Proton Independent Electrocatalytic Transfer Hydrogenation of Styrene with [(^{tBu}PCP)Ir(H)(Cl)] and Water

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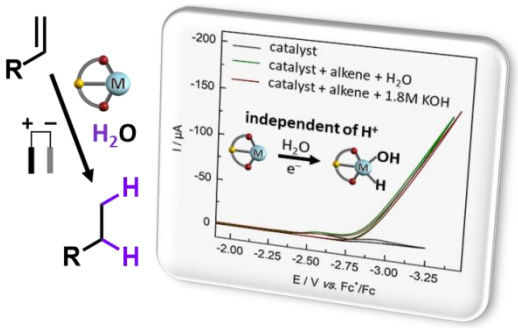
ABSTRACT: A new pathway of electrocatalytic transfer hydrogenation with neutral water as the H-donor was discovered using [(^{tBu}PCP)Ir(H)(Cl)] (**1**) as the catalyst and styrene as a model substrate in THF electrolyte. Cyclic voltammetry experiments with **1** revealed that two subsequent reductions at –2.55 and –2.84 V *vs*. Fc^+/Fc trigger the elimination of Cl^- and afford the highly reactive anionic Ir(I) hydride complex [(^{tBu}PCP)Ir(H)]$^-$ (**2**). The identity of **2** and its reactivity were further investigated by LIFDI-MS, which confirmed **2** as reactive species in the alkene hydrogenation cycle. Bulk electrolysis and chronoamperometry for electro-hydrogenation of styrene established ethylbenzene as the only product, formed with high faradaic efficiency of 96% and a turnover frequency of 1670 h^{-1} at an electrolysis potential of –3.1 V, with insignificant H_2 formation. Importantly, the electro-hydrogenation performance of **1** remained constant upon addition of KOH to the electrolyte, which suggests a reaction mechanism that is independent of free H^+. Instead, the reactive Ir-hydrides are regenerated by oxidative addition of H_2O to the complex, which creates a reaction cascade that is reminiscent of metal-hydride formation in classical transfer hydrogenation systems. As such, the herein presented study on electrocatalytic transfer hydrogenation (e-TH) with H_2O as the H-donor is different from the plethora of other electro-hydrogenation studies that operate *via* H^+ reduction, often in low-pH electrolyte. These findings may inspire the general, pH independent use of H_2O as H-donor in conjunction with electrochemistry, to replace isopropanol or formate as intrinsically reducing H-donors in the many existing examples of classical transfer hydrogenation.



INTRODUCTION

Hydrogenation of organic molecules is a process of paramount importance for the synthesis of base- and fine chemicals, pharmaceutically active compounds, and energy carriers, as well as for biomass valorization, both on industrial and laboratory scale.[1–7] To avoid challenges of handling gaseous H_2 at high temperatures and pressures necessary for chemical hydrogenation (CH), transfer hydrogenation (TH) has matured as a powerful alternative.[1,8,9] TH employs chemical H-donors such as predominantly used isopropanol or formic acid as a substitute for H_2. In both cases of CH and TH, the reduction equivalents for the net reduction of substrates during hydrogenation are provided by H_2 or the H-donor as chemical reducing agents, respectively.

For increased atom economy and cost efficiency, it would be desirable to enable H_2O as a cheap and abundant H-donor for TH instead of isopropanol or formate.[10] However, H_2O cannot provide the necessary reduction equivalents, which is why existing examples of hydrogenation with H_2O depend on the use of external reducing agents including Zn powder,[10–12] In powder,[13] or bis(pinacolato)diboron.[14,15] Electrochemistry can be an elegant substitute for such sacrificial electron donors, which has led to a third branch of hydrogenation catalysis, namely electrocatalytic hydrogenation (ECH). Remarkable examples of ECH have been reported for the conversion of alkenes to alkanes,[16,17] selective semi-hydrogenation of alkynes to alkenes,[18,19] exhaustive hydrogenation of arenes,[20–22] selective hydrogenation of arenes to 1,4-dienes,[23] hydrogenation of organic carbonyls,[24,25] or the de-oxygenation of biomass.[26–28] ECH has even proven to be a powerful method for the synthesis of selectively deuterated alkenes.[29] Both, noble metal electrodes and molecular catalysts are employed for these conversions.[30] The dominant common aspect of all these examples is that they rely on H^+ reduction, often in highly acidic electrolyte. The working principle is to either generate H_2 or surface hydrides *in situ* at the electrode for immediate consumption by a coupled hydrogenation reaction.[31] Examples of molecular ECH catalysts likewise operate by formation of reactive metal-hydride species *via* H^+ reduction, with a remarkable exception by Peters and coworkers, who elegantly separated redox reactive metal center and proton acceptor site in their anilinium cobaltocene catalyst.[25] While these existing systems succeed at avoiding external H_2 gas feeds or sacrificial electron donors for hydrogenation, several drawbacks impede application. In many cases faradaic efficiencies for hydrogenated products are low,

