Supplementary Information: Methanol Dehydrogenation by Iridium NHC Complexes

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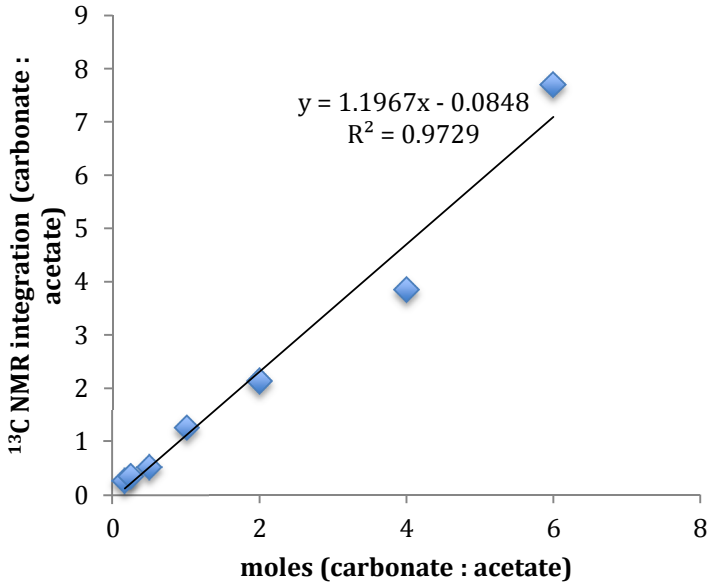
Table of Contents

General Methods

Chemicals were obtained from commercial suppliers and were used as received. Compounds **1a-4c**, as well as $[Cp^*IrCl_2]_2$ were prepared according to literature procedures. [1] Draeger tubes were purchased from Grainger (item # 29XM65, manufacturer model # CH 19701). NMR spectra were recorded on Agilent DD2-400, -500 -600 or Bruker AMX-500 spectrometers. Chemical shifts are reported with respect to residual internal protio solvent for ^1H and $^{13}C\{^1H\}$ NMR spectra. The chemical shift δ is reported in units of parts per million (ppm).

Quantitation of carbonate using $^{13}C\{^1H\}$ NMR.

The carbonate product from formic acid dehydrogenation was quantitated by $^{13}C\{^1H\}$ NMR using a calibration curve generated from samples with known amounts of carbonate and acetate (used as an internal standard in the reaction) (Figure S1). The data were fit by a straight line with the formula $y = 1.1967x - 0.0848$ (eq. S1), which was subsequently used to calculate the moles of carbonate in a sample given the moles of acetate standard and the relative $^{13}C\{^1H\}$ NMR integrations of carbonate and acetate. Finally, a blank sample containing KOH dissolved in a methanol/water mixture showed no detectable carbonate by $^{13}C\{^1H\}$ NMR.



moles carbonate: moles acetate	^{13}C NMR integral (carbonate) : integral (acetate)
0.17	0.27
0.25	0.35
0.5	0.52
1	1.25
2	2.13
4	3.85
6	7.69

Figure S1. ^{13}C NMR calibration curve for carbonate. Calibration curve comparing relative $^{13}C\{^{1}H\}$ integration of carbonate and acetate with relative amounts of carbonate and acetate in sample.

Gas burette monitoring of acceptorless methanol dehydrogenation.

The same gas burette setup described previously was used.[2] To a Schlenk tube equipped with a stir bar were added compound **4a** (1.6 mg, 0.004 mol%) and KOH (1.34 g, 20.3 mmol). The Schlenk was then coupled to a condenser connected to the burette. After evacuating and filling the system with argon 3-5 times, dry and degassed methanol (3.0 mL) was added under positive argon flow and the reaction flask was heated to 115 ˚C. Subsequently, the Schlenk flask was closed to the argon line and the condenser was opened to the burette using a 3-way stopcock. The water level in the burette was recorded as a function of time. Gas volume was converted to moles of H_2 using the Van der Waals equation (eq. S2). After stopping the reaction, the amounts of formate and carbonate detected by NMR with an internal standard were compared with the moles of gas produced, with good agreement (> 94 %).

$V_m = \frac{RT}{p} + b - \frac{a}{RT} = 23.96 \frac{L}{mol}$
$R = 8.3145\ m^3 Pa \cdot mol^{-1}$
T = 292 K
p = 101,325 Pa
$a = 2.49 * 10^{-10} Pa \cdot m^3 \cdot mol^{-2}$
$b = 26.7 * 10^{-6} m^3 \cdot mol^{-1}$

Equation S2. Van der Waals equation used for calculation of H_2 molar volume.

