Cobaltocene-mediated catalytic hydride transfer: strategies for electrocatalytic hydrogenation

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Abstract
The selective electrocatalytic hydrogenation of organics with transition metal hydrides is a promising strategy for electrosynthesis and energy storage. We report the electrocatalytic hydrogenation of acetone with a cyclopentadienone-iridium complex in a tandem electrocatalytic cycle with a cobaltocene mediator. The reductive protonation of cobaltocenium with mild acids generates $(C_5H_5)Co^{I}(C_5H_6)$ ($CpCo^{I}(CpH)$), which functions as an electrocatalytic hydride mediator to deliver a hydride to cationic Ir(III) without generating hydrogen. Electrocatalytic hydride transfer by $CpCo^{I}(CpH)$ to a cationic Ir species leads to the efficient (Faradaic efficiency > 90 %) electrohydrogenation of acetone, a valuable hydrogenation target as a liquid organic hydrogen carrier (LOHC). Hydride–transfer mediation presents a powerful strategy to generate metal hydrides that are inaccessible by stepwise electron/proton transfer.

Introduction

Energy conversion strategies are critical to our future. Directing electrical energy into specific chemical bonds for energy storage is a complex challenge.[1-2] Nature offers some lessons. Biological energy conversion strategies rely critically on enzymatic redox cascades, wherein ubiquitous nicotinamide (NAD(P)H) and flavin ($FADH_2$) enzyme cofactors facilitate coupled proton and electron reductions by transporting hydride equivalents ($2e^-$, $1H^+$) in protic environments to effect hydrogenation of substrates.[3] Abiotic analogs to these reductive cofactors are rare,[4] but could provide new opportunities for the electrocatalytic generation of metal hydrides, which are key intermediates for selective reduction reactions (Figure 1).

Selective catalytic electrohydrogenation of unsaturated substrates,[5] obviating the use of molecular hydrogen, presents a formidable challenge, as direct proton reduction to H_2 is competitive with electroreduction.[6-7] The electroreduction of carbonyls such as CO_2,[8-9] ketones, or aldehydes is of interest both for fine chemical synthesis and for energy storage applications utilizing liquid organic hydrogen carriers (LOHC).[6-7,10-13] Both applications benefit from high selectivity for electroreduction relative to the hydrogen evolution reaction (HER), which is typically reported as the Faradaic efficiency (FE): the percentage of charge passed during electrolysis that is incorporated into the reduced substrate. Electrohydrogenation of carbonyls is particularly challenging; while some strategies with heterogenous catalysts have been reported,[6,14-15] only a few molecular systems exist that operate with high FE.[7,16-19] To investigate selective electrohydrogenation reactions, we targeted the electrocatalytic reduction of acetone to isopropanol as a prototype electrochemical energy storage reaction.[11] The thermodynamic window of opportunity to selectively hydrogenate acetone is exceedingly narrow as the reversible electrochemical potential for the reduction of acetone to isopropanol ($E° = 0.08$ V vs $Fc^{0/+}$ in MeCN) is extremely close to that of hydrogen evolution (-0.028 V).[20] Furthermore, hydrogenation catalysts often proceed through metal hydride intermediates, many of which liberate H_2 under the protic conditions necessary for electrocatalytic hydrogenation.[6-7,21] If HER and ketone reduction are both fast, it is almost impossible to selectively electrohydrogenate ketones at any reasonable operating overpotential.[20,22]

Herein, we report two advances to enable highly selective electrohydrogenation: the development and electrochemical characterization of a modestly hydridic and acid-stable metal hydride[23] that can reduce ketones by a bifunctional mechanism,[24] and an electrochemical mediator[4,9,25-26] that selectively generates that metal hydride under electroreductive conditions in a tandem electrocatalytic cycle (Figure 1). We show that cobaltocene, long utilized as a simple reducing agent,[27] can function as an efficient electrocatalytic hydride donor with reactivity analogous to nature's NAD(P)H and $FADH_2$ cofactors.

