Strategic Applications of Electrochemistry in Ammonia Oxidation and Alkyl Halide Reduction

Thesis by

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In Partial Fulfillment of the Requirements for
the Degree of
Doctor of Philosophy

CALIFORNIA INSTITUTE OF TECHNOLOGY
Pasadena, California

2023
(Defended February 28, 2023)

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ACKNOWLEDGEMENTS

Although I do not come from an academic lineage, I want to first thank my parents for instilling in me an academic spirit. Growing up, I was always told that school was my first priority, and because of the sacrifices that my parents made, I was able to make this encouragement a reality. Despite the fact that my parents' understanding of the "schoolwork" that I now undertake is more limited than when they would help me with school assignments, they still remain fully committed to supporting me in my aspirations, even at the cost of me being far away from home. Likewise, my brother has been a staunch supporter of my academic aspirations despite this drawing me out of state. For this, I thank them, and I hope that one day these sacrifices will help me in finding a suitable job closer to home.

In the academic sphere, I have been blessed by a long list of teachers throughout my primary, secondary, and collegiate education. Each of these teachers has invigorated or inspired my learning in diverse ways, and there are too many to name individually. However, several of my scientific instructors bear mentioning. Having no particular talent or early interest in science, I credit a middle school teacher, Meeta Evers, for introducing science as a method, and often a fun one, for exploration rather than rote repetition. In high school, I enjoyed the unmatched teaching of Ed Bolton for two years. His dynamic, thorough, and (again) fun presentation of chemistry spurred my interest such that I entered college as a biochemistry major.

Before I even attended my first class, I had already found my first academic mentor in Prof. David Sherrill, my first research advisor. His dedication to the scientific community is such that he continually publishes popular theoretical chemistry course content on his website (vergil.chemistry.gatech.edu/). While teaching myself linear algebra during the summer prior to my first year, I encountered his course material online and was instantly hooked. My first day in Atlanta, I impetuously knocked on his door to meet the person that had published all the interesting material I had read online. (I later realized that this may not always be the most courteous way of connecting with someone, but this method is responsible for introducing me to a large number of incredible academic mentors throughout my undergraduate studies.) Prof. Sherrill kindly met with me and offered to introduce me to his research, and shortly thereafter I began my first foray into academic research. Although

I have drifted away from theoretical chemistry, I am grateful to Prof. Sherrill for his patience and enthusiasm in mentoring me as a young student and especially for paying for my attendance at a large number of conferences, including one at which he arranged for me to be an invited speaker.

The foreshadowing of my shift to experimental chemistry can be found in my enthusiasm for Prof. Gary Schuster's organic chemistry class that I enrolled in during my first semester at Georgia Tech. What I have always admired about organic chemists is their panache—and Prof. Schuster demonstrated this in abundance, a trait that helped initiate my interest in experimental chemistry. After doing rather poorly on the first exam, I showed up to his office hours and we chatted for a long time. I continued to stop by his office, but over time the purpose shifted from discussing organic chemistry specifically to chemistry and academia in general. Prof. Schuster truly introduced me into the academic world—its ways, its purposes, and its strategies—in a way that I would have remained wholly ignorant of without his guidance. Furthermore, he succeeded in disrupting my myopic vision of chemistry such that I became interested in myriad topics besides theoretical chemistry. By way of his advice, I eventually joined the group of Pete La Pierre in my final semester of undergraduate studies.

Prior to this shift, however, I first must mention Prof. E. Kent Barefield. As my instructor for both inorganic chemistry and an advanced synthesis lab, Prof. Barefield is the experimental chemistry analogue of Meeta Evers in that his lab course marked the first time I realized that lab work can be exciting rather than, again, rote repetition. We learned to develop our own synthetic protocols, a skill rarely taught in teaching laboratories, and we performed experiments that were on the frontier of scientific research. Of course, this also meant that some experiments failed. Adapting to failure is a crucial skill in scientific research, and I credit this class with first developing my capabilities to do so. Two aspects of inorganic chemistry caught my eye under the instruction of Prof. Barefield. First, inorganic chemistry often involves pretty colors and beautiful crystals. I will forever remember the beautiful green crystals of dibromobis(triphenylphosphine) nickel(II) that we prepared in his class, and this enthusiasm for crystals has served me well throughout my PhD. Second, inorganic chemistry is theoretically beautiful, a trait that helped bridge my interest in theoretical chemistry with a growing enjoyment of experimental chemistry. The arguments of crystal field and molecular orbital theory continue to fascinate and inspire me, even as organic chemistry looms in my future.

In my last semester as an undergraduate, Prof. Pete La Pierre kindly introduced me to experimental chemistry in a research setting. Pete and his students, especially Dominic Russo (fellow undergraduate), provided unmatched training in synthetic inorganic chemistry that provided an excellent foundation for my PhD research. Considering how sparse my research progress was in Pete's group, I am especially grateful.

In addition to these professors, I fondly thank Prof. Joseph Sadighi, Prof. Charlie Liotta, Prof. JC Gumbart, Prof. Bill Baron, and many others for their contributions to broadening my perspective on chemistry and the academic world as a whole.

At Caltech, I was fortunate to be in the final class for which research rotations were optional, which allowed me to begin research with Prof. Jonas Peters in the summer and never look back. Jonas provides a superlative combination of training in scientific excellence and precision writing as well as access to the exact research essentials needed for success. Jonas also offered a range of sage advice, and I may have done well to have taken it to heart sooner rather than later. In particular, Jonas loved to tell me "a PhD is a marathon, not a sprint," to which I liked to respond that I used to be a sprinter. In fact, a PhD is a grueling slugfest, and 'running slower' at times may have helped me get to my destination sooner than 'sprinting.'

In the Peters Group, I overlapped with many excellent scientists, several of whom I highlight for the role they played in shaping my training:

Nina Gu—My first mentor, Nina helped me hit the ground running, and with her help I finally collected my first crystal structure.

Matt Chalkley—Both friend and colleague, Matt taught me a number of excellent lessons. The most important of all he imparted early: there is no credit for projects left unfinished. This mindset was crucial in helping me develop scientific discipline in the face of the fun prospect of starting a new project when the going gets tough.

Pablo Garrido-Barros—Pablo was an unmatched mentor in developing my appreciation for and capacity to perform electrochemical experiments. However, Pablo is also a great friend and first-rate cook, two traits that I value even more highly from our time together. I will always remember Pablo's diligence in working on our first paper together, including the late nights that often turned into early mornings.

Heejun Lee—A true synthetic mastermind, Heejun inspired me to tackle challenging synthetic problems. I will always be amazed by his encyclopedic knowledge of not only reaction conditions, but also yields and byproducts.

Meaghan Deegan—Meaghan helped shape my outlook on maintaining exceedingly high standards of scientific rigor, a lesson that we should all maintain as our foremost duty in the laboratory.

