Supporting Information

Alcohol-assisted hydrogenation of carbon monoxide to methanol using molecular manganese catalysts

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2. General Methods

All catalytic and stoichiometric reactions were performed under argon atmosphere using standard Schlenk and glovebox techniques. The used glassware was dried under vacuum at high temperatures, evacuated, and refilled with argon at least three times. The solvents were purified using solvent purification systems and were stored and handled under argon. Chemicals were purchased from Sigma-Aldrich, Alfa-Aesar, abcr, Acros Organics, TCI chemicals and used without further purification. NMR-spectra were recorded on Bruker AV-300, AV-400, DPX-300, AV-600 spectrometers at the indicated temperatures with the chemical shifts ($\delta$) given in ppm relative to TMS and the coupling constants ($J$) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale (Acetonitrile-$d_3$: $\delta_H = 1.94$ ppm and $\delta_C = 118.3$, 1.3 ppm; CDCl$_3$: $\delta_H = 7.26$ ppm and $\delta_C = 77.1$ ppm; CD$_2$Cl$_2$: $\delta_H = 5.32$ ppm and $\delta_C = 54.00$ ppm; C$_6$D$_6$: $\delta_H = 7.16$ ppm and $\delta_C = 128.1$ ppm; THF-$d_8$: $\delta_H = 1.72$ ppm, 3.58 ppm and $\delta_C = 67.2$ ppm, 25.3 ppm; toluene-$d_8$: $\delta_H = 2.08$, 6.97, 7.01, 7.09 ppm and $\delta_C = 137.5, 128.9, 127.9, 125.1, 20.4$ ppm; DMSO-$d_6$: $\delta_H = 2.50$ ppm and $\delta_C = 39.5$ ppm).\(^1\)

Note: Catalytic reactions involving pressurized carbon monoxide and hydrogen were carried out in an in-house built stainless steel reactor equipped with a pressure transducer and external electrical heating. Safety advice: Conducting high-pressure experiments present a significant risk. They must be conducted by following appropriate safety procedures in conjunction with the use of suitable equipment.

3. Synthesis of Manganese and Cobalt Pincer Complex

Manganese pincer complexes 3, 4, 5, and 7 were prepared according to the reported literature: A. Kaithal, M. Hölscher, W. Leitner. *Angew. Chem. Int. Ed.* 2018, 57, 13449-13453.\(^2\)

Manganese pincer complexes 6 was prepared according to the reported literature: M. Schlagbauer, F. Kallmeier, T. Irrgang, R. Kempe. *Angew. Chem.* 2020, 132, 1501–1506.\(^3\)

Manganese pincer complex 8 was prepared according to the reported literature: A. Kaithal, S. Sen, C. Erken, T. Weyhermüller, M. Hölscher, C. Werlé, W. Leitner. *Nat. Commun.* 2018, 9, 4521.\(^4\)

Cobalt pincer complex 9 was prepared according to the reported literature: H. H. Cramer, B. Chatterjee, T. Weyhermüller, C. Werlé, W. Leitner, *Angew. Chem. Int. Ed.* 2020, 59, 15674-15681.\(^5\)

4. Standard Procedure for Catalyst Optimization

Molecular complexes (1 - 9) and NaO\textsubscript{t}Bu (9.6 mg, 0.10 mmol) were measured into a glass inlet equipped with a stirring bar inside a glovebox. The glass inlet was closed with a septum and transferred into the bottom part of the 10 mL steel autoclave, where it was opened under a stream of argon. After sealing,
the autoclave was evacuated and purged with argon three times. Ethanol (1 mL) and toluene (0.5 mL) were added at room temperature through a valve under argon. The autoclave was sealed, pressurized with CO (5 bar) and H₂ (50 bar), and heated at 150 °C for 24 h. After the reaction was completed, the autoclave was cooled to room temperature and slowly vented while stirring. Mesitylene (43.2 mg, 0.36 mmol) was added as an internal standard to the reaction mixture, and the resulting sample was analyzed by NMR spectroscopy.

