Electronic Supplementary Material (ESI) for Dalton Transactions.

# Electronic Supplementary Information

# Highly efficient dehydrogenation of formic acid in aqueous solution catalysed by an easily available water-soluble iridium(III) dihydride.

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**Contents**

### *Preparation and characterization of cis,mer-[IrH$_2$Cl(mtppms)$_3$]*

*m*tppms (monosulfonated triphenylphosphine sodium salt) was prepared as described in the literature.[1]

*m*tppms (965 mg, 2.4 mmol) was dissolved in 40 mL of 96% EtOH under Ar(g) and heated to reflux temperature, followed by addition of $IrCl_3x3H_2O$ (115 mg, 0.3 mmol) as a warm solution in 10 mL of 96% EtOH. The reaction mixture was refluxed with stirring for 8 h. After 1.5-2 h light yellow precipitation was observed. The cooled reaction mixture (suspension) was stirred overnight and the pale yellow solid product was collected by filtration. The complex was washed with 10 mL abs.EtOH, three times with 10 mL diethylether and dried in vacuum. Yield: 409 mg, 87.7 %. The product is soluble in water and MeOH, poorly soluble in ethanol and insoluble in organic solvents such as acetone, diethyleter and dichloromethane.

$\delta_H$ (360 MHz, $CD_3OD$, ppm) *hydride region*: $H_{(x)}$ -21.71 (tdd) $J_{HP(A)}$ 15.9; $J_{HP(B)}$ 11.4; $J_{HH(Y)}$ 4.9; $H_{(Y)}$ -11.10 (tdd) $J_{HP(A)}$ 20.3; $J_{HP(B)}$ 130.3; $J_{HH(X)}$ 4.9; *phenyl region*: 6.7-8.3 ($CH_{aryl}$) $\delta_P$ (146 MHz, $CD_3OD$, ppm) $P_{(A)\{H\}}$ 8.21 (d) $J_{PP(B)}$ 13.4; $P_{(B)\{H\}}$ -0.76 (t) $J_{PP(A)}$ 13.4; $\delta_C$ (90 MHz, $CD_3OD$, ppm): *phenyl region*: 128.06-145.66 ($C_{aryl}$)

IR (KBr): $\nu$/cm$^{-1}$ 3420, 3057 (O-H, water); 2249, 2145 (Ir-H, hydride); 1619, 1482, 1436, 1400 (=C-H, aromatic); 1222, 1192 (S=O);

Anal. Calcd for [IrH$_2$Cl(*m*tppms)$_3$]×6H$_2$O, C54H56IrClNa3O15P3S3 (1430.769): C, 45.33; H, 3.95; S, 6.72, Found: C, 45.20; H, 3.84; S, 6.75.

MS (ESI): m/z for [M-NaCl-2H] calcd 1262.06, found 1261.92

1. F. Joó, J. Kovács, Á. Kathó, A. C. Bényei, T. Decuir, D. J. Darensbourg, *Inorg. Synth.* 1998, **32**, 1.

***General procedure for catalytic FA decomposition in atmospheric gas burette***

*cis,mer*-[$IrH_2Cl$(*m*tppms)$_3$] (7.0 mg) together with *m*tppms (2.0 mg; if required) were placed into a jacketed flask connected to a thermostated gas burette. After deoxygenation, 4.5 mL of deoxygenated water was added under Ar followed by 0.5 mL of $HCOOH/HCOO^-$ solution (150 μL of 90 % (m/m) HCOOH and 33.0 mg HCOONa). The reactions were followed by recording the increase of gas volume.

***General procedure for catalytic FA decomposition in Parr-reactor***

*cis,mer*-[$IrH_2Cl$(*m*tppms)$_3$] (7.0 mg) was placed into the reactor which was then deoxygenated by an $N_2$ (or Ar) flow. 20 mL of deoxygenated water was added under $N_2$ (or Ar) and the reactor was heated to the operating temperature. When the temperature stabilized, the appropriate amount of $HCOOH/HCOO^-$ solution (e.g. 6.00 mL of 90 % (m/m) HCOOH containing 680.0 mg HCOONa) was quickly added through the injection valve. The reactions were followed by recording the increase of reactor pressure.

***Re-use of the catalyst***

When FA decomposition was complete (100% FA conversion) indicated by a pressure of 80-81 bar, the reactor pressure was decreased to atmospheric level and another amount of cc.HCOOH (5.00 mL) was quickly added through the injection valve. The new cycle of FA dehydrogenation was followed by recording the increase of reactor pressure.

***Gas analysis***

5.0 mL samples were taken from the gas phase of FA dehydrogenation experiments with a gas-tight syringe and analyzed on a Shimadzu GC2010 gas chromatograph using a Varian Plot, Molsieve 5A, 30mx0.32mm column at 65°C with He as carrier gas and a thermal conductivity detector at 70°C. The GC analysis showed this gas to be $H_2:CO_2 = 1:1$ mixture virtually free from CO (<10 ppm - detection limit).

***HPLC analysis***

The reaction mixture was analyzed by HPLC - Waters 501 pump, Supelcogel® 610H column, Waters 490E multiwavelength UV-Vis detector (λ = 210, 205 and 254 nm), sample volume 10 μl, eluent 0.1% $H_3PO_4$ in water, flow rate 1 ml/min. Formate was detected in 210 nm and its concentration was determined by the peak area using a calibration curve.

