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Communication

Electroreduction of Benzaldehyde with a Metal–Ligand Bifunctional Hydroxycyclopentadienyl Molybdenum(II) Hydride

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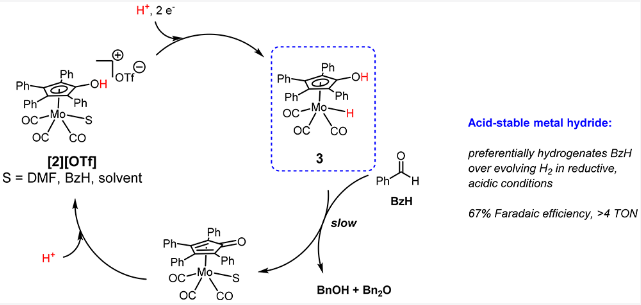
ABSTRACT: An electrocatalytic system for the hydrogenation of benzaldehyde to benzyl alcohol and dibenzyl ether is described. The molybdenum hydride $(C_5Ph_4OH)Mo(CO)_3(H)$ (**3**) is shown to be the actively hydrogenating species. This hydride is demonstrated to be remarkably acid-stable, leading to a *ca.* 67% Faradaic efficiency for aldehyde reduction over hydrogen evolution despite strongly acidic and reducing conditions. Hydride **3** is prepared via 1-proton-2-electron reduction of cation $[(C_5Ph_4OH)Mo(CO)_3(CH_3CN)][OTf]$ ([**2**][**OTf**]), which is generated by protonation of the Mo(0) precursor $[(C_5Ph_4O)Mo(CO)_3(L)]$(**1**).



INTRODUCTION

Electrocatalytic hydrogenation is a promising alternative to thermal catalytic hydrogenation for the upgrading and refining of biofuels[1−9] as well as a strategy for the storage of energy[10,11] in liquid organic hydrogen carriers.[12,13] Despite considerable effort, advances in electrocatalytic hydrogenation have been limited by challenges in the development of stable catalysts that exhibit a high selectivity for hydrogenation over hydrogen evolution.[3] While several electroreduction systems have been reported that exhibit high selectivities for hydrogenation over hydrogen evolution,[4,8,9,14] a mechanistic understanding of the factors that lead to high Faradaic efficiencies are limited.[4,5,8,15]

The thermodynamic challenges for selective electrocatalytic reduction are formidable; the thermodynamic potential for the reduction of acetone or other organic substrates is so similar to that of the reduction of protons to hydrogen ($\Delta E = 0.13$ V, eq 1) that any selectivity based purely on thermodynamics would be extremely challenging. The kinetics are critical; for any selective electrocatalytic hydrogenation catalyst, the rate of substrate hydrogenation must be higher than that of hydrogen evolution even when both are thermodynamically favorable.[16−18] For heterogeneous electrode catalysts, recent insights suggest that particular step edges or surface sites can exhibit selectivities for electrocatalytic hydrogenation,[4,5] particularly for situations where the substrate binds to the surface sites more avidly than hydrogen atoms (H_{abs}), leading to high surface coverages of the substrate.[8]

$$R(R')C{=}O \ + 2\,H^+ \ + 2\,e^- \rightleftharpoons R(R')CH{-}OH \qquad E^0 = 0.12\ V^{16}\ \text{(vs. NHE, R,R' = Me)} \quad (1)$$

Molecular electrocatalysts provide an opportunity to investigate the molecular details of individual proton and electron transfer steps and to test different hypotheses that might lead to high selectivities for electroreduction vs hydrogen evolution. To this end, we became interested in testing whether bifunctional molecular catalysts,[19] which have proven effective for transfer hydrogenation, might prove effective as selective electrohydrogenation catalysts (Figure 1). Metal hydrides are common intermediates in molecular electrohydrogenation catalytic cycles; competitive protonation of the metal hydride can lead to hydrogen evolution, overwhelming the desired reduction of the organic carbonyl.

The potential advantages of bifunctional catalysts for electrohydrogenation are based on the hypothesis that hydrogen evolution from the reduced, substrate-reactive form should be disfavored due to the electronic and geometric separation of the hydrogen equivalents LX-H and M-H. In addition, to the extent that bifunctional M-H/LX-H activation[19] might facilitate reduction of the carbonyl, the selectivity for reduction of the substrate over hydrogen evolution (by protonation of the metal hydride) might be enhanced.