given that H_2 evolution (HER) remains the dominant process.[32] Also poor solubility of most relevant organic substrates in acidic aqueous electrolytes requires less convenient emulsion electrolysis with the use of surfactants.[33,34] The requirement of high proton activity may interfere with functional groups of substrates that cannot tolerate low pH, and the harsh conditions of acidic electrolyte can lead to side reactions. Exemplarily, for ECH of toluene to methylcyclohexane on Pt electrodes in acid electrolyte, side reactions as severe as C–C bond cleavage to yield CH_4 and cyclohexane were observed.[33] Finally and importantly, with H_2O oxidation (OER) at the counter electrode, low pH electrolytes cause high overpotentials, catalyst degradation, and sluggish kinetics of the coupled oxidation reaction.[35] This generates a high cell potential and limits overall achievable process efficiencies. For the multitude of these reasons, it would be desirable to establish ECH reactions that proceed in organic electrolyte with neutral pH water, or even in alkaline media, instead of under acidic conditions.

Drawing from extensive literature on TH,[1,8] and inspired by examples that show metal-hydrides can also be formed by oxidative addition of H_2O to low-valent transition metal complexes instead of by H^+ reduction,[36] we hypothesized that a proton independent pathway of electrocatalytic transfer hydrogenation (e-TH) should be accessible. For the herein presented proof of principle study, the electrochemically accessible redox reactivity of the Ir(III) pincer complex [(^{tBu}PCP)Ir(H)(Cl)] (**1**) and electrochemically triggered chemical reactions were investigated. The e-TH performance of **1** was monitored upon addition of H_2O as the H-donor under neutral and alkaline conditions, with styrene as a model substrate in organic electrolyte. Successful production of ethylbenzene indeed suggested independence of H^+ activity in the electrolyte. Mechanistic studies and stoichiometric control reactions revealed that the e-TH at room temperature proceeds *via* an EC mechanism, in which a fleeting anionic Ir(I) hydride complex is electro-generated as the key reactive species. The combined results suggest that the iridium hydride is regenerated by oxidative addition of water in reminiscence of classical transfer hydrogenation. This represents a major difference compared to existing electro-hydrogenation catalysts that are principally driven by *in situ* proton reduction, and may inspire the general development of such e-TH reactivity.

RESULTS AND DISCUSSION

[(^{tBu}PCP)Ir(H)(Cl)] (**1**, with ^{tBu}PCP–H = 1,3-bis((di-tert-butylphosphino)methyl)benzene) was synthesized according to literature procedures,[37,38] and studied by cyclic voltammetry (CV) to elucidate its ECH reactivity. At first, a CV of **1** was recorded in organic electrolyte (0.1 M Bu_4NPF_6 (tetrabutylammonium hexafluorophosphate) in THF, all potentials referenced *vs*. Fc^+/Fc) to reveal fundamental redox reactivity of the complex (Figure 1). In the examined potential window between +0.3 and –3.3 V (SI, Figure S1),

