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Manganese-Catalyzed Sequential Hydrogenation of CO_2 to Methanol via Formamide

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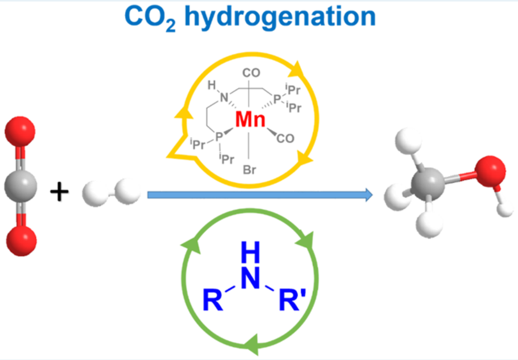
Supporting Information

ABSTRACT: Mn(I)-PNP pincer catalyzed sequential one-pot homogeneous CO_2 hydrogenation to CH_3OH by molecular H_2 is demonstrated. The hydrogenation consists of two parts—N-formylation of an amine utilizing CO_2 and H_2, and subsequent formamide reduction to CH_3OH, regenerating the amine in the process. A reported air-stable and well-defined Mn-PNP pincer complex was found active for the catalysis of both steps. CH_3OH yields up to 84% and 71% (w.r.t amine) were obtained, when benzylamine and morpholine were used as amines, respectively; and a TON of up to 36 was observed. In our opinion, this study represents an important development in the nascent field of base-metal-catalyzed homogeneous CO_2 hydrogenation to CH_3OH.

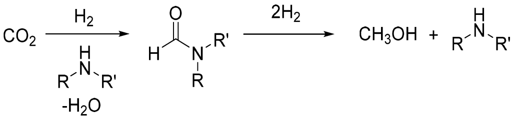


KEYWORDS: *homogeneous hydrogenation, CO_2 capture and utilization, Mn-pincer catalyst, methanol economy, CO_2 reduction to methanol*

The rapid increase in atmospheric CO_2 level due to human activities over the last three centuries has prompted the development of carbon capture processes. While most capture efforts have been focused on concentrated anthropogenic CO_2 sources like flue gases and various industrial activities, capture from diffuse sources like air has also gained attention.[1] Once captured, the CO_2 can be used as a feedstock for the synthesis of value-added products such as formic acid, methanol, methane, and higher hydrocarbons.[2] Among these, methanol represents a particularly attractive product as it can be used as a fuel (in direct methanol fuel cells, internal combustion engines, etc.), drop-in fuel additive, C1 source in organic transformations, or as a chemical precursor for the production of higher hydrocarbons.[3] Industrially, CH_3OH is produced from synthesis gas (CO, H_2, and CO_2) at high temperature and pressure over $Cu/ZnO/Al_2O_3$-based heterogeneous catalysts.[4] CH_3OH can also be produced from CO_2 hydrogenation with similar heterogeneous catalysts.[5] In the last 5 years, homogeneous catalysts, mainly based on noble metals like Ru and Ir, have also been reported for direct[6] and indirect[7] CO_2 reduction to CH_3OH with molecular H_2 at much lower temperatures and pressures.[8]

One of the promising pathways for CO_2 to CH_3OH reduction is via a formamide intermediate in the presence of an amine, first developed by the Sanford group (Scheme 1).[6e] The presence of an amine in the system provides a unique opportunity for its integration with carbon capture processes as was demonstrated by our group by converting directly CO_2 captured from air into CH_3OH.[6f] Such an integrated carbon capture and utilization process from diffused sources can facilitate the installation of small CCU units in remote areas, isolated from large carbon emission sources.

