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FIRST-ROW ORGANOOMETALLICS FOR HEAVY-METAL APPLICATIONS, AND AN ATOMICALLY-PRECISE IRON OXIDE NANoclUSTER

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Research Background

Through my studies in chemistry, I've established a true passion for inorganic chemical synthesis and analysis. I've performed three years of undergraduate research in four different groups, and I've been awarded four research fellowships; these experiences have given me a sense of creativity and independence that cannot be established within the confines of a classroom. This text summarizes my research experiences and independent studies in the field of inorganic chemistry.

My first research experience was in the Varga Group where I conducted biochemical analysis involving UV-visible studies of membrane proteins. After a summer of biochemical research, I became interested in synthetic work, so I performed two semesters of organic synthesis in the Hoberg Group. I then participated in the 2015 NSF-REU Program at the University of Utah with Dr. Janis Louie, wherein I synthesized iron organometallics for [2+2+2] cycloaddition. With Dr. Louie, I grew interested in organometallic catalysis and inorganic chemistry (as the work involved ligand synthesis, isolation of reactive intermediates and precatalysts, and mechanistic investigations), and I concluded that I'd like to pursue this class of chemistry in the long-term. Upon returning to UW, I explored inorganic chemistry further through graduate-level courses in physical inorganic, organometallic, and solid-state inorganic chemistry. I also began my work with Dr. Elliott Hulley, with whom I've been synthesizing iron organometallics with bifunctional ligand frameworks in an effort to establish a first-row olefin metathesis catalyst. I've developed synthetic approaches to several iron organometallics and a ligand-stabilized magic number iron oxide cluster, Fe$_9$O$_6$, the existence of which was predicted by Sun et al. sixteen years ago. These research experiences have allowed me to explore some molecular intricacies of a material world, and they've taught me to envision my own chemical systems.
Part One: Organometallic Catalysis

A fundamental challenge for chemical synthesis lies in the development of simple techniques for the manipulation of organic compounds. Organic compounds are composed mostly of carbon, nitrogen, oxygen, and hydrogen, and this category of materials encompasses most bioactive compounds, polymers, and other industrial products. In the chemical drawings throughout this text, carbon atoms are shown as black points in the chemical structures, and hydrogen are not explicitly illustrated. An organometallic complex is a molecule containing a single metal atom surrounded and bound by an organic ligand framework, which can be systematically modified to alter the properties of the metal atom. (Figure 1)

![Organometallic Complexes](image)

Organometallic reagents have revolutionized the field of organic synthesis through their use as stoichiometric reagents or as homogeneous, solution-phase catalysts. Stoichiometric usage of organometallics is exemplified by the highly reactive and well-known Grignard (R-MgBr) and organolithium (R-Li) reagents. In later years, organometallic catalysts have been developed to facilitate a variety of organic transformations including C-N, C-O, C-C bond formation and various cycloaddition reactions. The modern frontiers of organometallic research largely focus on the development of catalysts capable of new bond formation...
transformations, and the generation of organometallic systems for nitrogen fixation, CO₂ reduction, C-H activation, and phosphorous transfer. Another sector of organometallic research, one that I’m more familiar with, focuses on the replacement of heavy-metal catalysts with first-row counterparts. In this article, I present three organometallic projects toward this goal: iron catalyzed [2+2+2] cycloaddition for synthesis of substituted 2-aminopyridines, photoredox coupled C-N bond formation, and iron organometallics toward olefin metathesis.

I. Iron-Catalyzed [2+2+2] Cycloaddition

My interest for inorganic chemistry was sparked at the University of Utah where I served as a Summer 2015 NSF-REU Fellow in Prof. Janis Louie’s lab. I spent two months in Salt Lake City performing about 70 hours of research each week synthesizing iron organometallics with di-aldiminopyridine (PDAI) ligands (Fig. 2), and conducting kinetic studies on a catalytic cycle using variable temperature – nuclear magnetic resonance spectroscopy (VT-NMR), and gas chromatography with a flame ionization detector (GC-FID). This complex was the first organometallic that I had any real hands-on experience with, and it is a versatile catalyst for [2+2+2] cycloaddition to form 4,6-substituted 2-aminopyridines, [2+2] cycloaddition and has also been used to accomplish nitrogen fixation.2,3,4

