Supporting Information for

Reversible Catalytic Dehydrogenation of Alcohols for Energy Storage

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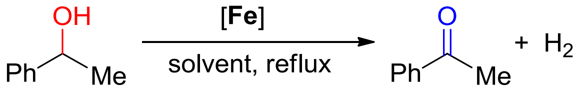
General Experimental Information. Unless otherwise noted, all the organometallic compounds were prepared and handled under a nitrogen atmosphere using standard Schlenk and glovebox techniques. Dry and oxygen-free solvents such as THF and pentane were collected from an Innovative Technology PS-MD-6 solvent purification system (1) and used throughout the experiments. Toluene was vacuum distilled from a purple solution of Na and benzophenone and stored over 4Å molecular sieves. It is necessary to degas toluene thoroughly by multiple freeze-pump-thaw cycles prior to use in the catalytic reactions. $CDCl_3$ was used without further purification. ^1H and ^{13}C NMR were recorded on a Bruker Avance-400 spectrometer. Chemical shift values in ^1H and ^{13}C NMR spectra were referenced internally to the residual solvent resonances. GC-MS spectra were recorded on a Shimadzu QP2010 instrument. All the products isolated from the dehydrogenation and hydrogenation reactions are known compounds (2-12).

Synthesis of Iron and Iridium Complexes. Complexes $(PNP^{Pri})Fe(H)(CO)BH_4$ (**1**) and $(PNP^{Pri})Fe(H)(CO)Br$ (**2**) have been prepared accordingly procedures previously reported in the literature (13-15). $[Ir(trop_2DACH)][OTf]$, **5**, was prepared following (16), and $[Ir(trop_2DAD)][OTf]$, **6**, was prepared following (17). Authentic samples of $[Ir(trop_2DACH\text{-}1H)]$ and $[Ir(trop_2DACH\text{-}2H)][K(18\text{-}C\text{-}6)]$ were prepared following (18). Oxidants were prepared following literature procedures: $[Fe(\eta^5\text{-}C_5H_4Me)_2]BF_4$, (19) (although the preparation followed was actually for $[Fe(\eta^5\text{-}C_5Me_5)_2]BF_4$); $[Fe(\eta^5\text{-}C_5H_4C(O)Me)Cp]BF_4$, (20) (see pg. 904); $[Fe(\eta^5\text{-}C_5H_4C(O)Me)_2]BF_4$ (21).

Catalytic Dehydrogenation of 1-Phenylethanol. In a glovebox, an iron complex (25 µmol), KO^tBu (if required), and 1-phenylethanol (833 µmol or 2.5 mmol) were mixed with 5 mL of solvent in a 50 mL flame-dried Schlenk flask. A condenser was attached to the flask and the whole set up was brought outside the glovebox. The Schlenk flask containing the homogeneous mixture was then stirred under reflux for 24 hours. During the reflux, the solution was continuously bubbled with N_2 (~1 atm) and the liberated H_2 gas was allowed to escape through an outlet port (a needle). After the reaction, the solution was allowed to cool to room temperature, filtered through a short silica gel column, and eluted with THF (10-15 mL). The resulting filtrate was evaporated under vacuum to afford an oily material. ^1H NMR spectrum was recorded in $CDCl_3$ for this material and the percentage conversion for each reaction was calculated from the ^1H NMR integrations. The results are summarized in Table S-1. A control experiment without any catalyst did not yield any product (entry 6).

Table S-1. Iron-Catalyzed Dehydrogenation of 1-Phenylethanol



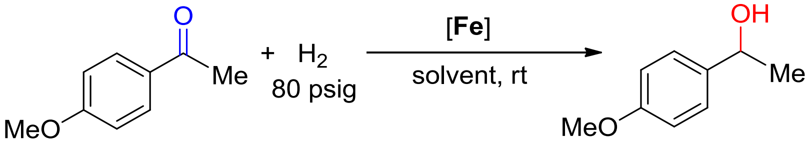
entry	catalyst (loading)	solvent	additive	time (h)	NMR conv. (%)
1	**1** (3 mol%)	THF	-	24	87
2	**1** (3 mol%)	toluene	-	24	100
3	**1** (1 mol%)	toluene	-	24	100
4[a]	**2** (3 mol%)	THF	KO^tBu	24	79
5	**2** (3 mol%)	THF	-	24	<5
6	-	toluene	-	24	0

