Computational Investigation of Small Molecule Catalysis by Cobalt, Rhodium, and Iridium Molecular Catalysts

Thesis by

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DEDICATION

For Kevin

"She is trying to guide his way home, from the waters that keep them apart."
-Roy Khan

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There are few times in one's life where one has the opportunity thank the people around them who have lent support and laughter. As I conclude my formal education and experience the emotional upheaval that comes with it, it feels appropriate to *attempt* to thank as many people as I can. No person walks the path to and through graduate school alone and it is through the grace and love of other people that I have been able to come this far. I have been blessed with an amazing group of friends, family, and mentors who have walked with me at various parts of this journey. I stress that this is an attempt to acknowledge how much of my success is owed to others, but these words feel inadequate when compared to the love and dedication of those mentioned here.

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ABSTRACT

Global energy demands are predicted to increase through 2040. In the spirit of meeting these demands, work focusing on increasing the efficiency of existing energy technologies, as well as improving energy storage is necessary. This work takes a catalytic approach to these challenges, focusing on Co, Rh, and Ir catalysts with pincer and bipyridine ligands. Density functional theory (DFT) can be used in order to gain a deeper understanding of how these catalysts behave. In the realm of improving existing technologies, the mechanism for oxidation of methane to methanol by Phebox Ir (Phebox = bis(oxazolinyl)phenyl) is investigated with a focus on understanding how subtle substitutions to the ligand can help or hinder this reaction. It is shown that in this catalyst, two unwanted intermediates on the potential energy surface (an Ir^{IV} state leading to catalyst deactivation and an Ir^{V} state leading to over-oxidation) can potentially be avoided by adding trifluoromethyl groups to the ligand. For production of fuels from solar energy, two reactions are studied. Experimentally, CO_2 reduction to formate by (POCOP)Ir (POCOP = C_6H_3-2,6-[OP(*t*Bu)$_2$]$_2$) has been shown to selectively occur at moderate potentials. The mechanism by which this catalyst reduces CO_2 is elucidated. In particular, the impressive product selectivity afforded this catalyst for formate over hydrogen production is rooted in kinetics: high barriers for protonation inhibit the creation of H_2 adducts. In addition to this, substitutions to the ligand and metal center are investigated to further illuminate the relationship between kinetics and thermodynamics. Hydrogen evolution in Cp*Rh(bpy) (bpy = 2,2'-bipyridine, Cp* = pentamethylcyclopentadienyl) is investigated, centering on unexpected protonation at the Cp* ligand rather than the metal center. This state is on the path for hydrogen evolution in the case of using weak acids, but in the presence of strong acids, the path through the traditional hydride is most likely. Finally, the attachment of these catalysts to electrode surfaces is discussed with the aim of making molecular catalysts a more viable option in industry It is shown that chlorine present in the attachment process enables easy catalyst dissociation from the surface. Several non-halogen options are discussed as replacements. Throughout the thesis two themes emerge: the constant interaction between thermodynamics and kinetics to control mechanistic paths and products, and the ability of small modifications to have huge impacts on catalytic cycles.

PUBLISHED CONTENT AND CONTRIBUTIONS

D.W. Shaffer, **S.I. Johnson**, J.W. Ziller, R.J. Nielsen, W.A. Goddard, A.L. Rheingold, J.Y. Yang; Reactivity of a Series of Isostructural Cobalt Pincer Complexes with CO_2, CO, and H^+. *Inorganic Chemistry.* 2014. 53 (24) 13031.http://dx.doi.org/10.1021/ic5021725

S.I.J. helped devise the computational mechanism, calculated all structures used in the manuscript, prepared the data and figures for the computational work, and participated in writing the manuscript.

M. Zhou, M., **S.I. Johnson**, Y. Gao, T.J. Emge, R.J. Nielsen, W.A. Goddard III, A.S. Goldman, Activation and Oxidation of Mesitylene C–H Bonds by (Phebox)Iridium(III) Complexes. *Organometallics.* 2015. 34, 2879−2888 http://dx.doi.org/10.1021/acs.organomet.5b00200

S.I.J. calculated all structures in the computational work, prepared the computational data, aided in explaining experimental results in accordance with computational results, and wrote the computational section of the manuscript.

