

Electrocatalysis

International Edition: DOI: 10.1002/anie.201807510
German Edition: DOI: 10.1002/ange.201807510**H₂ Oxidation Electrocatalysis Enabled by Metal-to-Metal Hydrogen Atom Transfer: A Homolytic Approach to a Heterolytic Reaction**

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Abstract: Oxidation of H₂ in a fuel cell converts the chemical energy of the H–H bond into electricity. Electrocatalytic oxidation of H₂ by molecular catalysts typically requires one metal to perform multiple chemical steps: bind H₂, heterolytically cleave H₂, and then undergo two oxidation and two deprotonation steps. The electrocatalytic oxidation of H₂ by a cooperative system using Cp*Cr(CO)₃H and [Fe(diphosphine)(CO)₃]⁺ has now been investigated. A key step of the proposed mechanism is a rarely observed metal-to-metal hydrogen atom transfer from the Cr–H complex to the Fe, forming an Fe–H complex that is deprotonated and then oxidized electrochemically. This “division of chemical labor” features Cr interacting with H₂ to cleave the H–H bond, while Fe interfaces with the electrode. Neither metal is required to heterolytically cleave H₂, so this system provides a very unusual example of a homolytic reaction being a key step in a molecular electrocatalytic process.

Electrochemical reactions are inherently charge-transfer reactions, involving oxidation or reduction at an electrode. Homolytic reactions, such as hydrogen atom transfers, are not typically involved in electrocatalytic reactions of molecular complexes.^[1] In contrast, hydrogen on metal surfaces is generally considered in terms of hydrogen atom reactivity in heterogeneous catalysis.^[2] We discovered an electrocatalytic oxidation of H₂ that is enabled by a key step involving a hydrogen atom transfer between two metals. In stark contrast to previously reported molecular electrocatalysts for oxidation of H₂, the proposed mechanism does not require that either metal heterolytically cleave H₂.

Electrocatalytic oxidation of H₂ in fuel cells converts the chemical energy in the H–H bond into electricity, providing a carbon-neutral source of energy. Hydrogenases in nature catalyze the oxidation of H₂ under mild conditions, using Fe and/or Ni.^[3] [NiFe]-hydrogenases catalyze the oxidation of H₂,^[4] with some of them being used in fuel cells.^[5] A biomimetic model of the [NiFe]-hydrogenase was reported as an electrocatalyst for oxidation of H₂.^[6] Bimetallic complexes of Ni/Ru and Ni/Fe oxidize H₂,^[7] providing insights into the function of hydrogenases. Apart from electrocata-

lysts, several metal complexes catalyze the oxidation of H₂ using chemical oxidants.^[8]

We designed synthetic molecular electrocatalysts for oxidation of H₂ using biologically inspired functionality and earth-abundant metals,^[9] including mononuclear complexes of Ni,^[10] Fe,^[11] and Mn.^[12] These molecular catalysts require one metal to perform diverse roles: it must bind H₂, then heterolytically cleave the H₂, prior to the removal of two electrons and two protons. The electronic characteristics and thermodynamic requirements favoring each of those steps can differ substantially, contributing to the challenges of designing efficient molecular catalysts. We envisaged a cooperative pathway in which one metal reacts with H₂, breaking the H–H bond, and forming a metal hydride that can be transferred as a hydrogen atom to a different metal complex that completes the electrocatalytic oxidation of hydrogen. This “division of chemical labor” separates the role of cleaving H₂ from the requirement of the electrocatalytic oxidation and proton transfers.

Our approach shares some similarity to the use of organic molecular mediators to remarkably improve transition-metal electrocatalysts for alcohol oxidation or O₂ reduction.^[13] Here we report the successful design of a cooperative catalysis system in which a chromium complex cleaves the H–H bond, forming a Cr–H bond that donates a hydrogen atom to an iron complex that undergoes deprotonation and oxidation. This new approach to the design of molecular electrocatalysts is initiated by homolytic cleavage of H₂ for a reaction that requires heterolytic rupture of metal hydride bonds, thereby taking advantage of the diversity of mechanistic pathways for cleaving H–H and M–H bonds.

