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Supporting Information

A Stable Manganese Pincer Catalyst for the Selective Dehydrogenation of Methanol

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Supporting Information

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1. General procedures

1.1 General experimental details

All reactions were performed under Argon atmosphere with exclusion of air using standard Schlenk techniques. Formic acid (FA), N,N-dimethyl-n-octylamine (DMOA), propylene carbonate, (PC) dioxane, terc-amyl alcohol, and triglyme were refluxed and distilled following standard procedures and stored under Argon atmosphere. Heptane, toluene, tetrahydrofuran (THF), EtOH and MeOH were dried by passing through a column of anhydrous alumina using a solvent purification system equipment from *Innovative Technology* and stored under Argon atmosphere. Water was degassed overnight by bubbling Argon overnight. KOH, tBuOK, LiOH and $LiBF_4$ were used and stored as received.

^{1}H NMR spectra were obtained at 300 MHz (Bruker AV-300) or 400 MHz (Bruker AV-400). $^{13}C\{1H\}$ NMR spectra were obtained at 75 MHz or 101 MHz. $^{31}P\{^{1}H\}$ NMR spectra were obtained at 121 MHz or 162 MHz. NMR chemical shifts are reported in ppm downfield from tetramethylsilane and were referenced to the residual proton resonance and the natural abundance ^{13}C resonance of the solvents. ^{31}P NMR chemical shifts are reported in ppm downfield from H_3PO_4 and referenced to an external 85% solution of phosphoric acid. Abbreviations used in the reported NMR experiments: b, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet.

IR-spectroscopy measurements were performed on a Vertex-80-FTIR spectrometer (BRUKER) with a MCT detector. The sample solutions were filled in a sealed IR-cell with CaF_2 windows and an optical path length of 0.012 mm which was purged with Argon prior to use. The temperature of the cell was controlled by a thermostat at 25 °C. The spectra were taken with 256 scans and a resolution of 1 cm^{-1}.

The synthesis of the complex **1** was done following a slightly modification of the reported procedure[1]: To a solution of THF (16 mL) containing $[MnBr(CO)_5]$ (231 mg, 0.84 mmol), $[HN(CH_2CH_2P(iPr)_2)_2]$ (308 mg, 1 mmol) was added dropwise, obtaining an orange-yellowish solution. The solution was stirred at room temperature for 15 minutes. After the reaction was refluxed for 3 hours, it was cooled down to room temperature and the solvent was removed in *vacuo*. The yellow powder was dissolved in toluene and filtered through celite. The product was washed with heptane and dried in *vacuo*.

[1] S. Elangovan, C. Topf, S. Fischer, H. Jiao, A. Spannenberg, W. Baumann, R. Ludwig, K. Junge, M. Beller, *J. Am. Chem. Soc.* **2016**, *138*, 8809–8814.

1.2 Calculation of TON

The measured gas volumes were corrected by a blank value (gas evolution measured in a reaction performed using same conditions but no catalyst added).
The turnover number (TON) was calculated by equation **(SI1):**

$$TON = \frac{\frac{V_{obs} - V_{blank}}{(V_{m,H_2,25°C} + V_{m,CO_2,25°C})}}{n_{cat}} \qquad (\boldsymbol{SI1})$$

where V_{obs} and V_{blank} are the gas volume measured in the catalytic reaction and blank reaction, respectively.
The calculation of $V_{m,H_2,25°C}$ was carried out using Van der Waals equation (equation (**SI2**)):

$$V_{m,H_2,25°C} = \frac{RT}{p} + b - \frac{a}{RT} = 24.48\ \frac{L}{mol} \qquad (\boldsymbol{SI2})$$

Where:

R: 8.3145 $m^3 \cdot Pa \cdot mol^{-1} \cdot K^{-1}$;
T: 298.15 K;
P: 101325 Pa;
a: $24.7 \cdot 10^{-3} \cdot Pa \cdot m^6 \cdot mol^{-2}$;
b: $26.6 \cdot 10^{-6}\ m^3 \cdot mol^{-1}$

The calculation of $V_{m,CO_2,25°C}$ was carried out using Van der Waals equation (equation (**SI3**)):

$$V_{m,CO_2,25°C} = \frac{RT}{p} + b - \frac{a}{RT} = 24.36\ \frac{L}{mol} \qquad (\boldsymbol{SI3})$$

Where:

R: 8.3145 $m^3 \cdot Pa \cdot mol^{-1} \cdot K^{-1}$;
T: 298.15 K;
P: 101325 Pa;
a: $36.5 \cdot 10^{-2} \cdot Pa \cdot m^6 \cdot mol^{-2}$;
b: $42.7 \cdot 10^{-6}\ m^3 \cdot mol^{-1}$

The equation (**SI1**) could be simplified when no CO_2 was released in the gas phase (MeOH and EtOH dehydrogenation) as it is shown in the equation (**SI4**):

$$TON = \frac{V_{obs} - V_{blank}}{V_{m,H_2,25°C} \cdot n_{cat}} \qquad (\boldsymbol{SI4})$$

1.3 GC calibrations

Gas content was determined by gas-phase GC. A GC sample was taken from the reaction system and was analyzed by one of the two available systems:

GC a): HP Plot Q / FID – hydrocarbons, Carboxen / TCD - permanent gases, He carrier gas.

GC b): Carboxen / TCD / Methanizer / FID - permanent gases, He carrier gas.

The gas integration was calibrated using certified gas mixtures from commercial suppliers (Linde and Air Liquide) with the following gas vol%:

GC a):

H_2: 1%, 10%, 25%, 50%, 100%

CO: 10 ppm, 100 ppm, 250 ppm, 1000 ppm, 1%, 10%

CO_2: 1%, 50%

CH_4: 1%

GC b):

H2: 1%, 10%, 25%, 50%, 100%

CO: 1 ppm, 2 * 10 ppm, 75 ppm, 100 ppm, 250 ppm, 1000 ppm, 1%, 10%

CO_2: 1%, 50%

CH_4: 1%

The systems allow for the determination of H_2, Ar, CH_4, CO and CO_2 within the ranges:

$H_2 \geq 0.5$ vol% - 100 vol%

CO ≥ 10 ppm [GC a)], CO down to 1 ppm [GC b)]

$CO_2 \geq 100$ ppm - 100 vol% [GC a)], down to 1 ppm [GC b)]

$CH_4 \geq 1$ ppm [GC b)]

GC analysis provides the relative composition of the different components of the collected gas. H_2, CO_2, CO, and CH_4 amounts were determined and their ratios established.

2. Burette measurements

Figure S1 depicts the setup of activity measurements with manual burettes.