L. Aguirre Quintana; **S.I. Johnson**; S.L. Corona; W. Villatoro; W.A. Goddard III; M. K. Takase; D. G. VanderVelde; J. R. Winkler; H. B. Gray; and J.D. Blakemore; Proton-Hydride Tautomerism in Hydrogen Evolution Catalysis. *Proceedings of the National Academy of Sciences* 2016, 113 (23), 6409-6414. http://dx.doi.org/10.1073/pnas.1606018113

S.I.J. participated in the conception of the project, guided undergraduate students to calculate structures, calculated structures herself, analyzed computational data and created figures representing the data, and participated in writing the manuscript.

S.I. Johnson; R.J. Nielsen; W.A. Goddard III. Selectivity for HCO_2^- over H_2 in the Electrochemical Catalytic Reduction of CO2 by (POCOP)IrH_2. *ACS Catalysis.* 2016, 6362-6371. http://dx.doi.org/10.1021/acscatal.6b01755

S.I.J. helped devise the mechanism, calculated most of the structures within the paper, analyzed the data and helped to prepare the manuscript.

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NOMENCLATURE

Bipyridine (bpy). 2,2'-bipyridine, a nitrogen-based heterocycle which is commonly used as a ligand in organometallic catalysis

Hydride. H^-, a proton and two electrons.

HOMO. Highest occupied molecular orbital

HSOMO. Highest singly-occupied molecular orbital

Ligand. An organic molecule bound to a metal center

LUMO. Lowest unoccupied molecular orbital

Ortho. See Phenyl Substutition section below.

Meta. See Phenyl Substutition section below.

NHE. Normal Hydrogen Electrode

Para. See Phenyl Substutition section below.

Phebox. Bis(oxazolinyl)phenyl ligand

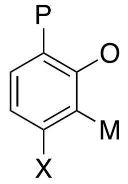
POCOP. C_6H_3-2,6-[OP(*t*Bu)$_2$]$_2$ ligand

SHE. Standard hydrogen electrode

Turnover Number (TON). Number of full catalytic cycles a catalyst completes

Turnover Frequencies (TOF). Number of turnovers in a given time span

Phenyl substitutions. If a group X is bound to a phenyl ring, as shown below, the ortho, meta, and para positions are indicated by O, M, and P, respectively.



Chapter 1

INTRODUCTION

Current US and Global Energy Scenario

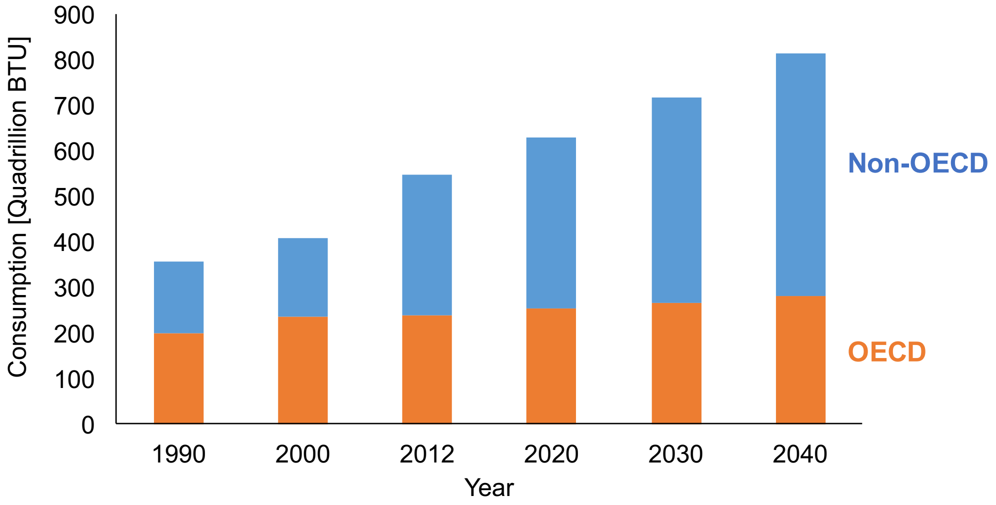


Figure 1.1: Global demand for energy, divided into contributions from developed (OECD) and developing countries. Figure courtesy of the US Energy Information Administration.[1]

