CO_2

$\downarrow$ + H_2O

$CO_{2(aq)}$ $\rightleftharpoons$ H_2CO_3

$\updownarrow$ - H^+ $pK_1 = 6.40$

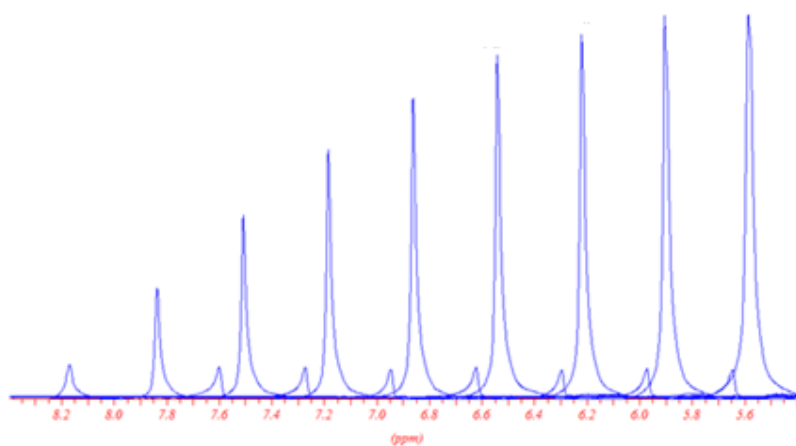HCO_3^-

$\updownarrow$ - H^+ $pK_2 = 10.30$

CO_3^{2-}

**Supplementary Figure 1. Protonation equilibria of the CO_2 in water.**

Supplementary Figure 2. Hydrogenation of CO$_2$ with [RuCl$_2$(PTA)$_4$]. ^{1}H NMR signal of $\underline{H}$COOH as a function of time in the hydrogenation of carbon dioxide to formic acid. [RuCl$_2$(PTA)$_4$] (2.76 mM) was dissolved in H$_2$O (2 mL) under N$_2$ atmosphere in a medium pressure sapphire NMR tube. This solution was pressurized at room temperature to 50 bar with CO$_2$ and completed to 100 bar with H$_2$. The system was heated to 60°C and the reaction was followed by ^{13}C NMR (100 MHz) spectroscopy. Figure 2 shows the evolution of the ^{1}H NMR signal in aqueous solution (H$_2$O) of $\underline{H}$COOH at 8.16 ppm (time difference between spectra $\Delta t = 143$ min). Reaction time: 148h.
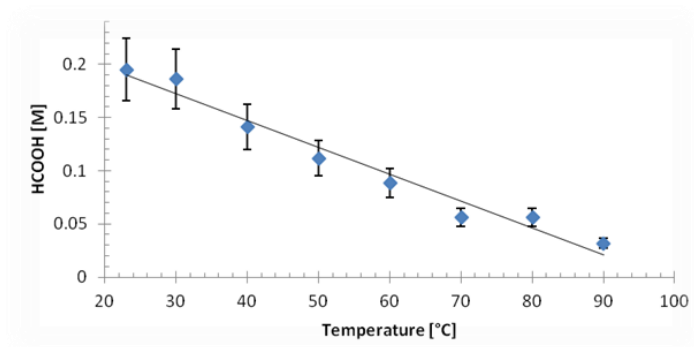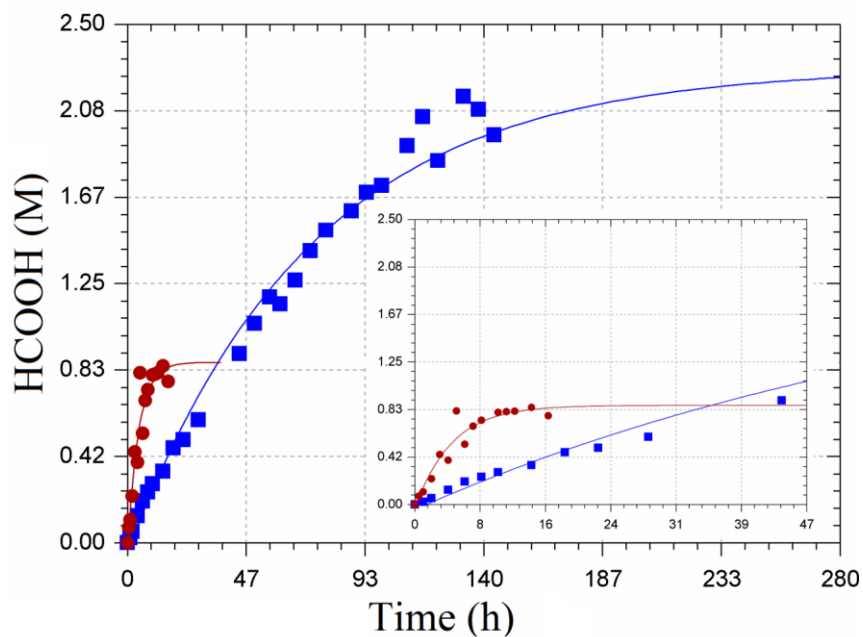
**Supplementary Figure 3. Effect of temperature on the catalytic hydrogenation of CO$_2$ with [RuCl$_2$(PTA)$_4$] in water.** Reaction conditions: [RuCl$_2$(PTA)$_4$] (2.76 mM), P(total) = 100 bar, P(H$_2$)/P(CO$_2$) ratio of 1, in aqueous solution (2 mL) ([DSS] = 0.0130 M), average values of several (2-6) measurements with a reproducibility is ± 15 %. The trend line is shown as a guide and is not a mathematical fit of the data. The formic acid syntheses were followed for 6 to 570 h, depending on the temperature.
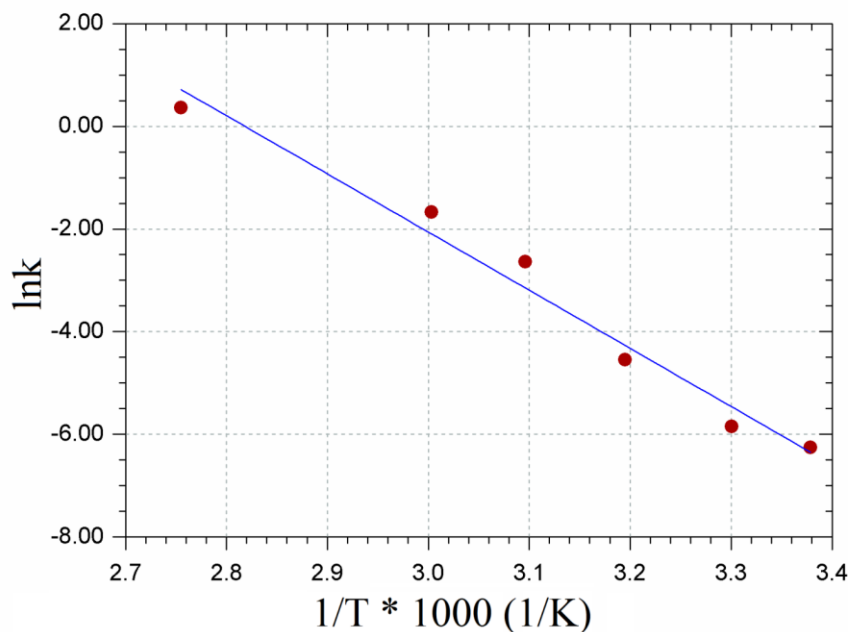
