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Electrochemical and chemical routes to hydride loss from an iridium dihydride†

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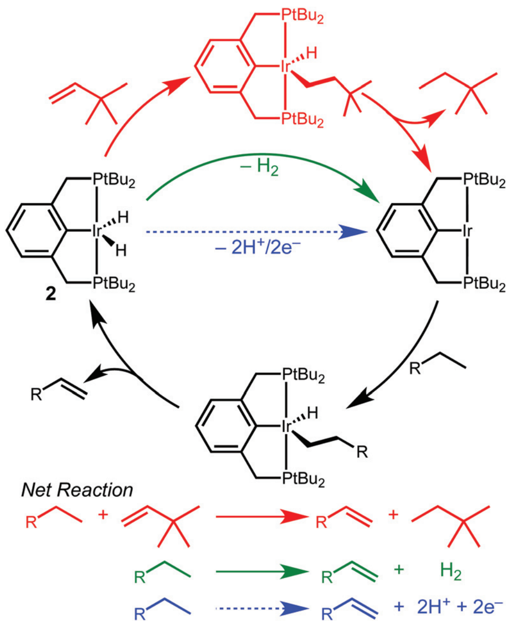
With a view towards replacing sacrificial hydrogen acceptors in alkane dehydrogenation catalysis, electrochemical methods for oxidative activation of a pincer-ligated iridium hydride intermediate were explored. A $1H^+/2e^-$ oxidation process was observed in THF solvent, with net hydride loss leading to a reactive cationic intermediate that can be trapped by chloride. Analogous reactivity was observed with the concerted hydride transfer reagent Ph_3C^+, connecting chemical and electrochemical hydride loss pathways.

Iridium complexes supported by tridentate ^{R_4}PCP (^{R_4}PCP = κ^3-C_6H_3-2,6-$(CH_2PR_2)_2$) pincer ligands are prolific dehydrogenation catalysts, enabling landmark transformations such as the dehydrogenation,[1,2] metathesis,[3] coupling[4,5] and dehydroaromatization[6] of alkanes.[7] Efficient dehydrogenation reactions require a sacrificial hydrogen acceptor, typically an olefin. The hydrogen acceptor alters the overall reaction thermodynamics and activates the iridium dihydride species.[7–9] In transfer dehydrogenation, catalyst activation occurs by insertion of the sacrificial olefin into one Ir–H bond, followed by C–H bond-forming reductive elimination with the other Ir–H bond, generating a highly reactive 14e⁻ intermediate capable of alkane C–H bond activation (Scheme 1).

The requirement of an added stoichiometric reagent represents a significant limitation in dehydrogenation reactions.[8,10] In considering new strategies to promote dehydrogenation reactions, we were drawn to electrochemical methods that could *decouple* the catalyst activating and hydrogen accepting steps.[11,12] We envisioned electrochemical oxidation of (^{R_4}PCP)Ir(H)$_2$ at an anode, generating a catalytic intermediate while releasing $2H^+/2e^-$ (Scheme 1) that could be used to drive any range of reactions at the cathode.



Scheme 1

Electrochemical dehydrogenation relies on (sometimes coupled) electron transfer and proton transfer steps,[13,14] while chemical dehydrogenation often involves concerted hydride transfer.[7,15,16] Recent reports have started to draw connections between chemical and electrochemical processes, however. For example, inspired by a report of (^{R_4}PCP)Ir-catalyzed hydrogenation of CO_2 to formate,[17] Brookhart and Meyer developed an analogous electrochemical reduction of CO_2 to formate catalyzed by (^{tBu_4}POCOP)Ir complexes (^{tBu_4}POCOP = κ^3-C_6H_3-2,6-$(OP^tBu_2)_2$).[18–20] A striking oxidative example involves two different catalysts for the same alcohol oxidation reaction that operate by two different mechanisms, either a concerted H_2 loss mechanism or an outer-sphere electron transfer mechanism in which a chemical oxidant (not an electrode) and a base facilitate $2H^+/2e^-$ loss.[21]

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Studies of electrochemical reactions that parallel well-known organometallic oxidations can help bridge the divide between chemical and electrochemical methods. This report focuses on the oxidation of a pincer-ligated iridium dihydride. Net loss of hydride ($H^+/2e^-$) is promoted by *either* electrochemical or chemical methods to produce an iridium monohydride species.

