

Electrohydrogenation: Enabling Science for Renewable Fuels

Investigators

Professor Robert M. Waymouth, Professor, Chemistry
Professor Christopher E. D. Chidsey, Professor, Chemistry
Kate Waldie, Graduate Student, Chemistry
Srinivasan Ramakrishnan, Graduate Student, Chemistry
Wei-Wei Wu, Graduate Student, Chemistry
Elizabeth McLoughlin, Graduate Student, Chemistry

Abstract

A wide range of transition metal based complexes active towards reducing carbon dioxide, carbonyls and protons have been developed. The electrochemical reduction of such substrates is increasingly relevant in the context of storing electrical energy in chemical bonds. For the two-electron reduction of CO₂, we made important advances on two key fronts: (a) achieving a single step two-electron transfer in earth-abundant metal complexes, and (b) reducing CO₂ with a singly reduced metal complex. Both these results help in achieving the desired chemistry with maximum energy efficiency. In addition, we have discovered a rapid Mn-based transfer hydrogenation catalyst.

Introduction

The goal of this project was to develop energy-efficient catalysts for electrohydrogenation reactions to create liquid fuels from renewable feedstock such as CO₂ and water. This would serve the ultimate goal of using renewable electricity to make energy dense liquid fuels from CO₂ and biomass.

Aim 1: To apply concepts from transfer hydrogenation to develop new catalysts for the energy efficient and rapid activation and reduction of CO₂ and carbonyl 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 electrocatalytic reduction of CO₂ and other carbonyl containing molecules.

Background

The large-scale storage of renewable electricity is still a missing piece in the quest for a truly sustainable energy system. The electrochemical reduction of CO₂ and/or upgradation of biomass to energy dense liquid fuels constitute grand challenges to realize energy storage in chemical bonds.¹ The challenge primarily stems from the thermodynamic and kinetic inertness of CO₂ towards reduction.² While transition metal based heterogeneous electrocatalysts are known to reduce CO₂,³⁻⁵ the selectivity is often poor leading to a mixture of products that are difficult to separate. With homogeneous transition metal complexes on the other hand, the reaction coordinate can be controlled via *a priori* design of specific metal-ligand-substrate interactions to achieve optimal catalytic selectivity.⁶

While high turnover rates are critical for large-scale implementation, our objective is to develop new strategies for CO₂ electrohydrogenation with maximum selectivity at low

overpotentials. It is our view that the gaps in the understanding of mechanistic details of product selectivity and driving forces are the major impediments to further progress in this field.

The innovation of our approach is based on the hypothesis that catalysts that mediate transfer hydrogenation of ketones (Figure 1) are promising candidates as catalysts for electrocatalytic hydrogenation for both thermodynamic and kinetic reasons. Thermodynamically, the reversible potential for hydrogenation of CO₂ 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 CO₂.

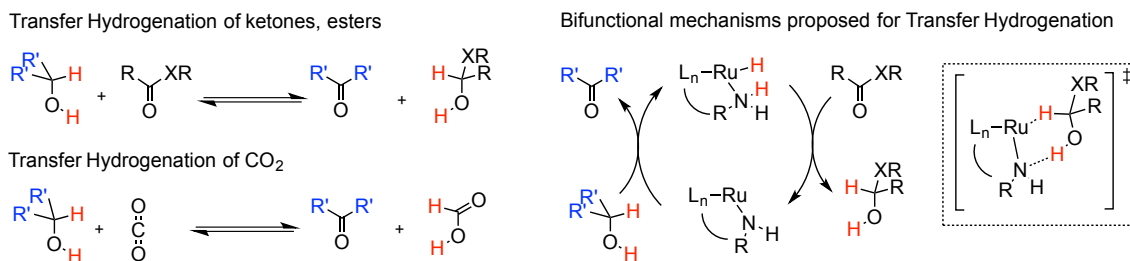


Figure 1: Transfer Hydrogenation of Ketones, Esters and CO₂.

The bifunctional mechanisms (Figure 1) proposed for certain classes of ketone transfer hydrogenation catalysts^{7,8} provide a promising strategy for lowering the kinetic barriers for CO₂ activation and reduction.⁹ 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).¹⁰

Several recent studies have shown that homogeneous molecular catalysts can utilize hydrogen to reduce CO₂ or esters,^{11,12} what distinguishes our approach is our strategy for translating this promising chemical reactivity into efficient electrohydrogenation reactivity.

