

Supporting Information

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**Hydrogenation of Carbon Dioxide to Methanol by Using
a Homogeneous Ruthenium–Phosphine Catalyst****

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General

Safety advice: High-pressure experiments with compressed gases represent a significant safety risk and must be conducted only following appropriate safety procedures and in conjunction with the use of suitable equipment.

For complex synthesis and catalytic experiments, moisture and oxygen were excluded by working in a glove box or by using Schlenk techniques. Argon 4.8 (Messer, Germany) was used as inert gas. Glassware was dried under vacuum under heating with a heat gun, evacuated and refilled with argon at least three times. All solvents were purified by distillation prior to use. Tetrahydrofuran, toluene and pentane were degassed by bubbling argon with a frit, dried by passing over activated alumina in steel columns and stored over molecular sieves. Dioxane and ethanol were degassed by distillation under argon and dried over molecular sieves. All reagents were commercially supplied by Aldrich, Fluka, Alfa Aesar and Heraeus Precious Metals and used as received unless stated otherwise. Reaction gases hydrogen (5.0) and carbon dioxide (4.6) were supplied by Linde and PraxAir and used without further purification.

NMR spectra were recorded with spectrometers Bruker AV600, AV400 or AV300 at room temperature in deuterated solvents. Chemical shifts ***d*** are given in ppm relative to tetramethylsilane (¹H and ¹³C) and 85% phosphoric acid (³¹P). First order spin multiplicities are abbreviated as singlet (s), doublet (d), triplet (t), quadruplet (qua), quintet (qui), sextet (sext) and septet (sep). Couplings of higher order or overlapped signals are denoted as multiplet (m), broadened signals as (bs). First order coupling constants *J* are given in Hz. Assignments are based on attached proton tests (ATP) and 2-D correlation spectroscopy (HSQC, HMQC, HMBC).

Gas chromatography was performed on a *Trace GC* gas chromatograph (Thermo Scientific) equipped with a SSL Inlet (250 °C, Split 83 mL/min), a FS-Innopeg-2000 column (60 m, inner diameter 0.25 mm, film thickness 0.25 µm) and a flame ionization detector (250 °C) using helium as carrier gas and a temperature program: 10 min isothermal at 50 °C, ramp to 200 °C (8 °C/min), 30 min at 200 °C.

Synthesis of complex 2:

A 35 mL schlenk tube was charged with 159.5 mg (0.5 mmol) [Ru(cod)(methylallyl)₂] and 312.0 mg 1,1,1-tris(diphenylphosphinomethyl)ethane (Triphos) in 25 mL toluene. After heating for 2 h at 110 °C, the resulting solution was concentrated in vacuo and treated with 10 mL of pentane. The precipitating complex was isolated and washed 3 times with 10 mL pentane. After drying, complex **2** was obtained as a bright yellow powder in 76 % yield.

¹H-NMR (600 MHz, d²-dichloromethane): δ 7.16-7.07 (m, 18H, C_{Ar}-H), 6.99 (m, 12H, C_{Ar}-H), 2.28 (bs, 6H, P-CH₂), 1.67 (bs, 6H, C-CH₂), 1.44 (s, 3H, CH₃).

¹³C-NMR (125 MHz, d²-dichloromethane): δ 141.0 (m, C_{Ar}), 132.2 (m, C_{Ar}-H), 127.6 (s, C_{Ar}-H), 127.3 (s, C_{Ar}-H), 106.5 (bs, C(CH₂)₃²⁻), 43.2 (m, C(CH₂)₃²⁻), 38.9 (q, J_{C-P}=9.7 Hz, CH₃), 38.2 (m, (Ph₂PCH₂)₃C-CH₃), 35.6 (m, P-CH₂) ppm.

³¹P-NMR (243 MHz, d⁸-toluene): δ 34.4 (s, 3P) ppm.

HR-MS (EI) C₄₁H₄₅P₃Ru: Calc.: 780.177 m/z. Found: 780.178 m/z.

