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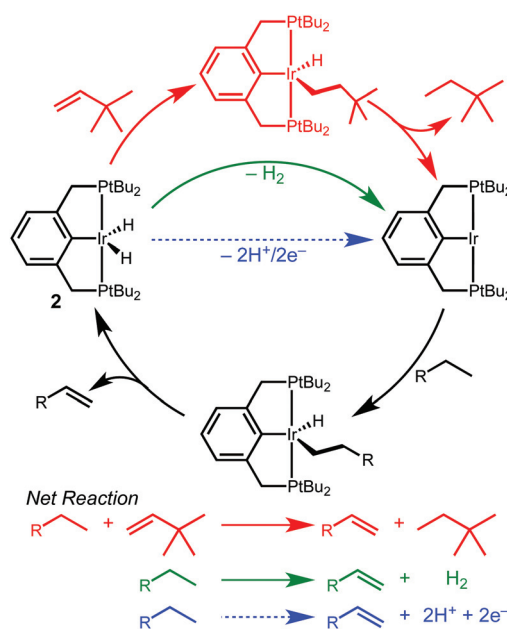
Electrochemical and chemical routes to hydride loss from an iridium dihydride†

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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 $1\text{H}^+/2\text{e}^-$ 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^4PCP ($\text{R}^4\text{PCP} = \kappa^3\text{-C}_6\text{H}_3\text{-2,6-(CH}_2\text{PR}_2)_2$) pincer ligands are prolific dehydrogenation catalysts, enabling landmark transformations such as the dehydrogenation,^{1,2} metathesis,³ coupling^{4,5} and dehydroaromatization⁶ 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 $(\text{R}^4\text{PCP})\text{Ir}(\text{H})_2$ at an anode, generating a catalytic intermediate while releasing $2\text{H}^+/2\text{e}^-$ (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 $(\text{R}^4\text{PCP})\text{Ir}$ -catalyzed hydrogenation of CO_2 to formate,¹⁷ Brookhart and Meyer developed an analogous electrochemical reduction of CO_2 to formate catalyzed by $(\text{tBu}_4\text{POCOP})\text{Ir}$ complexes ($\text{tBu}_4\text{POCOP} = \kappa^3\text{-C}_6\text{H}_3\text{-2,6-(OP}^t\text{Bu}_2)_2$).^{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 $2\text{H}^+/2\text{e}^-$ 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 ($\text{H}^+/\text{2e}^-$) is promoted by *either* electrochemical or chemical methods to produce an iridium monohydride species.

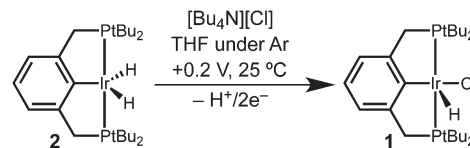
The dihydride complex was prepared according to previously reported procedures by dehydrohalogenation of $(^t\text{Bu}_4\text{PCP})\text{Ir}(\text{H})(\text{Cl})$ (**1**) under an H_2 atmosphere.^{1,22} This procedure affords a mixture of the five-coordinate dihydride $(^t\text{Bu}_4\text{PCP})\text{Ir}(\text{H})_2$ (**2**) and $(^t\text{Bu}_4\text{PCP})\text{Ir}(\text{H})_4$ (**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 $[\text{Bu}_4\text{N}][\text{PF}_6]$ supporting electrolyte was assessed by a CV sweep to oxidative potentials, a single irreversible feature was observed at -0.08 V vs. $\text{Cp}_2\text{Fe}^{+/0}$ (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. $\text{Cp}_2\text{Fe}^{+/0}$ 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. $\text{Cp}_2\text{Fe}^{+/0}$. 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 $^{31}\text{P}\{^1\text{H}\}$ 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



Scheme 2

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.

Controlled potential electrolysis of a THF solution containing **2** and excess LiCl or $[\text{Bu}_4\text{N}][\text{Cl}]$ was conducted at 0.2 V vs. $\text{Cp}_2\text{Fe}^{+/0}$ (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 $^{31}\text{P}\{^1\text{H}\}$ 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 $\text{THF}-d_8$ showed a triplet hydride resonance far upfield (δ -42.9) in the ^1H NMR spectrum that is diagnostic of $(^t\text{Bu}_4\text{PCP})\text{Ir}(\text{H})(\text{Cl})$ (**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) $\text{Ir}(\text{H})(\text{Cl})$ 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 $\text{CpM}(\text{CO})_3\text{H}$ ($\text{M} = \text{Cr}, \text{M}, \text{W}$),²⁶ which may involve a concerted proton-coupled electron transfer event in the tungsten case.²⁷ In contrast, the Rh analogue $(^t\text{Bu}_4\text{PCP})\text{Rh}(\text{H}_2)$, 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 $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ in $\text{THF}-d_8$, 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. $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ and 5 equiv. $[\text{Bu}_4\text{N}][\text{Cl}]$ led to a color change from pale orange to a much brighter orange, coinciding with