As the global population increases, worldwide energy demand will grow with it. The overall predicted energy demand can be seen in Figure 1.1. In this figure, energy demand has been divided into to two categories: demand from developed countries (defined by the US Energy Information Administration as countries belonging to the Organization for Economic Cooperation and Development [OECD])[1] and demand from developing economies. While demand in OECD countries is predicted to plateau and even decrease into the future, demand in developing countries will cause global energy demand to increase. The plateau in the US is attributed to increased appliance and vehicle efficiency, as well as a population shift to warmer regions, that require less heating.[2] Increasing demands in developing countries stems from higher demands for liquid fuels, personal travel, and materials in the industrial sector.[1]

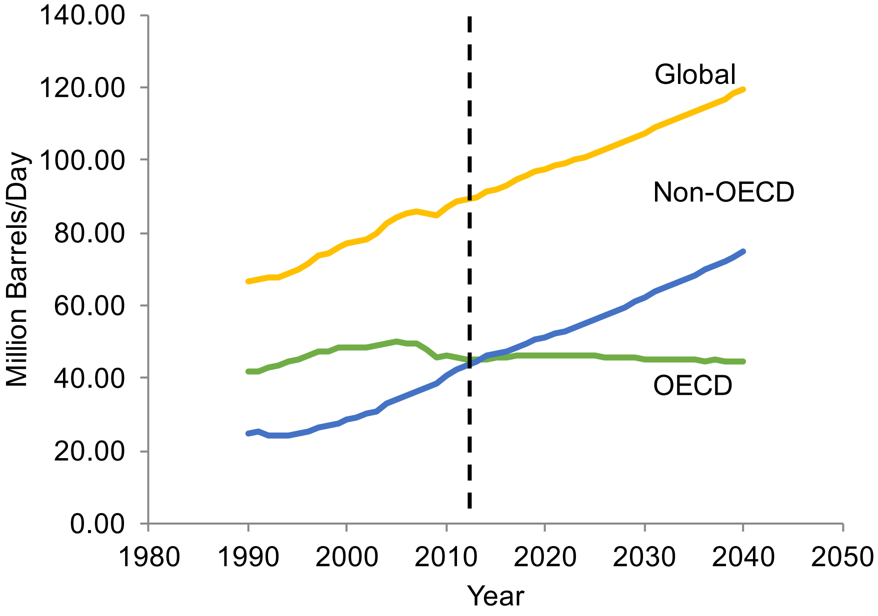


Figure 1.2: Global demand for petroleum and liquid fuels with projection. Increasing demand is largely driven by demand in growing economies. Figure courtesy of the US Energy Information Administration.[1]

In the United States, energy use can be divided into the following sectors: industrial, commercial, residential, and transportation. The largest consumer of energy is the industrial sector, comprising nearly one third of the U.S.'s energy use. This amount is predicted to grow into the future. Transportation contributes approximately 25% of the total energy use and is predicted to stay nearly the same. These two sectors are unique in that they are both significant users of petroleum and liquid fuels. According to the U.S. Energy Information Administration, "there are few substitutes for petroleum in construction, mining, agriculture, and manufacturing applications."[2] Furthermore, petroleum accounted for 92% of the transportation sector's energy usage (in 2010)[3]. The demand for petroleum and liquid fuels is not likely to subside. In fact, petroleum is the largest single source of fuel used in the United States, accounting for approximately 35% of primary energy use when divided by source.[2,3] In 2015, the U.S. net imported 4.21 million barrels of petroleum per day, with the top suppliers being Canada (40%), Saudi Arabia (11%), and Venezuela (9%).[4] Foreign petroleum sources composed about 24% of

US petroleum consumption in 2015. Demand for petroleum and liquid fuels is also projected to grow globally, as seen in Figure 2[5].

The fastest growing energy sources in the United States are natural gas and renewable sources, including wind, solar, hydropower, and geothermal sources. Natural gas, a mixture of methane and other light hydrocarbons, is largely used in the US for industrial and electric power, and heating. One stumbling block for natural gas's expansion into the transportation sector or as a replacement for petroleum is its gaseous nature, which makes it difficult to store and transport.[6] While gas-to-liquid (GTL) technologies exist, including liquefied natural gas (LNG) and compressed natural gas (CNG), these technologies often encounter issues with storage and are relegated to fleet vehicles or ships[7,8], or are prohibitively expensive[9]. Solar energy is the fastest growing renewable energy source and is predicted to continue growing 6% per year on average from 2015 to 2040.[2] Like natural gas, solar energy is faced with issues in energy storage.[10-12]

