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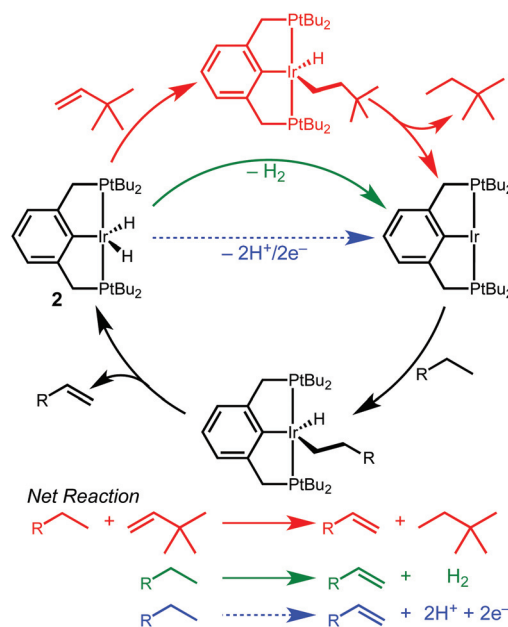
## Electrochemical and chemical routes to hydride loss from an iridium dihydride†

A. G. Walden,<sup>a</sup> A. Kumar,<sup>b,c</sup> N. Lease,<sup>b</sup> A. S. Goldman<sup>b</sup> and A. J. M. Miller<sup>\*a</sup>

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  $\text{Ph}_3\text{C}^+$ , connecting chemical and electrochemical hydride loss pathways.

Iridium complexes supported by tridentate  $\text{R}^4\text{PCP}$  ( $\text{R}^4\text{PCP} = \kappa^3\text{-C}_6\text{H}_3\text{-2,6-(CH}_2\text{PR}_2)_2$ ) pincer ligands are prolific dehydrogenation catalysts, enabling landmark transformations such as the dehydrogenation,<sup>1,2</sup> metathesis,<sup>3</sup> coupling<sup>4,5</sup> and dehydroaromatization<sup>6</sup> of alkanes.<sup>7</sup> 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.<sup>7–9</sup> 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  $14\text{e}^-$  intermediate capable of alkane C–H bond activation (Scheme 1).

The requirement of an added stoichiometric reagent represents a significant limitation in dehydrogenation reactions.<sup>8,10</sup> In considering new strategies to promote dehydrogenation reactions, we were drawn to electrochemical methods that could *decouple* the catalyst activating and hydrogen accepting steps.<sup>11,12</sup> 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,<sup>13,14</sup> while chemical dehydrogenation often involves concerted hydride transfer.<sup>7,15,16</sup> 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  $\text{CO}_2$  to formate,<sup>17</sup> Brookhart and Meyer developed an analogous electrochemical reduction of  $\text{CO}_2$  to formate catalyzed by  $(\text{t}^{\text{Bu}}\text{POCOP})\text{Ir}$  complexes ( $\text{t}^{\text{Bu}}\text{POCOP} = \kappa^3\text{-C}_6\text{H}_3\text{-2,6-(OP}^t\text{Bu}_2)_2$ ).<sup>18–20</sup> A striking oxidative example involves two different catalysts for the same alcohol oxidation reaction that operate by two different mechanisms, either a concerted  $\text{H}_2$  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.<sup>21</sup>

<sup>a</sup>Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599-3290, USA. E-mail: ajmm@email.unc.edu

<sup>b</sup>Department of Chemistry and Chemical Biology, Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08903, USA

<sup>c</sup>Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati - 781039, Assam, India

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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 ( $\text{H}^+/2\text{e}^-$ ) is promoted by either electrochemical or chemical methods to produce an iridium monohydride species.

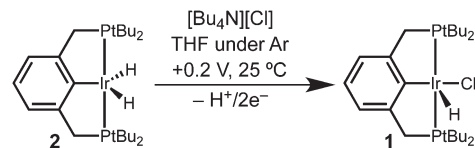
The dihydride complex was prepared according to previously reported procedures by dehydrohalogenation of  $(^t\text{Bu}_4\text{PCP})\text{Ir}(\text{H})(\text{Cl})$  (**1**) under an  $\text{H}_2$  atmosphere.<sup>1,22</sup> This procedure affords a mixture of the five-coordinate dihydride  $(^t\text{Bu}_4\text{PCP})\text{Ir}(\text{H})_2$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

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  $\text{s}^{-1}$ .