Results: May 15, 2016 – August 31, 2016.

New catalysts and new reactivity: Our synthetic efforts have focused on two areas: 1) to explore the reductive chemistry of highly active transfer hydrogenation catalysts, and 2) to design new complexes for reduction of CO₂, carbonyl containing compounds and/or protons.

Two-electron reduction at Cobalt: Engineering Metal-Ligand Interactions

The electrochemical reduction of CO₂ to formic acid is a two-electron two-proton process. The addition of a second electron to a molecular catalyst often results in high overpotentials due to on-site electrostatic repulsion. Precious metal complexes such as those of Ir, Rh and Pd are known to undergo a single step two-electron reduction thereby avoiding such overpotentials. However, there are no guiding principles for achieving this multi-electron redox behavior with first row metal complexes.

We discovered that a Co(III) complex with a redox-active phenylazopyridine ligand undergoes a reversible two-electron reduction at a modest potential of -0.16 V vs. Fc⁺/Fc (Fc = Ferrocene) in acetonitrile. This noble metal-like behavior was not found with the analogous Co(III) bipyridine and pyrazole complexes (Figure 2). Using spectroscopic and computational tools based on density functional theory, we showed how the alignment of metal d-orbitals and ligand π* orbitals in the singly-reduced intermediate state is a descriptor for achieving multi-electron reductions in earth-abundant metal complexes (Figure 2).

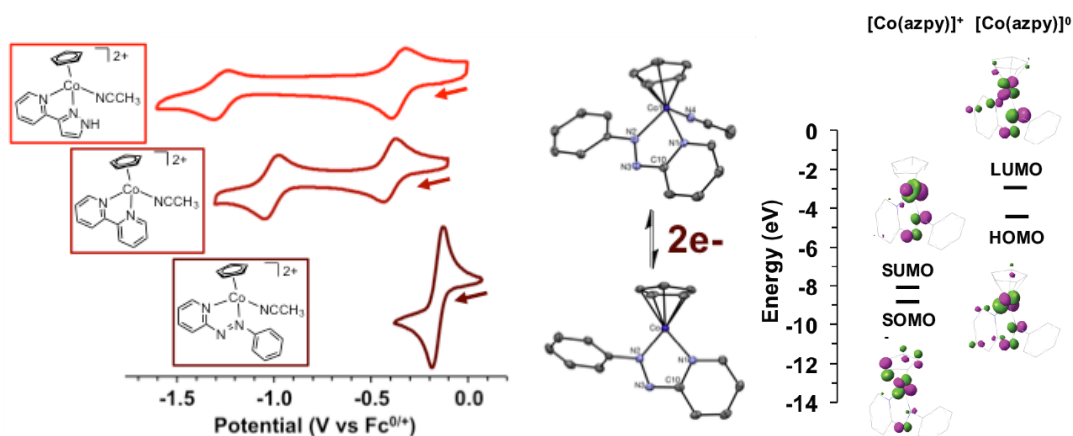


Figure 2. (Left) Cyclic Voltammograms of CpCo(III) complexes bearing different nitrogen based bidentate ligands. The phenylazopyridine complex alone shows a unique two-electron reduction. (Right) The metal and ligand orbital occupancies in the singly and doubly reduced states of this complex show substantial metal-ligand cooperativity.

The Cobalt phenylazopyridine system as an electrochemically regenerable H-atom donor

Further studies on the Co(III) phenylazopyridine complex with X-ray absorption spectroscopy revealed that the two-electron reduction of the Co(III) complex occurs at the metal rather than the ligand to form a Co(I) complex. Under acidic conditions, the nitrogen of the azopyridine ligand that is not coordinated to the metal is protonated after the two-electron reduction (Figure 3). Protonation at the ligand rather than at the Co center is supported by low-temperature ¹H-NMR spectroscopy as well as X-ray crystallography. Interestingly, X-ray absorption measurements reveal that the electronic structure of the doubly reduced Co center does not change upon protonation, i.e. Co remains in a Co(I) oxidation state. The pK_a of the protonated species was measured to be ca. 12.1 in MeCN.