[a] 10 mol% of KO^tBu was used with respect to catalyst **2**

General Procedure for the Iron-Catalyzed Dehydrogenation of Alcohols (Table 1). In a glovebox, a 50 mL flame-dried Schlenk flask was charged with catalyst **1** (10 mg, 25 µmol), an alcohol substrate (2.5 mmol or 25 mmol), and 5 mL of toluene. After attaching a condenser to the Schlenk flask, the solution was stirred at 120 °C for a specific time under a constant N_2 flow. A needle was placed through the septum on top of the condenser to remove the liberated H_2 gas. After the reaction, the solution was allowed to cool to room temperature, filtered through a short silica gel column, and eluted with THF. The resulting filtrate was evaporated under vacuum to afford the pure product. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of the products were recorded in $CDCl_3$ and matched with the chemical shifts reported in the literature. Percentage yields were also calculated for these isolated products.

General Procedure for the Iron-Catalyzed Hydrogenation of 4'-Methoxyacetophenone. In a glovebox, a 25 mL stainless steel Parr pressure reactor was loaded with an iron complex (25 µmol), KO^{t}Bu (if required), 4'-methoxyacetophenone (375 mg, 2.5 mmol), and 5 mL of toluene (or THF). The reactor was sealed, flushed with H_2 three times, and finally placed under 80 psig of H_2 pressure. The solution was then stirred at room temperature for 8 hours. After the reaction, the solution was filtered through a short silica gel column and eluted with THF. The resulting filtrate was evaporated to dryness to afford the pure hydrogenation product. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of the product were recorded in $CDCl_3$ and matched with the reported spectra in the literature. The results are summarized in Table S-2. For all of the reactions, quantitative conversions were achieved.

Table S-2. Iron-Catalyzed Hydrogenation of 4'-Methoxyacetophenone



entry	catalyst (loading)	solvent	additive	time (h)	NMR conv. (%)
1	**1** (1 mol%)	toluene	-	8	100
2^{a}	**2** (1 mol%)	THF	KO^{t}Bu	8	100
3	**3** (1 mol%)	toluene	-	8	100

^{a} 10 mol% of KO^{t}Bu was used with respect to catalyst **2**

Catalytic Dehydrogenation of 1-Phenylethanol with Complex 4. In a glovebox, a flame-dried 50 mL Schlenk flask was charged with catalyst **4** (9.7 mg, 25 µmol), 1-phenylethanol (302 µL, 2.5 mmol), and toluene (5 mL). The solution inside the flask was then stirred at 120 °C for 24 hours under a constant N_2 flow. H_2 was allowed to escape through an outlet port. After the reaction, the solution was allowed to reach room temperature, filtered through a short silica gel column, and eluted with THF. The resulting filtrate was evaporated under vacuum to afford an oily material. ^{1}H NMR spectrum recorded for this residue in $CDCl_3$ showed quantitative formation of acetophenone.

