

Efficient Interconversion of Chemical and Electrical Energy: Electrocatalysis with Discrete Transition Metal Complexes

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Introduction

This project aims to develop efficient electrocatalysts for ambient-temperature direct-hydrocarbon fuel cells. While the efficient catalysis of H_2 oxidation in fuel cells is well established, the challenges of making, transporting and storing H_2 motivate the development of efficient catalysts for the oxidation of hydrocarbons. Developing an efficient fuel cell to use the established hydrocarbon fuels is an important investment for reducing CO_2 emissions and improving the efficiency of energy utilization. The energy density of long-chain hydrocarbons in inexpensive tanks is 8 kWh/L, twice that of methanol and much better than any practical H_2 storage system¹. Moreover, a hydrocarbon fuel cell could also be a more efficient means than a combustion engine to use CO_2 -neutral fuels such as biofuels or synthetic fuels from solar energy. Finally, even in the H_2 fuel cell, the catalysis of O_2 reduction remains a severe problem, with the majority of the waste heat caused by poor catalysis of this reaction². This heat must be removed from the fuel cell across a relatively small temperature gradient at significant capital and operating expense.

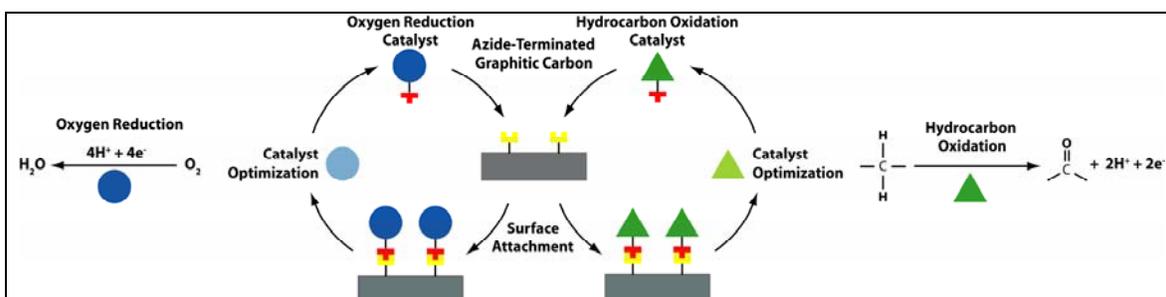


Figure 1. Schematic of research efforts

The dominant approach to improving electrocatalysis to date has been the empirical optimization of solid-state catalysts dispersed on graphitic electrodes. There is a need for a sustained and focused effort to understand and precisely tailor the reactivity of new types of electrocatalysts that fully utilize each of the expensive atoms in the catalysts to bind and activate the reactants. We are exploring how best to do this with stable ligands that present individual transition metal ions in specific arrangements to optimize electrocatalysis. Figure 1 depicts the relationship among our various efforts to

understand and optimize O₂ reduction and hydrocarbon oxidation catalysts based on transition metal complexes immobilized and site-isolated on graphitic electrodes like those used in PEM fuel cells.

Intimate contact of the reactants with metal atoms is required for efficient electrocatalysis, but neither hydrocarbons nor O₂ can displace other ligands from metal atoms. Thus, a good catalyst must have open coordination sites on the metal atoms at which the hydrocarbon or O₂ can bind and react. In this project, we have focused in particular on ligands that maintain open coordination sites around individual copper and palladium atoms. We have also explored ligands to position two or more metal atoms in a well defined environment that maintains such open coordination sites. Finally, we have explored methods to attach ligands covalently to graphite electrodes like those used as electrodes in PEM fuel cells in order to provide strong electronic coupling between the electrode and the metal atoms and to immobilize and site-isolate the metal complexes. Site-isolation prevents aggregation of the complexes, helping to maintain open coordination sites on the metal atoms.

In the most recent (second) year of this project, we have invented means to modify graphitic surfaces with azide groups (-N₃) for the covalent attachment of various ethynyl-terminated (HC≡C-) catalyst species by the recently discovered Sharpless-Meldal “click” reaction^{3,4}. We have submitted a patent application⁵ and published a journal article on this method⁶. We have recently demonstrated this “click” attachment of an ethynyl derivative of one of our mononuclear catalysts to an azide-modified graphitic electrode and demonstrated its electrocatalytic activity. We have submitted one manuscript for publication detailing our study of alcohol oxidation by phenanthroline complexes⁷ of palladium and will soon submit a paper on the reduction of O₂ by mononuclear phenanthroline complexes of copper. We have made progress on two families of ligands for multinuclear metal complexes and have begun to explore the electrocatalysis of O₂ reduction with copper complexes of one of these ligand families.