We recently found that the Fe^I cation [Fe(P^{Et}N^{Me}P^{Et})(CO)₃]⁺[BAR^F₄][−] (**1**⁺) (P^{Et}N^{Me}P^{Et} = (Et₂PCH₂)₂NMe); Ar^F = 3,5-bis(trifluoromethyl)phenyl) is a stable 17-electron complex.^[14] In contrast to the slow formation of the iron hydride [HFe(P^{Et}N^{Ph}P^{Et})(CO)₃]⁺, [**1H**]⁺, directly from H₂, we discovered that [**1H**]⁺ is produced rapidly by a novel metal-to-metal hydrogen atom transfer from CpCr(CO)₃H (Cp = C₅H₅), Cp*Cr(CO)₃H (Cp* = C₅Me₅), or CpMo(CO)₃H to [**1**]⁺ (Figure 1). These Cr or Mo hydrides react with [**1**]⁺, generating the cationic iron hydride and the corresponding Cr or Mo metal-centered radicals, which dimerize. The Cr–Cr dimers are in equilibrium with their corresponding metal-centered radicals, Cp(CO)₃Cr^{•[15]} or Cp*(CO)₃Cr^{•[16]} whereas the dimerization in the Mo complex is essentially irreversible owing to the much stronger Mo–Mo bond^[17] compared to the Cr–Cr bond. Reactions analogous to the one shown in Figure 1 are found with [Fe(P^{Et}N^{Ph}P^{Et})(CO)₃]⁺, which has a Ph substituent on the pendant amine, and with [Fe(depp)-

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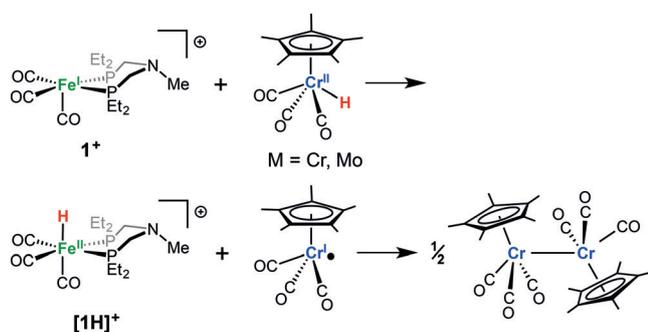


Figure 1. Metal-to-metal hydrogen atom transfer occurs readily using $\text{CpM}(\text{CO})_3\text{H}$ ($M = \text{Cr}, \text{Mo}$) or $\text{Cp}^*\text{Cr}(\text{CO})_3\text{H}$ (shown here).

$(\text{CO})_3]^+$ (depp = 1,3-bis(diethylphosphino)propane) bearing no pendant amine in the diphosphine ligand.

The successful metal-to-metal hydrogen atom transfer reactions, coupled with the ability of the Cr complexes to react directly with H_2 , point the way to electrocatalytic oxidation of H_2 by exploiting both of these reactions in a cooperative catalytic cycle. A cyclic voltammogram of **1** is shown in Figure 2; its reversible $\text{Fe}^{+/0}$ couple occurs at $E_{1/2} = -0.36$ V vs. $\text{Cp}_2\text{Fe}^{0/+}$. In the presence of excess $\text{Cp}^*\text{Cr}(\text{CO})_3\text{H}$, the electrochemically generated **[1]**⁺ is consumed, and is not observed on the return scan. A new cathodic wave is observed corresponding to the $[\text{Cp}^*\text{Cr}(\text{CO})_3]^{0/-}$ couple, as expected following hydrogen atom transfer from $\text{Cp}^*\text{Cr}(\text{CO})_3\text{H}$ to the electrochemically generated iron radical cation.

When an amine base is added, increased current is observed coincident with the $\text{Fe}^{+/0}$ redox couple, consistent with catalytic turnover (Figure 3). The base 2-methylpyridine ($\text{p}K_{\text{a}}^{\text{MeCN}} = 13.32$ ^[18] for 2-methylpyridinium) deprotonates **[1H]**⁺, but does not appreciably deprotonate $\text{Cp}^*\text{Cr}(\text{CO})_3\text{H}$