Christian Johansen—Christian's capacity for reading the scientific literature will always amaze me, and I thank him for his numerous, scrupulous corrections in my presentations and writings.

Marcus Drover—In what was often an intense scientific atmosphere, I thank Marcus for his general friendliness and encouragement to always be excited about science.

Joe Derosa—Although we did not get the chance to work on chemistry together, Joe was a constant friend in the group and a foremost companion in keeping me sane as I worked towards finishing my PhD.

Additionally, I thank my committee members: Prof. Ryan Hadt, Prof. Garnet Chan, Prof. Harry Gray, and Prof. Greg Fu. Their diverse research interests encouraged me to think outside of my, at times, narrow interests, and their insightful comments led to several large advancements in my research. In particular, a discussion with Ryan Hadt during my candidacy meeting provided the theoretical framework that inspired me to explore spin state as a handle for improving the iron complexes we have developed for ammonia oxidation.

Finally, I thank those who kept me going during my PhD. First and foremost, my love and soon to-be wife, Sara Dibrell. A gift from God and love at first sight, Sara accompanied me on more journeys than can be briefly mentioned. Working only one floor above me, it was a blessing to see you at work almost every day! Your confidence in, and loyalty to, me stabilized my life throughout the joys, and trials, of this PhD.

The other Mike of “The Mikes”—Michael Daugherty. A friend from day one, even after moving to Berkeley. Thank you for all the fun we had at Caltech and throughout California, especially your commitment to our annual Thanksgiving camping trips, even when they were cold and rainy.

Outside of Caltech, I enjoyed the constancy of my soccer team in playing almost every week: Jorge, Alfredo, Ben, Jamie, and more. They reminded me that there is a rhythm to life outside of graduate school, a lesson that is not always easy to remember.

Most importantly, I thank the triune God incarnated in Jesus Christ. No amount of scientific training could have prepared me for the challenges involved in completing my PhD. My faith in Christ and knowledge that my worth is independent of my works sustained me throughout many unexpected challenges that for long periods felt insurmountable. Relatedly, I thank my church community that provided encouragement and friendship here on Earth: Pat, Isaiah, Dan, Brian, Genti, Mark, Peter, Glenn, and many more. Your advice and patience throughout my many challenges has been invaluable.

ABSTRACT

This thesis describes the strategic application of electrochemistry in the development of catalytic systems for two challenging processes: alkyl halide reduction and ammonia oxidation. In the case of alkyl halide reduction, the ability to precisely tune electrochemical potential favored the use of electrochemistry as compared to chemical reagents. By contrast, for ammonia oxidation, electrochemistry was specifically targeted due to motivations in the eventual development of ammonia fuel cell technology. The first chapter introduces these and other advantages of electrochemistry, as well as details regarding the thermodynamic potentials and kinetic barriers associated with alkyl halide reduction or ammonia oxidation. The second chapter details our development of photoelectrochemical methodology to employ a strongly luminescent dicopper system for outer-sphere, single-electron transfer reduction of benzyl chlorides. The third chapter marks the beginning of our work in molecular iron-mediated ammonia oxidation catalysis, in which we develop our hypothesis that catalyst structures featuring *cis*-labile coordination sites should mediate ammonia oxidation. We disclose the first iron electrocatalyst ($[(TPA)Fe(MeCN)_2]^{2+}$) as well as a framework for the analysis of metrics such as overpotential, catalytic rate, and catalyst stability. The fourth chapter introduces a hypothesis for catalyst improvement—favoring low-spin electronic structures—and a model system for testing: ($[(BPM)Fe(MeCN)_2]^{2+}$). Using this second-generation catalyst, improved stability, enhanced activity, and lowered overpotential were observed. The fifth chapter explores the validity of the *cis*-labile and low-spin hypotheses via Hammett-type substituent studies on both the $[(TPA)Fe(MeCN)_2]^{2+}$ and the $[(BPM)Fe(MeCN)_2]^{2+}$ platforms. This study resulted in the development of a further enhanced molecular electrocatalyst for ammonia oxidation and revealed mechanistic information pertinent to the development of future catalytic systems.

PUBLISHED CONTENT AND CONTRIBUTIONS

Zott, M. D.; Canestraight, V. M.; Peters, J. C. Mechanism of a Luminescent Dicopper System That Facilitates Electrophotochemical Coupling of Benzyl Chlorides via a Strongly Reducing Excited State. *ACS Catal.* **2022**, *12*, 10781–10786. DOI: 10.1021/acscatal.2c03215.

M. D. Z. helped conceptualize the project and performed all experiments other than some luminescence and UV-vis titrations. M. D. Z. wrote the manuscript.

Zott, M. D.; Peters, J. C. Enhanced Ammonia Oxidation Catalysis by a Low-Spin Iron Complex Featuring *Cis* Coordination Sites. *J. Am. Chem. Soc.* **2021**, *143*, 7612–7616. DOI: 10.1021/jacs.1c02232

M. D. Z. conceptualized the project, performed the experiments, and wrote the manuscript.

Zott, M. D.;‡ Garrido-Barros, P.;‡ Peters, J. C. Electrocatalytic Ammonia Oxidation Mediated by a Polypyridyl Iron Catalyst. *ACS Catal.* **2019**, *9*, 10101–10108. DOI: 10.1021/acscatal.9b03499

M. D. Z. discovered the catalyst; solved and analyzed the crystal structures; performed and analyzed Mössbauer measurements; contributed to electrochemical and UV-vis studies; and contributed to the writing of the manuscript.

TABLE OF CONTENTS

ABBREVIATIONS AND SYMBOLS

A. Area

ANA. Ammonia Nucleophilic Attack

AO. Ammonia Oxidation

BDD. Boron Doped Diamond

BDFE. Bond Dissociation Free Energy

bpyPy$_2$Me *or* **BPM**. 6-(1,1-bis(pyridin-2-yl)ethyl)-2,2'-bipyridine

C. Charge

cm^{-1}. Wavenumbers

CPC. Controlled Potential Coulometry

CV. Cyclic Voltammetry (or Voltammogram)

°C. Degrees Celsius

δ. Isomer shift

Δ_{eq}. Quadrupole splitting

ΔG. Gibbs free energy

dap. 2,9-dianisyl-1,10-phenanthroline

DBU. 1,8-Diazabicyclo[5.4.0]undec-7-ene

DCA. Dicyanoanthracene

DFT. Density Functional Theory

DME. 1,2-dimethoxyethane

DPV. Differential Pulse Voltammetry (or Voltammogram)