To test this hypothesis, we targeted the Shvo type[20−23] Mo complex $(C_5Ph_4OH)Mo(CO)_3(H)$ **3**[24] as a candidate for an acetone electroreduction catalyst. The Mo complex **3** had been previously shown to reduce acetone to isopropanol stoichiometrically and to function as a transfer hydrogenation catalyst for the reduction of ketones and aldehydes with isopropanol as a hydrogen donor.[24]

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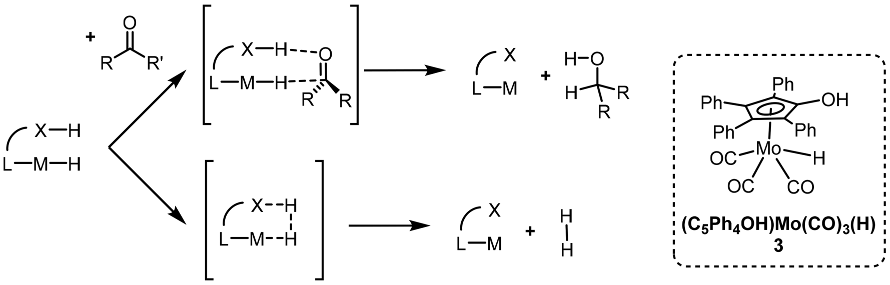
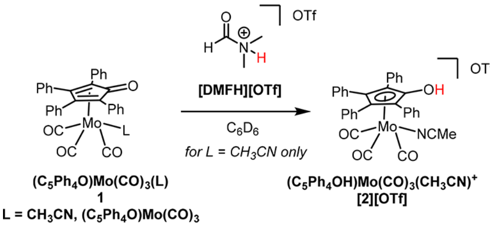


Figure 1. Competitive hydrogenation of carbonyl compounds vs hydrogen evolution with bifunctional catalysts (L = dative atom in backbone, X = O, NH).

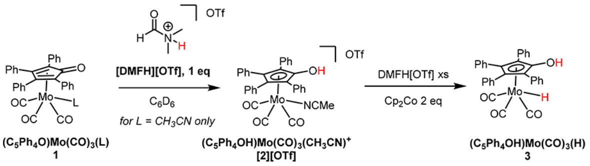
RESULTS AND DISCUSSION

A sample of the Mo(0) compound $[(C_5Ph_4O)Mo(CO)_3(L)]$ was prepared following the literature procedure[25] and was used without further purification. Rigorous analysis of the crude product by multiple characterization methods revealed it to be a mixture of the acetonitrile adduct $(C_5Ph_4O)Mo(CO)_3(CH_3CN)$ **1a** and the related, known[25] Mo^0 dimer $[(C_5Ph_4O)(CO)_3Mo]_2$ **1b** (see Supporting Information (SI)).