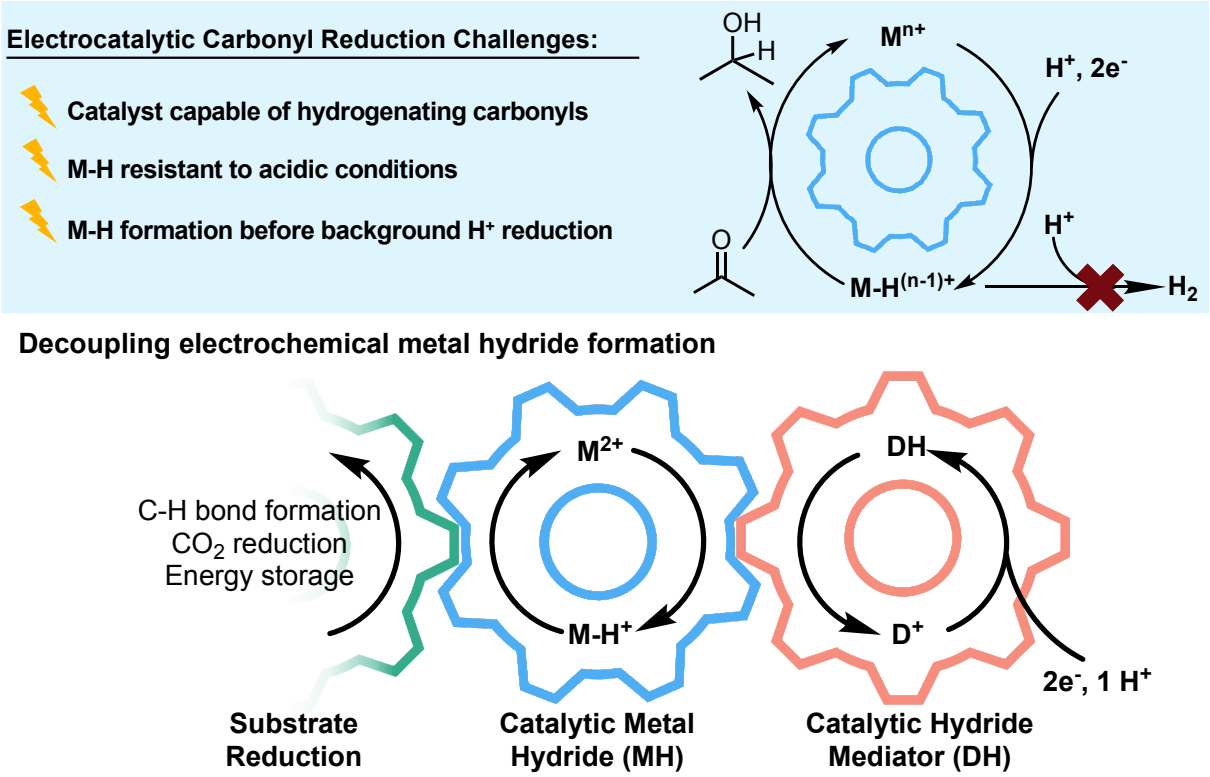


Figure 1. Challenges associated with electrocatalytic carbonyl reduction, or electrohydrogenation: Design of catalytic systems with the appropriate reactivity is a complex challenge, made more difficult by the need to ensure the putative catalyst is capable of interfacing with an electrode for turnover. Electrocatalytic mediators address the latter challenge by decoupling the electrode interface step from catalyst design, allowing drop-in additives for regenerating active catalyst species.

Results and Discussion

To develop metal hydrides for the selective electrocatalytic reduction of acetone, we targeted a modestly hydridic metal hydride that would be resistant to protonation and HER under the protic conditions necessary for electroreduction. The cationic Ir(III) hydride $[(C_5Tol_2Ph_2OH)(dmbpy)IrH]^+$ **$[Ir^{III}\text{-}H]^+$** is a promising candidate as it is tolerant to strong acids but reacts stoichiometrically with acetone to generate isopropanol.[23] Since the ability of metal hydrides to protonate and release hydrogen is related to the thermodynamic hydricity (ΔG_H-) of the metal hydride and the pK_a of the acid employed,[28] we measured the thermodynamic hydricity of **$[Ir^{III}\text{-}H]^+$** in acetonitrile. Treatment of the synthetically accessible $(C_5Tol_2Ph_2O)(dmbpy)IrH$ **$Ir^{I}\text{-}H$** with 2.5 equivalents of *4*-cyanoanilinium trifluoromethanesulfonate in MeCN-d_3 ($[^{4\text{-}CN}PhNH_3][OTf]$, pK_a 7 in MeCN[29]) generates the cationic hydride **$[Ir^{III}\text{-}H]^+$** (Figure 2A).[23]

Subsequent protonation of **[Ir^{III}-H]$^+$** establishes an equilibrium with H_2 and a dicationic Ir(III) species formulated as **[Ir^{III}-OTf][OTf]**. Protonation of **[Ir^{III}-H]$^+$** under these conditions was slow, reaching equilibrium with H_2 over several days, indicating that this metal hydride should be slow to release hydrogen with acids weaker than [$^{4\text{-CN}}$PhNH$_3$][OTf]. The equilibrium constant for this second protonation under one atmosphere of H_2 was measured by ^{1}H NMR, providing an experimental measure of the thermodynamic hydricity of **[Ir^{III}-H]$^+$** of ΔG_{H^-} = 64 kcal/mol in MeCN.[30-31] This value indicates that the hydricity of **[Ir^{III}-H]$^+$** is slightly higher (less hydridic) than the analogous [Cp*Ir(dmbpy)H]$^+$ (ΔG_{H^-} = 61.5 kcal/mol).[32] The modest hydricity of **[Ir^{III}-H]$^+$** indicates that it should be thermodynamically incompetent to directly deliver a hydride to acetone (ΔG_{H^-} (iPrO-)~ 20 kcal/mol in MeCN).[20,33-34] The observation that **[Ir^{III}-H]$^+$** can reduce acetone highlights the importance of the bifunctional[24] activation of acetone[23] by the OH group of the hydroxycyclopentadienyl ligand to facilitate hydride delivery, even with a modestly hydridic Ir-H.

With the appropriate hydride reactivity established, we performed several stoichiometric reactions to evaluate the competence of the Ir cyclopentadienone complexes to function as electroreduction catalysts. We sought to mimic electrochemical conditions by generating **[Ir^{III}-H]$^+$** via sequential protonation and reduction of the ($C_5Tol_2Ph_2O$)(dmbpy)IrCl **Ir^{I}-Cl** complex. Treatment of **Ir^{I}-Cl** with five equiv. of [$^{4\text{-CN}}$PhNH$_3$][OTf] results in protonation at the cyclopentadienone ligand to generate [($C_5Tol_2Ph_2OH$)(dmbpy)IrCl]$^+$ **[Ir^{III}-Cl]$^+$**. Further treatment of this solution of **[Ir^{III}-Cl]$^+$** and [$^{4\text{-CN}}$PhNH$_3$][OTf] with two equiv. of cobaltocene **Cp$_2$Co^{II}** in acetonitrile generated **[Ir^{III}-H]$^+$** (Figure 2A, S21). Under these conditions, the formation of **[Ir^{III}-H]$^+$** was accompanied by vigorous bubbling, which we attribute to hydrogen evolution from reductive protonation of **Cp$_2$Co^{II}** by [$^{4\text{-CN}}$PhNH$_3$][OTf].[26,35] As we had previously shown that **[Ir^{III}-H]$^+$** reacts with acetone to generate isopropanol,[23] these stoichiometric experiments suggested that the iridium cyclopentadienone complexes exhibit the appropriate reactivity for the electrocatalytic reduction of acetone.

