

Transformation of CO<sub>2</sub>

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## Low-Temperature Hydrogenation of Carbon Dioxide to Methanol with a Homogeneous Cobalt Catalyst

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Dedicated to Professor Lutz Friedjan Tietze on the occasion of his 75th birthday

**Abstract:** Herein we describe the first homogeneous non-noble metal catalyst for the hydrogenation of CO<sub>2</sub> to methanol. The catalyst is formed *in situ* from [Co(acac)<sub>3</sub>], Triphos, and HNTf<sub>2</sub> and enables the reaction to be performed at 100 °C without a decrease in activity. Kinetic studies suggest an inner-sphere mechanism, and *in situ* NMR and MS experiments reveal the formation of the active catalyst through slow removal of the acetylacetonate ligands.

Methanol is currently produced globally on a scale exceeding 70 million tons per year.<sup>[1]</sup> This large-scale production stems from its utility as a precursor for various important industrial products, such as formaldehyde, acetic acid, and bulk chemicals, including propene and other olefins produced by methanol-to-olefin (MTO), methanol-to-propene (MTP), and methanol-to-gasoline (MTG) processes.<sup>[2]</sup> Furthermore, methanol attracts significant attention as a hydrogen-storage material (12.5 wt % H<sub>2</sub>) and a drop-in liquid fuel as well as an energy carrier in methanol fuel cells. Its industrial utility combined with these promising energy applications has led to multiple proposals of a so-called “methanol economy”, in which methanol would be the central carbon and energy feedstock in a sustainable energy economy.<sup>[3]</sup>

Currently, methanol is produced from fossil fuels, especially natural gas, via syngas (mixture of CO, CO<sub>2</sub>, and H<sub>2</sub>).<sup>[4]</sup> For the more sustainable production<sup>[5]</sup> of methanol, the direct reduction of CO<sub>2</sub> is a highly interesting option if green hydrogen or renewable energy is used. In such a way, it would be possible to recycle atmospheric carbon as part of a carbon capture and recycling strategy (CCR), thus avoiding additional CO<sub>2</sub> emissions and replacing nonsustainable carbon sources.<sup>[6]</sup> So far, the hydrogenation of CO<sub>2</sub> to methanol has been studied intensively with heterogeneous catalysts.<sup>[7]</sup> A large library of active catalysts has been developed, but most require high temperatures (> 200 °C) to operate. In contrast, homogeneous catalysts are potentially more active and energy efficient systems with high tunability through mech-

anistic insight. Despite these advantages, only recently have there been the first reports of homogeneous catalysts for CO<sub>2</sub> hydrogenation to methanol.<sup>[1b,8]</sup> Most of these catalysts are based on ruthenium phosphine complexes, which indeed functioned under milder conditions (125–165 °C). Moreover, detailed mechanistic insight into an active catalyst has been obtained.<sup>[9]</sup>

Notably, Laurency and co-workers recently reported indirect methanol production from CO<sub>2</sub> at room temperature by the use of a formic acid disproportionation strategy in the presence of a homogeneous iridium catalyst.<sup>[10]</sup> However, for cost-effective production, catalysts that are based on abundant, non-noble metals (such as iron, cobalt, or copper) will be needed. To the best of our knowledge, no homogeneous non-noble metal catalysts for CO<sub>2</sub> hydrogenation to methanol are currently known. This need, coupled with a recent interest in cobalt-catalyzed hydrogenation reactions,<sup>[11]</sup> prompted us to investigate the ability of various cobalt complexes to catalyze the direct hydrogenation of CO<sub>2</sub> to methanol.

The starting point for our investigation was a recent elegant study by de Bruin and co-workers,<sup>[12]</sup> who demonstrated that Co(BF<sub>4</sub>)<sub>2</sub>/Triphos (Triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane) catalyzed the hydrogenation of esters and carboxylic acids. Interestingly, under similar conditions, little formation of methanol from carbon dioxide was observed (TON = 3; Table 1, entry 1). Variation of the reaction parameters led to an improved turnover number (TON) of 16 at 140 °C (Table 1, entry 2). Other cobalt precursors tested only afforded small amounts of ethyl formate and no desired methanol (Table 1, entries 3–6). Remarkably, the addition of BF<sub>3</sub>·Et<sub>2</sub>O to [Co(acac)<sub>3</sub>] (acac = acetylacetonate) in the presence of Triphos gave the same catalytic activity as observed for Co(BF<sub>4</sub>)<sub>2</sub> (Table 1, entry 7). This result highlights the importance of the weakly coordinating counterion in the system; this counterion might be needed to stabilize an active cationic cobalt complex.

