

# Electrohydrogenation: Enabling Science for Renewable Fuels

## Investigators

Professor Robert M. Waymouth, Professor, Chemistry  
Professor Christopher E. D. Chidsey, Professor, Chemistry  
Dr. Kristen Brownell, Graduate Student, Chemistry  
Dr. Anthony DeCrisci, Postdoctoral Student, Chemistry  
Kate Waldie, Graduate Student, Chemistry  
Dr. Sung-Kwan Kim, Postdoctoral Student, Chemistry  
Andrew Ingram, Graduate Student, Chemistry

## Abstract

A series of molecular metal hydrides derived from transfer hydrogenation catalysts have been shown to activate and/or reduce methyl formate, carbon dioxide and protons. These advances illustrate the potential of highly reactive transfer hydrogenation catalysts to act as catalyst precursors for the reduction of CO<sub>2</sub> and other biomass-derived feedstocks to energy dense liquid fuels. In the first year of this project, we have tested several well-defined molecular complexes designed to activate and reduce carbon-dioxide and alkyl formates. These studies have helped illuminate the electronic and structural features of coordination complexes whose metal and coordinated ligands can function cooperatively to react readily with carbon dioxide or its partial reduction products, such as alkyl formates.

## Introduction

The goal of this project is to develop energy-efficient catalysts for electrohydrogenation reactions to create and upgrade liquid fuels. The ultimate goal is to develop efficient strategies for the use of renewable sources of electricity to produce liquid fuels from CO<sub>2</sub> and to upgrade biomass to energy-dense liquid fuels.

**Aim 1:** To apply concepts from transfer hydrogenation to develop new catalysts for the energy efficient and rapid activation and reduction of CO<sub>2</sub>, formates and C=O containing molecules derived from biomass.

**Aim 2:** To apply concepts of proton-coupled electron transfer as a strategy for the electrochemical generation of metal hydrides.

**Aim 3:** To develop energy efficient catalysts for the electrohydrogenation of CO<sub>2</sub> and other C=O containing molecules.

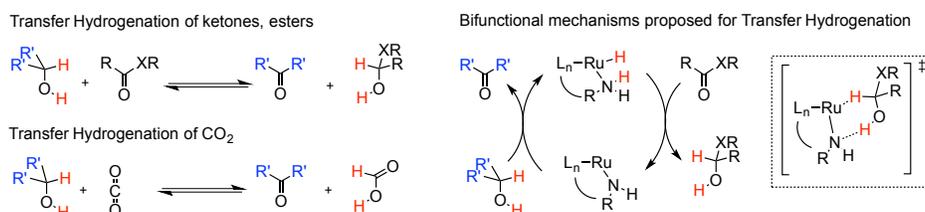
## Background

A sustainable energy economy will require the use of renewable sources as principal energy inputs. The energy-efficient conversion of electricity to chemical fuels is a critical component of a future energy economy, as intermittent renewable energy cannot be widely utilized unless it can be captured and stored. The storage of intermittent electricity, either by reduction of CO<sub>2</sub> to liquid fuels or by up-grading biomass, are grand challenges: few efficient electrohydrogenation catalysts exist.[1-2] The reduction of CO<sub>2</sub>, either by chemical hydrogenation or electroreduction, is a formidable challenge[3] as CO<sub>2</sub> is both kinetically and thermodynamically inert and the products of CO<sub>2</sub> partial reduction, formic acid and formates, are likewise resistant to reduction.[4] Our ultimate

objective is to develop new families of electrocatalysts for the electrohydrogenation of CO<sub>2</sub> to energy-rich liquid fuels, such as methanol. The direct electrohydrogenation of CO<sub>2</sub> would provide a strategy for the conversion of renewable electrical energy to liquid fuels.