Growth in energy production to meet the rising demand often comes at a cost, especially when demand is met by fossil fuels. In 2015, China declared a red flag alert in Beijing due to hazardous pollution from coal plants north of the city.[13] CO_2 concentration in the atmosphere is predicted to increase without policies and technologies aimed at reducing emission.[14] Unmitigated increase in greenhouse gas emission (including CO_2 and CH_4) is predicted by the Environmental Protection Agency (EPA) to have devastating effects on both the American environment and economy. Some of these effects include the loss of 35% of Hawaiian coral leading to recreational and tourism losses of $1.1 billion, $3.1 billion in predicted damages due to sea level rise and storm surge, and impacts on human health due to extreme temperatures and reduced air quality.[15] These losses represent damages to business, challenges to infrastructure, and decreasing ability for the economy to compete globally. Thus it is imperative to find and use clean liquid energy sources that also lower greenhouse gas emissions. Additionally, production of liquid fuels in the US presents a chance to improve energy security while also providing opportunities for strengthening the economy via export. Research aimed at meeting future demands can be directed in two broad thrusts: 1) improving existing energy technologies in terms of efficiency, or 2) investigating new methods of harvesting and storing energy. In this work, both approaches will be taken.

In the realm of existing energy technologies, natural gas is one of the fastest growing fuel sources in the US. However, much of the natural gas resources are tied up in stranded wells. These wells exist either in geographically isolated locations or locations that lack proper infrastructure. This includes methane trapped with other liquid hydrocarbons which is too difficult to transport.[16,17] Especially in this case, the infrastructure present is tailored to the transportation of liquid products. At room temperature and pressure, methane is a gas. As previously mentioned, there are some physical processes such as LNG and CNG meant to make methane easier to transport and their difficulty has been described.[13] However, there are also chemical processes aimed at converting methane into a transportable liquid. One such process is steam reformation of methane (SRM) to syngas, which can then be combined with the Fischer-Tropsch process to make higher order hydrocarbons.[6,9,18] Steam reformation occurs at temperatures in excess of 900 °C, requiring expensive alloys for reactors and plant components.[9] This in turn makes SRM a difficult option for wells in isolated locations, as the capital cost associated with the plant renders the process economically unviable, except in the case of very high oil prices.[2] Presently, methane recovered from isolated wells is typically flared to release CO_2 or released as methane directly, which has dire environmental impacts.[14,15,19] It also represents a source of waste in the process. Alternatively, chemical oxidation of methane to methanol, which is a liquid at room temperature, presents an attractive solution. Improvements made here could reduce the amount of energy required to transport natural gas, as well as enable more efficient recovery of energy resources from stranded wells. However, significant challenge lies in gently breaking the C-H bond, which at 105 kcal/mol is quite strong. Once one bond is broken, the remaining C-H bonds become weaker, leading to over-oxidation in most cases.

Solar energy presents an attractive option among renwables due to its large supply.[11] Utility-scale photovoltaics have grown in capacity from approximately 250 MW nationwide in 2010 to over 4000 MW in 2014, nearly a 16-fold increase.[20] The National Renewable Energy Lab's benchmark utility-scale installed price for PV has fallen, from $4.39 in 2009 to $1.77 in early 2015, largely attributed to decreasing costs of solar modules.[20] However, one challenge of solar energy is its intermittency: weather events, clouds, and the diurnal nature of the earth's solar cycle present a need for storage technologies. Batteries are problematic due to their low specific energies, implying that for a given energy storage capacity, they are quite heavy relative to conventional liquid fuels. This is particularly relevant in the transportation sector, as the amount of energy required for long trips becomes intractably large. Their specific energies range from ~20 W•h/kg for redox flow batteries to ~160 W•h/kg for conventional lithium ion batteries.[21] By comparison, the specific energy of gasoline is around 170,000 W•h/kg.[22]

In order to achieve this kind of energy density, we can take a lesson from nature: photosynthesis is the process by which plants store solar energy as sugars made from water and CO_2. By modifying this process to use sunlight to split water and provide protons and electrons to make fuels of our choosing, we create a process called *artificial photosynthesis*.[10,11] The harvested protons and electrons can be used to make hydrogen or can be combined with CO_2 to make carbon-based fuels. One advantage of using CO_2 as a feedstock is that one could close the loop in the carbon cycle. Fuels made from CO_2 release CO_2 when burned, which is then recovered to make more fuel. Unfortunately, these reactions can be incredibly complex and energy intensive. Even the basic case of $2H^+ + 2e^- \rightarrow H_2$ can have puzzling and varied routes.[23,24] The one-electron reduction of CO_2 to the anionic radical occurs at -1.90 V vs SHE in water[25], too high for commodity fuel production. CO_2 reduction can also have a variety of routes and products.[9,26,27]