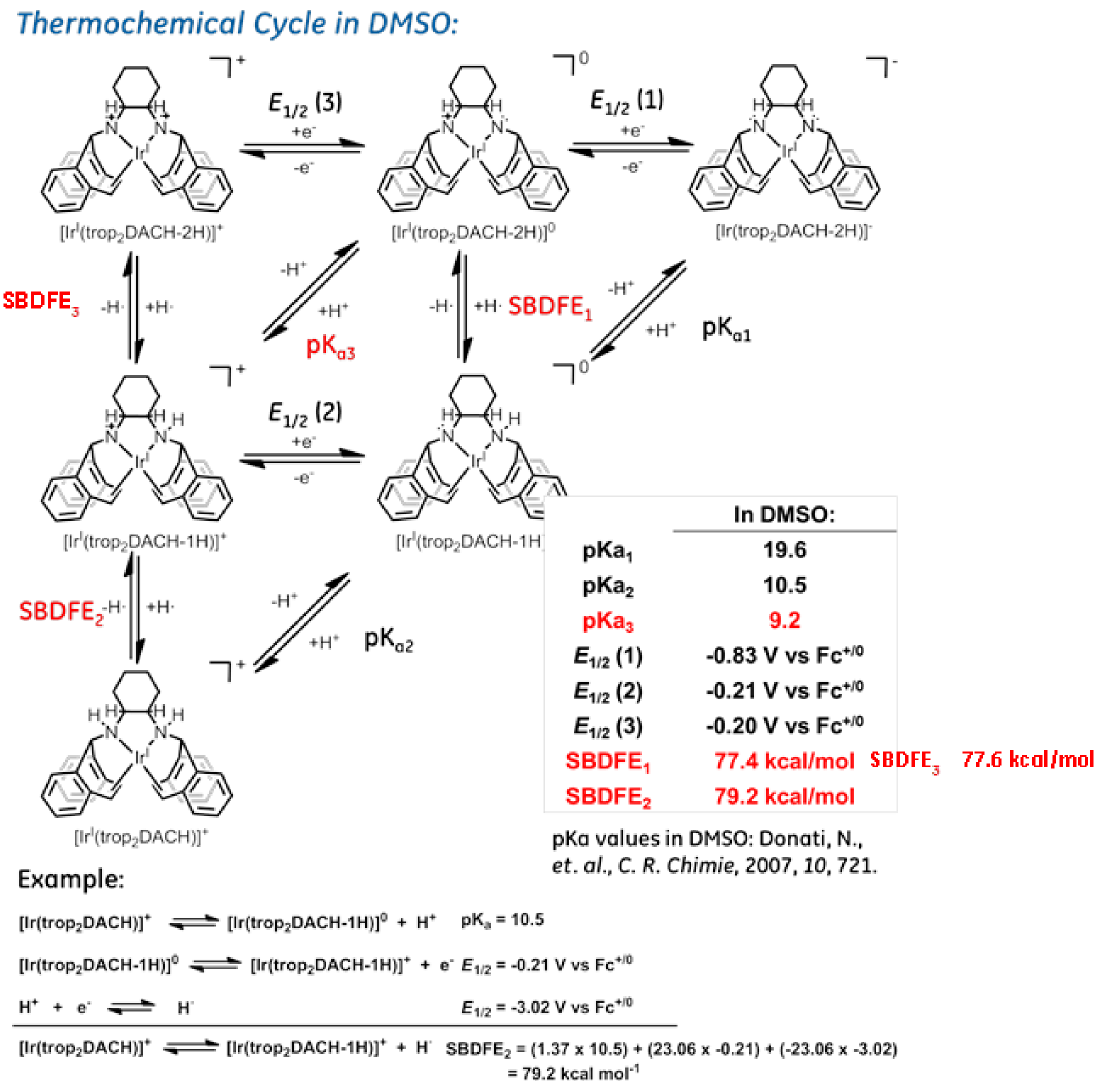
Catalytic Dehydrogenation of Benzyl Alcohol with Complex 1. In a glovebox, a flame-dried 50 mL Schlenk flask was charged with catalyst **2** (10 mg, 25 µmol), benzyl alcohol (259 µL, 2.5 mmol), and toluene (5 mL). The solution inside the flask was then stirred at 120 °C for 8 hours under a constant N_2 flow. H_2 was allowed to escape through an outlet port. After the reaction, the solution was allowed to reach room temperature, filtered through a short silica gel column, and eluted with THF. The resulting filtrate was evaporated under vacuum to afford an oily material. ^{1}H NMR spectrum recorded for this residue in $CDCl_3$ showed quantitative formation of benzyl benzoate. No trace of benzaldehyde was found in the ^{1}H NMR spectrum.

Oxidative Dehydrogenation of 4-Methoxybenzyl Alcohol with Complexes 5 and 6. Dehydrogenations with **5** used 0.03 mol% and **6** used 0.1 mol% catalyst, however both used 1.5 mmol alcohol, 3 mmol oxidant, and 3 mmol sodium phenolate as base at room temp in *o*-DCB (reaction volume ~5 mL). ^{1}H NMR yields were determined against hexamethylbenzene as an internal standard based on peak integration of either methoxy or aromatic protons. $E_{½}$ values are reported relative to $Fc^{+/0}$ and were measured in *o*-DCB/0.08M *n*-Bu_4NPF_6 as electrolyte at 0.1 V/s with Pt working and counter electrodes, and Ag-wire/10mM $AgNO_3$ solution as reference electrode in CH_3CN/0.1M *n*-Bu_4NPF_6 electrolyte.