Supplementary Figure 4. Arrhenius plot of the temperature dependence of the reaction. Determination of the plot using the pseudo first order rate constants (k) obtained from the kinetics curves (from Figure 2, t/°C: 23, 30, 40, 50, 60 and 90; with k/h^{-1} values: 0.00192, 0.00289, 0.0106, 0.0717, 0.188 and 1.44, respectively). Reaction conditions: [RuCl$_2$(PTA)$_4$] (2.76 mM), P(total) = 100 bar, P(H$_2$)/P(CO$_2$) ratio of 1, reaction time 6 - 570 h depending on the temperature, in aqueous solution (2 mL). From the Arrhenius plot of the temperature dependence of the rate constants (Figure 4), the activation enthalpy was determined, giving a value of + 95.5 kJ/mol, which is somewhat higher than the data of + 86 kJ/mol obtained for the same catalytic system at neutral pH.[27] In other catalytic systems known for the hydrogenation of the HCO$_3^-$ salts, the activation enthalpy values are much smaller, for example +36 kJ/mol with [RhCl(TPPMS)$_3$] catalyst, [32, 54] with [RhCl(TPPTS)$_3$][55] it is 25 kJ/mol, with K[RuCl(edta-H)][56] it is +31 kJ/mol, or in the hydrogenation of bicarbonate with a heterogeneous Pd catalyst [57, 58] it is +39 kJ/mol. In all these cases it is important to note that the addition of either an amine, an alcohol or a base is necessary for the reaction to proceed.