Keys to Catalysis

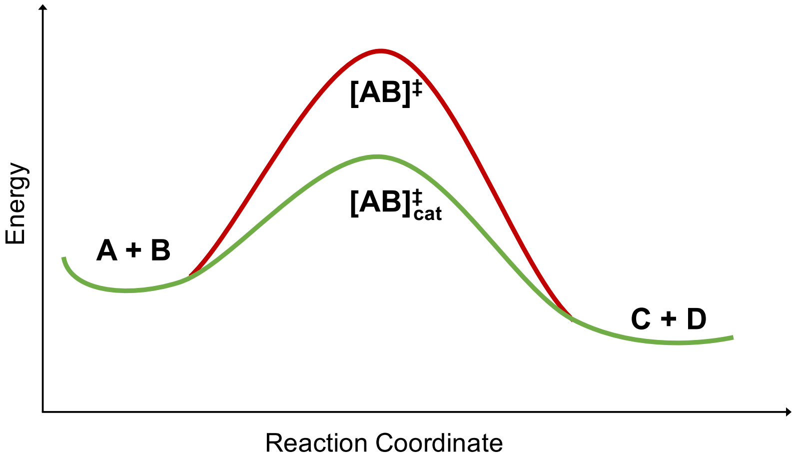


Figure 1.3: Model potential energy surface for catalyzed and uncatalyzed reactions.

One common thread between these two seemingly disparate energy problems is that they both involve high energy reactions with stable, small molecules. In order to reduce the energy requirement for these reactions (and thus lower their cost), we turn to catalysis. The potential energy surface (PES) for a model reaction ($A + B \rightarrow C + D$) is seen in Figure 1.3. In this reaction, A and B represent our reactants and C + D are the products. These complexes are all referred to as *intermediates*. On a PES, intermediates are defined as minima. Moving along our reaction coordinate from A and B to C and D (left to right), we encounter a barrier in the energy surface, which is denoted as $[AB]^{\ddagger}$. The double dagger superscript is indicative of AB's status as a *transition state*. We define the transition state as the energy maximum in this figure, which features a two-dimensional PES. However, real PESs are usually multi-dimensional, so we define the transition state more rigorously as the saddle point in a PES dividing products and reactants in quasi-equilibrium.[28,29] The transition state energy (or activation energy) is related to the reaction rate coefficient, which helps to determine how quickly a reaction will progress. This was seen empirically by Svante Arrhenius, a Swedish chemist, and appears as his Arrhenius equation[30]. The related Eyring equation can be derived from transition state theory and has a similar functional form.[31] The Arrhenius equation can be seen in Eq. 1, where E_a is the activation energy, R is the gas constant, T is the temperature, and A is a pre-exponential factor.

$$k = Ae^{\frac{-E_a}{RT}} \tag{1}$$

The rate constant *k* is then related to the actual rate of reaction by multiplying it by some function of the reactant concentration.[18] This is a simplified description of the field of chemical kinetics and for further reference, the reader is referred to texts focusing solely on the topic.[32-34]

In Figure 1.3, there are two barriers, $[AB]^{\ddagger}$ and $[AB]^{\ddagger}_{cat}$, which represent the uncatalyzed and catalyzed reactions, respectively. In the uncatalyzed case there is a higher barrier.

The catalyst is a material that lowers a reaction's barrier without affecting its thermodynamics, resulting in a faster reaction. A popular metaphor is that of traveling through a mountain range: one can walk directly over a mountain but will expend a lot of energy. This represents the uncatalyzed case. Alternatively, one can take a mountain pass or a tunnel through the mountain, metaphorically choosing the catalyzed route. In both cases, one starts and ends in the same place, but the amount of energy expended (and inherently the time it takes) varies by case. By definition, at the end of the reaction, the catalyst is unchanged and can proceed with more catalysis. A reaction which is aided by a molecule or surface, but the molecule or surface is changed at the end and does not react in the same way is said to be *stoichiometric*, whereas a reaction in which a molecule aids in reaction and is returned to its original state to aid again is referred to as *catalytic*. In order to be catalytic, a catalyst's PES must have moderate barriers, but also must have intermediates that are not too low in energy. These create thermodynamic sink states, which are difficult to overcome. One common type of sink occurs when something binds too strongly to the catalyst, effectively poisoning it. If something does not bind at all, catalysis cannot be done. This is called the Sabatier principle (a.k.a. the Goldilocks principle). Catalysis relies on optimization of all factors.

