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Electronic Supplementary Information

Manganese (I) κ^2-NN complex-catalyzed Formic acid Dehydrogenation

Alexander Léval, Henrik Junge and Matthias Beller

Leibniz-Institut für Katalyse e.V., Albert-Einstein Straße 29a, Rostock, 18059, Germany.

Content:

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1. Generalities.

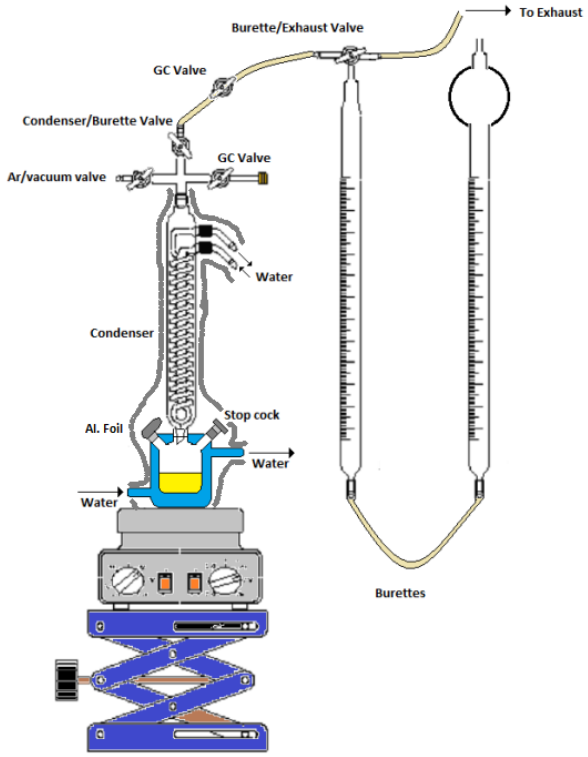
Unless noted, all reagents were bought from chemical suppliers and used without any purification. Every reaction was carried out under an inert atmosphere of argon by the means of standard Schlenk technique. Formic acid (99-100% purity) was purchased from BASF. Triglyme and *N,N*-dimethyl-N-octylamine (DMOA) were previously distilled. Formic acid (HCOOH, FA), N,N-dimethyl-N-octylamine (DMOA), triglyme and water were all degassed prior to their use (argon bubbling). Each organic solvent used in synthesis was collected from an SPS machine, stored under argon with drying agent (molecular sieve 4Å) and degassed prior to their utilization (argon bubbling). All synthesized complexes and ligands were prepared under an argon atmosphere. Complexes were stored under argon and ligands in atmospheric conditions.

Thin layer chromatography - TLC - was performed on aluminum backed hand-cut silica plates (5 cm × 10 cm, TLC silicagel 60 F254, Merck Millipore) and visualized using ultraviolet light (wavelength: 254 nm). Column chromatography was done on using silica (0.035-0.070 mm, silicagel 60, Fluka Chemika). The solvents were purchased from commercial sources (technical grade) and used without any further purification. **^{1}H, ^{13}C** and **^{19}F NMR spectroscopy** were carried out on Bruker AV-300, AV-400 or Fourier 300 spectrometer. NMR spectra were treated and interpreted using MestReNova (version 14.0.1-23559). All NMR data, in the manuscript and in the ESI experimental, are expressed as chemical shift in parts per million (ppm) relative to TMS and attribution was done according to the the residual solvent. The multiplicity of each signal is designed as follow; s (singlet), d (doublet), t (triplet), b (broad), m (multiplet). **Infrared spectroscopy** was carried out with a Bruker-ALPHA FT-IR ATR spectrometer with a spectral range of 7500 to 375 cm^{-1} (wavelength range: 1.3 to 27 mm). The spectra are exploited on OMNIC 7.3 or Origin 8.6. **Gas chromatography** was used to analyze the content of the gas phase with a CO quantification limit of 78 ppm or 10 ppm (when described). The samples were analyzed on Agilent Technologies 6890N (10 ppm CO detection limit) or Agilent Technologies 7890A (78 ppm CO detection limit) GC system.

2. Dehydrogenation of formic acid

General set-up. DH of FA was carried out with a double walled 3-neck reactor directly connected to a heating source (thermostat). A condenser was connected to the reactor and gas evolution was measured with a double burettes system. Due to light sensitivity, the reactor and the condenser were wrapped in aluminum foil (**figure S1**).

Figure 1: Manual burette set-up for the DH off FA [α].



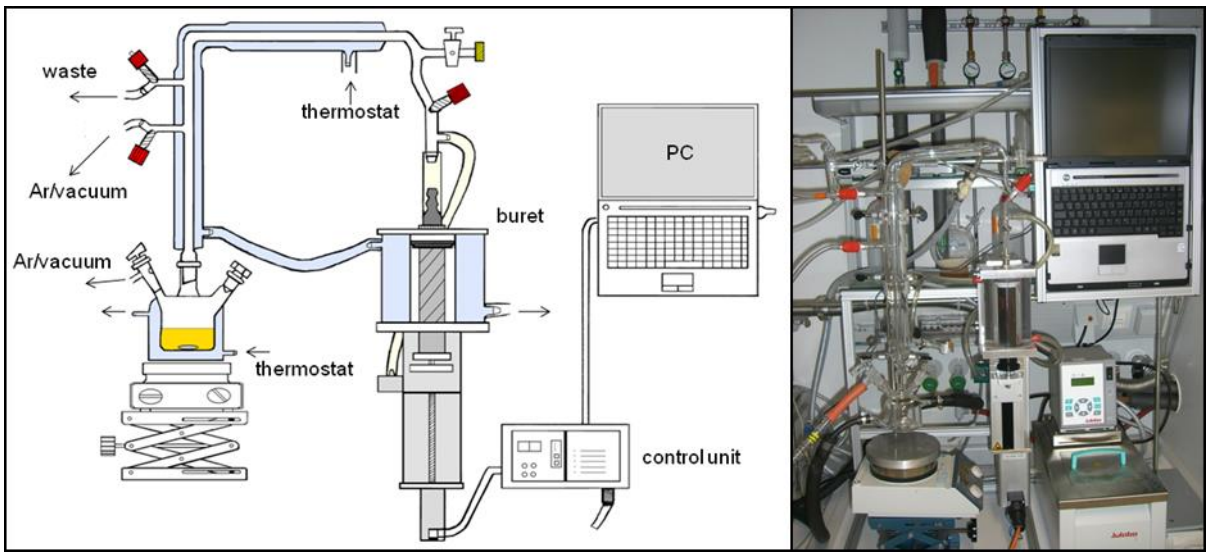
[α] Specificities: Water heated from thermostat, condenser cooled with tap water, gas released to the exhaust. Content of the gas phase analyzed by GC.

General procedure for the dehydrogenation of formic acid using manual burettes. A 3-neck double walled reactor was attached to a condenser connected to a manual burettes system. The apparatus was evacuated 6 times and refilled with Ar then flushed with argon for 15 minutes. Additives (when used) were added under argon overpressure and the setup was evacuated for 5 minutes, then back filled with Ar. The HCOOH : DMOA solution (11 : 10 molar ratio) was added under an argon overpressure. The setup was heated to the desired temperature while being flushed with argon. When the desired temperature was reached, the burette was closed, and the system was equilibrated for 30-60 min. The catalyst was introduced into the reactor with a mini-Teflon cup and the setup was vented to the open air in order to release the overpressure. The argon/vacuum line was closed, and the timer was started. After 180 minutes, a gas sample of the reaction was analyzed by gas chromatography.

General procedure for the continuous dehydrogenation of formic acid on automatic burettes. A 3-neck double walled reactor was attached to a condenser connected to an automatic burettes system. The apparatus was evacuated 6 and refilled with Ar then flushed with argon for 15 minutes. Additives

(when used) were added under argon overpressure and the setup was evacuated for 5 minutes then refiled with Ar. The HCOOH : DMOA solution (11 : 10 molar ratio) was added under an argon overpressure. The setup was heated to the desired temperature while being flushed with argon. When the desired temperature was reached, the burette was closed, and the system was equilibrated for 30-60 min. The catalyst was dropped into the reactor with a mini-Teflon cup and the setup was vented to the open air in order to release the pressure in the burette. The timer was then started. The automatic gas burette is equipped with a pressure sensor allowing continuous monitoring of the gas evolution through an automatic controlling unit. The gas evolution curves were collected by a computer. A 5 mL degassed syringe was used to obtain a gas sample analyzed by gas chromatography.

Figure 2: Automatic burette set-up for the DH of FA.



3. Calculation of the hydrogen volume, the TON and the TOF.

Turnover number (TON):

Gas evolution corrected by blank volume corresponding to the gas evolution of the same reaction using an empty Teflon cup without any catalyst. The turnover number (TON) is calculated with the following equation:

$$\mathrm{TON} = \frac{\frac{V_{obs} - V_{blank}}{V_{m_{H_2}} + V_{m_{CO_2}}}}{n_{cat}}$$

Where:

- $\mathrm{V_{obs}}$ is the gas evolution measured in the catalytic reaction.