$\boldsymbol{E}$. Potential

$\boldsymbol{E}_{\mathbf{1/2}}$. Half-Wave Potential

$\boldsymbol{E}°$. Standard Potential

$\boldsymbol{E}°_{\mathbf{cat}}$. Standard Potential for Catalysis

EC. Electrochemical-Chemical

$\boldsymbol{E}_{\mathbf{onset}}$. Onset Potential

$\boldsymbol{E}_{\mathbf{p}}$. Peak potential

$\boldsymbol{E}_{\mathbf{p/2}}$. Half-peak potential

Eq. Equation

equiv. Equivalent

ET. Electron Transfer

eV. Electron Volt

$\boldsymbol{\eta}$. Overpotential

F. Faraday’s constant

Fc. Ferrocene

FE. Faradaic Efficiency

GC. Gas Chromatography *or* Glassy Carbon

GJ. Gigajoules

h. Hours

I2N. Interaction of Two Nitrogens

K. Kelvin

k'_{obs}. Second order observed rate constant

kcal. Kilocalorie

L. Two-electron donor ligand

LFER. Linear Free Energy Relationship

LSV. Linear Sweep Voltammetry (or Voltammogram)

λ. Wavelength

M. Molar

Me. Methyl

mL. Milliliters

mm. Millimeters

MS. Mass Spectrometry

μB. Bohr magneton

nm. Nanometers

NpMI. *N*-arylmaleimide

ν. Frequency

R. Gas constant

RT. Room Temperature

s. Seconds

S. Electron Spin

SHE. Standard Hydrogen Electrode

SI. Supporting Information

SV. Stern-Volmer

T. Temperature

THF. Tetrahydrofuran

TOF. Turnover Frequency

TON. Turnover Number

TPA. Tris(2-pyridylmethyl)amine

τ_0. Fluorescence lifetime

UV-Vis. Ultraviolet-visible

V. Volt

XRD. X-ray Diffraction

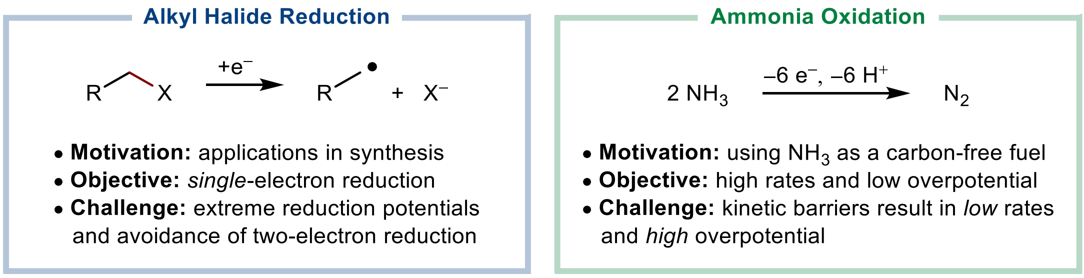
Chapter 1

Introduction

1.1 Opening Remarks

Electron transfer is a common mechanistic step in a wide range of chemical reactions.[1] This step is so prevalent that its appearance is seen in contexts as diverse as pharmaceutical synthesis,[2] qubit engineering,[3] biosensing,[4] sustainable fuels,[5,6] and many others. This is unsurprising given that, at least in our current conceptualization of physical reality, electrons are one of the primary subatomic particles, and their precise energies and arrangements in both atoms and molecules—the electronic structures—dictate chemical reactivity. Thus, by combining synthetic strategies to tune chemical structure with electrochemical methods that permit precise control over chemical potential, chemical reactions can be tuned in a well-controlled manner.[7,8,9,10] In this thesis, I develop reactions that follow this framework: carefully selected electrocatalyst structures are synergistically paired with an electrode at precisely tuned electrochemical potentials to address the specific challenges of enabling single-electron reduction of alkyl halides and multi-electron oxidation of ammonia (Scheme 1.1).

Scheme 1.1. Electron transfer in alkyl halide reduction and ammonia oxidation.



1.2 Electron Transfer Methods

To physically mediate electron transfer, numerous strategies exist, of which I highlight three prevalent in synthesis and sustainability chemistry: (1) chemical electron transfer, (2) photocatalysis, and (3) electrochemical bias.[2,11,12] Each strategy is distinct with respect to factors such as ease of tunability, electron transfer kinetics, and chemical compatibility, all of which can be influenced by characteristics such as the redox potential and the spatiotemporal availability of the electron transfer agent. We will first establish a framework for considering these principles using chemical reagents as an example, and then discuss the advantages and disadvantages of each strategy.

Chemical electron transfer reagents can be organic, inorganic, or organometallic in nature and typically promote either single- or multi-electron transfer in an irreversible fashion. Thus, they are commonly employed as stoichiometric reagents. As a simple example, an alkali metal such as lithium reacts via single-electron transfer with a proton, forming a lithium cation and a hydrogen atom (eventually released in the form of elemental hydrogen; Equation 1.1). To quantify the propensity of reagents to donate or receive electrons, their electrochemical potential can be analyzed versus a reference reaction, establishing a thermodynamic scale.[13] One such reference is the half-reaction describing reduction of protons to hydrogen, a component of Equation 1.1, which comprises the standard hydrogen electrode (SHE) that determines the potential reference of 0 V vs SHE. Since the reduction potential for Li^+/Li vs SHE is −3.1 V,[14] the reaction is highly favorable.

$$2\ Li + 2\ H^+ \longrightarrow 2\ Li^+ + H_2 \quad \text{(Equation 1.1)}$$

The thermodynamic driving force can be related to the reaction kinetics for electron transfer. For example, several models, such as Marcus theory, exist to quantify this relationship.[1] Kinetic factors that can be categorized as spatiotemporal strongly influence the experimentally observable reaction rates. For a heterogeneous reductant like lithium, the reaction rate is a function of surface area, with higher surface area resulting in higher reaction rate due to mass transfer effects. Furthermore, the reacting substrate (for Equation 1.1, H^+) must be brought within close proximity to the electron transfer agent. With soluble reaction components, this difficulty is obviated when the redox reagent is uniformly dispersed. Electron transfer is generally very fast, but temporal limitations can result in significantly reduced rates. For example, inner-sphere electron transfers that rely on complexation of the redox reagent and the substrate are regulated by the equilibrium between complexed and uncomplexed states.

An extensive discussion on advantages and disadvantages of chemical redox reagents, as well as details regarding their preparation and use, has been reviewed by Connelly and Geiger.[11] In brief, some advantages include superior applicability to large-scale reactions, compatibility with non-polar solvents, and, when soluble, extremely fast reaction rates. However, the greatest limitation of chemical redox reagents is their limited tunability, since any change in redox potential requires synthetic modifications. Such modifications may be challenging experimentally, and the resultant shifts in redox potential are discrete. While shifts can occasionally be brought about in a narrow capacity via solvent or electrolyte effects, more commonly, covalent modification via attachment of electron-donating or -withdrawing groups is required. Considering compatibility, chemical reagents can also be problematic given that they are used in a stoichiometric fashion. Thus, for a reductant such as lithium or an oxidant such as a nitrosonium salt, the product species (lithium cation or nitric oxide) can interact chemically with other reaction components.