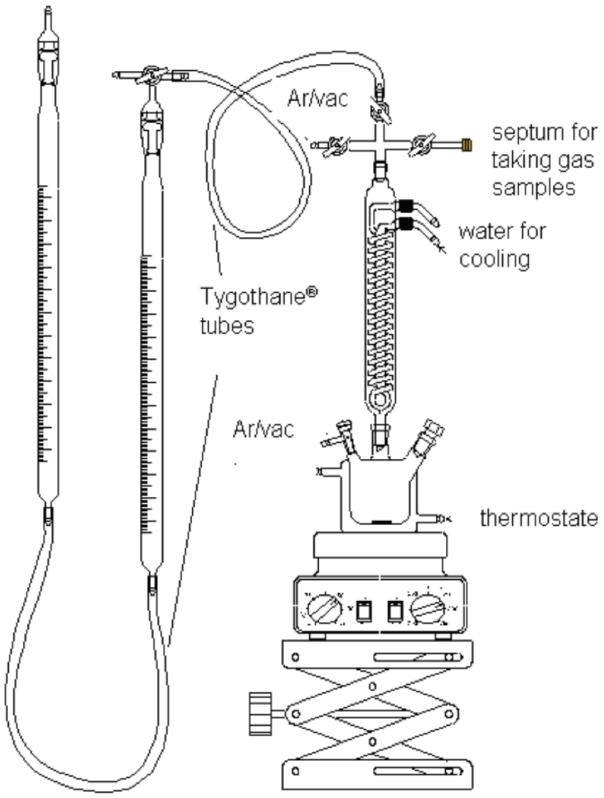


Figure SI1. Manual burette setup.

Automatic burette equipment:
The automatic burette equipment has been developed at the Leibniz-Institut für Katalyse e.V. Rostock together with MesSen Nord (Stäbelow). It can also be used for measuring the gas uptake in hydrogenation reactions. A detailed description of the equipment is provided in H.-J. Drexler, A. Preetz, T. Schmidt, D. Heller in *The Handbook of Homogeneous Hydrogenation*, Vol. 1 (Eds.: J. G. De Vries, C. J. Elsevier), Wiley-VCH, Weinheim, **2007**, pp. 257–293.

2.1 General procedure for the dehydrogenation of methanol

A solution (5mL) of MeOH and H_2O in a ratio 9:1 (volume) containing a defined amount of base and a defined amount of additives (ligand and additional solvent) was heated to 90°C and let it equilibrate for 20 min. Then, the manganese precursor ($MnBr(CO)_5$) or the different catalysts (8.4 µmol) were added in a teflon crucible, setting this point as the starting point for measuring the evolved gas volume using a manual or automatic burette. After running the reaction during the desired time, a GC sample was taken to determine the identity of the gas components.

2.2 General procedure for the dehydrogenation of ethanol

a solution (5mL) of EtOH and H_2O in a ratio 9:1 (volume) containing KOH (2.2444 g, 40 mmol) was heated to the 92°C and let it equilibrate for 20 min. Then catalyst **1** (4.18 mg, 8.4 µmol) was added was added in Teflon crucible, setting this point as the starting point for measuring the evolved gas volume using a manual or automatic burette. After running the reaction during the desired time, a GC sample was taken to determine the identity of the gas components.

2.3 General procedure for the dehydrogenation of paraformaldehyde

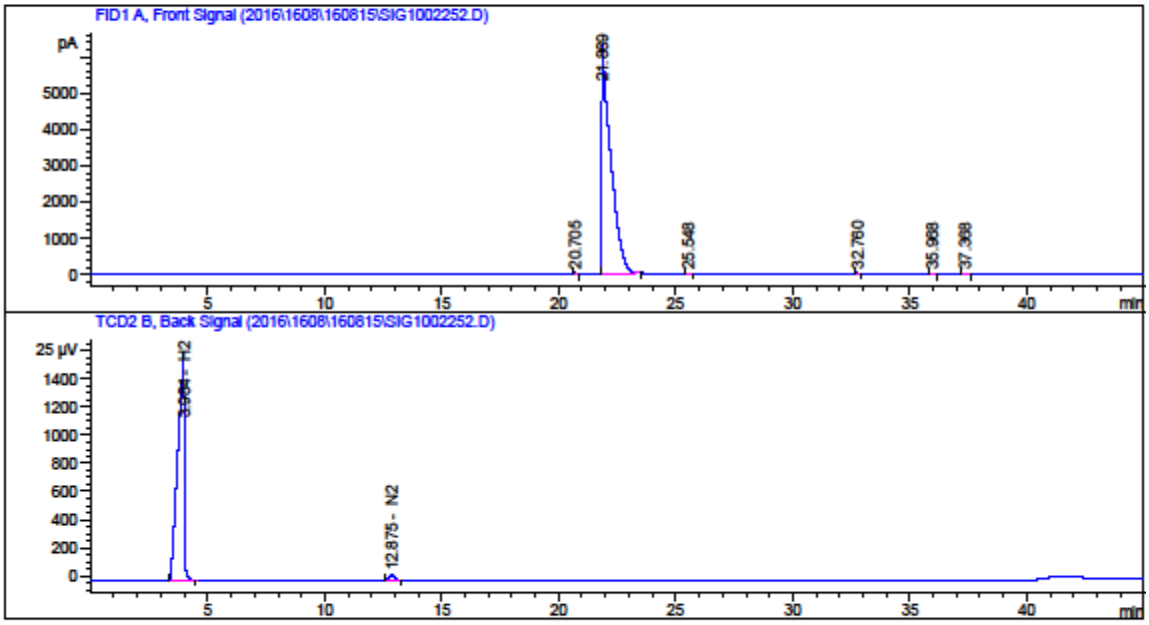
Paraformaldehyde (120 mg, 0.004 mol) was added to a mixture of *t*BuOH (36 mL) and KOH (aq) solution (4 mL), obtaining a final composition of 9:1 *t*BuOH/H_2O, 0.05M KOH, 0.1 M paraformaldehyde. The catalyst **1** (8.28 mg, 16.72 µmol) was added at the end. The mixture was heated and the reaction monitoring was started when the set temperature (81°C) was reached. After running the reaction during the desired time, a GC sample was taken to determine the identity of the gas components.

2.4 General procedure for the dehydrogenation of formic acid

A solution of formic acid and DMOA (11:10 molar ratio mixture, 5mL) was added to PC (5mL) in a reactor vessel. The mixture was heated to the desired 60°C and let it equilibrate for 20 min. Catalyst **1** (2.64 mg, 5.3 µmol) was added employing a Teflon crucible, setting this point as the starting point for measuring the evolved gas volume using a manual or automatic burette. After running the reaction during the desired time, a GC sample was taken to determine the identity of the gas components.