- V_{blank} is the gas evolution measured in the catalytic reaction.
- $V_{m,H_2,25°C}$ and $V_{m,CO_2,25°C}$ are the molar volumes of H_2 and CO_2 respectively calculated with the viral expansion of the Van der Walls equation.

Calculation of H_2 molar volume:

$$V_{m\,H_2} = \frac{R \cdot T}{p} + b - \frac{a}{R \cdot T}$$

Where:

- R = 8.3145 $m^3.Pa.mol^{-1}.K^{-1}$
- T = 273.15 + room temperature (°C) K
- P = 101325 Pa
- a = 24.9 × 10^{-3} $Pa.m^6.mol^{-2}$
- b = 26.7 × 10^{-6} $m^3.mol^{-1}$

Calculation of CO_2 molar volume:

$$V_{m_{CO_2}} = \frac{R \cdot T}{p} + b - \frac{a}{R \cdot T}$$

Where:

- R = 8.3145 $m^3.Pa.mol^{-1}.K^{-1}$
- T = 273.15 + room temperature (°C) K
- P = 101325 Pa
- a = 36.5 × 10^{-2} $Pa.m^6.mol^{-2}$
- b = 42.7 × 10^{-6} $m^3.mol^{-1}$

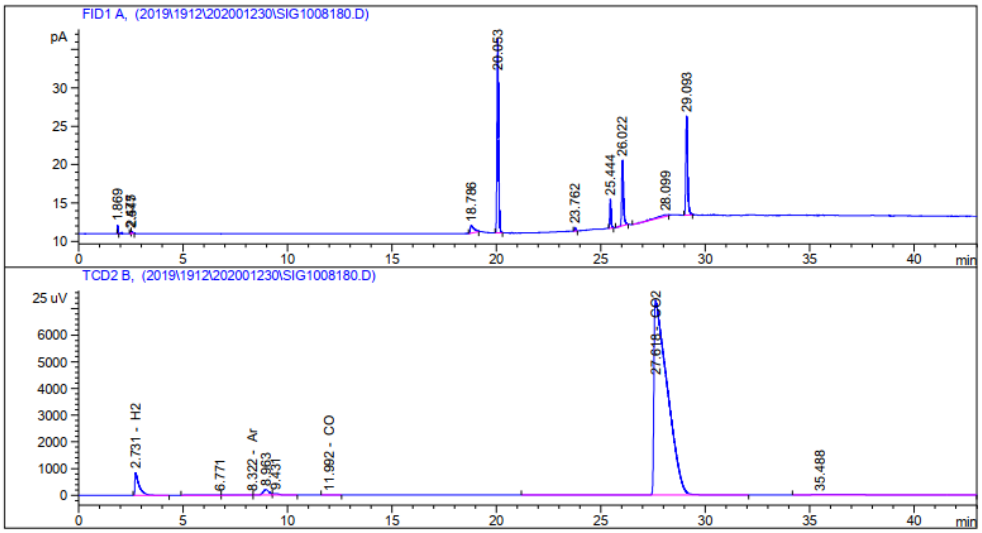
Turnover number frequency (TOF):

The turnover number frequency (TOF) was calculated with the experimental TON value. The unit of the TON (s^{-1}, min^{-1}, h^{-1}) is linked to the temporal unit (s, min, h)

$$\mathrm{TOF} = \frac{\mathrm{TON}}{\mathrm{time}}$$

4. Typical GC chromatogram.

Figure 3: Typical GC chromatogram for the DH of FA [a].

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=====================================================================
                    External Standard Report
=====================================================================

Sorted By             :      Retention Time
Calib. Data Modified  :      02/10/2019 15:21:51
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: FID1 A,
Signal 2: TCD2 B,

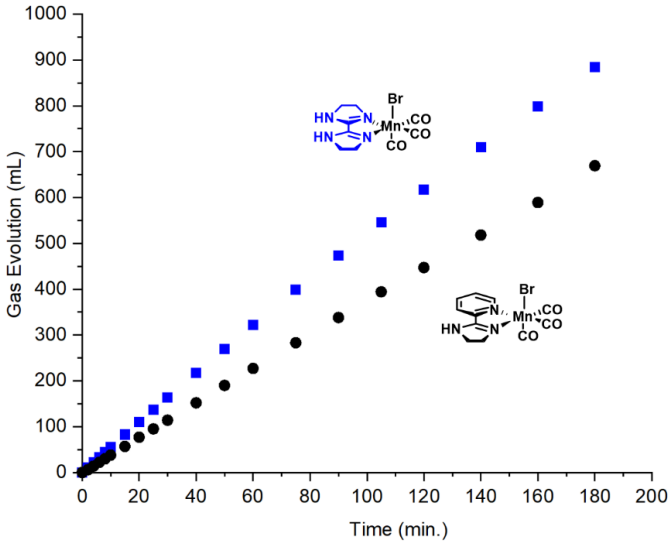
RetTime Sig Type     Area     Amt/Area    Amount   Grp   Name
 [min]                                    [vol%]
-------|--|------|----------|----------|----------|--|---------------
  2.731  2 BB     1.13265e4  4.42275e-3   50.09452    H2
  8.322  2 VV      149.55252 1.48702e-3 2.22388e-1    Ar
 11.992  2 BB       16.77317 2.30403e-4 3.86459e-3    CO
 21.000  2            -         -          -         CH4
 27.618  2 BB     3.24172e5  1.55051e-4   50.26312    CO2

