Electronic Supplementary Information

Homogeneously-catalysed hydrogen release/storage using the 2-methyllindole/2-methylindoline LOHC system in molten salt-organic biphasic reaction systems

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Experimental procedures

Synthesis. All chemicals were obtained from commercial suppliers and used as received. Manipulations of moisture and oxygen sensitive compounds were done under inert argon gas atmosphere. The $[PPh_4][NTf_2]$ salt was synthesised by ion exchange of 10.17 g (35.41 mmol) $Li[NTf_2]$ (Iolitec) and 13.27 g (35.41 mmol) $[PPh_4]Cl$ (Sigma Aldrich) in water. The precipitated product was filtrated and washed thoroughly with water to remove chloride impurities (until the filtrate was tested negative with $AgNO_3$). Finally, the salt was dried in vacuum. Yield 20.88 g (95.2%). ^{1}H NMR (δ, 293 K, acetone-d_6): 7.78 ppm (16 H, m), 7.95 ppm (4 H, t); ^{13}C NMR (δ, 293 K, acetone-d_6): 117.81 ppm (1 C), 118.70 ppm (1 C), 130.50 ppm (8 C, d), 134.91 ppm (8 C, d), 135.54 ppm (4 C, d); Elemental Analysis: Calculated: C: 50.41%; H: 3.25%; N: 2.26%; S: 10.35%; Found: C: 50.67%; H: 3.00%; N: 2.23%; S: 10.26%; DART-MS (ESI$^+$): m/z = 279.06 for $[NTf_2]^+$, m/z = 339.09 for $[PPh_4]^+$; (ESI$^-$): m/z = 278.92 for $[NTf_2]^-$.

Characterisation and analysis. The purity and identity of synthesised compounds were determined by NMR, elemental analysis and DART-MS (Direct Analysis in Real Time Mass Spectrometry). ^{1}H and ^{13}C NMR spectra were recorded on a Jeol ECX-400 NMR spectrometer with chemical shifts reported in ppm relative to acetone-d_6 (^{1}H: 2.05 ppm; ^{13}C: 29.84 ppm, 206.26 ppm) or chloroform-d_1 (^{1}H: 7.26 ppm; ^{13}C: 77.16 ppm). The determination of the carbon, hydrogen, nitrogen and sulfur content was performed on a Carlo Erba EA 1106, 1107 and 1108 instrument. The DART-MS analysis was performed on a JMS-T100LP AccuTOF LC-plus 4G (Jeol) with a He plasma ionisation from ionSense, operating in both positive and negative-ion mode. The m/z values refer to the most abundant isotope. ICP analysis was performed by Nicola Taccari[a] on a Perkin Elmer Plasma 400. The water insoluble samples were treated with HNO3 in a microwave oven (180 °C).

The process of the dehydrogenation was monitored with gas chromatography (GC) using a Varian 3900 gas chromatograph equipped with a FID (Flame Ionization Detector) and a Factor Four^{TM} capillary VF-1ms 15 m x 0.25 mm x 0.25 µm column. The temperature of both the injector and FID detector was 280 °C. The initial heating ramp of the column was from 60 to 150 °C with a heating rate of 10 °C min^{-1}, where after the temperature was further raised to 280 °C with a heating rate of 20 °C min^{-1} followed by hold for 5 min. The GC was calibrated with respect to 2-methylindole and 2-methylindioline using reference samples.

Procedure for catalytic dehydrogenation. The following procedure corresponds to the optimised reaction conditions: The catalyst (0.05 mmol), 52.7 mg PPh_3 (0.20 mmol), 1.24 g $[PPh_4][NTf_2]$ (2.0 mmol) and 10 mL extracting solvent Bu_2O (73.75 mmol) were added to a 50 mL three-necked round bottom flask in air, where after the flask was flushed with argon while heating to 130 °C. Then, the catalyst was activated by purging the reaction mixture with H_2 while stirring for 15 min, which turned the solution colour from red to yellow within the first couple of minutes. The hydrogen atmosphere was then exchanged with argon leaving the system under 1 bar of argon with an oil blubber outlet. The reaction was started by addition of 1.33 g 2-methylindoline (10.0 mmol), where after the solution was heated for up to 24 h under vigorously stirring (1500 rpm). Reaction yields were determined by GC-FID analysis using toluene as dilution solvent. ICP analysis of the reaction solutions confirmed only negligible loss of iridium from the molten salt phase during reactions (under detection limit).