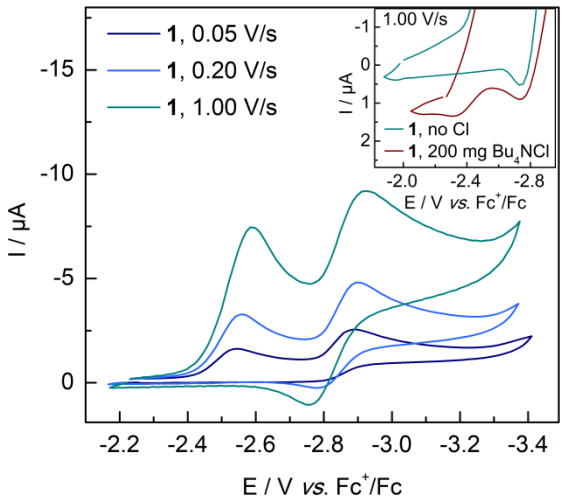


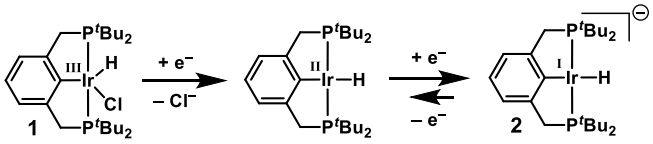
Figure 1. CV of **1** (4 mg) in THF with Bu_4NPF_6 (350 mg in 3 mL) recorded at scan rates between 0.05 and 1 V/s using a GC disc (1 mm) working electrode, a Pt wire counter electrode, and a silver wire pseudo reference electrode. Inset: Control experiment showing that upon addition of 200 mg of Bu_4NCl to the electrolyte solution, also the first reduction event becomes quasi reversible.

1 features an irreversible reduction at a peak potential of –2.55 V, and a second reduction event at a half wave potential of –2.84 V, which shows quasi-reversibility at scan rates above 0.1 V/s (Figure 1). The first reduction event is assigned to an Ir(III)/Ir(II) reduction, which generates a fleeting anionic Ir(II) complex that instantly seeks charge neutrality by eliminating a Cl^- ligand to yield the proposed intermediate Ir(II) species [(^{tBu}PCP)Ir(H)]. This hypothesis is supported by the fact that the addition of chloride ions to the electrolyte in form of excess Bu_4NCl (tetrabutylammonium chloride) renders the reduction at –2.55 V also quasi reversible at high scan rates (inset Figure 1 and SI, Figure S2), as Cl^- dissociation from the reduced Ir complex is hampered (or re-coordination of Cl^- is favored) in media with high chloride activity.

The second reduction event at –2.84 V is ascribed to an Ir(II)/Ir(I) couple, in which the proposed Ir(II) complex [(^{tBu}PCP)Ir(H)] is reduced by another electron. At scan rates below 0.1 V/s, this reduction event is also irreversible, likely because of the well-known high reactivity of Ir(I) complexes that even activate C–H bonds of alkanes.[39] However, the fact that at higher scan rates the second reduction event becomes more and more reversible (see Figure 1), strongly suggests that the Ir(I) complex formed remains an anionic species [(^{tBu}PCP)Ir(H)]$^-$ (**2**) that does not lose its hydride ligand. In fact, based on quantum chemical calculations by Ahlquist *et al.* an anionic hydride species related to **2**, but in a (^{tBu}POCOP)$^-$ pincer ligand environment, was previously proposed as the active species for electrochemical CO_2 reduction to formate with the POCOP analogue of complex **1**.[40,41] Further experimental evidence for the existence of such previously only theoretically proposed anionic Ir(I) hydrides like **2**, is now provided by

negative mode LIFDI-MS data (liquid injection field desorption/ionization mass spectrometry) obtained from *in situ* reduced solutions of **1** that were treated with electride solutions of $[K(2.2.2\text{-cryptand})]^+$ as a source of solvated electrons (SI, section 2 for details).[42] Indeed, a prominent molecular ion peak at 587.25 m/z with the expected isotope pattern was observed as experimental evidence for the formation of **2** upon chemical two-electron reduction of **1** (SI, Figure S16). Accordingly, the electrochemical response of **1** presented in Figure 1 is interpreted as shown in Scheme 1.

Scheme 1. Proposed Underlying Reactivity of the two Consecutive Electrochemical Reduction Events Observed for Complex 1.