Reductive Hydrogenation of *p*-anisaldehyde with Complexes 5 and 6. All hydrogenations used 1 mol% catalyst, 1.25 mmol aldehyde, 3.13 mmol reductant, and 6.26 mmol phenol as acid at room temp in *o*-DCB (reaction volume ~10 mL). ^{1}H NMR yields were determined against hexamethylbenzene as an internal standard based on peak integration of either methoxy or aromatic protons. $E_{½}$ values were measured in *o*-DCB/0.08M *n*-Bu_4NPF_6 as electrolyte at 0.1 V/s with Pt working and counter electrodes, and Ag-wire/10mM $AgNO_3$ solution as reference electrode in CH_3CN/0.1M *n*-Bu_4NPF_6 electrolyte.

Thermochemical cycle

$E_{½}^1$, $E_{½}^2$, and $E_{½}^3$ values were determined in DMSO from authentic samples of [Ir(trop$_2$DACH-1H)] and [Ir(trop$_2$DACH-2H)][K(18-C-6)], prepared following (18). Values of pK_{a1} and pK_{a2} for **5** were reported in the same reference. From this data, we followed (22) to derive bond dissociation energies and pK_a values to complete a thermochemical cycle (below).



	In DMSO:
pKa$_1$	19.6
pKa$_2$	10.5
pKa$_3$	9.2
$E_{1/2}$ (1)	-0.83 V vs Fc$^{+/0}$
$E_{1/2}$ (2)	-0.21 V vs Fc$^{+/0}$
$E_{1/2}$ (3)	-0.20 V vs Fc$^{+/0}$
SBDFE$_1$	77.4 kcal/mol
SBDFE$_2$	79.2 kcal/mol

SBDFE$_3$ 77.6 kcal/mol

pKa values in DMSO: Donati, N., *et. al.*, *C. R. Chimie*, 2007, *10*, 721.

Example:

$[Ir(trop_2DACH)]^+ \rightleftharpoons [Ir(trop_2DACH\text{-}1H)]^0 + H^+$ pK_a = 10.5

$[Ir(trop_2DACH\text{-}1H)]^0 \rightleftharpoons [Ir(trop_2DACH\text{-}1H)]^+ + e^-$ $E_{1/2}$ = -0.21 V vs Fc$^{+/0}$

$H^+ + e^- \rightleftharpoons H^\cdot$ $E_{1/2}$ = -3.02 V vs Fc$^{+/0}$

$[Ir(trop_2DACH)]^+ \rightleftharpoons [Ir(trop_2DACH\text{-}1H)]^+ + H^\cdot$ SBDFE$_2$ = (1.37 x 10.5) + (23.06 x -0.21) + (-23.06 x -3.02)
= 79.2 kcal mol^{-1}

Figure S1. Thermochemical cycle based on $[Ir(trop_2DACH)]^+$ in DMSO solvent.

CV data of 6 in the presence of sodium phenolate

CVs were measured in *o*-DCB/0.08M *n*-Bu_4NPF_6 as electrolyte at 0.1 V/s with Pt working and counter electrodes, and Ag-wire/10mM $AgNO_3$ solution as reference electrode in CH_3CN/0.1M *n*-Bu_4NPF_6 electrolyte. The 2 (quasi)reversible waves observed for 1mM **6** at -1.35 and -0.63 V are two consecutive one electron reductions of the bis-imine ligand (blue voltammogram). Two additional (quasi)reversible waves were observed for 1mM **6** in the presence of excess phenolate (4mM NaOPh) at -0.33 and -0.06 V *vs* Fc$^{+/0}$ (red voltammogram). An electrochemistry scheme for the associated redox processes may be found below.