5. Standard Procedure for Temperature Optimization

Mn-MACHO-iPr complex 3 (4.95 mg, 0.01 mmol) and NaO'Bu (9.6 mg, 0.10 mmol) were measured into a glass inlet equipped with a stirring bar inside a glovebox. The glass inlet was closed with a septum and transferred into the bottom part of the 10 mL steel autoclave, where it was opened under a stream of argon. After sealing, the autoclave was evacuated and purged with argon three times. Ethanol (1 mL) and toluene (0.5 mL) were added at room temperature through a valve under argon. The autoclave was sealed, pressurized with CO (5 bar) and H₂ (50 bar), and heated at a specific temperature for 8 h. After the reaction was completed, the autoclave was cooled to room temperature and slowly vented while stirring. Mesitylene (43.2 mg, 0.36 mmol) was added as an internal standard to the reaction mixture, and the resulting sample was analyzed by NMR spectroscopy.

6. Standard Procedure for Base Optimization

Mn-MACHO-iPr complex 3 (4.95 mg, 0.01 mmol) and base (0.10 mmol) were measured into a glass inlet equipped with a stirring bar inside a glovebox. The glass inlet was closed with a septum and transferred into the bottom part of the 10 mL steel autoclave, where it was opened under a stream of argon. After sealing, the autoclave was evacuated and purged with argon three times. Ethanol (1 mL) and toluene (0.5 mL) were added at room temperature through a valve under argon. The autoclave was sealed, pressurized with CO (5 bar) and H₂ (50 bar), and heated at 150 °C for 8 h. After the reaction was completed, the autoclave was cooled to room temperature and slowly vented while stirring. Mesitylene (43.2 mg, 0.36 mmol) was added as an internal standard to the reaction mixture, and the resulting sample was analyzed by NMR spectroscopy.

7. Standard Procedure for Pressure Optimization

Mn-MACHO-iPr complex 3 (4.95 mg, 0.01 mmol) and NaO'Bu (9.6 mg, 0.10 mmol) were measured into a glass inlet equipped with a stirring bar inside a glovebox. The glass inlet was closed with a septum and transferred into the bottom part of the 10 mL steel autoclave, where it was opened under a stream of argon. After sealing, the autoclave was evacuated and purged with argon three times. Ethanol (1 mL) and toluene (0.5 mL) were added at room temperature through a valve under argon. The autoclave was sealed, pressurized with CO and H₂, and heated at 150 °C for 8 h. After the reaction was completed, the autoclave was cooled to room temperature and slowly vented while stirring. Mesitylene (43.2 mg, 0.36 mmol) was added as an internal standard to the reaction mixture, and the resulting sample was analyzed by NMR spectroscopy.
0.36 mmol) was added as an internal standard to the reaction mixture, and the resulting sample was analyzed by NMR spectroscopy.

8. **Standard Procedure for Turnover Number (TON) Optimization**

Mn-MACHO-Pr complex 3 (1 – 2.5 μmol) and NaO’Bu (9.6 mg, 0.10 mmol) were measured into a glass inlet equipped with a stirring bar inside a glovebox. The glass inlet was closed with a septum and transferred into the bottom part of the 10 mL or 20 mL steel autoclave, where it was opened under a stream of argon. After sealing, the autoclave was evacuated and purged with argon three times. Ethanol (1 mL) and toluene (0.5 mL) were added at room temperature through a valve under argon. The autoclave was sealed, pressurized with CO and H₂, and heated at 150 °C for 12 h. After the reaction was completed, the autoclave was cooled to room temperature and slowly vented while stirring. Mesitylene (43.2 mg, 0.36 mmol) was added as an internal standard to the reaction mixture, and the resulting sample was analyzed by NMR spectroscopy.