**Figure S1** – $^1$H NMR spectra of *cis,mer*-[IrH$_2$Cl(*m*tppms)$_3$]

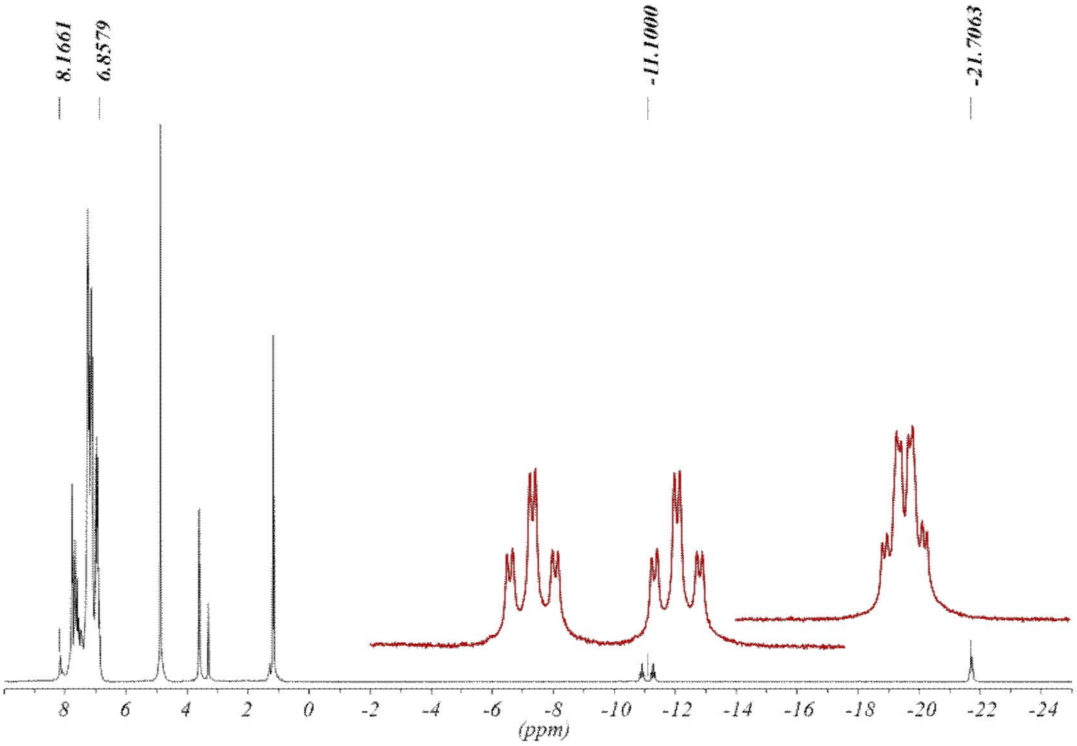


**Figure S2** – $^{31}$P{H} NMR spectra of *cis,mer*-[IrH$_2$Cl(*m*tppms)$_3$]

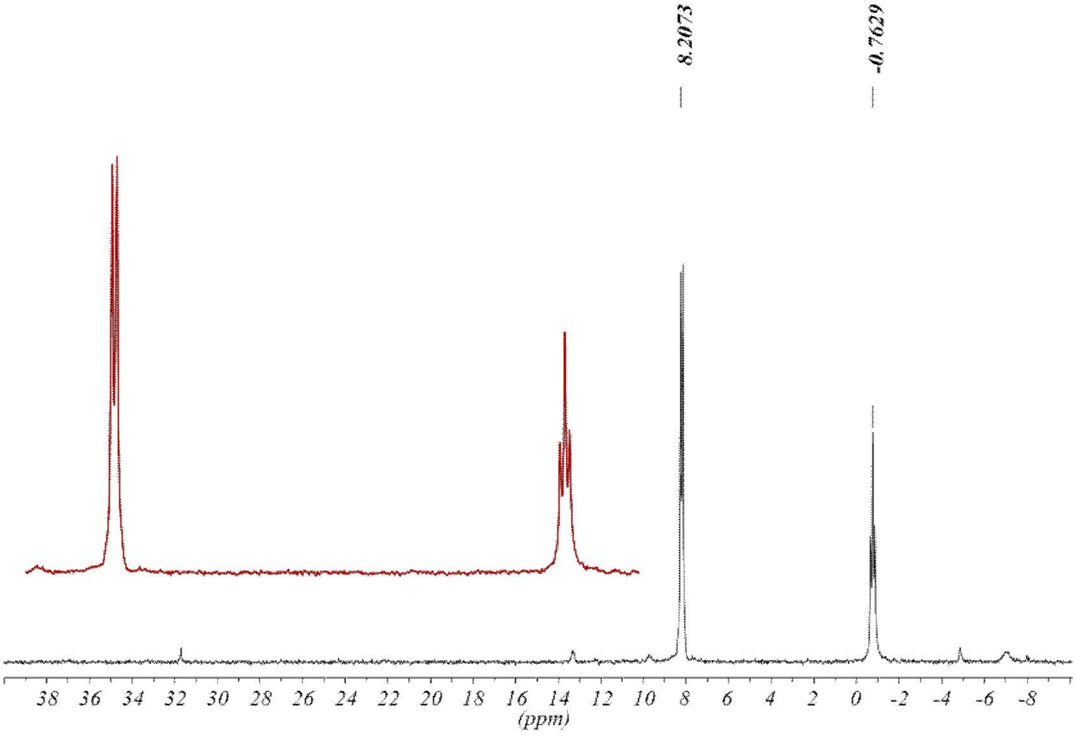
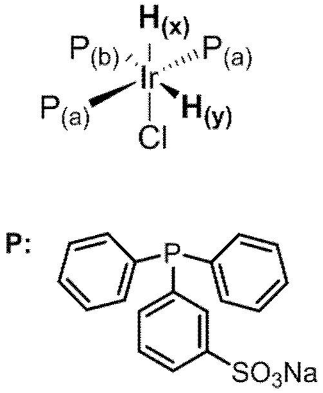