Results

Covalent Attachment of Metal Complexes to Carbon Electrodes

A one-step method to prepare azide-modified graphitic surfaces using iodine azide as the reagent has been developed.^{5,6} The azide groups were introduced at the graphitic edges, presumably via a Hassner addition⁸ of IN₃ to the double bonds and rapid elimination of HI (Figure 2). The prevalence of the reaction on the edge plane of highly oriented pyrolytic graphite and the absence of reaction on the basal plane suggested that the azides are formed predominantly at the edges of graphene sheets.

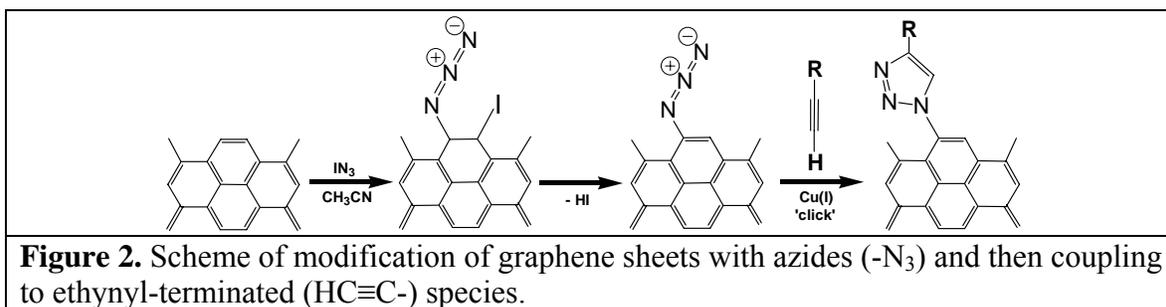


Figure 2. Scheme of modification of graphene sheets with azides (-N₃) and then coupling to ethynyl-terminated (HC≡C-) species.

Figure 3 shows nitrogen 1s x-ray photoelectron spectra (XPS) obtained from smooth, but randomly oriented, graphitic surfaces formed by the pyrolysis of photoresist. Figure 3a shows the XPS data after treatment with iodine azide. The peaks at 399 eV and 403 eV with a peak area ratio of 2:1 confirm the presence of the azide group.⁹ Figure 3b shows the XPS data obtained at the same surface after undergoing the click reaction with 20 μ M ethynylferrocene in the presence of a Cu(I) species to catalyze the click reaction. The loss of the peak at 403 eV and broadening of the peak at 399 eV are consistent with formation of the expected click product, the 1,2,3-triazole linkage. As expected, the area under the broader peak at 399 eV after the click reaction is equal to the area under the peaks at 403 and 399 eV before the click reaction. These observations suggest that the azide present on the surface forms the 1,2,3-triazole with 100 % yield.

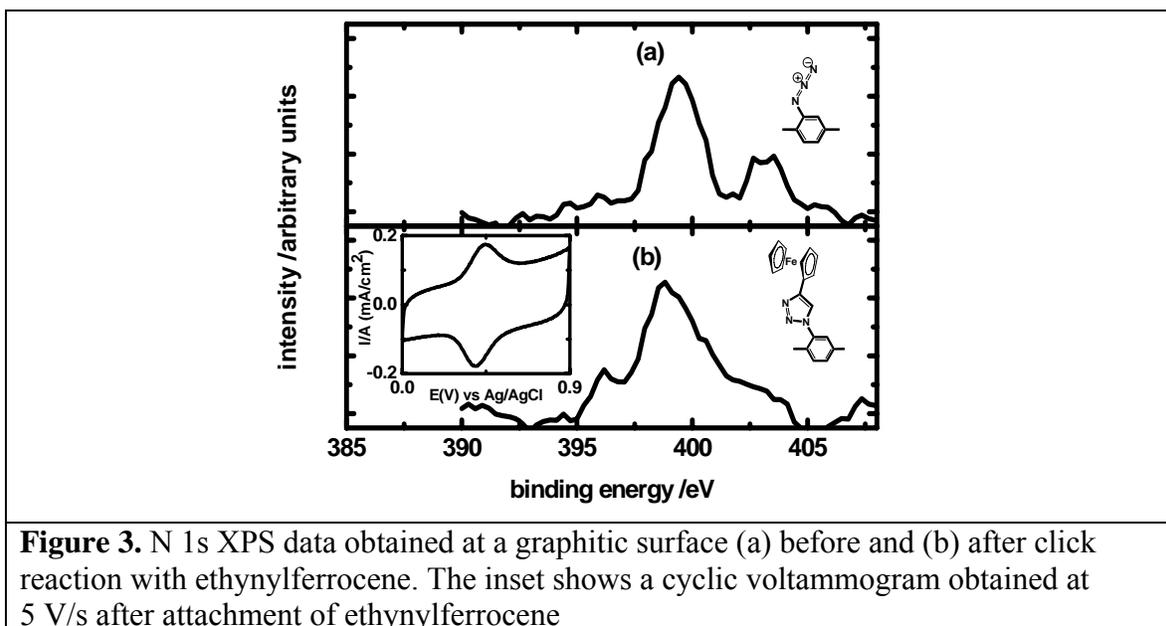
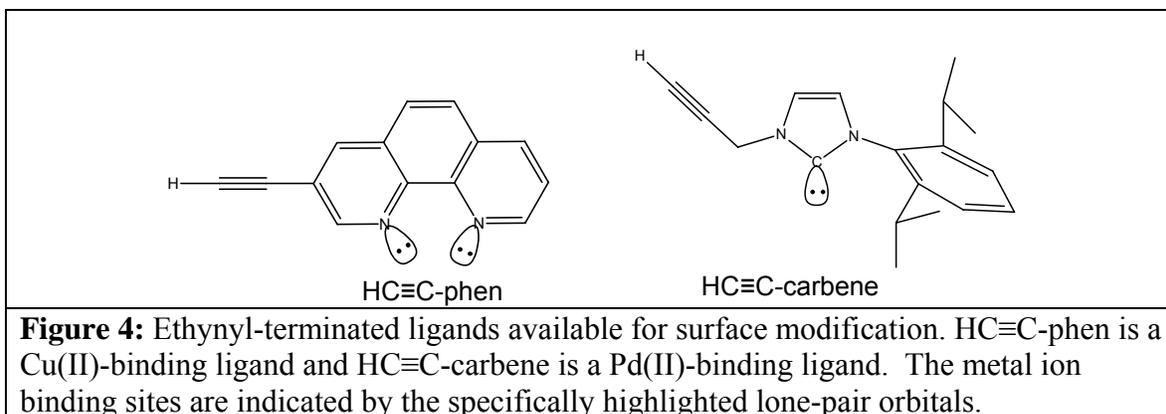