Electrochemical methods are the most developed alternatives to chemical reagents. Unlike chemical reagents that have discrete redox potentials, the electrochemical potential can be continuously tuned using a potentiostat. This allows for modifications to reaction driving force, small or large, to be readily interrogated. Furthermore, electrochemical cells can be engineered such that the byproducts of electron transfer do not come in contact with the reaction components of interest by utilizing a multi-compartment cell, since inert electrodes can serve solely as a conduit for electrons rather than as reagents themselves. This permits extensive engineering of the electrode surface to promote compatibility.[15] Since the potentiostat records both potential and current, a large number of electroanalytical methods exist for mechanistic investigations, and even extremely fast reactions can routinely be studied using voltametric methods. Some limitations of electrochemistry include the requirement of electrolyte, the typical reliance on polar solvents, and the difficulty of reaction setup.

Finally, photocatalysis is a growing strategy for effecting electron transfer in both redox-neutral and net-reductive or -oxidative transformations. Photocatalysis, like chemical redox strategies, relies on chemical compounds with unique redox properties and excited state lifetimes. The primary advantages of photocatalysis are the ability to access extreme redox potentials without jeopardizing compatibility, as well as the ease of favoring single-electron over multi-electron transfer. Since photon energies are high—blue light (440 nm) is equivalent to 65 kcal/mol (2.8 eV)—substrates that would typically be challenging to selectively activate using chemical reagents become accessible. The preference for single-electron transfer arises from the fact that most photocatalyst structures are only photoactive in an oxidative or reductive capacity in a single oxidation state; upon gaining or losing an electron, their redox and photochemical properties become dramatically altered. This facilitates the generation of substrate-derived radical intermediates that are rapidly consumed in subsequent chemical steps. This prevents additional redox chemistry from occurring, since the photocatalyst must be turned over before an electron transfer of the same polarity occurs. One dual advantage/disadvantage is that in the quenched (i.e., post electron-transfer) state, the photocatalyst can again absorb energy via light and photosensitize a reaction of the opposite polarity. This establishes the basis for redox-neutral photocatalysis, an important and broad field, but can be detrimental to promoting purely reductive or oxidative transformations. Photocatalysts share the challenge of discrete redox potentials with chemical reagents but face the additional challenge that leveling effects are often observed when attempting to make a given photosensitizer more potent. That is, changing the ground state potential often compensatorily moves the excitation energy in the opposite direction, resulting in minimal perturbation of the net excited state redox potential. Additionally, the mass-transfer phenomena governing reaction rates with heterogeneous redox reagents find a parallel in photosensitizers in that photosensitizers are only active in the excited state, and excited state lifetimes are often short (less than several microseconds). While this can promote selectivity, it also challenges reaction scaleup and limits overall reaction rate.

1.3 Reaction-Specific Considerations

The specific reactions of interest, single-electron alkyl halide reduction and multi-electron ammonia oxidation (AO), feature distinct thermodynamic and kinetic challenges. Both reactions typically incur high overpotential (the amount of input energy required in excess of the thermodynamic minimum), but the origin of the overpotential is distinct. In this section, we discuss the fundamental reaction-specific challenges and considerations for alkyl halide reduction and ammonia oxidation.

1.3.1 Alkyl halide reduction

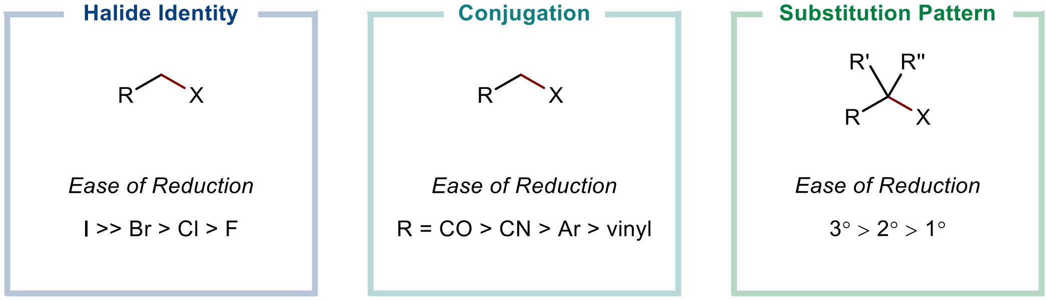
The research objective of single-electron alkyl halide reduction to produce alkyl radicals (Equation 1.2) is substantially motivated by synthetic utility as the resultant radicals can be employed in a wide variety of transformations.[16,17,18] As such, the primary constraints include chemoselectivity; amenability to primary, secondary, and tertiary alkyl halides; and compatibility with other reaction components (e.g., catalysts, other reagents, additives).

$$\text{R–X} + e^{-} \longrightarrow \text{R}\bullet + \text{X}^{-} \text{ (Equation 1.2)}$$

While large overpotential is a challenge inherent to the reaction class, it is limiting only insofar as it affects chemoselectivity, substrate applicability, and compatibility. Overpotential, and the requisite applied potential, vary dramatically depending on the precise structure of the alkyl halide.[19,20,21]

Factors that contribute to the effective reduction potential of alkyl halides include halide identity, conjugation, and substitution pattern (Scheme 1.2). In general, reduction is easier (i.e., $E°$ is less negative) in the order I > Br > Cl > F. Thus, fluorides and chlorides are more challenging to reduce than are analogous bromides and iodides. When the halogen-bearing carbon is in conjugation with π-bonds, as in allylic or benzylic systems, or with electron-withdrawing groups, the reduction event also becomes easier. Finally, increased substitution at the halogen-bearing carbon makes reduction easier in the order tertiary > secondary > primary. Generally, the effect of these factors on $E°$ is in the range of 100–1000 mV, with halide identity being the most influential factor. Thus, the exact reaction outcome can be subject to many, potentially competing, factors.

Scheme 1.2. Effects of alkyl halide structure on reduction potential.

