Methanol Formation

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Efficient Disproportionation of Formic Acid to Methanol Using Molecular Ruthenium Catalysts[**]

*Solène Savourey, Guillaume Lefèvre, Jean-Claude Berthet, Pierre Thuéry, Caroline Genre, and Thibault Cantat**

***Abstract:** The disproportionation of formic acid to methanol was unveiled in 2013 using iridium catalysts. Although attractive, this transformation suffers from very low yields; methanol was produced in less than 2 % yield, because the competitive dehydrogenation of formic acid (to CO_2 and H_2) is favored. We report herein the efficient and selective conversion of HCOOH to methanol in 50 % yield, utilizing ruthenium(II) phosphine complexes under mild conditions. Experimental and theoretical (DFT) results show that different convergent pathways are involved in the production of methanol, depending on the nature of the catalyst. Reaction intermediates have been isolated and fully characterized and the reaction chemistry of the resulting ruthenium complexes has been studied.*

The efficient conversion of carbon dioxide to methanol is a key process in devising a methanol economy based on a closed carbon cycle.[1] Such an achievement requires the development of catalysts and methods to promote the six-electron reduction of CO_2 using carbon-free energy input with a high overall Faraday efficiency. The most obvious solution would rely on the direct electro-reduction of CO_2 to methanol [Eq. (1)]; yet current state-of-the-art catalysts proceed with only a low faradaic yield and a low selectivity at high overpotentials.[2] In contrast, hydrogen formation from the (photo)electro-reduction of water has witnessed compelling successes recently and such carbon-free sources of H_2 could serve for the reduction of CO_2 to methanol [Eq. (2)].[3] The hydrogenation of CO_2 to methanol has indeed been the focus of considerable effort and catalysts are proposed to overcome the kinetic stability of these two nonpolar gases.[4,5] In this respect, the conversion yield starting from H_2 is still limited because high H_2 pressure is required, leading to an overall low faradaic efficiency. An interesting alternative would consist in utilizing formic acid (FA) as a C−H bond shuttle in the reduction of CO_2 to methanol [Eq. (3)]. This strategy relies on the two-electron reduction of CO_2 to FA, in an electrochemical cell, and this methodology is now technically and economically available, thanks to efficient electrocatalysts.[6] Disproportionation of FA is then required to produce methanol. Although decomposition of FA usually proceeds by dehydrogenation or dehydration to form CO_2 and CO [Eqs. (4) and (5)],[7] Miller, Goldberg et al. showed, for the first time in 2013, that a molecular complex could promote the disproportionation of FA to methanol.[8] Using $[(C_5Me_5)Ir(bpy)(H_2O)][OTf]_2$ (bpy = 2,2′-bipyridine, OTf = trifluoromethanesulfonate) as a catalyst, aqueous solutions of FA could be converted to MeOH at 80 °C. Though promising, this strategy currently suffers from the use of expensive iridium catalysts and the yields of methanol do not exceed 1.9 %.[8] This effect primarily results from poor selectivity as 88 % of the reacted FA undergoes dehydrogenation instead of disproportionation. Catalysts with improved activity and selectivity are highly desirable to reach the potential of this approach. Herein, we report the efficient disproportionation of FA to methanol, with methanol yields of up to 50.2 %, using ruthenium molecular catalysts. Mechanistic insights are also provided, based on the isolation of reactive catalytic intermediates and DFT calculations.

CO_2 electroreduction

$$CO_2 + 6\,H^+ + 6\,e^- \xrightarrow{\text{catalyst}} CH_3OH + H_2O \qquad (1)$$

CO_2 hydrogenation

$$\begin{tikzcd} & CO_{2(g)} + 3\,H_{2(g)} \arrow[r, "\text{catalyst}", "\Delta G^\circ_2(298) = -2.2\text{ kcal/mol}"'] & CH_3OH_{(l)} + H_2O \qquad (2) \\ 6\,H^+ + 6\,e^- \arrow[ur, "\text{catalyst}"] & & \end{tikzcd}$$