2.5 GC spectra

2.5.1 MeOH dehydrogenation

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 12.000            -          -           -        O2
 12.875 BB      681.89880 3.12982e-3    2.13422    N2
 16.600            -          -           -        CO
 29.400            -          -           -        CH4
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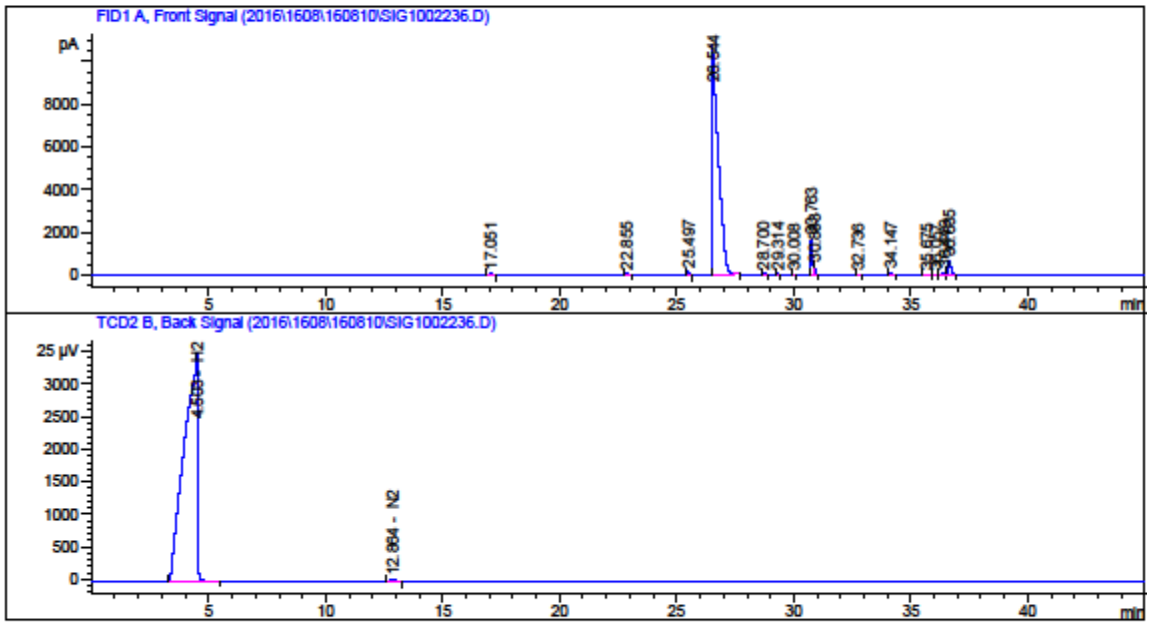
Figure SI2. GC spectra. Reaction conditions: MeOH/H_2O (5 mL, ratio 9:1), KOH (8 M), **1** (8.4 µmol, 1.68 mM); T_{set}: 92°C.

2.5.2 EtOH dehydrogenation

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Signal 2: TCD2 B, Back Signal

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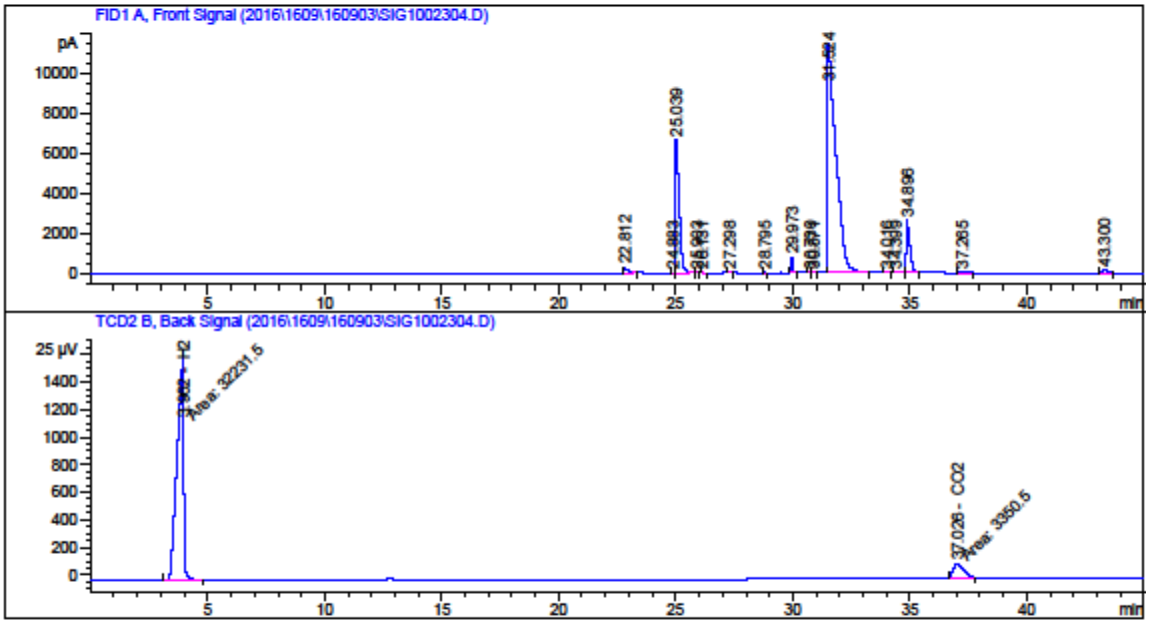
 12.000            -          -           -          O2
 12.864 BB      520.86621 3.12854e-3    1.62955     N2
 16.600            -          -           -          CO
 29.400            -          -           -          CH4
```

Figure SI3. GC spectra. Reaction conditions: EtOH/H_2O (5 mL, ratio 9:1), KOH (8 M), **1** (8.4 µmol, 1.68 mM); T_{set}: 92°C.

2.5.3 Para-formaldehyde dehydrogenation

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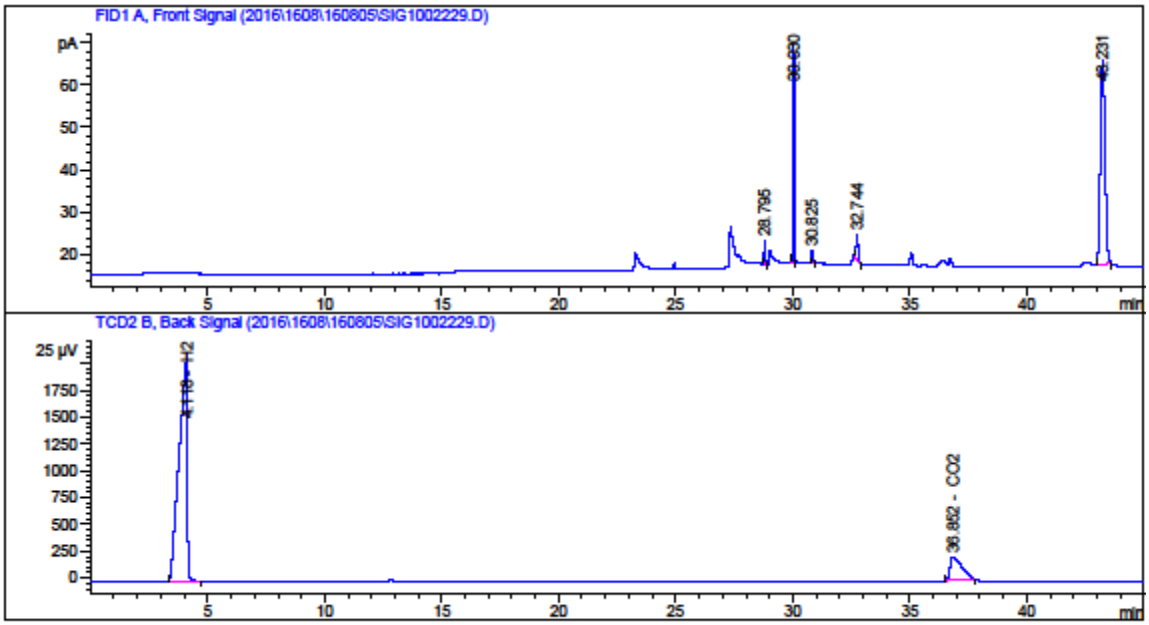
 12.000            -          -           -        O2
 12.800            -          -           -        N2
 16.600            -          -           -        CO
 29.400            -          -           -        CH4
 37.026 MM     3350.50342 1.70664e-3    5.71810    CO2

Totals :                                15.65350
```