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 hydrido-chloride complex **1**, which exhibited a quasi-reversible oxidation around  $0.5$  V vs.  $\text{Cp}_2\text{Fe}^{+/0}$  in  $\text{CH}_2\text{Cl}_2$  at fast scan rates in a prior study.<sup>24</sup>

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 submerged 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  $1.9$   $\text{e}^-$  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,<sup>25</sup> 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  $2\text{e}^-$  oxidation ( $2.3$   $\text{e}^-$  per Ir). Analysis by  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy now revealed a single phosphorous-containing species ( $\delta$  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 ( $\delta$   $-42.9$ ) in the  $^1\text{H}$  NMR spectrum that is diagnostic of  $(^t\text{Bu}_4\text{PCP})\text{Ir}(\text{H})(\text{Cl})$  (**1**). All of the  $^{31}\text{P}$  and  $^1\text{H}$  NMR signals closely matched the previously reported values.<sup>22</sup>

The electrochemical conversion of dihydride **2** to hydrido-chloride **1** represents a net hydride abstraction *via* the loss of  $2\text{e}^-$  to the anode and loss of  $\text{H}^+$  (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).<sup>24</sup> The stability of the product, hydrido-chloride **1**, towards further oxidation at the potentials applied during electrolysis is critical to the success of the reaction.<sup>24</sup>

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  $\text{CpM}(\text{CO})_3\text{H}$  ( $\text{M} = \text{Cr}, \text{M}, \text{W}$ ),<sup>26</sup> which may involve a concerted proton-coupled electron transfer event in the tungsten case.<sup>27</sup> 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,<sup>28</sup> does not undergo oxidative hydride loss: reversible  $1\text{e}^-$  oxidation is observed in  $\text{CH}_2\text{Cl}_2$ , and  $\text{H}_2$  loss is observed in coordinating solvents.<sup>29</sup>

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

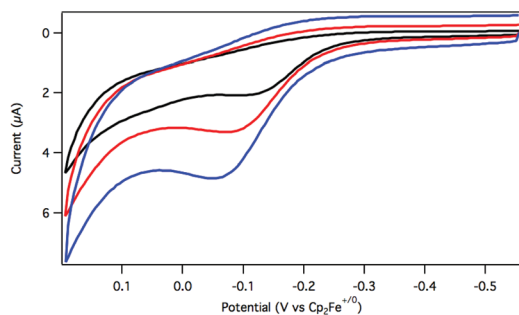
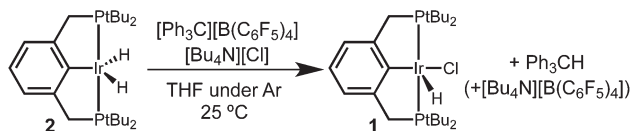
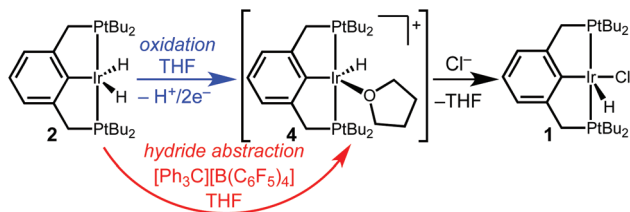


Fig. 1 Cyclic voltammetry of **2** at  $25$   $\text{mV s}^{-1}$  (black),  $100$   $\text{mV s}^{-1}$  (red), and  $250$   $\text{mV s}^{-1}$  (blue) in THF solution with  $0.1$  M  $[\text{Bu}_4\text{N}][\text{PF}_6]$  electrolyte. Glassy carbon working electrode, platinum counter electrode, Ag wire 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  $^1\text{H}$  NMR spectroscopy (Scheme 3). Triphenylmethane is also observed by  $^1\text{H}$  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  $1\text{H}^+/2\text{e}^-$  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 dichloro-methane adduct, is an active hydrosilylation catalyst.<sup>30,31</sup>

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)<sup>32–34</sup> 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  $\text{H}_2$ , but decompose under  $\text{N}_2$  or air to a mixture of products with distinct electrochemical responses.<sup>35</sup>

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