Curious to explore the chemical reactivity of the electrochemically produced anionic Ir(I) hydride **2**, we investigated the electrocatalytic hydrogenation of styrene as a model alkene with water as the H-donor. In analogy to quantum chemical calculations by Ahlquist *et al.* who predict CO_2 insertion into Ir–H bonds of anionic hydrides such as **2**, a direct activation of alkenes *via* formation of Ir(I)-alkyls could occur.[40] Alternatively, according to Jensen *et al*. Ir(I) ions in $(^{tBu}PCP)^-$ ligand environment can undergo oxidative addition of H_2O to form a reactive hydroxo-hydrido species.[43] For **2**, the oxidative addition of water

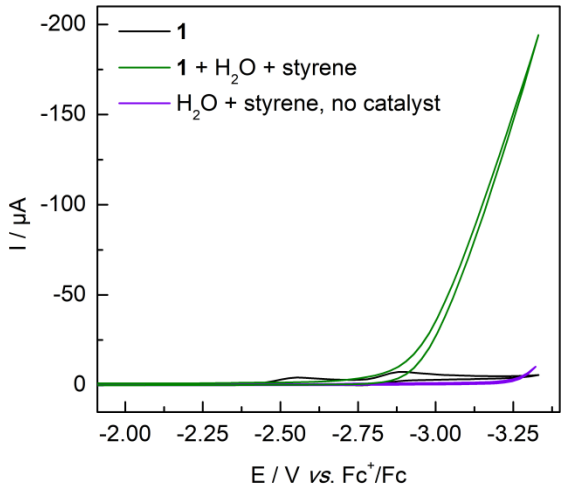


Figure 2. CV of **1** (4 mg) in THF with Bu_4NPF_6 (350 mg in 3 mL) recorded at a scan rate of 0.2 V/s using a GC disc (1 mm) working electrode, a Pt wire counter electrode, and a silver wire pseudo reference electrode (black trace). The green trace shows the catalytic current response after addition of 100 µL degassed H_2O and 100 µL styrene. The purple trace shows the CV response of the identical electrolyte solution with H_2O and styrene, but in absence of catalyst **1**.

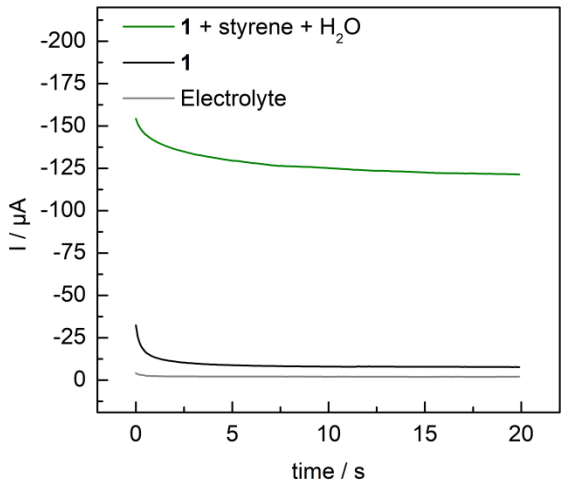


Figure 3. Chronoamperometry data obtained at an applied potential of –3.1 V for the electrolyte (3.00 mL of 0.1 M Bu_4NPF_6 in THF with 100 µL of H_2O) (grey), after addition of 3 mg **1** (black), and after addition of 100 µL styrene (green) to reach catalytic conditions.

would yield the fleeting anionic Ir(III) complex $[(^{tBu}PCP)Ir(H)_2(OH)]^-$, proposed to spontaneously decay into charge neutral complex $[(^{tBu}PCP)Ir(H)_2]$,[40] a well-known species active for alkene hydrogenation.[44] Besides activation of H_2O molecules, the reduction of free H^+, as in classical ECH, could occur as an alternative pathway to form the dihydride complex $[(^{tBu}PCP)Ir(H)_2]$ from anionic **2**.[45,46] Accordingly, multiple reaction cascades for alkene hydrogenation can be envisioned with **2** as the active species and water as the H-donor. To evaluate the actual ECH reactivity of **1** and associated reactive species, we herein provide experimental characterization along with mechanistic consideration for the different possible reaction pathways.