Totals :                                 100.58389
```

[a]Reaction conditions: HCOOH (38 mmol in a 11 : 10 molar ratio of HCOOH : DMOA), [Mn(BisIm)(CO)$_3$Br] (0.15 mol%, 57 µmol, 20.1mg) Tset (95°C). Gas chromatogram from long term experiment (Cycle 10). Gas evolution monitored with manual burettes, corrected by blank volume (0.2 mL) and content of the gas phase analyzed by gas chromatography (GC). Ratio Vol%H_2/(Vol%H_2 +Vol%CO_2) of 0.5 for each cycle (**Table S1** †). CO content of 39 ppm (quantification limit of 10 ppm) (**Table S1** †).

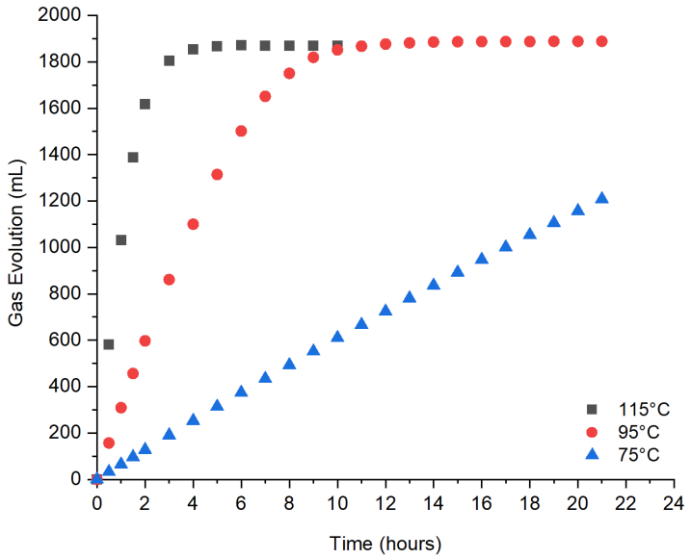
5. Gas Evolution Plot.

Figure 4: [Mn(BisIm)(CO)$_3$Br] vs. [Mn(PyIm)(CO)$_3$Br] in FA : DOMA mixture (11 : 10 molar ratio)[a].



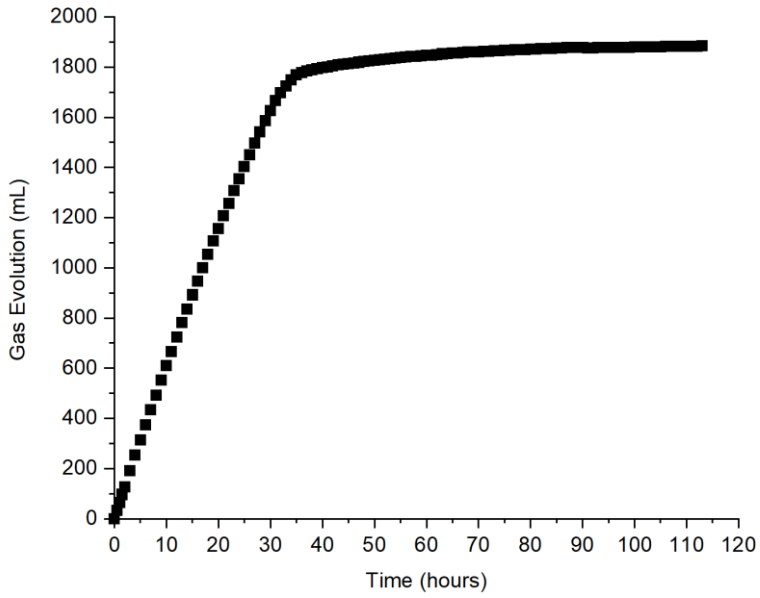
[a]Reaction conditions: HCOOH (38 mmol in a 11 : 10 molar ratio of HCOOH : DMOA), Cat. (0.015 mol%), T_{set} (95 °C), time (180 min). Gas evolution monitored with automatic burettes, corrected by blank volume (0.2 mL) and content of the gas phase analyzed by gas chromatography (GC). Ratio H_2 : CO_2 always 1 : 1 (**Table S1** †). CO content: 367 and 345 ppm for [Mn(BisIm)(CO)$_3$Br] and [Mn(PyIm)(CO)$_3$Br], respectively (**Table S1** †).

Figure 5: Temperature investigation: 75, 95 and 115 °C[a].



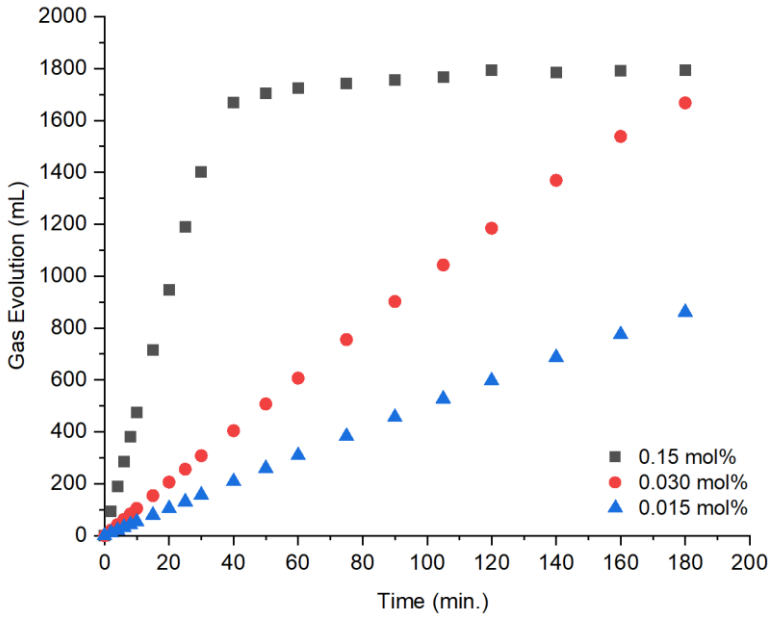
[a]Reaction conditions: HCOOH (38 mmol in a 11 : 10 molar ratio of HCOOH : DMOA), [Mn(BisIm)(CO)$_3$Br] (0.015 mol%), T_{set}, Time (180 min). Gas evolution monitored with automatic burettes, corrected by blank volume (0.2 mL) and content of the gas phase analyzed by gas chromatography (GC). Ratio H_2 : CO_2 always 1 : 1 (**Table S1** †). CO content: 169, 367 and 520-ppm for 75, 95 and 115°C, respectively (**Table S1** †).

Figure 6: Temperature investigation: 95°C[a].



[a]Reaction conditions: HCOOH (38 mmol in a 11 : 10 molar ratio of HCOOH : DMOA), [Mn(BisIm)(CO)$_3$Br] (0.015 mol%), T_{set} (95°C), Time (180 min). Gas evolution monitored with automatic burettes, corrected by blank volume (0.2 mL) and content of the gas phase analyzed by gas chromatography (GC). Ratio H_2 : CO_2 always 1 : 1 (**Table S1** †). CO content: 169 ppm (**Table S1** †).

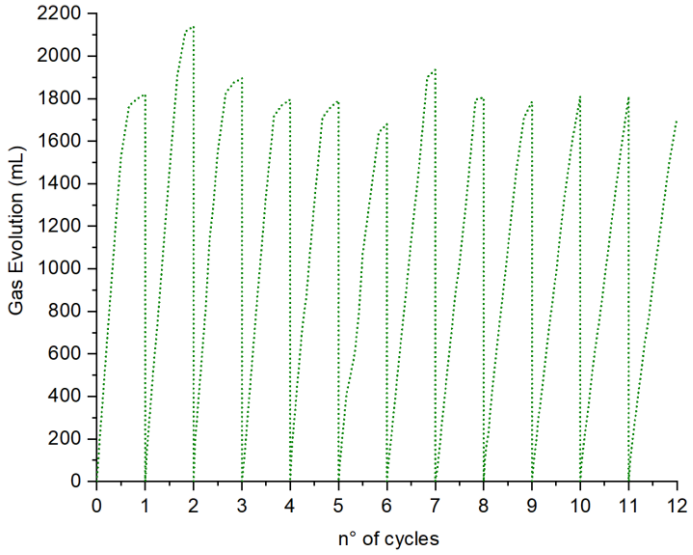
Figure 7: Catalytic loading investigation[a].



[a]Reaction conditions: HCOOH (38 mmol in a 11 : 10 molar ratio of HCOOH : DMOA), [Mn(BisIm)(CO)$_3$Br], T_{set} (95 °C), Time (180 min). Gas evolution monitored with automatic burettes, corrected by blank volume (0.2 mL) and content of the gas

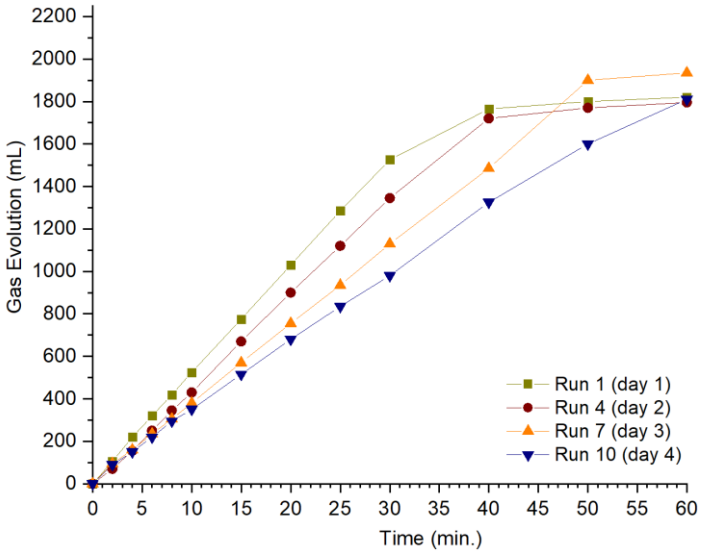
phase analyzed by gas chromatography (GC). Ratio H_2 : CO_2 always 1 : 1 (**Table S1** †). CO content: 367, 235 and 79 ppm for 0.015, 0.030 and 0.15 mol%, respectively (**Table S1** †).

Figure 8: Long term experiment: consecutive FA addition[a].



[a]Reaction conditions: HCOOH (38 mmol in a 11 : 10 molar ratio of HCOOH : DMOA), [Mn(BisIm)(CO)$_3$Br] (0.15 mol%, 57 µmol, 20.1 mg) T_{set} (95 °C), time for one cycle (60 min), 1.4 mL of FA (37 mmol) added every 60 minutes. A total of 3 cycles per day were carried out. The set-up was cooled and let under argon overnight. The reaction was carried out over 4 days (12 injections of FA). Gas evolution monitored with manual burettes, corrected by blank volume (0.2 mL) and content of the gas phase analyzed by gas chromatography (GC). Ratio H_2 : CO_2 always 1 : 1 for each cycle (**Table S1** †). CO content in between 39 and 60 ppm (quantification limit of 10 ppm) (**Table S1** †).

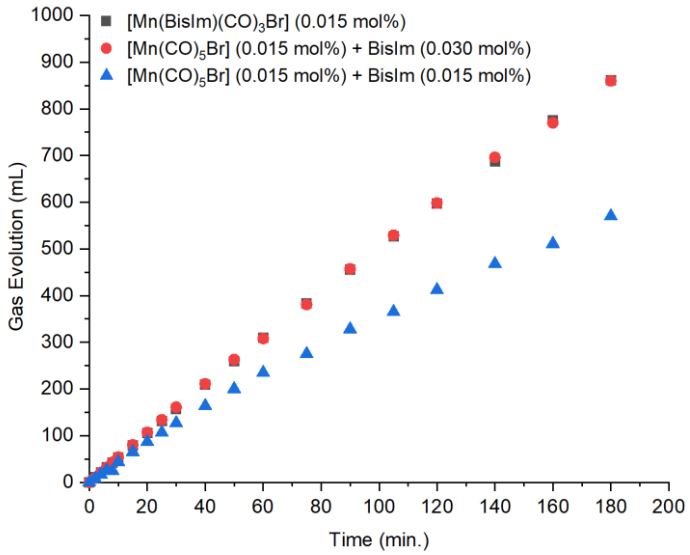
Figure 9: Cycle comparison: activity loss[a].



[a]Reaction conditions: HCOOH (38 mmol in a 11 : 10 molar ratio of HCOOH : DMOA), [Mn(BisIm)(CO)$_3$Br] (0.15 mol%, 57 µmol, 20.1 mg) T_{set} (95 °C), time for one cycle (60 min), 1.4 mL of FA (37 mmol) added every 60 minutes. A total of 3 cycles per day were carried out. The set-up was cooled and let under argon overnight. The reaction was carried out over 4 days

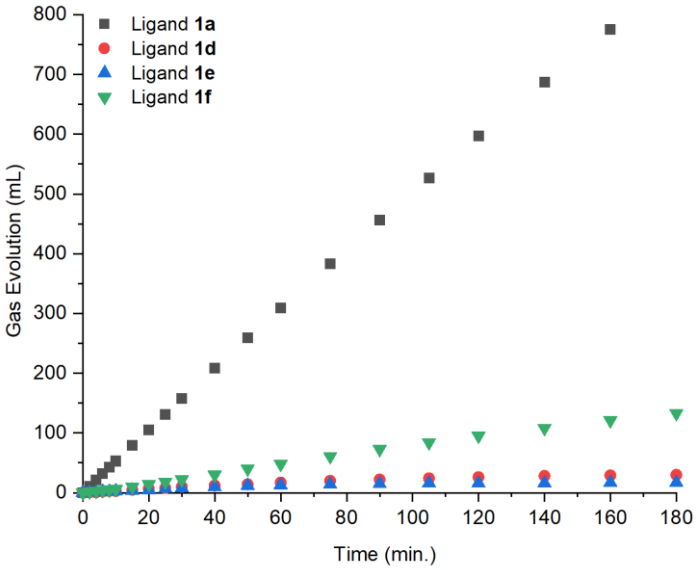
