Supporting Information for

Highly Efficient Ir-Catalyst for the Solventless Dehydrogenation of Formic Acid: The Key Role of an N-heterocyclic Olefin

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Experimental procedure

General:

All experiments were carried out under an inert atmosphere using standard Schlenk techniques. The solvents were dried by known procedures and distilled under argon prior to use or obtained oxygen- and water-free from a Solvent Purification System (Innovative Technologies). All other commercially available starting materials were purchased from Sigma-Aldrich, Merck and J. T. Baker and were used without further purification. H₂ gas (>99.5 %) was obtained from Infra. ¹H, ¹³C{¹H}, ³¹P{¹H} and ¹⁹F spectra were recorded either on a Bruker ARX 300 MHz or a Bruker Avance 400 MHz instruments. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (¹H, ¹³C{¹H}). Coupling constants, J, are given in Hz. Spectral assignments were achieved by combination of ¹H-¹H COSY, ¹³C APT and ¹H-¹³C HSQC/HMBC experiments. C, H, and N analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. GC-MS spectra were recorded on a Hewlett-Packard GC-MS system.

General procedure for the dehydrogenation of formic acid.

All the reactions were performed in a Man on the Moon series X102 kit micro-reactor with a total volume of 19 ml. Formic acid and water were degassed prior to use.

- Formic acid (neat) dehydrogenation.

500 µL (13 mmol) of formic acid was added to 44 mg (5 mol%, 0.65 mmol) of sodium formate at 0ºC under an argon atmosphere. After closing the reactor and placing it into a thermostated oil bath at 353K the pressure measurement was started. Once the pressure was stabilized, a solution of catalyst (2 mg, 0.016 mol%, 0.002 mmol) in 20 µL of formic acid was added with a syringe. The gas formation was measured until the reaction generated 1 bar of pressure. The amount of gases (CO₂ + H₂) produced during the reaction was calculated using the Ideal Gas Law.

- Formic acid dehydrogenation in H₂O.

A solution of 3 mg (10 mol%, 0.04 mmol) of sodium formate in water (2 mL) was prepared under an argon atmosphere. After closing the reactor and placing it into a thermostated oil bath at 353K the pressure measurement was started. Once the pressure was stabilized, a solution of catalyst (4 mg, 1 mol%, 0.004 mmol) in 20 µL (0.4 mmol) of formic acid was added with a syringe. The gas formation was measured until the reaction generated 1 bar of pressure. The amount of gases (CO₂ + H₂) produced during the reaction was calculated using the Ideal Gas Law.
- Formic acid dehydrogenation under optimized conditions (100 mol% of H₂O).

500 µL (13 mmol) of formic acid was added to 264 mg (30 mol%, 3.9 mmol) of sodium formate and 235 µL (100 mol% 13 mmol) of water at 0°C under an argon atmosphere. After closing the reactor and placing it into a thermostated oil bath at 363 K the pressure measurement was started. Once the pressure was stabilized, a solution of catalyst (2 mg, 0.016 mol%, 0.002 mmol) in 20 µL of formic acid was added with a syringe. The gas formation was measured until the reaction generated 1 bar of pressure. The amount of gases (CO₂ + H₂) produced during the reaction was calculated using the Ideal Gas Law.
Reactivity of [Ir(PCP)(COD)]BF₄ (1) with HCOOH in CD₂Cl₂ (preparation of 5).

HCOOH (13 µL, 0.35 mmol) and an excess of pyridine (50 µL, 0.60 mmol) were added to a solution of 1 (80 mg, 0.087 mmol) in 5 mL of dichloromethane. The resulting mixture was stirred for 18 h at 50 oC. After this time the solvent was removed under vacuum. Crystals of [Ir(H)₂(PCP)(py)]BF₄ (5) suitable for X-ray diffraction were obtained by slow diffusion of pentane into a saturated dichloromethane solution of the crude. HRMS (ESI) m/z calcd. for C₃₇H₃₉IrN₃P₂BF₄ (M - pyridine - BF₄) 701.1822, found 701.1828.

¹H NMR
Reactivity of [Ir(PCP)(COD)]BF₄ (1) with HCOOH/HCOONa in CD₃CN.

An excess of HCOOH (6 µL, 0.15 mmol) and an excess of sodium formate (10 mg, 0.15 mmol) were added to a solution of 1 (30 mg, 0.037 mmol) in 3 mL of acetonitrile. The resulting mixture was stirred for 18 h at 80 °C. After this time the solvent was removed under vacuum and the solid (compound 5) was washed with diethyl ether.

¹H NMR
Reactivity of [Ir(H)₂(PCP)(py)]BF₄ (5) with 3,5-dimethylpyridine in CD₂Cl₂ (preparation of 6)

To a solution of 5 in CH₂Cl₂, prepared as described above, an excess of 3,5-dimethylpyridine was added at room temperature, resulting in the formation of a mixture of a monohydride and a dihydride complex. Crystals of [Ir(H)₂(PCP)(Me₂py)]BF₄ (6) suitable for X-ray diffraction were obtained by slow diffusion of pentane into a saturated dichloromethane solution of the crude mixture.

³¹P NMR

¹H NMR
Dehydrogenation HCOOH in DMSO-d$_6$ using 1 as catalyst.