Treatment of a freshly prepared sample of $[(C_5Ph_4O)Mo(CO)_3(L)]$ with [DMFH][OTf] in toluene resulted in the formation of a precipitate. Washing of this precipitate with toluene and recrystallization from a mixture of dichloromethane/hexanes afforded red-orange crystals. Notably, treatment of a sample of pure dimer $[(C_5Ph_4O)(CO)_3Mo]_2$ **1b** with [DMFH][OTf] shows no protonation activity by ^{1}H NMR (SI, Figure S12), suggesting that exclusively $(C_5Ph_4O)Mo(CO)_3(CH_3CN)$ **1a** undergoes productive protonation. Microanalysis and high-resolution mass spectrometry (HRMS) of these crystals are consistent with the formation of the cationic $[(C_5Ph_4OH)Mo(CO)_3(CH_3CN)][OTf]$, ([**2**][**OTf**]), with coordinated acetonitrile and outer-sphere triflate (eq 2).[24] The complex [**2**][**OTf**] is soluble in chlorinated solvents and acetonitrile, sparingly soluble in aromatic solvents and is air-stable over several hours as a solid or in dichloromethane solution, with noticeable darkening of the solid or its solutions after a period of several days. To assess the feasibility of generating a Mo(II) hydride from the protonation and reduction of Mo(0) carbonyls, a sample of $[(C_5Ph_4O)Mo(CO)_3(L)]$ was dissolved in C_6D_6 and treated with excess [DMFH][OTf], then two equivalents of cobaltocene (Cp_2Co) as a chemical reductant. ^{1}H NMR analysis of the resulting solution revealed a new resonance at δ −3.83 ppm, consistent with the formation of a Mo−H (eq 3).[24] High-resolution mass spectrometry (electrospray ionization, acetonitrile, negative detection mode, −3.0 kV) of an aliquot of this C_6D_6 solution corroborates our successful generation of $(C_5Ph_4OH)Mo(CO)_3(H)$ **3** (SI, Figure S7; M − [H$^+$], *m/z* calcd 567.0488, obsd 567.0483) from **1**, acid, and cobaltocene. The reductive protonation of $[(C_5Ph_4OH)Mo(CO)_3(CH_3CN)][OTf]$, ([**2**][**OTf**])] was also investigated and monitored by ^{1}H NMR spectroscopy. In the presence of 2 equiv of Cp_2Co, protonation of [**2**][**OTf**] with either [DMFH][OTf] (1.1 equiv) or $HBF_4{\cdot}Et_2O$ (1.5 equiv) in C_6D_6 afforded $(C_5Ph_4OH)Mo(CO)_3(H)$ **3** in yields of 48% or 65%, respectively. The **3** so generated is capable of reducing benzaldehyde to benzyl alcohol (SI, Figure S11). Reductive protonation of [**2**][**OTf**] with excess acid (5.1 equiv. $HBF_4{\cdot}Et_2O$, 2 equiv of Cp_2Co) afforded a lower yield of the Mo−H **3** (22%), but when this solution was monitored by ^{1}H NMR over the course of 3 h, the amount of **3** in solution did not decrease appreciably (final yield 19%). This latter result suggests that the Mo−H **3** is relatively stable in the presence of acid. This conclusion is corroborated by the fact that **3**, independently prepared from **1** and excess isopropanol in benzene, is unreactive toward excess [DMFH][OTf] (SI, Table S2). The incomplete conversion of [**2**][**OTf**] to **3** is likely a consequence of competitive protonation of Cp_2Co and hydrogen evolution under these conditions.[26,27]



(2)



(3)

The cyclic voltammetry of **1** (∼1 mM) in *ortho*-difluorobenzene (ODFB) reveals an irreversible reductive feature at *ca.* −1700 mV vs Fc$^{+/0}$ on a cathodic sweep at 100 mV/s (SI, Figure S13). Addition of 1.0 mM [DMFH][OTf] to this solution results in the appearance of a new reductive wave at −1000 mV vs Fc$^{+/0}$, which we tentatively assign as the two-electron-one-proton reduction of [**2**][**OTf**] (formed *in situ* after the addition of acid) to **3**.

This same feature appears in the cyclic voltammogram of independently prepared [**2**][**OTf**] with excess acid (SI, Figure S14A). In the absence of acid, [**2**][**OTf**] displays a reductive feature at a slightly more anodic potential, approximately −900 mV vs Fc$^{+/0}$ (SI, Figure S14A). Voltammetric scan rate studies under acid-free conditions reveal that this feature only becomes quasi-reversible at high (1+ V/s) rates Figures 2, SI, S15), possibly indicative of a fast, reduction-induced rearrangement of the [**2**]$^+$ fragment, such as ligand dissociation. These reduction events are independent from that for [DMFH][OTf] alone (SI, Figure S14B).