Figure 3. N 1s XPS data obtained at a graphitic surface (a) before and (b) after click reaction with ethynylferrocene. The inset shows a cyclic voltammogram obtained at 5 V/s after attachment of ethynylferrocene

The inset of Figure 3b shows the cyclic voltammogram obtained at this ethynylferrocene-modified graphitic surface in 1 M aqueous perchloric acid. Well defined ferrocene oxidation and re-reduction peaks are observed ($E^0 = +0.42$ V vs Ag/AgCl/KCl). The peak currents vary linearly with scan rate from 1 to 10 V/s with little or no peak splitting as expected for rapid electron transfer to surface-immobilized ferrocene. The charge under these peaks gives a surface coverage of 2.0×10^{13} molecules/cm². Similar experiments on mechanically abraded edge planes of highly oriented graphite surfaces give ferrocene surface coverages up to 40 times higher. Higher coverages are expected on the edge planes both due to the favorable orientation of the graphene sheets and also due to the very rough texture of this face as prepared by mechanical abrasion. The azide-modified graphitic surfaces are ideal platforms for the immobilization of discrete transition-metal complexes because the 1,2,3-triazole linker is hydrolytically and oxidatively stable and because it should fully conjugate the graphene planes of the electrode with the molecular orbitals of the transition-metal complex, allowing very rapid electron transfer to and from the electrocatalytic metal atoms¹⁰.



We have prepared the two ethynyl-terminated ligands shown in Figure 4: the phenanthroline ligand, HC≡C-phen, and the nitrogen-stabilized carbene-based ligand, HC≡C-carbene. The click reaction has been successfully used to attach these ligands to azide-modified edge-plane graphite surfaces. Electrochemical data show that these ligand-modified surfaces bind Cu(II) ions. Figure 5 shows the electrochemical response of a graphitic electrode after treatment with a Cu(II) salt before (curve a) and after (curve b) click reaction with HC≡C-phen. The inset in Figure 5 shows the linear dependence of electrochemical peak current on scan rate expected for a surface-immobilized species. Rinsing the surface with organic solvents such as chloroform and acetonitrile does not alter the electrochemical response for the covalently-attached complex, whereas these treatments do remove physisorbed phen-based complexes. The area under the electrochemical peaks indicates that the coverage of the electroactive species is about 9×10^{14} molecules per cm^2 . This is similar to the calculated coverage of ethynylferrocene covalently attached to a similar azide-modified surface. The redox potential of the covalently-attached copper complex is 295 mV vs. NHE, a full 270 mV more positive than the parent copper phenanthroline complex physisorbed onto an edge-plane graphite electrode, presumably due to the electron-withdrawing nature of the triazole linker.

The covalently-attached copper complex electrocatalyzes the reduction of O_2 in air-saturated solutions (Figure 5, curve c) at potentials negative of the redox potential of the surface-attached Cu(phen) complex. Preliminary kinetic results indicate that O_2 is reduced by 4 electrons to $2 \text{H}_2\text{O}$. Exposing the surface to 2,9-dimethyl-1,10-phenanthroline decreased the O_2 -reduction current, consistent with the added phenanthroline binding to the open coordination sites on the surface-bound copper complex.