Disproportionation of formic acid

$$\begin{tikzcd} & 3\,HCO_2H_{(l)} \arrow[r, "\text{catalyst}", "\Delta G^\circ_3(298) = -25.8\text{ kcal/mol}"'] & CH_3OH_{(l)} + 2\,CO_{2(g)} + H_2O_{(l)} \qquad (3) \\ 3\,(CO_2 + 2\,H^+ + 2\,e^-) \arrow[ur, "\text{catalyst}"] & & \end{tikzcd}$$

Dehydrogenation of formic acid

$$HCO_2H_{(l)} \xrightarrow[\Delta G^\circ_4(298) = -7.8\text{ kcal/mol}]{} CO_{2(g)} + H_{2(g)} \qquad (4)$$

Dehydration of formic acid

$$HCO_2H_{(l)} \xrightarrow[\Delta G^\circ_5(298) = -3.2\text{ kcal/mol}]{} CO_{(g)} + H_2O_{(l)} \qquad (5)$$

Ruthenium complexes are well-established catalysts in reduction chemistry and their potential was recently illustrated, by the groups of Milstein, Beller, and Leitner, in the

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[*] S. Savourey, Dr. G. Lefèvre, Dr. J.-C. Berthet, Dr. P. Thuéry, Dr. C. Genre, Dr. T. Cantat
CEA, IRAMIS, NIMBE, CNRS UMR 3299
91191 Gif-sur-Yvette (France)
E-mail: thibault.cantat@cea.fr
Homepage: http://iramis.cea.fr/Pisp/thibault.cantat/index.htm

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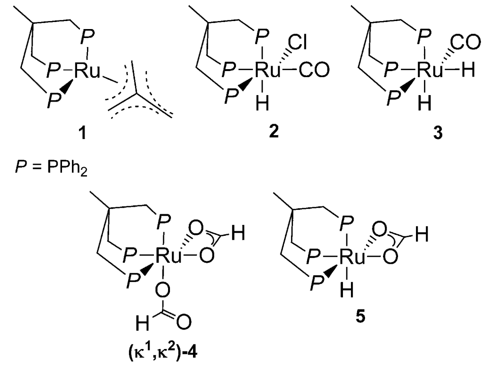
hydrogenation of a variety of reluctant substrates, such as CO_2, carbonates, carbamates, and amides.[9] In addition, ruthenium is less expensive than iridium ($75 per oz vs. $830 per oz in 2013). The disproportionation of formic acid was thus investigated, utilizing ruthenium(II) complexes supported by external phosphine ligands (Scheme 1, Table 1, and Table S1). To our delight, we observed that heating a THF solution of FA in a sealed vessel at 150 °C, in the presence of 0.6 mol% [Ru(COD)(methylallyl)$_2$] and 0.6 mol% $CH_3C(CH_2PPh_2)_3$ (triphos), resulted in the complete conversion of FA to produce methanol in 5.0% yield, after 1 h (entry 1, Table 1). This result corresponds to a 5.0% selectivity for the formation of methanol, meaning that 5.0% of the reacted C–H bonds in FA are efficiently converted to methanol. The remaining 95.0% of the C–H bonds are transformed to H_2 via dehydrogenation [Eq. (4)] and H_2 evolution was indeed confirmed by ^{1}H NMR spectroscopy. When $H^{13}CO_2H$ was utilized, $^{13}CH_3OH$ was formed and $^{13}CO_2$ was identified as the only organic by-product in this transformation and no trace of carbon monoxide, formaldehyde, or methylformate could be observed by ^{13}C NMR spectroscopy. The absence of CO was further confirmed by GC analysis of the gas mixture at the end of the reaction (see the Supporting Information (SI)). Interestingly, the reaction proceeds well in the absence of any additive or buffer, while pH < 2 must be maintained with HBF_4 when catalyst $[(C_5Me_5)Ir(bpy)(H_2O)](OTf)_2$ is utilized.[8]



Scheme 1. Precursor **1**, deactivated complexes **2** and **3**, and reaction intermediates **4** and **5** characterized from the ruthenium-catalyzed disproportionation of HCOOH to CH_3OH.