Scheme 1. CO_2 Hydrogenation to CH_3OH via Formamide



The development of first-row transition-metal-based catalysts is important because of the high abundance and low cost of such metals compared to more widely studied catalysts based on noble metals such as Pt, Ru, and Ir. It should be noted however that the cost and accessibility of the ligand should also be taken into consideration while designing such catalysts. Other crucial and most desirable features include high activity, high selectivity, and high durability, along with the ease of recyclability. Despite the growing attention that base-metal catalysis has received in recent years, surprisingly, only one study involving base-metal catalysts has been reported for the important process of CO_2 to CH_3OH reduction under homogeneous conditions.[9] That study, published by the Beller group in early 2017, employed an in situ generated Co-based catalyst to reduce CO_2 to CH_3OH with a TON of up to 78. Mn-based catalysts have been explored extensively for C−H activation.[10] In 2016, Beller et al. reported the catalytic

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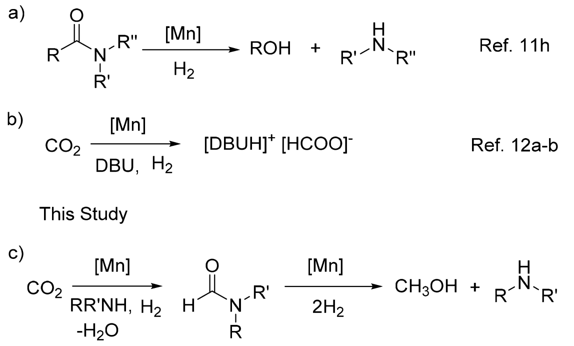
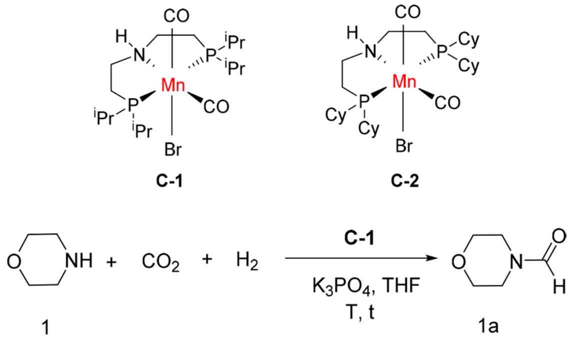
hydrogenation of aldehydes, ketones, and nitriles in the presence of Mn(I) complexes.[11a] Since then, several studies have successfully employed Mn(I) complexes for formic acid decomposition,[11b] N-alkylation,[11c] aqueous methanol reforming,[11e] N-formylation through CH_3OH dehydrogenation,[11f] ester hydrogenation,[11d,g] amide hydrogenation,[11h] alcohol deoxygenation,[11i] aminomethylation,[11j] and transfer hydrogenation.[11k] Based on some of these results, we wondered whether such catalysts based on inexpensive Mn(I) would be able to reduce CO_2 to CH_3OH. During the course of this study, two articles have surfaced, reporting successful CO_2 reduction to formate salts and formamide.[12] In the present study, we show for the first time that CO_2 can be sequentially reduced in the same pot by 3 eq. of H_2 to CH_3OH in the presence of Mn(I) catalyst **C-1** and an amine (Scheme 2, Table 1).[13] A maximum TON of 36 was achieved, which is comparable to the TON reported earlier with Co-based homogeneous catalysts.

