Electrohydrogenation: Enabling Science for Renewable Fuels

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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 CO\(_2\), we made important advances on two key fronts: (a) achieving a single step two-electron transfer in earth-abundant metal complexes, and (b) reducing CO\(_2\) 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 CO\(_2\) and water. This would serve the ultimate goal of using renewable electricity to make energy dense liquid fuels from CO\(_2\) and biomass.

Aim 1: To apply concepts from transfer hydrogenation to develop new catalysts for the energy efficient and rapid activation and reduction of CO\(_2\) 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 CO\(_2\) 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 CO\(_2\) 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 CO\(_2\) towards reduction.\(^2\) While transition metal based heterogeneous electrocatalysts are known to reduce CO\(_2\),\(^3-5\) 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 \textit{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 CO\(_2\) 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 CO\textsubscript{2} 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\textsubscript{2}.

**Figure 1:** Transfer Hydrogenation of Ketones, Esters and CO\textsubscript{2}.

The bifunctional mechanisms (Figure 1) proposed for certain classes of ketone transfer hydrogenation catalysts\textsuperscript{7,8} provide a promising strategy for lowering the kinetic barriers for CO\textsubscript{2} activation and reduction.\textsuperscript{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).\textsuperscript{10}

Several recent studies have shown that homogeneous molecular catalysts can utilize hydrogen to reduce CO\textsubscript{2} or esters,\textsuperscript{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 CO\textsubscript{2}, carbonyl containing compounds and/or protons.
Two-electron reduction at Cobalt: Engineering Metal-Ligand Interactions

The electrochemical reduction of CO\textsubscript{2} 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\textsuperscript{+}/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](image)

**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 \textsuperscript{1}H-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 pKa 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.

![Diagram of protonated complex](image)

**Figure 3**: Square scheme for the protonated complex. All values are listed in MeCN and referenced to Fc/Fc$^+$. $^a$Irreversible two-electron-one-proton oxidation $^b$Two-electron cathodic wave $^c,d$Calculated values.

**Initiation of CO$_2$ 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 CO$_2$ at diffusion controlled rates. The subsequent reactivity of this CO$_2$ bound species in an EC mechanism leads to the products in a highly exergonic fashion (Figure 4).

Activation of CO$_2$ 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 [CpRu(bpy)(CH$_3$CN)]PF$_6$ or [Ru-S]$^+$ in acetonitrile at 100 mV/s. The reaction coordinate free energy diagram from DFT calculations ($E_1 =$ reduction potential of the [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 [((Ph)_4CpOH)Mo(CO)_3(CH_3CN)] (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.](image)

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

<table>
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<th>Catalyst</th>
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<td>0.99415</td>
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**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


Talks


References

(7) Morris, R. H. Exploiting Metal-Ligand Bifunctional Reactions in the Design of Iron Asymmetric


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