Our objective is to develop new approaches to CO<sub>2</sub> activation and electrochemical hydrogenation at low overpotential. While both energy efficiency ("overpotential" and Faradaic efficiency) and current density (rate) are critical for large-scale implementation, it is our view that *the gaps in our understanding of the energetic requirements of critical chemical steps for reversible electrohydrogenation are the major impediments to further progress*. In the first year of this project, we have investigated a family of molecular catalysts to illuminate the molecular processes in electrocatalytic hydrogenation reactions.

The innovation of our approach is based on the hypothesis that catalysts that mediate transfer hydrogenation of ketones (Fig 1) are promising candidates as catalysts for electrohydrogenation for both thermodynamic and kinetic reasons. Thermodynamically, the reversible potential for hydrogenation of CO<sub>2</sub> to methanol (-0.031 V vs. RHE, 25°C) is similar to that for the reversible potential of acetone hydrogenation to isopropanol (0.12 V vs. RHE, 25°C). That the M-H intermediates are generated rapidly from isopropanol in transfer hydrogenation reactions means that these hydrides are formed readily and reversibly at potentials that correspond to the thermodynamic potential for ketone hydrogenation. This provides a compelling argument that the formation of these M-H complexes is thermodynamically feasible at potentials close to that for the hydrogenation of C=O bonds of ketones, formates and CO<sub>2</sub>.



**Figure 1:** Transfer Hydrogenation of Ketones, Esters and CO<sub>2</sub>.

The bifunctional mechanisms (Fig 1) proposed for certain classes of transfer hydrogenation of ketones catalysts provide a promising strategy for lowering the kinetic barriers for CO<sub>2</sub> activation and reduction. One of the key principles derived from studies of homogeneous transfer hydrogenation is the concept of dual-site cooperativity, whereby a redox-active transition metal such as Ru, Fe, or Ni is in close proximity to heteroatoms, such as O, N, or S such that a hydride and a proton are delivered to the C=O bond in one step to effect the overall hydrogenation (Fig. 1).[5]

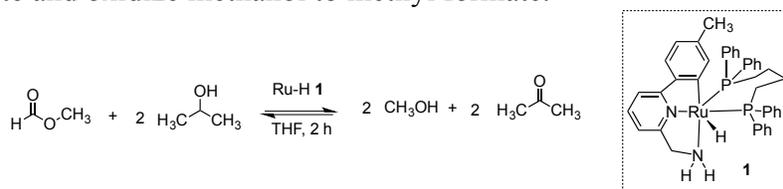
Several recent studies have shown that homogeneous molecular catalysts can utilize hydrogen to reduce CO<sub>2</sub> or esters;[4,6] what distinguishes our approach is our strategy for translating this promising chemical reactivity into efficient electrohydrogenation reactivity.

## Results

*Enhancing the analytical infrastructure for catalyst design/discovery:* A major focus in the initial stage of this project has been to enhance the laboratory's infrastructure and analytical capabilities to rapidly characterize, discover, and optimize new chemical and electrochemical catalysts. We have designed and prototyped a custom electrolysis cell using a carbon cloth working electrode that can assay candidate complexes in a matter of hours. Testing of our prototype cells is currently underway. In addition, we have designed, purchased, and installed a custom gas chromatograph that is able to quantify liquid and gaseous electrolysis products at the ppm level directly from electrolysis solutions without additional sample preparation.

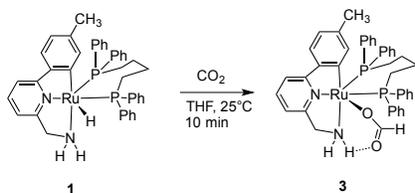
*New catalysts and new reactivity:* Our synthetic efforts have focused on two areas: 1) exploring the reductive chemistry of highly active transfer hydrogenation catalysts, and 2) designing new complexes for reduction of carbonyl containing compounds and/or protons.

*Reversible reduction of methyl formate; oxidation of methanol.* In the last year, we have generated a family of high activity transfer hydrogenation catalysts[7] based on metal hydrides. We have recently shown that these complexes can reversibly hydrogenate methyl formate and oxidize methanol to methyl formate.



