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# Production of Methane by Catalytic Decarboxylation of Methyl Formate as a Liquid Surrogate

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**ABSTRACT:** Methane is a widely utilized molecule, primarily sourced from fossil fuels and it finds numerous applications in the energy sector. More sustainable sources of methane include the conversion of organic wastes or gaseous CO<sub>2</sub>. An alternative would be to use a sustainable C<sub>1</sub> intermediate able to form methane. To this end, this work demonstrates the utilization of methyl formate as a liquid surrogate for methane, and its selective decomposition by catalytic decarboxylation. This reaction exhibited excellent yields, exceeding 90%, and the method can be expanded to produce several alkanes from alkyl formates.

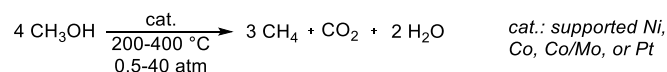
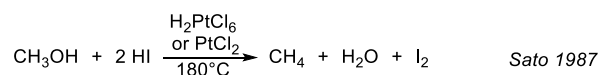
## INTRODUCTION

Natural gas is mostly composed of methane and accounts for 25 % of the primary energy consumed in the world, totaling 3.94 billion m<sup>3</sup> in 2022.<sup>1-2</sup> The current extraction of natural gas is primarily sourced from fossil fuels. However, efforts to transition towards more sustainable productions have led to the development of alternative methods. Some companies aim to reduce their carbon footprint by producing and using local, low-carbon energy. Biogas facilities employ anaerobic digestion to produce methane,<sup>3-4</sup> and methane can also be produced by the chemical hydrogenation of CO<sub>2</sub> to methane (the Sabatier reaction).<sup>5-10</sup> The former method relies on methanogens, capable of digesting organic wastes in anaerobic conditions.<sup>11-15</sup> This process produces methane in a mixture with CO<sub>2</sub>, which requires further purification. Conversely, the direct CO<sub>2</sub> hydrogenation to methane, often proceeds at elevated temperature and pressure (200-400°C, 5-15 bar).

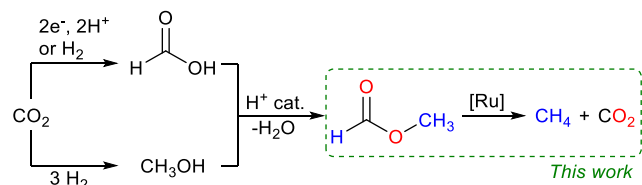
To achieve methane production from sustainable sources and milder conditions, one idea involves conducting the reaction in stages through an intermediary C<sub>1</sub> molecule capable of yielding methane. Methanol emerges as a viable candidate for this intermediary because it is the C<sub>1</sub> compound with the closest oxidation state to methane. It can be produced from CO<sub>2</sub> hydrogenation,<sup>16-18</sup> a process implemented in Iceland with the “George Olah CO<sub>2</sub> to renewable methanol plant” demonstrates the maturity of the process.<sup>19</sup> Nevertheless, the reduction of the C–O bond of methanol is challenging and requires most of the time heterogeneous metal catalysts working under harsh conditions (typical conditions use 300-400°C, under 0.5-40 bar of H<sub>2</sub>).<sup>20-26</sup> In the homogenous phase, Sato imagined in 1987 a reaction to form methane from methanol in the presence of two equivalents of a strong acid (HI) and a platinum catalyst (Scheme 1, top).<sup>27</sup> Low amount of methane was also observed by Foster when using an iridium catalyst and an iodide promoter in the carbonylation of methanol.<sup>28</sup> Although the reaction conditions are harsh, Sato’s strategy remains, to our knowledge, one of the few homogeneous paths, together with hydrosilylation,<sup>29-31</sup> to produce methane starting from methanol. In a broader context, many strategies are used for directly reducing

alcohols to alkanes in organic synthesis, including the Barton-Mac Combie reaction, the use of hydrosilanes,<sup>32-35</sup> the oxidation-Wolff Kischner sequence,<sup>36-38</sup> the dehydration-hydrogenation sequence,<sup>39-41</sup> and others.<sup>42-44</sup> However, these methods do not apply to methanol and require relatively toxic reagents and/or generate waste that adds to processing challenges. As an alternative to these shortcomings, we propose to reduce methanol with formic acid (FA) via the intermediate formation of methyl formate, FA being itself obtainable from CO<sub>2</sub> electroreduction<sup>45-47</sup> or hydrogenation (Scheme 1, bottom).<sup>48-51</sup>

### Literature examples for the reduction of methanol to methane



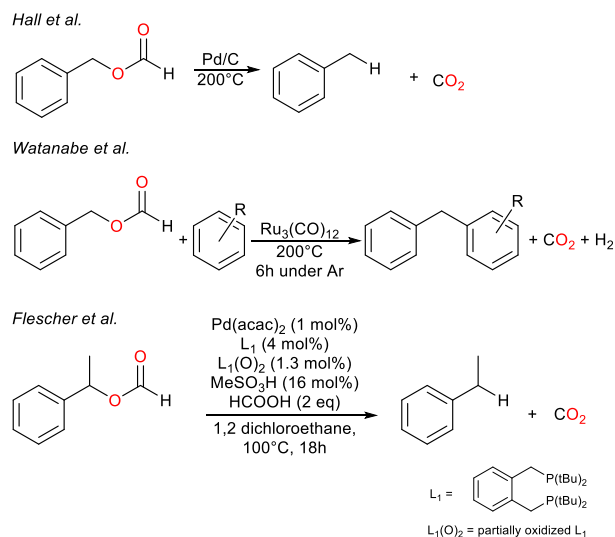
### Proposed strategy: utilization of methyl formate



