  (step iii, Path B). This would be followed by hydrogenation of  $\text{CO}_2$  to formic acid (FA, step iv), a thermodynamically unfavorable reaction that would be driven to the right by amidation of FA to afford DMF (step vi) or deprotonation of FA to yield dimethylammonium formate (DMFA, step v). Selective hydrogenation of DMF (step ii) would then release  $\text{CH}_3\text{OH}$ . Importantly, Jessop has previously demonstrated the Ru-catalyzed conversion of DMC to DMF via steps iii–vi.<sup>21</sup>

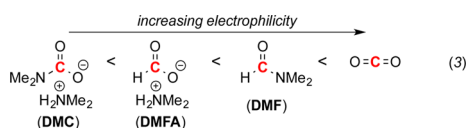
Both of the paths in Scheme 3 involve DMF as a key intermediate. We conducted independent experiments that confirm that **6** is a competent and selective catalyst for the hydrogenation of DMF to  $\text{CH}_3\text{OH}$  (eq 1). Furthermore, the



addition of 0.5 mmol of DMF at the onset of the **6**-catalyzed hydrogenation of DMC results in a 4-fold increase in the quantity of  $\text{CH}_3\text{OH}$  produced (eq 2). Both of these results are consistent with the proposed intermediacy of DMF in this transformation.



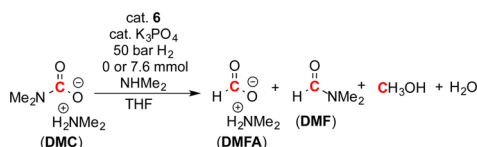
We next sought to utilize the proposed pathways in Scheme 3 and eqs 1 and 2 to further optimize the **6**-catalyzed hydrogenation of DMC. Since catalyst decomposition appears to be problematic at 155 °C, we focused on strategies for lowering the reaction temperature. Scheme 3 implicates four different carbonyl-containing intermediates that could accumulate under the reaction conditions: DMC, DMFA, DMF, and CO<sub>2</sub>. Among these possibilities, DMC is expected to be the most difficult to hydrogenate (since it is the least electrophilic) while CO<sub>2</sub> should be the most reactive toward hydrogenation (since it is the most electrophilic) (eq 3). Thus, assuming that there is some



equilibrium between DMC and CO<sub>2</sub> during the reaction, this analysis suggests that Path B should be accessible under milder conditions than Path A.

To test this hypothesis, we lowered the temperature for the DMC hydrogenation reaction to 95 °C (Table 2, entry 2). The

**Table 2. Optimization of **6**/NHMe<sub>2</sub>-Catalyzed Hydrogenation of DMC<sup>a</sup>**



entry	temp (°C)	[DMC] (M)	added NHMe <sub>2</sub> (mmol)	conv DMC (%)	TON	
					CH <sub>3</sub> OH	DMF+DMFA
1	155	0.32	none	22	19	3
2	95	0.32	none	10	<1	10
3 <sup>b</sup>	95	1.89	none	39	<1	385
4 <sup>b</sup>	95	1.89	7.6	87	<1	872
5 <sup>b,c</sup>	95 → 155	1.89	7.6	58	306	270

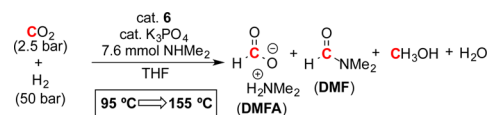
<sup>a</sup>Conditions: 50 bar H<sub>2</sub>, 5 μmol of **6**, 0.25 mmol of K<sub>3</sub>PO<sub>4</sub>, 18 h, 1.5 mL of DMC solution in THF. <sup>b</sup>2.6 mL of DMC solution. <sup>c</sup>95 °C for 18 h then 155 °C for 18 h. TONs determined by <sup>1</sup>H NMR spectroscopic analysis.<sup>19</sup>