(12 injections of FA). Gas evolution monitored with manual burettes, corrected by blank volume (0.2 mL) and content of the gas phase analyzed by gas chromatography (GC). Ratio H_2 : CO_2 always 1 : 1 for each cycle (**Table S1** †). CO content in between 39 and 60 ppm (quantification limit of 10 ppm) (**Table S1** †).

Figure 10: *In-situ* system[a].



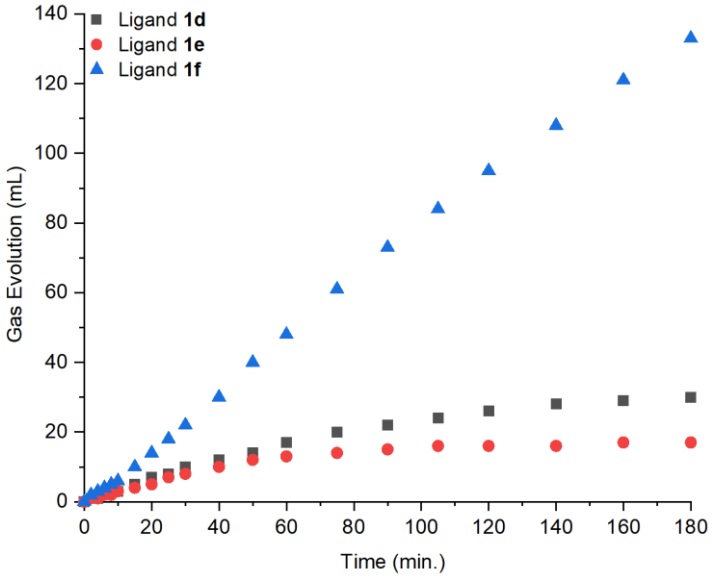
[a]Reaction conditions: HCOOH (38 mmol in a 11 : 10 molar ratio of HCOOH : DMOA), $[Mn(CO)_5Br]$ (0.015 mol%), Ligand **1a** (0.030 or 0.015 mol%), T_{set} (95 °C), Time (180 min). Gas evolution monitored with manual burettes, corrected by blank volume (0.2 mL) and content of the gas phase analyzed by gas chromatography (GC). Ratio H_2 : CO_2 always 1 : 1 (**Table S1** †). CO content: 367, 369 and 112 ppm for $[Mn(BisIm)(CO)_3Br]$, $[Mn(CO)_5Br]$ (0.015 mol%) + BisIm (0.030 mol%), and $[Mn(CO)_5Br]$ (0.015 mol%) + BisIm (0.015 mol%), respectively (**Table S1** †).

Figure 11: Benzoylated ligand (**1d**, **1e** and **1f**) in comparison to ligands **1a**[a].



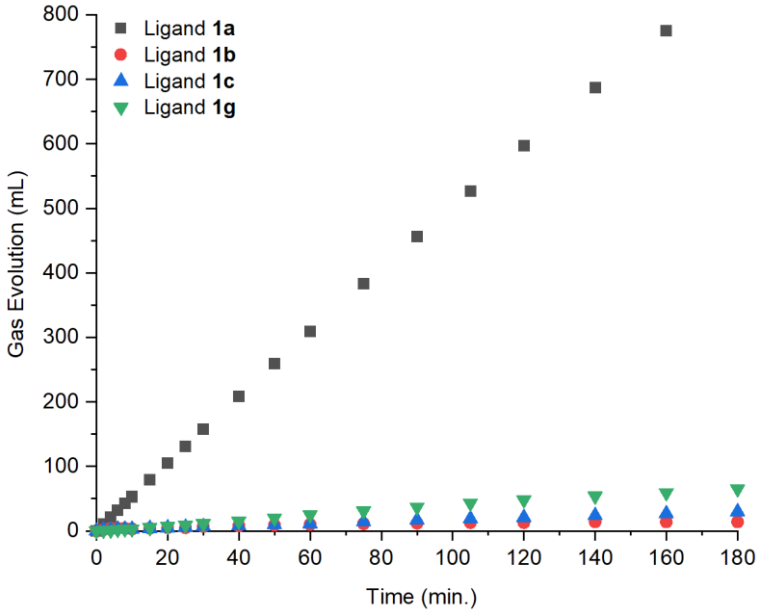
[a]Reaction conditions: HCOOH (38 mmol in a 11 : 10 molar ratio of HCOOH : DMOA), $[Mn(CO)_5Br]$ (0.015 mol%), Ligand (0.030 mol%), T_{set} (95 °C), Time (180 min). Gas evolution monitored with manual burettes, corrected by blank volume (0.2 mL) and content of the gas phase analyzed by gas chromatography (GC). Ratio H_2 : CO_2 always 1 : 1 (**Table S1** †). CO content: 369 ppm, 0.26%, 0.40% and 0.31% for ligand **1a**, **1f**, **1d** and **1e** , respectively (**Table S1** †).

Figure 12: Benzoylated ligands **1d**, **1e** and **1f**[a].



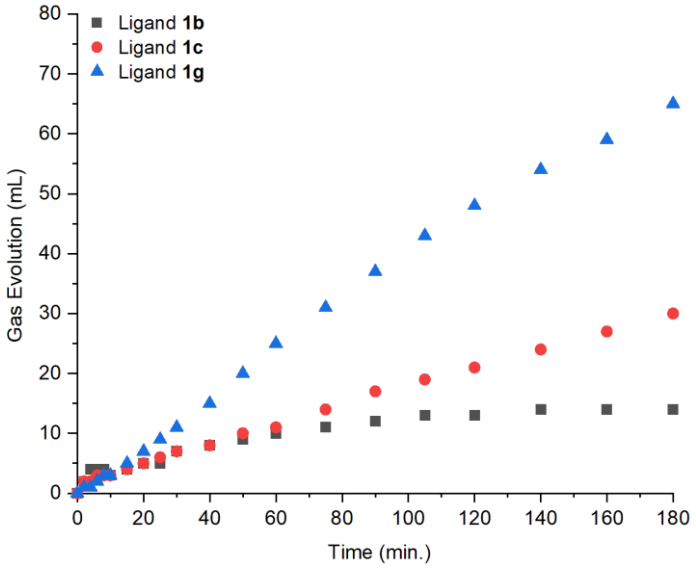
[a]Reaction conditions: HCOOH (38 mmol in a 11 : 10 molar ratio of HCOOH : DMOA), $[Mn(CO)_5Br]$ (0.015 mol%), Ligand (0.030 mol%), T_{set} (95 °C), Time (180 min). Gas evolution monitored with manual burettes, corrected by blank volume (0.2 mL) and content of the gas phase analyzed by gas chromatography (GC). Ratio H_2 : CO_2 always 1 : 1 (**Table S1** †). CO content: 0.26%, 0.40% and 0.31% for ligand **1f**, **1d** and **1e**, respectively (**Table S1** †).

Figure 13: Ligands , **1b**,**1c** and **1g** in comparison with ligand **1a**[a].



[a]Reaction conditions: HCOOH (38 mmol in a 11 : 10 molar ratio of HCOOH : DMOA), $[Mn(CO)_5Br]$ (0.015 mol%), Ligand (0.030 mol%), T_{set} (95 °C), Time (180 min). Gas evolution monitored with manual burettes, corrected by blank volume (0.2 mL) and content of the gas phase analyzed by gas chromatography (GC). Ratio H_2 : CO_2 always 1 : 1 (**Table S1** †). CO content: 369 ppm, 0.18%, 0.28% and 0.19% for **1a**, **1c**, **1b** and **1g**, respectively (**Table S1** †).

Figure 14: Ligands **1b**, **1c** and **1g**[a].



[a]Reaction conditions: HCOOH (38 mmol in a 11 : 10 molar ratio of HCOOH : DMOA), $[Mn(CO)_5Br]$ (0.015 mol%), Ligand (0.030 mol%), T_{set} (95 °C), Time (180 min). Gas evolution monitored with manual burettes, corrected by blank volume (0.2 mL) and content of the gas phase analyzed by gas chromatography (GC). Ratio H_2 : CO_2 always 1 : 1 (**Table S1** †). CO content: 0.18%, 0.28% and 0.19% for **1c**, **1b** and **1g**, respectively (**Table S1** †).

6. Table with GC ratios and CO content.

Table 1: CO content and H_2 : CO_2 ratios for the DH of FA[a].

Experiment	$H_2 : CO_2$[b] (mL)	H_2 Vol%[c]	CO_2 Vol%[c]	CO[c] (ppm)	Yield[d] (%)	TON	TOF (h^{-1})
Activity **2c** *95 °C, FA : DMOA (11 : 10)*	669	50	50	345	36	2403	801
Table 1, entry 1 *75 °C, 0.015 mol% (3 h)*	191	45	55	169*	10	686	229
75 °C, 0.015 mol% (113 h)	1880	45	55	169*	>99	6753	60
Table 1, entry 2 *95 °C, 0.015 mol% (3 h)*	861	48	52	367	46	3091	1030
95 °C, 0.015 mol% (12 h)	1876	48	52	367	>99	6738	562
Table 1, entry 3 *115 °C, 0.015 mol% (3 h)*	1805	48	52	520*	97	6484	2161
115 °C, 0.015 mol% (4 h)	1853	48	52	520*	>99	6620	1672

Table 1, entry 4 *95 °C, 0.030 mol% (3 h)*	1667	50	50	235*	90	2967	989
Table 1, entry 5 *95 °C, 0.15 mol% (3 h)*	1794	50	50	79*	97	656	219