Scheme 2. Mn(I)-Catalyzed Reductions



In the initial stage of this study, we investigated the effectiveness of Mn-pincer complexes **C-1** and **C-2** for the reduction of CO_2 to formamide in the presence of morpholine (**1**) (Table 1).[14,15] Such Mn(I)-PNP pincer catalysts were previously reported, as mentioned earlier, as active for aldehyde, ketone and nitrile reduction, formic acid decomposition, and for CH_3OH dehydrogenation.[11a,b,e] Satisfyingly, catalyst **C-1** was also able to reduce CO_2 in the presence of **1**, K_3PO_4 and molecular H_2 at 120 °C in THF, and the corresponding product, 4-formylmorpholine (**1a**), was observed through ^1H NMR in 65% yield after 24 h (Table 1, entry 1). Decreasing the reaction temperature to 110 °C increased the yield to 77% (entry 2). However, decreasing the temperature further was found to produce less **1a** after 24 h (entry 3). A higher yield was observed with a longer reaction time (entry 4), increasing catalyst loading (entry 5), or when the reaction was performed at a higher pressure of 70 bar (entry 6). Catalyst **C-2**, $MnBrPNP^{Cy}(CO)_2$ was less effective than **C-1** for this reduction (entry 7). Among solvents, THF was found to be the most suitable, while less polar solvents such as toluene, cyclopentyl methyl ether (CPME), and cyclohexane provided lower yields (entry 8−10). *t*-BuOK was found to be similarly effective as K_3PO_4 as an initial activator of catalyst **C-1** (entry 11). Further, catalyst **C-1** was reported in the literature as being air stable even after 25 days, leading us to wonder whether the reaction could be performed in the absence of an inert atmosphere. Selective N-formylation products were observed (conversion 59%, yield 53%) even when the reaction was set up without using a glovebox with commercially bought chemicals (see SI), but the yield was lower (Table 1, entry 12; compared to entry 5). Upon opening the reaction vessel, a brownish yellow solution was observed instead of a yellow solution, generally obtained when reactions were performed under inert atmosphere, indicating a probable catalyst decomposition taking place with the reaction set up in air.

Table 1. Optimization of N-Formylation of 1[a]



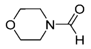
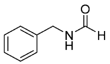
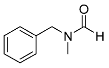
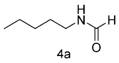
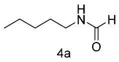
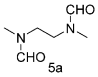
entry	*P* (bar)	*T* (°C)	time (h)	solv.	yield (%)[b]
1	60	120	24	THF	65
2	60	110	24	THF	77
3	60	100	24	THF	53
4	60	110	36	THF	92
5[c]	60	110	24	THF	93
6	70	110	24	THF	90
7[d]	60	110	36	THF	66
8	60	110	36	Ph−CH_3	65
9[c]	60	110	24	CPME	43
10[c,e]	60	110	24	Cy	32
11[c,e]	60	110	24	THF	95
12[c,f]	60	110	36	THF	53

[a]Reaction conditions: morpholine (2 mmol), cat. (0.5 mol %), K_3PO_4 (2.5 mol %), solvent (2 mL), CO_2: H_2 (1:1). [b]Yields were determined w.r.t amine from ^1H NMR spectra (N−CHO peaks) using 1,3,5-trimethoxybenzene (TMB) as an internal standard. [c]Morpholine (1 mmol), cat. (2 mol %), K_3PO_4 (10 mol %). [d]Catalyst **C-2** (0.5 mol %) was used. [e]*t*-BuOK (10 mol %) was used instead of K_3PO_4. [f]Set up in benchtop condition, Na_2CO_3 (10 mol %) was used as *t*-BuOK and K_3PO_4 are too hygroscopic to store under an open atmosphere. NMR yield calculations error = ± 5%.

Among various amines, benzylamines reacted to afford formamide products in high yields. For example, benzylamine (**2**) and *N*-methylbenzylamine (**3**) were converted to the corresponding −NCHO products, **2a** and **3a**, after 24 h at 2 mol % catalyst loading and a CO_2:H_2 (1:1) pressure of 60 bar in 93% and 94% yields, respectively (Table 2, entry 2−3). On the other hand, alkyl amines, such as primary amylamine (**4**) and secondary *N,N'*-dimethylethylenediamine (**5**) produced moderate *N*-formyl yields even at higher pressures and catalyst loadings (entry 4−6).