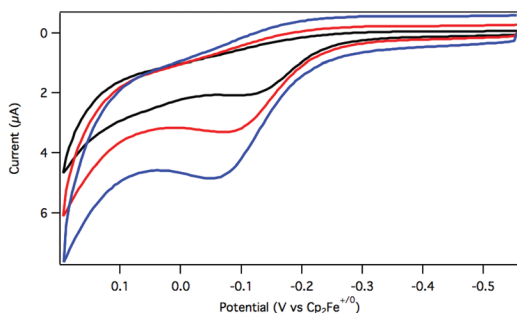
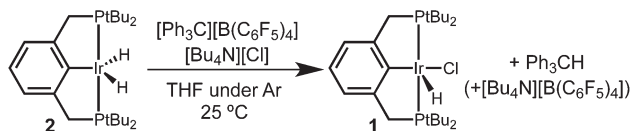
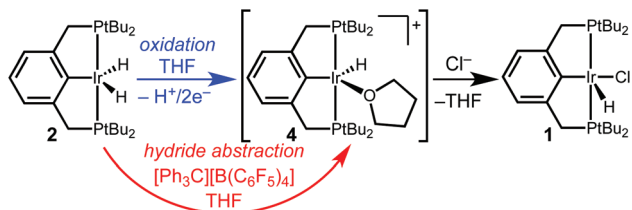


Fig. 1 Cyclic voltammetry of **2** at 25 mV s^{-1} (black), 100 mV s^{-1} (red), and 250 mV s^{-1} (blue) in THF solution with 0.1 M $[\text{Bu}_4\text{N}][\text{PF}_6]$ electrolyte. Glassy carbon working electrode, platinum counter electrode, Ag wire pseudo-reference electrode, 298 K.





Scheme 3



Scheme 4

the appearance of the characteristic signals of hydrido-chloride complex **1** by $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectroscopy (Scheme 3). Triphenylmethane is also observed by ^1H 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 $1\text{H}^+/2\text{e}^-$ process (*via* one of the pathways described above) to generate a reactive monohydride cation, $[(^t\text{Bu}_4\text{PCP})\text{Ir}(\text{H})]^+$ (**4**). Chemical hydride transfer from **2** to $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ would also afford **4**. We are not aware of any prior reported isolation of cation **4**. An analogous $[(^t\text{Bu}_4\text{POCOP})\text{Ir}(\text{H})]^+$ 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 hydrido-chloride **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