**Figure S3** – Structure and NMR-shifts (coupling constants) of *cis,mer*-[$IrH_2Cl$(*m*tppms)$_3$]



| | (ppm) | ***J*** (Hz) | | |
|---|---|---|---|---|
| $\delta\ [H_{(x)}]$ | -21,71 (tdd) | 15,9 ($P_{(a)}$) | 11,4 ($P_{(b)}$) | 4,9 ($H_{(y)}$) |
| $\delta\ [H_{(y)}]$ | -11,10 (tdd) | 20,3 ($P_{(a)}$) | 130,3 ($P_{(b)}$) | 4,9 ($H_{(x)}$) |
| $\delta\ [P_{(a)}\{H\}]$ | 8,21 (d) | 13,4 ($P_{(b)}$) | | |
| $\delta\ [P_{(b)}\{H\}]$ | -0,76 (t) | 13,4 ($P_{(a)}$) | | |

**Figure S4** – IR spectrum of *cis,mer*-[$IrH_2Cl$(*m*tppms)$_3$]

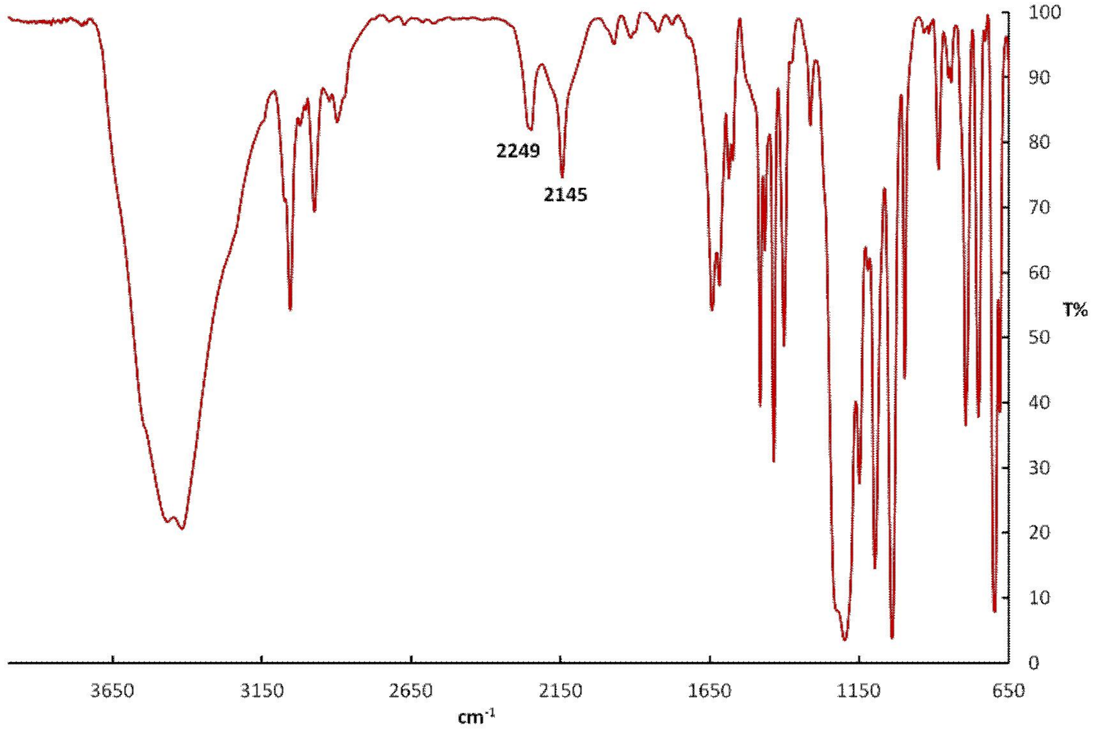
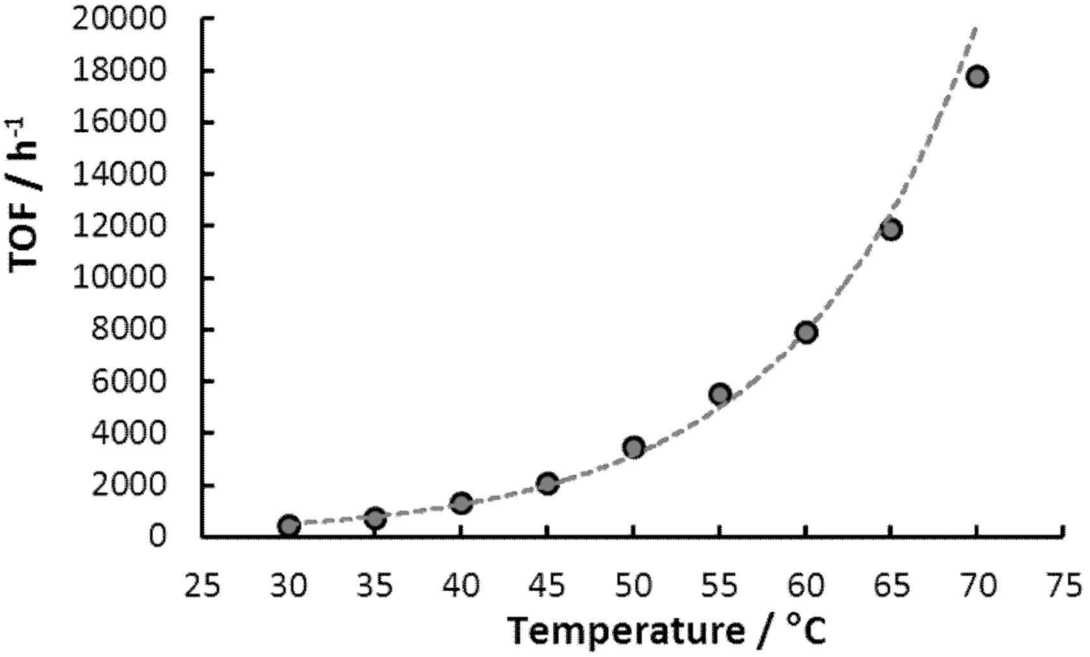
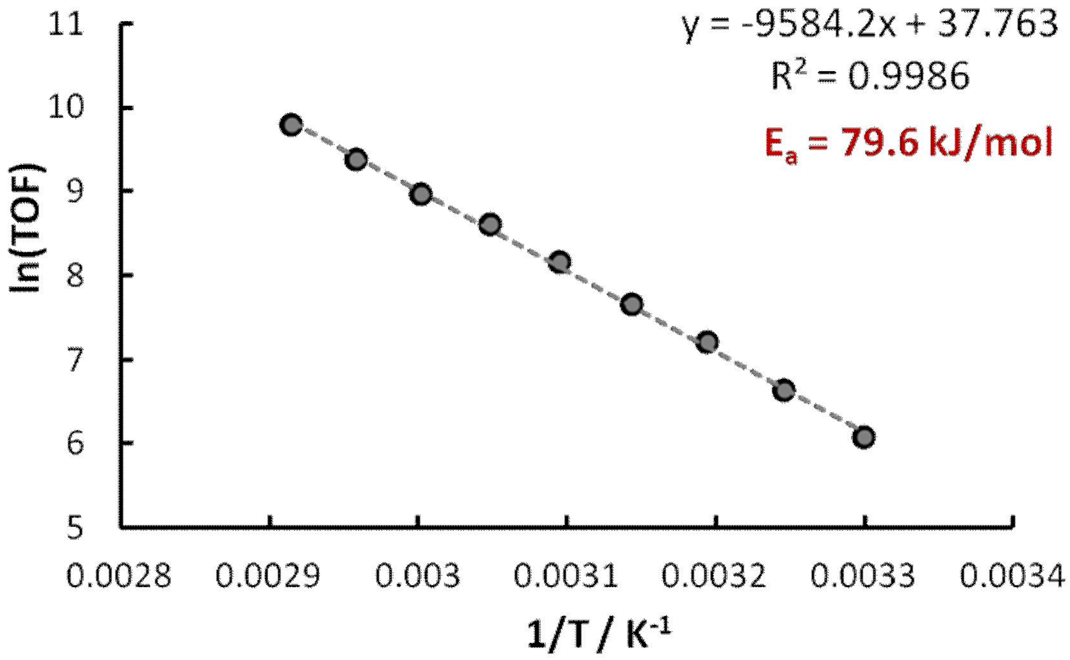