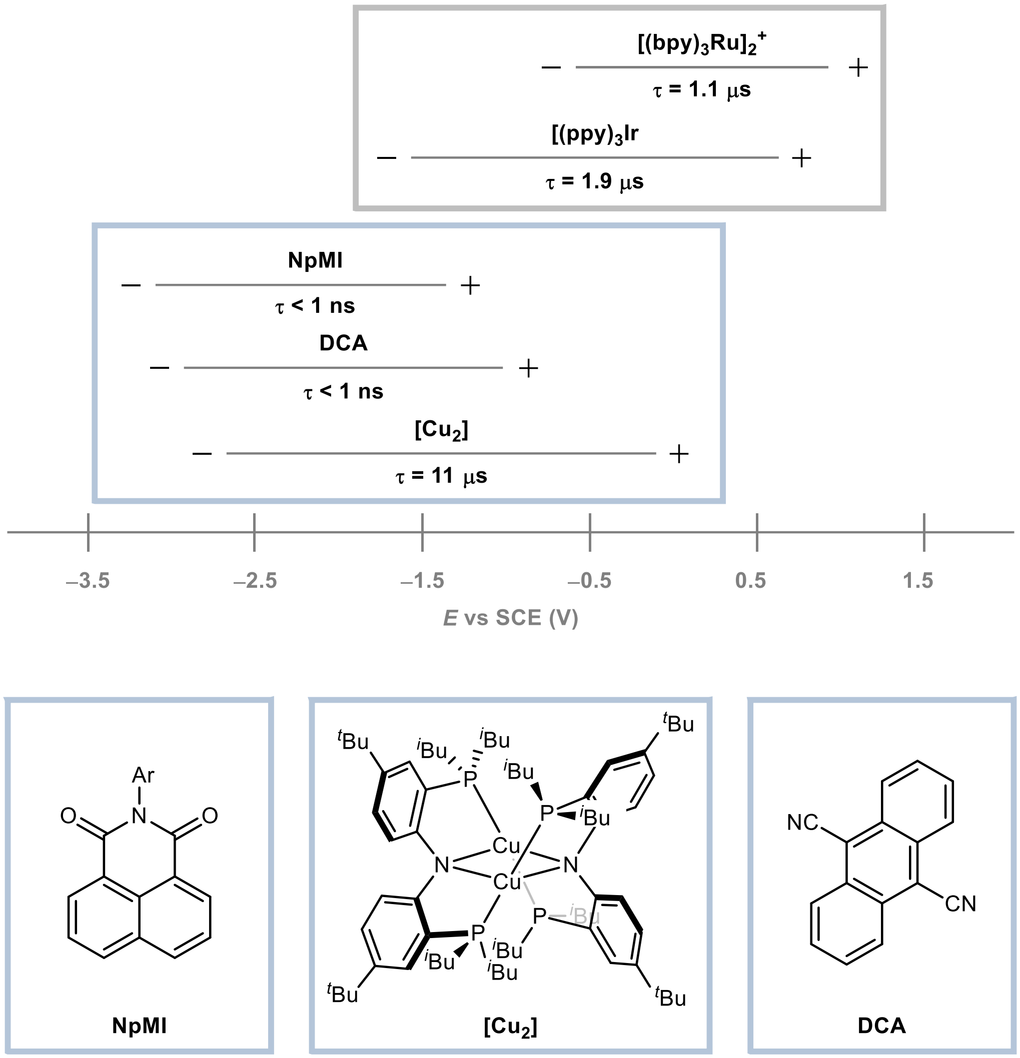


The reaction outcome of electron transfer to alkyl halides is further complicated by the presence of two closely spaced redox events: single electron reduction of the alkyl halide to the alkyl radical (E^{I}) and subsequent single electron reduction of the alkyl radical to an alkyl anion (E^{II}; Equation 1.3).[19,22] Net, these are single-electron and two-electron reduction processes, respectively. For easily reduced alkyl halides, such as alkyl iodides, precise control over the electrochemical potential can readily afford selective single-electron reduction for production of alkyl radicals since often $E^{I} > E^{II}$ (both values are negative). However, the more negative reduction potentials of some bromide and most chloride or fluoride substrates is such that a potential inversion is observed, i.e., the reduction of the alkyl halide bond is more challenging than is the reduction of the resultant alkyl radical, $E^{I} < E^{II}$. Therefore, additional controls must be employed to favor single-electron transfer and mitigate two-electron reduction.

$$R\bullet + e^{-} \longrightarrow R^{-} \text{ (Equation 1.3)}$$

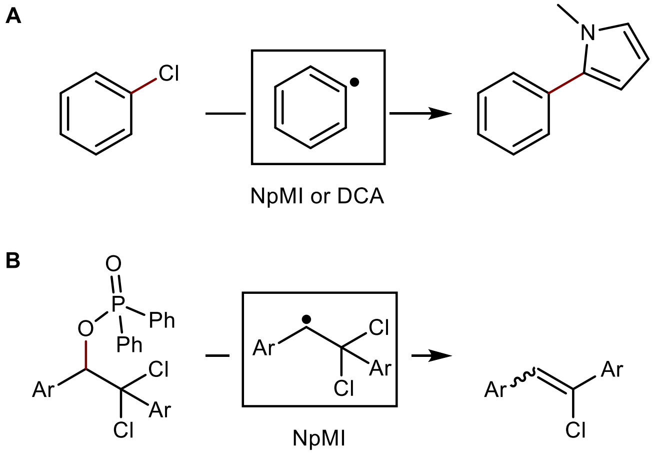
For alkyl halides susceptible to two-electron reduction, the primary means to control single- versus two-electron transfer is via the electron transfer method (see Sec 1.2). In direct electrolyses (i.e., without any electron transfer mediator), two-electron reduction to alkyl anions is almost always observed for bromide and chloride electrophiles that are not stabilized by conjugation due to the extremely negative potentials required for activation. Chemical reagents vary in their propensities to effect single- versus two-electron transfer. Simple, strongly reducing reagents such as alkali or alkaline metals or their adducts with polyaromatics (e.g., lithium napthalenide) generally promote two-electron reduction. Some specially designed reagents/catalysts that typically rely on inner-sphere Lewis-acid activation of the alkyl-halides can favor single-electron reduction by operating at lower reduction potentials, disfavoring reduction of the alkyl radical produced by the initial alkyl halide reduction.[23,24,25] However, the most developed method by which to produce alkyl radicals from alkyl halides is photochemistry. Photocatalysts by design favor single-electron transfer processes, and a variety of complex transformations exist wherein alkyl iodide and bromide substrates are transformed into reactive alkyl radical intermediates. Unfortunately, photocatalysts are typically insufficiently reducing to activate alkyl chloride or fluoride substrates that are not adjacent to conjugated systems or electron-withdrawing groups. Thus, the most efficacious method for alkyl radical generation is typically unsuitable for one of the broadest and most economical/environmentally friendly class of alkyl halides, chloride electrophiles.

The dearth of photocatalytic methodologies for single-electron reduction of chloride electrophiles motivated our group and others to explore electrophotocatalysis.[26] Electrophotocatalysis takes advantage of the benefits of electrochemistry and photochemistry. For single-electron processes, a photochemical electron-transfer mediator can be paired with an electrode; the photocatalyst provides the means to favor single-electron processes, and the electrode provides a convenient means to precisely tune the electrochemical potential. While most photocatalysts rely on both reductive and oxidative quenching cycles to effect redox neutral transformations, the use of an electrode to turn the photocatalyst over, rather than an additional quenching cycle, permits net-reductive or net-oxidative transformations to be readily performed at extreme redox potentials (Scheme 1.3). Considering the hypothesis that chloride electrophiles were generally inert due to inadequate photocatalyst redox potentials, the advantages of electrophotocatalysis promised a solution to this chemical challenge.