Controlled-potential electrolysis of a 5 mM ODFB solution of [**2**][**OTf**] and 6 mM [DMFH][OTf] at −700 mV (vs Fc$^{+/0}$) in the presence of 100 mM $TBAPF_6$ was carried out for 1 h. An aliquot of the resulting solution was diluted into C_6D_6 and analyzed by ^{1}H NMR with solvent suppression of the ODFB resonances (see SI). A resonance at δ −4.04 ppm was

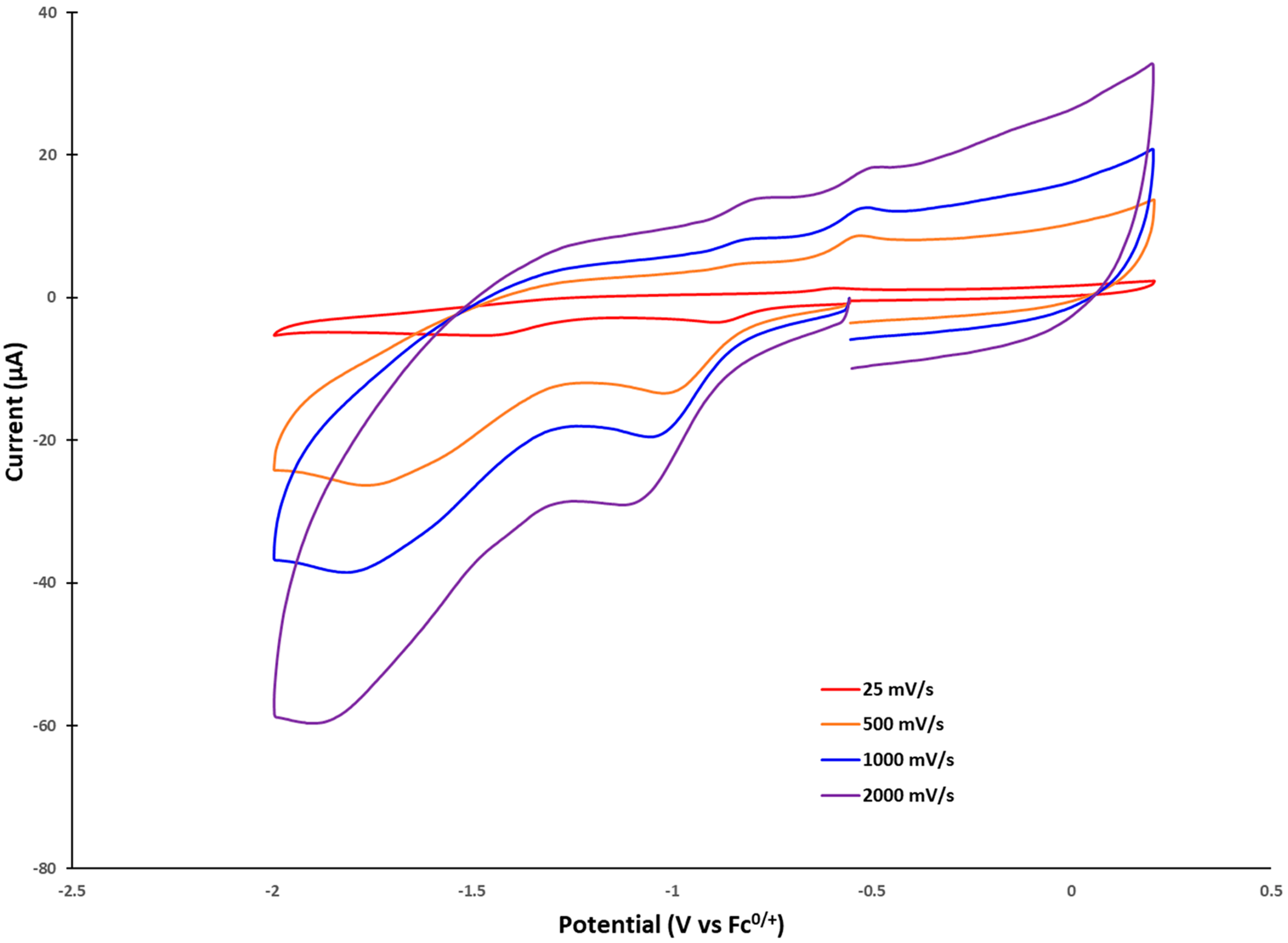


Figure 2. A selection of traces from a CV scan rate study of [**2**][**OTf**] in 5 mL of 100 mM $^{n}Bu_4NPF_6$ in ODFB. The complete study is available in SI, Figure S15.