To investigate this effect in more detail, we studied the use of various Lewis and Brønsted acids in combination with [Co(acac)<sub>3</sub>]/Triphos (Table 1, entries 8–15). The addition of HBF<sub>4</sub>·Et<sub>2</sub>O improved the catalytic activity further (Table 1, entry 8). Unfortunately, other Brønsted acids, such as PTSA or triflic acid, turned out to be inactive (Table 1, entries 9 and 10). The addition of some other metal triflates gave catalytically active systems, although they were less active than that with HBF<sub>4</sub>·Et<sub>2</sub>O (Table 1, entries 12 and 13). Remarkably, when HNTf<sub>2</sub> (Tf = trifluoromethanesulfonyl) was tested, the highest TON of 31 was observed for the formation of methanol (Table 1, entry 14). In contrast, only a trace

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**Table 1:** [Co]/Triphos-catalyzed CO<sub>2</sub> hydrogenation to methanol: Variation of the catalyst and reaction conditions.<sup>[a]</sup>

Entry	[Co]	Additive	TON CH <sub>3</sub> OH <sup>[b]</sup>	TON HCOOEt <sup>[b]</sup>
1 <sup>[c]</sup>	Co(BF <sub>4</sub> ) <sub>2</sub> ·6 H <sub>2</sub> O	–	3	n.d.
2	Co(BF <sub>4</sub> ) <sub>2</sub> ·6 H <sub>2</sub> O	–	16	2
3	Co(ClO <sub>4</sub> ) <sub>2</sub> ·6 H <sub>2</sub> O	–	<1	2
4	CoSO <sub>4</sub> ·7 H <sub>2</sub> O	–	0	0
5	Co(NO <sub>3</sub> ) <sub>2</sub> ·6 H <sub>2</sub> O	–	0	3
6	[Co(acac) <sub>3</sub> ]	–	<1	2
7	[Co(acac) <sub>3</sub> ]	BF <sub>3</sub> ·Et <sub>2</sub> O	16	1
8	[Co(acac) <sub>3</sub> ]	HBf <sub>4</sub> ·Et <sub>2</sub> O	23	3
9	[Co(acac) <sub>3</sub> ]	PTSA <sup>[d]</sup>	0	2
10	[Co(acac) <sub>3</sub> ]	HOTf	<1	2
11	[Co(acac) <sub>3</sub> ]	Al(OTf) <sub>3</sub>	<1	1
12	[Co(acac) <sub>3</sub> ]	Yb(OTf) <sub>3</sub>	12	3
13	[Co(acac) <sub>3</sub> ]	Sn(OTf) <sub>2</sub>	10	4
14	[Co(acac) <sub>3</sub> ]	HNTf <sub>2</sub>	31	1
15	[Co(acac) <sub>3</sub> ]	LiNTf <sub>2</sub>	<1	1
16	[Co(acac) <sub>2</sub> ]	HNTf <sub>2</sub>	18	1
17	Co(OAc) <sub>2</sub> ·4 H <sub>2</sub> O	HNTf <sub>2</sub>	22	1
18	Co(BF <sub>4</sub> ) <sub>2</sub> ·6 H <sub>2</sub> O	HNTf <sub>2</sub>	28	1
19 <sup>[e]</sup>	[Co(acac) <sub>3</sub> ]	HNTf <sub>2</sub>	36	1
20 <sup>[e,f]</sup>	[Co(acac) <sub>3</sub> ]	HNTf <sub>2</sub>	0	1
21 <sup>[e,g]</sup>	[Co(acac) <sub>3</sub> ]	HNTf <sub>2</sub>	0	0
22 <sup>[e]</sup>	–	HNTf <sub>2</sub>	0	0
23 <sup>[e,h]</sup>	[Co(acac) <sub>3</sub> ]	HNTf <sub>2</sub>	40	1
24 <sup>[e,h,i]</sup>	[Co(acac) <sub>3</sub> ]	HNTf <sub>2</sub>	50	2