Figure 2: General reaction scheme for the synthesis of 4,6-substituted 2-aminopyridines from acetylene and cyanamide starting materials.
My work in the Louie Group involved the synthesis of a reactive \textsuperscript{ipr}PDAI precatalyst, (\textsuperscript{ipr}PDAI)\textit{Fe(\textit{C}_4\textit{H}_6)}, which could be added to a solution of benzene and mixed with N,N-dimethylcyanamide and acetylene to catalyze the regioselective generation of 2-aminopyridines. (Fig. 2) The organic substrates must be added to the catalyst sequentially (first cyanamide, then acetylene) to avoid production of unwanted benzene side products. 2-aminopyridines are an important class of bioactive compounds used as anti-inflammatory drugs for rheumatoid and osteoarthritis and as antihistamines, and are also being pursued as potential agents for prion inhibition.\textsuperscript{5} In a graduate level course on organometallic chemistry, I illustrated this catalyst's utility by proposing a synthetic approach toward a potential prion inhibitor. (Fig. 3)

![Proposed Prion Inhibitor, Tripeleennamine, and Piroxicam](image)

Figure 3: A series of bioactive products that incorporate 2-aminopyridines into their structures. 2-aminopyridine groups are highlighted in blue. Tripeleennamine and piroxicam are regularly prescribed; the compound on the left is a proposed prion inhibitor suggested a synthetic approach

One of my responsibilities was to assist a graduate student in mechanistic investigations of this catalytic cycle (Fig. 4), which we initially assumed took eight hours to complete. For a standard catalytic reaction, a general rule-of-thumb is that the rate of catalysis increases or decreases by a factor of two for a given a change of 10 degrees Fahrenheit. In the interest of performing timely experiments, and not monopolizing the NMR spectrometer for a full eight hours, we increased the temperature to obtain a reaction time of about three hours. With the reaction vessel inside of a heated NMR spectrometer probe,
we recorded spectra of the reaction mixture once every two minutes for the extent of the proposed reaction time.

Figure 4: A proposed catalytic cycle for [2+2+2] cycloaddition of two acetylenes and one dimethylcyanamide to form a substituted 2-aminopyridine.
Our results were peculiar, as they showed no loss of starting material or arrival of product; rather, with each experiment we acquired 90 spectra that looked almost identical. Our initial assumption was that our catalyst had oxidized, and that the reaction had not proceeded at all, and so we synthesized a fresh batch of precatalyst, but upon repeating the experiment, we once again obtained 90 identical spectral with no changes from first to last.

Earlier that summer, when first introducing me to the reaction, my partner had pointed out that once the last substrate, acetylene, was added to the reaction mixture, the vessel heated up dramatically. With only 1 mL of solution in a glass vial, I could feel a stark temperature increase through the thick rubber gloves of the glove box. At first, I assumed that the heat was produced by the loss of butadiene, C₄H₆, from the precatalyst, but after all the frustration of not understanding our results, it occurred to me that losing butadiene would be an endothermic process so it shouldn’t produce heat, it should require it. We then recognized that the catalytic reaction involved breaking two C-C π-bonds and one C-N π-bond, and forming two C-C σ-bonds and one C-N σ-bond. Given that σ-bonds are stronger and lower in energy than π-bonds, this process would release a significant amount of heat. As such, we concluded that the heat was probably produced by the reaction itself, and that the spectra weren’t all the same because the reaction hadn’t begun, but rather because it had already finished by the time it was in the NMR spectrometer.

Now that we’d had properly assessed the reaction, on the last day of my fellowship in Utah we searched for an NMR spectrum of purified 2-aminopyridine product. Upon comparing the spectrum of purified product to the 90 spectra of the crude reaction mixture, it became clear that the mixture’s main component was product, not starting material, and that the reaction was finished before NMR analysis had commenced. Finally, we understood our perplexing results; if we wanted to probe the kinetics of the catalytic cycle, we ought to
cool the reaction down rather than heating it up. While I was frustrated to leave without concrete experimental data, I was astonished to learn that this catalyst was far more active than we assumed. I left Utah ready for more surprises, and understanding that assumptions don’t cut it in research; our expectations are often shattered. Only a thorough, relentless approach will coax any useful information out of the unknown, and if this approach is taken, some truly amazing results can be obtained.

