## Dalton Transactions



View Article Online

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**Cite this:** *Dalton Trans.*, 2016, **45**, 9766

Received 5th February 2016, Accepted 4th March 2016 DOI: 10.1039/c6dt00522e

www.rsc.org/dalton

## Electrochemical and chemical routes to hydride loss from an iridium dihydride<sup>†</sup>

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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<sub>3</sub>C<sup>+</sup>, connecting chemical and electrochemical hydride loss pathways.

Iridium complexes supported by tridentate <sup>R<sub>4</sub></sup>PCP (<sup>R<sub>4</sub></sup>PCP =  $\kappa^3$ -C<sub>6</sub>H<sub>3</sub>-2,6-(CH<sub>2</sub>PR<sub>2</sub>)<sub>2</sub>) 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 14e<sup>–</sup> 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 (<sup>R<sub>4</sub></sup>PCP)Ir(H)<sub>2</sub> 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.



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 (<sup>R</sup><sub>4</sub>PCP)Ir-catalyzed hydrogenation of CO<sub>2</sub> to formate,<sup>17</sup> Brookhart and Meyer developed an analogous electrochemical reduction of CO<sub>2</sub> to formate catalyzed by (<sup>tBu</sup><sub>4</sub>POCOP)Ir complexes (<sup>tBu</sup><sub>4</sub>POCOP =  $\kappa^3$ -C<sub>6</sub>H<sub>3</sub>-2,6-(OP<sup>t</sup>Bu<sub>2</sub>)<sub>2</sub>).<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 H<sub>2</sub> loss mechanism or an outer-sphere electron transfer mechanism in which a chemical oxidant (not an electrode) and a base facilitate 2H<sup>+</sup>/2e<sup>-</sup> loss.<sup>21</sup>

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<sup>†</sup>Electronic supplementary information (ESI) available: Experimental details, electrochemical data, and NMR spectra. See DOI: 10.1039/c6dt00522e

Studies of electrochemical reactions that parallel wellknown 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<sub>2</sub> atmosphere.<sup>1,22</sup> 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).<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  $[Bu_4N][PF_6]$  supporting electrolyte was assessed by a CV sweep to oxidative potentials, a single irreversible feature was observed at  $-0.08 \text{ V} vs. \text{ Cp}_2\text{Fe}^{+/0}$  (Fig. 1). No return reduction process was apparent, even as the scan rate was increased to  $1 \text{ V s}^{-1}$ .

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.<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 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<sup>-</sup> per Ir, but an aliquot analyzed by <sup>31</sup>P{<sup>1</sup>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



Fig. 1 Cyclic voltammetry of 2 at 25 mV s<sup>-1</sup> (black), 100 mV s<sup>-1</sup> (red), and 250 mV s<sup>-1</sup> (blue) in THF solution with 0.1 M [Bu<sub>4</sub>N][PF<sub>6</sub>] electrolyte. Glassy carbon working electrode, platinum counter electrode, Ag wire pseudo-reference electrode, 298 K.



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  $[Bu_4N][Cl]$  was conducted at 0.2 V  $\nu$ s. Cp<sub>2</sub>Fe<sup>+/0</sup> (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<sup>-</sup> oxidation (2.3 e<sup>-</sup> per Ir). Analysis by <sup>31</sup>P{<sup>1</sup>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 THF-*d*<sub>8</sub> showed a triplet hydride resonance far upfield ( $\delta$  –42.9) in the <sup>1</sup>H NMR spectrum that is diagnostic of (<sup>*t*Bu<sub>4</sub></sup>PCP)Ir(H)(Cl) (1). All of the <sup>31</sup>P and <sup>1</sup>H NMR signals closely matched the previously reported values.<sup>22</sup>

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<sup>+</sup> (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, hydridochloride 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  $CpM(CO)_3H$  (M = Cr, M, 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 (<sup>HBu</sup><sub>4</sub>PCP)Rh(H<sub>2</sub>), which is best described as a Rh(I) dihydrogen complex,<sup>28</sup> does not undergo oxidative hydride loss: reversible 1e<sup>-</sup> oxidation is observed in CH<sub>2</sub>Cl<sub>2</sub>, and H<sub>2</sub> 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  $[Ph_3C][B(C_6F_5)_4]$  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



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  $1\text{H}^+/2\text{e}^-$  process (*via* one of the pathways described above) to generate a reactive monohydride cation,  $[(^{tBu_4}\text{PCP})\text{Ir}(\text{H})]^+$  (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  $[(^{tBu_4}\text{POCOP})\text{Ir}(\text{H})]^+$  species, isolated as an acetone or dichloromethane adduct, is an active hydrosilylation catalyst.<sup>30,31</sup>

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)<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.

## Acknowledgements

The authors acknowledge funding from NSF Center for Enabling New Technologies through Catalysis (CENTC), CHE-1205189. The Templeton group generously provided access to an argon-filled glovebox.  $2^{\rm Solutions}$  containing hydrides 2 and 3 are stable under Ar or H<sub>2</sub>, but decompose under N<sub>2</sub> or air to a mixture of products with distinct electrochemical responses.<sup>35</sup>

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