[a] Standard reaction conditions: [Co] (0.14 mmol), Triphos (0.28 mmol), additive (0.36 mmol), THF (8 mL), EtOH (3 mL), H<sub>2</sub> (60 bar), CO<sub>2</sub> (20 bar), 140 °C, 24 h. [b] TON = mmol product (mmol catalyst)<sup>-1</sup>. [c] Reaction conditions: [Co] (0.028 mmol), Triphos (0.028 mmol), THF (15 mL), H<sub>2</sub> (70 bar), CO<sub>2</sub> (35 bar), 100 °C, 22 h. [d] PTSA = *p*-toluenesulfonic acid. [e] The reaction was carried out with 0.42 mmol of HNTf<sub>2</sub>. [f] No Triphos was used. [g] No CO<sub>2</sub> was used. [h] The reaction was carried out at 100 °C. [i] The reaction was carried out at 70 bar H<sub>2</sub> and 20 bar CO<sub>2</sub>. n.d. = not determined.

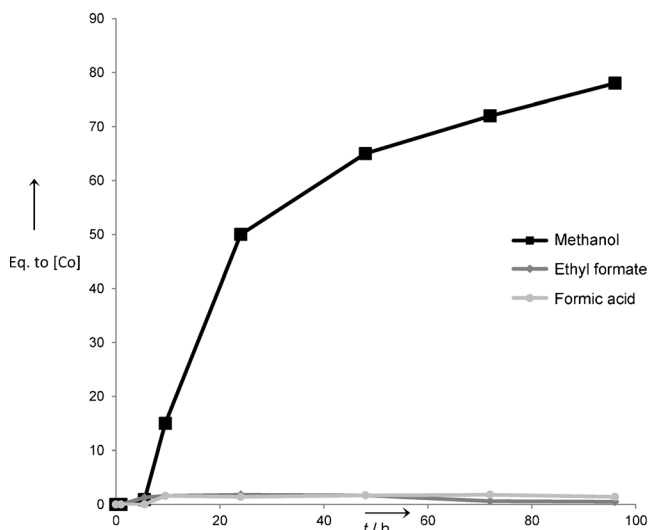
amount of methanol was detected when LiNTf<sub>2</sub> was used (Table 1, entry 15).

Among several cobalt precursors tested in the presence of Triphos and HNTf<sub>2</sub>, [Co(acac)<sub>3</sub>] afforded the most active system (Table 1, entries 16–18). Fine tuning of the [Co]/HNTf<sub>2</sub> ratio (see Figure S1 in the Supporting Information) revealed that a 1:3 relationship afforded the highest activity for the formation of methanol, whereas the best results were obtained when two equivalents of Triphos were used with respect to cobalt (see Table S1 in the Supporting Information). Other multidentate phosphine ligands did not show significant activity in this reaction (see Table S2).

To confirm that indeed a cobalt/phosphine-catalyzed hydrogenation of CO<sub>2</sub> to methanol was taking place under the reaction conditions, we carried out various control experiments. Without the ligand Triphos, no methanol was formed, although a small amount of ethyl formate was produced (Table 1, entry 20). In the absence of either [Co(acac)<sub>3</sub>] or CO<sub>2</sub>, no hydrogenation products were observed

(Table 1, entries 21 and 22). To our delight, this catalyst system was also active at a lower temperature: The performance of the system was virtually identical at 100 °C, with the formation of methanol with a TON of 40 (Table 1, entry 23). Apart from the Ru catalyst system recently reported by Leitner, Klankermayer, and co-workers,<sup>[9]</sup> this catalyst is the first homogeneous or heterogeneous catalyst able to hydrogenate CO<sub>2</sub> to methanol at 100 °C. Interestingly, our system did not show a decrease in activity. Finally, when the hydrogen pressure was increased from 60 to 70 bar, the TON increased slightly to 50 (Table 1, entry 24; see also Table S3). When a Co(BF<sub>4</sub>)<sub>2</sub>/Triphos/HNTf<sub>2</sub> system was tested at 100 °C, very low activity was detected, thus indicating the formation of a different catalyst species (see Table S4).