- 1 M. Gupta, C. Hagen, R. J. Flesher, W. C. Kaska and C. M. Jensen, *Chem. Commun.*, 1996, 2083–2084.
- 2 A. Kumar, T. Zhou, T. J. Emge, O. Mironov, R. J. Saxton, K. Krogh-Jespersen and A. S. Goldman, *J. Am. Chem. Soc.*, 2015, **137**, 9894–9911.
- 3 A. S. Goldman, A. H. Roy, Z. Huang, R. Ahuja, W. Schinski and M. Brookhart, *Science*, 2006, **312**, 257–261.
- 4 D. C. Leitch, Y. C. Lam, J. A. Labinger and J. E. Bercaw, *J. Am. Chem. Soc.*, 2013, **135**, 10302–10305.
- 5 J. A. Labinger, D. C. Leitch, J. E. Bercaw, M. A. Deimund and M. E. Davis, *Top. Catal.*, 2015, **58**, 494–501.
- 6 R. Ahuja, B. Punji, M. Findlater, C. Supplee, W. Schinski, M. Brookhart and A. S. Goldman, *Nat. Chem.*, 2011, **3**, 167–171.
- 7 J. Choi, A. H. Roy, MacArthur, M. Brookhart and A. S. Goldman, *Chem. Rev.*, 2011, **111**, 1761–1779.
- 8 K. Krogh-Jespersen, M. Czerw, N. Summa, K. B. Renkema, P. D. Achord and A. S. Goldman, *J. Am. Chem. Soc.*, 2002, **124**, 11404–11416.
- 9 K. B. Renkema, Y. V. Kissin and A. S. Goldman, *J. Am. Chem. Soc.*, 2003, **125**, 7770–7771.
- 10 W. Xu, G. P. Rosini, K. Krogh-Jespersen, A. S. Goldman, M. Gupta, C. M. Jensen and W. C. Kaska, *Chem. Commun.*, 1997, 2273–2274.
- 11 P. Driscoll, E. Deunf, L. Rubin, O. Luca, R. H. Crabtree, C. Chidsey, J. Arnold and J. Kerr, *ECS Trans.*, 2011, **35**, 3–17.
- 12 B. Rausch, M. D. Symes and L. Cronin, *J. Am. Chem. Soc.*, 2013, **135**, 13656–13659.
- 13 C. Costentin, M. Robert and J.-M. Savéant, *Chem. Rev.*, 2010, **110**, PR1–PR40.
- 14 D. R. Weinberg, C. J. Gagliardi, J. F. Hull, C. F. Murphy, C. A. Kent, B. C. Westlake, A. Paul, D. H. Ess, D. G. McCafferty and T. J. Meyer, *Chem. Rev.*, 2012, **112**, 4016–4093.
- 15 S. E. Clapham, A. Hadzovic and R. H. Morris, *Coord. Chem. Rev.*, 2004, **248**, 2201–2237.
- 16 C. R. Waidmann, A. J. M. Miller, C.-W. A. Ng, M. L. Scheuermann, T. R. Porter, T. A. Tronic and J. M. Mayer, *Energy Environ. Sci.*, 2012, **5**, 7771–7780.
- 17 R. Tanaka, M. Yamashita and K. Nozaki, *J. Am. Chem. Soc.*, 2009, **131**, 14168–14169.
- 18 P. Kang, C. Cheng, Z. Chen, C. K. Schauer, T. J. Meyer and M. Brookhart, *J. Am. Chem. Soc.*, 2012, **134**, 5500–5503.
- 19 P. Kang, T. J. Meyer and M. Brookhart, *Chem. Sci.*, 2013, **4**, 3497–3502.
- 20 P. Kang, S. Zhang, T. J. Meyer and M. Brookhart, *Angew. Chem., Int. Ed.*, 2014, **53**, 8709–8713.
- 21 P. J. Bonitatibus, S. Chakraborty, M. D. Doherty, O. Siclován, W. D. Jones and G. L. Soloveichik, *Proc. Natl. Acad. Sci. U. S. A.*, 2015, **112**, 1687–1692.



- 22 C. J. Moulton and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1976, 1020–1024.
- 23 T. J. Hebden, K. I. Goldberg, D. M. Heinekey, X. Zhang, T. J. Emge, A. S. Goldman and K. Krogh-Jespersen, *Inorg. Chem.*, 2010, **49**, 1733–1742.
- 24 F. Novak, B. Speiser, H. A. Y. Mohammad and H. A. Mayer, *Electrochim. Acta*, 2004, **49**, 3841–3853.
- 25 M. Gupta, W. C. Kaska and C. M. Jensen, *Chem. Commun.*, 1997, 461–462.
- 26 O. B. Ryan, M. Tilset and V. D. Parker, *J. Am. Chem. Soc.*, 1990, **112**, 2618–2626.
- 27 M. Bourrez, R. Steinmetz, S. Ott, F. Gloaguen and L. Hammarström, *Nat. Chem.*, 2015, **7**, 140–145.
- 28 K. Huang, J. H. Han, C. B. Musgrave and E. Fujita, *Organometallics*, 2007, **26**, 508–513.
- 29 M. D. Doherty, S. J. Konezny, V. S. Batista and G. L. Soloveichik, *J. Organomet. Chem.*, 2014, **762**, 94–97.
- 30 J. Yang and M. Brookhart, *J. Am. Chem. Soc.*, 2007, **129**, 12656–12657.
- 31 J. Yang and M. Brookhart, *Adv. Synth. Catal.*, 2009, **351**, 175–187.
- 32 W. E. Geiger and F. Barrière, *Acc. Chem. Res.*, 2010, **43**, 1030–1039.
- 33 R. J. LeSuer, C. Buttolph and W. E. Geiger, *Anal. Chem.*, 2004, **76**, 6395–6401.
- 34 A. P. Abbott and D. J. Schiffrin, *J. Chem. Soc., Faraday Trans.*, 1990, **86**, 1453–1459.
- 35 R. Ghosh, M. Kanzelberger, T. J. Emge, G. S. Hall and A. S. Goldman, *Organometallics*, 2006, **25**, 5668–5671.