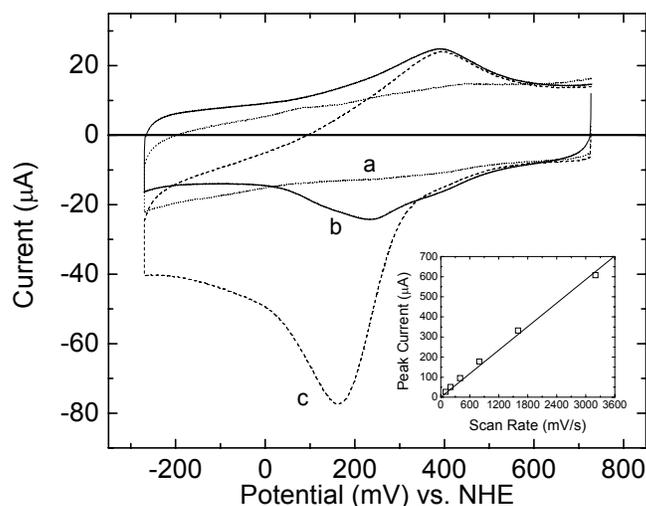


Figure 5. Cyclic voltammograms in 0.1M NaClO₄, 0.04M acetate buffer, pH 4.8. (a) Azide-terminated edge-plane graphite surface exposed to HC≡C-phen in the absence of Cu(I) catalyst and then treated with Cu(NO₃)₂(aq), (b) azide-terminated edge-plane graphite surface exposed to HC≡C-phen in the presence of Cu(I) catalyst and then treated with Cu(NO₃)₂(aq), and (c) same as (b) but in air-saturated solution showing electrocatalysis of O₂ reduction.

In upcoming work, we will form surface-bound Pd(II) and Ru(II) complexes of both of the ligands in Figure 4. XPS and voltammetric studies will be conducted at flat graphitic surfaces and rough edge-plane graphitic surfaces to determine the redox behavior and surface coverage of the Pd and Ru species formed on the surface. Rotating disk electrodes (RDE) will be used to study the electrocatalytic properties of the surface-immobilized Pd and Ru species towards alcohol oxidation. Similar characterization studies will also be conducted with ethynyl-terminated polynuclear metal complexes.

Mononuclear Cu Electrocatalysts for O₂ Reduction

Prior to developing complex multinuclear metal catalysts for O₂-reduction to H₂O, we have tried to fully understand the mechanism by which simple, mononuclear complexes catalyze this reaction. Last year, we reported that, in an expansion of Anson's work on Cu(I) complexes of 1,10-phenanthroline (phen) and 2,9-dimethyl-1,10-phenanthroline (2,9-Me₂-phen) adsorbed onto edge-plane graphite (EPG) as O₂-reduction catalysts,^{11,12} we obtained or synthesized a large library of phen-derivatives. We inferred that these catalysts follow a general mechanism involving an initial one-electron reduction from Cu^{II}(phen) to Cu^I(phen), followed by a binding of O₂ to form an Cu^{II}(phen)-O₂⁻ complex. This is then further reduced by 3 electrons to H₂O and Cu^{II}(phen).

Using this library of ligands, we identified systematic trends in the standard redox potential, E^0 , of their Cu complexes—specifically, a positive shifts in potential as electron-withdrawing substituents are added to the ligand backbone, and as the size of the substituents in the 2,9-positions adjacent to the coordinating nitrogens are increased. These trends are explained as follows: more electron-withdrawing substituents preferentially stabilize the lower oxidation state of the complex, here the Cu^I complex,

thereby increasing E^0 up to 130 mV compared to unsubstituted phen. Alternatively, adding substituents in the 2,9-positions increases E^0 up to 310 mV by distorting the energetically preferred square-planar geometry of Cu^{II} complex, which makes it energetically favorable to reduce the Cu^{II} complex to Cu^{I} , and thus increases the reduction potential. A comprehensive study of the O_2 -reduction kinetics of the Cu-complexes of six ligands has been conducted this year. Using a standard rotating disk kinetic analysis,¹² O_2 -reduction rates were determined at different potentials in the absence of mass-transfer effects. Figure 6 shows both how the maximum rate of O_2 reduction (at -300mV vs NHE) change as the E^0 of the catalysts are varied and also how the rate of O_2 reduction at E^0 varies with E^0 . The slow decrease in the maximum O_2 -reduction rate with increasing E^0 is expected for a system in which O_2 -binding is the rate-limiting step—as Cu^{I} is preferentially stabilized, it becomes less favorable to form the $\text{Cu}^{\text{II}}(\text{ligand})\text{-O}_2^-$ complex. On the other hand, the O_2 -reduction rates at E^0 follow two distinct trends with increasing E^0 —a steep decrease in rate as the substituents become more electron-withdrawing, and a more shallow decrease in rate with the increasing size of 2,9-substituents. The reduction rate at E^0 for all six complexes is slower than one half of the maximum O_2 -reduction rate, which is the rate that would be the expected rate if O_2 -binding were the rate limiting step at E^0 . Based on these data, we conclude that one or more of the subsequent reduction steps is rate limiting at E^0 . The slow rate of these subsequent reductions make mononuclear Cu complexes poor choices for efficient electrocatalysts for O_2 reduction. For instance, the O_2 -reduction rate for $\text{Cu}(\text{Et}_2\text{-phen})$ measured at its E^0 (-605 mV vs reversible O_2 reduction) is 0.2 turnovers $\text{Cu}^{-1} \text{s}^{-1}$ comparable to nanoparticulate Pt-catalysts at the significantly lower overpotential of -350 mV vs reversible O_2 reduction.¹³