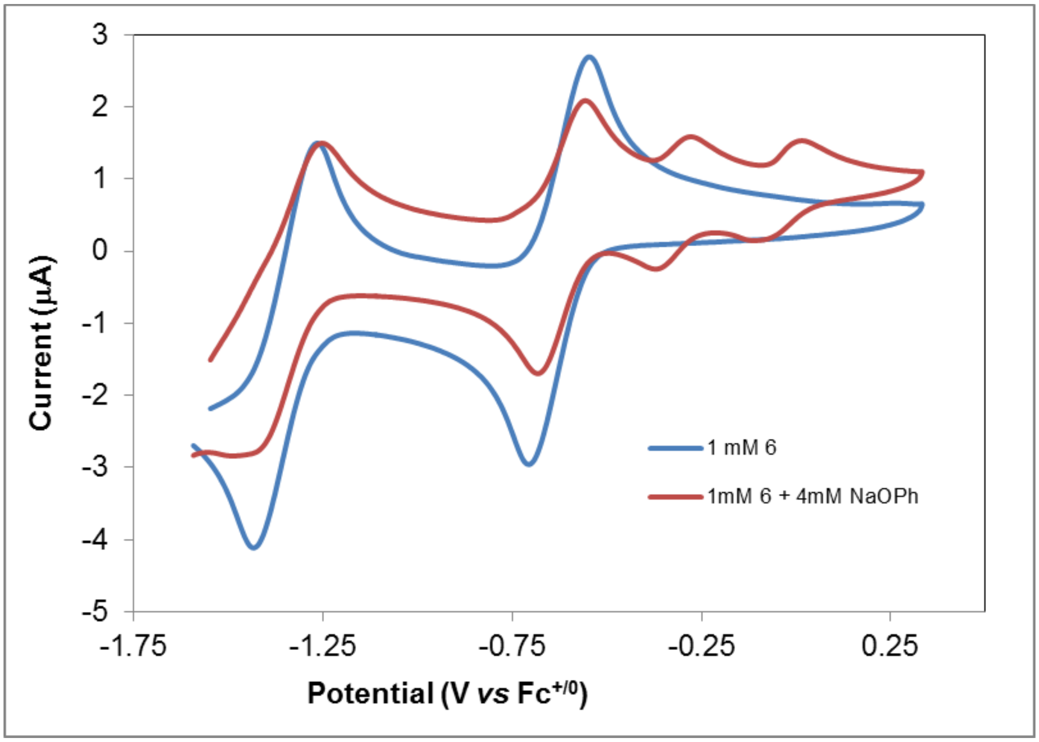


Figure S2. Cyclic voltammogram of complex **6** in *o*-DCB (blue) and in the presence of sodium phenolate (red).

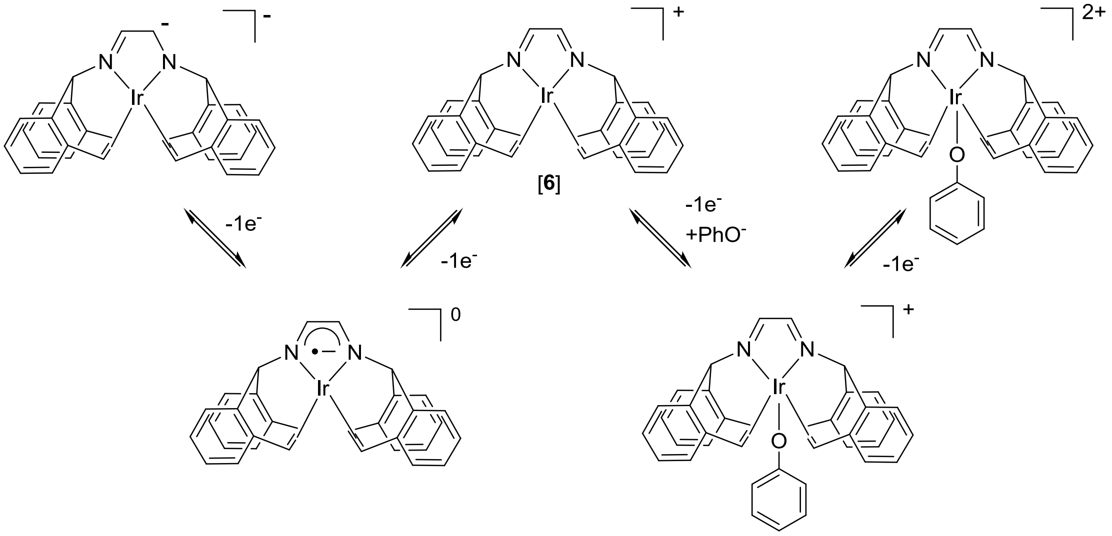


Figure S3. Scheme of electrochemical reactions of complex **6.**

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and decamethylferrocenium pentacyanopropenide, $[Fe(C_5Me_5)_2]^{+\cdot}$ $[C_3(CN)_5]^-$ *Journal of the American Chemical Society* 109(3):769-781.

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