Table 1, entry 6 *$LiBF_4$ (10 mol%)*	608	49	51	215*	33	2183	728
Table 1, entry 7 *LiCl (10 mol%)*	611	48	52	137	33	2194	731
Cycle 1 *95 °C, 0.15 mol% (60 min.)*	1820	50	50	b.q.	98	654	218
Cycle 2 *95 °C, 0.15 mol% (60 min.)*	2140	50	50	b.q.	>99	769	256
Cycle 3 *95 °C, 0.15 mol% (60 min.)*	1865	49	51	b.q.	>99	670	223
Cycle 4 *95 °C, 0.15 mol% (60 min.)*	1795	49	51	b.q.	97	645	215
Cycle 5 *95 °C, 0.15 mol% (60 min.)*	1790	49	51	b.q.	96	643	214
Cycle 6 *95 °C, 0.15 mol% (60 min.)*	1680	49	51	b.q.	91	603	201
Cycle 7 *95 °C, 0.15 mol% (60 min.)*	1935	49	51	b.q.	>99	695	232
Cycle 8 *95 °C, 0.15 mol% (60 min.)*	1805	48	52	b.q.	97	648	216
Cycle 9 *95 °C, 0.15 mol% (60 min.)*	1785	50	50	b.q.	96	641	214
Cycle 10 *95 °C, 0.15 mol% (60 min.)*	1810	51	49	60*	98	650	217
Cycle 11 *95 °C, 0.15 mol% (60 min.)*	1810	50	50	39*	98	650	217
Cycle 12 *95 °C, 0.15 mol% (60 min.)*	1710	49	51	42*	92	614	205
Overall 12 cycles *95 °C, 0.15 mol% (12 h)*	21945	49	51	47	99	7883	657
in-situ (2 : 1)	570	49	51	369*	31	2047	682
in-situ (1 : 1)	860	50	50	112*	46	3089	1030
Table 2, entry 1 *Ligand **1a***	860	50	50	112*	46	3089	1030
Table 2, entry 2 *Ligand **1b***	14	61	39	2765	1	50	17
Table 2, entry 3 *Ligand **1c***	30	71	29	1750	2	107	36
Table 2, entry 4 *Ligand **1d***	30	42	58	3988*	2	107	36
Table 2, entry 5 *Ligand **1e***	17	55	45	3132	1	60	20
Table 2, entry 6 *Ligand **1f***	133	56	44	3640	7	477	159
Table 2, entry 7 *Ligand **1g***	65	55	45	1918	3	233	78
Activity **2b** *95 °C, FA : DMOA (11 : 10)*	715	50	50	94	39	2568	856
Pre-activation (2 : 1) *Et_2O, 40 °C, 30 min.*	8	69	31	2375	<1	28	7
Pre-activation (1 : 1) *Et_2O, 40 °C, 30 min.*	6	55	45	785	<1	21	9

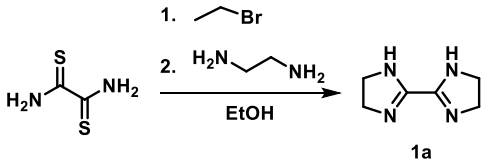
[a]Reaction conditions detailed under the corresponding table/experiment in this work. [b]Gas evolution monitored with manual burettes. [c]Content of the gas phase analyzed by GC with a CO detection limit of 78 ppm, b.q. stands for "bellow quantification limit". When specified by "*", the GC was carried out with a CO detection limit of 10 ppm. [d]Yield calculated according to the obtained gas mixture and based on the initial formic acid quantities.

7. Synthesis.

General procedure for the synthesis of non-aromatic adjacent bisheterocycles:

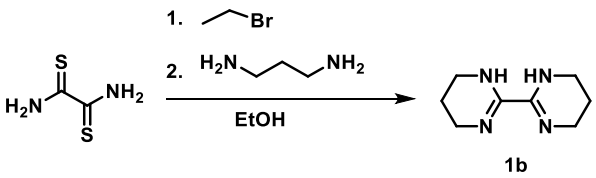
This procedure was adapted from existing literature precedence[1]. A three neck round bottom flask was equipped with a condenser (bubbler, argon/vacuum entry). The apparatus was dried under vacuum. Dithiooxamide (1 eq.) was suspended in ethanol (10 mL) and bromoethane (EtBr, 2.42 eq.) was dropwisely added. The mixture was heated to 60 °C and stirred for 4 hours. Ethylene diamine (6.75 eq.) was added dropwise over the course of an hour. After the addition, the suspension was heated to 80 °C for 20 minutes. The solution was then cooled by an ice bath and stirred 45 min at 0 °C. Filtration afforded the product in moderate to good yields.

Figure S15: 4,4',5,5'-tetrahydro-1*H*,1'*H*-2,2'-biimidazole synthesis (**1a**).



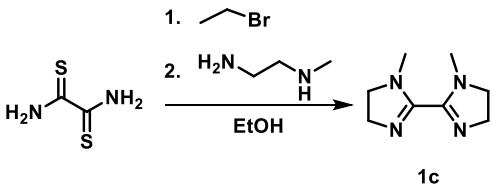
Grey solid, 77% yield. **^{1}H NMR** (300 MHz, DMSO-d_6) δ (ppm) 6.66 (bs, 2H), 3.50 (bs, 8H). NMR data in accordance with reported literature[5].

Figure S16: 1,1',4,4',5,5',6,6'-octahydro-2,2'-bipyrimidine synthesis (**1b**).



Grey solid, >99% yield. **^{1}H NMR** (300 MHz, DMSO-d_6) δ (ppm) 5.09 (bs, 2H), 2.73 (t, J = 6.8, 6.8 Hz, 8H), 1.60 (p, J = 6.84, 6.84, 6.85, 6.85 Hz, 4H). NMR data in accordance with reported literature[5].

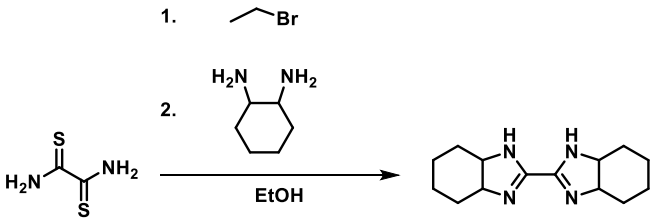
Figure S17 : 1,1'-dimethyl-4,4',5,5'-tetrahydro-1*H*,1'*H*-2,2'-biimidazole synthesis (**1c**).



1c

Purified by column chromatography with MeOH (100%), thick yellow/brown oil, 99% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ (ppm) 3.57 (bt, *J* = 5.9 Hz, 4H), 3.25 (bt, *J* =6.0 Hz, 4H), 3.01 (s, 6H, Me). **^{13}C NMR** (75 MHz, $CDCl_3$) δ (ppm) 146.9, 49.6, 43.6, 37.5. **ESI-TOF**: m/z = 167. **IR (ATR)**: 3353, 2927, 2848, 1671, 1585, 1479, 1397, 1337, 1256, 1207, 1085, 1062, 956, 857, 632, 523 cm^{-1}.