Quantification of carbon monoxide formed in acceptorless dehydrogenation reaction

Adventitious CO was quantified using a Draeger tube (Carbon monoxide 8/a, designed

for measurement of CO in 95 % H_2). A methanol dehydrogenation reaction was run with precatalyst **4a** and a gas burette setup similar to that used for following the reaction progress[2] with a few changes. A large reservoir (1 L) was used to collect H_2, and a small but efficient reflux condenser was used to minimize the amount of Ar in the collected gas. After evolution of 1 L of gas, the gas was slowly passed through the Draeger tube by means of a short Tygothane tube connected to the third outlet of the burrete using the 3-way stopcock. The CO concentration was determined as described in the instructions included with the detector tubes.

Figure S2. Draeger tube used for CO detection. Extent of discoloration due to CO marked with black line.

Homogeneity studies

The homogeneous nature of the active catalyst was supported through several experiments. First, simple iridium starting materials ($IrCl_3$, IrO_2 Ir^0 nanoparticles) showed poor activity for methanol dehydrogenation (Table X1, entries 17-19), arguing against breakdown of bis-NHC precatalysts to form such species. Second, poisoning experiments were carried out with precatalyst **4a** (Table S2). Under standard reaction conditions (0.004 mol % **4a**, 1.34 g KOH, 3 mL degassed MeOH) the addition of Hg(0) did not have a significant effect on catalyst activity, while addition of excess PPh_3 (50 eq.) considerably hindered catalysis.

Table S1. Poisoning experiments with Hg(0) and PPh_3.

Entry	Catalyst	Additive	TON
1	**4a**	Hg(0)	1690
2	**4a**	PPh_3	11

The effects of Hg(0) and PPh_3 on catalyst performance were further studied using gas burette measurements (Figure S2). A standard reaction was prepared (0.004 mol % **4a**, 1.34 g KOH, 3 mL MeOH), and catalyst activity was monitored using the burette as described above. After the addition of a drop of Hg(0) at 45 min, the cool reaction mixture was stirred until the reaction was restarted at t = 1h 10min by raising the temperature to reflux. The reaction then proceeded normally. In contrast, when PPh_3 (50 eq.) was added to the cooled reaction mixture at t = 2h 5min, the reaction barely got going on attempted restart at t = 2h 40 min. The lack of poisoning by Hg(0), which

deactivates many heterogeneous catalysts, and deactivation by excess PPh_3, which can shut down homogeneous catalysts by coordinating vacant sites, are consistent with a homogeneous active species.[3]

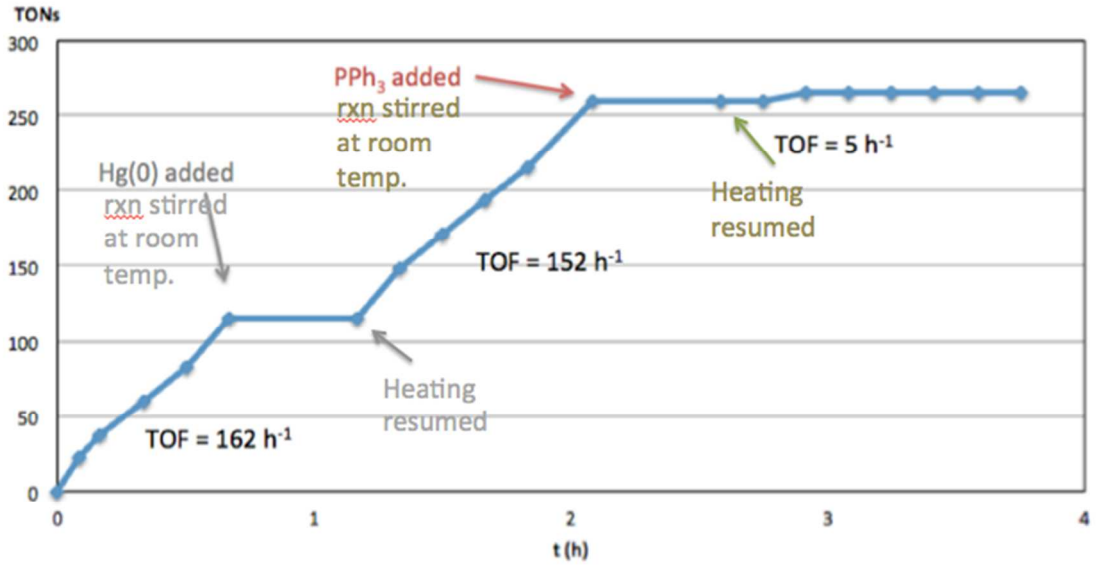


Figure S3. Effect of Hg(0) and PPh_3 on catalyst performance
Reaction run with 1.9 x 10^{-3} mmol $[Ir(IMe)_2(CO)_2]BF_4$ (0.0025 mol %) and 1.34 g KOH (15 % H_2O by mass, 20.0 mmol) in 3 mL degassed MeOH at reflux in gas burette.