### Scheme 1. top: Representative examples for the reduction of methanol to methane. Bottom: strategy for the use of methyl formate as a liquid surrogate for methane

Methyl formate is readily obtained by esterification of FA with methanol. It has been recently proposed as a hydrogen energy carrier thanks to ruthenium catalysts.<sup>52</sup> When using it as a liquid surrogate for methane, the main challenge relies in designing an efficient decarboxylation of this alkyl formate. Research into the decomposition of methyl formate has mainly focused on its decarbonylation via isomerization to acetic acid.<sup>53</sup> In some conditions, methane could be seen, like in Pruet’s

work on the isomerization of methyl formate with an iridium catalyst and methyl iodide as a promoter in the presence of water, which led to the inhibition of the formation of acetic acid in favor of methane.<sup>54</sup> Only few examples have been reported in the literature for the decarboxylation of organic formates and they mostly concern activated benzyl formates (Scheme 2). In 1970, Hall used palladium on carbon at 200 °C to convert benzyl formate to toluene with a yield of 97%.<sup>55</sup> Watanabe used benzyl formate as a benzylating reagent for arenes through decarboxylation using  $[\text{Ru}_3(\text{CO})_{12}]$  at 200 °C.<sup>56</sup> However, the reactive benzyl cation or radical formed under these conditions can activate the C–H bond in benzene, making recombination with the hydride to form toluene challenging with  $[\text{Ru}_3(\text{CO})_{12}]$  alone. In 2015, Fleischer demonstrated a single-step esterification and reductive decarboxylation from benzylic alcohols and formic acid using a palladium complex and an acid additive.<sup>57</sup> To our knowledge, the only example of activation of the C–O bond of an alkyl formate other than benzyl formate has been reported by Jenner, who showed that under CO,  $[\text{Ru}_3(\text{CO})_{12}]$ , and methyl iodide as an additive, methyl formate isomerizes to acetic acid at 200 °C.<sup>58–60</sup> Interestingly, minor quantities of methane were also formed as side-products. Herein, we report on the selective decarboxylation of methyl formate into methane, its scale up, and the extension of the catalytic methodology to other alkyl formates.

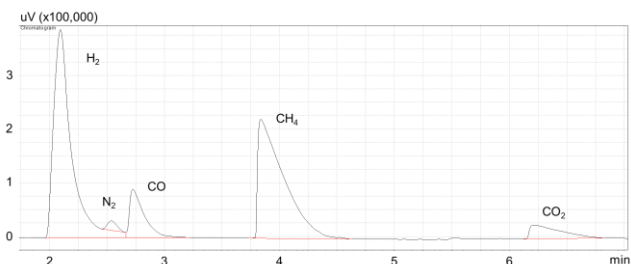


**Scheme 2:** State of the art in the decarboxylation of benzyl formates

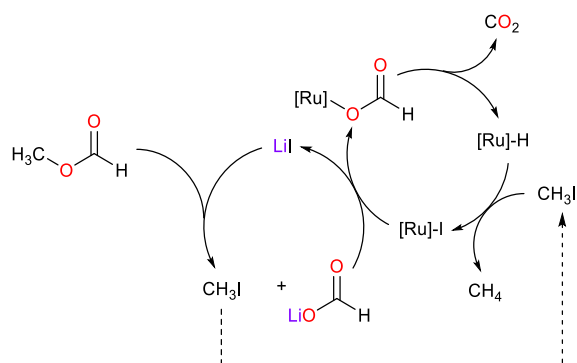
## RESULTS AND DISCUSSION

Starting with the system proposed by Jenner, we wished to quantify the amount of methane produced in the absence of CO, upon decomposition of methyl formate with  $[\text{Ru}_3(\text{CO})_{12}]$ : When methyl formate is heated at 160 °C in the presence of 3 mol% of  $[\text{Ru}_3(\text{CO})_{12}]$  and 20 mol% of LiI in THF, we observed after 24 h a conversion of 55 % of the starting methyl formate, and some methane could be observed in  $^1\text{H}$  NMR. However, we also observed the formation of 14 % of methanol and 13 % of methyl iodide, from the decarbonylation and nucleophilic substitution of methylformate respectively. No other liquid product was observed in  $^1\text{H}$  NMR, leading us to conclude that the remainder consisted of methane and  $\text{CO}_2$ , both identifiable in the GC chromatogram (Figure 1).