Figure SI4. GC spectra. Reaction conditions tBuOH (36mL), H_2O (4mL), KOH (0.05M), paraformaldehyde (4 mmol, 0.1M), **1** (16,72 µmol, 0.418 mM); T_{set}: 81°C.

2.5.4. Formic acid dehydrogenation

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Signal 1: FID1 A, Front Signal


Signal 2: TCD2 B, Back Signal

RetTime  Type     Area      Amt/Area    Amount   Grp   Name
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 12.000            -          -          -         O2
 12.574            -          -          -         N2
 16.600            -          -          -         CO
 29.400            -          -          -         CH4
 36.852 BB     7774.96191 1.72772e-3   13.43296    CO2

Totals :                               29.20818
```

Figure SI5. GC spectra. Reaction conditions: PC (5mL), 11 mol FA/10 mol DMOA (5mL), **1** (5.3 µmol, 0.53 µM); T_{set}: 60°C.

3. Optimisation reactions

Table SI1. Influence of the different conditions on the activity of the catalyst.

Entry	Catalyst (µmol)	MeOH (mL)	H_2O (mL)	Additive	Solvent (mL)	T (°C)	VH_2 (5h) [mL]	TON (5h)
1	**1** (8.4)	9	1	KOH (8 M)	-	90	20	98
2	**1** (8.4)	4.5	0.5	KOH (8 M)	triglyme (5)	90	18	88
3	**1**(8.4)	4.5	0.5	KOH (8 M)	*t*-myl alcohol (5)	90	23	114
4	**1** (8.4)	4.5	0.5	KOH (8 M)	toluene (5)	90	6	31
5	**1** (8.4)	4.5	0.5	KOH (8 M)	dioxane (5)	90	26	126
6	**1** (8.4)	4.5	0.5	*t*BuOK (8 M)	triglyme (5)	90	7	34
7	**1** (8.4)	4.5	0.5	LiOH (8 M)	triglyme (5)	90	-	-
8	**1** (8.4)	4.5	0.5	$LiBF_4$ (1 mM)	triglyme (5)	90	-	-
9	**1** (8.4)	5	-	KOH (8 M)	-	90	18	90
10	**1** (8.4)	4.5	0.5	KOH (8 M)	-	90	11	54
11	**1** (8.4)	2.5	2.5	KOH (8 M)	-	90	-	-
12	**1** (8.4)	4.5	0.5	KOH (8 M), 10 eq. of PNP*i*PR ligand	-	90	28	138

4. Longterm test with different solvents

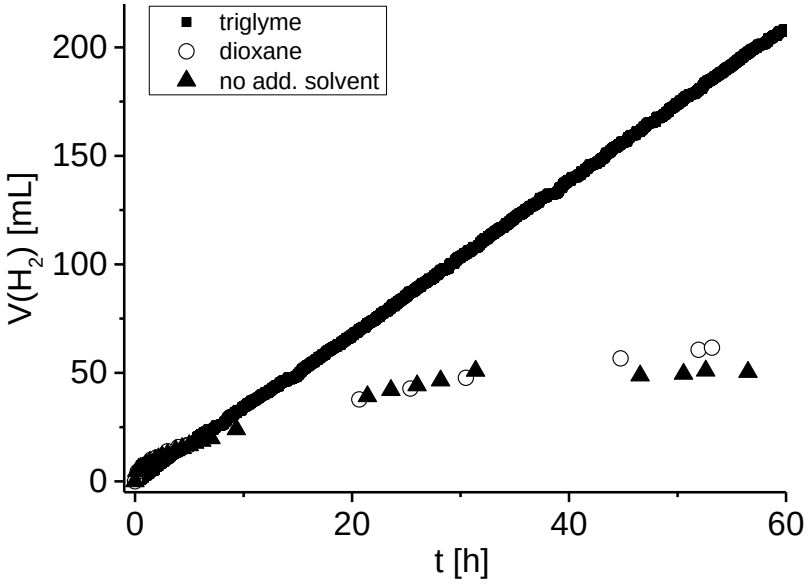


Figure SI6. Reaction conditions: MeOH/H_2O (5 mL, ratio 9:1), KOH (8 M; molarity based on total MeOH + H_2O volume), **1** (8.4 µmol, 0.84 mM), T_{set} 92 °C. Reactions performed without additional solven and with dioxane as solvent were performed in the manual burette set-up, while the reaction performed with the addition of triglyme was performed in the automatic burette set-up.

5. Longterm reaction of precursor $Mn(CO)_5Br$ plus 10 eq. of ligand

