Liquid-phase Hydrogenation of Carbon Monoxide to Methanol using a Recyclable Manganese-based Catalytic System

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1 Supporting Data and Graphs

1.1 Supporting Data for Optimization Reactions

 Table S1: Hydrogenation of carbon monoxide with different Mn-MACHO complexes. The reaction mixture was analyzed by ¹H-NMR.

Entry	Solvent	P-Subst.	MeOH	п	п	п	S to	TON
		Mn-	Vol%	(Methyl	(Dodecyl	(MeOH)	MeOH	(MeOH)
		1	(%)	formate)	formate)	(mmol)	(%)	(1110011)
		catalyst		(mmol)	(mmol)			
1	NMP	iso-Propyl	33	-	-	-	-	-
2	γ- Valerolacton	<i>iso</i> -Propyl	33	-	-	-	-	-
3	1-Dodecanol	cyclohexyl	25	0.25	0.08	5.26	94	1034
4	1-Dodecanol	<i>tert</i> -Butyl	25	-	-	-	-	-

Conditions: CO (10 bar), H_2 (50 bar), Catalyst (5 µmol), NaO'Bu (50 µmol), Solvent + Methanol (1.5 mL), 150 °C, 4 h, 20 mL autoclave. Selectivities calculated as molar fraction of total products detected (methanol, methyl and dodecyl formate).



Figure S1: Exemplary ¹H NMR Spectrum (400 MHz, toluene-*d*₈) of a reaction sample for screening reaction. δ = 3.01 (d, 3 H, CH₃-OH (Methanol)), 3.18 (d, 3 H, CH₃-OC (Methyl formate)), 3.54 (m, 4 H, CH₂ (THF)), 7.45 (d, 1 H, OOCH (Methyl formate)), 7.58 (s, 1 H, OOCH (Dodecyl formate)) ppm.



Figure S2: Picture of an exemplary reaction solution before (left) and after (right) reaction.

Table S2: Hydrogenation of carbon monoxide with Mn-1 at different temperatures and reaction times. The reaction mixture was analyzed by ¹H-NMR.

Entry	Т	t	n (Methyl	n (Dodecyl	n (MeOH)	S to MeOH	TON
	(°C)	(h)	formate)	formate)	(mmol)	(%)	(MeOH)
			(mmol)	(mmol)			
1	120	5	0.65	0.26	-0.58	-	-
2	130	5	0.50	0.20	0.93	57	441
3	140	5	0.37	0.13	2.82	94	1034
4	150	5	0.24	0.08	4.66	94	2360
5	160	5	0.15	0.05	5.35	96	2816
6	170	5	0.13	0.04	5.37	97	2555
7	150	20	0.22	0.05	7.33	97	3576
8	160	20	0.10	0.03	9.11	99	4555
9	170	20	0.13	0.04	8.53	98	4169

Conditions: CO (10 bar), H₂ (50 bar), **Mn-1** (2 μ mol), NaOMe (50 μ mol), 25% Methanol in 1-Dodecanol (1.5 ml), *T*, *t*, 20 mL autoclave. Selectivities calculated as molar fraction of total products detected (methanol, methyl and dodecyl formate).

Table S3: Theoretical yield calculations based on ideal gas equation at 20°C.

Vessel	V (vessel) ^a (ml)	V (solution) (ml)	V (gas) (ml)	p (CO) (bar)	Y _{theo} c (mmol)
Autoclave	23.5	1.5+0.3 ^b	21.7	10	8.9
Reactor	320	70	250	20	205
Reactor after base addition	320	80	240	20	197

a) measured experimentally (incl. vessel head and piping). b) volume of magnetic stir bar. c) deviations in the manual CO pressurization can result in varying theo. yields.

Table S4: Hydrogenation of carbon monoxide with **Mn-1** under optimized conditions with different methanol content. Details to Table 3. The reaction mixture was analyzed by 1H-NMR.

Entry	Т	t	MeOH wt%	<i>n</i> (Methyl	n (Dodecyl	n (MeOH)
	(°C)	(h)	(%)	formate)	formate)	(mmol)
				(mmol)	(mmol)	
1	10	80	25	0.08	0.03	9.57
2	10	80	10	0.03	-	9.60
3	10	80	0	0.06	0.04	9.30
4	15	75	0	-	-	14.92

Conditions: CO (10 bar), H₂ (50 bar), **Mn-1** (2 μ mol), NaOMe (50 μ mol), 25% Methanol in 1-Dodecanol (1.5 ml), *T*, *t*, 20 mL autoclave. Selectivities calculated as molar fraction of total products detected (methanol, methyl and dodecyl formate).

The drop in catalyst activity at temperatures above 160 °C is hypothesized to be attributed to a thermal deactivation and decomposition of the active molecular complex. Besides a significant colour difference (clear, slight yellow vs. cloudy, brown) of the reaction mixtures after reaction, ³¹P NMR measurements support this hypothesis.