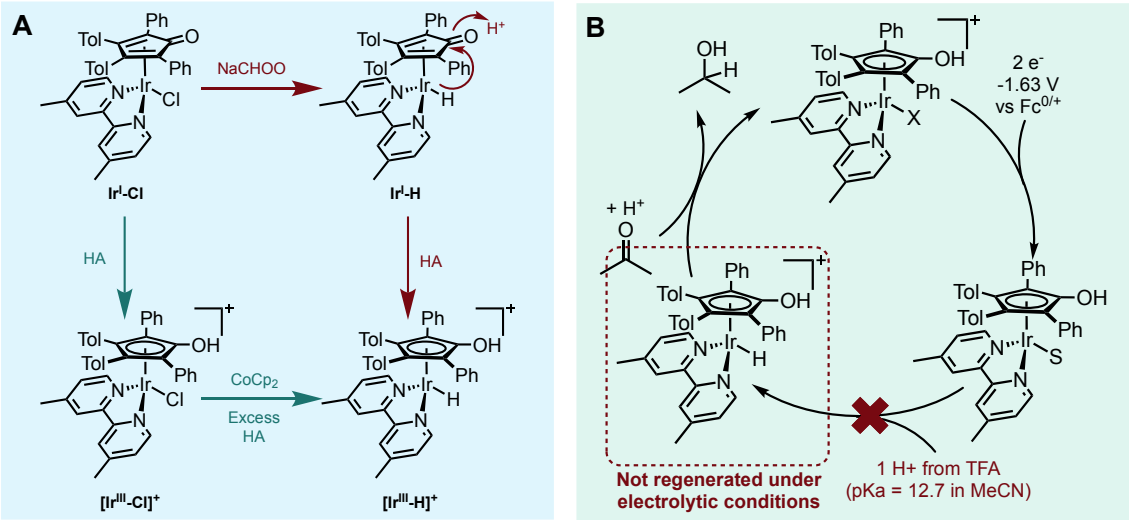


Figure 2.A. Stoichiometric experiments to generate catalytically relevant [($C_5Tol_2Ph_2O$)(dmbpy)IrX] (X = H$^-$ or Cl$^-$) species **B.** Attempted direct electrocatalytic reduction of acetone with hydroxycyclopentadienyl Ir catalysts by controlled potential electrolysis at the Ir(III) reduction potentials was unsuccessful in the absence of cobaltocenium.

Table 1. Summary of key results in the controlled potential electrolysis (CPE) of 1.2 mM Ir^{I}-H conducted on a glassy carbon rod electrode in the presence of various acids and concentrations of $[Cp_2Co]PF_6$, operated at -1.32 V vs $Fc^{0/+}$ in acetone.

	Ir:Co Ratio	Acid Identity	[Acid] (mM)	Charge (C)	µmol iPrOH	TON_{Ir}	TON_{Co}	FE (%)
1	1:1	TFA	16	-11.9	42.9	4.8	3.8	55
2	1:1	SA	60	-15.3	83.6	9.7	8.3	95
3	1.:0.1	SA	60	-5.99	34.9	4.1	37.8	85
4	1:1	SA	120	-17.0	87.2	9.7	8.7	89
5[a]	No Co	TFA	16	-6.34	10.7	1.2	N/A	5.6
6[a]	No Co	SA	60	-3.18	11.3	1.2	N/A	14.5
7[b]	No Ir	SA	60	-1.13	N/A	N/A	0	0

[a]operated at -1.61 V vs $Fc^{0/+}$. [b]No isopropanol detected by ^{1}H NMR.

Although these stoichiometric results were promising, attempts to demonstrate the electrocatalytic reduction of acetone with the iridium cyclopentadienone complexes in the absence of cobaltocene were unsuccessful. Several lines of evidence implicate a special role of cobaltocene beyond its ability to function as a single electron reductant. The reduction potentials of the Ir^{III} hydroxycyclopentadienyl complexes $\mathbf{[Ir^{III}\text{-}Cl]^+}$ and $\mathbf{[Ir^{III}\text{-}X]^+}$ (X = trifluoroacetate) were measured by generating these complexes in-situ with 16 mM trifluoroacetic acid (TFA). For these experiments, the weaker acid TFA (pK_a 12.7 in MeCN)[35-36] was employed, as attempts to measure the redox potentials of $\mathbf{[Ir^{III}\text{-}Cl]^+}$ and $\mathbf{[Ir^{III}\text{-}X]^+}$ (X = trifluoroacetate) with $[^{4\text{-}CN}PhNH_3][OTf]$ were obscured by background reduction of the acid (see Figure S38).[29] The reduction potentials observed for these Ir(III) species are both negative of -1.6 V vs $Fc^{0/+}$ (Figures S34-36), at least 300 mV more negative than that of the $Cp_2Co^{II/III}$ couple (-1.33 V vs. $Fc^{0/+}$), indicating that reduction by cobaltocene should be endergonic by approximately 7 kcal/mol.

Furthermore, controlled potential electrolysis (CPE) of 1.2 mM $\mathbf{Ir^{I}\text{-}H}$ precatalyst at -1.61 V vs. $Fc^{0/+}$ with 16 mM TFA in acetone over four hours did not catalytically generate isopropanol in the absence of cobaltocenium (Figure 2B). Under these conditions, only a stoichiometric amount of isopropanol (1 equiv. per Ir) could be detected, which we attribute to the protonation of the $\mathbf{Ir^{I}\text{-}H}$ precatalyst to the cationic $\mathbf{[Ir^{III}\text{-}H]^+}$ (Figure 2A), which then reacts with acetone to generate one equivalent of isopropanol.

These results indicated that cobaltocene is necessary for the formation of the catalytically relevant $\mathbf{[Ir^{III}\text{-}H]^+}$. When CPE was repeated in the presence of both cobaltocenium hexafluorophosphate $\mathbf{[Cp_2Co^{III}]^+}$ and $\mathbf{Ir^{I}\text{-}H}$ at 1.2 mM with TFA as the proton source, productive electrocatalytic hydrogenation of acetone was observed (Table 1, entry 1). CPE operated at the reduction potential of $\mathbf{[Cp_2Co^{III}]^+}$ (-1.32 V) in acetone with 1:1 $\mathbf{Ir^{I}\text{-}H}$ precatalyst, $\mathbf{[Cp_2Co^{III}]^+}$ (1.2 mM each) and 16 mM TFA over 4 h generated 43 µmols of isopropanol at 55 % FE, corresponding to a turnover number with respect to iridium (TON_{Ir}) of 4.8 and TON_{Co} of 3.8. We attribute the remaining FE to HER as the electrolysis was accompanied by modest gas evolution at the cathode, which likely stems from the reductive protonation of $\mathbf{Cp_2Co^{II}}$ with TFA (pK_a 12.7 in MeCN).[35-36]

The electrocatalytic yield and efficiency improved considerably when the weaker salicylic acid (SA, pK_a = 16.7 in MeCN[29]) was used in place of TFA. A CPE operated under the same conditions above but with 60 mM SA in place of TFA showed no evidence of HER, generating

Table 2. Summary of results for CPE of 1.2 mM Ir^{I}-H conducted on carbon cloth working electrodes in the presence of various concentrations of $[Cp_2Co]PF_6$, operated at -1.32 V vs $Fc^{0/+}$ in acetone.