Formic acid (10 µL, 0.25 mmol), sodium formate (1.5 mg, 10 mol%, 0.025 mmol), complex 1 (2.2 mg, 1 mol%, 0.0023 mmol) and 0.3 mL of DMSO-d$_6$ were placed in a Young NMR tube under an argon atmosphere. The resulting solution was placed in a thermostated oil bath at 353K and monitored by NMR.

$^1$H NMR after 150 min:
$^{31}$P NMR after 150 min:
IR Spectrum of the mixture of gases obtained from catalysis

The region between 2200 and 2050 cm$^{-1}$, where the bands of gaseous CO would be expected, shows no traces of the by-product.

**Figure S1.** IR Spectrum of the gaseous products obtained under optimized reaction conditions (100 mol% of H$_2$O and 30 mol% of HCOONa and 0.016 mol% I).
Reaction profiles

**Figure S2.** Optimization of $\text{H}_2\text{O}$ mol% 

**Figure S3.** Optimization of $\text{HCOONa}$ mol% (at 5 mol% $\text{H}_2\text{O}$ loading)
Figure S4. Optimization of HCOONa mol% (at 100 mol% H\textsubscript{2}O loading)
Arrhenius plots

\[ \ln K = \left(-\frac{E_a}{R}\right)(1/T) + \ln A \]
\[ r^2 = 0.9967 \]
\[ E_a = 19.9 \pm 0.8 \text{ Kcal/mol} \]

Figure S5. Arrhenius plot for the dehydrogenation of FA using complex 1 (conditions: 100 mol% of H₂O and 30 mol% of HCOONa and 0.016 mol% 1).

\[ \ln K = \left(-\frac{E_a}{R}\right)(1/T) + \ln A \]
\[ r^2 = 0.9889 \]
\[ E_a = 24.5 \pm 1.8 \text{ Kcal/mol} \]

Figure S7. Arrhenius plot for the dehydrogenation of FA using complex 1 in the absence of H₂O (conditions: 30 mol% of HCOONa and 0.016 mol% 1).
Recycling experiments

**Figure S8.** Recycling experiments for the dehydrogenation of FA (20 µL) using complex 1 in H$_2$O (2 mL). Conditions: 10 mol% of HCOONa, 1 mol% 1, 80 ºC.
Crystal structure determination. X-ray diffraction data were collected at 100.0(2) K on an APEX SMART Bruker diffractometer with graphite–monochromated Mo–Kα radiation ($\lambda = 0.71073$ Å) using narrow $\omega$ rotations (0.3–0.6°). Intensities were integrated and corrected for absorption effects with SAINT-PLUS,1 and SADABS2 programs, both included in APEX2 package. The structures were solved by the Patterson method with SHELXS-20133 and refined by full matrix least–squares on $F^2$ with SHELXL-20144 under WinGX.5

Crystal data and structure refinement for 5. C$_{38}$H$_{41}$BCl$_2$F$_4$IrN$_3$P$_2$, $M = 951.59$ g mol$^{-1}$, monoclinic, P2$_1$/n, $a = 15.5008(17)$ Å, $b = 11.5673(13)$ Å, $c = 21.116(2)$ Å, $\beta = 97.5830(10)^\circ$, $V = 3753.1(7)$ Å$^3$, $Z = 4$, $D_{\text{calc}} = 1.684$ g cm$^{-3}$, $\mu = 3.838$ mm$^{-1}$, $F(000) = 1888$, 0.260 x 0.060 x 0.040 mm, $\theta_{\text{min}}/\theta_{\text{max}}$ 2.061/26.371°, 1.537/25.027°, limiting indexes –18$\leq$h$\leq$18, –13$\leq$k$\leq$13, –25$\leq$l$\leq$25, reflections collected/unique 32133/6587 [R(int) = 0.0854], data/restraints/parameters 6587/0/466, GOF = 1.194, $R_1 = 0.0788$, $wR^2 = 0.1577$, largest diff. peak/hole 2.959/-2.104 e Å$^{-3}$. CCDC deposit number 1858260.

Crystal data and structure refinement for 6. C$_{40}$H$_{45}$BCl$_2$F$_4$IrN$_3$P$_2$, $M = 979.64$ g mol$^{-1}$, triclinic, $P$–1, $a = 11.0544(15)$ Å, $b = 13.3742(18)$ Å, $c = 14.3388(19)$ Å, $\alpha = 84.204(2)^\circ$, $\beta = 84.669(2)^\circ$, $\gamma = 72.812(2)^\circ$, $V = 2010.4(5)$ Å$^3$, $Z = 2$, $D_{\text{calc}} = 1.618$ g cm$^{-3}$, $\mu = 3.585$ mm$^{-1}$, $F(000) = 976$, 0.280 x 0.120 x 0.120 mm$^3$, $\theta_{\text{min}}/\theta_{\text{max}}$ 2.061/26.371°, limiting indexes –13$\leq$h$\leq$13, –16$\leq$k$\leq$16, –17$\leq$l$\leq$17, reflections collected/unique 20667/8144 [R(int) = 0.0448], data/restraints/parameters 8144/9/482, GOF = 1.058, $R_1 = 0.0463$ [I>2$\sigma$(I)], $wR^2 = 0.1174$ (all data), largest diff. peak/hole 2.262/-2.004 e Å$^{-3}$. CCDC deposit number 1858261.

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2 SADABS program; University of Göttingen: Göttingen, Germany, 1999.