The decarboxylation reaction thus led to the formation of methane in 28 % yield. In order to improve the efficiency and the selectivity, we considered a plausible mechanism with intertwined catalytic cycles that involve: (i) facilitating the cleavage of the C–O bond of methyl formate by nucleophilic substitution, using lithium iodide, to form methyl iodide and lithium formate, (ii) decarboxylating the formate on the catalyst to form a metal hydride intermediate and (iii), transferring this hydride equivalent to methyl iodide, yielding methane (Scheme 3).<sup>61</sup>



**Figure 1:** Analysis of the head fraction of the gaseous phase of the experiment with  $\text{Ru}_3(\text{CO})_{12}$  as a catalyst (3 mol%) and lithium iodide as an additive (20 mol%) after 3 days of reaction at 160 °C



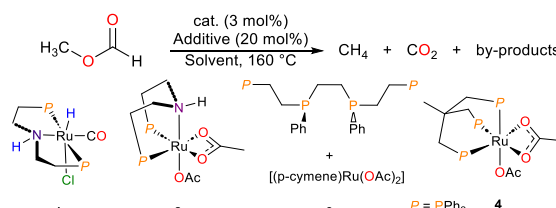
**Scheme 3.** Proposed mechanism for the formation of methane from methyl formate

First, a screening of catalysts was performed, using four ruthenium complexes known for their ability to form hydride species and/or perform decarboxylation reactions.<sup>62–63</sup> The decarboxylation of methyl formate was first tested with 3 mol% of  $[(\text{MACHO})\text{RuH}(\text{CO})\text{Cl}]$  **1**, efficient in the transfer hydrogenation of esters.<sup>62</sup> After 3 days at 160 °C in the presence of 20 mol% of LiI, we observed 23 % conversion, but only methyl iodide and methanol were observed by  $^1\text{H}$  NMR in 15 and 8 % yield respectively (Table 1, Entry 1). The acetate complex  $[(\text{MACHO})\text{Ru}(\text{OAc})_2]$  **2** led to lower conversion and only side-products were detected. (Table 1, Entry 2.). The combination of rac-P4 and  $[(p\text{-cymene})\text{Ru}(\text{OAc})_2]$  **3** was also tested, as it was described by Gonsalvi *et al.* to be efficient in the decarboxylation of formic acid to  $\text{H}_2$  and  $\text{CO}_2$ .<sup>63</sup> The conversion is significant (95 %) after 3 days, and only traces of methyl iodide and 7 % methanol are observed (Table 1, Entry 3). Finally,  $[(\text{triphos})\text{Ru}(\text{OAc})_2]$  **4**, also used in the disproportionation of formic acid,<sup>64–65</sup> was found to be the most efficient catalyst and full conversion was observed after 24 h, resulting in the selective formation of methane in 95 % yield: only traces of methanol and methyl iodide were observed (Table 1, Entry 4). Lowering the temperature to 100 °C was however detrimental to the catalytic activity, which drastically decreased, and only 8% of methyl formate was converted into methanol and methyl iodide:

no methane was observed in  $^1\text{H}$  NMR (Table 1, Entry 5). Blank experiments (Table 1, Entries 5 and 6) confirmed that both LiI and the ruthenium complex are required to obtain methane. Furthermore, LiI alone is able to form iodomethane, which supports our mechanistic hypothesis where iodomethane is a key intermediate of the reaction.

The influence of the solvent was then tested: replacing THF with an apolar solvent, benzene- $d_6$ , led to a very low (12 %) conversion and mostly methyl iodide was observed (Table 1, Entry 8.). In acetonitrile, the reaction did not form methane or methyl iodide, and only methanol as well as unidentified peaks were detected (Table 1, Entry 9), which may arise from the decomposition of acetonitrile.<sup>66</sup> In DMF- $d_7$ , methane was formed in 73 % yield, albeit together with 24 % of methanol after three days of reaction (Table 1, Entry 10).

**Table 1 Optimization of reaction conditions**



Entry	Cat.	Addit.	Solvent	Conv. (%) <sup>[a]</sup>	CH <sub>3</sub> I (%) <sup>[a]</sup>	CH <sub>3</sub> OH (%) <sup>[a]</sup>	CH <sub>4</sub> (%) <sup>[b]</sup>
1	1	LiI	THF- $d_8$	23	15	8	-
2	2	LiI	THF- $d_8$	14	< 5	< 5	-
3	3	LiI	THF- $d_8$	95	< 5	7	86
4 <sup>[c]</sup>	4	LiI	THF- $d_8$	100	< 5	< 5	95
5	4	-	THF- $d_8$	-	-	-	-
6	-	LiI	THF- $d_8$	14	11	< 5	-
7 <sup>[c,d]</sup>	4	LiI	THF- $d_8$	8	5	< 5	-
8	4	LiI	C <sub>6</sub> D <sub>6</sub>	12	8	< 5	-
9	4	LiI	CD <sub>3</sub> CN	80	- <sup>[e]</sup>	9	- <sup>[e]</sup>
10	4	LiI	DMF- $d_7$	97	-	24	73
11	4	LiI / LiBF <sub>4</sub>	THF- $d_8$	19	19	-	-
12	4	LiBr	THF- $d_8$	69	< 5 <sup>[f]</sup>	< 5	64
13	4	NaI	THF- $d_8$	< 5	-	-	-
14	4	KI	THF- $d_8$	< 5	-	-	-
15	4	Ph <sub>4</sub> PI	THF- $d_8$	< 5	-	-	-

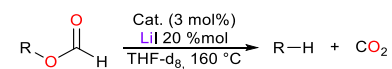
Reaction conditions : 0.14 mmol MeOCHO, 3 mol% catalyst, additive 20 mol%, 0.6 mL solvent, 3 days, 160 °C, [a] Determined by  $^1\text{H}$  RMN of crude mixture, mesitylene was used as internal standard, [b] computed by difference between conversion and yield of liquid products (ESI for more details), [c] reaction time of 24 h, [d] 100 °C, [e] degradation of acetonitrile, [f] CH<sub>3</sub>Br