**Figure 2:** Reversible hydrogenation of methyl formate, oxidation of methanol.

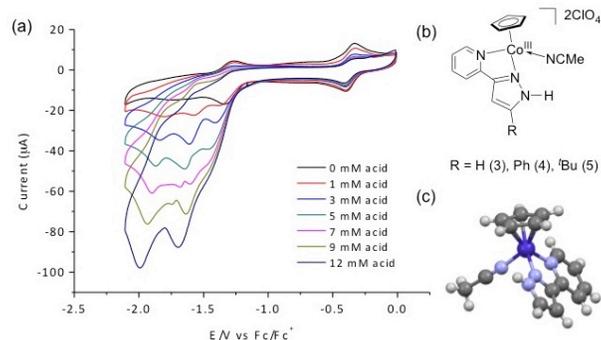
We have also shown that the Ru(II)-hydride **1** reacts readily with CO<sub>2</sub> at room temperature to generate the Ru(II)-formate. Theoretical studies imply that the cooperative influence of the pendant N-H group is important in stabilizing the incipient Ru-formate, illustrating the important role of cooperative ligand effects. The reactivity of the Ru-H manifested in Figures 2 and 3 reveal that appropriately designed metal hydrides are capable of mediating the reduction of both CO<sub>2</sub> and formates, precisely the type of reactivity needed to efficiently reduce carbon dioxide to energy rich molecules such as methanol.



**Figure 3:** Rapid insertion of CO<sub>2</sub> into Ru-H 1.

To illuminate the molecular features that influence this reactivity, we have carried out theoretical calculations coupled to a series of kinetic and thermodynamic studies on the reactions of these ruthenium hydrides with ketones, esters and CO<sub>2</sub>. These studies are providing molecular design parameters to enable us to tune the reactivity of these complexes and to illustrate the fundamental electronic features that are required for efficient reduction of CO<sub>2</sub>, esters and ketones.

*Earth abundant Cobalt complexes for electroreduction of protons:* We have also investigated a new family of earth-abundant metal complexes derived from cobalt to test for metal-ligand cooperativity in the reduction of protons to dihydrogen. We prepared piano-stool cobalt hydride complexes containing pyrazole groups as pendant acids/bases to test if the acid-base behavior of the ligand can facilitate proton reduction or reactivity with polar carbonyl and alcohol containing compounds. Initial studies reveal that these are active electrocatalysts for the reduction of protons to dihydrogen in acetonitrile (Fig 4), albeit at rather negative potentials. The onset of electrocatalytic current occurs at potentials corresponding to the reduction of Co(II) to Co(I), similar to that observed for other Co complexes.[8,9] These studies reveal that, under these conditions, the pyridyl pyrazole ligand does not appear to exhibit the desired cooperative behavior, at least in the hydrogen evolution reaction.



**Figure 4.** (a) Electroreduction of protons with the cobalt complex  $[\text{CpCo}(\text{Hpzpy})(\text{MeCN})][\text{ClO}_4]_2$  (**3**) as a function of acid concentration. Conditions: glassy carbon electrode, 1mM **3**, 0.1 M  $[\text{NBu}_4][\text{ClO}_4]$  in  $\text{CH}_3\text{CN}$ , acid: *p*-toluenesulfonic acid monohydrate (PTSA), scan rate 100 mV/s (In  $\text{N}_2$  glovebox) (b)  $[\text{CpCo}(\text{Hpzpy}-\text{R})(\text{MeCN})][\text{ClO}_4]_2$  (R= H (**3**), Ph (**4**),  $t\text{Bu}$  (**5**)) (c) X-ray structure of **3**; hydrogen atom and  $\text{ClO}_4$  anions are omitted for clarity.

## Progress

In the first few months of this project, we have commissioned new electrochemical cells and analytical methods for evaluating new catalysts for electrocatalytic reduction reactions. Preliminary reactivity studies have provided promising leads for the generation of reactive ruthenium hydrides that can activate and reduce carbon dioxide and alkyl formates. Initial investigations with earth-abundant cobalt complexes reveal electrocatalytic behavior for the reduction of protons. Should our ongoing efforts to develop efficient electrohydrogenation catalysts for the reduction of  $\text{CO}_2$  to methanol prove successful, this research will provide a strategy for the more widespread use of renewable and/or intermittent energy sources, such as wind, hydroelectric and solar energy.