9. **Control Experiments to Investigate the Proposed Reaction Network**

9.1. **Hydrogenation of CO Using Complex I in the Absence of a Base (Scheme 2a)**

9.1.1. **Synthesis of complex I**

A PTFE sample vial was charged with Mn-MACHO-Pr complex 3 (50 mg, 0.1 mmol), NaO’Bu (11.53 mg, 0.12 mmol) and toluene (0.5 mL). The resulting solution was stirred for half an hour at room temperature leading to a color change from yellow to orange-red. Filtration of the reaction mixture over celite followed by removing the solvent under vacuo led to the isolation of complex I (38.5 mg, 0.092 mmol, 92%) as a dark red solid. The analytical data of the complex are consistent with those previously reported in the literature.²

\[
\text{CO} + \text{H}_2 \xrightarrow{\text{I (0.01 mmol)}} \text{CH}_3\text{OH} \quad \text{TON (8)}
\]

Mn-complex I (4.15 mg, 0.01 mmol) was measured into a glass inlet equipped with a stirring bar inside a glovebox. The glass inlet was closed with a septum and transferred into the bottom part of the 10 mL steel autoclave, where it was opened under a stream of argon. After sealing, the autoclave was evacuated and purged with argon three times. Ethanol (1 mL) and toluene (0.5 mL) were added at room temperature through a valve under argon. The autoclave was sealed, pressurized with CO (5 bar), H₂ (50 bar), and heated to 150 °C. After 8 h, the autoclave was cooled to room temperature and slowly vented while stirring. Mesitylene (43.2 mg, 0.36 mmol) was added as an internal standard to the reaction mixture, and the resulting sample was analyzed by NMR spectroscopy.
mixture, and the resulting sample was analyzed by NMR spectroscopy. \( \delta_{\text{standard}} = 6.64 \text{ (s, 3H), } \delta_{\text{MeOH}} = 3.17 \text{ (s, 1H)}. \)

**Figure S1:** \(^1\)H NMR (400 MHz, tol-d8, 298 K) reaction mixture spectrum for the reaction of CO and H\(_2\) using complex I.

### 9.2. The Reaction of Ethanol with Carbon Monoxide in the Presence of a Base (Scheme 2b)

NaO\(^\text{Bu}\) (9.6 mg, 0.1 mmol) was measured into a glass inlet equipped with a stirring bar inside a glovebox. The glass inlet was closed with a septum and transferred into the bottom part of the 10 mL steel autoclave, where it was opened under a stream of argon. After sealing, the autoclave was evacuated and purged with argon three times. Ethanol (1.0 mL) was added at room temperature under argon. The autoclave was sealed, pressurized with CO (5 bar), and heated at 150 °C. After 8 h, the autoclave was cooled to room temperature and slowly vented while stirring. Mesitylene (43.2 mg, 0.36 mmol) was added as an internal standard to the reaction mixture, and the resulting sample was analyzed by NMR spectroscopy. \( \delta_{\text{standard}} = 6.64 \text{ (s, 3H), } \delta_{\text{formate}} = 7.64 \text{ (s, 1H)}. \)
9.3. The Reaction of Carbon Monoxide with Hydrogen in the Absence of Ethanol (Scheme 2c)

\[
\text{CO} + 2 \text{H}_2 \xrightarrow{\text{NaO}^\text{t} \text{Bu} (0.1 \text{ mmol})} \xrightarrow{\text{tol.}, 150 \degree \text{C}, 8 \text{ h}} \text{CH}_3\text{OH}
\]

Mn-MACHO-iPr complex 3 (4.95 mg, 0.01 mmol) and NaO^tBu (9.6 mg, 0.10 mmol) were measured into a glass inlet equipped with a stirring bar inside a glovebox. The glass inlet was closed with a septum and transferred into the bottom part of the 10 mL steel autoclave, where it was opened under a stream of argon. After sealing, the autoclave was evacuated and purged with argon three times. Toluene (1 mL) was added at room temperature through a valve under argon. The autoclave was sealed, pressurized with CO (5 bar) and H\textsubscript{2} (50 bar), and heated at 150 °C for 8 h. After the reaction was completed, the autoclave was cooled to room temperature and slowly vented while stirring. Mesitylene (43.2 mg, 0.36 mmol) was added as an internal standard to the reaction mixture, and the resulting sample was analyzed by NMR spectroscopy. (\(\delta_{\text{standard}} = 6.63 \text{ (s, 3H)}, \delta_{\text{MeOH}} = 3.04 \text{ (s, 3H)}\)).
9.4. The reaction of Ethyl Formate with CO and H$_2$ Using Complex 3 (Scheme 2d)