**Figure S5** – Effect of temperature on FA dehydrogenation by *cis,mer*-[$IrH_2Cl$(*m*tppms)$_3$]



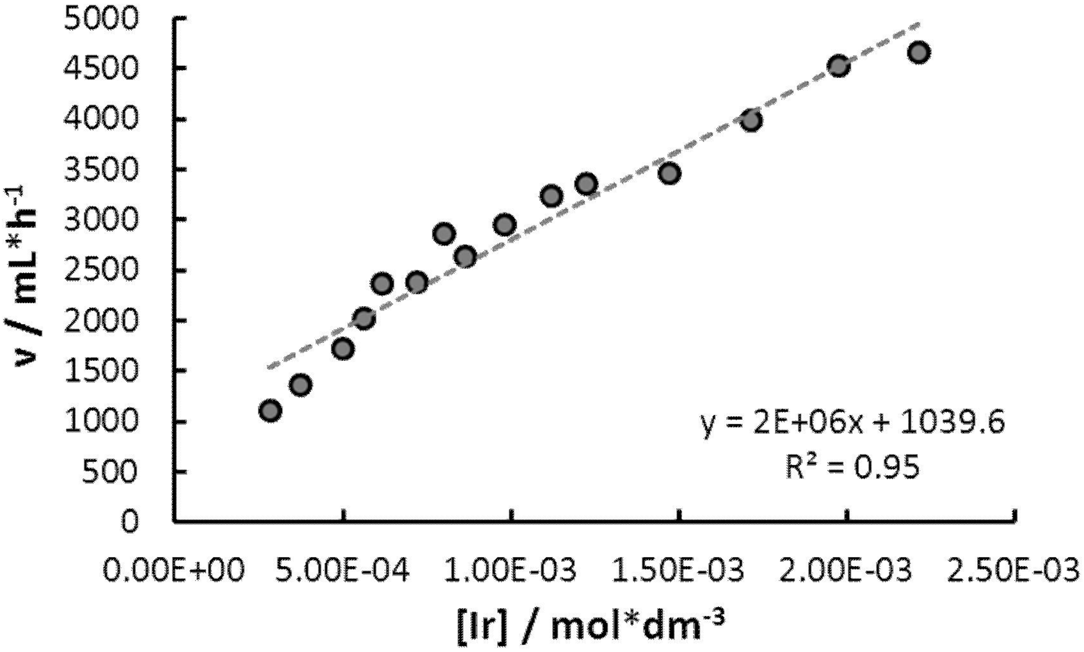
$n_{Ir}$ = 4.9x10$^{-6}$ mol; $n_{HCOOH}$ = 3.58x10$^{-3}$ mol; $n_{HCOONa}$ = 4.9x10$^{-4}$ mol; V = 5.0 mL; gas burette

**Figure S6** – Effect of temperature on FA dehydrogenation by *cis,mer*-[$IrH_2Cl$(*m*tppms)$_3$] – Arrhenius-plot



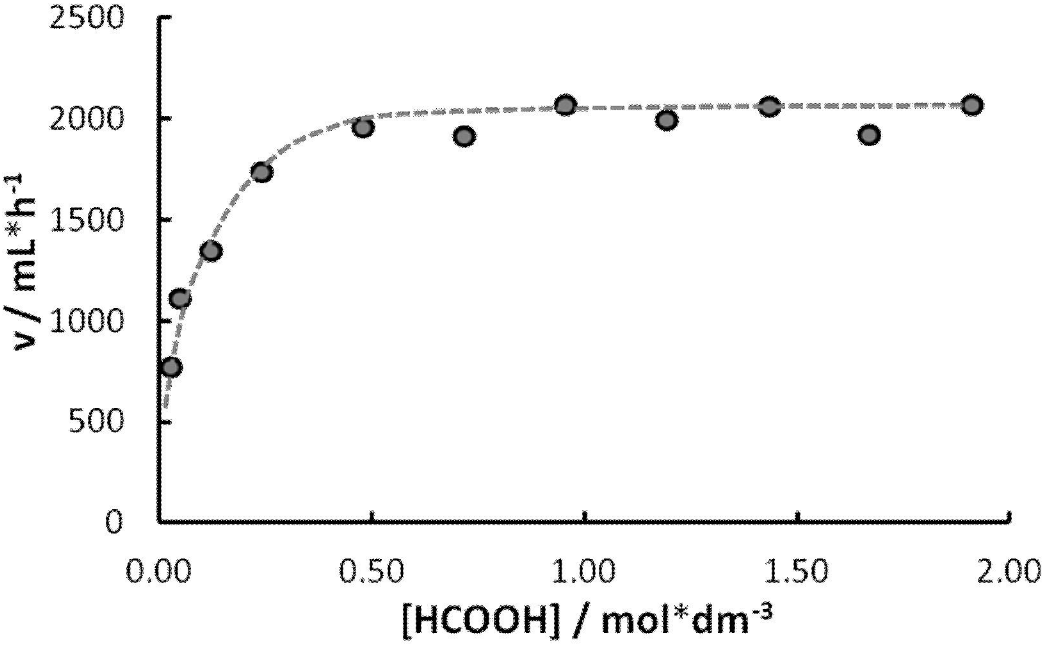
$n_{Ir}$ = 4.9x10$^{-6}$ mol; $n_{HCOOH}$ = 3.58x10$^{-3}$ mol; $n_{HCOONa}$ = 4.9x10$^{-4}$ mol; V = 5.0 mL; gas burette