	Ir:Co Ratio	[SA] (mM)	Charge (C)	µmol iPrOH	TON_{Ir}	TON_{Co}	FE (%)
1	1:1	60	-19.9	107	12.9	11.9	96
2	1.:0.333	60	-19.16	101	12.1	35	92
3	1:0.1	60	-18.09	96.3	11.4	114	93
4	1:0.1	120	-33.2	146	17.4	173	80
5	1:0.1	600	-55.5	139	17.0	165	46

isopropanol (TON_{Ir} = 9.7) with 95% FE. Under these conditions, doubling the concentration of SA slightly degrades selectivity (Table 1, entry 4). The cobalt loading could be decreased to $1/10^{th}$ the iridium concentration which yields a lower TON_{Ir} of 4.1, but the associated TON_{Co} of 38 compares very well to other reductive electrocatalytic mediators (Table 1, entry 3).[9,26] Control experiments confirm that electrocatalytic hydrogenation requires both iridium and cobalt for productive catalysis (Table 1, entries 5-7). A CPE experiment with a methoxycyclopentadienyl Ir(III) complex yielded a substoichiometric quantity of isopropanol (0.79 equiv. relative to Ir, Figure S66), indicating the importance of the bifunctional hydroxycyclopentadienyl ligand in electrohydrogenations with the modestly hydridic Ir(III) hydride.

The electrocatalytic hydrogenation of acetone with the Ir/Co catalyst system was also carried out with a high surface area carbon cloth electrode (Table 2). Under these conditions, the turnover numbers increased but still yielded high Faradaic efficiencies for isopropanol. A lower Co loading (1:0.1 iridium : cobalt) led to only a modest decrease in the yield of isopropanol with a TON_{Ir} of 11, but a higher TON_{Co} of 114 while maintaining 93 % FE. Increasing the SA concentration to 120 mM at 1:0.1 iridium : cobalt loading produces a TON_{Ir} of 17 and TON_{Co} of 173 at 80 % FE. No pinacol products, a common result of one electron / one proton reduction of ketones, were detected in any of these CPE studies.

Cobaltocenium as an electrocatalytic PCET mediator

As the mismatch in reduction potentials for $\mathbf{Cp_2Co^{II}}$ and the Ir(III) complexes indicates that cobaltocene is unlikely to function as an electron transfer (ET) mediator,[27,37] we sought to test whether the reductive protonation of cobaltocenium might generate an intermediate that can function as a PCET mediator,[4,38] effecting either a net hydrogen atom transfer (HAT, $1e^-$, $1H^+$) or a net hydride transfer ($2e^-$, $1H^+$).[39] Electrocatalytic PCET mediators have been shown to facilitate both oxidative[38,40-41] and reductive[9,25-26,42-44] electrocatalytic reactions by providing alternate pathways to high-energy electron transfer/proton transfer (ET/PT) steps. Peters *et al.*[42-43] showed that cobaltocene and its permethylated analog Cp^*_2Co can facilitate electrocatalytic nitrogen reduction via proton-coupled electron transfer (PCET) with strong acids such as $[^{4\text{-CN}}PhNH_3][OTf]$ at -35 °C. For these studies the authors invoked HAT from $[Cp^*Co(Cp^*H)]^+$ as the primary mechanism but suggested that Cp*Co(Cp*H) might also mediate hydride transfer.[43] Nevertheless, the challenges of utilizing cobaltocenes[26] as reductive mediators have long been appreciated, due to its tendency to generate hydrogen with strong acids[26,35-36] through the intermediacy of $\mathbf{[CpCo^{II}(CpH)]^+}$, and/or $\mathbf{CpCo^{I}(CpH)}$.[26,35-36] We sought to test whether, with appropriately weak acids, the reductive protonation of cobaltocene would generate $\mathbf{CpCo^{I}(CpH)}$ which could serve as a net-hydride donor to generate the key $\mathbf{[Ir^{III}\text{-}H]^+}$ intermediate without generating hydrogen.

To interrogate the role of cobaltocene in electrocatalytic acetone reduction, we investigated the cyclic voltammetry (CV) of cobaltocenium with acids of varying strength. When a 1.2 mM solution of **$[Cp_2Co^{III}]^+$** in acetone was titrated up to 2.5 mM [*N,N*-dimethyl-4-cyanoanilinium][trifluoromethanesulfonate] ($[^{4\text{-CN}}PhNMe_2H][OTf]$), the $Co^{III/II}$ redox feature became less reversible with increasing acid concentration and a new feature with an $E_{1/2}$ of approximately -0.42 V vs $Fc^{0/+}$ appeared anodic of the $Co^{III/II}$ couple (Figure 3C, blue trace). Notably, this oxidative feature disappeared upon addition of 1.2 mM **$[Ir^{III}$-OTf][OTf]**, implicating a reaction between this species and the hydroxycyclopentadienyl iridium complex. A CV of independently synthesized **$CpCo^{I}$(CpH)**[45] shows a matching oxidative feature observed in acetone (Figure 3C, black trace). As this feature is irreversible at scan rates up to 1 V/s, its $E_{1/2}$ was estimated to be -0.42 V by the inflection point.[46]

For weaker acids such as TFA (Figure 3C, teal trace) or SA (Figure S42), the appearance of the oxidative feature at -0.42 V vs. $Fc^{0/+}$ was less pronounced, but could be enhanced by scanning beyond -2.4 V, the reduction potential of the $Co^{II/I}$ couple in acetone (Figures S43-45). The latter behavior is consistent with the reductive protonation of cobaltocenium to **$CpCo^{I}$(CpH)** by an ET-ET-PT mechanism, as described by Geiger *et al.*[36] To confirm the formation of **$CpCo^{I}$(CpH)** at -1.33 V vs $Fc^{0/+}$, a controlled potential electrolysis (CPE) of a solution of 10 mM **$[Cp_2Co^{III}]^+$** and 100 mM SA in acetone was carried out at -1.33V vs. $Fc^{0/+}$. Under these conditions, a significant quantity of **$CpCo^{I}$(CpH)** was generated, as identified by CV (Figure S56-57). Additionally, CV acquired following the CPE of 1.2 mM **$[Cp_2Co^{III}]^+$** in acetone with 60 mM SA (Table 1, entry 7) showed a strong oxidative feature matching **$CpCo^{I}$(CpH)** (Figure S58), indicating that this complex can form at -1.33 V vs $Fc^{0/+}$ with SA by a ET-PT-ET mechanism, but too slowly or in too small a quantity with this acid to be observed by CV.