Supplementary Figure 5. Temperature effect on the rate and equilibrium of the catalytic hydrogenation of CO_2 with [RuCl$_2$(PTA)$_4$] in DMSO. 50°C (blue square); 90°C (brown circle). Reaction conditions: [RuCl$_2$(PTA)$_4$] (2.76 mM), P(total) = 100 bar, P(H$_2$)/P(CO_2) = 1, DMSO (2 mL), average values of several (2-6) measurements, reproducibility is ± 15 %. The reaction times were 16 h at 90°C and 150 h at 50°C.
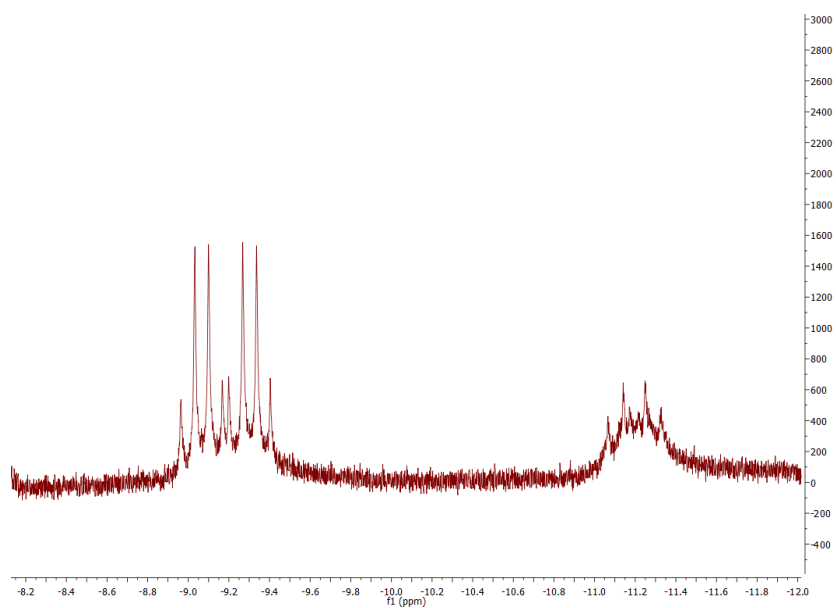
Supplementary Figure 6. ^{1}H NMR spectra showing the hydride region during the mechanistic study of the carbon dioxide hydrogenation with [RuCl$_2$(PTA)$_4$] in DMSO. The multiplet centered at -9.2 ppm corresponds to [RuH(PTA)$_4$Cl] and the multiplet centered at -11.2 ppm corresponds to [RuH$_2$(PTA)$_4$]. Reaction conditions: [RuCl$_2$(PTA)$_4$] (2.76 mM), P(total) = 100 bar, P(H$_2$)/P(CO$_2$) ratio of 1, t = 50°C, DMSO (2 mL containing DSS, 0.0130 M).
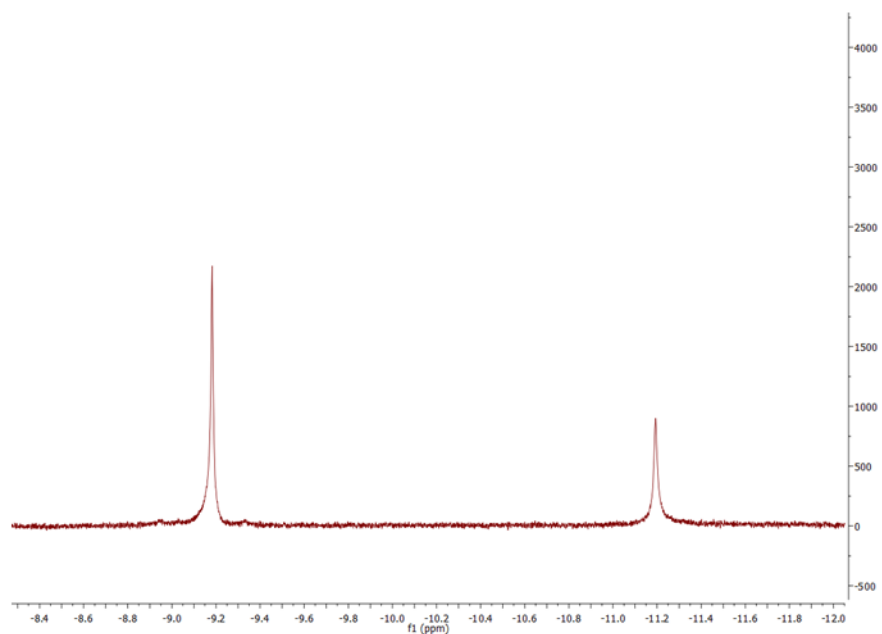
Supplementary Figure 7. ^{1}H{^{31}P} NMR spectra showing the hydride region during the mechanistic study of the carbon dioxide hydrogenation with [RuCl$_2$(PTA)$_4$] in DMSO. The singlet at – 9.2 ppm correspond to [RuH(PTA)$_4$Cl] and the singlet at -11.2 ppm to [RuH$_2$(PTA)$_4$]. Reaction conditions: 2.76 mM [RuCl$_2$(PTA)$_4$], P(total) = 100 bar, P(H$_2$)/P(CO$_2$) ratio of 1, t = 50°C, reaction volume of 2 mL (DSS solution of 0.0130 M in DMSO).