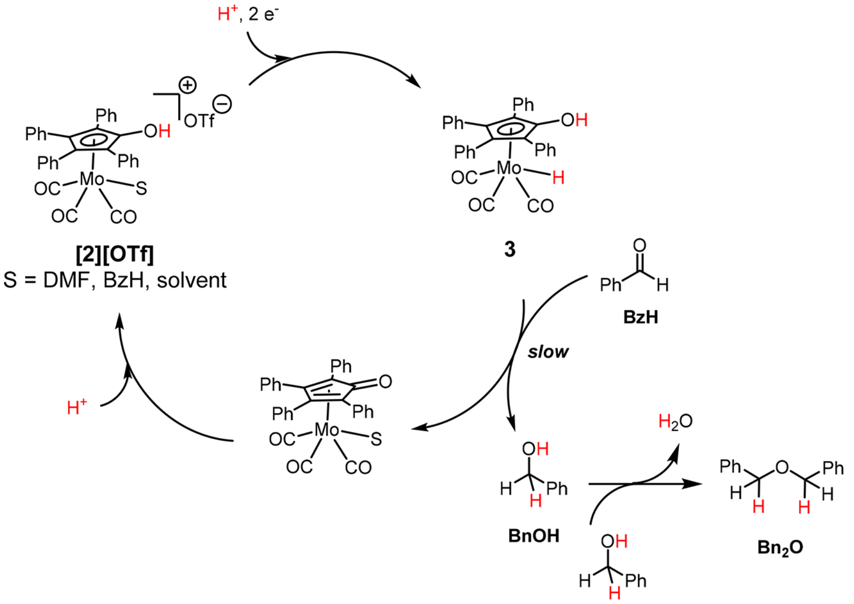


Figure 3. Proposed electrocatalytic mechanism for the reduction of benzaldehyde by [**2**][**OTf**] (S = ODFB).

observed, consistent with the formation of $(C_5Ph_4OH)Mo(CO)_3(H)$ **3** (SI, Figure S17). These results indicate that the reductive protonation of **1** to give **3** can be carried out both chemically and electrochemically. Analysis of the charge passed during the controlled-potential electrolysis reveals that 1.7 mol electrons/initial mol [**2**][**OTf**] were transferred over the course of the 1 h electrolysis. The total charge passed is approximately 15% less than that predicted for the 2-electron 1-proton reduction of [**2**][**OTf**], which might be attributed to the partial decomposition of [**2**][**OTf**] under the reaction conditions.

As stoichiometric experiments had shown that $(C_5Ph_4OH)Mo(CO)_3(H)$ **3** can be generated electrochemically from $[(C_5Ph_4OH)Mo(CO)_3(CH_3CN)][OTf]$ ([**2**][**OTf**]), and previous studies had shown that **3** can reduce benzaldehyde,[24] the electrocatalytic reduction of aldehydes was investigated with [**2**][**OTf**]. Initial experiments by cyclic voltammetry were uninformative, as titration of benzaldehyde into a [**2**][**OTf**]/[DMFH][OTf] solution, even at very low scan rates (*i.e.*, 25 mV/s), did not show any evidence of an enhanced current at −1000 mV. This was not unexpected, as previous studies[24] had shown that catalytic reduction of aldehydes by $(C_5Ph_4OH)Mo(CO)_3(H)$ **3** only occurs over the course of hours at 65 °C (99% conversion after 12 h, 65 °C).

To investigate the electrocatalytic reduction of aldehydes, controlled-potential electrolysis of an ODFB solution of 1 mM [**2**][**OTf**], 100 mM [DMFH][OTf], and 100 mM benzaldehyde at −900 mV (vs $Fc^{0/+}$) were carried out for 2 h. Analysis of the resulting solution by ^1H NMR (see SI) after 2 h revealed the formation of benzyl alcohol (BnOH) and dibenzyl ether (Bn_2O), with turnover number of TON = 4.4 and a Faradaic efficiency of approximately 67% (averaged from two runs). The results of this experiment are summarized in the SI, Table S3. A control experiment with no Mo (SI, Figures S22, S23) showed very low yield (0.3%) and Faradaic efficiency (1.7%), confirming the catalytic role of Mo. Similarly, an experiment with no applied potential showed no conversion (SI, Figure S24), indicating the requirement of an electrochemical step in the catalytic cycle.