To test if **$CpCo^{I}$(CpH)** is competent to generate an Ir-H under conditions similar to electrocatalysis, 42 μmol of **$CpCo^{I}$(CpH)** was treated 5 equiv. SA per Co atom in acetonitrile-d_3 (CD_3CN). Tracking this solution by ^1H NMR revealed minimal loss of **$CpCo^{I}$(CpH)** over the course of one hour. Upon mixing with 16 μmol of **$[Ir^{III}$-Cl]$^+$**, complete transformation to the cationic **$[Ir^{III}$-H]$^+$** occurred before the first NMR spectrum could be acquired (less than five minutes, Figures S9-S11). These data demonstrate that **$CpCo^{I}$(CpH)** is reasonably stable in the presence of SA and rapidly transfers a net hydride equivalent to **$[Ir^{III}$-Cl]$^+$** to form **$[Ir^{III}$-H]$^+$** (Figure 3B). A kinetic isotope effect (KIE) of 4.4 was measured for net hydride transfer from **$CpCo^{I}$(CpH)** to **$[Ir^{III}$-Cl]$^+$** by competition between **$CpCo^{I}$(CpH)** (1.8 mM) and its deuterated analog, **$CpCo^{I}$(CpD)** (1.8 mM) and **$[Ir^{III}$-Cl]$^+$** (1.8 mM) in CD_3CN with 60 mM SA (Table S3). This primary kinetic isotope effect for hydrogen transfer between **$CpCo^{I}$(CpH)** and **$[Ir^{III}$-Cl]$^+$** is consistent with either direct hydride transfer[47] or initial hydrogen atom transfer (HAT)[48-49] followed by reduction by the resulting **Cp_2Co^{II}**.

Evidence for electrocatalytic hydride transfer was observed by CV when **$[Ir^{III}$-X]$^+$** was treated with a substoichiometric amount of **$[Cp_2Co^{III}]^+$** and salicylic acid (SA). A 0.4 mM solution of **$[Cp_2Co^{III}]^+$** with 60 mM SA in acetone showed only the $Co^{III/II}$ couple, which is fully reversible in the presence of this weak acid (Figure 3D, black trace). The addition of 2 mM **$[Ir^{III}$-X]$^+$** (X = salicylate) to this solution resulted in a large increase in current, accompanied by the loss of reversibility in the $Co^{III/II}$ couple (Figure 3D, red trace). A solution of 2.0 mM **$[Ir^{III}$-X]$^+$** in acetone with 60 mM SA showed no reductive features at the potential of the $Co^{III/II}$ couple (Figure 3D, blue trace). These data indicate an electrocatalytic current which is only observed in the presence of acid and both **$[Ir^{III}$-X]$^+$** and **$[Cp_2Co^{III}]^+$**, suggesting rapid electrocatalytic reductive protonation of **$[Cp_2Co^{III}]^+$** and net hydride transfer to iridium mediated by **$CpCo^{I}$(CpH)**. Applying plateau

analysis to this peak–shaped wave provides a lower boundary on the turnover frequency (TOF) of 2.2 s^{-1} (Eq. S8-S11).[50] Though only a lower boundary, this TOF is considerably faster than the k_{obs} of 2.5 hr^{-1} determined by NMR experiments for the hydrogen transfer from **$[Ir^{III}$-H$]^+$** to acetone (Figures S30-31).

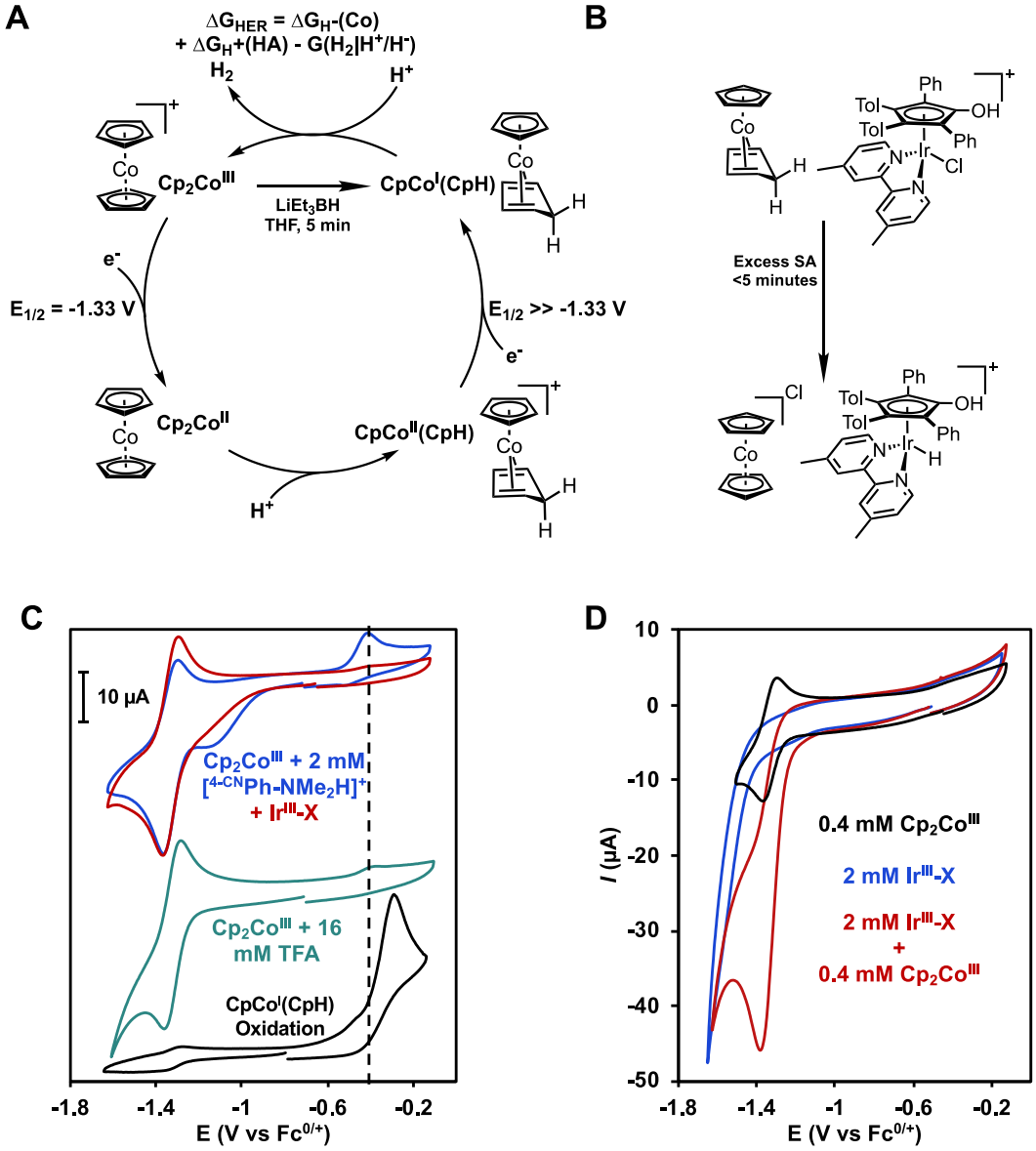
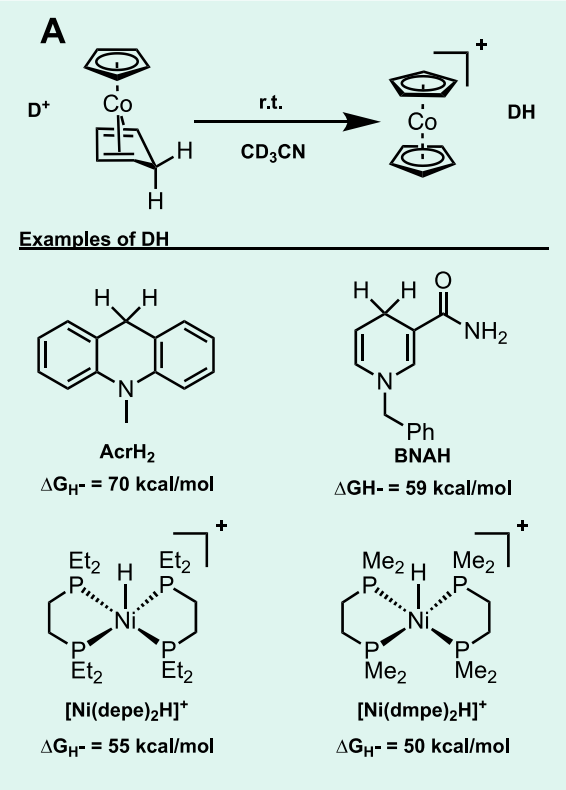