Scheme 1.3. Redox properties of various strongly reducing photocatalysts and their associated lifetimes. Redox neutral systems are highlighted in gray boxes, net-reductive or -oxidative systems are highlighted in blue boxes. Potentials of oxidative quenching (−) and reductive quenching (+) are marked with − and +, respectively.

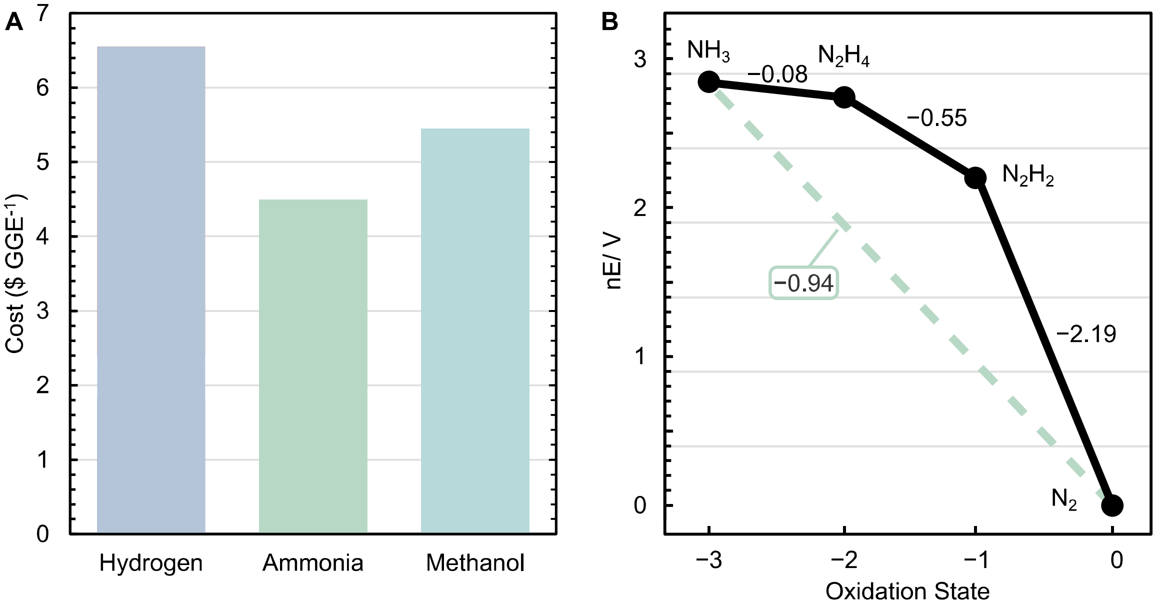
Indeed, electrophotocatalytic activation of challenging to reduce chloride electrophiles was reported for the first time in 2020.[27,28] Concurrently, in independent publications from the Wickens group and collaboratively the Lin and Lambert groups, protocols to convert aryl chlorides into aryl radicals were disclosed (Scheme 1.4A). Aryl chlorides incur similar challenges as discussed for alkyl chlorides, such as extremely negative reduction potentials and the potential for two-electron reduction. In both examples, organic photocatalysts (*N*-arylmaleimide, NpMI; dicyanoanthracene, DCA) were made more reducing by single-electron cathodic reduction followed by photoexcitation, reaching excited-state potentials in excess of −3.2 V vs SCE, albeit with short lifetimes on the scale of 1 ns or lower. While the precise mechanistic course of the reactions (namely, the identity of the photoreductant) has been brought under question by the Nocera group as a result of short photoexcited state lifetimes,[29] products characteristic of aryl radicals can be generated in synthetically useful quantities by reaction with common radical trapping agents. Subsequent work by the Barham group using NpMI revealed that similar protocols effect C–O cleavage in phosphinated alcohols, although *alkyl (benzylic) chlorides* were not reduced (Scheme 1.4B).[30] One potential factor responsible for the inertness of alkyl chlorides to NpMI is that aryl chlorides have lower free energies of activation for reduction than do alkyl chlorides as a result of a stepwise reduction pathway, and the associated kinetic penalty may prevent the use of photocatalysts with short lifetimes. Thus, we became interested in developing a protocol for alkyl chloride reduction via electrophotocatalysis, the details of which comprise Chapter 2.



Scheme 1.4. Carbon radical generation via activation of challenging to reduce (A) aryl chloride and (B) alkyl phosphinate substrates under electrophotocatalysis.

1.3.2 Ammonia oxidation

Interest in ammonia oxidation, specifically the conversion of two equivalents of ammonia to dinitrogen, is burgeoning given recent appreciation for its capacity to serve as a method for carbon-free energy production.[31,32,33,34,35] The notably high volumetric energy density of ammonia (13.6 GJ·m^{-3}) bests methanol, a comparable fuel that can also be readily produced in a carbon-neutral fashion, and it is more readily condensed and safer to transport than hydrogen.[36] Under a unified set of conditions, a complete technoeconomical analysis for hydrogen, methanol and ammonia produced using renewable energy found ammonia to feature the lowest source-to-tank cost (Scheme 1.5A).[37] While these beneficial attributes augur well for the future development of ammonia fuel technologies, high combustion temperatures for ammonia pose challenges to its immediate and widespread adoption.



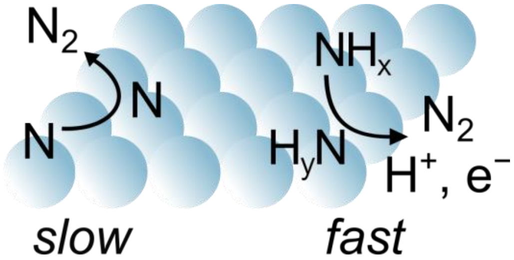
Scheme 1.5. Sustainable fuel economic and thermodynamic metrics. (A) Source-to-tank costs for various fuels generated under carbon-neutral conditions with renewable energy. (B) Frost-Latimer diagram illustrating ammonia oxidation thermodynamics in acetonitrile using ammonia as base ($pK_a = 16.5$) with Fc/Fc^+ as the reference potential.

A solution that promises to efficiently facilitate use of ammonia as fuel is electrochemical oxidation in a fuel cell. The theoretical potential for ammonia oxidation is very low, 0.09 V vs SHE (pH = 0) in aqueous conditions and −0.94 V vs Fc/Fc^+ in acetonitrile using ammonia as base (Scheme 1.5B).[38] Thus, when ammonia oxidation is paired with oxygen reduction, the maximum cell potential is comparable to a hydrogen fuel cell. Unfortunately, highly efficacious catalysts are required for ammonia oxidation since anodic oxidation on inert electrodes typically incurs an overpotential in excess of 1 V. The overpotential often observed for ammonia oxidation is unsurprising given the complexity of this six-electron, six-proton process. By analyzing the overall reaction in one- or two-electron steps, key contributors to the overpotential become apparent.