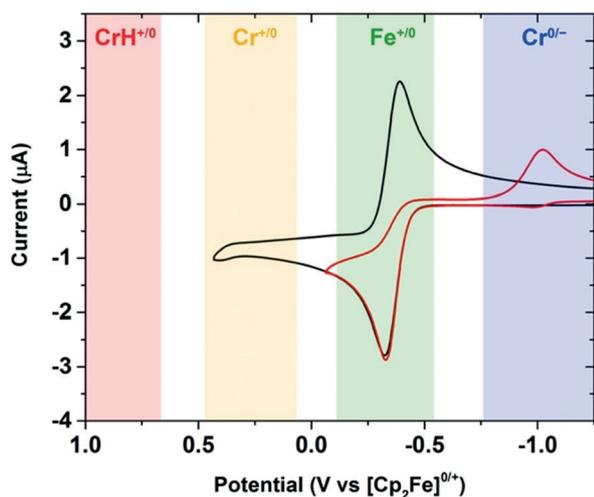


Figure 2. Cyclic voltammograms of a solution containing **1** (0.4 mM) (black trace) and **1** with $\text{Cp}^*\text{Cr}(\text{CO})_3\text{H}$ (40 mM) (red trace) in PhF with $[\text{Bu}_4\text{N}][\text{B}(\text{C}_6\text{F}_5)_4]$ (100 mM). The irreversible reduction wave at approximately -0.9 V vs. $\text{Cp}_2\text{Fe}^{0/+}$ corresponds to the $[\text{Cp}^*\text{Cr}(\text{CO})_3]^{0/-}$ couple. Approximate window for the $[\text{Fe}(\text{diphosphine})(\text{CO})_3]^{+/0}$ couple (green band), the $[\text{Cp}^*\text{Cr}(\text{CO})_3]^{0/-}$ couple (blue band), the $[\text{Cp}^*\text{Cr}(\text{CO})_3]^{+/0}$ couple (yellow band), and the $[\text{Cp}^*\text{Cr}(\text{CO})_3\text{H}]^{+/0}$ couple (red band).

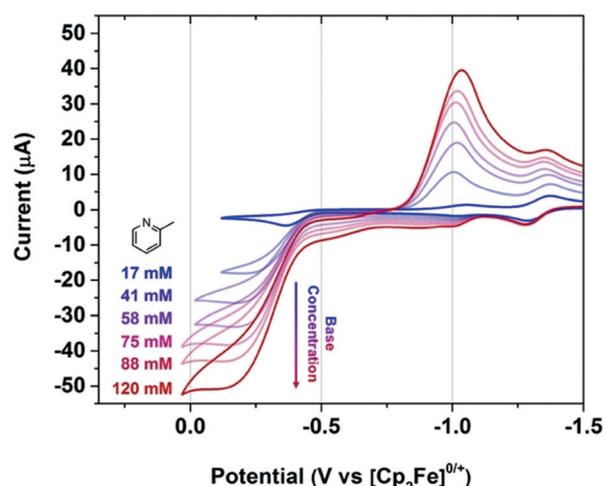
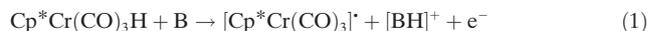


Figure 3. Cyclic voltammograms of a solution containing **1** (0.4 mM) and $\text{Cp}^*\text{Cr}(\text{CO})_3\text{H}$ (100 mM) in PhF with $[\text{Bu}_4\text{N}][\text{B}(\text{C}_6\text{F}_5)_4]$ (100 mM) at increasing concentrations of 2-methylpyridine under argon. Scan rate: 500 mV s^{-1} . The solid blue trace contains no 2-methylpyridine. $[\text{Cp}_2\text{Co}][\text{B}(\text{C}_6\text{F}_5)_4]$ is used as an internal reference (-1.33 V vs. $[\text{Cp}_2\text{Fe}]^{0/+}$).

($\text{p}K_{\text{a}}^{\text{MeCN}} = 16.1$ ^[19]). Based on experiments on protonation of **1** by 2,6-di-*tert*-butylpyridinium tetrakis(pentafluorophenyl)borate in MeCN, we determined the $\text{p}K_{\text{a}}^{\text{MeCN}}$ of **[1H]**⁺ to be 10.7(3). Increased oxidative catalytic current is observed near the $\text{Fe}^{+/0}$ couple, with a simultaneous increase in the cathodic current at -0.9 V, similar to the reported value of the $[\text{Cp}^*\text{Cr}(\text{CO})_3]^{0/-}$ couple.^[20] The catalytic reaction under the conditions of the cyclic voltammetric studies is shown in Equation (1).