General procedure for formate ester hydrogenation experiments

All high pressure batch experiments were conducted in stainless steel autoclaves (inner volume = 13 mL) equipped with a glass inlet and a magnetic stir bar. Prior to use, the autoclave was dried at 60 °C in high vacuum and repeatedly filled with argon. Under an argon atmosphere, catalyst **1** (0.025 mmol), Triphos (0.05 mmol), ethyl formate (2.5 mmol), 1.0 mL THF and 1.0 mL of a solution of methane sulfonic acid in THF (3.7 mg/mL) were weighed into a Schlenk tube. The reaction solution was transferred to the autoclave via cannula. The autoclave was pressurized with H₂ to 30 bar and the mixture stirred and heated at 140 °C in an oil bath. After 24 h, the autoclave was cooled to ca. 0 °C in an ice bath and then carefully vented. The reaction solution was analyzed by ¹H-NMR with internal standard mesitylene (Figure 1).

General procedure for CO₂ hydrogenation experiments

All high pressure batch experiments were conducted in stainless steel autoclaves (inner volume = 13 mL) equipped with a glass inlet and a magnetic stir bar. Prior to use, the autoclave was dried at 60 °C in high vacuum and repeatedly filled with argon. Under an argon atmosphere, catalyst **1** (0.025 mmol), triphos (0.05 mmol), ethanol (10 mmol), 0.5 mL THF and 1.0 mL of a solution of methane sulfonic acid in THF (3.7 mg/mL) were weighed into a Schlenk tube. The reaction solution was transferred to the autoclave via cannula. The autoclave was pressurized with CO₂ to 10 bar and then H₂ was added up to a total pressure of 40 bar. The reaction mixture was stirred and heated to 140 °C in an oil bath. After 24 h, the autoclave was cooled to ca. 0 °C in an ice bath and then carefully vented. The reaction solution was analyzed by ¹H-NMR with internal standard mesitylene (Figure 2) and the results confirmed by gas chromatography using heptane as internal standard (Figure 3).

TON's were found to be reproducible within ±5% in two independent runs for selected experiments (Δ TON = ±5%).