The first one-electron oxidation of ammonia can be considered in two cases wherein electron-transfer is coupled to, or independent of, electron transfer. Experimental thermodynamic data indicates a gas-phase bond-dissociation free energy value of 99.4 kcal/mol.[39] Thus, the N–H bonds in ammonia are extremely strong; as an example, this value exceeds the C–H bond-dissociation free energy of methane. Under non-aqueous (acetonitrile) electrochemical conditions, the mechanism of the first electron transfer from ammonia has been extensively investigated by Manthiram and coworkers.[40] Their analysis indicated that the first electron transfer occurs *without* coupled proton transfer, and this electron transfer is the rate-determining step in ammonia oxidation at inert electrodes such as glassy carbon. From DFT calculations, this step occurs at a potential of 1.77 V vs the computational hydrogen electrode, a theoretical electrode that is analogous to the experimental SHE. This potential is notably above the thermodynamic potential for the entire six-electron ammonia oxidation reaction.

The oxidation of ammonia by two- or four-electrons is more challenging to study experimentally in a direct fashion, but available thermodynamic data allows for the construction of a Frost-Latimer diagram (Scheme 1.5B).[38] Looking at the Frost-Latimer diagram, the slope of a line between any two chemical intermediates gives the thermodynamic potential vs Fc/Fc^+ for the given transformation. Thus, the line between NH_3 and N_2 has a slope of −0.94 V as previously discussed. Since most chemical processes proceed via one- or two-electron steps, it is interesting to consider the available two-electron pathways. The first available two-electron oxidation, the conversion of NH_3 to N_2H_4, has a potential of −0.08 V. Similar to the case of one-electron oxidation, this potential is substantially above that of the overall six-electron process; therefore, it is expected that proceeding via this pathway would incur a substantial overpotential. For each subsequent two-electron transformation (N_2H_4 to N_2H_2 and N_2H_2 to N_2), oxidation becomes easier, which can be rationalized by the ability of the increasing N–N bond order to facilitate reactivity. If any of these N–N bond containing intermediates were generated, it is more easily oxidized than is ammonia. This motivates research into catalyst designs that lower the activation barrier for N–N formation.

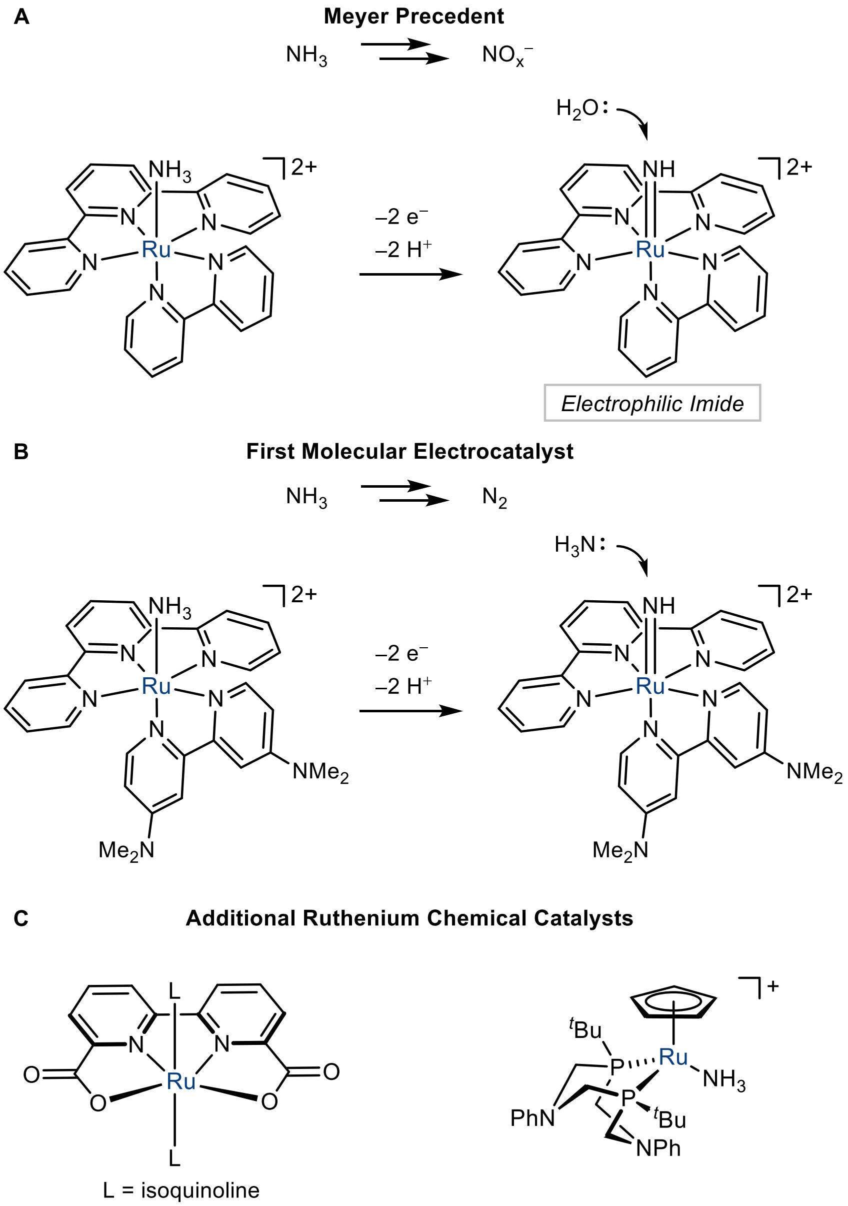
The interplay of these thermodynamic factors can be integrated into an analysis of the available experimental data governing the mechanism of ammonia oxidation under catalytic conditions. Electrochemical ammonia oxidation underwent its first wave of intense interest in the 1960s, and the mechanistic hypotheses then established that persist to this day.[41,42,43,44] Namely, the reaction course is proposed to follow either the Oswin-Salomon[41] or the Gerischer-Mauerer[42] mechanisms (Scheme 1.6). The Oswin-Salomon mechanism proposes that N–N bond formation during electrocatalytic ammonia oxidation with platinum electrodes proceeds via the coupling of two metal nitrides. By contrast, the Gerischer-Mauerer mechanism proposes that N–N formation proceeds prior to removal of all hydrogen atoms from the ammonia-derived nitrogen. The Gerischer-Mauerer mechanism is now widely accepted to be correct, i.e., early N–N coupling of nitrogenous, ammonia-derived fragments that still contain hydrogen is most efficient. If ammonia-derived nitrides are produced, these are instead considered catalyst poisons.[45] Unfortunately, even heterogeneous catalysts using the most recent, carefully designed platinum alloys incur high overpotential despite decades of concerted research into improving overpotential.[46,47,48] Furthermore, surface coverage by metal-nitrides still remains a substantial problem insofar as its contributes to catalyst poisoning that limits catalyst durability.