Figure S18: 3a,3'a,4,4',5,5',6,6',7,7a,7',7'a-dodecahydro-1*H*,1'*H*-2,2'-bibenzo[*d*]imidazole synthesis (**1g**).



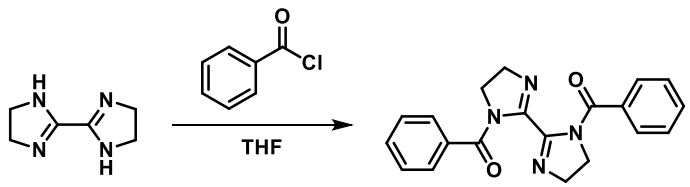
1g

White solid with slight orange taint, 61% yield. **^{1}H NMR** (300 MHz, DMSO-d_6) δ (ppm) 6.43 - 4.45 (bs, 2H), 2.50 - 3.38 (bm, 4H), 1.94 - 1.77 (bs, 4H), 1.30 - 1.00 (bs, 8H). **^{13}C NMR** (75 MHz, DMSO-d_6) δ (ppm) 55.0, 34.2, 21.9, HN-C=N not detected. **ESI-TOF**: m/z = 247. **IR (ATR)**: 3238, 3171, 2924, 2854, 2349, 2337, 2322, 1593, 1498, 1461, 1444, 1363, 1302, 1275, 1234, 1148, 1113, 1091, 1067, 1049, 992, 910, 840, 731, 681, 569, 518, 463 cm^{-1}.

General procedure for the acylation of 2,2'-Bisimidazoline:

Procedure adapted from existing literature[2]. In a previously dried flask, **1a** (2 mmol) was dissolved in dry and degassed THF (10 mL). The corresponding acyl chloride (1 mmol) was dropwisely added to the solution under a stream of argon. The reaction medium was stirred overnight at room temperature. The brown bisimidazoline chloride salt was removed by filtration. The solvent was removed under vacuum and the crude product was purified by column chromatography using MeOH: DCM (5 : 95).

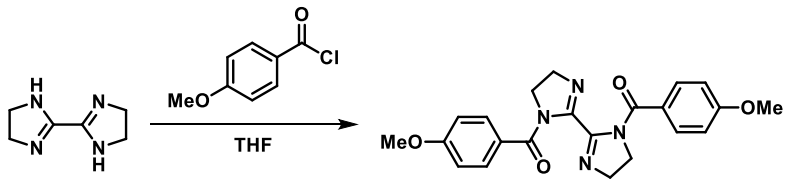
Figure S19: (4,4',5,5'-tetrahydro-1*H*,1'*H*-[2,2'-biimidazole]-1,1'-diyl)bis(phenylmethanone) synthesis (**1d**).



1d

Purified by column chromatography with MeOH : DCM (5 : 95, R_f=0.51), white solid, 63% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ (ppm) 7.59 - 7.35 (m, 10H), 4.09 - 3.81 (bm, 4H), 3.81 - 3.17 (bs, 4H). **^{13}C NMR** (76 MHz, $CDCl_3$) δ (ppm) 167.1, 151.9, 134.6, 132.6, 131.3, 128.3, 127.8, 54.5, 48.1. **ESI-TOF**: m/z = 347. **IR (ATR)**: 2253, 1666, 1368, 1095, 904, 726, 650 cm^{-1}.

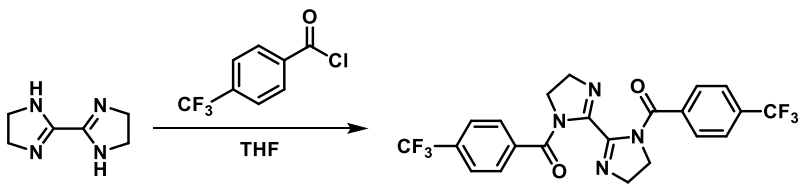
Figure S20: (4,4',5,5'-tetrahydro-1*H*,1'*H*-[2,2'-biimidazole]-1,1'-diyl)bis((4-methoxyphenyl)methanone) (**1e**).



1e

Purified by column chromatography with MeOH : DCM (5 : 95, R_f=0.48), white solid with slight yellow taint, 35% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ (ppm) 7.50 - 7.40 (m, 4H), 6.89 - 6.76 (m, 4H), 3.90 - 3.80 (bm, 4H), 3.78 - 3.76 (bs, 6H), 3.73 - 3.55 (bs, 4H). **^{13}C NMR** (76 MHz, $CDCl_3$) δ (ppm) 168.1, 167.6, 167.0, 162.1, 130.2, 126.7, 113.5, 55.4, 54.5, 48.4. **ESI-TOF**: m/z = 407. **IR (ATR)**: 2900, 2253, 1657, 1606, 1511, 1363, 1257, 1173, 1030, 904, 841, 726, 650 cm^{-1}.

Figure S21: (4,4',5,5'-tetrahydro-1H,1'H-[2,2'-biimidazole]-1,1'-diyl)bis((4-(trifluoromethyl)phenyl)methanone) synthesis (**1f**).

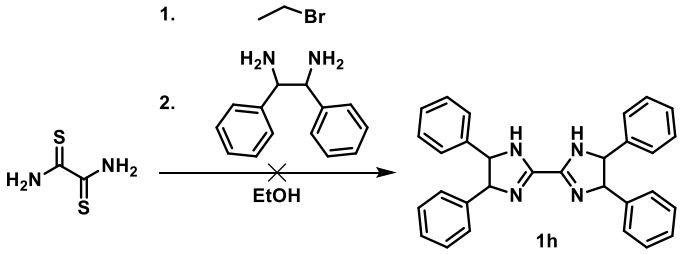


1f

Purified by column chromatography with MeOH : DCM (5 : 95, R_f=0.56), white solid with slight yellow taint, 51% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ (ppm) 7.75 - 7.45 (m, 8H), 4.20 - 3.85 (bm, 4H), 3.84 - 3.50 (bs, 4H). **^{19}F{^{1}H}**

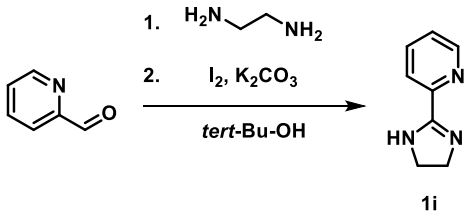
NMR (283 MHz, $CDCl_3$) δ (ppm) 63.12 (6F). **ESI-TOF**: m/z = 483. **IR (ATR)**: 2952, 1669, 1618, 1514, 1382, 1322, 1278, 1168, 1126, 1066, 1018, 995, 910, 850, 766, 724, 459 cm^{-1}.

Figure 22: Unsuccessful 4,4',5,5'-tetraphenyl-4,4',5,5'-tetrahydro-1*H*,1'*H*-2,2'-biimidazole synthesis (**1h)**.



This procedure was adapted from existing literature precedence[3]. A three neck round bottom flask was equipped with a condenser (bubbler, argon/vacuum entry). The apparatus was dried under vacuum. Dithiooxamide (1 eq.) was suspended in ethanol (10 mL) and bromoethane (EtBr, 2.42 eq.) was dropwisely added. The medium was heated to 60 °C and stirred for 4 hours. Diphenylethylenediamine (6.75 eq.) was added dropwise over the course of an hour. After the addition, the reaction mixture was heated at 80 °C for 20 minutes. The solution was then cooled with an ice bath and the was stirred 45 min. at 0 °C. Filtration afforded a white solid. The resulting analysis showed no evidence of **1h**. Only the diphenylethylenediamine as the starting material was observed.