Table 1: Catalytic disproportionation of formic acid to methanol.

$$3\,HCO_2H \xrightarrow[\text{solvent, } T(^\circ C)\ \ 1-72\text{ h}]{0.6\text{ mol\% cat. } ([Ru(COD)(methylallyl)_2] + L)} CH_3OH + 2\,CO_2 + H_2O$$

Entry	FA [mmol]	L	Additive (1.5 mol%)	Solv. (0.3 mL)	T [°C]	t[a] [h]	CH_3OH yield [%]
1	0.6	triphos	–	THF	150	1	5.0
2	2.4	3 PPh_3	–	THF	150	1	< 0.1
3	2.4	2 dppe	–	THF	150	1	< 0.1
4	2.4	$(OP)_3$	–	THF	150	1	0.5
5	2.4	**1**[b]	–	THF	150	1	9.7[b]
6	2.4	triphos	–	THF	80	17	7.6
7	2.4	triphos	–	THF	40	72	1.0
8	2.4	triphos	–	THF	150	1	11.9
9[c]	4.8	triphos	–	THF	40	72	1.0
10[c]	4.8	triphos	–	THF	80	17	26.7
11[d]	0.8	triphos	–	THF	150	1	0.5
12[e]	1.6	triphos	–	THF	150	1	7.5
13	2.4	triphos	–	$CHCl_3$	150	1	1.2
14	2.4	triphos	–	C_7H_8	150	1	5.8
15	2.4	triphos	–	C_6H_6	150	1	7.4
16	2.4	triphos	NEt_3	THF	150	1	6.8
17	2.4	triphos	H_2O	THF	150	1	11.6
18	2.4	triphos	EtOH	THF	150	1	11.9
19	2.4	triphos	MSA	THF	150	1	50.2

Reaction conditions: cat. [Ru(COD)(methylallyl)$_2$] (0.6 mol%); yields determined by ^{1}H NMR spectroscopy in deuterated solvents, using mesitylene as an internal standard. [a] Reaction time required to achieve 100% conversion. [b] cat.: [Ru(triphos)(tmm)](0.6 mol%) (tmm = trimethylene methane). [c] 0.3 mol% cat. [d] 1 mol% cat. [e] 2 mol% cat.

Different supporting ligands and ruthenium precursors were then screened so as to improve the catalytic activity and selectivity (Table 1 and Table S1). With PPh_3, 1,2-bis(diphenylphosphino)ethane (dppe), $P(CH_2CH_2PPh_2)_3$ (PP_3), and 2,6-bis(diisopropylphosphinomethyl)pyridine as ligands, dehydrogenation of FA was observed with no formation of methanol (entries 2 and 3 in Table 1; experiments with the latter two ligands described in Table S1). However, replacing the triphos ligand with the triphosphinite $CH_3C(CH_2OPPh_2)_3$ $(OP)_3$ ligand led to the conversion of FA to methanol in 0.5% yield (entry 4, Table 1).

Importantly, the reaction temperature and the initial concentration of FA strongly influence the catalytic activity (entries 1 and 6–12, Table 1). Decreasing the initial quantity of FA from 2.4 to 0.8 mmol is accompanied by a decrease in MeOH yield from 11.9 to 0.5% (entries 8, 11, and 12). Noticeably, [Ru(COD)(methylallyl)$_2$] is known to react with triphos to afford complex **1** (Scheme 1), which was structurally characterized (Figure S14).[5b] The catalytic activity of **1** is similar to that of [Ru(COD)(methylallyl)$_2$] + triphos and MeOH was obtained in 9.7% yield (vs. 11.9% yield) with the isolated complex **1** (entries 5 and 8). Although the disproportionation reaction is efficient at 150 °C, it also proceeds well at 80 °C and is significantly slowed down only at temperatures below 40 °C. For example, the transformation of 2.4 mmol FA affords MeOH in 11.9 and 7.6% yield at 150 and 80 °C, respectively, while the yield drops to 1.0% at 40 °C (entries 6–8, Table 1). The nature of the solvent was also found to impact the outcome of the reaction. While the formation of MeOH proceeds equally well in toluene and benzene, it is considerably slower in $CHCl_3$ where MeOH is formed in a low 1.2% yield (entries 13–15, Table 1). In fact, the catalytic system was found to degrade in $CHCl_3$ at 150 °C, and yellow crystals of **2** deposited from the crude mixture within 24 h. X-ray analysis reveals that **2** is a ruthenium(II) hydrido chloride complex that coordinates one triphos ligand and one molecule of CO (Figure 1). The extra chloride ligand likely results from the abstraction of a Cl atom from the solvent by a Ru–H species.[10]