Acceptorless methanol dehydrogenation

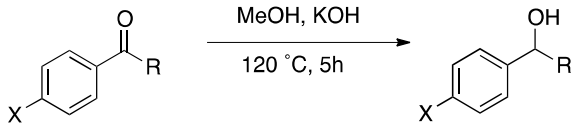
^{1}H NMR analysis of the reaction mixture after a standard reaction (0.004 mol % **4a**, 1.34 g KOH, 3 mL MeOH) showed predominantly formate with no detectable methoxymethane, methylformate or acetate, which are observed in some systems for methanol dehydrogenation.[4] A reaction was also run with formate and precatalyst **4a**. Sodium formate (3 mmol, 0.003 mmol **4a**, 1.34 g KOH, 3 mL H_2O, 15 h, 115 ˚C) gave conversion to carbonate (174 TON), as quantified by $^{13}C\{^1H\}$ NMR.

Table S2. Transfer hydrogenation of heterocycles

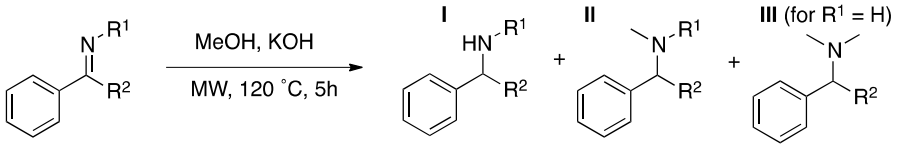
Entry	Substrate	Yield (%)[a]
1	acridine	>95
2	quinoxaline	<5
3	quinaldine	<5

Experiments run under MW irradiation (120 ˚C, 5 hours) with **4a** (6.5 μmol, 5 mol%), substrate (0.13 mmol), KOH (0.65 mmol) and dry and degassed methanol (0.5 mL). [a]Yields determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard.

Table S3. Negative controls for transfer hydrogenation reactions



Entry	R	X	Equiv. KOH *vs*. substrate	Yield (%)[a]
1	Ph	H	1	<5
2	Ph	H	5	14
3	Ph	CF_3	1	9
4	Ph	OMe	5	5



Entry	R^1	R^2	Equiv. KOH *vs*. substrate	Yield I[a]	Yield II[a]	Yield III[a]
5	Ph	H	1	<5	<5	-
6	Bn	H	1	<5	<5	-

Entry	Substrate	Equiv. KOH *vs*. substrate	Yield (%)[a]
7	acridine	5	<5

Experiments run under MW irradiation (120 ˚C, 5 hours) with substrate (0.13 mmol) KOH (0.13 - 0.65 mmol) and dry and degassed methanol (0.5 mL). [a]Yields determined by ^{1}H NMR using 1,3,5- trimethoxybenzene as an internal standard.

^{1}H NMR analysis of side products from acetophenone transfer hydrogenation reaction