The catalytic current increases at higher concentrations of chromium hydride and base. The pseudo first-order rate constant k_{obs} (equivalent to TOF) can be determined using $i_{\text{cat}}/i_{\text{p}}$ according to Equation (2), where i_{cat} is the observed catalytic current, and i_{p} is the peak current observed in the absence of catalysis.^[21]

$$\frac{i_{\text{cat}}}{i_{\text{p}}} = \frac{n}{0.4463} \sqrt{\frac{RTk_{\text{obs}}}{Fv}} \quad (2)$$

In Equation (2), n is the number of electrons transferred ($n=1$ for these reactions), R is the gas constant, T is the temperature in Kelvin, F is the Faraday constant, and v is the scan rate. At constant chromium hydride concentration, the observed rate increases linearly at low concentrations of 2-methylpyridine, and reaches a plateau at higher concentrations (Figure 4, upper). The slope of the plot of k_{obs} vs. $[\text{2-methylpyridine}]$ in this linear region gives the second-order rate constant for deprotonation of **[1H]**⁺ by 2-methylpyridine ($4900 \text{ M}^{-1} \text{ s}^{-1}$). The second-order rate constant for deprotonation of $[\text{HFe}(\text{depp})(\text{CO})_3]^+$ by 2-methylpyridine was found to be similar ($2600 \text{ M}^{-1} \text{ s}^{-1}$), suggesting the pendant amine has minimal, if any, influence on the deprotonation of the iron hydride. At constant $[\text{2-methylpyridine}]$ concentration, the

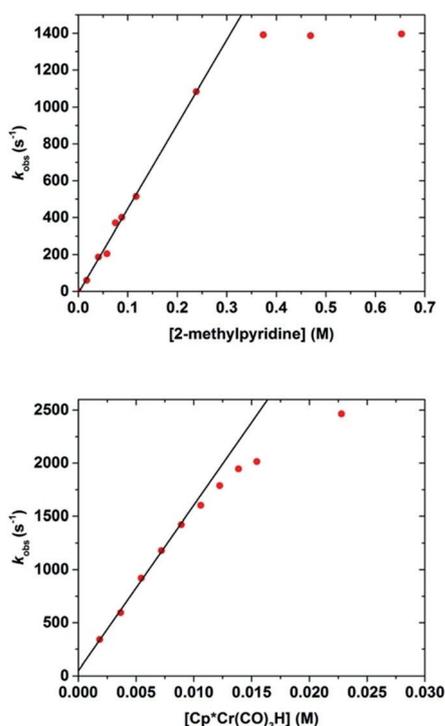


Figure 4. Top: Plot of k_{obs} vs. [2-methylpyridine] at [Cp*Cr(CO)₃H] = 100 mM. Conditions: PhF, 0.4 mM **1**, 100 mM [Bu₄N][B(C₆F₅)₄], scan rate 500 mVs⁻¹. Bottom: Plot of k_{obs} vs. [Cp*Cr(CO)₃H] at constant [2-methylpyridine] = 800 mM. Conditions: PhF, 0.4 mM **1**, 100 mM [Bu₄N][B(C₆F₅)₄], scan rate 15 Vs⁻¹.

observed rate increases linearly with increasing [Cp*Cr(CO)₃H] concentration (Figure 4, lower). The slope of the linear region of this plot gives a lower limit of the second-order rate constant for the metal-to-metal hydrogen atom transfer step of $1.4 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ (see the Supporting Information for more details on the analysis of the kinetics).

The chromium hydride is regenerated from Cp*(CO)₃Cr* by H₂, giving electrocatalytic oxidation of H₂. The third-order rate constant for reaction of H₂ with Cp*(CO)₃Cr* has been reported as $330 \text{ M}^{-1} \text{ s}^{-1}$.^[22] A controlled potential electrolysis (CPE) was performed under H₂ (1 atm) with Cp*Cr(CO)₃H, **1**, and 2,6-di-*tert*-butylpyridine as the base. This bulkier base was used to avoid the slow disproportionation reaction of the Cp*Cr(CO)₃ radical with non-sterically encumbered amine bases^[23] which becomes appreciable over the course of the CPE experiment. The Faradaic efficiency was determined to be 95% by comparing the quantity of acid generated to the number of electrons passed during the electrolysis. Lower limits of turnover numbers of 5 for Cr and 21 for Fe were determined. Analyzing the solution by cyclic voltammetry after the CPE gives a catalytic wave of similar magnitude as the solution prior to the CPE, indicating little or no degradation of the Fe compound. In contrast, CPE using the Cr only system gives a Faradaic efficiency of only 54% using *N,N*-diisopropylethylamine as the base.