Another decomposition pathway of the Ru catalyst was also identified when the disproportionation of FA was carried out in benzene and toluene; after 24 h at 150 °C, crystals of [Ru(κ^3-triphos)(CO)(H)$_2$] (**3**) were obtained.[11] Although **3** proves inactive in the disproportionation of FA, it catalyzes

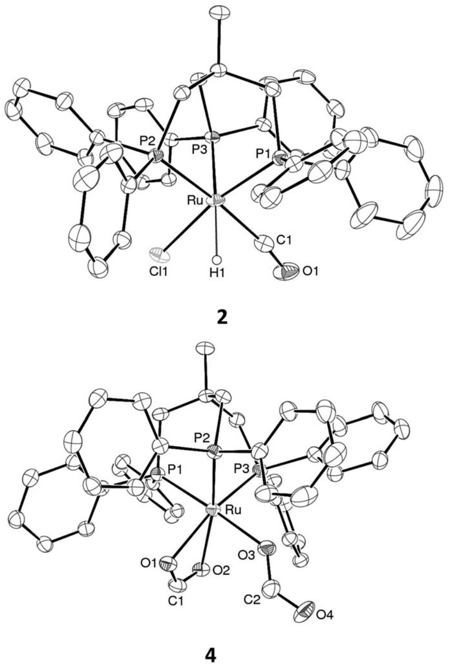
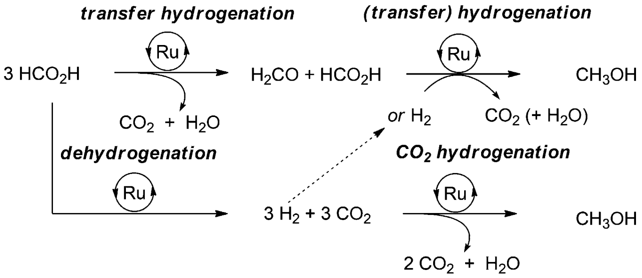


Figure 1. ORTEP views of complexes **2** (top) and **4**·THF (bottom). Solvent molecules and hydrogen atoms are omitted. Displacement ellipsoids are drawn at the 30% probability level.

efficiently its dehydrogenation [Eq. (4)], in agreement with a recent report by Peruzzini, Gonsalvi et al.[7b,c] Because the formation of CO complexes **2** and **3** was only observed 23 h after the complete conversion of FA, it is unlikely that **3** results from the dehydration of FA [Eq. (5)]. Moreover, Cole-Hamilton et al. have recently shown that ruthenium(II) carbonyl complexes can form by decarbonylation of aldehydes or alcohols under reducing conditions, and a similar route could account for the generation of **2** and **3** in the presence of methanol and/or formaldehyde.[9e,12] Based on these findings, the efficient disproportionation of 4.8 mmol HCOOH to MeOH was achieved in 26.7% yield using 0.3 mol% [Ru(COD)(methylallyl)$_2$] + triphos as a catalyst, after 17 h at 80 °C (entry 10, Table 1). This result corresponds to a complete conversion of FA and a selectivity of 26.7% for MeOH production and it affords a catalytic turnover number (TON) of 26 (TOF = 1.5 h^{-1}). In comparison, MeOH was only obtained in 1.9% yield (as a mixture of MeOH and methylformate), at best, with 0.002 mol% [(C$_5$Me$_5$)Ir(bpy)(H$_2$O)][OTf]$_2$, after 24 h at 80 °C.[8] Although the catalytic activity of iridium is somewhat greater than that of the present ruthenium system (TON = 156, TOF = 6.5 h^{-1}) it exhibits a low selectivity for MeOH production (7%).