Figure 3.A. Scheme of reductive protonation of **Cp_2Co^{II}** by reduction of **$[Cp_2Co^{III}]^+$** in the presence of acid. **B.** Schematic of **$[Ir^{III}$-H$]^+$** formation by treatment of **$[Ir^{III}$-Cl$]^+$** with **$CpCo^I(CpH)$** in the presence of 5 equivalents of SA relative to the Ir concentration. **C.** CV traces collected in neat acetone showing the appearance of an oxidative feature upon reduction of **$[Cp_2Co^{III}]^+$** with acids matches an external standard of **$CpCo^I(CpH)$**. **D.** CV traces in neat acetone show a catalytic current response only when 0.4 mM Ir, 2 mM Co and 60 mM SA are present. Each of the CV traces contain 60 mM SA. All CV traces were collected at 50 mV/s.

The crucial thermodynamic parameter to improve our understanding of this apparent net-hydride transfer is the thermodynamic hydricity of **$CpCo^I(CpH)$**. To provide an experimental measurement, and to generally improve our understanding of the reactivity of **$CpCo^I(CpH)$,** we

studied several hydride transfer reactions to acceptors of known hydricity, performed in acetonitrile as there is no established hydricity scale in acetone (Figure 4A). The addition of 4 equivalents of 10-methylacridinium perchlorate ([AcrH][ClO_4]) to **$CpCo^{I}(CpH)$** in CD_3CN cleanly generated 10-methylacridine ($AcrH_2$, ΔG_{H^-} = 70 kcal/mol) within 5 minutes, along with cobaltocenium **$[Cp_2Co^{III}]^+$**. Similarly, **$CpCo^{I}(CpH)$** reacts quantitatively with 1-benzylnicotinamide hexafluorophosphate in CD_3CN to generate 1-benzyl-1,4-dihydronicotinamide (BNAH, ΔG_{H^-} = 59 kcal/mol) and **$[Cp_2Co^{III}]^+$**. These experiments reveal that **$CpCo^{I}(CpH)$** is a competent hydride donor to generate the $FADH_2$ and NADH analogs $AcrH_2$ and BNAH, respectively.[3] No evidence of single-electron transfer or HAT reactivity was observed for either organic hydride acceptor.[51]

Reaction of **$CpCo^{I}(CpH)$** with bis-(1,2-dimethylphosphinoethane)nickel(II) tetrafluoroborate ([Ni^{II}(dmpe)$_2$][BF_4]$_2$), yields an equilibrium mixture of [Ni^{II}(dmpe)$_2$][BF_4]$_2$, the nickel-hydride, [Ni^{II}(dmpe)$_2$H][BF_4] (ΔG_{H^-} = 50 kcal/mol), **$CpCo^{I}(CpH)$** and cobaltocenium. The equilibrium constant was determined from the ^{1}H NMR spectra, which provides an experimental measure of the hydricity of **$CpCo^{I}(CpH)$** of ΔG_{H^-} = 49 kcal/mol, slightly higher than that computationally proposed by Peters, *et al.*[26] Critically, the measured hydricity and reduction potentials of **$CpCo^{I}(CpH)$** allow calculation of the Bond Dissociation Free Energy (BDFE)[51] and pK_a in acetonitrile for **$CpCo^{I}(CpH)$** (Figure 4B).[26] The pK_a of **$CpCo^{I}(CpH)$** (41)[52] was calculated from the hydricity and our experimentally measured $Co^{II/I}$ reduction potential, which yields an estimate of the BDFE of **$CpCo^{I}(CpH)$** of 54 kcal/mol. This calculated BDFE and $E_{1/2}$ estimated from irreversible oxidation **$CpCo^{I}(CpH)$** allows further calculation of the pK_a (7.4) and BDFE (33 kcal/mol) of **$[CpCo^{I}(CpH)]^+$**, which show the cationic Co(II) complex to be much more reactive than the corresponding neutral Co(I) for both PT and HAT.