The overpotential for H₂ oxidation was determined by comparing the $E_{1/2}$ of the Fe⁺⁰ couple, where the electrocatalytic wave occurs, to the thermodynamic potential of H₂

oxidation/H⁺ reduction for the base/conjugate acid pair, which was determined by measuring the open circuit potential of a 1:1 base:conjugate acid solution under H₂ (1 atm) using a freshly prepared Pt wire electrode.^[24] Using 2,6-di-*tert*-butylpyridine as the base in the bulk electrolysis ($pK_{\text{a}}^{\text{MeCN}} = 11.4$ ^[23,25] for 2,6-di-*tert*-butylpyridinium), the overpotential using **1** was determined to be 0.38 V.

The proposed mechanism for the cooperative electrocatalytic oxidation of H₂ using both the Cr and Fe complexes is shown in Figure 5. The key step enabling this new approach

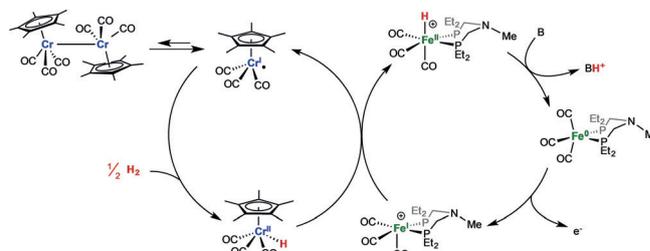


Figure 5. Proposed mechanism for the electrocatalytic oxidation of H₂ by a cooperative mechanism involving metal-to-metal hydrogen atom transfer.

to the design of electrocatalysts is metal-to-metal hydrogen atom transfer, a type of reaction that has received minimal attention. The formation of CpCr(CO)₃H from H₂ and [CpCr(CO)₃]⁺ has been studied in detail,^[26] and has been used in catalytic organic reactions developed by Norton and co-workers.^[27] Hoff and co-workers reported the kinetics and thermochemistry of metal-to-metal hydrogen atom transfers involving a series of Cr complexes.^[28] Hydrogen atom transfer self-exchange between Tp*Mo(CO)₃H (Tp* = hydrido-tris(3,5-dimethylpyrazolyl)borate) and [Tp*Mo(CO)₃]⁺ is slow (estimated $k < 9 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ at -34°C).^[29] In contrast, hydrogen atom transfer from CpW(CO)₃H to photochemically generated [CpW(CO)₃]⁺ is fast, with an estimated lower limit of $k > 1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ at 25°C .^[30] To the best of our knowledge, metal-to-metal hydrogen atom transfer has never been proposed in any catalytic reaction. In contrast, hydrogen atom transfers from metal hydrides to organic compounds have been studied in detail. Kinetics of hydrogen atom transfers from metal hydrides to alkenes and organic radicals have been reported,^[31] and versatile organic synthetic methods were reported recently using radical-based reactivity of organic compounds.^[27,32] Hydrogen atom transfers in the opposite direction, carbon-to-metal, have been reported for a few reactions where the formation of a very strong Os–H bond provides the driving force.^[33]

Following the formation of the Fe–H bond by metal-to-metal hydrogen atom transfer, the cationic iron hydride is deprotonated by the exogenous amine base. Electrochemical oxidation of the Fe⁰ complex to Fe^I regenerates the cationic Fe complex. This mechanism differs substantially from those proposed previously for molecular electrocatalysts for oxidation of H₂, which typically proceed through alternating deprotonation and oxidation steps, with one metal complex undergoing two different oxidation steps and two unique

deprotonation steps. In contrast, deprotonation in this cooperative catalyst system occurs through only one iron hydride species, and catalysis proceeds through only one electrochemical oxidation. This mechanism may be considered as a metal-mediated oxidation of hydrogen atoms, with two trips around the cycle being required for oxidation of each molecule of H₂. This unusual mechanism offers some advantages by requiring just one oxidation step and one deprotonation step. In traditional molecular electrocatalysts, the two oxidations typically occur at different potentials, and the two deprotonations occur for intermediates that have different pK_a values, making it much more likely that some increase in overpotential is incurred because of the need to use a base sufficiently strong for both deprotonation steps.