In order to enhance further the productivity of MeOH, it is necessary to increase the selectivity of the reaction and favor the reduction of FA. In this respect, detailed experimental and mechanistic studies by Klankermayer, Leitner et al. have shown that acid promoters, such as methanesulfonic acid (MSA), could significantly boost the catalytic activity of [Ru(COD)(methylallyl)$_2$] + triphos or **1** in hydrogenation reactions, by facilitating the formation of reactive Ru–H species.[13] This strategy has been successfully utilized by the groups of Beller, Leitner, and Klankermayer to promote the methylation of amines with CO$_2$/H$_2$.[9c,d] Following this approach, the disproportionation of FA was explored using 0.6 mol% [Ru(COD)(methylallyl)$_2$] + triphos and 1.5 mol% MSA, at 150 °C (entry 19, Table 1). Under these conditions, FA is fully decomposed within 1 h leading to the formation of MeOH in 50.2% yield. To the best of our knowledge, this result represents the best selectivity obtained for the disproportionation of FA to MeOH.

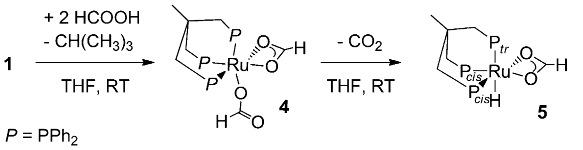
Different pathways can be proposed based on the possible organic intermediates involved in the disproportionation of FA (Scheme 2). FA can first undergo a catalytic reduction to formaldehyde by transfer hydrogenation using a second equivalent of FA. Since formaldehyde is highly reactive towards reduction, it is readily reduced to MeOH either by transfer hydrogenation (with a third equivalent of FA) or by hydrogenation (from the competitive dehydrogenation of FA).[14] Additionally, the competitive dehydrogenation of FA to H$_2$ and CO$_2$ can also converge to methanol, as long as the catalyst is able to promote the difficult hydrogenation of CO$_2$ to methanol (Scheme 2). In fact, the Leitner group demonstrated in 2013 that [**1**/MSA] was an efficient catalyst in the hydrogenation of CO$_2$ to MeOH above 120 °C in the presence of alcohols as promoters.[4b] Monitoring the product distribution for the disproportionation of FA catalyzed by [**1**/MSA] reveals that the dehydrogenation of FA is strongly favored at short reaction times and only 0.5% MeOH is formed once FA is fully consumed. Yet, MeOH production then increases over time via hydrogenation of CO$_2$ assisted by the catalytic amount of methanol formed at an earlier stage (Figure S7).[15] Importantly, in the absence of MSA, a distinct reaction profile was observed and the production of MeOH follows the consumption of FA and stops once FA is fully converted. In addition, the hydrogenation of CO$_2$ is unlikely under the mild conditions (< 120 °C) in the absence of MSA.[5b] These findings suggest that **1**, in the absence of MSA, promotes the disproportionation of FA via transfer hydrogenation. This conclusion also sheds some light on the influence of the initial concentration of FA on the selectivity of the reaction (vide supra). Indeed, both the dehydrogenation and the disproportionation of FA produce gases and, in a closed vessel, doubling the initial quantity of FA nearly generates a twofold increase in pressure (Entries 8, 11, 12 in Table 1). Yet, while the dehydrogenation of 1 mole FA produces 2 moles of gases,



Scheme 2. Proposed pathways for the disproportionation of formic acid to methanol.

its disproportionation to MeOH generates only 2/3 mole of gas. According to le Châtelier's law, the disproportionation of FA is thus favored over dehydrogenation, at high pressure (i.e. at high initial concentration of FA), leading to an increased selectivity towards MeOH production.

Using [Ru(COD)(methylallyl)$_2$] + triphos (or **1**) as a catalyst, the disproportionation of FA therefore proceeds by means of an unexplored transfer hydrogenation pathway and we then turned our attention to the role of the metal catalyst in this transformation. Complex **1** reacts at RT with 2 equiv FA in THF to afford the new complex **4** [Eq. (6)]. Crystals of **4** were successfully grown from a THF solution and its X-ray structure reveals the formation of a ruthenium(II) bis-formate complex, namely [Ru(triphos)(κ^1-OCHO)(κ^2-OCHO)]. A single C–H bond signal was observed for the two formate ligands in the ^{1}H (8.49 ppm) and ^{13}C NMR (172.3 ppm) spectra of **4**, revealing fluxional behavior at RT. Interestingly, **4** decarboxylates within minutes at RT to afford complex **5**. Based on ^{1}H, ^{13}C, and ^{31}P NMR and ESI-MS data, complex **5** can be formulated as the ruthenium(II) hydrido formate complex [Ru(triphos)(H)(κ^2-OCHO)], characterized by a typical [Ru]-H signal at $\delta = -2.42$ (dt, $^2J_{\mathrm{PcisH}} = 20$ Hz, $^2J_{\mathrm{PtransH}} = 124$ Hz) and a [Ru]-OCOH singlet at $\delta = 8.24$.[16] Notably, both **4** and **5** exhibit catalytic activity similar to that of **1** in the disproportionation of FA, thereby confirming their implication in this reaction. Furthermore, addition of 2 equiv FA to a THF solution of **4** resulted in the formation of a mixture of methanol, H$_2$, CO$_2$, and **5** within 48 h at RT [Eq. (7)]. This reactivity confirms that MeOH production does not result from the hydrogenation of CO$_2$ (which requires high H$_2$ pressure)[5b] but rather from the transfer hydrogenation of FA.