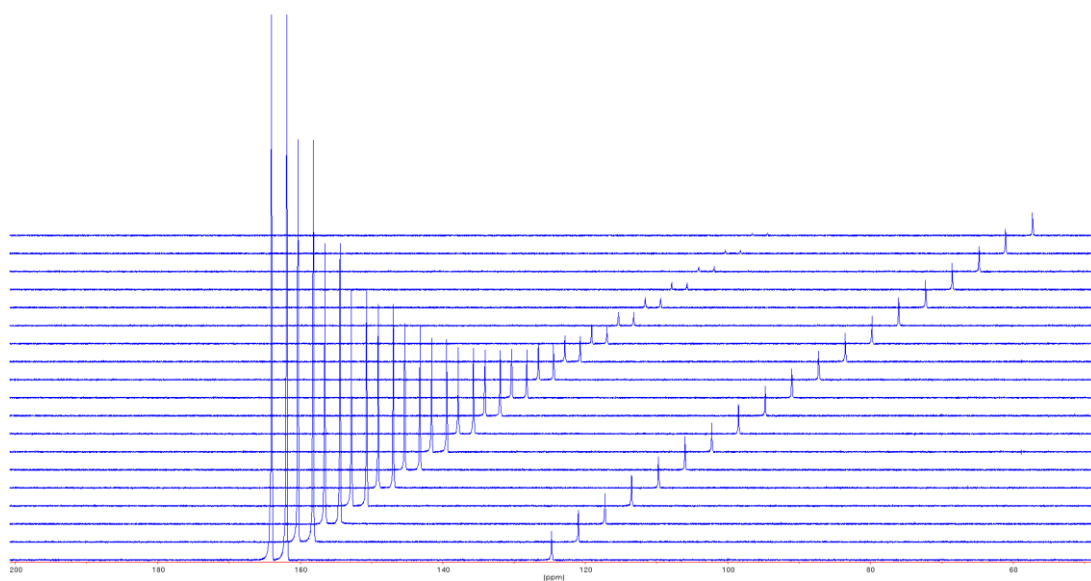
Supplementary Figure 8. Hydrogen production from HCOOH in DMSO. ^{13}C NMR signals of H**C**OOH in the formic acid dehydrogenation reaction into carbon dioxide and hydrogen in d^6-DMSO. [RuCl$_2$(PTA)$_4$] (10.2 mM) was dissolved in d^6-DMSO (2 mL) in a 10 mm NMR tube. The system was heated to 80°C and the reaction was followed by ^{13}C NMR (100 MHz) spectroscopy. Figure 8 shows the evolution of the ^{13}C NMR doublet of H**C**OOH at 163 ppm and signal corresponding to the dissolved **C**O$_2$ at 124.7 ppm (time difference between spectra Δt = 1h). Reaction time: 20 h.
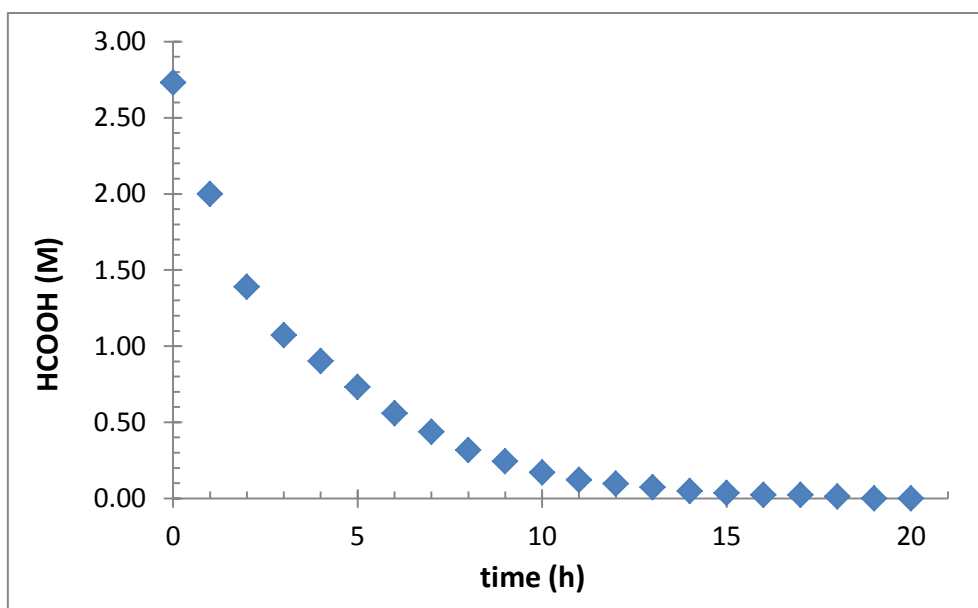
Supplementary Figure 9. Hydrogen production from HCOOH in DMSO. Decrease of the formic acid concentration in the dehydrogenation of formic acid into carbon dioxide and hydrogen in d^6-DMSO as function of time. The [HCOOH] was determined *in situ* by quantitative ^{13}C NMR spectroscopy.[51] [RuCl$_2$(PTA)$_4$] (10.2 mM) was dissolved in d^6-DMSO (2 mL) in a 10 mm NMR tube. The system was heated to 80°C and the reaction was followed by ^{13}C NMR (100 MHz) spectroscopy.