The spectra consist of three important regions. Active catalyst species occur in the 80-90 ppm region. Due to the coordination of various solvent (Methanol, 1-Dodecanol) and intermediate species (Methyl / Dodecyl formate ester), multiple signals occur in this region. Free (deactivated) ligand species are visible between 5 and -5 ppm. We were not able to assign structures to the signals occurring between 60 and 65 ppm. However, we hypothesize that these signals correspond to inactive catalyst complexes or cluster.

While the ratio of active catalyst species to residual complex and ligand signals is only slightly raised after 20 h at 150 °C (1:0.19 to 1:0.30), a significant increase occurs after 20 h at 170 °C (1:0.81). These results indicate significantly reduced catalyst stability at 170 °C. We aim to further verify our hypothesis in the future by gaining deeper insights into the catalyst stability and deactivation mechanisms.



Figure S3: ³¹P NMR spectra of the reaction mixture before the reaction and after 20 h at 150 °C and 170 °C. Conditions: CO (10 bar), H₂ (50 bar), (1) (2 μ mol), NaOMe (50 μ mol), 25% Methanol in 1-Dodecanol (1.5 ml), *T*, *t*, 20 mL autoclave.

3,0 - NMR - IR 2,5 2,5 2,0 2,0 n_{NMR} (mmol) ntensity 1,5 1,5 1,0 - 1,0 0,5 0,0 0,5 0 200 400 600 800 1000 1200 1400 Time (min)

1.2 Supporting Data for Reaction Monitoring Reaction

Figure S4: Methyl formate concentration time profile followed by ¹H NMR measurements with internal standard THF and IR intensity at 1731 cm⁻¹. Conditions: CO (8 bar), H₂ (32 bar), (1) (48 µmol), NaOMe (2.4 mmol), 25% Methanol in 1-Dodecanol (25 ml), 150 °C, 280 mL reactor.



Figure S5: Dodecyl formate concentration time profile followed by ¹H NMR measurements with internal standard THF and IR intensity at 1602 cm⁻¹. Conditions: CO (8 bar), H₂ (32 bar), (1) (48 μ mol), NaOMe (2.4 mmol), 25% Methanol in 1-Dodecanol (25 ml), 150 °C, 280 mL reactor.



Figure S6: Pressure and total formate concentration (methyl formate + dodecyl formate) time profile based on ¹H NMR measurements with internal standard THF. Conditions: CO (8 bar), H₂ (32 bar), 1 (48 μ mol), NaOMe (2.4 mmol), 25% Methanol in 1-Dodecanol (25 ml), 150 °C, 280 mL reactor.



Figure S7: Exemplary ¹H NMR Spectrum (80 MHz, methanol) for reaction monitoring experiment. Relevant peak integrals between 3-4 ppm were deconvoluted using PEAXACT. δ = 3.33 (s, 3 H, CH₃-OH (Methanol)), 3.54 (m, 2 H, CH₂-OH (1-Dodecanol)), 3.70 (m, 4 H, CH₂ (THF)), 8.02 (s, 1 H, OOCH (Methyl formate)), 8.53 (m, 1 H, OOCH (Dodecyl formate)) ppm.

1.3 Supporting Data for Recycling Experiments



Figure S8: Exemplary ¹H NMR Spectrum (400 MHz, toluene-*d*₈) of the distillate of the recycling experiments. Sample does not contain any intermediates or 1-Dodecanol. Only methanol ($\delta = 3.18$ ppm (d, 3 H, CH₃-OH)) and residual NMR solvent peaks.

Table S5: Pressure after reaction at room temperature, isolated methanol quantities and leaching of the catalyst compo	nents
manganese and phosphorus (ppm and % of initial amount) per run in the catalyst recycling.	

D	<i>p</i> (bar)	n (MeOH,	Mn Le	eaching	P Leaching	
Kun	r.t. after reaction	isolated) (mmol)	ppm	%	ppm	%
1	57.1	208	< 0.2	< 0.03	2.3	0.27
2	58.0	212	< 0.2	< 0.03	2.8	0.34
3	55.4	213	< 0.2	< 0.03	2.6	0.32
4	63.7	201	< 0.2	< 0.03	3.5	0.39
5	98.0	82	< 0.2	< 0.01	3.0	0.13
6	56.6	201	< 0.2	< 0.03	3.4	0.38

2 Experimental

General considerations

All reactions were conducted under argon inert gas atmosphere unless stated otherwise with argon supplied by *AirLiquide* (99.9999 purity). Air sensitive chemicals were stored in a glovebox and standard Schlenk techniques were applied. The solvents were degassed and purified using standard solvent purification systems and techniques and were stored over molecular sieves and argon. Chemicals were purchased from Sigma-Aldrich, Alfa-Asear, abcr, Acros Organics, TCI chemicals. All chemicals were used as obtained from the vendors and degassed before application in catalytic reactions. Carbon monoxide (99.999% purity) and hydrogen (99.999% purity) for catalytic reactions were obtained from *AirLiquide*.