The successful design of this new type of electrocatalytic system requires electrochemical compatibility of all the components, as shown by the colored bands in Figure 2. Catalysis occurs at the [1]⁺⁰ redox couple (green band in Figure 2), which is flanked by the [Cp*Cr(CO)₃]⁺⁰ redox couple (yellow band) at more positive potentials and the [Cp*Cr(CO)₃]^{0/-} couple (blue band) at more negative potentials. The chromium hydride is oxidized (red band) at a higher potential. The Fe and Cr catalysts perform poorly as a single catalysts because of the poor yield of H₂ homolysis with [1]⁺ and the low Faradaic efficiency of the Cr complex. Electrocatalytic oxidation of H₂ using both metal complexes offers superior performance compared to using either metal alone.

Our results demonstrate that electrocatalytic oxidation of H₂ can be accomplished using a novel design strategy that distributes the tasks, incorporating homolytic (hydrogen atom transfer) reactivity that is seldom associated with molecular electrochemical reactions. In the cooperative catalysis using mediators reported here, electrocatalytic oxidation of H₂ is accomplished without requiring that either metal complex be capable of heterolytically cleaving H₂. We suggest that combining homolytic hydrogen atom transfers with the heterolytic reactivity normally associated with molecular electrocatalytic reactions offers an appealing approach in the design of electrocatalysts.^[34]

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Conflict of interest

The authors declare no conflict of interest.

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- [1] C. Costentin, H. Dridi, J.-M. Savéant, *J. Am. Chem. Soc.* **2014**, *136*, 13727–13734.
- [2] R. Prins, *Chem. Rev.* **2012**, *112*, 2714–2738.
- [3] W. Lubitz, H. Ogata, O. Rüdiger, E. Reijerse, *Chem. Rev.* **2014**, *114*, 4081–4148.
- [4] a) K. A. Vincent, J. A. Cracknell, J. R. Clark, M. Ludwig, O. Lenz, B. Friedrich, F. A. Armstrong, *Chem. Commun.* **2006**, 5033–5035; b) J. A. Cracknell, K. A. Vincent, F. A. Armstrong, *Chem. Rev.* **2008**, *108*, 2439–2461.
- [5] a) T. Matsumoto, S. Eguchi, H. Nakai, T. Hibino, K.-S. Yoon, S. Ogo, *Angew. Chem. Int. Ed.* **2014**, *53*, 8895–8898; *Angew. Chem.* **2014**, *126*, 9041–9044; b) S. Ogo, Y. Mori, T. Ando, T. Matsumoto, T. Yatabe, K.-S. Yoon, H. Hayashi, M. Asano, *Angew. Chem. Int. Ed.* **2017**, *56*, 9723–9726; *Angew. Chem.* **2017**, *129*, 9855–9858.
- [6] B. C. Manor, T. B. Rauchfuss, *J. Am. Chem. Soc.* **2013**, *135*, 11895–11900.
- [7] a) S. Ogo, *Chem. Commun.* **2009**, 3317–3325; b) S. Ogo, *Coord. Chem. Rev.* **2017**, *334*, 43–53.
- [8] a) J. M. Camara, T. B. Rauchfuss, *Nat. Chem.* **2012**, *4*, 26–30; b) M. Yuki, K. Sakata, Y. Hirao, N. Nonoyama, K. Nakajima, Y. Nishibayashi, *J. Am. Chem. Soc.* **2015**, *137*, 4173–4182; c) M. Yuki, K. Sakata, S. Kikuchi, H. Kawai, T. Takahashi, M. Ando, K. Nakajima, Y. Nishibayashi, *Chem. Eur. J.* **2017**, *23*, 1007–1012; d) M. R. Ringenberg, M. J. Nilges, T. B. Rauchfuss, S. R. Wilson, *Organometallics* **2010**, *29*, 1956–1965.
- [9] R. M. Bullock, M. L. Helm, *Acc. Chem. Res.* **2015**, *48*, 2017–2026.
- [10] a) J. Y. Yang, S. E. Smith, T. Liu, W. G. Dougherty, W. A. Hoffert, W. S. Kassel, M. Rakowski DuBois, D. L. DuBois, R. M. Bullock, *J. Am. Chem. Soc.* **2013**, *135*, 9700–9712; b) A. Dutta, J. A. Roberts, W. J. Shaw, *Angew. Chem. Int. Ed.* **2014**, *53*, 6487–6491; *Angew. Chem.* **2014**, *126*, 6605–6609.
- [11] T. Liu, D. L. DuBois, R. M. Bullock, *Nat. Chem.* **2013**, *5*, 228–233.
- [12] E. B. Hulley, N. Kumar, S. Raugei, R. M. Bullock, *ACS Catal.* **2015**, *5*, 6838–6847.
- [13] a) A. Badalyan, S. S. Stahl, *Nature* **2016**, *535*, 406–410; b) C. W. Anson, S. S. Stahl, *J. Am. Chem. Soc.* **2017**, *139*, 18472–18475.
- [14] G. M. Chambers, S. I. Johnson, S. Raugei, R. M. Bullock, unpublished results.
- [15] S. J. McLain, *J. Am. Chem. Soc.* **1988**, *110*, 643–644.
- [16] M. C. Baird, *Chem. Rev.* **1988**, *88*, 1217–1227.
- [17] J. R. Pugh, T. J. Meyer, *J. Am. Chem. Soc.* **1992**, *114*, 3784–3792.
- [18] I. Kaljurand, A. Kutt, L. Soovali, T. Rodima, V. Maemets, I. Leito, I. A. Koppel, *J. Org. Chem.* **2005**, *70*, 1019–1028.
- [19] E. J. Moore, J. M. Sullivan, J. R. Norton, *J. Am. Chem. Soc.* **1986**, *108*, 2257–2263.
- [20] T. C. Richards, W. E. Geiger, M. C. Baird, *Organometallics* **1994**, *13*, 4494–4500.
- [21] a) R. S. Nicholson, I. Shain, *Anal. Chem.* **1964**, *36*, 706–723; b) J. M. Savéant, E. Vianello, *Electrochim. Acta* **1965**, *10*, 905–920.
- [22] K. B. Capps, A. Bauer, G. Kiss, C. D. Hoff, *J. Organomet. Chem.* **1999**, *586*, 23–30.
- [23] A. E. Stigman, M. Stieglitz, D. R. Tyler, *J. Am. Chem. Soc.* **1983**, *105*, 6032–6037.
- [24] J. A. S. Roberts, R. M. Bullock, *Inorg. Chem.* **2013**, *52*, 3823–3835.
- [25] C. Bergquist, B. M. Bridgewater, C. J. Harlan, J. R. Norton, R. A. Friesner, G. Parkin, *J. Am. Chem. Soc.* **2000**, *122*, 10581–10590.
- [26] J. R. Norton, T. Spataru, D. M. Camaioni, S.-J. Lee, G. Li, J. Choi, J. A. Franz, *Organometallics* **2014**, *33*, 2496–2502.
- [27] G. Li, J. L. Kuo, A. Han, J. M. Abuyuan, L. C. Young, J. R. Norton, J. H. Palmer, *J. Am. Chem. Soc.* **2016**, *138*, 7698–7704.