The dihydride complex was prepared according to previously reported procedures by dehydrohalogenation of (^{tBu_4}PCP)Ir(H)(Cl) (**1**) under an H_2 atmosphere.[1,22] This procedure affords a mixture of the five-coordinate dihydride (^{tBu_4}PCP)Ir(H)$_2$ (**2**) and (^{tBu_4}PCP)Ir(H)$_4$ (**3**).[23] Samples could be stirred in pentane, filtered, and dried under vacuum to remove the dihydrogen ligand and provide pure **2**.‡

The oxidation of dihydride **2** was initially explored using cyclic voltammetry (CV). When a solution of **2** in argon-saturated THF containing $[Bu_4N][PF_6]$ supporting electrolyte was assessed by a CV sweep to oxidative potentials, a single irreversible feature was observed at −0.08 V *vs.* $Cp_2Fe^{+/0}$ (Fig. 1). No return reduction process was apparent, even as the scan rate was increased to 1 V s^{-1}.

An irreversible electrochemical oxidation is consistent with a rapid chemical reaction following electron transfer from **2** to the electrode. The dihydride **2** is more easily oxidized than the hydridochloride complex **1**, which exhibited a quasi-reversible oxidation around 0.5 V *vs.* $Cp_2Fe^{+/0}$ in CH_2Cl_2 at fast scan rates in a prior study.[24]

To identify the product formed at positive potentials under argon, a controlled potential electrolysis experiment was carried out. A high-surface-area reticulated vitreous carbon working electrode was submersed in a THF solution of dihydride **2** and polarized to 0.2 V *vs.* $Cp_2Fe^{+/0}$. The flow of current diminished as a gradual color change from pale orange to pale yellow was observed. The oxidation passed 239 mC of charge, corresponding to 1.9 e^- per Ir, but an aliquot analyzed by $^{31}P\{^1H\}$ NMR spectroscopy revealed a mixture of species.

Considering the possibility that oxidation of **2** would produce a reactive cationic species,[25] the oxidative electrochemistry was also carried out in the presence of a chloride ion source as a trapping agent. In the presence of LiCl (and with conditions otherwise similar to those described above), the CV response of **2** was essentially unchanged relative to chloride-free conditions, suggesting that chloride does not influence the initial oxidation process.

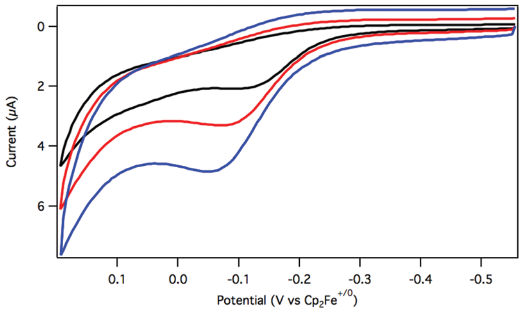
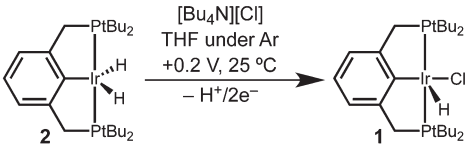


Fig. 1 Cyclic voltammetry of **2** at 25 mV s^{-1} (black), 100 mV s^{-1} (red), and 250 mV s^{-1} (blue) in THF solution with 0.1 M $[Bu_4N][PF_6]$ electrolyte. Glassy carbon working electrode, platinum counter electrode, Ag wire pseudo-reference electrode, 298 K.



Scheme 2

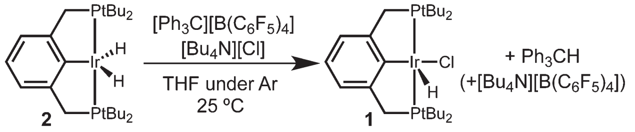
Controlled potential electrolysis of a THF solution containing **2** and excess LiCl or $[Bu_4N][Cl]$ was conducted at 0.2 V *vs.* $Cp_2Fe^{+/0}$ (Scheme 2). In the presence of chloride, the solution color changed from pale orange to a much brighter orange, and the 283 mC of charge passed corresponds to a $2e^-$ oxidation (2.3 e^- per Ir). Analysis by $^{31}P\{^1H\}$ NMR spectroscopy now revealed a single phosphorous-containing species (δ 69). The product was isolated from the electrolyte by removal of the THF under vacuum and extraction with pentane. Full NMR spectroscopic analysis in THF-d_8 showed a triplet hydride resonance far upfield (δ −42.9) in the ^1H NMR spectrum that is diagnostic of (^{tBu_4}PCP)Ir(H)(Cl) (**1**). All of the ^{31}P and ^1H NMR signals closely matched the previously reported values.[22]