Procedure for pressure swing experiment. 250.0 mg Crabtree catalyst ($[Ir(cod)(py)(PCy_3)]PF_6$) (0.31 mmol), 334.4 mg PPh_3 (1.27 mmol), 15.51 g $[PPh_4][NTf_2]$ (25.0 mmol) and 25 mL Bu_2O (147.5 mmol) was mixed in a Teflon cup in a 300 mL Parr reactor, whereupon the autoclave was sealed and flushed three times with argon. The autoclave was then heated to 130 °C, and the atmosphere exchanged and pressurized to approx. 5 bar of H_2 during activation of the catalyst for 15 min. After activation, the pressure was released and the atmosphere changed back to 1 bar argon and the autoclave heated and kept at 140 °C. Then, 16.40 g (123.1 mmol) 2-methylindoline was added to the reactor through a passable port, the autoclave sealed and stirred (780 rpm). Liquid samples (0.1 mL) were periodically removed from the reactor during the dehydrogenation reaction with a syringe via the same passable port and the reactor flushed with argon before proceeding. After 24 h of reaction, the reactor was pressurised with 30 bar H_2 for hydrogenation whereupon samples were again taken periodically using a syringe through a passable port. For each sampling, the pressure was released and then re-pressurised with 30 bar H_2 for the hydrogenation to proceed. Samples were analysed by GC-FID using toluene as dilution solvent.

Preliminary studies

A series of screening experiments were initially carried out to encircle the optimal catalyst and reaction media for the catalytic dehydrogenation reaction of different indolines.

The considered reaction media covered both different molten salts and extraction solvents. The indole yields obtained from dehydrogenation of indoline in different reaction media are summarised in Table S1. Among the molten salts, $[PPh_4][NTf_2]$ performed better compared to the other molten salts for this reaction and was accordingly chosen for further experiments. Among the different extraction agents, use of diphenyl ether, Ph_2O, induced quantitative yield after 24 h and slightly lower yield was obtained with dibutyl ether, Bu_2O. However, due to cost and toxicity concerns Bu_2O was chosen as the extraction solvent for the continued experiments.

Table S1: Overview of reaction media for the catalytic dehydrogenation of indoline[a]

Entry	Chemical formula	m.p. (°C)	b.p. (°C)	Catalytic yield (%)
Molten salt[b]	$[PPh_4][NTf_2]$	134	-[d]	68
	$[PPh_4OPh][NTf_2]$	88	-	53
	$Cs[NTf_2]$	122	-	41
	$[PMeBu_3][NTf_2]$	-	-	40
Extraction solvent[c]	Bu_2O	− 98	142	83
	Ph_2O	25	259	100

[a] Reaction conditions: 0.30 g indoline (2.5 mmol), 4.83 mg $[Ir(cod)(py)(PCy_3)]PF_6$ (Crabtree's catalyst) (0.006 mmol), molten salt (0.8 mmol), extraction agent (30 mmol), 125 °C, 24 h, argon atmosphere. [b] With 5 mL Bu_2O (30 mmol). [c] With 0.050 g $[PPh_4][NTf_2]$ (0.8 mmol). [d] - = Not available.

Subsequently, the performance of different catalysts and substrates was investigated and the results are presented in Figure S1. For the dehydrogenation of indoline, three different catalysts were tested and the commercially available Crabtree's catalyst was found to be the best performing of the considered catalysts. Furthermore, comparing the substrates indoline and 2-methylindoline (using $[Ir(cod)(NHC)(PPh_3)][PF_6]$ (NHC = N,N-dimethyl-benzimidazol-2-ylidene) as the catalyst), 2-methylindoline was significantly more reactive. Hence, to obtain a system with an optimised performance the most reactive substrate where combined with the most active catalyst giving rise to the examined dehydrogenation system composed of 2-methylindoline with Crabtree's catalyst in a biphasic medium of $[PPh_4][NTf_2]$ and Bu_2O.