II. Photoredox-Activated Organometallic Catalysis: High-Valent Nickel Species for C-N Bond Formation

Background

Organometallic cross-coupling reactions have afforded selective and efficient methods for C-C, C-N, and C-O bond formation. Many of these reactions, such as Suzuki-Miyaura aryl coupling and Buchwald-Hartwig C-N bond formation, are traditionally performed using heavy metals such as palladium. While heavy-metal catalysts are versatile and highly reactive, their toxicity and price have created a demand to replace them with first-row transition metal systems. Nickel catalysts have been developed for several C-C coupling reactions, but C-O bond forming reactions have been more limited due to the thermodynamic requirement that reductive elimination of the coupled product occur from a transient Ni$\text{III}$ state. Recently, C-O bond formation was accomplished via a photoredox generated Ni$\text{III}$ intermediate, and a “general strategy” for photoredox activation of organometallic catalysis was proposed. Herein, an analogous system is proposed that has been tailored to facilitate C-N bond formation.
Project Narrative

It is well established that reductive elimination of a C-O coupled product is an exergonic process for Pd$^{II}$ complexes, while this process is endergonic and disfavored for Ni$^{III}$ complexes. Acting on the assumption that reductive processes are more favored for species of higher oxidation state, Macmillan et al. showed that photoredox catalysis can be utilized to generate a Ni$^{III}$ alkoxide species \textit{in situ} and perform reductive C-O coupling.\(^7\) It is hypothesized that an amine with electronic character similar to an alcohol, such as a sulfonamide (pKa $\approx$ 12-17)\(^8\), may be used to perform aryl-sulfonamide C-N cross coupling. (Scheme I) The sulfonate group can be removed from a coupled sulfonamide product using LiAlH$_4$ or Red-al to yield a substituted amine.\(^9\)

The catalytic system employs an iridium sensitizer, [Ir(dF(CF$_3$)ppy)$_2$(dtppy)]PF$_6$ (2), to invoke two single electron transfer (SET) processes. A proposed photo-activated catalytic system is provided in scheme II, below. The first SET is an oxidation of a Ni(II)-nitride by a blue light sensitized *Ir$^{III}$ species to generate the reactive Ni$^{III}$ intermediate and facilitate reductive elimination of C-N product; the second SET is a reduction of the Ni$^I$ to Ni$^0$, which completes both catalytic cycles simultaneously. K$_2$CO$_3$ is used to deprotonate the sulfonamide\(^9\), which undergoes ligand exchange with a Ni$^{III}$ aryl bromide intermediate to produce a presumably unreactive Ni$^{III}$ aryl nitride complex. At this point, sensitization will generate a Ni$^{III}$ species capable of performing the critical C-N bond formation. After reductive
elimination of product, SET completes the catalytic cycles to reproduce the Ni$^0$ and Ir$^{III}$ catalysts. Quinuclidine, which strongly influenced the efficiency of photo-activated C-O bond formation, acts as an electron transport agent, shuttling electrons for the reduction of Ni$^{III}$ and oxidation of Ni$I$.\textsuperscript{7}

Figure 6: A scheme depicting a proposed catalytic cycle for photo-activated coupling of a substituted aryl halide to a monosubstituted sulfonamide.

Transition metal sensitizers with aromatic polypyridyl ligand frameworks are commonly employed for photoredox catalysis. They absorb in the visible range, exhibit a long-lived excited state, and have redox properties that can be tuned through ligand
modifications. Excitations in iridium polypyridyl complexes occur from a singlet $t_{2g}$ state to a ligand $\pi^*$ orbital. Rapid intersystem crossing is then facilitated by spin-orbit coupling in the presence of the large iridium atom to produce a redox active $^*\text{MLTC}^3$ excited state.\textsuperscript{11,12}

The iridium sensitizer (2), whose structure is shown above, was chosen on the basis of its triplet lifetime (2.3 $\mu$s), its excited state reduction potential ($E^0_{\text{red}} \left[ ^*\text{Ir}^{III}/\text{Ir}^{II} \right] = -1.21$ V), and its established ability to both reduce Ni\textsuperscript{II} species and oxidize Ni\textsuperscript{III} alkoxides.\textsuperscript{10,7} The fluoro substituents on the phenyl-pyridyl ligands result in a stabilization of the $t_{2g}$ orbital, which enhances the complex’s reducing strength. The oxidation potential of an Ni\textsuperscript{III} alkoxide complex was determined to be $+0.71$ V.\textsuperscript{13} Given the isoelectronic character of the sulfonamide relative to an alcohol, a similar oxidation potential is predicted for this system, and so electron transfer should be favorable. If Ni\textsuperscript{III} nitride oxidation is not observed, the ligand framework can be modified with more electron-withdrawing fluoro substituents to lower the $t_{2g}$ HOMO. The absorption spectrum of (2) exhibits two intense ligand centered ($^1\text{LC}$) transitions in the UV, and a weak $^1\text{MLCT}$ transition at 378 nm. The complex phosphoresces at blue-green light (470 nm) with 68% quantum yield.\textsuperscript{10} Self-quenching is prevented electrostatically by repulsion between charged metal centers, and sterically by the bulky tert-butyl substituents.\textsuperscript{10}

