



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

Received 5th February 2016,  
Accepted 4th March 2016

DOI: 10.1039/c6dt00522e

www.rsc.org/dalton

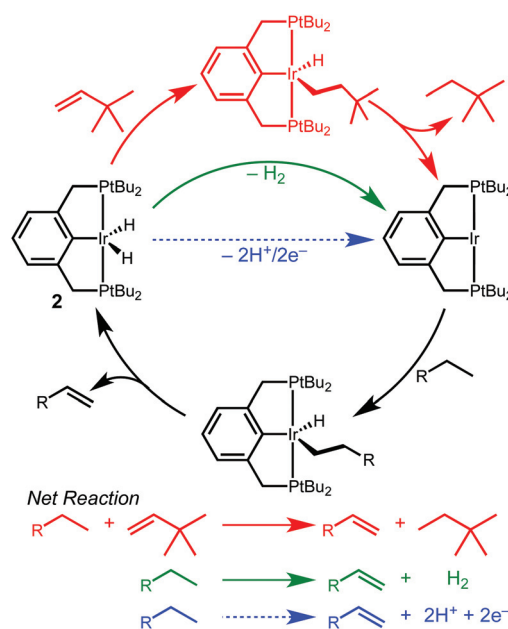
## Electrochemical and chemical routes to hydride loss from an iridium dihydride†

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

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



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.

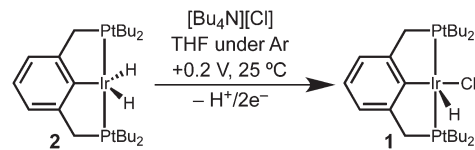
The dihydride complex was prepared according to previously reported procedures by dehydrohalogenation of  $(^t\text{Bu}_4\text{PCP})\text{Ir}(\text{H})(\text{Cl})$  (**1**) under an  $\text{H}_2$  atmosphere.<sup>1,22</sup> This procedure affords a mixture of the five-coordinate dihydride  $(^t\text{Bu}_4\text{PCP})\text{Ir}(\text{H})_2$  (**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 hydridochloride 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 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 hydridochloride **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, 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  $\text{CpM}(\text{CO})_3\text{H}$  ( $\text{M} = \text{Cr}, \text{M}, \text{W}$ ),<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 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

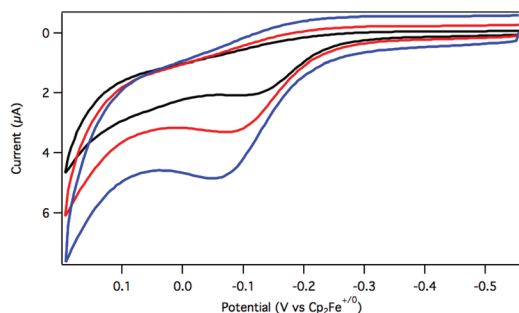
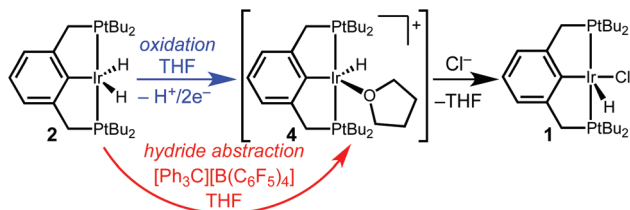


Fig. 1 Cyclic voltammetry of **2** at  $25$   $\text{mV s}^{-1}$  (black),  $100$   $\text{mV s}^{-1}$  (red), and  $250$   $\text{mV s}^{-1}$  (blue) in THF solution with  $0.1$  M  $[\text{Bu}_4\text{N}][\text{PF}_6]$  electrolyte. Glassy carbon working electrode, platinum counter electrode, Ag wire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

## 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.

## 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>

- M. Gupta, C. Hagen, R. J. Flesher, W. C. Kaska and C. M. Jensen, *Chem. Commun.*, 1996, 2083–2084.
- 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.
- A. S. Goldman, A. H. Roy, Z. Huang, R. Ahuja, W. Schinski and M. Brookhart, *Science*, 2006, **312**, 257–261.
- D. C. Leitch, Y. C. Lam, J. A. Labinger and J. E. Bercaw, *J. Am. Chem. Soc.*, 2013, **135**, 10302–10305.
- J. A. Labinger, D. C. Leitch, J. E. Bercaw, M. A. Deimund and M. E. Davis, *Top. Catal.*, 2015, **58**, 494–501.
- R. Ahuja, B. Punji, M. Findlater, C. Supplee, W. Schinski, M. Brookhart and A. S. Goldman, *Nat. Chem.*, 2011, **3**, 167–171.
- J. Choi, A. H. Roy MacArthur, M. Brookhart and A. S. Goldman, *Chem. Rev.*, 2011, **111**, 1761–1779.
- 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.
- K. B. Renkema, Y. V. Kissin and A. S. Goldman, *J. Am. Chem. Soc.*, 2003, **125**, 7770–7771.
- 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.
- P. Driscoll, E. Deunf, L. Rubin, O. Luca, R. H. Crabtree, C. Chidsey, J. Arnold and J. Kerr, *ECS Trans.*, 2011, **35**, 3–17.
- B. Rausch, M. D. Symes and L. Cronin, *J. Am. Chem. Soc.*, 2013, **135**, 13656–13659.
- C. Costentin, M. Robert and J.-M. Savéant, *Chem. Rev.*, 2010, **110**, PR1–PR40.
- 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.
- S. E. Clapham, A. Hadzovic and R. H. Morris, *Coord. Chem. Rev.*, 2004, **248**, 2201–2237.
- 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.
- R. Tanaka, M. Yamashita and K. Nozaki, *J. Am. Chem. Soc.*, 2009, **131**, 14168–14169.
- P. Kang, C. Cheng, Z. Chen, C. K. Schauer, T. J. Meyer and M. Brookhart, *J. Am. Chem. Soc.*, 2012, **134**, 5500–5503.
- P. Kang, T. J. Meyer and M. Brookhart, *Chem. Sci.*, 2013, **4**, 3497–3502.
- P. Kang, S. Zhang, T. J. Meyer and M. Brookhart, *Angew. Chem., Int. Ed.*, 2014, **53**, 8709–8713.
- 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.