Having explored the first reaction step in this sequential reduction process, we proceeded to investigate the feasibility of in situ reduction of the generated formamides. A study on catalyst **C-1**'s effectiveness for formamide reduction showed that at 70 bar of H_2 pressure, **1a** can be reduced to morpholine and CH_3OH with a 64% CH_3OH yield (TON = 128) at 0.5 mol % catalyst loading in THF after 24 h (Table 3, entry 1). Expectedly, when we subjected the in situ formamide from the reaction mixture from Table 1, entry 4 (T1, E4) to 70 bar H_2 pressure at 150 °C for 36 h, reduction of the in situ formed **1a** was indeed observed with 11% of CH_3OH formation (TON = 22) (Table 3, entry 2), although the TON was lower. 78% of

Table 2. N-Formylation of Various Amines[†]

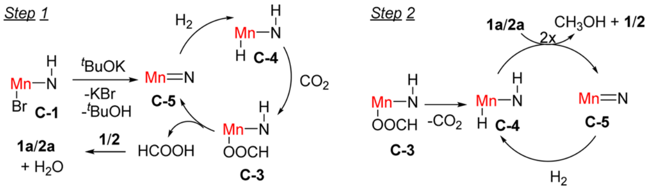
Entry	Product	**C-1** (mol %)	P (bar)	Time (h)	Yield (%)[a]
1	 1a	2	60	36	95
2	 2a	2	60	24	93
3	 3a	2	60	24	94
4	 4a	2	60	24	25
5[b]	 4a	4	70	36	53
6[b]	 5a	4	60	24	43

[†]Reaction conditions: amine (1 mmol), **C-1** (2 mol %), *t*-BuOK (10 mol %), THF (2 mL), CO_2: H_2 (1:1), 110 °C [a]Yields were determined w.r.t amines from ^1H NMR spectra (N−CHO peaks) using TMB as an internal standard. [b]Amine (0.5 mmol) *t*-BuOK (20 mol %). NMR yield calculations error = ± 5%.

unreduced **1a** was also observed. An increase in the catalyst loading and H_2 pressure to 2 mol % and 80 bar, respectively, increased both CH_3OH yield and TON (= 36), with only 6% of the in situ generated **1a** remaining in the reaction mixture after 36 h (entry 3). Generation of CH_3OH (~71%) and morpholine (~83%) were confirmed through ^1H and ^{13}C spectra (Figure S6). Similarly, when the reaction mixture from Table 2, entry 2 was used as the in situ formamide, 46% CH_3OH (TON = 23) was observed after 24 h at 80 bar and a **C-1** loading of 2 mol % (entry 4). A higher CH_3OH yield of 84% (TON = 21) was obtained when 4 mol % **C-1** was used (entry 5). Notably, no N−CH_3 side-products were observed through ^1H and ^{13}C NMR, and no trace of CO was detected in GC during hydrogenation of the in situ formed formamides.

Next, mechanistic studies were performed to gain an understanding of the active catalytic species formed in the reaction mixture. When 40 μmol of **C-1** was treated with 60 bar of CO_2: H_2 (1:1) in the presence of *t*-BuOK (0.3 mmol) and **1** (0.2 mmol) in THF-d_8 (1 mL) at 110 °C, a yellow solution was obtained after 6 h. The ^{31}P NMR spectrum of the solution showed the presence of a major peak at 87.4 ppm along with a minor peak due to catalyst **C-1** at 82.3 ppm (Figure S9B). In the ^1H NMR, one N−H triplet peak was observed at 7.1 ppm (*J* = 11.6 Hz) along with a singlet at 8.4 ppm (Figure S9A). Product **1a** was also observed as a sharp singlet at 7.98 ppm. The new ^1H and ^{31}P peaks were assigned to the complex Mn(OOCH)PNP^{iPr}(CO)$_2$ (**C-3**) (Figure S1), which is formed in the reaction mixture through CO_2 insertion into in situ formed complex MnHNP^{iPr}(CO)$_2$ (**C-4**) (Scheme 3, step 1).