Other additives were also tested, starting with LiBF<sub>4</sub> which, according to Han,<sup>67</sup> facilitates the cleavage of the C–O bond in aryl methyl ethers. In that case however, the catalytic activity was totally lost even though methyl iodide was still formed (Table 1, Entry 11). Switching lithium iodide to use larger cations such as potassium, PPh<sub>4</sub><sup>+</sup>, or sodium was also deleterious to the catalytic activity, and no conversion was observed (Table 1,

Entries 13, 14 and 15.). Replacing LiI with LiBr allowed the formation of methane in 64 % yield, with only traces of MeBr and MeOH (Table 1, Entry 12). Such modifications did not improve the catalytic activity further, and we continued to use 3 mol% of **4**, together with 20 mol% of LiI, in THF, at 160 °C, for the rest of the study. Incidentally, on this optimized system, when methyl formate and LiI are replaced by a 1:1 mixture of lithium formate and methyl iodide, we observed, after 24 h at 160 °C, a conversion of 78 % and an intense peak of methane in  $^1\text{H}$  NMR, confirming our previous mechanistic hypotheses.

We then tested this system to other alkyl formates to assess its versatility. The reactions were performed under optimized conditions, monitoring the reaction by  $^1\text{H}$  NMR until the maximum conversion was reached (Table 2). While full conversion for methyl formate was obtained in 24 hours (Table 2, Entry 1), ethyl formate was decomposed much more slowly (91 % conversion in 7 days), mainly producing ethane together with traces of the decarbonylation product (ethanol) and the elimination product, ethylene (Table 2, Entry 2). No reaction was observed with butyl formate. When benzyl formate was used, full conversion was observed in less than 48 hours, but the selectivity dropped, and only 48 % toluene was obtained (Table 2, Entry 3). Side-products include 32 % of benzyl alcohol and 8 % of benzaldehyde. These compounds may have been formed through decarbonylation of the formate, leading to benzyl alcohol. The latter can be further dehydrogenated to benzaldehyde.<sup>68</sup> To enhance selectivity, we employed the more sterically hindered catalytic system **3** expected to exhibit reduced C–H bond insertion in benzyl formate, thus minimizing decarbonylation. As anticipated, this led to improved selectivity, with 84% toluene observed after 48 hours of heating (Table 2, Entry 4).

**Table 2 Catalytic decarboxylation of selected alkyl formates**

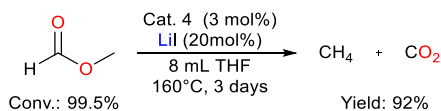


Entry	Substrate (R)	Cat.	Reaction time <sup>[b]</sup>	Conv. (%) <sup>[c]</sup>	Observed products
1	CH <sub>3</sub>	4	24 h	100	CH <sub>4</sub> < 5 % CH <sub>3</sub> OH < 5 % CH <sub>3</sub> I
2	CH <sub>3</sub> CH <sub>2</sub>	4	7 days	91	C <sub>2</sub> H <sub>6</sub> major 7% CH <sub>3</sub> CH <sub>2</sub> OH C <sub>2</sub> H <sub>4</sub> traces
3	Ph-CH <sub>2</sub>	4	48 h	100	48% PHCH <sub>3</sub> 32% PhCH <sub>2</sub> OH 8 % PhCHO 12% PhCH <sub>2</sub> I
4	Ph-CH <sub>2</sub>	3	48 h	98	84% PHCH <sub>3</sub> < 5 % PhCH <sub>2</sub> OH 8 % PhCHO

[a] Reaction conditions: 0.14 mmol alkyl formate, 3 mol% catalyst, LiI 20 mol%, 0.6 mL THF- $d_8$ , 160 °C. [b] Reaction time for maximum conversion. [c] Determined by  $^1\text{H}$  RMN of the crude mixture, mesitylene was used as internal standard

Finally, to showcase the applicability of the reaction on a larger scale, the decarboxylation of methyl formate was carried out in a 50 mL Parr autoclave (Scheme 4). For this experiment, the concentration of methyl formate and the volume of the reaction were increased respectively from 0.24 M and 0.6 mL at NMR scale to 0.7 M and 8 mL. After 3 days of reaction, we were

pleased to observe an increase in pressure from 1.0 to 5.9 bar, and GC analysis of the gas phase showed that it was composed of a 62/32/6 % mixture of methane, CO<sub>2</sub> and H<sub>2</sub> (the more soluble CO<sub>2</sub> was also detected by NMR, in the liquid mixture, accounting for the lower percentage than methane), corresponding to 91 % yield. In <sup>1</sup>H NMR, only traces of methyl formate remained, together with 7.5 % of methanol. The production of methane reached 132 mL (T = 285 K, ΔP = 4.9 bar) for a 0.36 mL input of methyl formate. This validated that methyl formate could indeed serve as a liquid surrogate containing 27 wt% of methane. It could be used as a means to transport it in a safe manner, and generate methane at high pressure for further use.