With the optimized system in hand, we wanted to gain more insight into the formation of the active catalyst as well as the mechanism of the reaction. To this end, we monitored over time the concentration of the three hydrogenation products: formic acid, ethyl formate, and methanol (Figure 1, Table 2). This homogeneous catalyst was stable and active for more than 4 days. The observed maximum TON corresponds to a methanol yield of 12 % with respect to CO<sub>2</sub> and is thus comparable to some of the homogeneous ruthenium-based systems developed by Olah, Prakash, and co-workers.<sup>[1b]</sup> The

**Figure 1.** Graph showing the concentration of methanol, ethyl formate, and formic acid with respect to time for CO<sub>2</sub> hydrogenation to methanol under the catalysis of [Co(acac)<sub>3</sub>]/Triphos/HNTf<sub>2</sub>. See Table 2 for the reaction conditions.**Table 2:** Monitoring of the concentration of methanol, ethyl formate, and formic acid with respect to time for CO<sub>2</sub> hydrogenation to methanol under the catalysis of [Co(acac)<sub>3</sub>]/Triphos/HNTf<sub>2</sub>.<sup>[a]</sup>

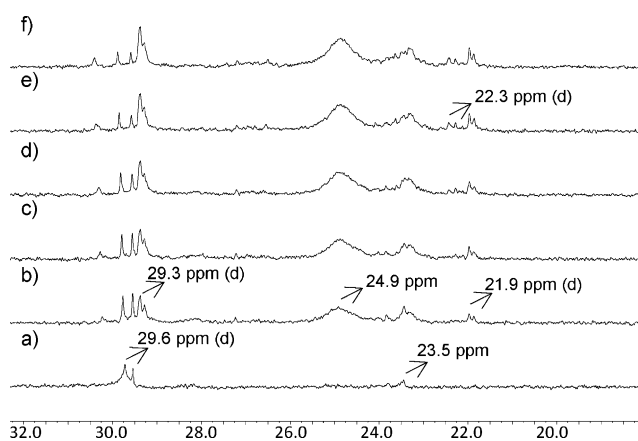
t [h]	1	5.5	9.5	24	48	72	96
TON CH <sub>3</sub> OH <sup>[b]</sup>	0	0.9	15	50	65	72	78
TON HCOOEt <sup>[b]</sup>	0	1.3	1.6	1.8	1.7	0.6	0.5
TON HCOOH <sup>[b]</sup>	0	0	1.6	1.4	1.7	1.8	1.4

[a] Reaction conditions: [Co(acac)<sub>3</sub>] (0.14 mmol), Triphos (0.28 mmol), HNTf<sub>2</sub> (0.42 mmol), THF (8 mL), EtOH (3 mL), H<sub>2</sub> (70 bar), CO<sub>2</sub> (20 bar), 100 °C. [b] TON = mmol product (mmol catalyst)<sup>-1</sup>.

formation of formic acid and ethyl formate over the course of the reaction raises the question as to whether these compounds are intermediates in the formation of methanol.<sup>[12]</sup> To examine this possibility, we carried out separate hydrogenation experiments of both compounds. Under the optimal reaction conditions (100 °C, 70 bar of H<sub>2</sub>, 5.6 mol % of [Co], 24 h; see the Supporting Information), formic acid and ethyl formate were hydrogenated to methanol in 59 and 66 % yield, respectively. The concentration–time graph in Figure 1 shows no significant accumulation of formic acid derivatives. If a stepwise mechanism for CO<sub>2</sub> hydrogenation to methanol is assumed, this result suggests that the hydrogenation of the intermediates is not rate-limiting. However, the relatively slow hydrogenation of either formic acid or ethyl formate contradicts this hypothesis. Furthermore, in control experiments in which no significant amount of methanol was formed, we still observed similar amounts of ethyl formate (Table 1, entries 6 and 20). On the basis of these observations, we propose that formic acid and ethyl formate are only formed as part of a minor reaction pathway. Thus, methanol formation mainly takes place through an inner-sphere mechanism. Notably, as compared to the [Ru]/Triphos system,<sup>[8b]</sup> the cobalt catalyst did not show a decrease in activity at 100 °C, which might indicate a different rate-limiting step in the inner-sphere mechanism. Previous reports support this difference in the rate-limiting step.<sup>[9,12]</sup> This intrinsic feature could provide potential for more energy efficient, cobalt-based systems. Interestingly, the addition of formic acid at the start of the reaction inhibited catalysis (see Scheme S1 in the Supporting Information). To exclude other intermediates/side products, we analyzed the gas phase of the reaction after a reaction time of 96 h (see the Supporting Information). Only CO<sub>2</sub>, H<sub>2</sub>, and a small amount of N<sub>2</sub> (probably originating from air) were detected, whereas CO, methane, or volatile ethers, such as DME or ethyl methyl ether, were not observed (detection limit: > 0.1 vol %). With this catalyst, CO was not hydrogenated to methanol (see Scheme S2), thus excluding the possibility of a CO-based pathway.