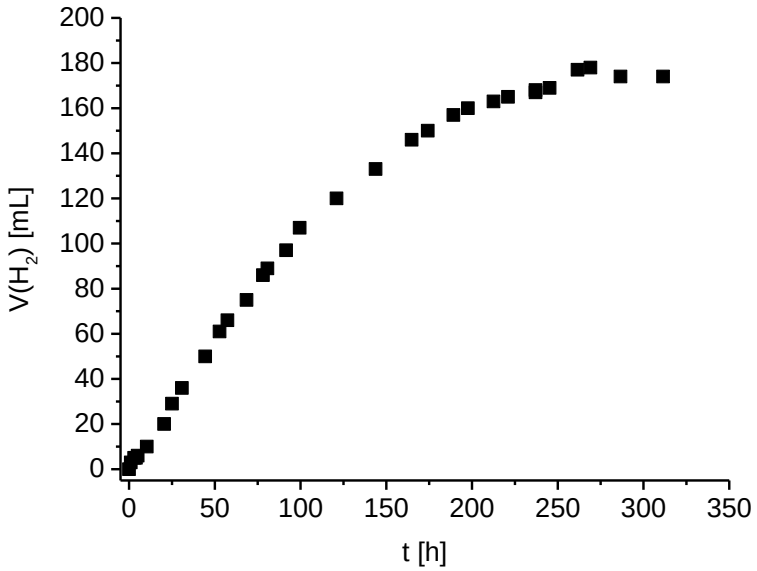


Figure SI7. Reaction conditions: MeOH/H_2O (20 mL, ratio 9:1), triglyme (20 mL), KOH (8 M; molarity based on total MeOH + H_2O volume), $Mn(CO)_5Br$ plus 10 eq. HPNP*i*Pr ligand (2.1 µmol, 0.05 mM); T_{set} 92°C.

6. NMR investigations

6.1 NMR of reaction solution

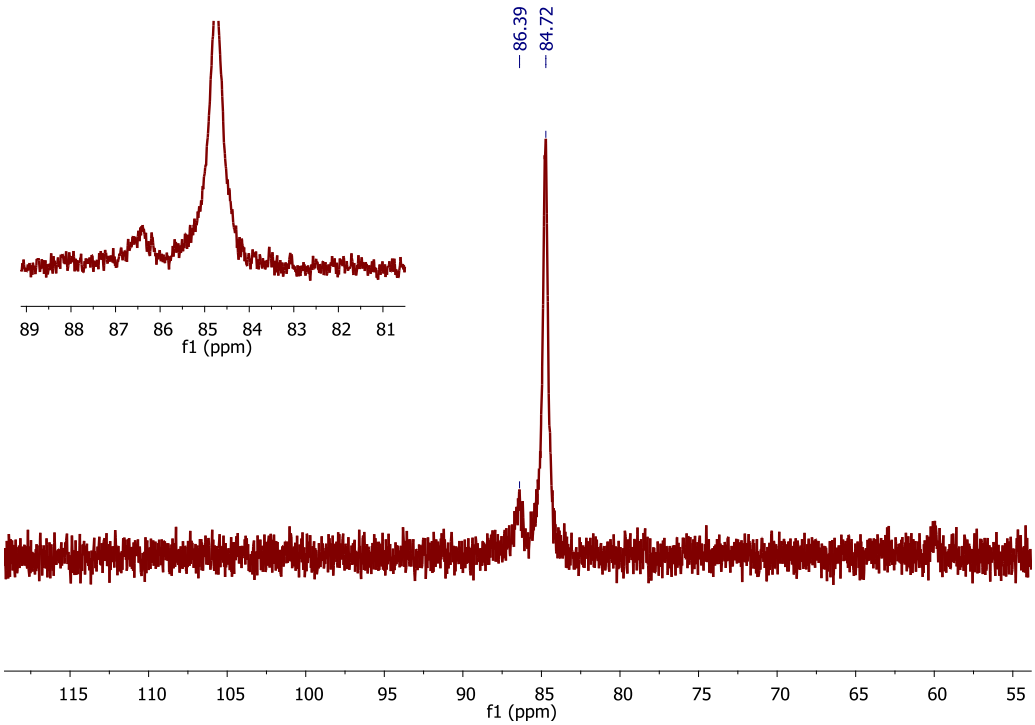


Figure SI8. ^{31}P NMR (297 K, 162 MHz, 9/1 MeOH/H_2O, a few drops of MeOD-d_4). **1** (10 mM) in 9:1 MeOH:H_2O solution containing 8 M KOH.

6.2 Light-triggered cleavage of the HNPNP*i*Pr ligand

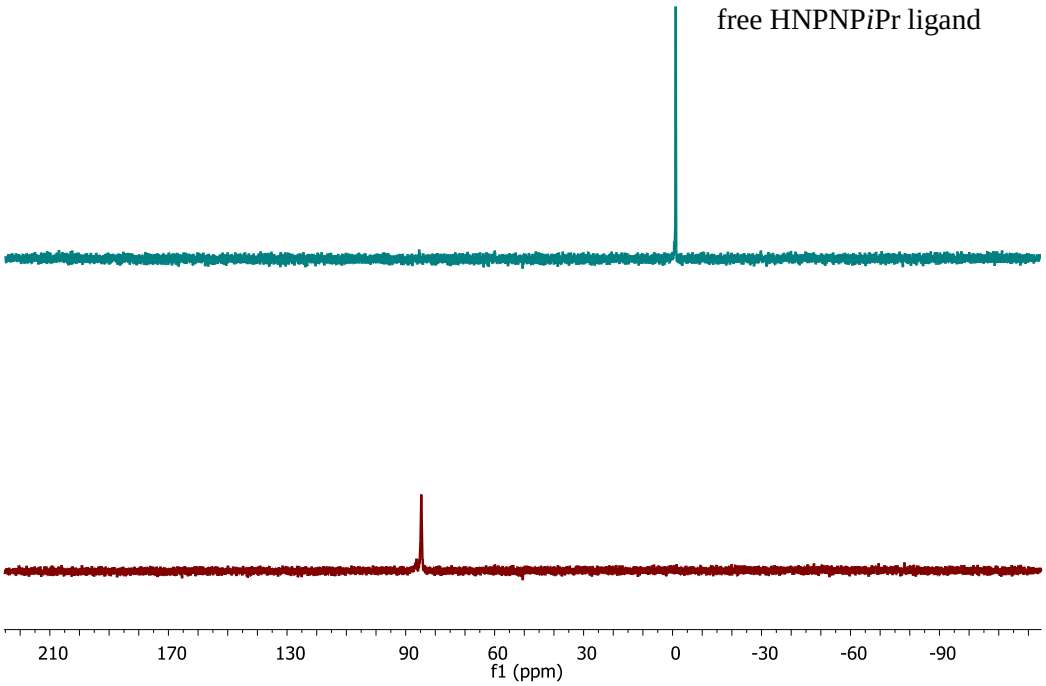


Figure SI9. ^{31}P NMR (297 K, 162 MHz, 9/1 MeOH/H_2O, a few drops of MeOD-d_4). Bottom: **1** (10 mM) in 9:1 MeOH:H_2O solution containing 8 M KOH. Top: After exposure to a Luxeon LED light source for 30 min.

6.3 NMR of the methoxide species 9

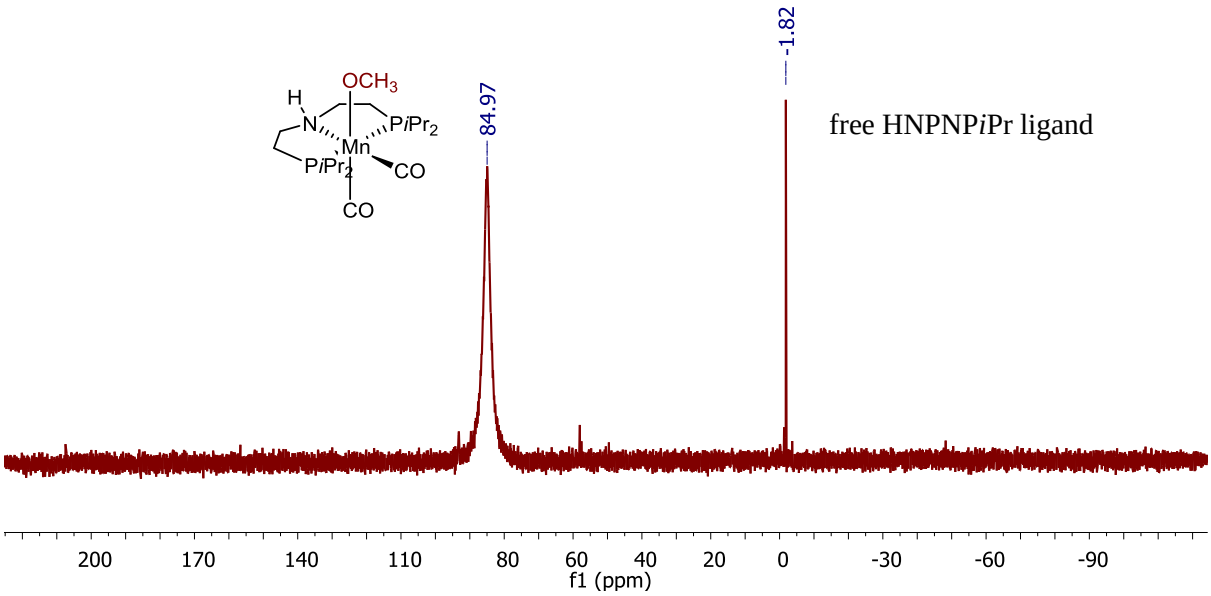


Figure SI10. ^{31}P NMR (296 K, 121.5 MHz, C_6D_6). Addition of 10 eq. of MeOH to amido species **8**. Spectrum was recorded after stirring for 1 hour. The amido species was generated *in-situ* by adding 3 eq. of NaO*t*Bu to the Mn complex **1**.

6.4 NMR of the hydroxide species 7

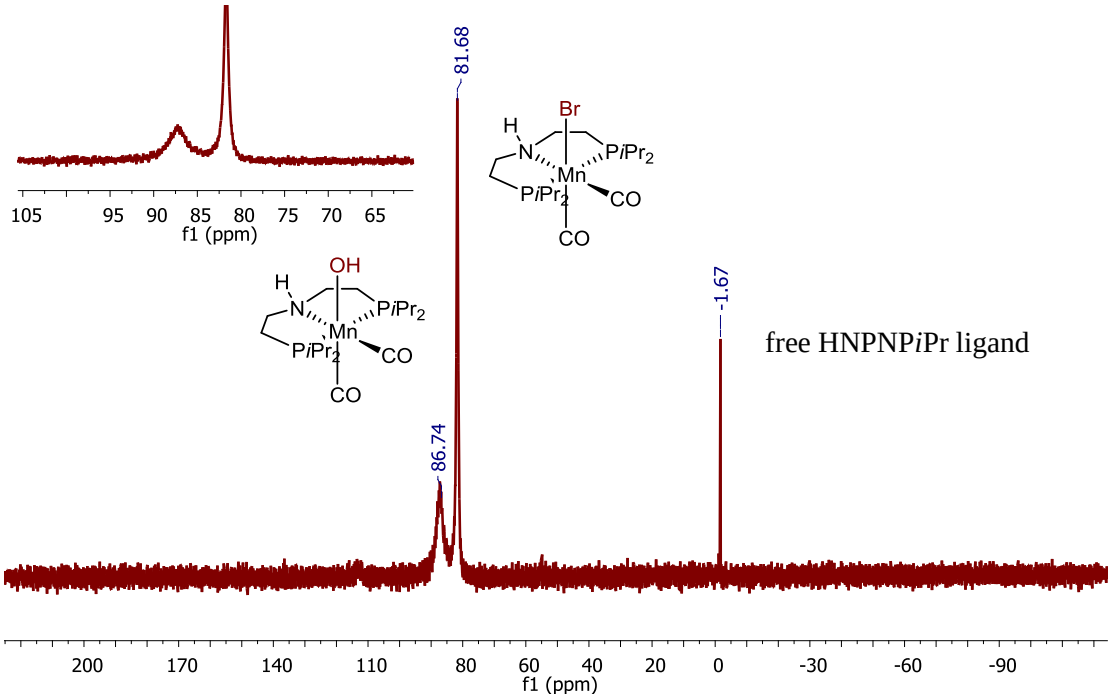


Figure SI11. ^{31}P NMR (296 K, 121.5 MHz, C_6D_6). Addition of 10 eq. of H_2O to amido species **8.** Spectrum was recorded after stirring for 1 hour. The amido species was generated *in-situ* by adding 3 eq. of NaO*t*Bu to the Mn complex **1**.

6.5 NMR of the formate species 11

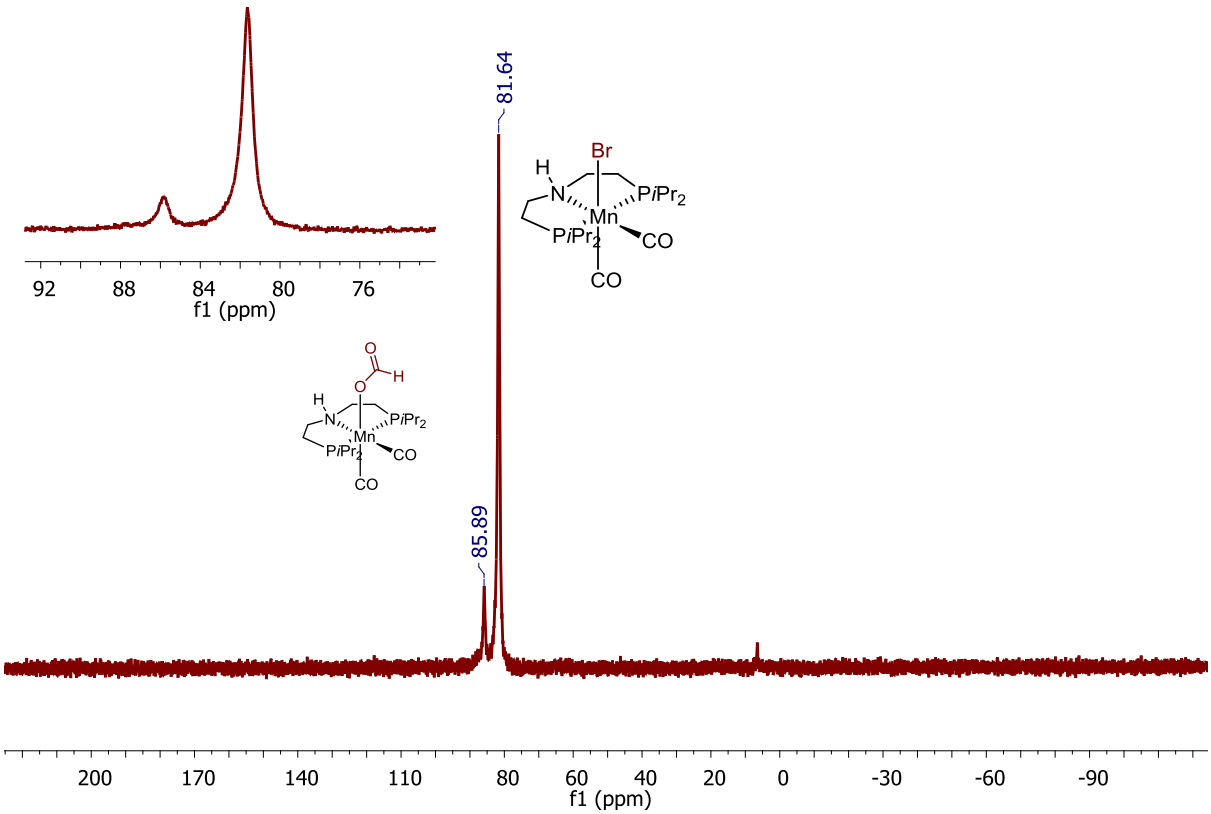


Figure SI12.^{31}P NMR (296 K, 121.5 MHz, C_6D_6). Addition of 10 eq. of formic acid to amido species **8**. Spectrum was recorded after stirring for 1 hour. The amido species was generated *in-situ* by adding 3 eq. of NaO*t*Bu to the Mn complex **1**.

7. IR investigations

7.1 Addition of KOH to 9:1 MeOH/H_2O solution containing Mn-iPr catalyst 1

To a 9:1 MeOH/H_2O solution containing 10 mM Mn-iPr catalyst in a Schlenk flask sequentially 0.5/1/10/800 eq. KOH were added (by the addition of a 8 M aqueous KOH sol.) and each time samples were taken and IR spectra were measured . Simultaneously, the same procedure was performed without catalyst in order to obtain IR background spectra.

7.2 Reaction monitoring