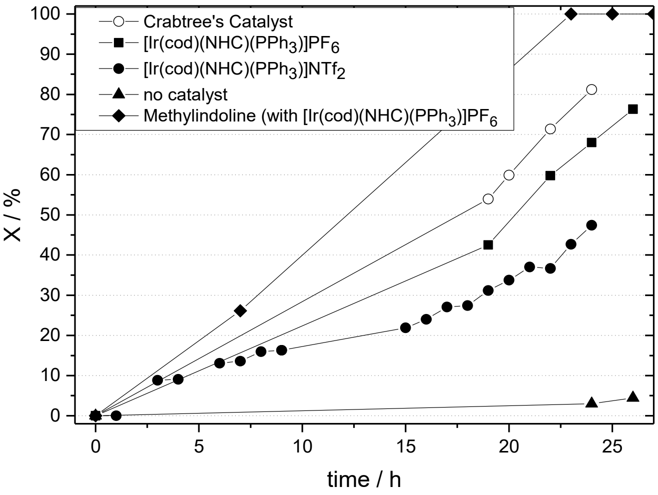

Figure S1: Comparison of three different catalyst in the dehydrogenation of indoline and 2-methylindoline. Reaction conditions: substrate (2.5 mmol), catalyst (0.006 mmol), $[PPh_4][NTf_2]$ (0.8 mmol), 5 mL Bu_2O (30 mmol), 125 °C in argon. X = Yield.

Kinetic studies

A kinetic study was performed for the optimised dehydrogenation system in the temperature interval between 120 and 140 °C. For 2-methylindoline conversions between 10 and 60% the reaction rate was considered to follow a pseudo-zero order rate law (i.e. rate = constant). Hence, the rate constant (*k*) was determined from linear regression of the conversion vs. time. The ln(***k***) was plotted against the inverse temperature in accordance to the Arrhenius rate equation ($\boldsymbol{k} = \exp(-\boldsymbol{E}_a/(R \cdot T))$) as presented in Figure S2. The study showed an excellent linear relation between ln(***k***) and T^{-1} and the system was found to exhibit good Arrhenius behaviour in the applied temperature range with an apparent activation energy of 127.3 kJ mol^{-1}.

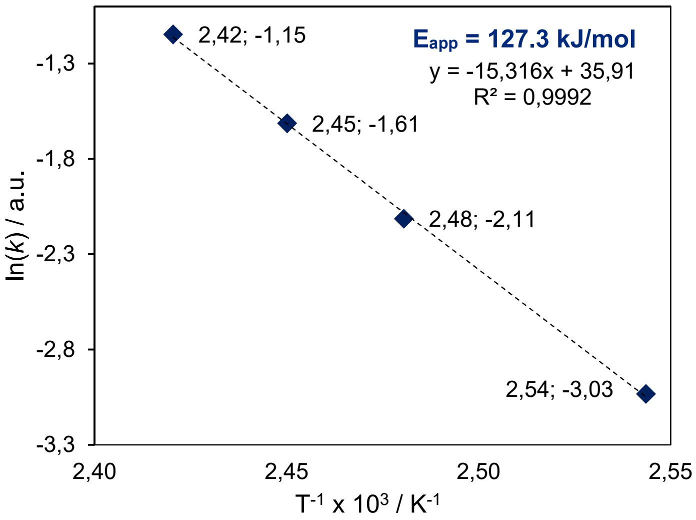

Figure S2: Arrhenius plot of the pseudo-zero order reaction rates for dehydrogenation 2-methylindoline using Crabtree's catalyst in the biphasic system of $[PPh_4][NTf_2]$ and Bu_2O at temperatures between 120 and 140 °C under 1 bar Ar. Each point is labelled with the data point values. Reaction conditions: 1.33 g 2-methylindoline (10.0 mmol), 40.2 mg $[Ir(cod)(py)(PCy_3)]PF_6$ (0.05 mmol), 52.5 mg PPh_3 (0.20 mmol), 1.24 g $[PPh_4][NTf_2]$ (2.0 mmol), 10 mL Bu_2O, 120-140 °C under 1 bar Ar.