Cyclic voltammetry experiments with catalyst precursor **1**, styrene, and water as the H-donor indeed yielded a strong catalytic current, visibly tied to the Ir(II)/Ir(I) reduction potential (Figure 2). Control experiments with either of the three components alkene, H_2O or catalyst missing did not yield a comparable catalytic current response (SI, Figure S3). Most importantly, the simple addition of water to complex **1** did also not facilitate catalytic water reduction to produce H_2, as evidenced by the lack of a catalytic current response in CV (SI, Figure S3), and no significant amount of H_2 being detected in GC-RGD headspace analysis (gas chromatograph with reducing gas detector) after bulk electrolysis experiments (SI, Figures S4 and S21). The desirable lack of competing H_2 evolution is likely due to the literature known water stability of iridium hydride functionalities.[43,45,47] Bulk electrolysis experiments performed at –3.1 V *vs*. Fc^+/Fc in the presence of styrene, H_2O, and catalyst precursor **1** revealed the formation of ethylbenzene as the hydrogenated product of styrene at high faradaic efficiency of 96% with a TON of 93, based on

^{1}H NMR analysis of the electrolyte solution after electrolysis (SI, Figures S5 and S10).

A turnover frequency (TOF) of 1670 h^{-1}, was determined for the hydrogenation of styrene with **1**, based on chronoamperometry experiments at –3.1 V following a protocol reported by Stahl and Rafiee (Figure 3 and eq. 1).[48]

$$TOF = \frac{[(Q_{cat} - Q_1) \times FE] \times 3600}{(Q_1 - Q_e) \times n \times t} \qquad (1)$$

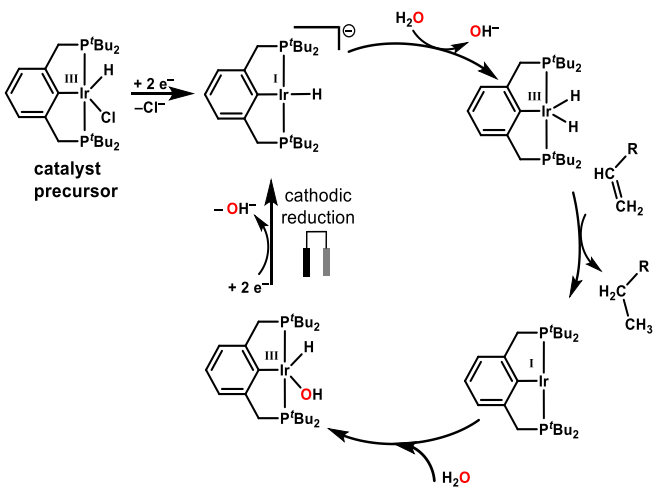
In eq. (1), Q_{cat} corresponds to the charge passed under catalytic conditions, Q_1 corresponds to the charge passed in the presence of catalyst **1** without substrate, Q_e corresponds to the charge passed for the blank electrolyte solution. *FE* is the faradaic efficiency as determined by bulk electrolysis (*vide supra*), *n* is the number of electrons transferred to produce one molecule of product (here: ethylbenzene, *n* = 2), and *t* is the time over which the charges were passed. Respective charges were determined by integrating over the experimental electrolysis currents as shown in Figure 3, excluding all charges passed during the first second, in order to eliminate capacitive current effects.

Together, the high selectivity and faradaic efficiency confirmed the excellent performance of catalyst **1** for electro-hydrogenation, which prompted us to further investigate the underlying catalytic reactivity.

Mechanistic Considerations. In order to understand the electrocatalyst's working principle, stoichiometric control reactions were performed. Based on the combined results (*vide infra*) and quantum chemical support published for CO_2 reduction on the related POCOP system,[40,45,46] the reaction cascade shown in Scheme 2 is proposed as a likely mode of operation for the electro-hydrogenation of alkenes with complex **1**.