The 9:1 MeOH/H_2O solution containing 10 mM Mn-iPr catalyst and 8 M KOH in a Schlenk flask with condenser was stirred for 1 hour before 0.5 mL sample was taken and measured by IR and NMR spectroscopy. The solution was heated to 90 °C and another sample was taken after the solution was stirred for 5 min at that temperature. Subsequent samples were taken after 120 min and 300 min. For referencing purposes, formic acid was added to a 9:1 MeOH/H_2O solution containing 8 M KOH and measured. A reference solution without catalyst was measured for all samples for background.

8. Computational studies

In our previous studies we have computed the structures, stabilities and catalytic properties of a set of PNP-ligand-based transition metal pincer complexes (M = Fe, Ru, Os, Mn, and Ir) in the hydrogenation and dehydrogenation reactions, where we have validated different density functional methods on the basis of experimental evidences. It is found that the B3PW91[2] density functional theory method in conjugation with the all-electron TZVP basis set[3] (LANL2DZ[4] for Ru, Os, and Ir) has the best agreement between computation and experiment in structures and energies. In this study, we have used the same models and methods for investigating the methanol water reforming reactions; i.e.; all stationary structures were optimized and subsequently characterized at the B3PW91/TZVP level either as energy minimums without imaginary frequencies or transition states with only one imaginary frequency by frequency calculations; and the imaginary model connects the initial and the final states. The thermal corrections to Gibbs free energy at 298 K from the frequency analysis are added to the total electronic energy, and we therefore used the corrected Gibbs free energy (ΔG) at 298 K for our energetic discussion and comparison. All calculations have been carried out by using the Gaussian09 program package[5].

With the availability of the experimental recorded IR spectra for the bromide complex **1**, we scaled the computed harmonic CO stretching frequencies. We obtained an average scaling factor of 0.9452 for the CO stretching frequencies; and this factor can be used to scale all CO frequencies of other complexes for the discussion of their changes upon the change of the reaction condition. The scaled IR spectra with a band width of 5 cm^{-1} are plotted in Figures SI13 and SI14.