NMR Measurements were carried out at ambient temperature using a *Bruker AVANCE NEO* 400-spectrometer (¹H: 400 MHz, ³¹P: 162 MHz) for the batch experiments. The continuous experiment was monitored with a *Magritek Spinsolve 80 Phosphorous*-spectrometer (¹H: 80 MHz). Chemical shifts were given in ppm and the residual solvent signal of deuterated solvent was referenced to trimethyl silane for ¹H NMR spectra and to phosphoric acid for ³¹P NMR spectra.

XRF-measurements were conducted on an *Xepos C* from *Spectro*. Samples were analyzed for manganese and phosphourous content.

Synthesis of Manganese Pincer Complex

Manganese pincer complexes were prepared according to the reported literature:

- *iso*-propyl^[1]
- cyclohexyl^[2]
- *tert*-butyl^[3]

General Procedure for Solvent & Catalyst Optimization

The reaction mixtures were prepared as stock solutions in the glovebox. Molecular complex $[Mn(CO)_2Br[HN(C_2H_4P'Pr_2)_2]]$, $[Mn(CO)_2Br[HN(C_2H_4P(C_6H_{11})_2)_2]]$ or $[Mn(CO)_2Br[HN(C_2H_4P'Bu_2)_2]]$ (10 µmol/ml) and NaO'Bu (9.6 mg/ml, 100.0 µmol/ml) were measured into a Schlenktube and dissolved in a stock solution of methanol with 9.2%wt THF as the internal standard. The 20 ml stainless steel autoclave was equipped with a stirring bar, closed and evacuated and purged with argon three times. The solvent (1 ml) and the stock solution (0.5 ml) were added at room temperature through the ball valve (5) under argon. The autoclave was pressurized *via* the needle valve (4) with CO (10 bar) and H₂ (50 bar) and heated to 150 °C for 4 h. After the reaction was completed, the autoclave was analyzed by NMR spectroscopy.



Figure S9: Picture of the applied autoclave consisting of a reaction vessel (1), a manometer (2), a rupture disk (3), a needle valve (4) and a ball valve or stopper (5).

General Procedure for Base Optimization

The reaction mixtures were prepared as stock solutions in the glovebox. Molecular complex $[Mn(CO)_2Br[HN(C_2H_4P^iPr_2)_2]]$ (0.7 mg/ml, 1.3 µmol/ml) and NaO/Bu or NaOMe were measured into a Schlenktube and dissolved in a stock solution of 1-Dodecanol containing 25%wt methanol with 2.9%wt THF as the internal standard. The 20 ml stainless steel autoclave was equipped with a stirring bar, closed and evacuated and purged with argon three times. The reaction mixture (1.5 ml) was added at room temperature through the ball valve (5) under argon. The autoclave was pressurized *via* the needle valve (4) with CO (10 bar) and H₂ (50 bar) and heated to 150 °C for 5 h. After the reaction was completed, the autoclave was analyzed by NMR spectroscopy.

General Procedure for Temperature Optimization

The reaction mixtures were prepared as stock solutions in the glovebox. Molecular complex $[Mn(CO)_2Br[HN(C_2H_4P^iPr_2)_2]]$ (0.7 mg/ml, 1.3 µmol/ml) and NaOMe (1.8 mg/ml, 33.3 µmol/mol) were measured into a Schlenktube and dissolved in a stock solution of 1-Dodecanol containing 25% wt methanol with 2.9% wt THF as the internal standard. The 20 ml stainless steel autoclave was equipped with a stirring bar, closed and evacuated and purged with argon three times. The reaction mixture (1.5 ml) was added at room temperature through the ball valve (**5**) under argon. The autoclave was pressurized *via* the needle valve (**4**) with CO (10 bar) and H₂ (50 bar) and heated to a specific temperature for 5 h or 20 h. After the reaction was completed, the autoclave was cooled to room temperature and slowly vented while stirring. The reaction mixture was analyzed by NMR spectroscopy.

General Procedure for Pressure Optimization

The reaction mixtures were prepared as stock solutions in the glovebox. Molecular complex $[Mn(CO)_2Br[HN(C_2H_4P^iPr_2)_2]]$ (0.7 mg/ml, 1.3 µmol/ml) and NaOMe (1.8 mg/ml, 33.3 µmol/mol) were measured into a Schlenktube and dissolved in a stock solution of 1-Dodecanol containing 25% wt methanol with 2.9% wt THF as the internal standard. The 20 ml stainless steel autoclave was equipped with a stirring bar, closed and evacuated and purged with argon three times. The reaction mixture (1.5 ml) was added at room temperature through the ball valve (**5**) under argon. The autoclave was pressurized *via* the needle valve (**4**) with CO and H₂ and heated to 150°C for 5 h. After the reaction was completed, the autoclave was cooled

to room temperature and slowly vented while stirring. The reaction mixture was analyzed by NMR spectroscopy.