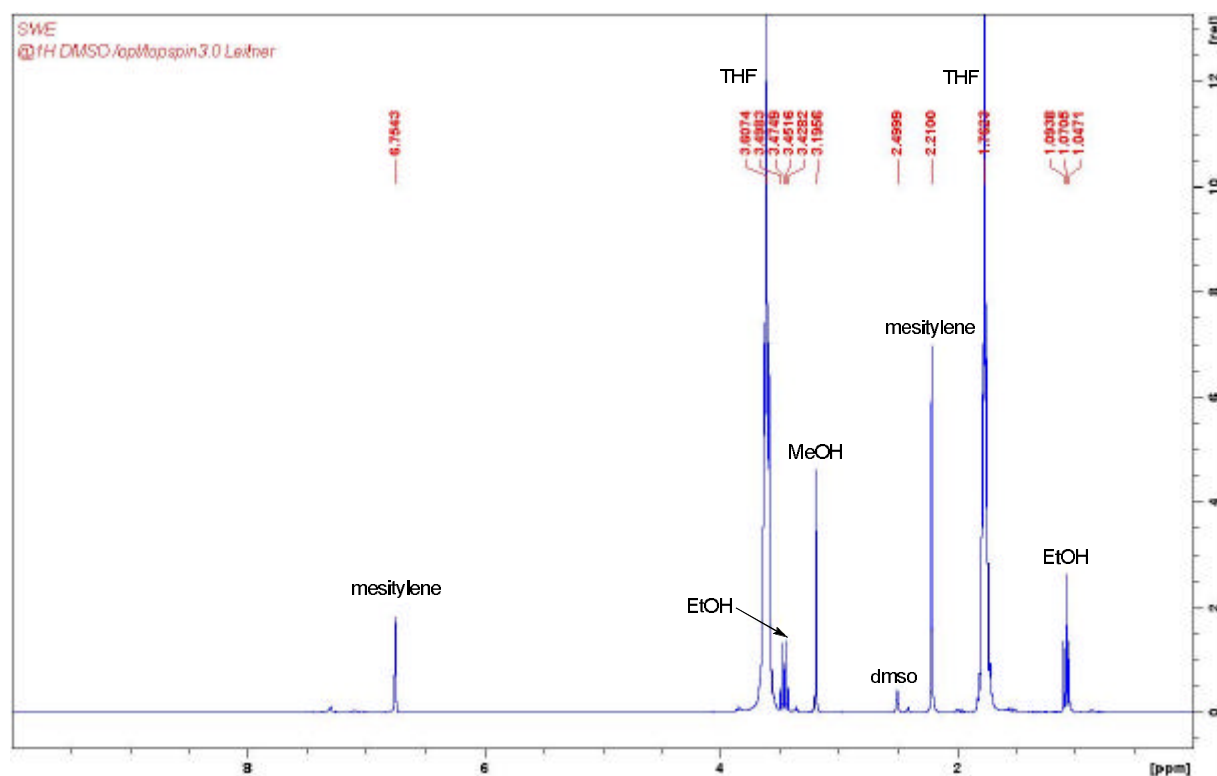


Figure 1: ¹H-NMR (300 MHz, d₆-dmsol) spectrum of reaction solution from ethyl formate hydrogenation with above described standard protocol with internal standard mesitylene.

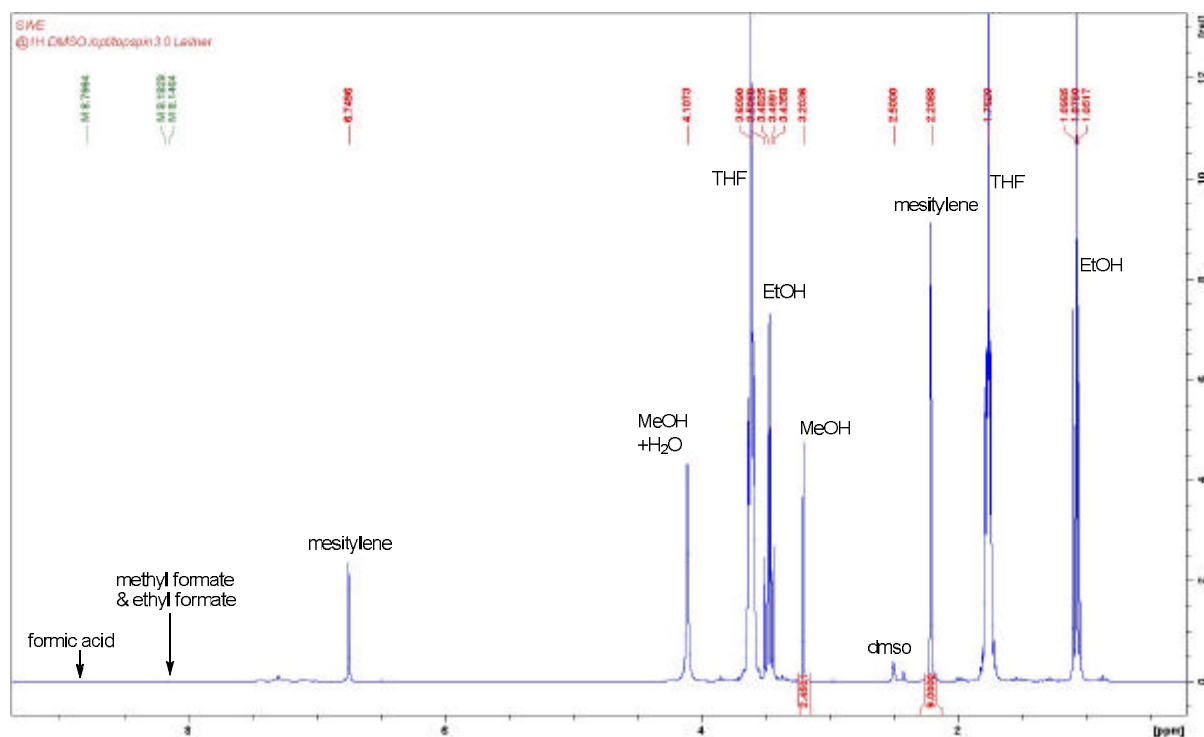


Figure 2: ^1H -NMR (300 MHz, d_6 -DMSO) spectrum of reaction solution from CO_2 hydrogenation with above described standard protocol with internal standard mesitylene.