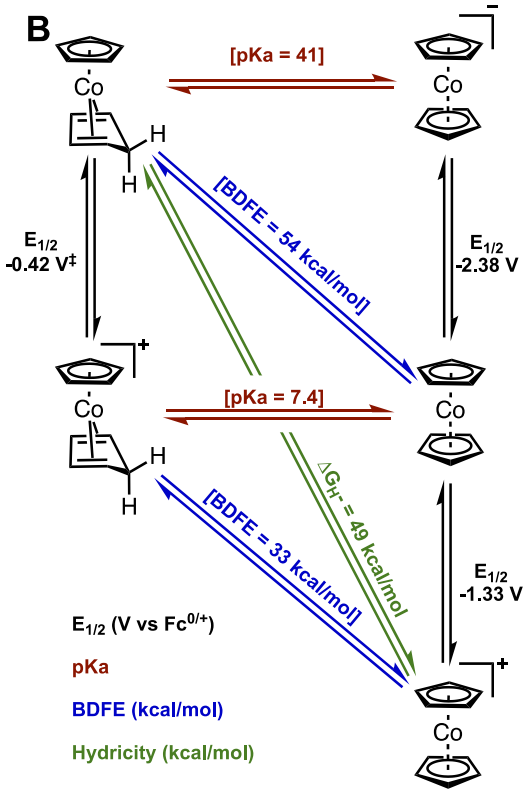


Figure 4.A. Reactivity of **$CpCo^{I}(CpH)$** with biomimetic ($AcrH_2$, $FADH_2$ type and BNAH, NADH type) and organometallic hydride acceptors. **B.** Thermochemical square scheme for **$CpCo^{I}(CpH)$** derived from the ΔG_H- and observed reduction potentials, calculated values are shown in brackets. ‡Estimated from the inflection point of an irreversible feature.[46]

Mechanistic Insights into Cobaltocene–Mediated Hydride Transfer

The observations that **$CpCo^{I}(CpH)$** is a competent hydride donor, that it can be generated electrochemically at -1.33 V in the presence of salicylic acid in acetone, and is capable of generating **$[Ir^{III}\text{-}H]^+$** lead us to propose the mechanism for mediated electrocatalytic hydrogenation of acetone summarized in Figure 5. In this mechanism, protonation of the cyclopentadienone ligand of **$Ir^{I}\text{-}X$** generates the cationic hydroxycyclopentadienyl **$[Ir^{III}\text{-}X]^+$** (X = salicylate). Hydride transfer from **$CpCo^{I}(CpH)$** to **$[Ir^{III}\text{-}X]^+$** generates the cationic **$[Ir^{III}\text{-}H]^+$**, which reduces acetone to regenerate **$Ir^{I}\text{-}X$**. The key hydride transfer mediator **$CpCo^{I}(CpH)$** is recycled by reductive protonation of cobaltocenium (**$[Cp_2Co^{III}]^+$**). Reduction of cobaltocenium at -1.33 V generates cobaltocene; protonation of cobaltocene generates the cationic **$[CpCo^{II}(CpH)]^+$** ($E_{1/2}$ = -0.42 V), which is rapidly reduced at an operating potential of -1.33 V to **$CpCo^{I}(CpH)$**.[26]

The low solubilities of the Ir precursors have precluded a detailed kinetic analysis of this tandem electrocatalytic cycle (Figure 5) by CV, but our data to date suggest that the turnover limiting step is the reduction of acetone by the (hydroxycyclopentadienyl) Ir hydride **$[Ir^{III}\text{-}H]^+$**. The hydrogenation of acetone by **$[Ir^{III}\text{-}H]^+$** is relatively slow in neat acetone with a k_{obs} = 2.5 h^{-1} (Figure S30-S31). Cyclic voltammetry (Figure 3D) suggests that the reductive protonation of **$[Cp_2Co^{III}]^+$** and delivery of hydride from **CpCo(CpH)** to the **$[Ir^{III}\text{-}X]^+$** cation is considerably faster than this, with an estimated k_{obs} of 2.2s^{-1}. Prior studies[26] suggested that hydrogen evolution by the reductive protonation of cobaltocene with $[^{4\text{-}CN}PhNH_3][OTf]$ in DME was slow and that this was due to rate-limiting protonation of **Cp_2Co^{II}** to generate **$CpCo(CpH)^+$**. An alternative interpretation consistent with our data is that reductive protonation of **Cp_2Co^{II}** is relatively fast, but that protonation of **CpCo(CpH)** and generation of hydrogen is the slow step in HER. Further studies are warranted to address this hypothesis, but this interpretation would be consistent with the kinetic stability of **CpCo(CpH)** observed in the presence of salicylic acid (Figure S9) and the observation that **$[Ir^{III}\text{-}H]^+$** can be formed competitively with HER from **Cp_2Co^{II}** and the stronger acid $[^{4\text{-}CN}PhNH_3][OTf]$ in CD_3CN (Figure S21).