- [28] G. Kiss, K. Zhang, S. L. Mukerjee, C. D. Hoff, G. C. Roper, *J. Am. Chem. Soc.* **1990**, *112*, 5657–5658.
- [29] J. D. Protasiewicz, K. H. Theopold, *J. Am. Chem. Soc.* **1993**, *115*, 5559–5569.
- [30] J.-S. Song, R. M. Bullock, C. Creutz, *J. Am. Chem. Soc.* **1991**, *113*, 9862–9864.
- [31] a) R. M. Bullock, E. G. Samsel, *J. Am. Chem. Soc.* **1990**, *112*, 6886–6898; b) D. C. Eisenberg, C. J. C. Lawrie, A. E. Moody, J. R. Norton, *J. Am. Chem. Soc.* **1991**, *113*, 4888–4895.
- [32] a) M. Yan, J. C. Lo, J. T. Edwards, P. S. Baran, *J. Am. Chem. Soc.* **2016**, *138*, 12692–12714; b) S. W. M. Crossley, C. Obradors, R. M. Martinez, R. A. Shenvi, *Chem. Rev.* **2016**, *116*, 8912–9000.
- [33] a) J. Zhang, D. C. Grills, K.-W. Huang, E. Fujita, R. M. Bullock, *J. Am. Chem. Soc.* **2005**, *127*, 15684–15685; b) A. Lewandowska-Andralojc, D. C. Grills, J. Zhang, R. M. Bullock, A. Miyazawa, Y. Kawanishi, E. Fujita, *J. Am. Chem. Soc.* **2014**, *136*, 3572–3578.
- [34] CCDC 1810833 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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