These measurements indicate that the Co(I)-NH complex is a competent hydrogen atom donor as the bond-dissociation free energy of the N-H bond is calculated to be approximately 67 kcal/mol. This value is supported by NMR studies, which reveal that the protonated species can donate a hydrogen atom to 2,6-di-*tert*-butyl-4-(4'-nitrophenyl)phenoxy radical (BDFE = 77 kcal/mol). These results reveal the rich chemistry of proton- and redox-active ligands and guide new approaches to electrochemically regenerable hydrogen atom donors. Such hydrogen atom donors can then be used to make metal hydrides at low driving forces.

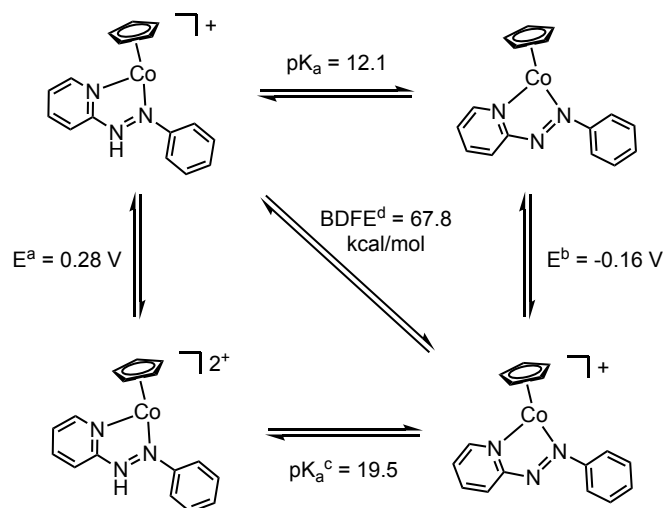


Figure 3: Square scheme for the protonated complex. All values are listed in MeCN and referenced to Fc/Fc^+ . ^aIrreversible two-electron-one-proton oxidation ^bTwo-electron cathodic wave ^{c,d}Calculated values.

Initiation of CO₂ Reduction by a Singly Reduced Ru(II)-Bipyridine Complex

A cyclopentadienyl Ru(II) bipyridine complex on single electron reduction was found to initiate a cascade of electrochemical and chemical steps leading up to the generation of a Ru(II)-bound CO complex and free carbonate, all at a potential that is ca. 100 mV positive of the first reduction of the Ru(II) complex. We found that the one-electron reduction of this complex is purely ligand based (bpy) and leads to binding of CO₂ at diffusion controlled rates. The subsequent reactivity of this CO₂ bound species in an EC mechanism leads to the products in a highly exergonic fashion (Figure 4).

Activation of CO₂ at the first reduction potential is therefore an alternate way of avoiding high overpotentials associated with multi-electron reductions.