**Scheme 4. Scale up for the decarboxylation of methyl formate into methane**

## CONCLUSION

In this communication, the decarboxylation of methyl formate to methane was achieved using a ruthenium triphos bis acetate catalyst and lithium iodide as an additive in THF, with yields up to 95 %. The reaction involves methyl iodide and lithium formate as key intermediates. A small scope of alkyl formates was tested and the reaction proved applicable to ethyl formate and benzyl formate. A scale-up reaction showcased the production of 132 mL of methane from 0.36 mL of methyl formate, the latter serving as a liquid surrogate containing 27 wt% methane.

## EXPERIMENTAL SECTION

### Catalytic decarboxylation of alkyl formate

In a typical experiment, a J. Young NMR tube was charged in a glovebox with the catalyst (4.2 μmol, 3 mol%), the additive (28 μmol, 20 mol%) and 0.6 mL of solvent. Then the tube was loaded with the internal standard (Mesitylene, 71 μmol) and the formate (0.14 mmol). The tube was immediately sealed and placed in an oil bath. The reaction progress was monitored using <sup>1</sup>H NMR spectroscopy over 3 days. The crude mixtures were analyzed using <sup>1</sup>H and <sup>13</sup>C spectroscopy. Identification of the corresponding alkanes, alcohols, or alkyl iodides, was confirmed through comparison to previous literature reports.

### Scaled-up decarboxylation of methyl formate

In a typical experiment, a vial was charged in a glovebox with the catalyst (174 μmol, 3 mol%), the additive (1.16 mmol, 20 mol%) and 8 mL of anhydrous THF. The internal standard (276 μmol of mesitylene) and methyl formate (5.79 mmol) were then added to the vial. The solution was collected from the vial with a syringe and injected into a Parr 50 mL stainless steel autoclave containing a glass insert. Before each reaction, autoclaves and inserts were washed out with acetone, heated for 2 h at 200 °C, and then cooled down and rinsed with acetone. Finally, the bottom part of the reactor and inserts were dried in the oven at 120 °C, and the top part was dried thanks to a heat gun.

The autoclave was purged with argon (3x10 bar) and heated to 160°C for three days. The reaction progress was monitored through the increase in pressure. After cooling down, a gas phase sample was taken with a gas-tight syringe and analyzed by gas chromatography. After depressurization, the crude mixture was transferred from the autoclave and measured, a 0.2 mL sample was collected diluted with THF-*d*<sub>8</sub>, and analyzed by <sup>1</sup>H and <sup>13</sup>C spectroscopy.

## ASSOCIATED CONTENT

### Supporting Information

Detailed experimental procedures, copy of NMR spectra and GC traces, calibration curves. The Supporting Information is available free of charge on the ACS Publications website.

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### Notes

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## REFERENCES

1. Natural gas consumption worldwide from 1998 to 2022. <https://www.statista.com/statistics/282717/global-natural-gas-consumption/> (accessed 19/03/2024).
2. BP *Statistical review of world energy*; 2023.
3. Molino, A.; Nanna, F.; Ding, Y.; Bikson, B.; Braccio, G., Biomethane production by anaerobic digestion of organic waste. *Fuel* **2013**, *103*, 1003-9.
4. Zamri, M. F. M. A.; Hasmady, S.; Akhiar, A.; Ideris, F.; Shamsuddin, A. H.; Mofijur, M.; Fattah, I. M. R.; Mahlia, T. M. I., A comprehensive review on anaerobic digestion of organic fraction of municipal solid waste. *Renew. Sust. Energ. Rev.* **2021**, *137*, 110637.
5. Garbarino, G.; Bellotti, D.; Riani, P.; Magistri, L.; Busca, G., Methanation of carbon dioxide on Ru/Al<sub>2</sub>O<sub>3</sub> and Ni/Al<sub>2</sub>O<sub>3</sub> catalysts at atmospheric pressure: Catalysts activation, behaviour and stability. *Int. J. Hydr. En.* **2015**, *40* (30), 9171-82.
6. Kirchner, J.; Anolleck, J. K.; Losch, H.; Kureti, S., Methanation of CO<sub>2</sub> on iron based catalysts. *Appl. Catal. B.-Environ.* **2018**, *223*, 47-59.
7. Li, W. H.; Nie, X. W.; Jiang, X.; Zhang, A. F.; Ding, F. S.; Liu, M.; Liu, Z. M.; Guo, X. W.; Song, C. S., ZrO<sub>2</sub> support imparts superior activity and stability of Co catalysts for CO<sub>2</sub> methanation. *Appl. Catal. B.-Environ.* **2018**, *220*, 397-408.
8. Aziz, M. A. A.; Jalil, A. A.; Triwahyono, S.; Ahmad, A., CO<sub>2</sub> methanation over heterogeneous catalysts: recent progress and future prospects. *Green Chem.* **2015**, *17* (5), 2647-63.
9. Len, T.; Luque, R., Addressing the CO<sub>2</sub> challenge through thermocatalytic hydrogenation to carbon monoxide, methanol and methane. *Green Chem.* **2023**, *25* (2), 490-521.
10. Su, X.; Xu, J.; Liang, B.; Duan, H.; Hou, B.; Huang, Y., Catalytic carbon dioxide hydrogenation to methane: A review of recent studies. *J. Energ. Chem.* **2016**, *25* (4), 553-65.
11. Söhngen, N. L., Sur le rôle du Méthane dans la vie organique. *Recl. Trav. Chim. Pays-Bas* **1910**, *29* (7), 238-74.
12. Stephenson, M.; Stickland, L. H., Hydrogenase: The bacterial formation of methane by the reduction of one-carbon

compounds by molecular hydrogen. *Biochemical Journal* **1933**, 27 (5), 1517-27.