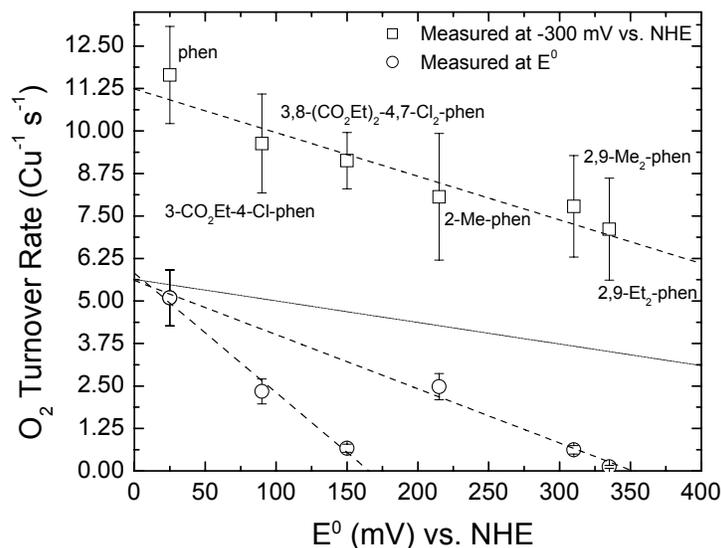


Figure 6. O_2 -reduction rates for Cu complexes measured at E^0 (circles) and -300 mV vs. NHE (squares) plotted against E^0 for each Cu complex. The dotted line is the rate at E^0 if O_2 -binding were rate-limiting. All data taken in 100 mM NaClO_4 , 40 mM acetate buffer, pH 4.8 except for 2,9-Me₂-phen taken in 92 mM acetate buffer, pH 4.2.

Multinuclear Cu Electrocatalysts for O₂ Reduction

The most efficient catalyst known for the reduction of a O₂ is fungal laccase¹⁴, an enzyme with three copper ions that collectively bind and reduce dioxygen. Building on our understanding of mononuclear species we have begun preliminary studies into O₂-reduction catalyzed by binuclear and higher Cu complexes. A proposed mechanism for the reduction of dioxygen with the binuclear ligand, dipyriddyipyrazole (dppy), is shown in Figure 7.

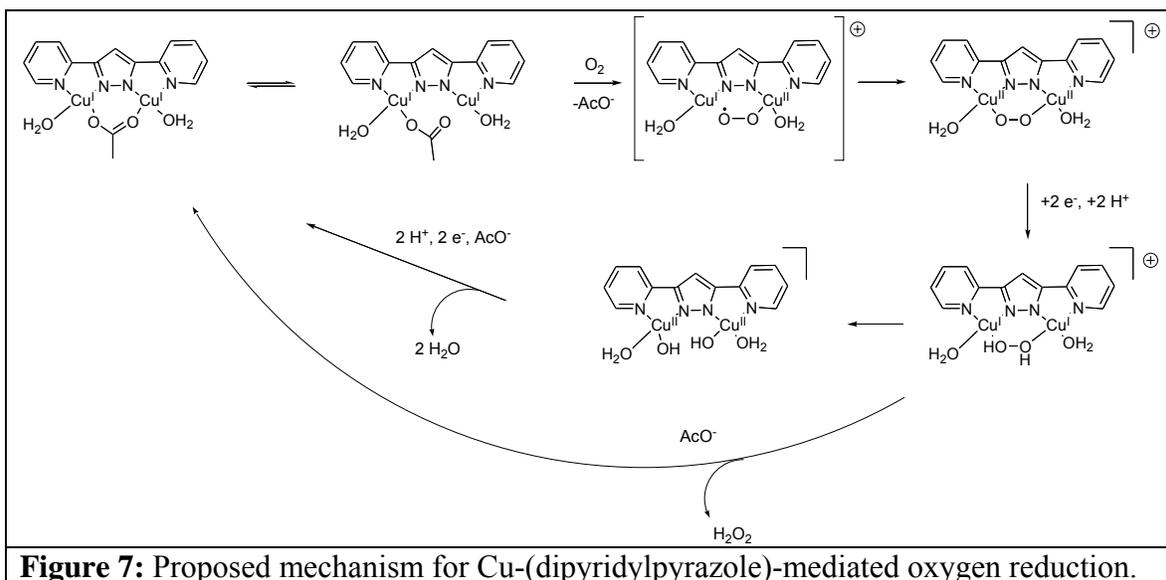


Figure 7: Proposed mechanism for Cu-(dipyridylpyrazole)-mediated oxygen reduction.