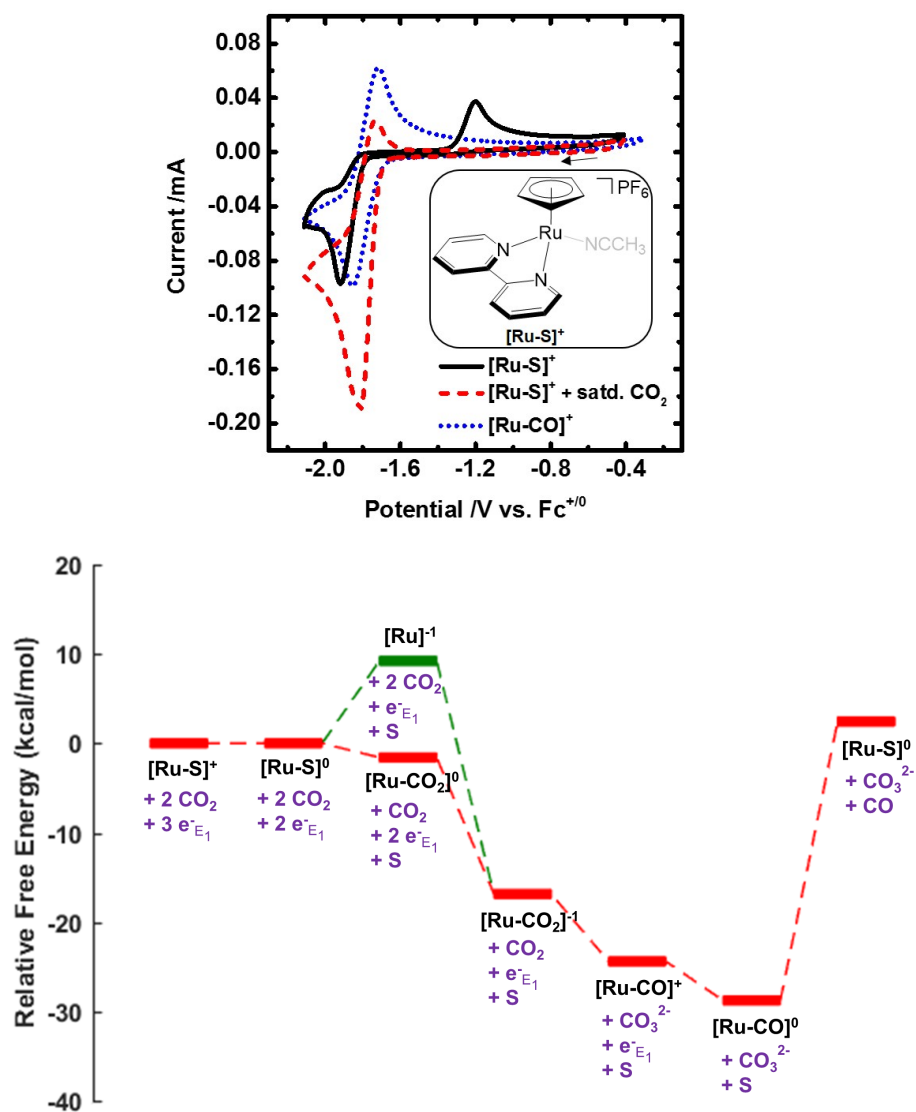


Figure 4. The cyclic voltammogram of $[\text{CpRu}(\text{bpy})(\text{CH}_3\text{CN})]\text{PF}_6$ or $[\text{Ru-S}]^+$ in acetonitrile at 100 mV/s. The reaction coordinate free energy diagram from DFT calculations (E_1 = reduction potential of the $[\text{Ru-S}]^{+/0}$ couple).

New Classes of Earth Abundant Complexes for Transfer Hydrogenation and Electroreduction

As part of our efforts to develop catalysts based on earth-abundant metals for transfer hydrogenation reactions and electrohydrogenation catalysts, we have generated a family of Cr, Mo, W, Fe, and Ru carbonyl complexes ligated by a redox and proton-active cyclopentadienone ligand.^{13,14} All of the novel phosphine-tethered Shvo-style^{15,16} complexes were active catalysts for the transfer hydrogenation of benzaldehyde with isopropanol as the dihydrogen source (Figure 5).

Specifically, the Mo complex (**Mo-2**) showed a three-fold higher reaction rate and greater than six-fold higher turnover number for transfer hydrogenation under the same reaction conditions compared to the analogous complex $[(\text{Ph})_4\text{CpOH}]\text{Mo}(\text{CO})_3(\text{CH}_3\text{CN})$ (**Mo-1**) that does not bear the phosphine moiety in its ligand backbone (Figure 6).

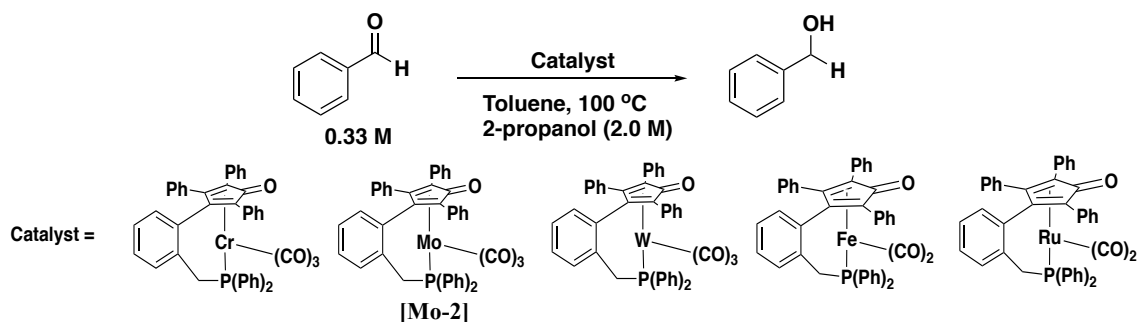
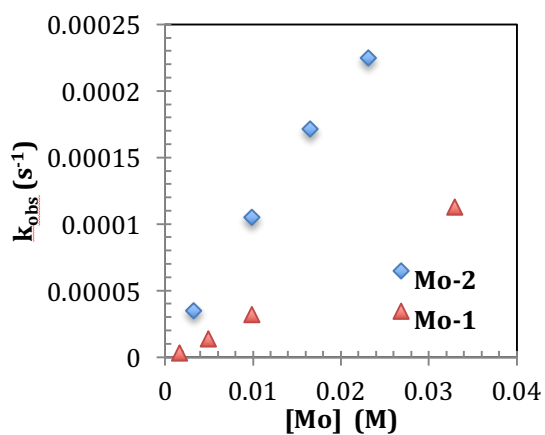