13. Barker, H. A., Studies upon the methane-producing bacteria. *Archiv. Mikrobiol.* **1936**, 7 (1-5), 420-38.

14. Miller, T. L.; Wolin, M. J., Oxidation of hydrogen and reduction of methanol to methane is the sole energy source for a methanogen isolated from human feces. *J Bacteriol* **1983**, 153 (2), 1051-5.

15. Keltjens, J. T.; Vogels, G. D., Conversion of Methanol and Methylamines to Methane and Carbon Dioxide. In *Methanogenesis*, Boston, MA, 1993; pp 253-303.

16. Jiang, X.; Nie, X.; Guo, X.; Song, C.; Chen, J. G., Recent Advances in Carbon Dioxide Hydrogenation to Methanol via Heterogeneous Catalysis. *Chem. Rev.* **2020**, 120 (15), 7984-8034.

17. Kar, S.; Goepfert, A.; Prakash, G. K. S., Integrated CO<sub>2</sub> Capture and Conversion to Formate and Methanol: Connecting Two Threads. *Acc. Chem. Res.* **2019**, 52 (10), 2892-903.

18. Sen, R.; Goepfert, A.; Surya Prakash, G. K., Homogeneous Hydrogenation of CO(2) and CO to Methanol: The Renaissance of Low-Temperature Catalysis in the Context of the Methanol Economy. *Angew. Chem. Int. Ed.* **2022**, 61 (42), e202207278.

19. Olah, G. A., Beyond oil and gas: the methanol economy. *Angew. Chem. Int. Ed.* **2005**, 44 (18), 2636-9.

20. Kiyoura, T.; Kogure, Y. Production of Methane. JPS6323826A, 1988/02/01/, 1988.

21. Shimizu, S.; Satou, S.; Konuki, K.; Nakajima, H.; Ikezoe, Y. Obtaining Method of Methane from Methanol with Hydrogen Polyiodide Solution. JPS5815927A, 1983/01/29/, 1983.

22. Saperstein, D. D. Catalytic process for obtaining methane from methanol. US4182926A, 1980/01/08/, 1980.

23. Spitz, P. H.; Frank, M. E. Liquid Phase Methanol Gasification. US3920716A, 1975/11/18/, 1975.

24. Balkenende, A. R.; Debokx, P. K.; Geus, J. W., Methane Formation from Methanol on Ni/SiO<sub>2</sub>, Ni/Al<sub>2</sub>O<sub>3</sub> and Ni/TiO<sub>2</sub> Catalysts. *Appl. Catal.* **1987**, 30 (1), 47-56.

25. Nuñez, G. M.; Fenoglio, R. J.; Resasco, D. E., Enhanced methane production from methanol decomposition over Pt/TiO<sub>2</sub> catalysts. *React. Kinet. Catal. Lett.* **1989**, 40 (1), 89-94.

26. Shan, J.; Xue, Y.; Wang, D.; Chen, Z.; Zhu, S., Direct production of ethanol with high yield from glycerol via synergistic catalysis by Pd/CoOx and Cu/SBA-15. *Appl. Catal. B.-Environ.* **2022**, 302, 120870.

27. Onuki, K.; Shimizu, S.; Nakajima, H.; Ikezoe, Y.; Sato, S., Study of Catalytic Reduction of Methanol for Methane-Methanol Thermochemical Hydrogen-Production Cycles. *Int. J. Hydr. En.* **1987**, 12 (8), 555-9.

28. Forster, D., Kinetic and spectroscopic studies of the carbonylation of methanol with an iodide-promoted iridium catalyst. *Journal of the Chemical Society, Dalton Transactions* **1979**, 1639-45.

29. Chen, J.; Falivene, L.; Caporaso, L.; Cavallo, L.; Chen, E. Y., Selective Reduction of CO<sub>2</sub> to CH<sub>4</sub> by Tandem Hydrosilylation with Mixed Al/B Catalysts. *J. Am. Chem. Soc.* **2016**, 138 (16), 5321-33.

30. Huang, W.; Roisnel, T.; Dorcet, V.; Orione, C.; Kirillov, E., Reduction of CO<sub>2</sub> by Hydrosilanes in the Presence of Formamidates of Group 13 and 12 Elements. *Organometallics* **2020**, 39 (5), 698-710.

31. Luconi, L.; Rossin, A.; Tuci, G.; Gafurov, Z.; Lyubov, D. M.; Trifonov, A. A.; Cicchi, S.; Ba, H.; Pham-Huu, C.; Yakhvarov, D.; Giambastiani, G., Benzoimidazole-Pyridylamido Zirconium and Hafnium Alkyl Complexes as Homogeneous Catalysts for Tandem Carbon Dioxide Hydrosilylation to Methane. *ChemCatChem* **2018**, 11 (1), 495-510.