Figure 7: Structure of a reactive intermediate that could potentially be used as an isolable starting point for mechanistic investigations.
Mechanistic investigations will be performed to gauge the influence of the iridium sensitizer and determine whether a transient Ni\textsuperscript{III} species is a critical intermediate. A Ni\textsuperscript{II} aryl nitride (3) should be isolated as a mechanistic probe. Stern-Volmer phosphorescence quenching experiments will be performed to determine whether emission of *Ir\textsuperscript{III} decreases in the presence of (3), quenching would signify the production of a Ni\textsuperscript{III} intermediate. Redox activity will also be measured using cyclic voltammetry. Complex (3) will be treated with blue-light in the absence of sensitizer, and with sensitizer in the absence of light to determine whether Ni\textsuperscript{III} is capable of product formation. Undesirable side products may results from direct sensitization of the sulfonamide substrate and generation of a radical species\textsuperscript{12}, but the presence of quinuclidine may prevent this process and nickel oxidation should be more favorable. As is noted for Buchwald-Hartwig coupling, B-hydride elimination may result in sulfonylimine side-product formation, though this process is kinetically disfavored in palladium-based systems and C-N coupling is observed.\textsuperscript{14} Computational studies will be performed to elucidate mechanistic information and intermediate energies. Substrate studies will provide information as to catalyst selectivity and functional group compatibility. Finally, the ligand framework of the iridium and nickel complexes and the sulfonyl alkyl substituent can be tuned to modify the electronics of the system and optimize catalytic efficiency.

**Conclusion**

Merging photoredox and organometallic catalysis may provide access to previously unattainable catalytic processes. My proposal seeks to adapt a strategy developed by MacMillan et al. to establish the first nickel based C-N cross coupling catalyst. The system proposed above would provide a cost-effective replacement for Buchwald-Hartwig C-N cross coupling, and it may promote new forms of selectivity and reactivity. Furthermore, this work
will test the proposed “general method” for photoredox activation of organometallic catalysis.

III. Iron Organometallics toward Olefin Metathesis – See CPAC for sources

Background

Metal carbenes (M=CR₂), also known as metal alkylidenes, are a class of organometallic complexes that are paramount to a number of industrial and pharmaceutical processes. They are the active catalyst for two important reaction types: olefin metathesis and cyclopropanation. Olefin metathesis, or the metal catalyzed scrambling of carbon-carbon double bonds, is a cornerstone to industrial polymer production and pharmaceutical synthesis. Cyclopropanation, the synthesis of substituted cyclopropanes, is a crucial reaction for the synthesis of several pharmacologically active compounds. Olefin metathesis occurs as a metal alkylidene coordinates to an olefin and undergoes [2+2]-insertion to form a metallacyclobutane intermediate, which then performs a retro-[2+2] to generate a new metal alkylidene and a new olefin. (Fig. 8, blue) Conversely, the metallacyclic intermediate can undergo reductive elimination to produce cyclopropane. (Fig. 8, red)

![Figure 8: A scheme depicting the mechanism of olefin metathesis (outlined in blue) and cyclopropanation (outlined in red).](image)

The 2005 Nobel Prize was awarded to Yves Chauvin, Robert Grubbs and Richard Schrock “for the development of the metathesis method in organic synthesis.” Grubbs and
Schrock utilized Chauvin’s mechanistic insight\textsuperscript{17}, which suggested the importance of a metal-bound alkylidene, to develop highly active single component ruthenium and molybdenum based catalysts that are still employed today.\textsuperscript{18,19} (Fig. 9) Given that efficient methods of C-C bond formation lie at the very foundation of organic chemistry, these catalysts revolutionized the modern approach to pharmaceutical and industrial organic synthesis. (Fig. 10)

Figure 9: The general structures of a Grubbs and Schrock olefin metathesis catalyst.