As already elucidated from CV analysis (*vide supra*), precatalyst **1** is converted into its active form **2**, by electrochemical reduction. Subsequently, **2** can either react

Scheme 2. Proposed Reaction Cascade for Electrocatalytic Hydrogenation of Styrene with Water.



with an alkene to form an anionic Ir(I) alkyl species, in analogy to quantum chemical calculations for CO_2 insertion,[40,45] or **2** could react with H_2O to yield charge neutral Ir(III) dihydride complex [(^{tBu}PCP)Ir(H)$_2$] under elimination of OH^-. In order to experimentally assess the feasibility of both pathways, solutions of Ir(III) complex **1** were again reduced chemically by addition of approximately two equivalents of solvated electrons in form of [K(2.2.2-cryptand)]$^+$ electride solution (SI, section 2 for details). The *in situ* generated Ir(I) species was quenched by addition of H_2O, and subsequently analyzed by ^{1}H NMR (SI, Figure S13) and LIFDI-MS (SI, Figure S18), to gain experimental insight into underlying reaction cascades of ECH with **1**. Quenching *in situ* generated **2** in THF-d_8 by addition of H_2O afforded the distinctive hydride signals of Ir(III)-dihydride complex [(^{tBu}PCP)Ir(H)$_2$] at –19.53 ppm,[49] as predicted by quantum chemical calculations,[40,45,46] together with unidentifiable decay products of highly reactive species **2** (SI, Figure S13). While the hydrogenation of alkenes by [(^{tBu}PCP)Ir(H)$_2$], as shown in Scheme 2 is well documented,[1] two reaction pathways were previously discussed for its formation from anionic Ir(I) hydrides like **2**; namely the oxidative addition of H_2O with subsequent elimination of OH^- from the anionic species [(^{tBu}PCP)Ir(H)$_2$(OH)]$^-$, or reductive O–H bond cleavage by **2** from coordinated H_2O under OH^- elimination.

For related Ir–POCOP complexes in acetonitrile, calculations by Ahlquist *et al*. yielded an activation barrier for reductive O–H bond cleavage that is energetically favored by *ca*. 36 kcal mol^{-1} compared to classical oxidative addition of H_2O; thus, rendering oxidative addition unlikely according to the transition state they found.[40] However, the anionic intermediate species analogous to [(^{tBu}PCP)Ir(H)$_2$(OH)]$^-$ that oxidative addition of H_2O to **2** would afford, was calculated at merely 2.4 kcal mol^{-1} higher energy than the transition state for reductive O–H bond cleavage. Utilizing our new preparative protocol for *in situ* synthesis of **2** and subsequent characterization of short-lived species by negative mode LIFDI-MS, we therefore investigated the potential formation of [(^{tBu}PCP)Ir(H)$_2$(OH)]$^-$ experimentally.

Interestingly, quenching samples of **2** with H_2O generated a molecular ion peak at 603.25 m/z, with a matching isotope pattern for the species [(^{tBu}PCP)Ir(OH)]$^-$ (Figure S18) as a potential fragment of [(^{tBu}PCP)Ir(H)$_2$(OH)]$^-$ that forms upon H_2 elimination. This possibility is supported by LIFDI-MS control experiments with independently synthesized tetrahydride species [(^{tBu}PCP)Ir(H)$_4$] (**3**), for which H_2 elimination was also observed, due to high vacuum and high temperatures on the LIFDI instrument's emitter (SI, Figure S19). Alternative formation of [(^{tBu}PCP)Ir(OH)]$^-$ v*ia* simple protonation of the hydride functionality in **2** to release H_2 with exchange of the hydride ligand for OH^- could explain the LIFDI-MS result. This pathway, however, is not supported by ^{1}H NMR reaction control performed in sealed J-Young NMR tubes, which did not show any H_2 formation. Hence, we consider oxidative addition of H_2O

to complex **2** plausible under our experimental conditions, likely in parallel to the widely accepted reductive O–H bond cleavage pathway to form Ir(III) dihydride [(^{tBu}PCP)Ir(H)$_2$].