The electrochemical conversion of dihydride **2** to hydridochloride **1** represents a net hydride abstraction *via* the loss of $2e^-$ to the anode and loss of H^+ (to solution or perhaps to a surface site on the electrode), followed by chloride binding. This two-step electrochemical–chemical (EC) transformation is consistent with the irreversible CV response (prior studies of (pincer)Ir(H)(Cl) also implicated an EC mechanism, but did not identify a product).[24] The stability of the product, hydridochloride **1**, towards further oxidation at the potentials applied during electrolysis is critical to the success of the reaction.[24]

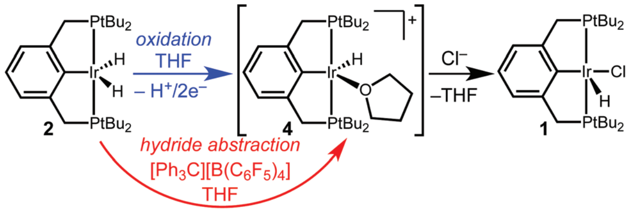
Analogous electrochemical hydride loss *via* a two-electron/one-proton oxidative process has been reported for a series of Group 6 complexes of the type $CpM(CO)_3H$ (M = Cr, M, W),[26] which may involve a concerted proton-coupled electron transfer event in the tungsten case.[27] In contrast, the Rh analogue (^{tBu_4}PCP)Rh(H_2), which is best described as a Rh(I) dihydrogen complex,[28] does not undergo oxidative hydride loss: reversible $1e^-$ oxidation is observed in CH_2Cl_2, and H_2 loss is observed in coordinating solvents.[29]

To further probe the hydride transfer reactivity, chemical methods that could effect an analogous hydride loss were explored. When dihydride **2** is allowed to react with the hydride abstractor $[Ph_3C][B(C_6F_5)_4]$ in THF-d_8, the solution changes color from pale orange to pale yellow. NMR spectroscopic monitoring revealed a mixture of products analogous to those observed in the initial electrolysis.

Hydride abstraction was next attempted in the presence of a chloride source. Treatment of dihydride **2** with 1 equiv. $[Ph_3C][B(C_6F_5)_4]$ and 5 equiv. $[Bu_4N][Cl]$ led to a color change from pale orange to a much brighter orange, coinciding with



Scheme 3



Scheme 4

the appearance of the characteristic signals of hydridochloride complex **1** by $^{31}P\{^{1}H\}$ and ^{1}H NMR spectroscopy (Scheme 3). Triphenylmethane is also observed by ^{1}H NMR spectroscopy, clearly identifying the fate of the hydride.

We suggest that the electrochemical and chemical hydride abstractions proceed *via* a shared intermediate, given the similar product distributions under various reaction conditions. As shown in Scheme 4, we hypothesize that oxidation of dihydride **2** occurs as a net $1H^+/2e^-$ process (*via* one of the pathways described above) to generate a reactive monohydride cation, $[(^{tBu_4}PCP)Ir(H)]^+$ (**4**). Chemical hydride transfer from **2** to $[Ph_3C][B(C_6F_5)_4]$ would also afford **4**. We are not aware of any prior reported isolation of cation **4**. An analogous $[(^{tBu_4}POCOP)Ir(H)]^+$ species, isolated as an acetone or dichloromethane adduct, is an active hydrosilylation catalyst.[30,31]

From this shared intermediate cation **4**, trapping with chloride ion can generate the hydridochloride **1**. In the absence of chloride, we suspect that cation **4** decomposes through reactions with itself and/or the solvent, the details of which are currently under investigation. The observation of identical products under electrochemical and chemical reaction conditions suggests that future electrochemical oxidations (even in non-polar solvents)[32–34] can be modeled after existing hydride abstraction reactions.

By implicating a key monohydride cation intermediate and building an analogy between well-defined organometallic hydride abstraction reactions and electrochemical oxidation processes, these joint chemical/electrochemical studies provide a foundation for future development of electrochemical dehydrogenation processes.

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Notes and references

‡ Solutions containing hydrides **2** and **3** are stable under Ar or H_2, but decompose under N_2 or air to a mixture of products with distinct electrochemical responses.[35]

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