[2] Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822-8824.

[3] Schaefer, A.; Huber, C.; Ahlrichs, R. *J. Chem. Phys.* **1994**, *100*, 5829-5835.

[4] P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 299-310.

[5] Frisch J. *et al.*, Gaussian 09, Revision C.01, Gaussian, Inc., Wallingford CT, 2010.

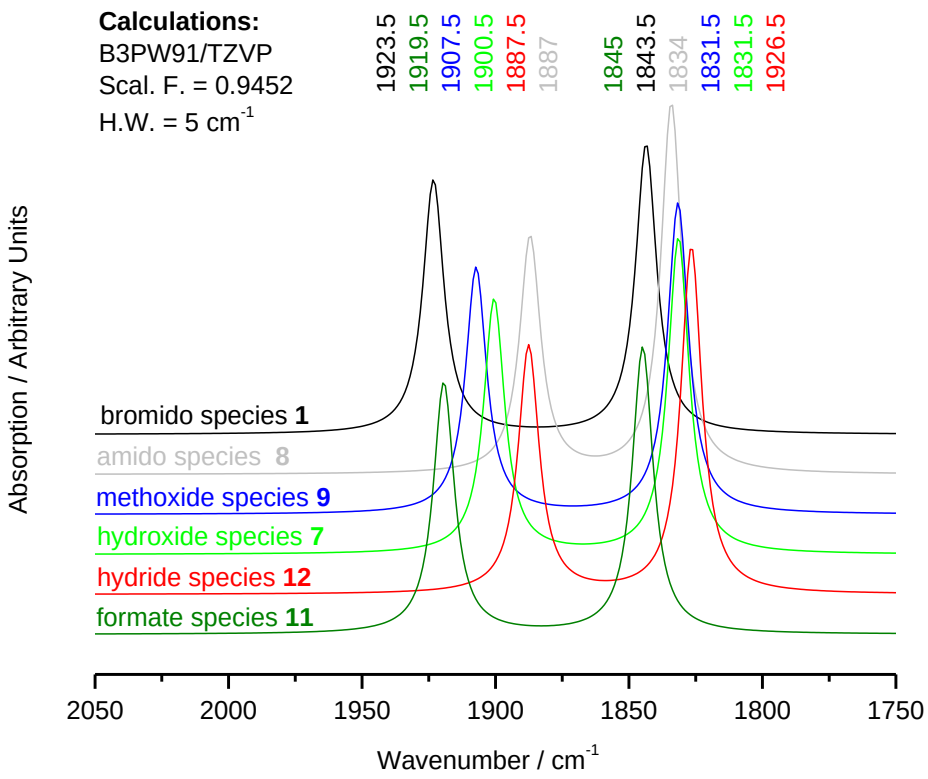


Figure SI13. DFT-calculated IR spectra for a range of Mn species.

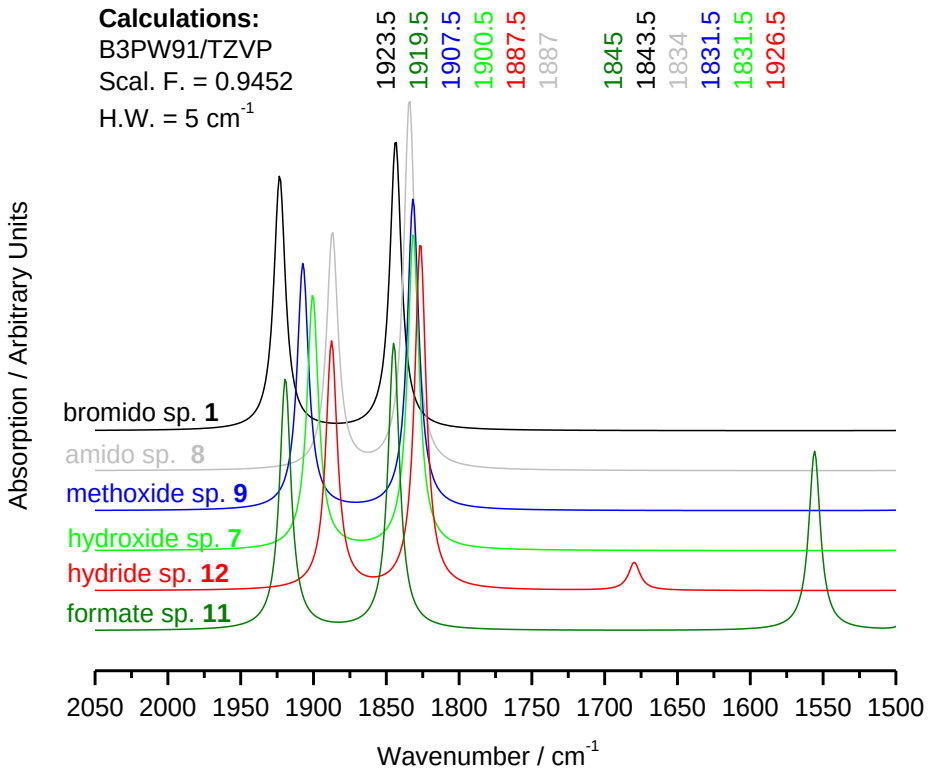
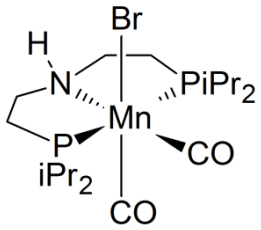


Figure SI14. DFT-calculated IR spectra for a range of Mn species with an extended scaling of the x-axis up to 1500 cm^{-1}.

Table SI2. B3PW91 Computed Cartesian Coordinates



C	0.354934	0.107189	-0.123069
P	0.085728	0.061594	1.758605
C	1.899079	-0.060683	2.281626
Mn	-1.459973	1.385021	2.891743
C	-0.975485	2.950655	2.182769
O	-0.638908	3.968923	1.756577
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H	0.241460	-2.402936	2.120743
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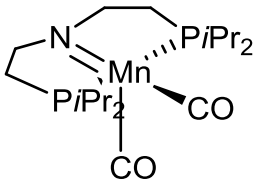

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O	0.612937	2.512569	4.843641
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H	-3.413942	-1.536370	4.786018
H	-1.186269	-1.986104	1.497659
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H	-0.514268	-1.752160	4.446211
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H	0.345248	-1.042475	-0.259285
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C	-2.550687	2.464519	6.922008
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C	-4.605072	4.307720	2.954361
C	-4.872749	2.038187	1.928009
H	-1.591451	-0.234450	-1.512840
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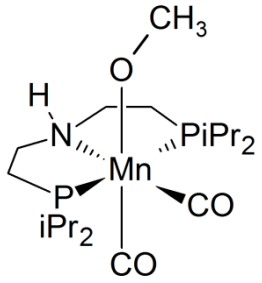

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C	0.951748	2.411381	-3.657883
P	0.398708	2.320618	-1.878368
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C	-1.700296	3.575424	-0.469315
C	1.224493	-3.529744	-0.928924
C	1.432195	-3.075531	0.514060
C	2.555057	-3.863099	-1.598384
C	-1.460440	-3.307891	-1.903252
C	-2.439428	-2.944141	-3.015828
C	-2.136655	-3.269141	-0.534036
C	1.659621	3.371744	-0.925669