A representative cyclic voltammogram after adsorbing dppy onto edge-plane graphite and loading the ligand with Cu^{II} is shown in Figure 8. In the absence of air, this complex has a single reversible peak at -170 mV vs. NHE that appears to be the reduction of both Cu^{II} sites simultaneously. The peak current exhibits a linear dependence on scan rate, indicating that the compound is adsorbed on the surface. In air-saturated electrolyte, there is a shoulder peak with an onset of +140 mV vs. NHE.

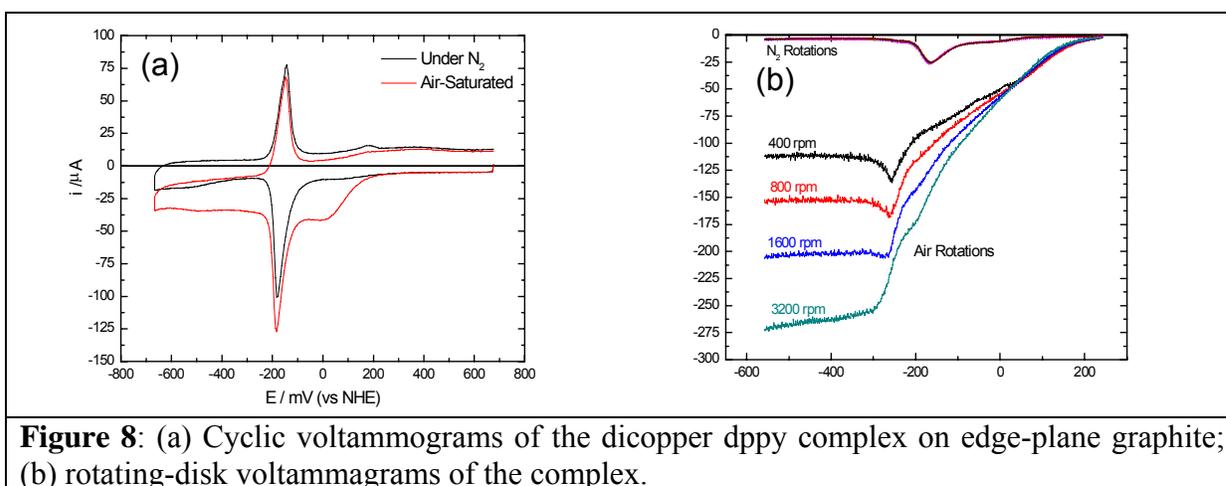


Figure 8: (a) Cyclic voltammograms of the dicopper dppy complex on edge-plane graphite; (b) rotating-disk voltammograms of the complex.

A rotating disk electrode experiment was also conducted to examine the kinetics of the dioxygen reduction mechanism. The peak at -170 mV, assign to the Cu(dppy) complex, significantly enhances the rate of oxygen reduction, showing that the species

responsible for the peak is electrocatalytic. However, the origin of the electrocatalysis at +140 mV is not yet well understood.

We intend to look at neutral analogs of the dppy ligand (dppy is anionic) such as dipyriddy 1,2,4-triazole ligands¹⁵⁻¹⁷ (Figure 9). There are a number of dicopper species with this type of ligand, but little is known about the electrochemistry of these species. The alkyl and amino 1,2,4-triazole ligands will be synthesized and their activity towards oxygen reduction investigated. Similar studies will be made with the 3,6-(2-pyridylthio)pyridazine (PTP) ligand^{18,19}.

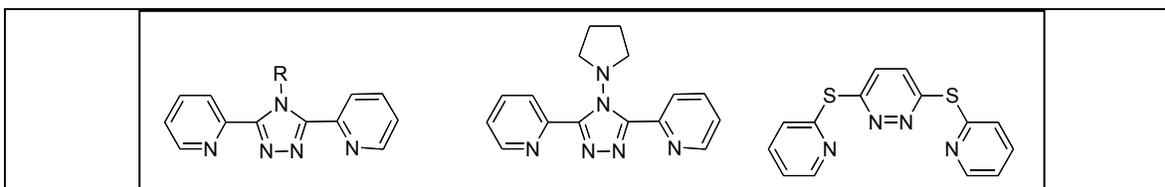


Figure 9: (a), (b): Proposed 4-substituted dipyriddy 1,2,4-triazole ligands; (c) the dipyriddythiopyridazine ligand

We are also exploring trinuclear and higher ligands for copper. Here, we are seeking a robust, generalizable strategy for the single-point covalent surface attachment of polyamine ligands to provide a multinuclear active site to the carbon electrode through a short tether that promotes site isolation and fast electron transfer. This architecture will be enabled by the pyridyl ethynyl aldehyde shown in Figure 10, which (a) can be linked to a polyamine ligand through a reductive amination coupling strategy, and (b) provides an ethynyl group that makes the molecule into a partner for click coupling to the azide-functionalized electrode surface. We have attached this pyridyl linker to a mononucleating polyamine ligand (Figure 10) and have synthesized trinucleating ligands²⁰ (Figure 11).