From these definitions, three concepts emerge: turnover, turnover number, and turnover frequency. Turnover is when the catalyst is returned to its original state to start another catalytic cycle. Turnover number (TON) is defined as the number of turnovers completed. Turnover frequency (TOF) is the turnovers completed in a given time span.[18] High TON and TOF are crucial in catalysis as they represent a fast and efficient reaction.[9] Other key characteristics of a good catalyst are high product and reactant *selectivity*, meaning that the catalyst only reacts with and produces desired molecules. Unwanted side reactions can poison a system[35], create side products that are difficult to separate,[36] or lead to a catalyst's deactivation and failure[37]. In terms of industrial catalysts, it is important to keep in mind the efficiency of a catalyst. To this goal, Sheldon describes the E-factor of a catalyst, defined as the ratio of undesired product to desired products.[38] Undesired products represent wasted energy and increased separations downstream. Different chemical sectors have different E-factors. For example, in the field of pharmaceuticals, an E-factor of 25-100 is suitable, since the desired products are quite expensive and can absorb costs associated with waste. However, in the field of bulk chemicals (which includes fuels), much smaller ratios of 1-5 are required for the economic viability of processes.[38] In efficient fuels catalysts, waste must be minimal.

Broadly, catalysis can be separated into several categories, including homogeneous catalysis, heterogeneous catalysis, and biocatalysis.[18] Homogenous catalysis refers to when the catalyst and substrates are of the same phase, most often in the liquid phase. Conversely, heterogeneous catalysis refers to situations where the catalyst and the product are of different phases. In industry, this typically involves a solid catalyst in liquid or gas substrate. Biocatalysis refers to enzymatic catalysis, where proteins perform reactions. Catalysts can further be separated into chemical catalysis and electrocatalysis[39], which work in an electrochemical cell[27]. Each type of catalyst has advantages and disadvantages, which will be discussed in Chapter 6. However, in this study we will focus on homogeneous, molecular catalysts with a single metal center surrounded by organic ligands.

A recent technoeconomic analysis of H_2 produced by photoelectrochemical cells found that while fuel-forming catalysts were not a large portion of the overall cost, they were the least abundant component of the cells, which was cause for alarm.[40] In this thesis, I study the PESs and mechanisms of existing, successful fuel-forming catalysts in order to determine the source of their selectivity, high TON and TOF, and resistance to degradation. With this in mind, I will work towards design of earth-abundant catalysts. The overarching focus will be on group 9 transition metals: Co, Rh, and Ir. I will also focus on two broad ligand structures: pincer catalysts and bipyridine-based (bpy) catalysts. These catalysts are all studied with the goal of improving energy sources, both established and emerging.

Ligand Classes

The first class of catalysts studied here are called pincer catalysts because they literally grip the metal like the pincers of a bug. A generalized form can be seen in Figure 1.4a and b.

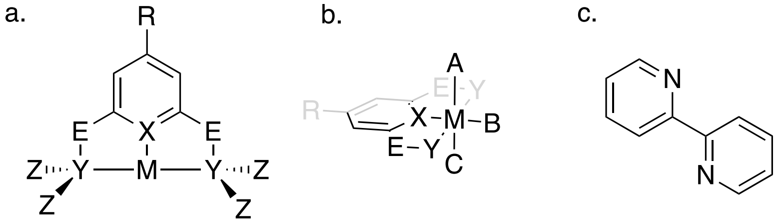


Figure 1.4: Schematic of a. an arbitrary pincer, b. the side view of the arbitrary pincer, and c. bipyridine.