Upon formation of [(^{tBu}PCP)Ir(H)$_2$], the hydrogenation cycle is proposed to follow the classical established pathway for hydrogenation of non-polar substrates by redox reactive metal catalysts,[1] which yields the Ir(I) complex [(^{tBu}PCP)Ir] as the next intermediate. [(^{tBu}PCP)Ir] is known to undergo oxidative addition of H_2O,[40,43] which replenishes the metal-hydride functionality *via* formation of [(^{tBu}PCP)Ir(H)(OH)]. Ahlquist and coworkers suggest that this formal oxidative addition of H_2O to Ir(I) proceeds through an Ir(I)-aquo intermediate [(^{tBu}PCP)Ir(H_2O)],[40] from which hydride formation occurs *via* proton relay across a water cluster around the Ir center. A two-electron electrochemical reduction of the Ir(III) hydroxo hydrido complex then regenerates the reactive Ir(I) hydride **2**, to close the catalytic cycle.

It was previously proposed that for CO_2 reduction with Ir pincer complexes, an alternative mechanism could exist in which CO_2 inserts into the Ir–H bond of anionic Ir(I) hydride like **2**, to form the C–H bond of formate.[40,45] In context of the herein presented ECH of styrene this implies the possibility for an alternative catalytic cycle, in which styrene inserts into the Ir-H bond of **2**. Investigating this possibility, LIFDI-MS quenching experiments were again employed, in which *in situ* generated **2** was reacted with styrene to potentially form the anionic alkyl species [(^{tBu}PCP)Ir(phenylethyl)]$^-$. Experimental results do not show a molecular ion peak in accordance with [(^{tBu}PCP)Ir(phenylethyl)]$^-$; thus, we conclude that despite thermodynamic feasibility for CO_2 insertion into the Ir-H bond of **2**, styrene does not react analogously as a dominant pathway, potentially because of steric hindrance of the larger substrate.

Additional NMR control reactions, in which Ir(III) complex **1** was reacted with one equivalent of styrene and H_2O in THF-d_8 yielded no detectable ethyl benzene or an identifiable iridium alkyl complex (SI, Figures S11 and S12); thus, excluding this complex as the active species during the catalytic cycle.

Importantly, the combined results on the reactivity of **1** suggest a so far unique electro-hydrogenation cycle that is driven by (formal) oxidative addition of H_2O rather than by the common path of H^+ reduction from a Brønsted acid. If the reactive hydride species are indeed regenerated by H_2O activation rather than by H^+ reduction, the catalytic current in CV experiments should be independent of proton activity. In line with this assumption, CV control experiments in which KOH was added to the electrolyte solution under catalytic conditions, to drastically reduce the activity of H^+, did show little to no effect on the catalytic current response (Figure 4). Even though the pH value is not a well-defined concept in organic solvents with small amounts of water, addition of KOH as a strong Brønsted

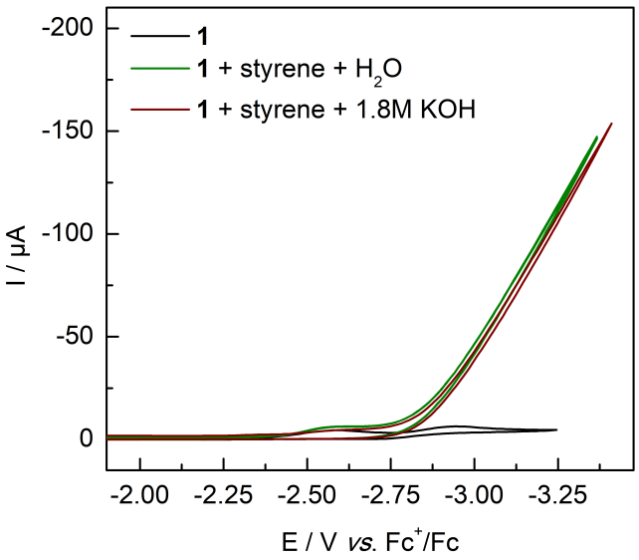


Figure 4. CV of **1** (3 mg) in THF with 0.1 M Bu_4NPF_6 recorded at a scan rate of 0.2 V/s using a GC disc (1 mm) working electrode, a Pt wire counter electrode, and a silver wire pseudo reference electrode. The black trace shows complex **1** without substrates, the green trace shows the catalytic current originating in the presence of H_2O and styrene, the brown trace shows the catalytic current response when KOH is added to the electrolyte to reduce proton activity.

base severely reduces H^+ activity in the electrolyte, while the activity of H_2O molecules remains high, independent of KOH addition. Accordingly, the control experiment presented in Figure 4 suggest a reaction mechanism for electro-hydrogenation with **1** that is indeed mediated by H_2O activation rather than by H^+ reduction, as proposed in Scheme 2.