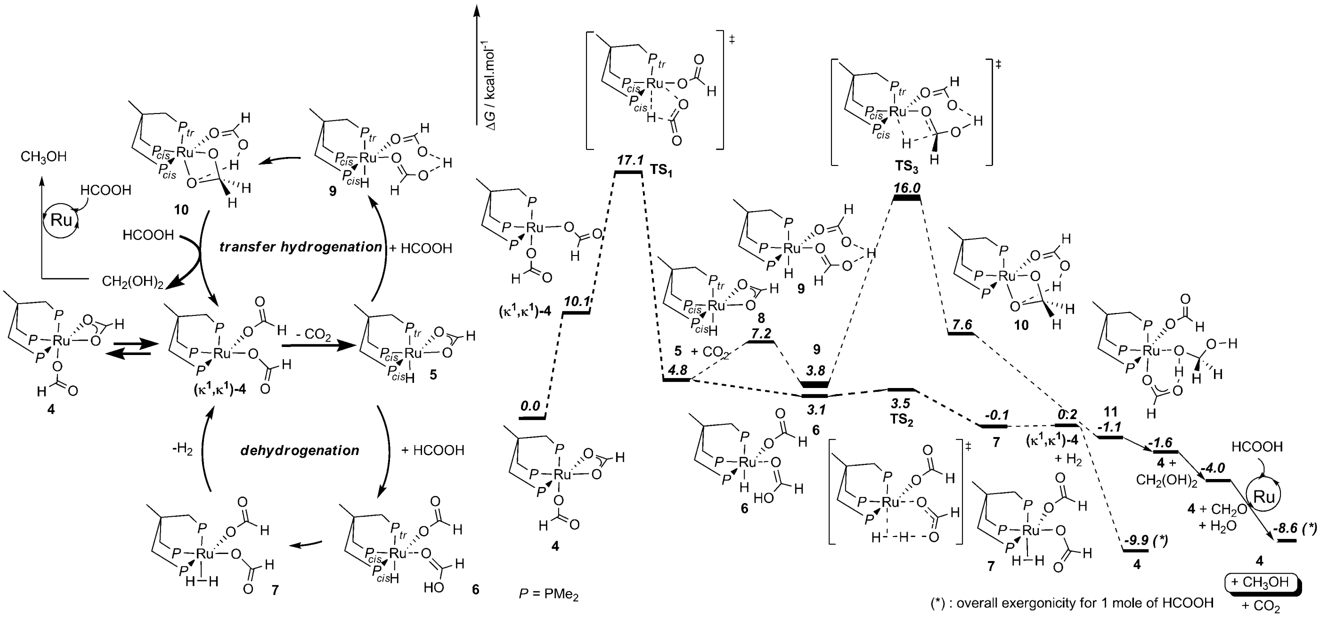


(6)