sole detectable hydrogenation products were DMF and DMFA (10% conversion of DMC, TON = 10, entry 2). At this temperature, the **6**-catalyzed hydrogenation of CO<sub>2</sub> to DMF is fast, while DMF hydrogenation is extremely slow (<1% conversion over 18 h).<sup>23</sup> Thus, Path B is expected to be the only accessible route to these products at this temperature. We next hypothesized that increasing the initial concentration of DMC would further accelerate Path B by increasing the equilibrium concentration of the reactive electrophile, CO<sub>2</sub>. As predicted, moving from 0.32 M (entry 2) to 1.89 M DMC (entry 3) resulted in a significant increase in conversion of DMC (39% conversion, TON (DMF + DMFA) = 385). Finally, we reasoned that the addition of exogenous NHMe<sub>2</sub> would further drive Path B by accelerating the trapping of the FA generated in step iv. Indeed, the addition of 7.6 mmol of NHMe<sub>2</sub> at the onset of the reaction resulted in high (87%) conversion of DMC over 18 h at 95 °C to form a mixture of DMF (870 turnovers) and DMFA (2 turnovers, entry 4).

The results in Table 2, entries 2–4, led us to examine a single pot, temperature ramp strategy for hydrogenating DMC to CH<sub>3</sub>OH. This approach involves initial equilibration of DMC to CO<sub>2</sub> and hydrogenation at 95 °C to build up a high concentration of DMF, followed by an increase in temperature to enable the **6**-catalyzed conversion of DMF to CH<sub>3</sub>OH. Gratifyingly, a temperature ramp of 95 °C for 18 h followed by 155 °C for 18 h afforded a mixture of CH<sub>3</sub>OH (31% yield, TON = 306) and DMF/DMFA (27% yield, TON = 270).

We next applied the same strategy to the direct hydrogenation of CO<sub>2</sub>. These reactions were conducted with 2.5 bar CO<sub>2</sub> and 50 bar H<sub>2</sub> using the same temperature ramp described in Table 3,

**Table 3. Catalyst **6**/NHMe<sub>2</sub>-Catalyzed Hydrogenation of CO<sub>2</sub> to CH<sub>3</sub>OH<sup>a</sup>**



entry	loading of <b>6</b> (mol %)	time (h)		conv CO <sub>2</sub> (%)	TON	
		at 95 °C	at 155 °C		CH <sub>3</sub> OH	DMF+DMFA
1	0.10	18	18	96	220	740
2	0.10	18	36	89	267	623
3 <sup>b</sup>	0.03	18	36	82	550	1870

<sup>a</sup>Conditions: 2.5 bar CO<sub>2</sub> (5 mmol), 50 bar H<sub>2</sub>, 5 μmol of **6**, 0.25 mmol of K<sub>3</sub>PO<sub>4</sub>. TONs determined by <sup>1</sup>H NMR spectroscopic analysis.<sup>19</sup> <sup>b</sup>1.7 μmol of **6**.

entry 5 (95 °C for 18 h ramping to 155 °C for 18 h). As shown in Table 3, entry 1, these conditions resulted in 96% conversion of CO<sub>2</sub> to a mixture of DMF/DMFA (74% yield, TON = 740) and CH<sub>3</sub>OH (22% yield, TON = 220).<sup>24</sup> Extending the time at 155 °C to 48 h resulted in a relatively small increase in the TON of CH<sub>3</sub>OH (27% yield, TON = 267) (entry 2). This is consistent with catalyst decomposition at this elevated temperature (*vide supra*). Finally, decreasing the loading of **6** to 0.03 mol % resulted in a further increase in the TON of CH<sub>3</sub>OH (19% yield, TON = 550). Overall, these results demonstrate that the combination of an amine and a Ru pincer catalyst can be used to convert both CO<sub>2</sub> and CO<sub>2</sub>-capture intermediates such as DMC to CH<sub>3</sub>OH.

In summary, this Communication describes the development of a homogeneous catalytic method that enables the capture and reduction of CO<sub>2</sub> to CH<sub>3</sub>OH using a combination of NHMe<sub>2</sub> and Ru catalyst **6**. Unlike previous examples of homogeneous catalytic CO<sub>2</sub> reduction, this process proceeds under basic conditions. The amine is proposed to play a dual role in this system, directly reacting with CO<sub>2</sub> to produce DMC and also intercepting formic acid to form DMF. Overall, the current process proceeds with high carbon efficiency, leading to up to 96% conversion of CO<sub>2</sub> to a mixture of DMF and CH<sub>3</sub>OH. We anticipate that this process can be improved further through the identification of more stable hydrogenation catalysts as well as through advances in reaction/reactor engineering. Both are currently under investigation in our group and will be reported in due course.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Experimental and spectroscopic details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## AUTHOR INFORMATION

## Corresponding Author

\*mssanfor@umich.edu

## Author Contributions

<sup>†</sup>N.M.R. and C.A.H. contributed equally to this work.

## Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This work was supported by NSF under the CCI Center for Enabling New Technologies through Catalysis (CENTC) Phase II Renewal, CHE-1205189. C.A.H. thanks the NSF for a Graduate Research Fellowship. N.M.R. and C.A.H. thank Rackham Graduate School for a Rackham Merit Fellowship.

## REFERENCES

- (1) (a) Kamijo, T.; Sorimachi, Y.; Shimada, D.; Miyamoto, O.; Endo, T.; Nagayasu, H.; Mangiaracina, A. *Energy Procedia* **2013**, *37*, 813. (b) Pera-Titus, M. *Chem. Rev.* **2013**, *114*, 1413.
- (2) (a) Figueroa, J. D.; Fout, T.; Plasynski, S.; McIlvried, H.; Srivastava, R. D. *Int. J. Greenh. Gas Control* **2008**, *2*, 9. (b) Yang, H.; Xu, Z.; Fan, M.; Gupta, R.; Slimane, R. B.; Bland, A. E.; Wright, I. J. *Environ. Sci.* **2008**, *20*, 14. (c) Macdowell, N.; Florin, N.; Buchard, A.; Hallett, J.; Galindo, A.; Jackson, G.; Adjiman, C. S.; Williams, C. K.; Shah, N.; Fennell, P. *Energy Environ. Sci.* **2010**, *3*, 1645.
- (3) (a) Corsten, M.; Ramirez, A.; Shen, L.; Koornneef, J.; Faaij, A. *Int. J. Greenh. Gas Control* **2013**, *13*, 59. (b) Appel, A. M.; Bercaw, J. E.; Bocarsly, A. B.; Dobbek, H.; DuBois, D. L.; Dupuis, M.; Ferry, J. G.; Fujita, E.; Hille, R.; Kenis, P. J. A.; Kerfeld, C. A.; Morris, R. H.; Peden, C. H. F.; Portis, A. R.; Ragsdale, S. W.; Rauchfuss, T. B.; Reek, J. N. H.; Seefeldt, L. C.; Thauer, R. K.; Waldrop, G. L. *Chem. Rev.* **2013**, *113*, 6621.
- (4) (a) Daresbourg, D. J. *Inorg. Chem.* **2010**, *49*, 10765. (b) Riduan, S. N.; Zhang, Y. G. *Dalton Trans.* **2010**, *39*, 3347. (c) Dibenedetto, A.; Angelini, A.; Stufano, P. J. *Chem. Technol. Biotechnol.* **2014**, *89*, 334.
- (5) (a) Leitner, W. *Angew. Chem., Int. Ed.* **1995**, *34*, 2207. (b) Grabow, L. C.; Mavrikakis, M. *ACS Catal.* **2011**, *1*, 365. (c) Choudhury, J. *ChemCatChem* **2012**, *4*, 609. (d) Li, Y. H.; Junge, K.; Beller, M. *ChemCatChem* **2013**, *5*, 1072. (e) Li, Y. N.; Ma, R.; He, L. N.; Diaio, Z. F. *Catal. Sci. Technol.* **2014**, *4*, 1498.
- (6) (a) Waller, D.; Stirling, D.; Stone, F. S.; Spencer, M. S. *Faraday Discuss. Chem. Soc.* **1989**, *87*, 107. (b) Spencer, M. S. *Top. Catal.* **1999**, *8*, 259.
- (7) Martino, G.; Courty, P.; Marcilly, C.; Kochloeff, K.; Lunsford, J. H. *Handbook of Heterogeneous Catalysis*; Wiley-VCH: Weinheim, 1997; p 1801.
- (8) For examples of the use of boranes and silanes to convert CO<sub>2</sub> to the CH<sub>3</sub>OH oxidation state with homogeneous metal catalysts, see: (a) Eisenschmid, T. C.; Eisenberg, R. *Organometallics* **1989**, *8*, 1822. (b) Riduan, S. N.; Zhang, Y.; Ying, J. Y. *Angew. Chem., Int. Ed.* **2009**, *48*, 3322. (c) Chakraborty, S.; Zhang, J.; Krause, J. A.; Guan, H. *J. Am. Chem. Soc.* **2010**, *132*, 8872. (d) Huang, F.; Lu, G.; Zhao, L.; Li, H.; Wang, Z. X. *J. Am. Chem. Soc.* **2010**, *132*, 12388. (e) Huang, F.; Zhang, C.; Jiang, J.; Wang, Z.