## Future Plans

In the next year, a key objective will be to develop novel strategies for generating reactive metal hydrides electrochemically. Here we plan to focus on the design of redox-active and proton-active ligands to facilitate the generation of metal hydrides by proton-coupled electron transfer. The promising electrocatalytic reduction chemistry of the

cobalt complexes will be extended to the more challenging electrocatalytic reduction of ketones, esters and carbon dioxide.

### Publications and Patents

1. Brownell, K. R. Investigations of Ruthenium Transfer Hydrogenation Catalysts for the Electrooxidation of Alcohols. *Ph.D. Thesis*, Stanford University, 2012.
2. De Crisci, A. G.; Reinecke, B. N.; Hedman, B.; Kanan, M. W.; Jaramillo, T. F.; Waymouth, R. M. The exploration of Heterogeneous Transfer Hydrogenation Catalysts for Alcohol Oxidation, *Poster Presentation*, GCEP Research Symposium, Oct. 10-11, 2012.

### References

1. A.T. Bell, B.C. Gates, D. Ray, *Basic Research Needs: Catalysis for Energy* (PNNL-17214), U.S. Department of Energy, Report from a Workshop held in August 6–8, 2007, Bethesda, Maryland (US) <http://science.energy.gov/bes/news-and-resources/reports/basic-research-needs/>.
2. Whipple, D. T.; Kenis, P. J. A., Prospects of CO<sub>2</sub> Utilization via Direct Heterogeneous Electrochemical Reduction. *J. Phys. Chem. Lett.* 1 (24), 3451-3458, 2010.
3. Benson, E. E.; Kubiak, C. P.; Sathrum, A. J.; Smieja, J. M., Electrocatalytic and homogeneous approaches to conversion of CO<sub>2</sub> to liquid fuels. *Chem. Soc. Rev.* 38 (1), 89-99, 2009.
4. Balaraman, E.; Gunanathan, C.; Zhang, J.; Shimon, L. J. W.; Milstein, D., Efficient hydrogenation of organic carbonates, carbamates and formates indicates alternative routes to methanol based on CO<sub>2</sub> and CO. *Nat Chem* 3 (8), 609-614, 2011.
5. Ikariya, T.; Blacker, A. J., Asymmetric transfer hydrogenation of ketones with bifunctional transition metal-based molecular. *Acc. Chem. Res.* 40 (12), 1300-1308, 2007.
6. Federsel, C.; Jackstell, R.; Beller, M., State-of-the-Art Catalysts for Hydrogenation of Carbon Dioxide. *Angew. Chem., Int. Ed.* 49 (36), 6254-6257, 2010.
7. Baratta, W.; Ballico, M.; Esposito, G.; Rigo, P., Role of the NH<sub>2</sub> functionality and solvent in terdentate CNN alkoxide ruthenium complexes for the fast transfer hydrogenation of ketones in 2-propanol. *Chem. Eur. J.* 14 (18), 5588-5595, 2008.
8. Koelle, U.; Ohst, S. Electrochemical Reduction of Protonated Cyclopentadienylcobalt Phosphine Complexes, *Inorg. Chem.*, 25, 2689-2964, 1986.
9. Marinescu, S. C.; Winkler, J.R.; Gray, H. B. Molecular mechanisms of Cobalt-catalyzed hydrogen evolution *Proc. Nat. Acad. Sci.* 109, 15127-15131, 2012.

### Contacts

Robert M. Waymouth: waymouth@stanford.edu  
Christopher Chidsey: chidsey@stanford.edu  
Kate Waldie: kwaldie@stanford.edu  
Sung-Kwan Kim: skkim1@stanford.edu  
Andrew Ingram: ajingram@stanford.edu