These pincers are tridentate ligands, meaning they bind to the metal in three places. They are typically planar due to the aryl ring in the middle (though non-aryl groups can be used[41]), though some bending an occur along the Y-M-Y axis[42]. In Fig. 1.4a, we see the different positions in the pincer ligand labeled. Each position in the pincer is unique, as it modifies the electronic structure of the catalyst in a different way.[42-46] The R groups can be used as a solvation aid[47], or to modify the electronics at the metal center without interfering sterically. The E groups can affect bending of the pincer, as well as be used in second sphere coordination to lower reaction barriers[48]. The Y and Z groups can be used to affect the sterics at the metal center, creating reaction pockets or blocking reaction sites at the metal.[42] Finally, the X position has significant control over the coordination of groups directly across the metal (position B in Fig. 1.4b).[49] In many of the systems studied here, full octahedral coordination is found around the metal, meaning six groups bind. Three positions are taken up by the pincer and the other three can be seen in the side view of Figure 1.4.b. Positions A and C are referred to as the axial positions, and B is referred to as the equatorial position. One of the reasons for the pincer ligand's ubiquity in catalysis is its modular nature: since each position of the pincer has a subtle effect, these groups are routinely swapped out to tune catalysts. Part of their modularity results from the synthetic processes used to make them.[43,50]

The second class of catalysts that will be investigated are bipyridine (bpy) based catalysts. Bpy is a non-innocent ligand (meaning that it is able to host an electron upon reduction)[51] that is found in many catalytic systems[52-57]. It often binds with transition metals through the nitrogen groups and can also be modified, such as to make vinyl bipyridine[58], though not as extensively as the pincer scaffold.

Role of Computation

In this study, I use density functional theory as the primary tool in order to understand the PES of these catalysts. Density functional theory is rooted in the Schrodinger equation, and in this work, primarily the time-independent version.[59] The Schrödinger equation allows for the solution of energy levels and wave function for a collection of electrons and nuclei. It can be seen in Eq. 2.

$$\hat{H}\Psi = E\Psi \tag{2}$$

In this equation, operator $\hat{H}$ is referred to as the Hamiltonian. In a system consisting of M nuclei and N electrons, $\hat{H}$ in atomic units as follows:

$$\hat{H} = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 - \frac{1}{2}\sum_{I=1}^{M}\frac{1}{M_I}\nabla_I^2 - \sum_{i=1}^{N}\sum_{I=1}^{M}\frac{Z_I}{r_{iI}} + \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{r_{ij}} + \sum_{I=1}^{M}\sum_{J>I}^{M}\frac{Z_I Z_J}{r_{IJ}} \qquad (3)$$

In this equation, the first two terms refer to the kinetic energy of the electrons and nuclei, respectively. The third term gives the interaction between electrons and the nuclei. The fourth and fifth terms give the interaction between pairs of electrons and pairs of nuclei, respectively. This equation can be solved exactly for the hydrogen atom and for "hydrogen-like" atoms, but additional electrons complicate the system intractably. Unfortunately, most interesting catalysis involves more than one or two electrons. Thus begins the journey into quantum chemical methods, which involves a collection of approximations made with the goal of solving the Schrödinger equation as exactly as possible for the multi-electron system.

The first major approximation is the Born-Oppenheimer Approximation, which approximates electrons as moving in a field of fixed nuclei. This is a consequence of the nuclear mass being much larger than that of the electron. This approximation reduces the problem to largely solving for electronic motion and effects, making the fifth term in Eq. 3 effectively a constant. The second major approximation is that of Hartree and Fock, which reduces the N-electron problem to N non-interacting one-electron problems, then introduces the Hartree-Fock (HF) potential to account for the electron-electron interactions. The reader is referred to the classic text by Szabo and Ostlund for further details.[60]

While the HF scheme was a large leap forward, it was plagued with error due to electron-electron interactions, as well issues with scaling to larger systems. In response to this, Hohenberg and Kohn proposed in their 1964 landmark theory the use of electron density rather than N-electron wave function.[61] This paper effectively gave birth to modern density functional theory. Through proof by contradiction, they were able to show that the electron density was a unique property of the system. It showed that the energy is functional of the 3-dimensional electron density. Previously, 3N-dimensional wave function had been used, so this represented a large improvement in scaling. It also showed that if the exact form of the of functional including quantum effects, the electron-electron interaction, and kinetic energy were known, an exact solution to the Schrodinger Equation would be found.[59] However, it gives no information on what this functional looks like.