**Figure S7** – Effect of catalyst concentration on FA dehydrogenation by *cis,mer*-[$IrH_2Cl$(*m*tppms)$_3$]



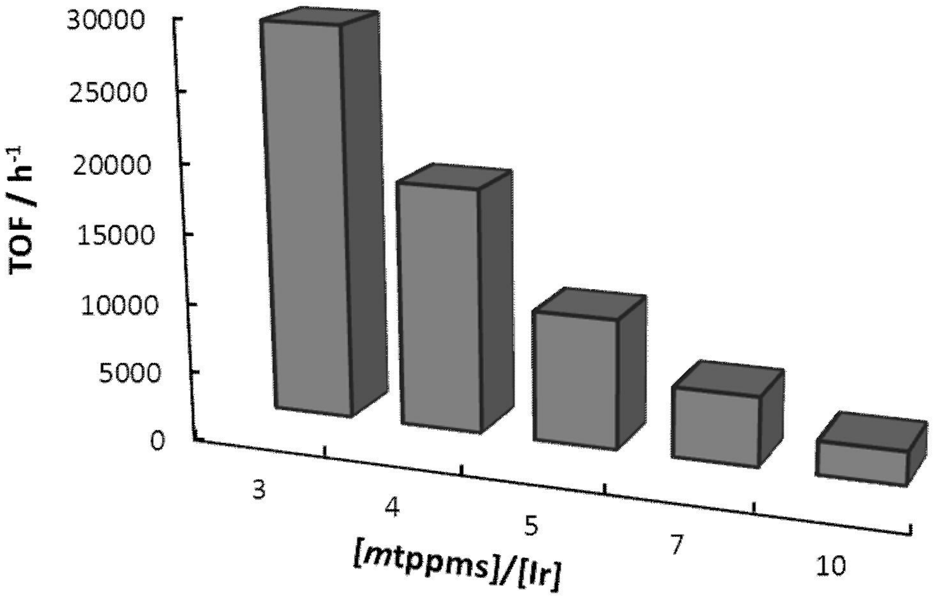
$n_{HCOOH}$ = 8.115x10$^{-3}$ mol; $n_{HCOONa}$ = 2x10$^{-3}$ mol; V = 5.0 mL; T = 60°C; v = ml gas / h
($n_{Ir}$ = 1.4x10$^{-6}$ – 1.105x10$^{-5}$ mol); gas burette

**Figure S8** – Effect of HCOOH concentration on FA dehydrogenation by *cis,mer*-[$IrH_2Cl$(*m*tppms)$_3$]



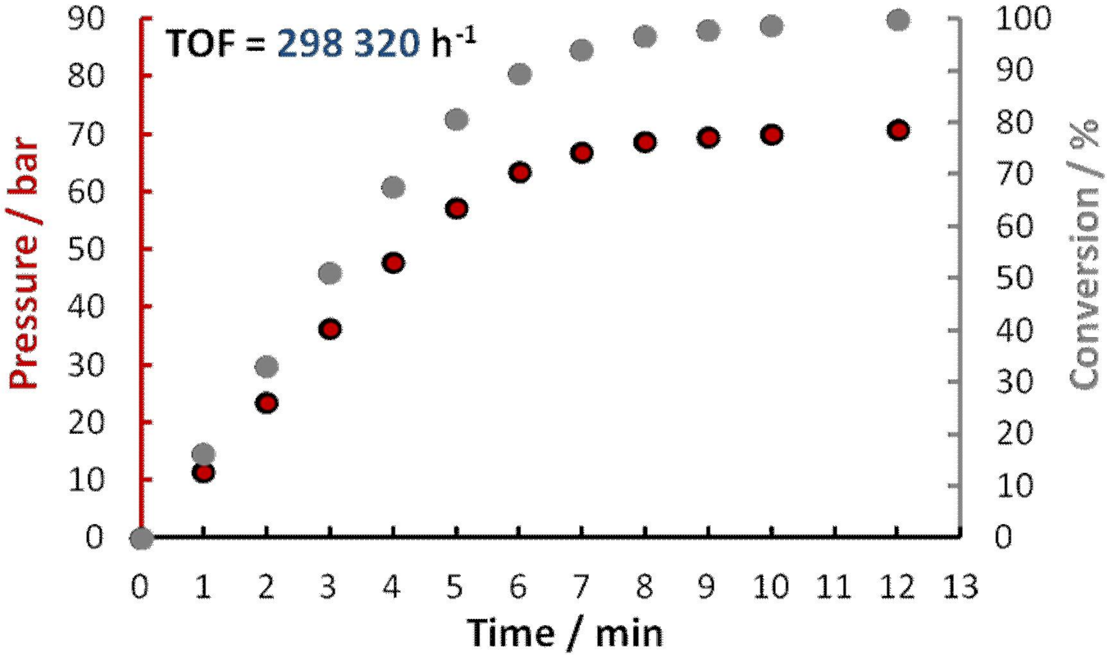
$n_{Ir}$ = 4.9x10$^{-6}$ mol; $n_{HCOONa}$ = 4.9x10$^{-4}$ mol; V = 5.0 mL; T = 60°C; v = ml gas / h;
($n_{HCOOH}$ = 1.195x10$^{-5}$ – 9.55x10$^{-3}$ mol); gas burette