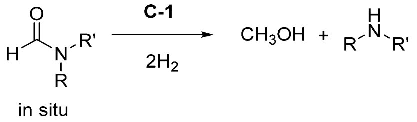
Scheme 3. A Plausible Mechanism



Interestingly, the complex **C-4** itself was not observed in the solution in either ^1H or ^{31}P NMR spectra, which can be due to its high reactivity. Complex **C-3** was found to be active for the reduction of pure **1a** to **1** and CH_3OH (Table S1, entry 2). We surmise that the complex **C-3,** formed during initial N-formylation step, gets decarboxylated during subsequent formamide reduction step at high H_2 pressure (70 bar) to form back active catalytic species **C-4,** which in turn reduces the in situ formed formamide (Scheme 3, step 2). Similar observations were recently reported by Gonsalvi et al. with another manganese-PNP complex.[12b] The presence of *t*-butoxide manganese species (**C-8**) (Figure S1) was also detected after the hydrogenation of in situ formed formamides (Figure S11−15).

Unfortunately, attempts of direct CH_3OH synthesis in one step with low CO_2 and high H_2 pressure failed to produce CH_3OH in the presence of **C-1**. When the reactor vessel was charged with 5 bar CO_2 and 85 bar H_2 and heated at 150 °C for 24 h in the presence of morpholine and **C-1**, only a minute amount (5%) of formamide was formed with no observable CH_3OH. When a stepwise temperature increase procedure was followed with an initial 24 h heating at 110 °C to allow the

Table 3. Hydrogenation of In Situ-Formed Formamides[a]



entry	formamide source	*P* (bar)	time (h)	N−CHO (%)[b]	amine (%)[b]	CH_3OH (%)[b,c]	TON
1	ex situ	70	24	trace	94	64	128
2	T1, E4	70	36	78	15	11	22
3	T2, E1	80	36	6	83	71	36
4	T2, E2	80	24	52	#	46	23
5[d]	T2, E2	80	36	5	#	84	21

[a]Reaction conditions: reaction mixtures from Table 1 or 2 (as specified) were subjected to H_2 pressure after the release of previous CO_2:H_2 (1:1) gas mixture. *T* = 150 °C. [b]Amount of formamide, amine, and CH_3OH were calculated w.r.t. amines from ^1H NMR spectra with TMB as internal standard. [c]Lower CH_3OH yields are due to losses, while releasing gases after reaction. [d]4 mol % of **C-1** loading. #benzyl CH_2 peak overlapped with THF peaks making quantification challenging. T1, E4 signifies Table 1, entry 4. NMR yield calculations error = ± 5%. TON = mol of CH_3OH formed per mol of **C-1**.

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formation of **1a**, followed by 36 h heating at 150 °C for subsequent formamide hydrogenation, 38% of **1a** was observed in the reaction mixture with only traces of CH_3OH formation. We suggest that under these conditions (5 bar CO_2, 85 bar H_2), the rates of both N-formylation and formamide reduction becomes sluggish (Table S2).

Finally, we decided to scale up the reaction with 10 mmol benzylamine at a low **C-1** loading (0.1 mol %) to observe the extent of catalytic efficiency of **C-1**. The first reduction step to formamide proceeded with 84% yield (TON_{N-CHO} = 840) after 48 h at 70 bar pressure (H_2: CO_2 = 1:1) and 110 °C. This is higher than the TON reported by Dubey et al. for formamide formation of secondary diethylamine using a Mn complex with 6,6′-dihydroxy-2,2′-bipyridine ligand. A TON_{MeOH} of 28 was observed for the subsequent hydrogenation of formed **2a** at 85 bar H_2 for 48 h. Thus, we conclude that the TON of **C-1** for CO_2 hydrogenation to CH_3OH is closer to the other reported first row transition-metal catalyst than the noble metal Ru-based pincer catalysts.[16]

In conclusion, CO_2 was hydrogenated to CH_3OH in the presence of an air-stable Mn(I)-pincer catalyst. This sequential CO_2 hydrogenation in the same pot produced CH_3OH in good yields with a maximum observed TON of 36. Our future efforts in this context will be toward direct CO_2 hydrogenation to CH_3OH by base-metal catalysts at lower pressures and temperatures.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.7b02066.

General information and experimental details (PDF)

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Notes

The authors declare no competing financial interest.

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