The stoichiometric and catalytic experiments are consistent with the mechanism outlined in Figure 3. In the presence of [DMFH][OTf], [**2**][**OTf**] is converted to the Mo−H **3** by a two-electron-one-proton reduction at the working electrode. The slow reduction of benzaldehyde by Mo−H **3** affords benzyl alcohol and the Mo(0) tetraphenylcyclopentadienone complex.[24] Competitive acid-catalyzed dehydration of benzyl alcohol generates dibenzyl ether. Protonation of the Mo(0) tetraphenylcyclopentadienone regenerates [**2**][**OTf**].

In light of previous studies showing that the rate of aldehyde reduction is slow at room temperatures, it is likely that the chemical step between benzaldehyde and **3** is turnover-limiting. The *ca.* 67% Faradaic efficiencies observed are noteworthy in that they imply that the Mo−H **3**, generated electrochemically in the presence of benzaldehyde, exhibits a selectivity for reduction of the aldehyde over protonation to release H_2 (hydrogen evolution reaction, HER). The origin of this selectivity is not clear, but has some precedent in the chemistry of ionic hydrogenation[28] with related Mo piano stool complexes. The related $Cp'Mo(H)(CO)_3$ (Cp′ = cyclopentadiene, pentamethylcyclopentadiene, pentabenzylcyclopentadiene[29]) complexes[28−31] were observed to react with triflic acid in CD_2Cl_2 to generate H_2 and $Cp'Mo(OTf)(CO)_3$,[30] but when protonation of either $CpMo(CO)_2(PPh_3)H$ (CH_3CN) or $CpMo(CO)_2(PPh_3)H$ (CH_2Cl_2) was carried out in the presence of a ketone (acetone or 3-pentanone), competitive reduction to the alcohol and hydrogen evolution were observed.[29,31] The bifunctional nature of the hydroxycyclopentadienyl ligand might also contribute to the observed selectivity for electrohydrogenation (Figure 1).

In summary, we report the electrohydrogenation of benzaldehyde with a Shvo-type Mo complex $(C_5Ph_4OH)Mo(CO)_3(H)$ **3**. Controlled potential electrolysis of benzaldehyde at −0.90 V (vs $Fc^{+/0}$) in *ortho*-difluorobenzene with the acid [DMFH][OTf] affords a mixture of the reduction products benzyl alcohol (BnOH) and dibenzyl ether (Bn_2O) with a Faradaic efficiency of approximately 67%. Stoichiometric experiments reveal that the reductive protonation of either the Mo(0) complex $[(C_5Ph_4O)Mo(CO)_3(L)]$ or the cationic Mo(II) complex $[(C_5Ph_4OH)Mo(CO)_3(CH_3CN)][OTf]$ affords the hydride $(C_5Ph_4OH)Mo(CO)_3(H)$ **3**, which was previously shown to be competent to reduce aldehydes. These studies provide support for an electrocatalytic mechanism involving the rate-limiting reduction of the aldehyde by the Mo−H **3** and subsequent reductive protonation of $[(C_5Ph_4O)Mo(CO)_3(L)]$ to regenerate the Mo−H **3**. The high Faradaic efficiencies observed with these metal−ligand bifunctional catalysts provide new design motifs for the design of selective electrocatalysts for electrohydrogenation relative to hydrogen evolution.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00630.

General experimental methods, syntheses, additional cyclic voltammograms, quantification procedures and calculations, procedures for controlled potential electrolysis studies, control experiments, and additional nuclear magnetic resonance studies (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Garedew, M.; Lin, F.; Song, B.; DeWinter, T. M.; Jackson, J. E.; Saffron, C. M.; Lam, C. H.; Anastas, P. T. Greener Routes to Biomass Waste Valorization: Lignin Transformation Through Electrocatalysis

for Renewable Chemicals and Fuels Production. *ChemSusChem* **2020**, *13*, 4214−4237.

(2) Carl, S.; Waldrop, K.; Pintauro, P.; Thompson, L. T.; Tarpeh, W. A. Selective Hydrogenation of Furfural in a Proton Exchange Membrane Reactor Using Hybrid Pd/Pd Black on Alumina. *ChemElectroChem* **2019**, *6*, 5563−5570.