Supplementary Table 1. Selective carbon dioxide hydrogenation into formic acid in water with different Ru(II) and Rh(I) catalysts.

Entry	Catalyst precursor	P_{total} [bar]	HCOOH[a] [M]	TON[b]
1	[RuCl$_2$(PTA)$_4$]	60	0.023	8
2	[RuCl$_2$(PTA)$_4$]	100	0.083	30
3	[RhCl(PTA)$_3$]	60	0.002	0.7
4	[RhCl(TPPMS)$_3$]	60	0.001	0.4
5	[RuCl$_2$(PTA)([9]aneS$_3$)]	100	0.046	17
6	[Ru(H$_2$O)$_4$(MePTA)$_2$](tos)$_4$	60	0.020	7
7	[RuCl$_2$(TPPMS)$_2$]	60	0.011	4
8	[RuCl$_2$(TPPTS)$_2$]$_2$	60	0.012	4
9	[RuCl$_2$(p-cymene)]$_2$	60	0.012	4
10	[RuCl$_2$(p-cymene)]$_2$ + 2 eq. TPPMS	60	0.021	8
11	[RuCl$_2$(p-cymene)]$_2$ + 2 eq. TPPTS	60	0.011	4
12	[RuCl(p-cymene)(1-methyl-3-(prop-2-enyl)-1H-(imidazol-3-ium)][BF$_4$]	100	0.042	15

The catalyst (c = 2.76 mM) was dissolved in H$_2$O (2 mL) under a N$_2$ atmosphere in a medium pressure sapphire NMR tube. The solution was pressurized at room temperature with CO$_2$ and completed by H$_2$ to the required pressure with a P(H$_2$)/P(CO$_2$) ratio of 1. Then the system was heated to 60°C and shaken until the equilibrium of the reaction was reached (72 – 96 h). The final yield of HCOOH was determined by ^{1}H NMR spectroscopy with the DSS as an internal standard. [a]average values of several (4-5) measurements with a reproducibility of ± 15%. [b]Turnover number (TON), the number of moles of CO$_2$ (or H$_2$) that one mole of catalyst converts into HCOOH.

Supplementary Table 2. Direct synthesis of formic acid from H_2 and CO_2 with [RuCl$_2$(PTA)$_4$] catalyst as function of temperature.