**Figure S9** – Effect of phosphine concentration on FA dehydrogenation by *cis,mer*-[$IrH_2Cl(m\text{tppms})_3$]



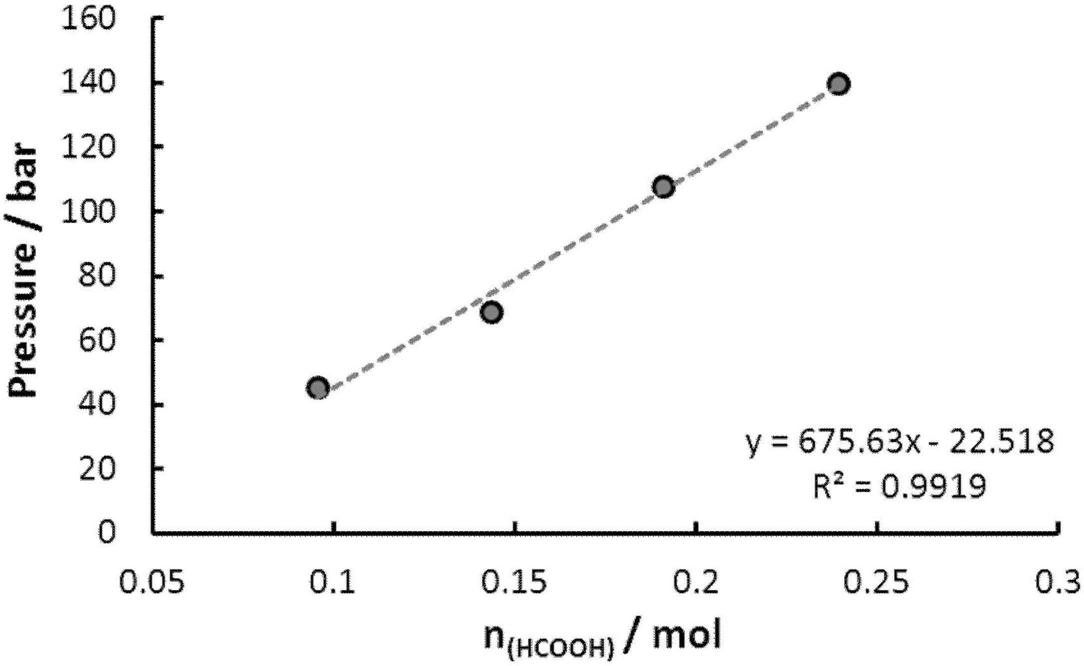
$n_{Ir}$ = 4.9x10$^{-6}$ mol; $n_{HCOONa}$ = 4.9x10$^{-4}$ mol; $n_{HCOOH}$ = 4.8x10$^{-3}$ mol; V = 5.0 mL; T = 60°C

**Figure S10** – Time course of HCOOH dehydrogenation in closed reactor



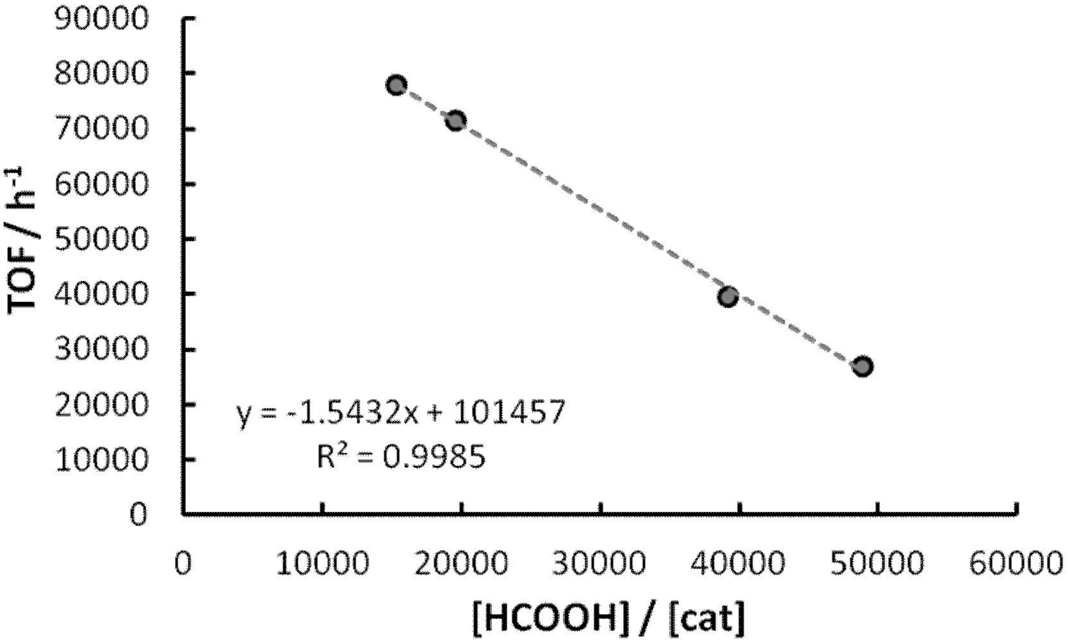
$n_{Ir}$ = 5x10$^{-6}$ mol; $n_{HCOONa}$ = 5x10$^{-2}$ mol; $n_{HCOOH}$ = 1.44x10$^{-1}$ mol; V = 20.0 mL; T = 100°C