C	3.030380	3.465828	-1.590266
C	1.791146	2.898131	0.519802
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H	1.623061	-0.049410	-3.401482
H	0.681686	3.361260	-4.125364
H	2.039523	2.332320	-3.660442
H	-0.705945	1.334647	-4.558303
H	0.824441	1.177414	-5.423711
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H	0.742856	-1.199286	-5.422153
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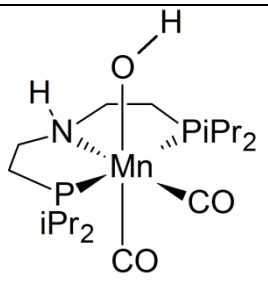

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C	1.771266	-3.474893	-0.271406
O	-1.937992	-0.074663	-2.227685
C	1.828409	0.044127	-1.663369
O	2.986570	0.070943	-1.534769
P	-0.179808	2.280783	-2.099906
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C	-2.037613	2.693444	-0.007890
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C	0.399703	-1.234215	-4.593635
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C	-2.713450	-3.381550	-2.245971
C	-1.858544	-2.810132	0.039919
C	-2.910967	3.187754	-2.304661
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H	1.488545	-1.273375	-4.512177
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H	-1.426759	2.335976	-4.185722
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H	1.434116	1.310608	-4.513884
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H	2.259939	1.916234	0.564042
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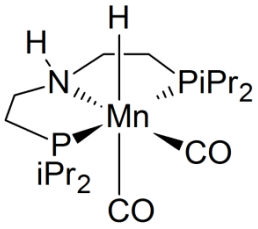

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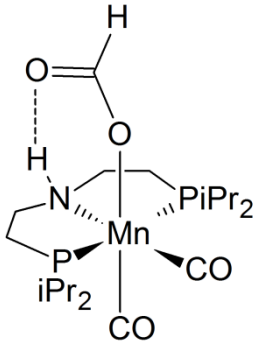

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C	-1.507031	-0.371213	-0.510415
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H	0.722980	2.619716	-0.753892
H	-3.465173	3.884104	2.832386
H	-3.119504	2.159255	2.857070
H	-2.322974	3.246163	4.006012
H	-2.930120	4.049489	0.418091
H	-1.341759	3.614709	-0.209169
H	-2.470303	2.350770	0.286184
H	-2.580214	-4.278594	0.399111
H	-2.260448	-2.547039	0.276575
H	-1.029425	-3.711827	-0.217394
H	-3.139254	-4.156602	2.818800
H	-2.053142	-3.429477	3.993789
H	-2.929199	-2.409762	2.841441
H	2.551965	-3.278176	-0.648279
H	0.946918	-2.553885	-0.753924
H	2.252879	-1.658124	0.014717
H	3.478776	-4.092208	1.449657
H	3.248795	-2.595039	2.346549
H	2.569955	-4.107845	2.957898
H	4.006959	0.165649	1.952189
O	2.997209	0.112448	3.696826