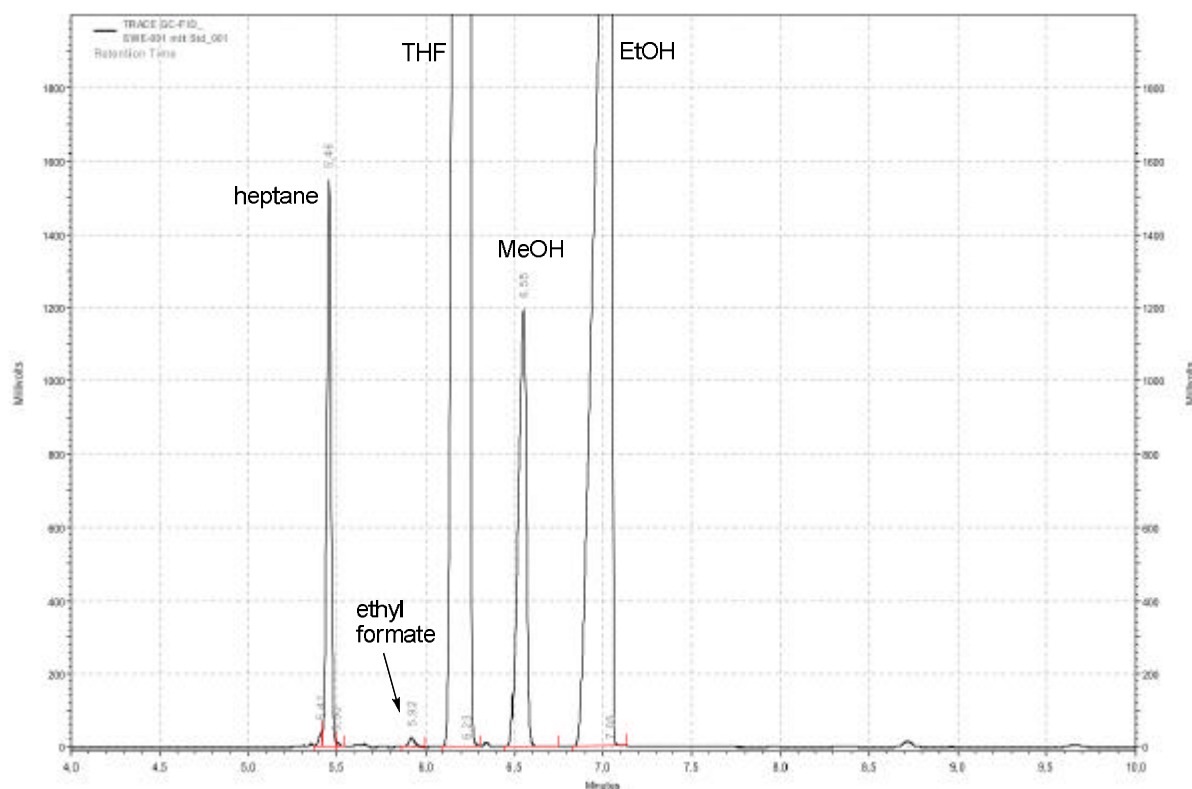


Figure 3: Representative gas chromatogram of reaction solution from CO₂ hydrogenation in ethanol/THF with internal standard heptane.

CO₂ hydrogenation in deuterated methanol

Figure 4 shows the ¹H-NMR (600 MHz, *d*₆-dms_o) of the CO₂ hydrogenation reaction in THF in the presence of *d*₄-methanol. Besides the singlet for CH₃OH also multiplets corresponding to CD₂H₂OH and CD₂HOH are observed. To exclude uncertainties arising from this scrambling phenomena, all other reactions were performed in the presence of ethanol instead of methanol (vide supra).