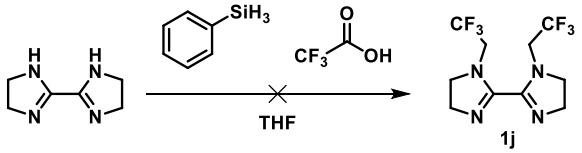
Figure 23: Synthesis of ligand 2-(4,5-dihydro-1*H*-imidazol-2-yl)pyridine (**1i**).



Procedure adapted from existing literature[4, 5]. A three neck round bottom flask (100 mL) was equipped with an Allhin condenser, mounted with an argon entry and a bubbler, was flamed under vacuum. *Tert*-butanol (30 mL) and 2-pyridinecarboxaldehyde (0.40 mL, 4.0 mmol, 1 eq.) were added to the flask under pressure of argon. Ethylene diamine (0.30 mL, 4.4 mmol, 1.1 eq.) was slowly added dropwise and the mixture was agitated at room temperature for 30 minutes. After addition of iodine (762 mg, 6.0 mmol, 1.5 eq.) and K_2CO_3 (1.07 g, 8.0 mmol, 2 eq.), the reaction mixture was heated to 70 °C for 180 minutes. Quenching with aqueous saturated sodium sulfite solution (Na_2SO_3, 40 mL), extraction with ethylacetate (EtOAc, 3 X 30 mL), washing with aqueous saturated sodium chloride (NaCl, 40 mL), drying with sodium sulfate (Na_2SO_4) and removal of the solvent under vacuum afforded a yellowish solid. Column chromatography utilizing a gradient from ethyl acetate :

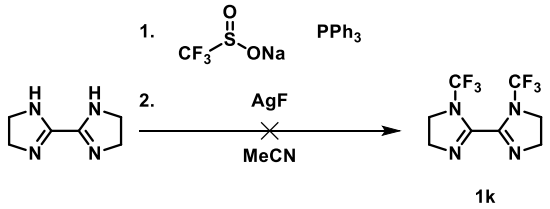
triethylamine (99 : 1, R_f=0.15) to methanol : ethyl acetate : triethylamine (9.5 : 89.5 : 1, R_f=0.24) afforded a light yellow solid (515 mg, 3.5 mmol, 88% yield). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.56 (ddd, *J* = 0.9, 1.8, 4.9 Hz, 1H), 8.13 (dt, *J* = 1.09, 1.09, 7.94 Hz, 1H), 7.75 (td, *J* = 1.75, 7.73, 7.77 Hz, 1H), 7.34 (ddd, *J* = 1.23, 4.85, 7.56 Hz, 1H), 3.83 (s, 4H). Data in accordance with previously reported procedures[4, 5].

Figure 24: Unsuccessful 1,1'-bis(2,2,2-trifluoroethyl)-4,4',5,5'-tetrahydro-1*H*,1'*H*-2,2'-biimidazole synthesis (**1j**).



Procedure adapted from literature precedence[6]. In a previously evacuated and dried 10 mL 2-neck round bottom flask equipped with an Allhin condenser, **1a** (1 mmol) was dissolved in dry and degassed THF (2 mL). The mixture was heated to 70 °C and both phenylsilane (4 mmol) followed by trifluoroacetic acid (3.5 mmol) were carefully loaded into the reaction medium by dropwise addition. The authors mention "copious H_2 gas evolution", no gaseous release was observed in our case. The reaction mixture was refluxed for 4 hours and cooled down to room temperature. The crude was concentrated under vacuum and diluted with diethyl ether. The organic phase was washed with saturated sodium bicarbonate solution. The organic layer was collected and dried over anhydrous sodium sulfate and concentrated under vacuum to afford a yellowish solid. Analysis (^{1}H, ^{13}C, ^{19}F{^{1}H} NMR and HRMS) showed major decomposition. Homeopathical amounts of the targeted ligand **1j** were detected on the HRMS (**ESI-TOF**: m/z = 483).

Figure 25: Unsuccessful 1,1'-bis(trifluoromethyl)-4,4',5,5'-tetrahydro-1*H*,1'*H*-2,2'-biimidazole synthesis (**1j**).

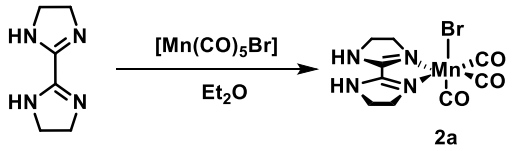


Procedure adapted from existing literature[7]. In a previously evacuated and flamed dried 25 mL 3-neck round bottom flask equipped with an Allhin condenser, **1a** (1 mmol) was loaded with acetonitrile (MeCN, 10 mL). Both sodium triflinate (3 mmol) and triphenylphosphine (6 mmol) were charged in the medium and the set-up was stirred for 60 minutes at room temperature (color change: brown → orange → yellow → pale light yellow). The lights of the laboratory were then shut off, the set-up was wrapped in aluminum foil and AgF was added (9 mmol). The reaction mixture was submerged in an 85 °C oil bath and refluxed for 4 hours. The solvent was removed under vacuum and the residue was purified by column chromatography (100% Ethylacetate). The analysis carried out (^{1}H, ^{13}C and ^{19}F{^{1}H} NMR) did not show any traces of targeted ligand **1k**.

General synthesis of complex [Mn(κ^2-NN)(CO)$_3$Br]:

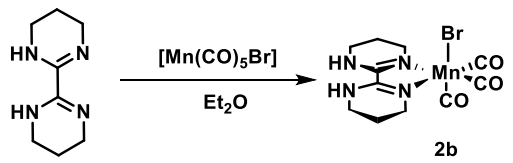