Mn-MACHO-Pr complex 3 (4.95 mg, 0.01 mmol) and NaO$^+$Bu (9.6 mg, 0.1 mmol) were measured into a glass inlet equipped with a stirring bar inside a glovebox. The glass inlet was closed with a septum and transferred into the bottom part of the 10 mL steel autoclave, where it was opened under a stream of argon. After sealing, the autoclave was evacuated and purged with argon three times. Ethyl formate (370.4 mg, 5 mmol) and toluene (1.0 mL) were added at room temperature through a valve under argon. The autoclave was sealed, pressurized with CO (15 bar), H$_2$ (50 bar), and heated to 150 °C. After 8 h, the autoclave was cooled to room temperature and slowly vented while stirring. Mesitylene (43.2 mg, 0.36 mmol) was added as an internal standard to the reaction mixture, and the resulting sample was analyzed by NMR spectroscopy. ($\delta_{\text{standard}} = 6.70$ (s, 3H), $\delta_{\text{MeOH}} = 3.33$ (s, 1H)).
Figure S4: $^1$H NMR (400 MHz, CDCl$_3$, 298 K) reaction mixture spectrum for the reaction of ethyl formate with CO and H$_2$.

9.5. The Reaction of Ethyl Formate with H$_2$ Using Complex 3

Mn-MACHO-iPr complex 3 (4.95 mg, 0.01 mmol) and NaO'Bu (9.6 mg, 0.1 mmol) were measured into a glass inlet equipped with a stirring bar inside a glovebox. The glass inlet was closed with a septum and transferred into the bottom part of the 10 mL steel autoclave, where it was opened under a stream of argon. After sealing, the autoclave was evacuated and purged with argon three times. Ethyl formate (370.4 mg, 5 mmol) and toluene (1.0 mL) were added at room temperature through a valve under argon. The autoclave was sealed, pressurized with H$_2$ (50 bar), and heated to 150 °C temperature. After 8 h, the autoclave was cooled to room temperature and slowly vented while stirring. Mesitylene (43.2 mg, 0.36 mmol) was added as an internal standard to the reaction mixture, and the resulting sample was analyzed by NMR spectroscopy. ($\delta_{(\text{standard})} = 6.66 \text{ (s, 3H)}, \delta_{\text{MeOH}} = 3.28 \text{ (s, 1H)}$).
Figure S5: $^1$H NMR (400 MHz, CDCl$_3$, 298 K) reaction mixture spectrum for the reaction of ethyl formate with H$_2$. 
10. A plausible Alternate Mechanism for the Direct Hydrogenation of CO
11. NMR Spectra for the Hydrogenation of CO to Methanol

Figure S6: $^1$H NMR (400 MHz, Tol-d8, 298 K), Table 1, entry 1.

Figure S7: $^1$H NMR (400 MHz, Tol-d8, 298 K), Table 1, entry 2.
Figure S8: $^1$H NMR (400 MHz, CDCl$_3$, 298 K), Table 1, entry 3.

Figure S9: $^1$H NMR (400 MHz, CDCl$_3$, 298 K), Table 1, entry 4.
Figure S10: $^1$H NMR (400 MHz, CDCl$_3$, 298 K), Table 1, entry 5.

Figure S11: $^1$H NMR (400 MHz, CDCl$_3$, 298 K), Table 1, entry 6.
Figure S12: $^1$H NMR (400 MHz, CDCl$_3$, 298 K), Table 1, entry 7.

Figure S13: $^1$H NMR (400 MHz, CDCl$_3$, 298 K), Table 1, entry 8.
Figure S14: $^1$H NMR (400 MHz, Tol-d$_8$, 298 K), Table 1, entry 9.