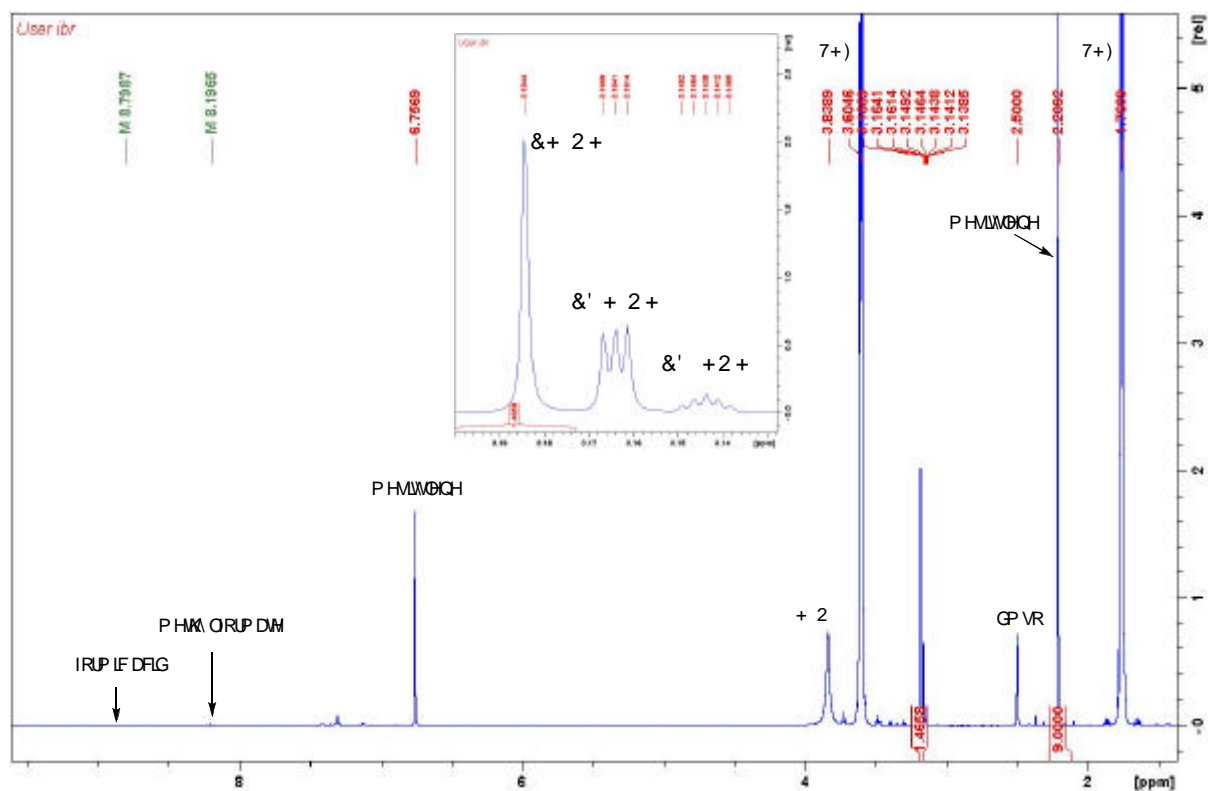


Figure 4: ^1H -NMR (600 MHz, d_6 -DMSO) spectrum of reaction solution from CO_2 hydrogenation in d_4 -methanol with internal standard mesitylene.

CO₂ hydrogenation in carbon-13 labelled and deuterated methanol

Figure 5 shows the ¹H-NMR (600 MHz, *d*₆-dmsO) of the CO₂ hydrogenation reaction in THF in the presence of ¹³CD₃OD. The signal for ¹²CH₃OH is accompanied by ¹³C-satellite signals with an integration of about 0.5 % in comparison to the intensity of the main signal. This corresponds to the natural abundance of ¹³C in CO₂ and further corroborates that the methanol observed is produced from CO₂ and does not stem from the ¹³CD₃OD. The signals for ¹³CD₂HOH and ¹³CD₂HOH further indicate deuterium scrambling between ¹³CD₃OD and CH₃OH or hydrogen.