-X.; Guan, H. *Inorg. Chem.* **2011**, *50*, 3816. (f) Riduan, S. N.; Ying, J. Y.; Zhang, Y. G. *ChemCatChem* **2013**, *5*, 1490. (g) Wang, B. J.; Cao, Z. X. *R. Soc. Chem. Adv.* **2013**, *3*, 14007. (h) LeBlanc, F. A.; Piers, W. E.; Parvez, M. *Angew. Chem., Int. Ed.* **2014**, *53*, 789. (i) Anker, M. D.; Arrowsmith, M.; Bellham, P.; Hill, M. S.; Kociok-Kohn, G.; Liptrout, D. J.; Mahon, M. F.; Weetman, C. *Chem. Sci.* **2014**, *5*, 2826.
- (9) For examples of the use of frustrated Lewis pairs for the conversion of CO<sub>2</sub> to CH<sub>3</sub>OH, see: (a) Ashley, A. E.; Thompson, A. L.; O'Hare, D. *Angew. Chem., Int. Ed.* **2009**, *48*, 9839. (b) Ménard, G.; Stephan, D. W. *J. Am. Chem. Soc.* **2010**, *132*, 1796. (c) Stephan, D. W.; Erker, G. *Angew. Chem., Int. Ed.* **2010**, *49*, 46. (d) Sgro, M. J.; Stephan, D. W. *Angew. Chem., Int. Ed.* **2012**, *51*, 11343. (e) Zhu, J.; An, K. *Chem.—Asian J.* **2013**, *8*, 3147. (f) Courtemanche, M. A.; Legare, M. A.; Maron, L.; Fontaine, F. G. *J. Am. Chem. Soc.* **2013**, *135*, 9326. (g) Courtemanche, M. A.; Legare, M. A.; Maron, L.; Fontaine, F. G. *J. Am. Chem. Soc.* **2014**, *136*, 10708. (h) Wang, T.; Stephan, D. W. *Chem. Commun.* **2014**, *50*, 7007. (i) Anker, M. D.; Arrowsmith, M.; Bellham, P.; Hill, M. S.; Kociok-Kohn, G.; Liptrout, D. J.; Mahon, M. F.; Weetman, C. *Chem. Sci.* **2014**, *5*, 2826. (j) Fontaine, F. G.; Courtemanche, M. A.; Legare, M. A. *Chem.—Eur. J.* **2014**, *20*, 2990.
- (10) For early reports of the Ru-catalyzed hydrogenation of CO<sub>2</sub> to a mixture of CO, CH<sub>3</sub>OH, and CH<sub>4</sub>, see: (a) Tominaga, K.; Sasaki, Y.; Kawai, M.; Watanabe, T.; Saito, M. *J. Chem. Soc., Chem. Commun.* **1993**, 629. (b) Tominaga, K.; Sasaki, Y.; Watanabe, T.; Saito, M. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 2837.
- (11) Huff, C. A.; Sanford, M. S. *J. Am. Chem. Soc.* **2011**, *133*, 18122.
- (12) For seminal work by Milstein demonstrating the 3- and 5-catalyzed hydrogenation of esters, amides, and carbonates, see: Balaraman, E.; Gunanathan, C.; Zhang, J.; Shimon, L. J. W.; Milstein, D. *Nat. Chem.* **2011**, *3*, 609.
- (13) (a) Wesselbaum, S.; vom Stein, T.; Klankermeyer, J.; Leitner, W. *Angew. Chem., Int. Ed.* **2012**, *51*, 7499. (b) Wesselbaum, S.; Moha, V.; Meuresch, M.; Brosinski, S.; Thenert, K. M.; Kothe, J.; Stein, T. v.; Englert, U.; Hölscher, M.; Klankermeyer, J.; Leitner, W. *Chem. Sci.* **2015**, *6*, 693.
- (14) For a related approach that generates methyl formate from CO<sub>2</sub>, see: Yadav, M.; Linehan, J. C.; Karkamkar, A. J.; van der Eide, E.; Heldebrand, D. J. *Inorg. Chem.* **2014**, *53*, 9849.