(3) Orella, M. J.; Roman-Leshkov, Y.; Brushett, F. R. Emerging opportunities for electrochemical processing to enable sustainable chemical manufacturing. *Curr. Opin. Chem. Eng.* **2018**, *20*, 159−167.

(4) Bondue, C. J.; Calle-Vallejo, F.; Figueiredo, M. C.; Koper, M. T. M. Structural principles to steer the selectivity of the electrocatalytic reduction of aliphatic ketones on platinum. *Nat. Catal.* **2019**, *2*, 243−250.

(5) Bondue, C. J.; Koper, M. T. M. Electrochemical Reduction of the Carbonyl Functional Group: The Importance of Adsorption Geometry, Molecular Structure, and Electrode Surface Structure. *J. Am. Chem. Soc.* **2019**, *141*, 12071−12078.

(6) Lopez-Ruiz, J. A.; Andrews, E.; Akhade, S. A.; Lee, M.-S.; Koh, K.; Sanyal, U.; Yuk, S. F.; Karkamkar, A. J.; Derewinski, M. A.; Holladay, J.; Glezakou, V.-A.; Rousseau, R.; Gutiérrez, O. Y.; Holladay, J. D. Understanding the Role of Metal and Molecular Structure on the Electrocatalytic Hydrogenation of Oxygenated Organic Compounds. *ACS Catal.* **2019**, *9*, 9964−9972.

(7) Lopez-Ruiz, J. A.; Sanyal, U.; Egbert, J.; Gutiérrez, O. Y.; Holladay, J. Kinetic Investigation of the Sustainable Electrocatalytic Hydrogenation of Benzaldehyde on Pd/C: Effect of Electrolyte Composition and Half-Cell Potentials. *ACS Sustainable Chem. Eng.* **2018**, *6*, 16073−16085.

(8) Singh, N.; Sanyal, U.; Ruehl, G.; Stoerzinger, K. A.; Gutierrez, O. Y.; Camaioni, D. M.; Fulton, J. L.; Lercher, J. A.; Campbell, C. T. Aqueous phase catalytic and electrocatalytic hydrogenation of phenol and benzaldehyde over platinum group metals. *J. Catal.* **2020**, *382*, 372−384.

(9) Song, Y.; Sanyal, U.; Pangotra, D.; Holladay, J. D.; Camaioni, D. M.; Gutierrez, O. Y.; Lercher, J. A. Hydrogenation of benzaldehyde via electrocatalysis and thermal catalysis on carbon-supported metals. *J. Catal.* **2018**, *359*, 68−75.

(10) Soloveichik, G. L. Liquid fuel cells. *Beilstein J. Nanotechnol.* **2014**, *5*, 1399−1418.

(11) Soloveichik, G. L. Flow Batteries: Current Status and Trends. *Chem. Rev.* **2015**, *115*, 11533−11558.

(12) Bourane, A.; Elanany, M.; Pham, T. V.; Katikaneni, S. P. An overview of organic liquid phase hydrogen carriers. *Int. J. Hydrogen Energy* **2016**, *41*, 23075−23091.

(13) Crabtree, R. H. Nitrogen-Containing Liquid Organic Hydrogen Carriers: Progress and Prospects. *ACS Sustainable Chem. Eng.* **2017**, *5*, 4491−4498.

(14) Fokin, I.; Siewert, I. Chemoselective Electrochemical Hydrogenation of Ketones and Aldehydes with a Well-Defined Base-Metal Catalyst. *Chem. - Eur. J.* **2020**, *26*, 14137−14143.

(15) Matanovic, I. ELECTROCATALYSIS Selectivity control for electroreduction of ketones. *Nat. Catal.* **2019**, *2*, 186−187.

(16) Green, S. K.; Tompsett, G. A.; Kim, H. J.; Kim, W. B.; Huber, G. W. Electrocatalytic Reduction of Acetone in a Proton-Exchange-Membrane Reactor: A Model Reaction for the Electrocatalytic Reduction of Biomass. *ChemSusChem* **2012**, *5*, 2410−2420.