Scheme 3 lays out a plausible pathway for methanol formation supported by the available data and by DFT computations. Competition between the decomposition of formic acid (leading to H$_2$ and CO$_2$) and its disproportionation to MeOH has been investigated using DFT techniques, with the simplified CH$_3$C(CH$_2$PMe$_2$)$_3$ ligand in place of

$$4 + 2\,\mathrm{HCOOH} \xrightarrow[\text{THF, RT}]{} 5 + \mathrm{CH_3OH / CO_2 / H_2} \qquad (7)$$

triphos. Both pathways rely on the formation of **5** and its generation from **4** proceeds through the decoordination of one κ^2-OCHO formate ligand and decarboxylation of the unsaturated [Ru(triphos)(κ^1-OCHO)$_2$] ((κ^1,κ^1)-**4**) intermediate. This step requires a relatively low activation energy of $\Delta G^{\neq} = 17.1$ kcal mol^{-1}, consistent with the experimental findings [Eq. (7)].[17] Coordination of an incoming molecule of FA can provide either complexes **6** or **9**, which only differ by the presence of an H-bond between the two formate ligands in **9**. Yet, these two intermediates evolve along different routes. The presence of an acidic O–H functionality in **6** can quench the Ru–H group to produce H$_2$ and regenerate **4** with a very low activation barrier (0.4 kcal mol^{-1}). In contrast, the intramolecular H-bond in **9** decreases the acidity of the O–H function and, at the same time, increases the electrophilic character of the (κ^2-OCHO) formate ligand, thereby facili-



Scheme 3. Computed pathways for the catalytic disproportionation of FA to methanol and FA dehydrogenation to H$_2$ and CO$_2$ (at the M06/6-31 + G* (H,C,O,P) + SDD (Ru) level of theory).

tating a hydride migration to produce the acetal intermediate **10** with an activation energy of 12.2 kcal mol^{-1}. Protonolysis of **10** with FA can then regenerate **4** with the release of $H_2C(OH)_2$, which dehydrates to formaldehyde prior to its easy reduction to methanol.[14] As outlined in the computed energy surface (Scheme 3), the facial coordination of triphos to the Ru^{II} center favors a facial arrangement of the two formate ions in **4** and likely facilitates the transfer hydrogenation in $\mathbf{TS_3}$. Overall, this mechanism highlights that the decarboxylation of a formate ligand to produce a reactive Ru hydride species is the rate-determining step (RDS) and it precedes the divergent dehydrogenation/disproportionation pathways. Experimentally, we found that the disproportionation of HCO_2D, catalyzed by **1** indeed yielded a mixture of CH_3OD, CH_2DOD, and CHD_2OD, resulting from a hydride scrambling enabled by the formation of H–D complex **7** (see SI). As a result, the selectivity for the production of MeOH is under thermodynamic control. While the dehydrogenation of one molecule of FA is favored at low pressure ($\Delta G = -9.9$ kcal mol^{-1} vs. -8.6 kcal mol^{-1} for the disproportionation route), the formation of methanol by transfer hydrogenation is favored at high pressure, in agreement with the experimental findings. Further work is underway in our laboratories to translate these conclusions into the design of earth-abundant metal catalysts with increased selectivity for the production of methanol from FA.

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[13] F. M. Geilen, B. Engendahl, M. Holscher, J. Klankermayer, W. Leitner, *J. Am. Chem. Soc.* **2011**, *133*, 14349.

[14] The ability of complex **4** to promote the reduction of formaldehyde to methanol by transfer hydrogenation from FA was confirmed experimentally (see SI).

[15] It is also possible that under the applied conditions the dehydrogenation of FA to CO_2 and H_2 is reversible and [**1**/MSA] promotes the formation of MeOH through transfer hydrogenation from FA.

[16] The NMR data recorded for **5** are consistent with those reported for its acetate analogue [Ru(triphos)(H)(OAc)], see: B. Chaplin, P. J. Dyson, *Inorg. Chem.* **2008**, *47*, 47381.

[17] It is interesting to note the role played by the kinetic *trans* effect related to the hydrido ligand. Two conformations can indeed be considered for the transition state leading to the complex **4**. A mechanism involving a distorsion of the (P_{trans}RuH) angle (145.3°) is strongly unfavored (see SI) with a computed barrier 31.2 kcal mol^{-1} higher than that for a structure in which the (P_{trans}RuH) angle still close to 180° (171.1°). The labilization of the PMe_2 *trans* ligand in **5** is attested by the relative position of the P_{trans} signal in $^{31}P\{^1H\}$ NMR, which is at higher field than the two P_{cis} peaks (see SI), and by the longer computed P_{trans}–Ru bond (2.36 Å vs. 2.22 and 2.23 Å for the two P_{cis}–Ru bonds).