Procedure adapted from existing literature[5, 8]. In a previously evacuated and dried 50 mL 3-neck round bottom flask, [Mn(CO)$_5$Br], diethyl ether (20 mL) and the corresponding ligand were charged under a pressure of argon. Aluminum foil was wrapped around the glassware (round bottom flask and condenser) to avoid light exposure. The reaction mixture was heated to reflux in diethyl ether (Et_2O) for 4 hours. In every case, an orange solid was precipitated and was filtered off and subsequently washed with Et_2O to afford the corresponding manganese complex. All complexes were stored under argon in the absence of light.

Figure S26: Synthesis of [Mn(BisIm)(CO)$_3$Br] (**2a**).



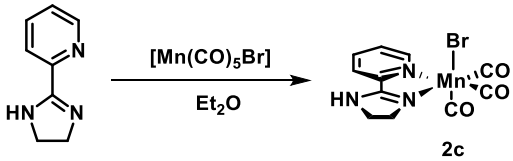
^{1}H NMR (300 MHz, DMSO-d^6) δ (ppm) 7.89 (s, 1H), 4.16 – 3.65 (m, 8H). **^{13}C NMR** (75 MHz, DMSO-d^6) δ (ppm) 158.6, 53.9, 46.2, CO resonance not detected. **CI-MS:** m/z = 277 [M-Br]. **IR (ATR):** 3232 (N-H), 2017 (CO), 1906 (CO). Data in accordance with previously reported procedure[5].

Figure S27: Synthesis of [Mn(BisTHP)(CO)$_3$Br] (**2b**).



^{1}H NMR (300 MHz, DMSO-d^6) δ (ppm) 7.89 (s, 2H), 4.18 – 3.59 (m, 12H). **^{13}C NMR** (75 MHz, DMSO-d^6) δ (ppm) 158.6, 53.9, 46.2, CO resonance not detected. **IR (ATR):** 3234 (N-H) 2019 (CO), 1901 (b, CO) cm^{-1}. **EI-MS:** m/z = 389 [M]. Data in accordance with previously reported procedure[5].

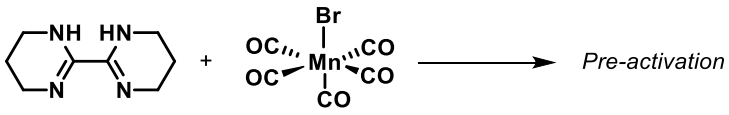
Figure S28: Synthesis of [Mn(PyIm)(CO)$_3$Br] (**2c**).



^{1}H NMR (400 MHz, DMSO-d^6) δ (ppm) 9.14 (d, J = 5.2 Hz, 1H), 8.71 (s, 1H), 8.28 – 8.14 (m, 2H), 8.11 – 8.04 (m, 1H), 7.80 – 7.70 (m, 1H), 4.22 – 3.82 (m, 4H). **^{13}C NMR** (101 MHz, DMSO-d^6) δ (ppm) 260.2, 251.2, 165.5, 154.3,

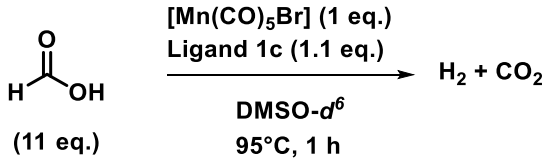
147.0, 139.3, 132.0, 127.6, 124.1, 54.2, 45.4. **CI-MS:** m/z = 286 [M-Br]. **IR (ATR):** 3252 (N-H), 2016 (CO), 1898 (b, CO) cm^{-1}. Data in accordance with previously reported procedure[5].

Figure S29: Pre-formation of the catalyst between **1b** and **[Mn(CO)$_5$Br]**.



In a 5 mL Schlenk flask previously evacuated and dried, **1b** (5 or 10 µmol) and [Mn(CO)$_5$Br] (5 µmol) were suspended in Et_2O (1 mL) under a stream of argon. The mixture was agitated in the absence of light for 30 minutes. The solvent was removed under vacuum and the obtained solid was scratched out and transferred to a Teflon crucible and directly used for the FA DH.

Figure S30: NMR-scale reaction between ligand **1c** and [Mn(CO)$_5$Br] in the presence of FA in DMSO-*d*^{6}.



In a 5 mL Schlenk flask previously evacuated and dried, **1c** (55 µmol, 26.5 mg) and [Mn(CO)$_5$Br] (50 µmol, 13.7 mg) were dissolved in DMSO-*d*^{6} (0.8 mL) under a stream of argon. The mixture was agitated in the absence of light for 5 minutes (light orange color) and immerged in a 95°C. After 5 additional minutes, a deep-red color change is noted. Formic acid is added to the reaction medium (55 µmol, 20 µL) and the mixture is stirred for 60 minutes (95°C). A gas sample is taken and analyzed by gas chromatography after 1 hour. The content of the flask was then transferred to a J. Young tube, via canula filtration, and analyzed by NMR.

Figure S31: ^{19}F NMR of NMR-scale reaction between **1c** and $[Mn(CO)_5Br]$ in the presence of FA in DMSO-d^6.

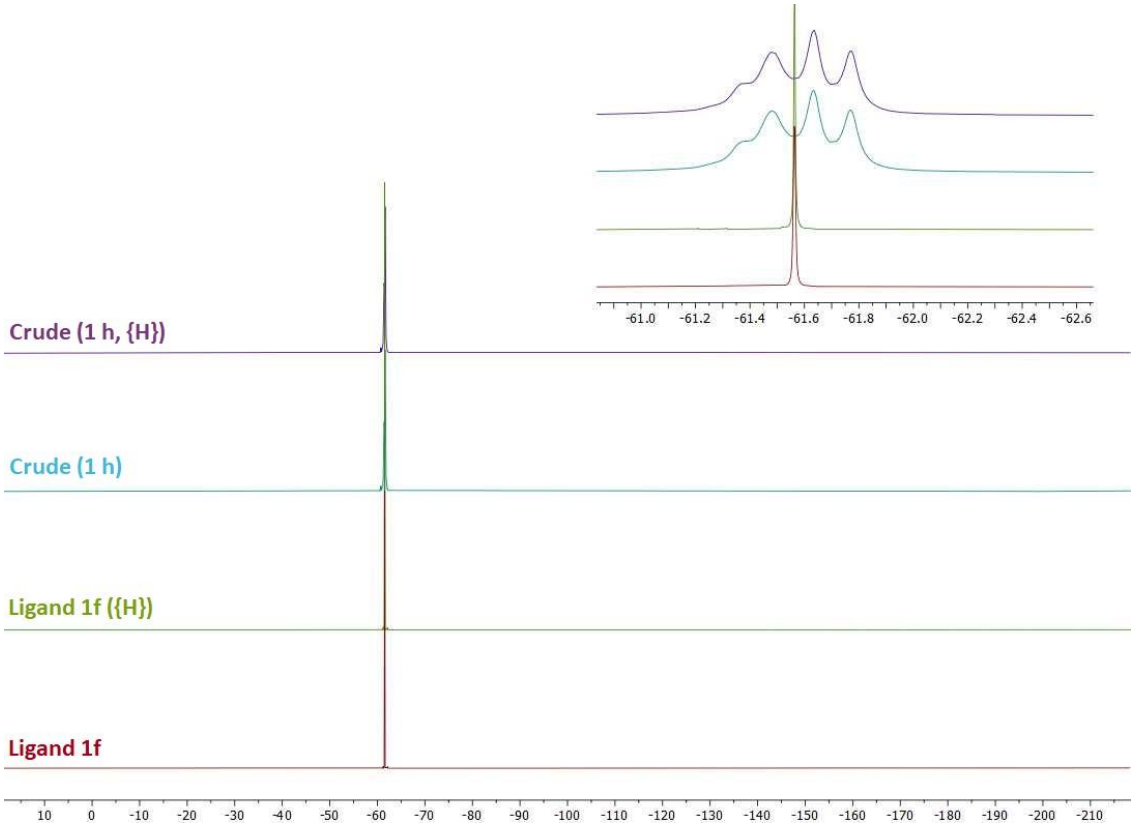


Figure S32: ^{1}H NMR of NMR-scale reaction between **1c** and $[Mn(CO)_5Br]$ in the presence of FA in DMSO-d^6.

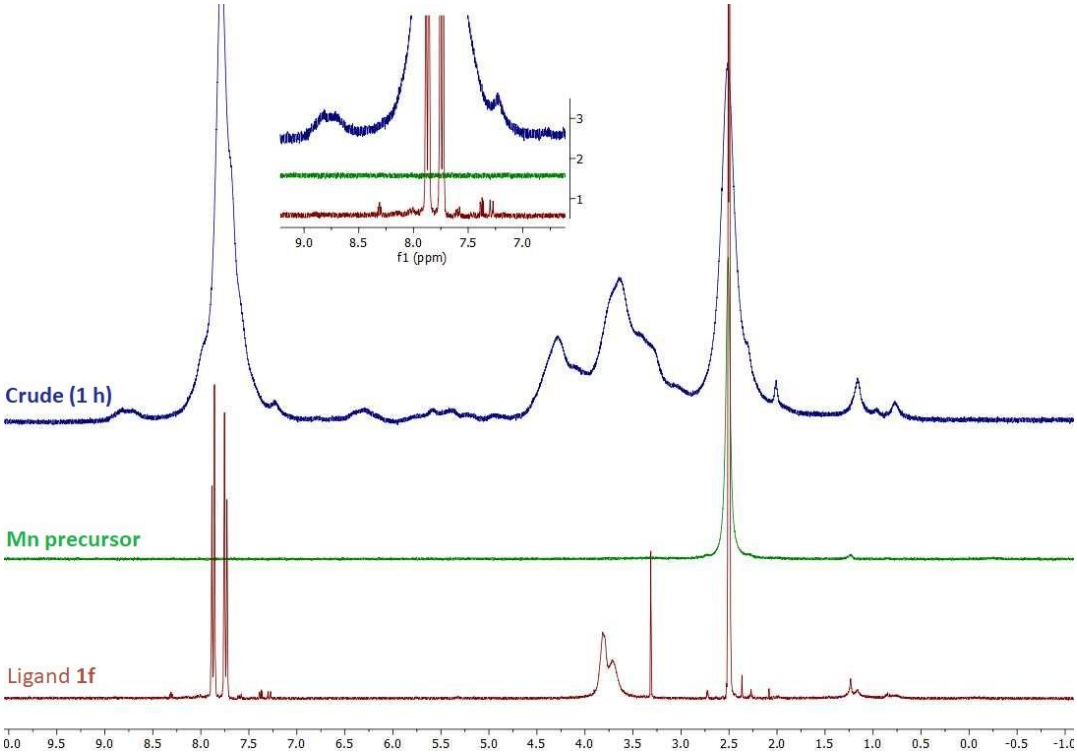
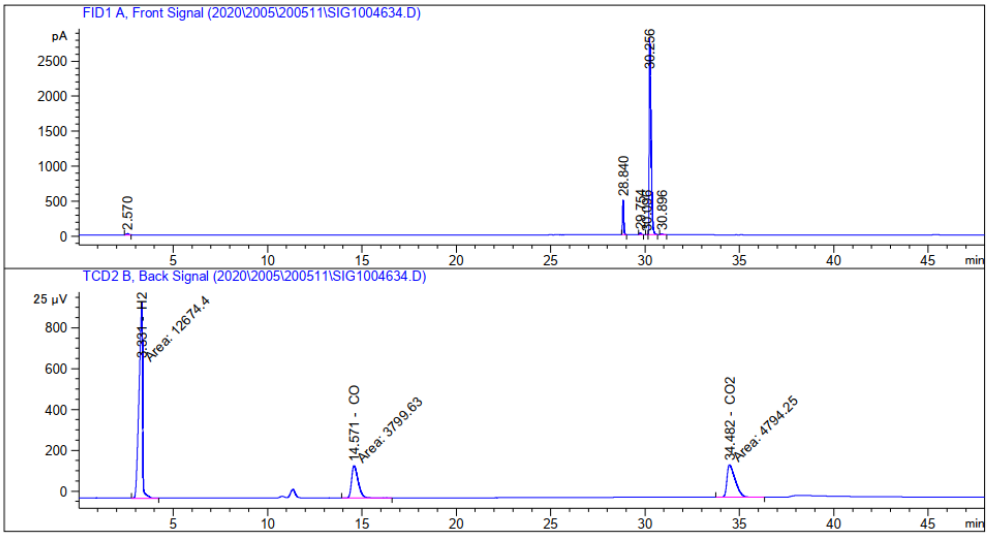


Figure S33: GC of NMR-scale reaction between **1c** and $[Mn(CO)_5Br]$ in the presence of FA in DMSO-d^6.



Signal 1: FID1 A, Front Signal

Signal 2: TCD2 B, Back Signal

RetTime [min]	Type	Area [25 µV*s]	Amt/Area	Amount [% Vol.]	Grp	Name
3.331	MM	1.26744e4	3.27511e-4	4.15101		H2
10.770		-	-	-		O2
11.339		-	-	-		N2
14.571	MM	3799.63135	3.55284e-3	13.49947		CO
26.900		-	-	-		CH4
34.482	MM	4794.24902	1.79476e-3	8.60454		CO2
Totals :				26.25503		

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