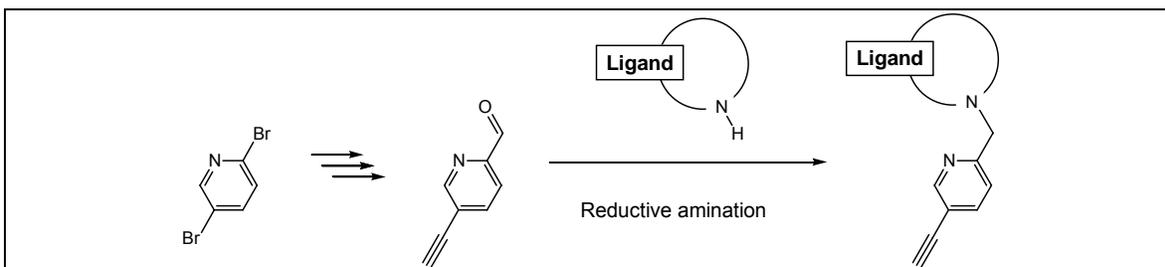


Figure 10. Reductive amination coupling of pyridyl linker to ligand

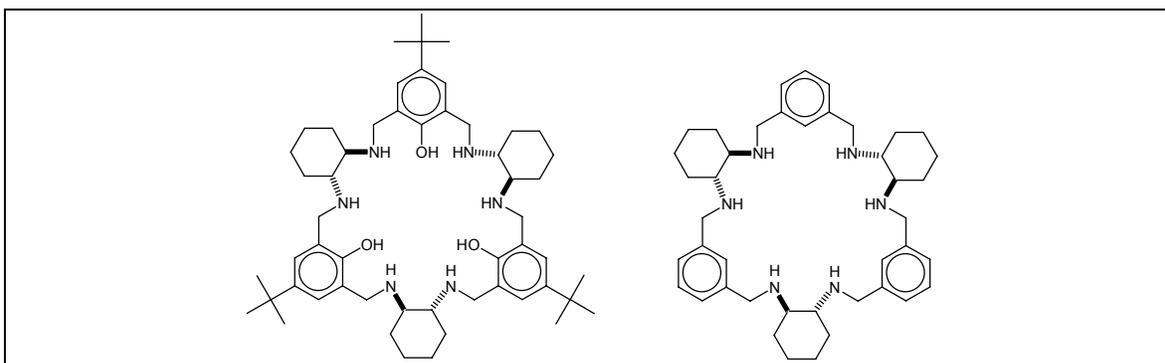


Figure 11. Trinucleating ligands

A Novel Mononuclear Pd Catalyst for C-H Oxidation

In our last report, we briefly described a catalyst for alcohol oxidation, [(2,9-dimethylphenanthroline)Pd(OAc)₂](OTf)₂ **1**, that exhibited unprecedented initial turnover frequencies (TOFs) under very mild conditions (room temperature, ambient air as oxidant). Through the study of **1**, we have identified two key requirements in catalyst design necessary to achieve very high TOFs: the active catalyst must (a) be cationic to afford an open coordination site and (b) contain a basic counterion for intramolecular deprotonation of the bound alcohol species. From Figure 12, which shows the reaction progress of aerobic 2-heptanol oxidation with different complexes, it is evident that neither requirement alone is sufficient (see curves for **2** and **3**). Complex **4** was also studied, and produced a significantly slower initial TOF compared to **1** due to its small dimer dissociation constant; only the monomeric forms of **1** and **4** are catalytically active.