32. Chatgililoglu, C.; Ferreri, C.; Landais, Y.; Timokhin, V. I., Thirty Years of (TMS)<sub>3</sub>SiH: A Milestone in Radical-Based Synthetic Chemistry. *Chem. Rev.* **2018**, 118 (14), 6516-72.

33. Cook, A.; MacLean, H.; St Onge, P.; Newman, S. G., Nickel-Catalyzed Reductive Deoxygenation of Diverse C-O Bond-Bearing Functional Groups. *ACS Catal.* **2021**, 11 (21), 13337-47.

34. Drosos, N.; Ozkal, E.; Morandi, B., Catalytic Selective Deoxygenation of Polyols Using the B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>/Silane System. *Synlett* **2016**, 27 (12), 1760-4.

35. Jang, D. O.; Kim, J. G.; Cho, D. H.; Chung, C. M., Radical deoxygenation of alcohols via their trifluoroacetate derivatives with diphenylsilane. *Tet. Lett.* **2001**, 42 (6), 1073-5.

36. Bauer, J. O.; Chakraborty, S.; Milstein, D., Manganese-Catalyzed Direct Deoxygenation of Primary Alcohols. *ACS Catal.* **2017**, 7 (7), 4462-6.

37. Huang, J. L.; Dai, X. J.; Li, C. J., Iridium-Catalyzed Direct Dehydroxylation of Alcohols. *Eur. J. Org. Chem.* **2013**, 2013 (29), 6496-500.

38. Dai, X. J.; Li, C. J., En Route to a Practical Primary Alcohol Deoxygenation. *J. Am. Chem. Soc.* **2016**, 138 (16), 5433-40.

39. Liu, C. J.; Sun, J. M.; Brown, H. M.; Marin-Flores, O. G.; Bays, J. T.; Karim, A. M.; Wang, Y., Aqueous phase hydrodeoxygenation of polyols over Pd/WO<sub>3</sub>-ZrO<sub>2</sub>: Role of Pd-WO<sub>3</sub> interaction and hydrodeoxygenation pathway. *Catal. Today* **2016**, 269, 103-9.

40. Paulino, P. N.; Perez, R. F.; Figueiredo, N. G.; Fraga, M. A., Tandem dehydration-transfer hydrogenation reactions of xylose to furfuryl alcohol over zeolite catalysts. *Green Chem.* **2017**, 19 (16), 3759-63.

41. Furuta, A.; Hirobe, Y.; Fukuyama, T.; Ryu, I.; Manabe, Y.; Fukase, K., Flow Dehydration and Hydrogenation of Allylic Alcohols: Application to the Waste-Free Synthesis of Pristane. *Eur. J. Org. Chem.* **2017**, 2017 (10), 1365-8.

42. Chenneberg, L.; Baralle, A.; Daniel, M.; Fensterbank, L.; Goddard, J.-P.; Ollivier, C., Visible Light Photocatalytic Reduction of O-Thiocarbamates: Development of a Tin-Free Barton-McCombie Deoxygenation Reaction. *Adv. Synth. Catal.* **2014**, 356 (13), 2756-62.

43. Williams, O. P.; Chmiel, A. F.; Mikhael, M.; Bates, D. M.; Yeung, C. S.; Wickens, Z. K., Practical and General Alcohol Deoxygenation Protocol. *Angew. Chem. Int. Ed.* **2023**, 62 (18), e202300178.

44. Anwar, K.; Merckens, K.; Aguilar Troyano, F. J.; Gómez-Suárez, A., Radical Deoxygenation Strategies. *Eur. J. Org. Chem.* **2022**, 2022 (26), e202200330.

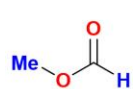
45. Al-Tamreh, S. A.; Ibrahim, M. H.; El-Naas, M. H.; Vaes, J.; Pant, D.; Benamor, A.; Amhamed, A., Electroreduction of Carbon Dioxide into Formate: A Comprehensive Review. *ChemElectroChem* **2021**, 8 (17), 3207-20.

46. Zhu, P.; Wang, H. T., High-purity and high-concentration liquid fuels through CO<sub>2</sub> electroreduction. *Nature Catal.* **2021**, 4 (11), 943-51.