Figure 10: Images depicting potential synthetic products of olefin metathesis with an organic polymer (top) and a complex natural product (bottom). In the natural product, metathesis sites are denoted with the abbreviation RCM, standing for ring closing metathesis.\textsuperscript{20}
While the importance of these catalysts cannot be overstated they leave room for improvement in that they are based on second row metals. Heavy metal catalysts are well studied and highly reactive, but they are expensive and have greater toxicity than first row catalysts. As such, they impart higher expenses on pharmaceutical and industrial manufacturing processes, and their use necessitates expensive separation procedures to ensure consumer safety.\textsuperscript{1} These ramifications of heavy metal catalysis have created a demand for the development of a generation of earth abundant first row catalysts.

Metal alkylidenes are highly reactive and unstable compounds, which compromises their stability when bound to a first row transition metal. In a computational study of the structural and electronic requirements for olefin metathesis Hoffmann suggested iron as a viable metal so long as the metallacycle intermediate has a d\textsuperscript{4} electron count.\textsuperscript{21} First row alkylidenes have been investigated in the past, but these compounds are isolated using electron-withdrawing carbonyl (CO) ligands, and as a result they are active to cyclopropanation, but not olefin metathesis.\textsuperscript{22} (Fig. 11) As such, there is a demand for research that explores organometallics with new ligand platforms capable of providing an electron rich metal center bound to a stable alkylidene.

\begin{center}
\textbf{Figure 11:} The structure of Pettit’s iron-bound alkylidene, which facilitated cyclopropanation, but not olefin metathesis.
\end{center}

The incorporation of a multifunctional ligand framework with pendent binding sites may be the key to the stabilization and isolation of a first row complex that acts as a metal carbene. The proposed system employs a pendent nucleophile to bind an iron bound
alkylidene, and stabilize it as a σ-ylide. This will allow for the reversible stabilization and
masking of an alkylidene as a σ-ylide until an olefin binds to an open coordination site, at
which point metathesis or cyclopropanation may proceed. (Fig. 12) If dissociation of the
nucleophile from the σ-ylide and in situ formation of a reactive alkylidene is disfavored,
metathesis may still proceed due to the isolobal relationship between the π-bonding orbital
of the alkylidene and the σ*-antibonding orbital of the ylide. (Fig. 13)

Figure 12: A schematic depicting the means by which the pendent binding group may dissociate from
the alkylidene carbon, and produce the reactive carbene state that can then undergo metathesis or
cyclopropanation.

Figure 13: A schematic representing the isolobal character between the reacting orbitals of a metal
alkylidene and a σ-ylide, which are highlighted in blue.

In Hulley’s lab we pursue the well-studied half-sandwich ligand framework that we
expect to provide a stable, electron-rich metal center. We’ve chosen to replace Pettit’s
electron-withdrawing carbonyl ligands with an electron-donating phosphine ligand.
Phosphorous-based σ-ylides have been extensively studied, though we wish to explore nitrogen ylides and determine their sigma bond donating strength. (Fig. 14)

Figure 14: The general structure of our proposed catalyst, though modifications can be made to the phosphine ligand and cyclopentadiene group.

**Synthetic Work**

We perform organic synthesis to yield novel ligand systems fit for metal bound ylide propagation. In the synthetic approach reported below, a multifunctional ligand framework is employed to promote C-H activation and the formation of a metal bound ylide. There are a variety of other viable ligand systems that may yield similar results. Exchange of the chloride counter ion for a BF$_{20}^-$ counter ion is noted to produce a more crystalline substance with greater solubility. Lithiation of the system may allow for other transmetallation based mechanisms of ylide formation. $^{31}$P NMR suggests lithiation was successful, as only one phosphorous peak is visible in the spectrum and no starting material is observed. (Fig. 16)

Figure 15: A schematic for the synthesis of an ylide-bearing phosphine ligand.
Figure 16: A schematic for salt exchange and lithiation of the imidazolyl phosphine ligand.