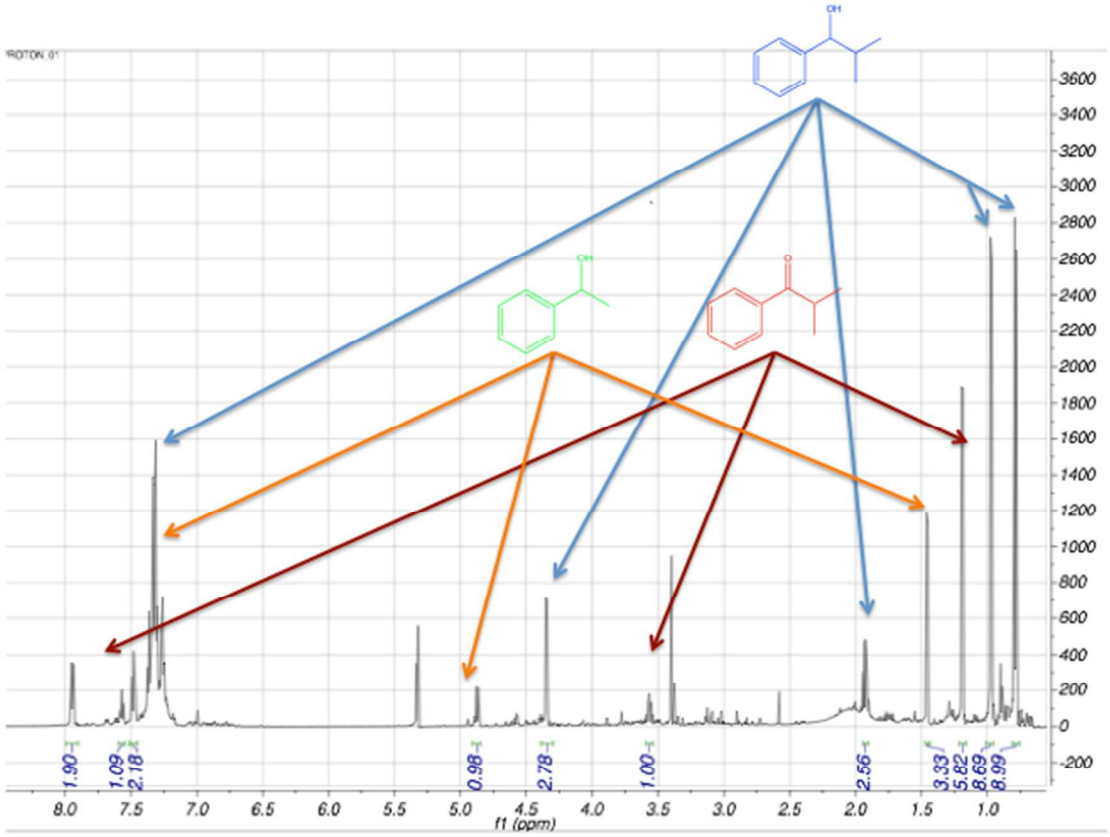


Figure S4. ^{1}H **NMR spectrum of products from acetophenone TH reaction with compound 4a and KOH.** ^{1}H NMR shifts of methylated products match those previously reported in the literature: α, α' dimethyl acetophenone[5], α, α' dimethyl 1-phenylethanol[6].

Figure S5. ^{1}H NMR of benzhydrol product

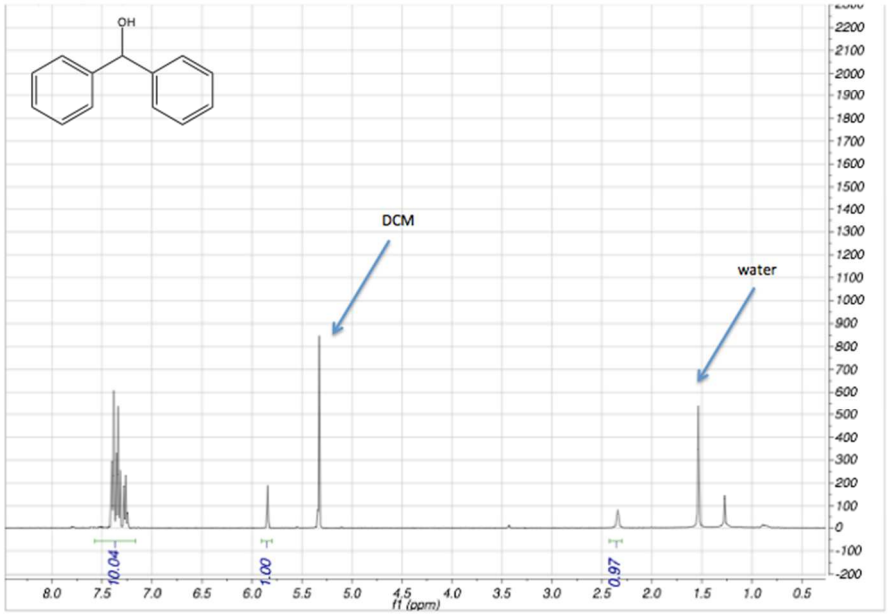
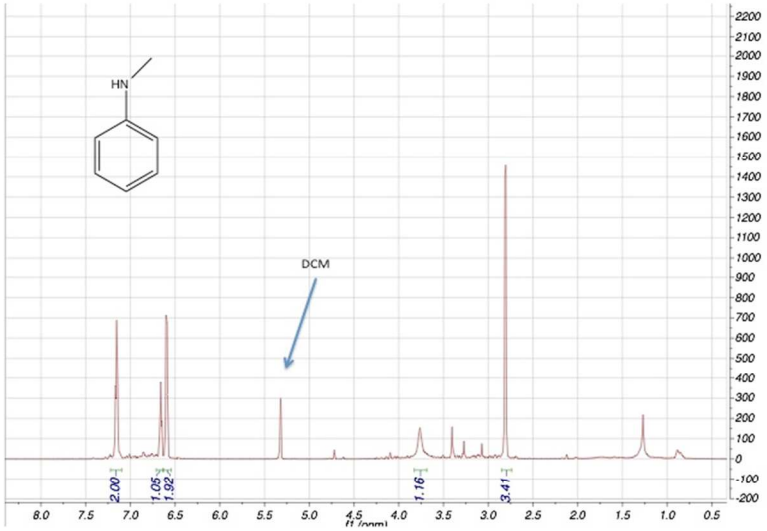


Figure S6. ^{1}H NMR of N-methylaniline product



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