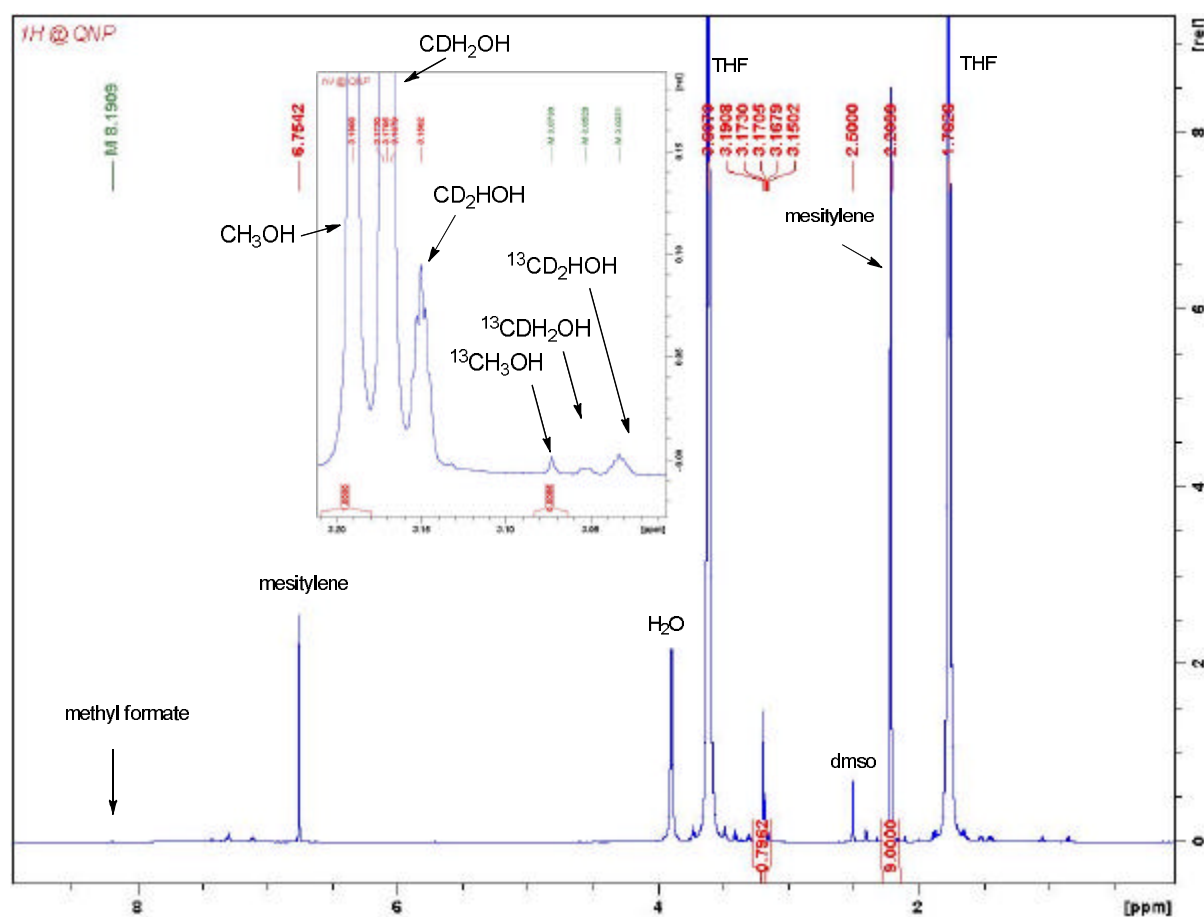


Figure 5: ¹H-NMR (600 MHz, *d*₆-dmsO) of reaction solution from CO₂ hydrogenation in THF in the presence of ¹³CD₃OD with internal standard mesitylene.

Further experimental data

Table S1. Additional variation of reaction parameters in the catalytic hydrogenation of carbon dioxide to methanol.^[a]

Entry	Cat. Ru(acac) ₃	Triphos (eq.)	Acid (eq.) ^[b]	Time [h]	pH ₂ [bar]	pCO ₂ [bar]	TON ^[c]
1	1	1	MSA (1.5)	24	30	10	45
2	1	3	MSA (1.5)	24	30	10	32
3 ^[d]	1	2	MSA (1.5)	24	30	10	68
4	1	2	MSA (1.5)	24	0	10	0

[a] Reaction conditions: Catalyst (25 μ mol), 1.5 mL THF, EtOH (10 mmol), 140 °C; [b] equivalents to catalyst; [c] TON = mmol MeOH/mmol catalyst; [d] 13 μ mol catalyst.

Table S2. Control experiments for formate ester hydrogenation^[a]

Entry	Cat.	Acid	R	pH ₂ [bar]	TON ^[b]
1	-	MSA (38 μ mol)	Et	30	0
2	1	MSA (38 μ mol)	Et	-	0

[a] Reaction conditions: Ru(acac)₃ (25 μ mol), Triphos (50 μ mol), substrate (2.5 mmol), 2 mL THF, 140 °C, 24 h; [b] TON = mol MeOH/mol catalyst.