General Procedure for Combined Optimization

The reaction mixtures were prepared as stock solutions in the glovebox. Molecular complex $[Mn(CO)_2Br[HN(C_2H_4P'Pr_2)_2]]$ (0.7 mg/ml, 1.3 µmol/ml) and NaOMe (A 3.6 mg/ml, 66.7 µmol/ml; **B** 5.4 mg/ml, 100.0 µmol/ml) were measured into a Schlenktube and dissolved in a stock solution of 1-Dodecanol containing 25%wt methanol with 2.9%wt THF as the internal standard. The 20 ml stainless steel autoclave was equipped with a stirring bar, closed and evacuated and purged with argon three times. The reaction mixture (1.5 ml) was added at room temperature through the ball valve (**5**) under argon. The autoclave was pressurized *via* the needle valve (**4**) with CO (10 bar) and H₂ (**A** 50 bar; **B** 80 bar) and heated to 150°C (**A**) or 160°C (**B**) for 1 h (initial TOF) and 4 h. After the reaction was completed, the autoclave was cooled to room temperature and slowly vented while stirring. The reaction mixture was analyzed by NMR spectroscopy.

General Procedure for Reaction Monitoring

The Reaction Monitoring experiment was performed in a 280 ml stainless-steel reactor. The reactor is connected to an *in situ* FTIR-device and a Benchtop NMR spectrometer through 1/16" stainless steel tubing. The reaction mixture was continuously pumped *via* a *FluSys WADose Lite HP* through the setup with a flow of 2 ml/min. The flow rate was controlled using a *Bronkhorst Mini CoriFlow* flowmeter. The setup is illustrated in Figure S7 (GC not used for this experiment). FTIR-measurements were performed using a *Bruker Vertex 70v* device equipped with a *Harrick Scientific* flow cell (HPL-C-13). The pathlength was 150 µm (PTFE spacer). The flow cell was equipped with diamond windows from Diamond Materials GmbH (Diameter: 13 mm, Central Thickness: 1300 µm, wedge: < 0.05°, Surface: polished, Ra < 20 nm). The NMR-measurements were performed with a *Bola* PTFE-tube (Outer diameter: 4 mm; Inner diameter: 2 mm).

Molecular complex $[Mn(CO)_2Br[HN(C_2H_4P'Pr_2)_2]]$ (0.7 mg/ml, 1.3 µmol/ml) and NaOMe (3.6 mg/ml, 66.7 µmol/mol) were measured in the glovebox into a Schlenktube and dissolved in 35 ml of a stock solution of 1-Dodecanol containing 25%wt methanol with 2.9%wt THF as the internal standard. The reactor was evacuated and purged with argon three times before the reaction mixture was added *via* a syringe. The reactor was then heated to 150 °C. Once the

reaction temperature was reached the pump for the sample loop and the measurements were started. Then 8 bar CO and 32 bar H_2 were added. FTIR-measurements were recorded every minute for the first 5.5 h and after that every 10 min. NMR spectra were recorded every minute for the first 90 min and after that every 4.5 min.



Figure S10: Left: Illustrative scheme of the reactor setup. Right: Construction of the reactor setup. GC not used for this experiment.

General Procedure for Catalyst Recycling

Recycling reactions were carried out in a 300 ml Parr reactor. Molecular complex $[Mn(CO)_2Br[HN(C_2H_4P'Pr_2)_2]]$ (0.7 mg/ml, 1.3 µmol/ml) and NaOMe (3.6 mg/ml, 66.7 µmol/mol) were measured in the glovebox into a Schlenktube and dissolved in 70 ml 1-Dodecanol. The stainless-steel reactor was closed and evacuated and purged with argon three times. The reaction mixture was added at room temperature under argon. The reactor was pressurized *via* a needle valve with CO (20 bar) and H₂ (100 bar) and heated to 150°C for 4 h. Then the reactor was cooled to room temperature and slowly vented while stirring. A vacuum pump with a liquid nitrogen cooling trap was connected to the reactor. The reactor was heated to 70 °C and the methanol was removed under reduced pressure (max. 50 mbar). After the reactor was cooled down to room temperature the reactor was again pressurized with the same gas amounts and the procedure was repeated in total 6 times. The distillates of each run were analyzed by NMR spectroscopy and XRF. Before the pressurization of the 6th run NaOMe (4.65 mmol) were added in 10 ml 1-Dodecanol to the reaction mixture.

3 References

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