However, this is easier said (and proved) than done! The Kohn-Sham approach[62] is a direct consequence of the Hohenberg-Kohn theorems, presents a blueprint for using the theorems iteratively to find a solution. Key to this blueprint is the separation of the Hamiltonian into portions that can be solved exactly for a non-interacting system and the remaining unknown portions (primarily those involving electron-electron interactions) are collected in a term called the exchange-correlation functional. More depth on this subject can be found in Koch and Holthausen.[59] The exchange-correlation functional puts the functional in density functional theory, as judicious choice of functional is key to accurate results. In this thesis, I primarily use B3LYP[63] and M06[64]. Both are hybrid functionals, which combine differing amounts of Hartree-Fock exchange and an empirically-fit function to derive the functional.

From these calculations, one can derive a variety of useful characteristics of a catalytic system.[59] One can calculate the geometry of intermediates on the PES, as well as the geometry of transition states (with help from transition state theory[28]). One can also glean energies from these calculations to infer which paths will be most likely. The energies in this thesis generally are Gibbs free energies in solution, except where otherwise mentioned. In each chapter, a separate methods section is present as there are subtle differences between the methods used in each chapter.

One advantage of computation in catalysis is that small adjustments can be made to the structure of the catalyst being studied. These adjustments can be as small as rotating a piece of the molecule to see an energy change to something as large as calculating an entirely new pathway for a related catalyst with new functional groups. In each case, the atomistic states along the pathways can be seen in full detail, a luxury often not afforded to experiment.[18] A potential molecule can be screened for an effect without the trial of making it in the lab. Molecules that do not exist yet can be predicted and some that cannot be made at all for various experimental reasons can be made computationally as a toy system. This freedom is attractive, but as Stan Lee wrote, “With great power comes great responsibility”. Errors exist in DFT calculations due to a variety of reasons including, for instance, errors in functionals[65], or unforeseen side reactions[37] so it is important to continually validate. In this study, I have worked closely with experimental groups to create constant iteration of explanation of observations and prediction of new catalysts.

Common Threads and Overview

Two overarching motifs can be seen in this thesis beyond the connection of energy sciences. The first is the capacity of small modifications in structure to have large effects on catalytic ability. Gaining a true intuition for how subtle atomic effects can improve a catalyst is the key to most chapters. This plays on one of the strengths of computational catalysis and can be used to help predict new generations of catalysts which build on the strength of previous generations. The second motif is the interplay of thermodynamics, represented by the energy of intermediates, and kinetics, represented by transition states. The connection between thermodynamics and kinetics cannot be stressed enough. However, while thermodynamics may dictate the overall boundaries of possibility for a catalytic system, kinetics dictate which path is actually taken. The wrestling of these two effects is a hallmark of many of the catalysts studied in this work and can be seen throughout.

The outline of the thesis is as follows. Chapter 2 focuses on an iridium-based catalyst competent for C-H activation in mesitylene, a methane surrogate. This chapter includes elucidation of the mechanism for this C-H activation, as well as predictions to help the catalyst improve their competence for selective methane activation. Chapter 3 is the first of two chapters focusing on iridium and cobalt catalysts for CO_2 reduction to formate. This chapter centers on the mechanism by which these catalysts actually complete this reduction, as well as investigating the effects of solvent on the thermodynamics of the reaction. A key point in this chapter is how this catalyst is able to avoid the thermodynamically-preferred hydrogen evolution, which is an unwanted side reaction. Chapter 4 follows this closely with investigating how subtle atomic changes to the ligands in these catalysts affect both the thermodynamics and kinetics of the system. Chapter 5 shifts to investigating a rhodium catalyst for desired hydrogen evolution, and looks to explain an unexpected experimental result. The chapter goes on to elucidate how this catalyst makes hydrogen and how modifications on the ligand affect that path. Finally, Chapter 6 is a departure from the realm of strict homogenous molecular catalysis, instead focusing on how to make these catalysts more viable for industrial purposes. Molecular catalysts typically are more active, with less side reactions than heterogeneous catalysts, yet separation of the catalyst from product can be expensive and can render these catalysts uneconomic except in the case of specialty chemicals.[18] Furthermore, in the field of electrocatalysis, physical closeness of a catalyst to an electrode can speed up processes by reducing the time required for diffusion-based electron transfer.[66,67] Thus, this chapter operates at the boundary between chemistry and materials science. It primarily focuses on meeting the challenge of robust attachment of bipyridine-based catalysts on Si electrodes. Much effort has been devoted to predicting new schemes for attachment.

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