This is contrasting the previously reported reaction mechanism for CO_2 reduction to formate by iridium pincer complexes in acetonitrile as proposed by Brookhart and coworkers. In their case, a *cationic* Ir(III) hydride is reported as the electro reactive species, which undergoes a concerted two-electron reduction to Ir(I) at a mild reduction potential of –1.4 V *vs*. NHE (corresponding to *ca*. –2.0 V *vs*. Fc^+/Fc).[50] The electro-generated Ir(I) was then reported to react with H^+ from water as a simple proton source to generate an Ir(III) di-hydride as the hydrogenating species for CO_2 reduction.[41]

Instead, the herein reported example of electrocatalytic alkene hydrogenation uses H_2O as H-donor in the sense of transfer hydrogenation. Reactive metal hydrides driving the catalytic hydrogenation are formed *via* intramolecular activation of the coordinated H-donor water, instead of by simple proton reduction. This renders the reported model system distinctly different from the majority of electro-hydrogenation examples reported in the literature, which rely on stoichiometric use of protons from Brønsted acids and thus, low pH electrolyte. Building on this finding, electrocatalytic transfer hydrogenation (e-TH) with water is an auspicious concept to be explored in more detail in the

future. Despite the potential to enable electrohydrogenation of substrates that cannot tolerate acidic media, it should be emphasized that electrohydrogenation at the working electrode requires water oxidation at the counter electrode as the second half reaction. As known from the Pourbaix diagram, H_2O oxidation is easier at high pH; thus, e-TH with water molecules instead of H^+ paves the way to operate electrolysis at drastically reduced cell potentials, given that water oxidation potentials are reduced by ~ 830 mV when switching from pH = 0 to pH = 14 electrolytes.[51] Acknowledging that both necessary overpotentials of e-TH half reaction and H_2O oxidation contribute to the cell potential, it is clear that catalyst **1** can merely serve as a model towards energy efficient e-TH. For actually energy efficient processes, hydrogenation overpotentials must be drastically reduced by catalyst design in the future.

CONCLUSIONS

In summary, the electrochemical reactivity of the Ir(III) complex [(^{tBu}PCP)Ir(H)(Cl)] (**1**) was investigated in THF electrolyte, which revealed the formation of anionic Ir(I) hydride complex [(^{tBu}PCP)Ir(H)]$^-$ (**2**) upon electrochemical reduction at –2.84 V *vs*. Fc^+/Fc. The existence of **2**, previously only postulated based on quantum chemical calculations, was now confirmed by LIFDI-MS experiments with *in situ* reduced samples of **1**. Cyclic voltammetry experiments revealed that **2** mediates electrocatalytic transfer hydrogenation (e-TH) of styrene as a model substrate with pH neutral H_2O as the H-donor and electrons provided by a glassy carbon working electrode as external reducing agent. Chronoamperometry experiments confirmed a high faradaic efficiency of 96% for the conversion of styrene to ethylbenzene as the only product according to ^{1}H NMR, with a turnover frequency of 1670 h^{-1} at an electrolysis potential of –3.1 V. Control experiments in which KOH was added to the electrolyte, in order to reduce the activity of H^+ during electro hydrogenation, yielded the same catalytic current as the addition of pure water. This result strongly suggests that the newly found e-TH reactivity of **1** as presented herein, is independent of protons and mediated by oxidative addition of H_2O to Ir(I) for generation of reactive iridium hydride species. As such, this H^+ independent example of e-TH may inspire pathways to generally enable H_2O as sustainable and abundant H-donor in the broad context of transfer hydrogenation. For electrocatalytic reaction design in general, the H^+ independency of e-TH with water will allow to optimize conditions of the reaction medium (electrolyte) for substrate compatibility and to support the OER at the counter electrode, without compromising catalytic performance at the working electrode.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information contains experimental details, synthesis procedures, relevant NMR data, additional electrochemical experiments and LIFDI-MS details.

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Notes

The authors declare no competing financial interest.

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