- (15) (a) Jacquet, O.; Frogneux, X.; Das Neves Gomes, C.; Cantat, T. *Chem. Sci.* **2013**, *4*, 2127. (b) Beydoun, K.; Vom Stein, T.; Klankermeyer, J.; Leitner, W. *Angew. Chem., Int. Ed.* **2013**, *52*, 9554. (c) Li, Y.; Sorribes, I.; Yan, T.; Junge, K.; Beller, M. *Angew. Chem., Int. Ed.* **2013**, *52*, 12156. (d) Beydoun, K.; Ghattas, G.; Thenert, K.; Klankermeyer, J.; Leitner, W. *Angew. Chem., Int. Ed.* **2014**, *53*, 11010. (e) Sorribes, I.; Junge, K.; Beller, M. *Chem.—Eur. J.* **2014**, *20*, 7878.
- (16) John, J. M.; Bergens, S. H. *Angew. Chem., Int. Ed.* **2011**, *50*, 10377.
- (17) Kuriyama, W.; Matsumoto, T.; Ogata, O.; Ino, Y.; Aoki, K.; Tanaka, S.; Ishida, K.; Kobayashi, T.; Sayo, N.; Saito, T. *Org. Process Res. Dev.* **2012**, *16*, 166.
- (18) (a) Balaraman, E.; Gnanaprakasam, B.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* **2010**, *132*, 16756. (b) Oldenhuis, N. J.; Dong, V. M.; Guan, Z. *Tetrahedron* **2014**, *70*, 4213.
- (19) TONs determined by GC-FID were in agreement with the values established by NMR. For example, for Table 3, entry 1, the TONs for methanol were 220 ± 31 (NMR) and 180 ± 23 (GC-FID). See Supporting Information (SI) for details.
- (20) (a) Noyori, R.; Ohkuma, T. *Angew. Chem., Int. Ed.* **2001**, *40*, 40. (b) Hamilton, R. J.; Bergens, S. H. *J. Am. Chem. Soc.* **2006**, *128*, 13700. (c) Clarke, M. L.; Diaz-Valenzuela, M. B.; Slawin, A. M. Z. *Organometallics* **2007**, *26*, 16. (d) Saudan, L. A.; Saudan, C. M.; Debieux, C.; Wyss, P. *Angew. Chem., Int. Ed.* **2007**, *46*, 7473. (e) Huff, C. A.; Sanford, M. S. *ACS Catal.* **2013**, *3*, 2412. (f) Dub, P. A.; Henson, N. J.; Martin, R. L.; Gordon, J. C. *J. Am. Chem. Soc.* **2014**, *136*, 3505.
- (21) (a) Jessop, P. G.; Hsiao, Y.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1994**, *116*, 8851. (b) Jessop, P. G.; Hsiao, Y.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1996**, *118*, 344. (c) Jessop, P. G. *The Handbook of Homogeneous Hydrogenation*; Wiley-VCH: Weinheim, 2008; p 489.
- (22) The direct hydrogenation of DMFA to CH<sub>3</sub>OH is another possible pathway. Although we cannot definitively rule this out, we believe that it is unlikely based on (i) the observed conversion of DMFA to DMF under the reaction conditions coupled with (ii) the higher electrophilicity of DMF versus DMFA. Additionally, the hydrogenation of HCO<sub>2</sub><sup>-</sup>NEt<sub>3</sub>H<sup>+</sup> (which cannot form the corresponding amide) under conditions similar to those in eq 2 yielded <10 turnovers of CH<sub>3</sub>OH (versus 99 turnovers for DMF hydrogenation). See SI for details.
- (23) 95 °C was selected because this temperature was found to be optimal for the hydrogenation of CO<sub>2</sub> to DMF (see Table S3 for details).
- (24) The use of <sup>13</sup>CO<sub>2</sub> for this reaction resulted in the formation of <sup>13</sup>CH<sub>3</sub>OH and H<sup>13</sup>C(O)NMe<sub>2</sub> as the products, as determined by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic analysis. See SI for details.