Notably, the concentration–time graph (Figure 1) shows a pronounced induction period of around 6–8 h. This feature prompted us to study the formation of the active catalyst *in situ* by high-pressure NMR spectroscopy. Thus, we followed the reaction for 8 h at 100 °C under 10 bar CO<sub>2</sub>/30 bar H<sub>2</sub> in [D<sub>8</sub>]THF (see Figure S2 for details). Figure 2 depicts the measured <sup>31</sup>P{<sup>1</sup>H} spectra in the 20–30 ppm region, which is in the range of phosphine ligands coordinated to cobalt.<sup>[13]</sup> Upon heating to 100 °C, a doublet at  $\delta_p = 29.6$  ppm appeared, along with a poorly resolved feature at  $\delta_p = 23.5$  ppm. After 1 h 25 min at 100 °C, the resolution of the doublet at  $\delta_p = 29.6$  ppm had increased, whereas the feature at  $\delta_p = 23.5$  ppm had increased in intensity. Furthermore, at this time, two new doublets appeared at  $\delta_p = 29.3$  and 21.9 ppm, which probably correspond to the same species, as well as a broad signal at  $\delta_p = 24.9$  ppm.

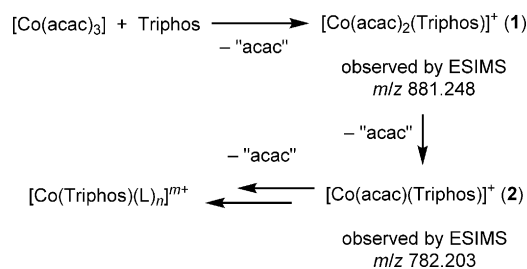
When heating was continued, the intensity of the pair of signals at  $\delta_p = 29.3$  and 21.9 ppm increased, along with an increase in intensity of the two broad features at  $\delta_p = 23.5$  and 24.9 ppm. The signal at  $\delta_p = 29.6$  ppm, however, appeared to decrease in intensity, thus indicating that the corresponding



**Figure 2.** <sup>31</sup>P{<sup>1</sup>H} spectra in the 20–30 ppm region for the mixture [Co(acac)<sub>3</sub>]/Triphos/HNTf<sub>2</sub> in [D<sub>8</sub>]THF under CO<sub>2</sub> (10 bar) and H<sub>2</sub> (30 bar) at 100 °C after: a) 5 min; b) 1 h 25 min; c) 3 h 10 min; d) 4 h 10 min; e) 5 h 50 min; f) 8 h.

species, which was formed upon heating, was consumed. Additionally, after heating for 5 h 50 min, a new doublet at  $\delta_p = 22.3$  ppm appeared. These results show that on a time-scale of several hours, after the initial formation of a cobalt–phosphine complex, the initial species is consumed, and multiple new complexes are formed.