47. Masel, R. I.; Liu, Z.; Yang, H.; Kaczur, J. J.; Carrillo, D.; Ren, S.; Salvatore, D.; Berlinguette, C. P., An industrial perspective on catalysts for low-temperature CO<sub>2</sub> electrolysis. *Nature Nanotech.* **2021**, *16* (2), 118-28.
48. Wang, W. H.; Himeda, Y.; Muckerman, J. T.; Manbeck, G. F.; Fujita, E., CO<sub>2</sub> Hydrogenation to Formate and Methanol as an Alternative to Photo- and Electrochemical CO<sub>2</sub> Reduction. *Chem. Rev.* **2015**, *115* (23), 12936-73.
49. Chen, X.; Liu, Y.; Wu, J. W., Sustainable production of formic acid from biomass and carbon dioxide. *Mol. Catal.* **2020**, *483*, 110716.
50. Zhai, S.; Jiang, S.; Liu, C.; Li, Z.; Yu, T.; Sun, L.; Ren, G.; Deng, W., Liquid Sunshine: Formic Acid. *J. Phys. Chem. Lett.* **2022**, *13* (36), 8586-600.
51. Jessop, P. G.; Hsiao, Y.; Ikariya, T.; Noyori, R., Homogeneous catalysis in supercritical fluids: Hydrogenation of supercritical carbon dioxide to formic acid, alkyl formates, and formamides. *J. Am. Chem. Soc.* **1996**, *118* (2), 344-55.
52. Sang, R.; Wei, Z.; Hu, Y.; Alberico, E.; Wei, D.; Tian, X.; Ryabchuk, P.; Spannenberg, A.; Razaq, R.; Jackstell, R.; Massa, J.; Sponholz, P.; Jiao, H.; Junge, H.; Beller, M., Methyl formate as a hydrogen energy carrier. *Nature Catal.* **2023**, *6*, 543-50.
53. Jüriling-Will, P.; Botz, T.; Franciò, G.; Leitner, W., A "Power-to-X" Route to Acetic Acid via Palladium-Catalyzed Isomerization of Methyl Formate. *ChemSusChem* **2022**, *15* (16), e202201006.
54. Pruett, R. L.; Kacmarcik, R. T., Reactions of formic acid. 1. The iridium-catalyzed synthesis of acetic acid from methyl formate. *Organometallics* **1982**, *1* (12), 1693-9.
55. Matthews, J. S.; Ketter, D. C.; Hall, R. F., Palladium-Catalyzed Reactions of Formate Esters. *J. Org. Chem.* **1970**, *35* (5), 1694-&.
56. Kondo, T.; Tantayanon, S.; Tsuji, Y.; Watanabe, Y., Ruthenium Complex Catalyzed Benzoylation of Arenes with Benzyl Formates - Decarbonylation and Decarboxylation of Alkyl Formates. *Tet. Lett.* **1989**, *30* (31), 4137-40.
57. Ciszek, B.; Fleischer, I., Homogeneous Palladium-Catalyzed Transfer Hydrogenolysis of Benzylic Alcohols Using Formic Acid as Reductant. *Chem. Eur. J.* **2018**, *24* (47), 12259-63.
58. Kheradmand, H.; Kiennemann, A.; Jenner, G., Homologation of carboxylic methyl esters via reductive carbonylation catalyzed by a cobalt-ruthenium mixed catalyst. *J. Organomet. Chem.* **1983**, *251* (3), 339-46.
59. Jenner, G.; Bitsi, G., Ruthenium-Catalyzed Carbonylation of Alcohols to Alkyl Formates. *J. Mol. Catal.* **1988**, *45* (2), 235-46.
60. Jenner, G., Homogeneous Catalytic Reactions Involving Methyl Formate. *Appl. Catal. A-Gen.* **1995**, *121* (1), 25-44.
61. Crochet, E.; Anthore-Dalion, L.; Cantat, T., Alkyl Formates as Transfer Hydroalkylation Reagents and Their Use in the Catalytic Conversion of Imines to Alkylamines\*\*. *Angew. Chem. Int. Ed.* **2023**, *62* (1), e202214069.
62. Kuriyama, W.; Matsumoto, T.; Ogata, O.; Ino, Y.; Aoki, K.; Tanaka, S.; Ishida, K.; Kobayashi, T.; Sayo, N.; Saito, T., Catalytic Hydrogenation of Esters. Development of an Efficient Catalyst and Processes for Synthesising (R)-1,2-Propanediol and 2-(1-Methoxy)ethanol. *Org. Proc. Res. Dev.* **2011**, *16* (1), 166-71.
63. Mellone, I.; Bertini, F.; Peruzzini, M.; Gonsalvi, L., An active, stable and recyclable Ru(II) tetraphosphine-based catalytic system for hydrogen production by selective formic acid dehydrogenation. *Catal. Sci. Technol.* **2016**, *6* (17), 6504-12.
64. Mellone, I.; Peruzzini, M.; Rosi, L.; Mellmann, D.; Junge, H.; Beller, M.; Gonsalvi, L., Formic acid dehydrogenation catalysed by ruthenium complexes bearing the tripodal ligands triphos and NP<sub>3</sub>. *Dalton Trans.* **2013**, *42* (7), 2495-501.
65. Savourey, S.; Lefevre, G.; Berthet, J. C.; Thuery, P.; Genre, C.; Cantat, T., Efficient disproportionation of formic acid to methanol using molecular ruthenium catalysts. *Angew. Chem. Int. Ed.* **2014**, *53* (39), 10466-70.
66. Mai, V. H.; Lee, S.-H.; Nikonov, G. I., Transfer Hydrogenation of Unsaturated Substrates by Half-sandwich Ruthenium Catalysts using Ammonium Formate as Reducing Reagent. *ChemistrySelect* **2017**, *2* (25), 7751-7.
67. Mei, Q.; Yang, Y.; Liu, H.; Li, S.; Liu, H.; Han, B., A new route to synthesize aryl acetates from carbonylation of aryl methyl ethers. *Sci. Adv.* **2018**, *4* (5), eaaq0266.
68. Tao, J. C.; Wen, L.; Lv, X. B.; Qi, Y.; Yin, H. L., Ruthenium(II)-PNN pincer complex catalyzed dehydrogenation of benzyl alcohol to ester: A DFT study. *J. Mol. Struct.* **2016**, *1110*, 24-31.

ToC Artwork:

Liquid surrogate of  
Methane



[Ru] catalyst