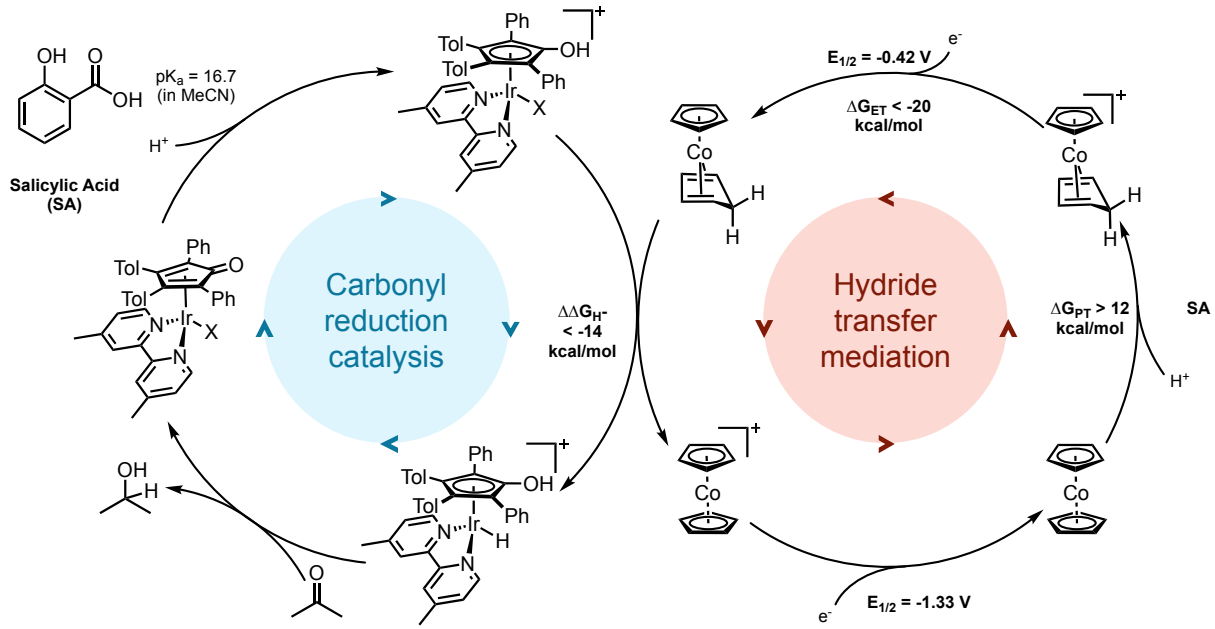


Figure 5. Proposed mechanism of cobaltocene-mediated electrohydrogenation. Under the conditions of electrocatalysis with the Ir precursor **Ir^{I}-H**, X is most likely the salicylate anion. Potentials are given in Volts referenced to the Ferrocene couple ($Fc^{+/0}$).

The measured hydricity values of **CpCo^{I}(CpH)** (ΔG_{H^-} = 49 kcal/mol) and **[Ir^{III}-H]$^+$** (ΔG_{H^-} = 64 kcal/mol) indicate that the proposed hydride transfer step (Figure 5) is exergonic by more than 14 kcal/mol, consistent with the rapid hydride transfer to **[Ir^{III}-X]$^+$** species observed in NMR and CV experiments. The pK_a of **[CpCo^{II}(CpH)]$^+$** (7.4) is 9.3 units more acidic than SA,[29] indicating that proton transfer from salicylic acid to **Cp$_2$Co** is endergonic by as much as 12 kcal/mol under the catalytic conditions.[53] Catalytic formation of **CpCo^{I}(CpH)** would therefore be driven by the rapid reduction of **[CpCo^{II}(CpH)]$^+$** (exergonic by ~20 kcal/mol) to generate **CpCo^{I}(CpH)**. This endergonic PT followed by a very exergonic ET implies a low steady-state concentration of **[CpCo^{II}(CpH)]$^+$**. The stoichiometric hydride transfer, electrolysis, and cyclic voltammetry data presented herein are consistent with a net-hydride transfer from **CpCo^{I}(CpH)** to form **[Ir^{III}-H]$^+$**, but the data do not allow us to rule out that Ir hydride formation from **CpCo^{I}(CpH)** occurs by initial hydrogen atom transfer, followed by rapid electron transfer.

Conclusions

The ability of cobaltocene, widely regarded as a one-electron reducing agent,[27] to perform selective catalytic net-hydride transfer[43,60] in the presence of weak acids enables a tandem electrocatalytic cycle to generate a metal hydride for the electrohydrogenation of acetone with very high Faradaic efficiency. We attribute the high FE for electroreduction to the combined thermodynamic stability of **[Ir^{III}-H]$^+$** and kinetic stability of **CpCo^{I}(CpH)** with SA. While the ΔG_{H^-} of **CpCo^{I}(CpH)** indicates it should be thermodynamically feasible to eliminate H_2 with SA (ΔG_{HER} = -4.3 kcal/mol in MeCN), **CpCo^{I}(CpH)** showed good transient stability to SA, indicating a kinetically trapped hydride donor. This is also true for NADH, as the protonation of NADH to generate hydrogen requires a catalyst.[54] Unlike NADH, however, the stability of intermediate **Cp$_2$Co^{II}** allows electrocatalytic cycling of a hydride donor under mild conditions without generating the highly reactive radical intermediates that complicate the electrochemical regeneration of cofactors or organic hydride donors like BNAH and $AcrH_2$.[3,55-56]

The ability to selectively access a net-hydride transfer reagent at room temperature with relatively weak acids is a major advancement in the use of metallocenes for electrocatalytic PCET reactions. The hydricity of **$CpCo^{I}(CpH)$** (ΔG_H-(MeCN) = 49 kcal/mol) and its ability to be efficiently electrochemically generated also suggests the possibility of a general method to access other catalytically relevant metal hydrides.[31] In addition, **$CpCo^{I}(CpH)$** might prove useful as an alternative to other hydride reducing agents,[57-58] or as a mediator to enable the electrocatalytic reduction of organic substrates with mild acids at mild potentials.[3,59]

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Supporting Information:
Additional experimental details, ^{1}H NMR spectra of synthesized compounds and supporting stoichiometric experiments, and electrochemical data for CV and CPE experiments (PDF).

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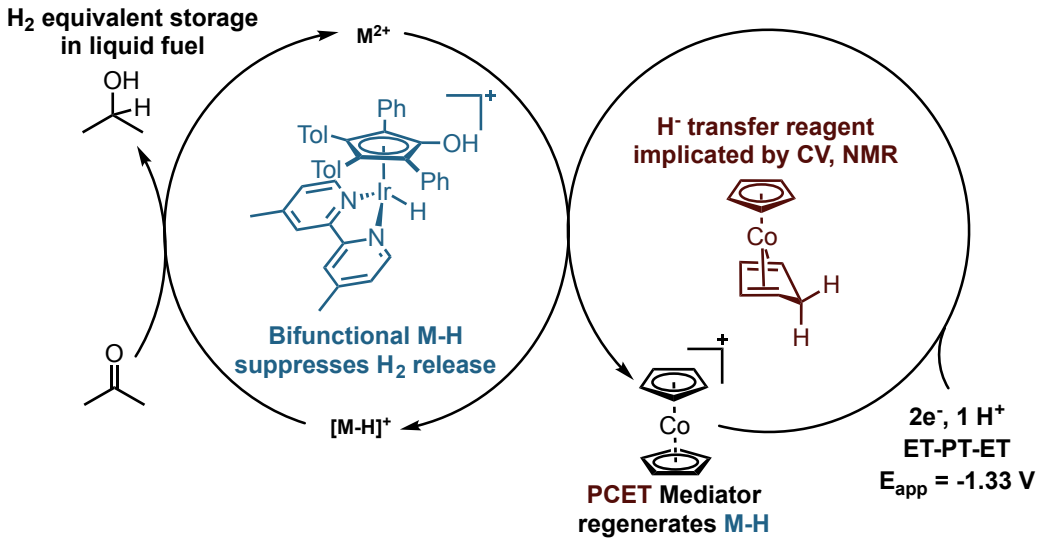
H2 equivalent storage
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PCET Mediator
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Eapp = -1.33 V