Scheme 1.6. Oswin-Salomon (slow) and Gerischer-Mauerer (fast) mechanisms of ammonia oxidation on platinum electrodes. The arrows represent N–N formation and, if necessary, further oxidation, to ultimately produce N_2.

The dearth of suitable catalysts and associated design principles thus motivates research into homogeneous complexes that catalyze ammonia oxidation. This would facilitate mechanistic studies, permitting validation of previous mechanisms—r the uncovering of new mechanisms. These fundamental discoveries would then inspire mechanistically directed development of more efficient heterogeneous catalysts. Furthermore, such molecular complexes could serve as active catalysts in their own right.

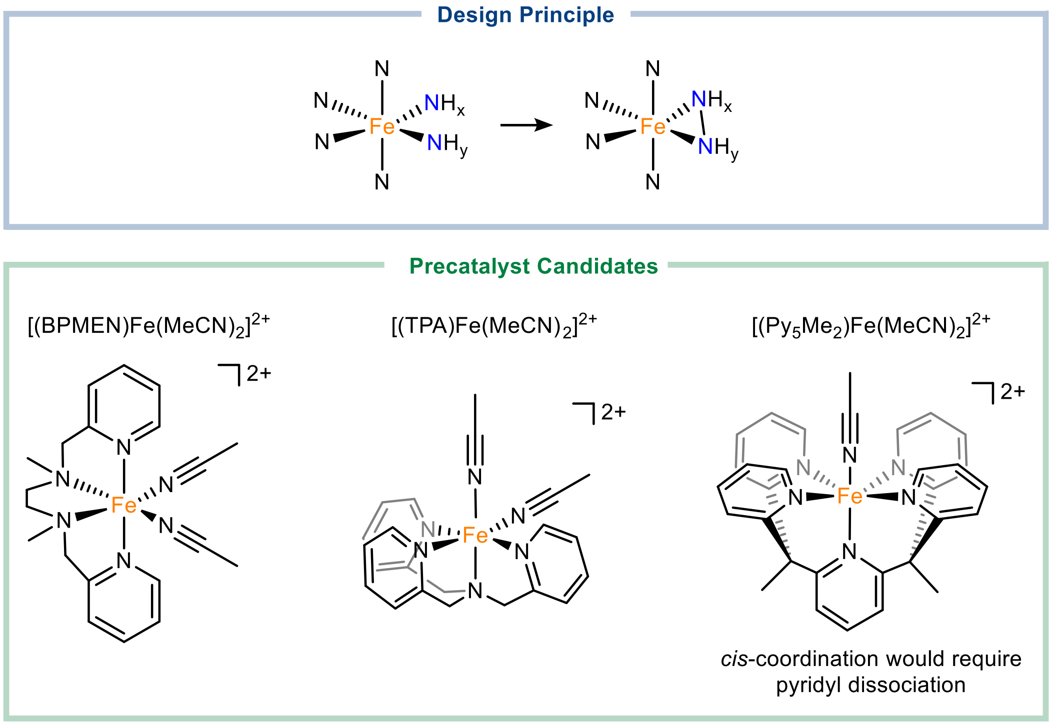
Given this context, at the onset of our research in 2018, it was striking that there were no reported transition metal systems that catalyzed ammonia oxidation over multiple cycles. In a stoichiometric fashion, Mayer demonstrated in 1981 that ruthenium polypyridyl complexes (Scheme 1.7A) can convert ammonia into nitrite and nitrate under oxidative electrochemical conditions.[49] Importantly, this work provided the first mechanistic insight into pathways that may be operative for ammonia oxidation in molecular systems: a disproportionation mechanism was proposed to furnish a high-valent Ru^{IV}=NH imido



Scheme 1.7. Early precedent in molecular ammonia oxidation using ruthenium catalysts. (A) Generation of an electrophilic imide that captures a water nucleophile and (B) ammonia oxidation catalysts inspired thereof. (C) Additional ruthenium catalysts featuring alternative designs.

complex that exhibited electrophilic character at nitrogen. Thus, water could serve as a nucleophile to generate an N–O bond. In 2019, Smith and coworkers developed this chemistry into the first example of electrocatalytic ammonia oxidation mediated by a molecular catalyst by working in anhydrous conditions, wherein N–N formation was proposed to follow an analogous mechanism (Scheme 1.7B).[50] Thus, at an applied potential of 0.2 V vs Fc/Fc^+, two equivalents of N_2 relative to ruthenium could be produced after 3 h. Within a short time period throughout 2019, two additional ruthenium catalysts (Scheme 1.7C) were reported using both electrochemical and chemical oxidation strategies, reaching a maximum of up to 14 equiv. N_2 under chemical catalysis (i.e., not electrocatalysis).[51,52,53]

Contemporaneous with the development of these early ammonia oxidation molecular catalysts, we were pursuing a catalyst design strategy that emulated the proposed mechanism for highly active ammonia oxidation heterogeneous catalysis: early coupling of NH_x and NH_y fragments (see Scheme 1.6). We became interested in a class of iron(II) water oxidation catalysts featuring neutral tetradentate ligands that enforce a coordination geometry marked by *cis* disposed, non-chelated coordination sites.[54] Using weakly coordinating triflate counterions in a high dielectric solvent such as acetonitrile, the triflate anions are completely displaced by acetonitrile.[55] Thus, we hypothesized that such a coordination sphere may be amenable to binding two ammonia-derived ligands *cis* to one another at an electrophilic metal, potentially allowing intramolecular N–N formation upon loss of protons following oxidation (Scheme 1.8). Since intermediates containing N–N bonds (e.g., hydrazine, diazene) are more readily oxidized than is ammonia, we considered it critical to intentionally design catalysts that feature properties capable of facilitating N–N coupling, the step that presumably would be rate- or potential-determining.



Scheme 1.8. Our motivation for investigating iron complexes featuring potential *cis* coordination sites for ammonia binding, and structures of our initial panel of proposed iron(II) ammonia-oxidation precatalysts.

Initially analyzing a panel of iron(II) complexes (Scheme 1.8), we found that $[(TPA)Fe(MeCN)_2]^{2+}$ exhibited the most promising activity for ammonia oxidation. The details of our studies into *cis*-ammonia coordination, electrocatalytic ammonia oxidation and mechanistic studies thereof are found in Chapter 3. Further development of $[(TPA)Fe(MeCN)_2]^{2+}$ inspired ammonia oxidation catalysts is the subject of Chapters 4 and 5.

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