**Figure S11** – Final pressures in a closed reactor as a function of the amount of FA



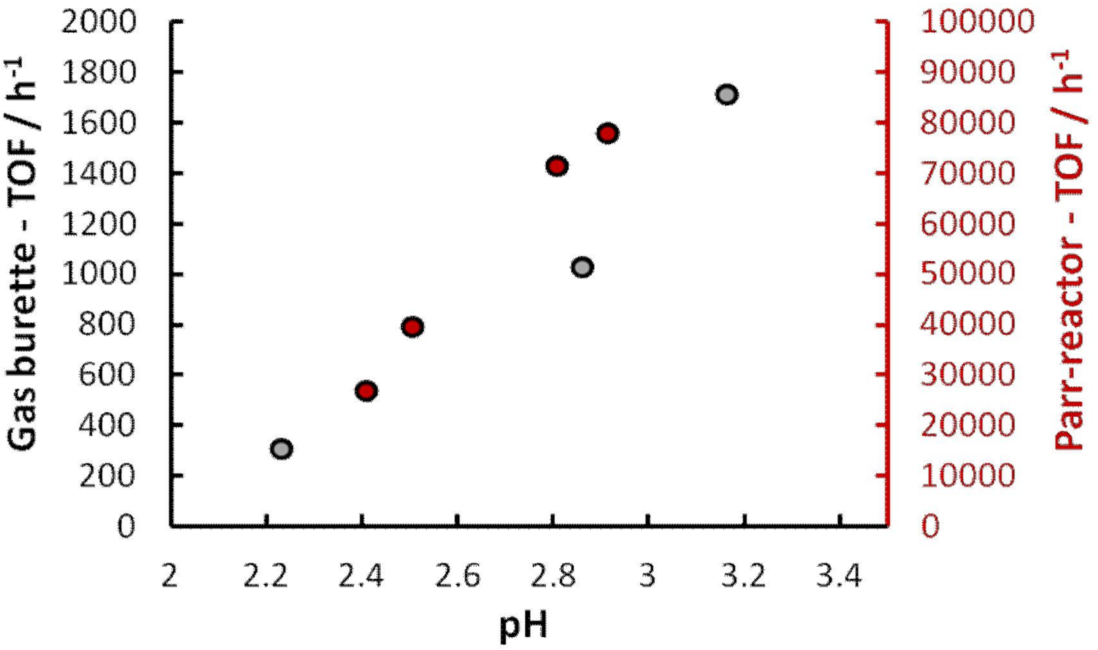
$n_{Ir}$ = 5x10$^{-6}$ mol; $n_{HCOONa}$ = 1x10$^{-2}$ mol; V = 20.0 mL; T = 80°C

**Figure S12** – Effect of the S/C ratio on the reaction rates in a closed reactor



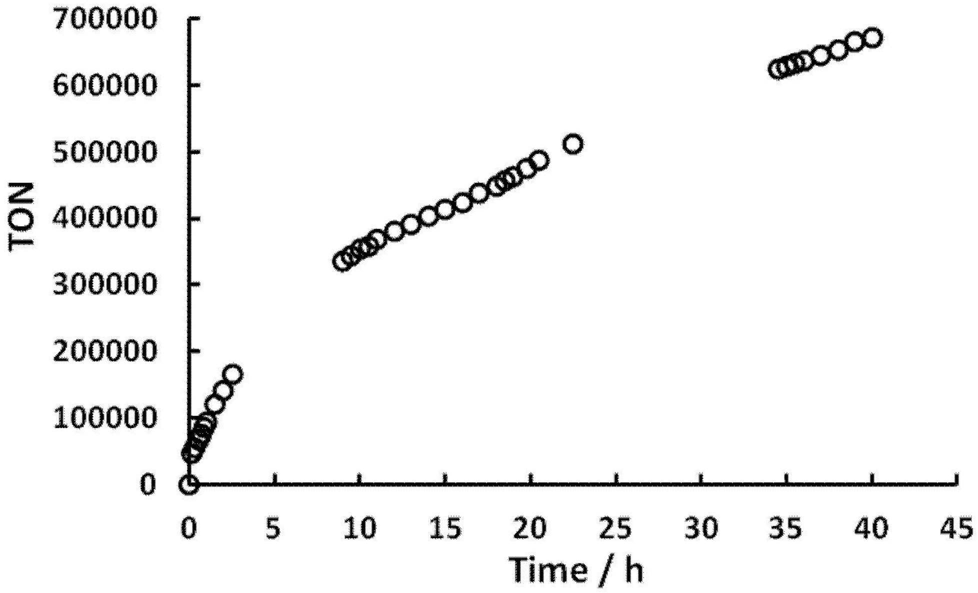
$n_{Ir}$ = 5x10$^{-6}$ mol; $n_{HCOONa}$ = 1x10$^{-2}$ mol; V = 20,0 mL; T = 80°C

**Figure S13** – The rate of FA dehydrogenation as a function of pH measured in the gas burette (atmospheric pressure, low S/C ratios) and in the closed Parr reactor (elevated pressures, high S/C ratios).



*Gas burette* (grey dots): $n_{Ir}$ = 9.9×10$^{-6}$ mol; $n_{HCOOH + HCOONa}$ = 1.00×10$^{-3}$ mol; V = 5.0 mL; T = 60°C. *Parr-reactor* (red dots): $n_{Ir}$ = 4.9×10$^{-6}$ mol; $n_{HCOOH + HCOONa}$ = 8.5x10$^{-2}$ - 2.5×10$^{-1}$ mol; V = 20.0 mL; T = 80°C

**Figure S14** – Long-term stability of *cis,mer*-[$IrH_2Cl$(*m*tppms)$_3$] in FA dehydrogenation; determination of TON as a function of time



Parr reactor: $n_{Ir}$ = 8.81×$10^{-8}$ mol; $n_{HCOOH}$ = 2.652x$10^{-1}$ mol; $n_{HCOONa}$= 1x$10^{-1}$ mol; V = 20.0 mL; T = 115°C. The reaction was followed by measuring the pressure inside the reactor and the final conversion at 40 h was determined by HPLC. At 40 h TON=674 000.