(17) Cunningham, D. W.; Barlow, J. M.; Velazquez, R. S.; Yang, J. Y. Reversible and Selective CO2 to HCO2- Electrocatalysis near the Thermodynamic Potential. *Angew. Chem., Int. Ed.* **2020**, *59*, 4443−4447.

(18) Boutin, E.; Merakeb, L.; Ma, B.; Boudy, B.; Wang, M.; Bonin, J.; Anxolabéhère-Mallart, E.; Robert, M. Molecular catalysis of CO_2 reduction: recent advances and perspectives in electrochemical and light-driven processes with selected Fe, Ni and Co aza macrocyclic and polypyridine complexes. *Chem. Soc. Rev.* **2020**, *49*, 5772−5809.

(19) Dub, P. A.; Gordon, J. C. Metal Ligand Bifunctional Catalysis: The "Accepted" Mechanism, the Issue of Concertedness, and the Function of the Ligand in Catalytic Cycles Involving Hydrogen Atoms. *ACS Catal.* **2017**, *7*, 6635−6655.

(20) Shvo, Y.; Czarkie, D.; Rahamim, Y.; Chodosh, D. F. A new group of ruthenium complexes: structure and catalysis. *J. Am. Chem. Soc.* **1986**, *108*, 7400−7402.

(21) Blum, Y.; Shvo, Y. Catalytically reactive (η^4-tetracyclone)$(CO)_2(H)_2$Ru and related complexes in dehydrogenation of alcohols to esters. *J. Organomet. Chem.* **1985**, *282*, C7−C10.

(22) Casey, C. P.; Singer, S. W.; Powell, D. R.; Hayashi, R. K.; Kavana, M. Hydrogen transfer to carbonyls and imines from a hydroxycyclopentadienyl ruthenium hydride: Evidence for concerted hydride and proton transfer. *J. Am. Chem. Soc.* **2001**, *123*, 1090−1100.

(23) Conley, B. L.; Pennington-Boggio, M. K.; Boz, E.; Williams, T. J. Discovery, Applications, and Catalytic Mechanisms of Shvo's Catalyst. *Chem. Rev.* **2010**, *110*, 2294−2312.

(24) Wu, W.; Seki, T.; Walker, K. L.; Waymouth, R. M. Transfer Hydrogenation of Aldehydes, Allylic Alcohols, Ketones, and Imines Using Molybdenum Cyclopentadienone Complexes. *Organometallics* **2018**, *37*, 1428−1431.

(25) Adams, H.; Bailey, N. A.; Hempstead, P. D.; Morris, M. J.; Riley, S.; Beddoes, R. L.; Cook, E. S. Cyclopentadienone complexes of molybdenum: synthesis of carbonyl, acetonitrile, phosphine and phosphido-bridged derivatives. *J. Chem. Soc., Dalton Trans.* **1993**, 91−100.

(26) Koelle, U.; Infelta, P. P.; Graetzel, M. Kinetics and mechanism of the reduction of protons to hydrogen by cobaltocene. *Inorg. Chem.* **1988**, *27*, 879−883.

(27) Chalkley, M. J.; Oyala, P. H.; Peters, J. C. Cp* Noninnocence Leads to a Remarkably Weak C-H Bond via Metallocene Protonation. *J. Am. Chem. Soc.* **2019**, *141*, 4721−4729.

(28) Bullock, R. M. Catalytic ionic Hydrogenations. *Chem. - Eur. J.* **2004**, *10*, 2366−2374.

(29) Namorado, S.; Antunes, M. A.; Veiros, L. F.; Ascenso, J. R.; Duarte, M. T.; Martins, A. M. Ionic hydrogenation of ketones with molybdenum pentabenzylcyclopentadienyl hydride catalysts. *Organometallics* **2008**, *27*, 4589−4599.

(30) Bullock, R. M.; Song, J.-S. Ionic Hydrogenations of Hindered Olefins at Low Temperature. Hydride Transfer Reactions of Transition Metal Hydrides. *J. Am. Chem. Soc.* **1994**, *116*, 8602−8612.

(31) Smith, K. T.; Norton, J. R.; Tilset, M. Single-step hydride transfer from CpMo(CO)(2)(PPh(3))H to protonated ketones. *Organometallics* **1996**, *15*, 4515−4520.