Entry	Temperature [°C]	P(H$_2$)/P(CO$_2$) [bar]	HCOOH [M]	TON
1	23	50/50	0.195	71
2	30	50/50	0.186	67
3	40	50/50	0.141	51
4	50	50/50	0.112	41
5	60	50/50	0.088	32
6	60	50/50	0.083	30
7	70	50/50	0.056	20
8	80	50/50	0.056	20
9	90	50/50	0.032	12
10[a]	135	70/50	0.024	40

Reaction conditions: [RuCl$_2$(PTA)$_4$] (2.76 mM), P(total) = 100 bar, P(H$_2$)/P(CO$_2$) ratio of 1, aqueous solution (2 mL) ([DSS] = 0.0130 M), average values of several (2-6) measurements, reproducibility is ± 15 %, [a] 135°C, 10 minutes, 0.597 mM [RuCl$_2$(PTA)$_4$]. The formic acid syntheses were followed for 6 h to 570 h, depending on the temperature.

Supplementary Table 3. Recycling experiments: carbon dioxide hydrogenation with [RuCl$_2$(PTA)$_4$] in water.

Cycle	HCOOH [M]	TON
1	0.151	15
2	0.120	27
3	0.131	40
4	0.174	58
5	0.142	72

Reaction conditions: [RuCl$_2$(PTA)$_4$] (10 mM), P(total) = 100 bar, P(H$_2$)/P(CO$_2$) ratio of 1, t = 60°C, water (2 mL, containing [DSS] = 0.0130 M), average values of several (2-3) measurements for each cycle, reproducibility is ± 15 %. The HCOOH concentrations were determined after 62 h reaction time.

Supplementary Table 4. Catalytic hydrogenation of carbon dioxide to formic acid in organic solvents.

Entry	Solvent	HCOOH [M]	TON
1	H_2O	0.10	36
2	DMSO	1.8	652
3	Ethanol	0.20	72
4	Methanol	0.20	72
5	Acetonitrile	0.20[a]	72
6	Propylene carbonate	0.20[a]	72
7	Toluene	-	-

Reaction conditions: 2.76 mM [RuCl$_2$(PTA)$_4$], P(total) = 100 bar, P(H$_2$)/P(CO$_2$) ratio of 1, t = 50°C, reaction time 120 h, reaction volume of 2 mL (DSS solution of 0.0130 M), average values of several (2-3) measurements, reproducibility is ± 15 %. [a]determined by the standard addition method.

Supplementary Table 5. Selective hydrogenation of carbon dioxide into formic acid in DMSO.

Entry	Catalyst precursor	Total pressure [bar]	HCOOH [M]	TON
1	$[RuCl_2(PTA)_4]$	100	1.93	699
2	$[RhCl(PTA)_3]$	100	0.011	4
3	$IrCl_3$ + 10 eq. PTA	100	0.003	1

Reaction conditions: catalyst (2.76 mM), P(total) = 100 bar, $P(H_2)/P(CO_2)$ ratio of 1, t = 50°C, DMSO (2 mL) (DSS solution of 0.0130 M), average values of several (2-3) measurements, reproducibility is ± 15 %. Reaction time: 120 h.

Supplementary Table 6. Production of formic acid as a function of pressure and of $P(H_2)/P(CO_2)$ pressure ratio.

Entry	Total pressure [bar]	$P(H_2)$ / $P(CO_2)$ ratio	HCOOH [M]	TON
1	50	1	0.39	141
2	60	1	0.53	192
3	70	1	0.95	344
4	80	1	1.19	431
5	90	1	1.22	442
6	100	1	1.93	699
7	100	1.5	1.39	504
8	100	2.3	1.29	467
9	100	4	1.56	565
10	100	9	0.95	344

Reaction conditions: [RuCl$_2$(PTA)$_4$] (2.76 mM), t = 50°C, reaction time 120 h, in DMSO solvent (2 mL), average values of several (2-6) measurements, reproducibility is ± 15.

Supplementary Table 7. Production of formic acid as a function of temperature.

Entry	Temperature [°C]	HCOOH [M]	TON
1	40	1.87	678
2	50	1.93	699
3	60	1.84	667
4	70	1.12	406
5	80	0.99	359
6	84	0.90	326
7	90	0.83	300

Reaction conditions: $[RuCl_2(PTA)_4]$ (2.76 mM), P(total) = 100 bar, $P(H_2)/P(CO_2)$ = 1, reaction time between 10 to 150 h, DMSO (2 mL), average values of several (2-6) measurements, reproducibility is ± 15 %.

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