Figure S15: $^1$H NMR (400 MHz, Tol-d$_8$, 298 K), Table 2, entry 1.
Figure S16: $^1$H NMR (400 MHz, Tol-d8, 298 K), Table 2, entry 2.

Figure S17: $^1$H NMR (400 MHz, CDCl$_3$, 298 K), Table 2 entry 3.
Figure S18: $^1$H NMR (400 MHz, Tol-d8, 298 K), Table 2, entry 4.

Figure S19: $^1$H NMR (400 MHz, CDCl3, 298 K), Table 2, entry 5.
Figure S20: $^1$H NMR (400 MHz, CDCl$_3$, 298 K), Table 2, entry 6.

Figure S21: $^1$H NMR (400 MHz, CDCl$_3$, 298 K), Table 2, entry 7.
Figure S22: $^1$H NMR (400 MHz, Tol-d$_8$, 298 K), Table 2, entry 8.

Figure S23: $^1$H NMR (400 MHz, CDCl$_3$, 298 K), Table 3, entry 1.
Figure S24: $^1$H NMR (400 MHz, CDCl$_3$, 298 K), Table 3, entry 2.

Figure S25: $^1$H NMR (400 MHz, CDCl$_3$, 298 K), Table 3, entry 3.
Figure S26: $^1$H NMR (400 MHz, CDCl$_3$, 298 K), Table 3, entry 4.

Figure S27: $^1$H NMR (400 MHz, CDCl$_3$, 298 K), Table 3, entry 5.
Figure S28: $^1$H NMR (400 MHz, CDCl$_3$, 298 K), Table 3, entry 6.

Figure S29: $^1$H NMR (400 MHz, CDCl$_3$, 298 K), Table 3, entry 7.
Figure S30: $^1$H NMR (400 MHz, CDCl$_3$, 298 K), Table 4, entry 1.

Figure S31: $^1$H NMR (400 MHz, CDCl$_3$, 298 K), Table 4, entry 2.
Figure S32: $^1$H NMR (400 MHz, CDCl$_3$, 298 K), Table 4, entry 3.

Figure S33: $^1$H NMR (400 MHz, Tol-d8, 298 K), Table 4, entry 4.
Figure S34: $^1$H NMR (400 MHz, Tol-d8, 298 K), Table 4, entry 5.

Figure S35: $^1$H NMR (400 MHz, Tol-d8, 298 K), Table 4, entry 6.
Figure S36: $^1$H NMR (400 MHz, Tol-d8, 298 K) spectrum for Scheme 4.
12. References

(1) Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I., NMR Chemical Shifts of Trace Impurities: Common Laboratory Solvents, Organics, and Gases in Deuterated Solvents Relevant to the Organometallic Chemist. *Organometallics* 2010, 29 (9), 2176-2179.

(2) Kaithal, A.; Hölscher, M.; Leitner, W., Catalytic Hydrogenation of Cyclic Carbonates using Manganese Complexes. *Angew. Chem. Int. Ed.* 2018, 57 (41), 13449-13453.

(3) Schlagbauer, M.; Kallmeier, F.; Irrgang, T.; Kempe, R., Manganese-Catalyzed β-Methylation of Alcohols by Methanol. *Angew. Chem. Int. Ed.* 2020, 59 (4), 1485-1490.

(4) Kaithal, A.; Sen, S.; Erken, C.; Weyhermüller, T.; Hölscher, M.; Werlé, C.; Leitner, W., Manganese-catalyzed hydroboration of carbon dioxide and other challenging carbonyl groups. *Nat. Commun.* 2018, 9 (1), 4521.

(5) Cramer, H. H.; Chatterjee, B.; Weyhermüller, T.; Werlé, C.; Leitner, W., Controlling the Product Platform of Carbon Dioxide Reduction: Adaptive Catalytic Hydrosilylation of CO2 Using a Molecular Cobalt(II) Triazine Complex. *Angew. Chem. Int. Ed.* 2020, 59 (36), 15674-15681.