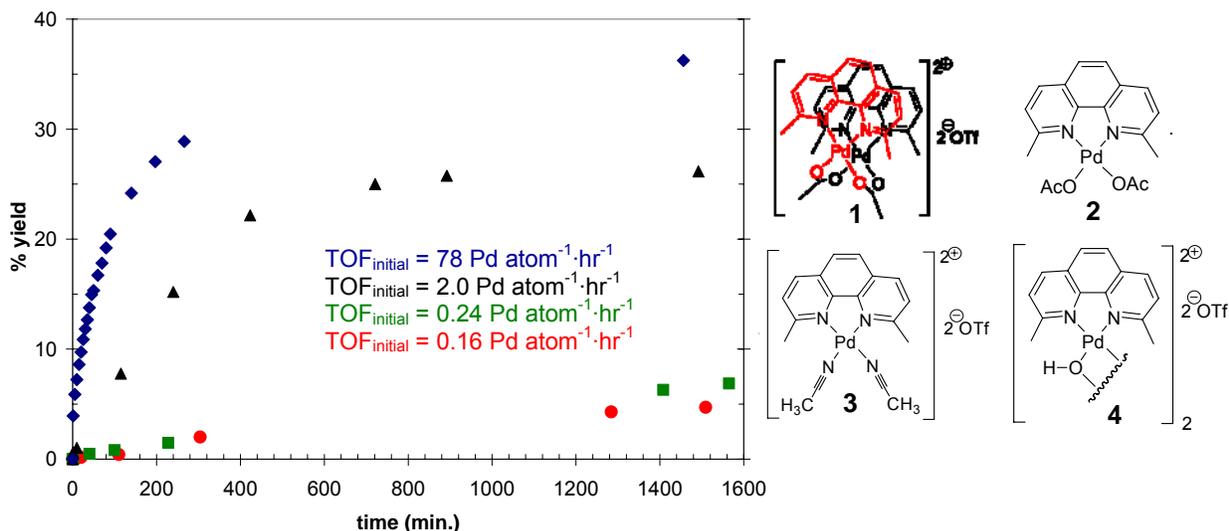


Figure 12. Reaction progress of air oxidation (1 atm) of 2-heptanol (0.5 M) with complexes **1** (◆), **2** (■), **3** (●), and **4** (▲) (3 mol % Pd) in acetonitrile (acetonitrile/dichloromethane, 1:1 for **2**; acetonitrile/dimethylsulfoxide, 1:1 for **4**) at room temperature.

Despite the fast initial TOF of catalyst **1**, the turnover number was only 12 after 24 h due to substantial slowing of the reaction rate over the course of the reaction. Palladium black formation and catalyst inhibition by products were ruled out as possible causes. To our surprise, the catalytically inactive, palladium carboxylate **5** (Figure 13) was isolated as the major palladium-containing product after the reaction.

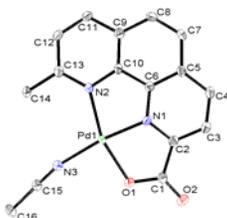


Figure 13. ORTEP-III plot of **5** with ellipsoids drawn at the 50% probability level.

To combat this deactivation of the catalyst, we employed other oxidants. Benzoquinone was found as a suitable oxidant for which no catalyst decomposition was observed. Benzoquinone also serves as a closer analogue to an electrode than oxygen. Motivated by this observation we began to explore the use of **1** for the oxidation of methanol with benzoquinone. The dominant product is methyl formate. Several pathways are possible (Figure 14). Isotopic labeling studies and model reactions suggest that methanol is oxidized first to formaldehyde, which reacts with methanol and is further oxidized to methyl formate (pathway D).

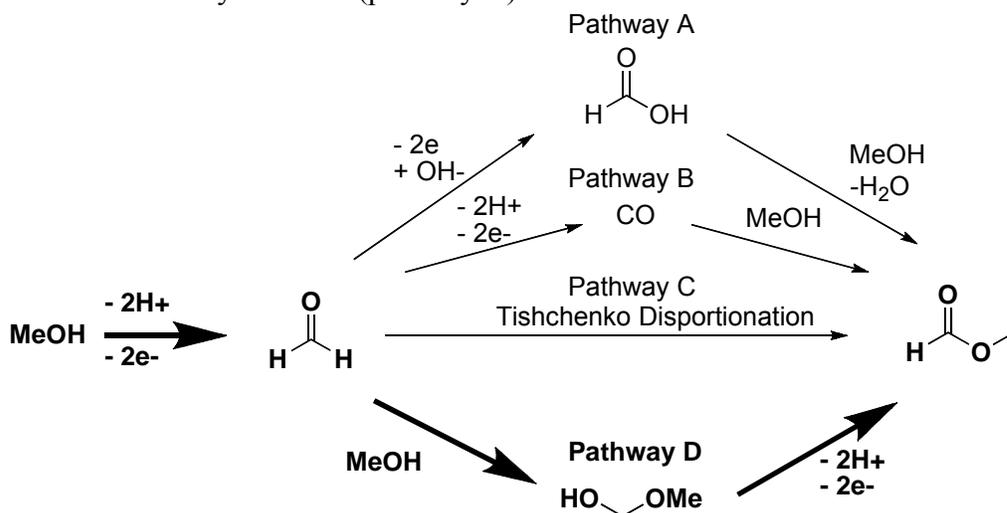


Figure 14. Possible pathways for the oxidation of methanol to methyl formate.

To date, adsorption of **1** onto edge-plane graphite has not given a viable electrocatalyst. We are now exploring click-immobilized analogs to **1** based on HC≡C-phen (Figure 4).

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