Figure 5. New family of metal complexes with redox- and proton-active ligands catalyze transfer hydrogenation of benzaldehyde with isopropanol.



Catalyst	k ($\text{M}^{-1} \text{s}^{-1}$)	R^2	TON
Mo-1	3.4×10^{-3}	0.99742	103
Mo-2	1.0×10^{-2}	0.99415	683

Figure 6. Observed rate and turnover number for **[Mo]** for the transfer hydrogenation of benzaldehyde in benzene at 65°C.

Progress

In the four month no-cost extension of this project, we have developed a simple design methodology for engineering single step two-electron reductions in earth-abundant metal complexes. We have also shown that the initiation of CO_2 reduction can take place after the addition of only one electron in an ECEC fashion as in the case of the Ru(II) bipyridine complex. Both results are important advances towards developing

catalysts that can operate with maximum energy efficiency (low overpotential). Further, we have explored the use of the protonated Co(I)-NH complex as an electrochemically regenerable H-atom donor that can make metal hydrides in situ. We have also developed a family of bifunctional proton-active and redox-active complexes out of earth-abundant metals for transfer hydrogenation reactions. Translation of this transfer hydrogenation activity to electrocatalysis will be a substantive step towards realizing reversible electrohydrogenation of CO₂ to liquid fuels.

Publications and Patents

1. Waldie, K.; Ramakrishnan, S.; Kim, S.; Maclaren, J.; Chidsey, C. E. D.; Waymouth, R. M. *J. Am. Chem. Soc.* **2017**, 139(12), 4540-4550.
2. Ramakrishnan, S.; Martinez, T. J.; Waymouth R. M.; Chidsey, C.E.D. ‘Thermodynamic Descriptors for Electrocatalytic CO₂ Reduction with Transition Metal Hydrides’ *Poster Presentation* at Theory and Applications of Computational Chemistry (TACC) Conference, Seattle, Aug 30, 2016.
3. McLoughlin, E. A.; Brown, T. A.; Samonina-Kosicka, J.; Zare, R. N.; Waymouth, R.M. “Electrochemistry Mass Spectrometry (EC/MS) Techniques to Examine Homogeneous Electrocatalytic Intermediates” *Poster Presentation* at CMAD Symposium. May 13, 2016.
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5. Samonina-Kosicka, J.; Rudeko, A.; Clark, M.; Kubiak, C. P.; Brown, T.A.; Zare, R. N.; Waymouth, R.M. “Mechanistic Studies of the CO₂ Electrochemical Reduction by the New Rhenium Tricarbonyl Azopyridine Complex” *Poster Presentation* at Johnson Symposium, Oct. 14, 2016.

Talks

1. Wu, Weiwei ‘Synthesis of Co and Mo hydroxycyclopentadienyl complexes and their catalytic activities in transfer hydrogenation’, ACS National Meeting, San Francisco CA, April 2017.

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Contacts

Robert M. Waymouth: waymouth@stanford.edu

Christopher Chidsey: chidsey@stanford.edu

Kate Waldie: kwaldie@stanford.edu

Srinivasan Ramakrishnan: saistrini@stanford.edu

Wei-Wei Wu: weiweiwu@stanford.edu

Elizabeth McLoughlin: emclough@stanford.edu