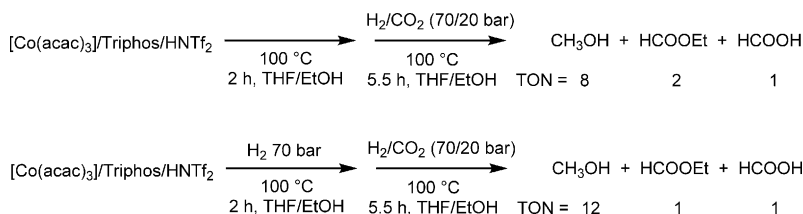
For a better understanding of the nature of the cobalt complexes formed under the reaction conditions, we carried out high-resolution electrospray ionization mass spectrometry (HRESIMS) experiments. In a sample taken after a reaction time of 1 h, two major cobalt species were detected: [Co(acac)<sub>2</sub>(Triphos)]<sup>+</sup> (**1**, [M]<sup>+</sup>, *m/z* 881.248) and [Co(acac)(Triphos)]<sup>+</sup> (**2**, [M]<sup>+</sup>, *m/z* 782.203; see Figure S3a). Since no methanol was observed after that time, we conclude that these two complexes are not catalytically active. In a sample taken after 16 h, **1** was no longer detected, whereas **2** was still present (see Figure S3b). This observation indicates that **1** is an intermediate consumed during the reaction and excludes the possibility that **2** is only a fragment of **1**. On the basis of these findings and the *in situ* NMR data, the following pathway for the formation of the active catalyst can be proposed (Scheme 1): After initial coordination of Triphos and [Co(acac)<sub>2</sub>(Triphos)]<sup>+</sup> formation, the remaining acac ligands are removed stepwise to liberate the active, cationic cobalt–Triphos species, which is stabilized by NTf<sub>2</sub><sup>-</sup>. The slow removal of the acac ligands explains the induction period of



**Scheme 1.** Proposed pathway for the formation of the active catalyst from [Co(acac)<sub>3</sub>]/Triphos.

several hours. A similar induction period was recently observed in iron-catalyzed hydrosilylation owing to the strong coordination of a carboxylate ligand.<sup>[14]</sup>

Following this reasoning, the induction period should be avoided if the removal of acac ligands is assisted before the reaction starts. Indeed, we found that when the reaction solution was heated at 100 °C for 2 h before H<sub>2</sub> and CO<sub>2</sub> were added, the formation of methanol after 5.5 h was improved by one order of magnitude (Scheme 2). Preheating in the presence of H<sub>2</sub> (70 bar) slightly improved the activity further, thus suggesting the reductive activation of the acac-containing precatalysts.



**Scheme 2.** Catalyst preformation from [Co(acac)<sub>3</sub>]/Triphos/HNTf<sub>2</sub> at 100 °C as well as at 100 °C in the presence of hydrogen. Reaction conditions: [Co(acac)<sub>3</sub>] (0.14 mmol), Triphos (0.28 mmol), HNTf<sub>2</sub> (0.42 mmol), THF (8 mL), EtOH (3 mL).

In conclusion, we have developed the first homogeneous non-noble metal catalyst able to hydrogenate CO<sub>2</sub> to methanol. Furthermore, the cobalt/Triphos-based system can catalyze the reaction at 100 °C without a decrease in activity, which is unprecedented. Kinetic in situ NMR and MS studies suggest an inner-sphere mechanism catalyzed by a cationic cobalt/Triphos complex, which is formed after slow removal of the acac ligands. Overall, we hope that this report will inspire the development of novel, homogeneous catalysts based on non-noble metals for more efficient hydrogenation reactions of CO<sub>2</sub> to methanol.

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## Conflict of interest

The authors declare no conflict of interest.

**Keywords:** carbon dioxide · cobalt · homogeneous catalysis · hydrogenation · methanol

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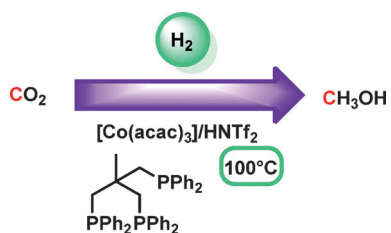
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## Communications

Transformation of CO<sub>2</sub>

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Low-Temperature Hydrogenation of  
Carbon Dioxide to Methanol with  
a Homogeneous Cobalt Catalyst



**A humble catalyst with modest needs:** A non-noble metal catalyst was developed for the efficient hydrogenation of CO<sub>2</sub> to methanol. The catalyst formed in situ from [Co(acac)<sub>3</sub>], 1,1,1-tris(diphenylphosphinomethyl)ethane (Triphos), and HNTf<sub>2</sub> was able to produce methanol from CO<sub>2</sub> at just 100°C (see scheme).