Our initial synthetic approach involved working with half-sandwich iron lithium bimetallic complexes bound to cyclooctadiene (COD) ligands. We expected the COD ligand to be labile enough for replacement with our phosphine ligand, and that the lithium ion would crash out in a LiBF$_{20}$ salt to allow for C-H activation and generation of the metal bound ylide complex. (Fig. 17)

![Figure 17: A schematic of the first synthetic approach we took to approach our target catalyst.](image)

We were able to obtain a single crystal X-ray diffraction structure of the bimetallic complex, which was developed by Furstner et al.\textsuperscript{23} (Fig. 18) We performed NMR scale reactions in an effort to synthesize the target catalyst, and the appearance of a hydride peak at -5.5 ppm after reaction with the bifunctional ligand suggests that the synthesis may have worked. (Fig. 19) These syntheses are challenging in that they require specialized glassware for air-free filtration, close manipulation of subzero temperatures, and the use of highly reactive lithium sand, which is difficult to make and handle. The difficulties associated with this synthetic method pushed us to investigate other avenues.
Figure 18: An XRD generated structure for [Li(DME)]Fe(Cp)(COD). The colors light blue, red, grey, and orange correspond to lithium, oxygen, carbon, and iron, respectively. Hydrogen are omitted for clarity.

Figure 19: NMR spectra of the bimetallic starting material, [Li(DME)]Fe(Cp)(COD) (top), and overlayed on a spectrum of the same sample after a stoichiometric amount of ligand was added. The peak at -5.5 ppm is indicative of a hydride, which suggests the reaction may have been successful.

Our synthetic approach then turned toward the development of a series of new mono- and di-alkyl iron organometallics. A slurry of FeCl\textsubscript{2} in TMEDA was stirred for two hours, collected on a frit, and washed with pentane to obtain Fe(TMEDA)\textsubscript{x}Cl\textsubscript{2} as a pale salmon colored powder.\textsuperscript{24} Empirical calculations were utilized to determine the mole ratio of FeCl\textsubscript{2} to Fe(TMEDA)\textsubscript{x}Cl\textsubscript{2} within the sample by mass, and this value was used to determine the moles of iron added by mass. A cold slurry of Fe(TMEDA)\textsubscript{x}Cl\textsubscript{2} in pentane was treated with one or two equivalents of neopentyl lithium (NpLi) or neophyl lithium (NphLi) to obtain the corresponding mono- or di-alkyl TMEDA complex. (Fig. 20) It is observed the Fe(R)\textsubscript{2}(TMEDA)
is initially formed so, the reaction is run for 12 hours to allow for conproportionation and formation of Fe(R)Cl(TMEDA). The mono- and di-alkyl complexes could be easily separated from one another, as the mono-alkyl product is much less soluble in pentane. Single crystals were grown from a saturation solution of the complex at -30 °C in the glove box, and a crystal structure was obtained for three of the four compounds. (Fig. 21)

Figure 20: A schematic depicting the synthetic method developed to yield a series of mono- and di-alkyl iron organometallics.
Figure 21: Crystal structures of Fe(Np)Cl(TMEDA) (top), Fe(Np)$_2$(TMEDA) (middle), and Fe(Nph)Cl(TMEDA) (bottom) shown from left to right, respectively. Ellipses represent uncertainty in atomic position as calculated by the diffractometer. Colors orange, blue, grey, and green correspond to elements iron, nitrogen, carbon, and chlorine, respectively.
These alkyl organometallics were then studied as starting materials for the formation of the desired half-sandwich platform. The mono-alkyl complexes, Fe(Np)Cl(TMEDA) and Fe(Nph)Cl(TMEDA), reacted rapidly with lithium cyclopentadiene (LiCp) salts to form an orange colored product. NMR data suggests that these reactions produce ferroocene derivatives and the dialkyl iron TMEDA complex rather than the desired half-sandwich complex. (Fig. 22) Alternatively, we treated the dialkyl complexes, Fe(Np)$_2$(TMEDA) and Fe(Nph)$_2$(TMEDA), with protonated cyclopentadiene (CpH) derivatives. This facilitated the slow formation of a purplish or greenish brown colored solution. NMR data of this solution suggests the formation of the desired half sandwich complex and a corresponding alkane byproduct. (Fig. 23) We are working to collect a crystal structure of this material to fully characterize it. We will also scale up the reaction to obtained more material and refine our purification methods.

![Figure 22: A schematic depicting the mechanism for the undesired formation of Fe(Np)$_2$(TMEDA) and ferroocene. Observed products are shown in boxes.](image)

![Figure 23: Reaction schematic for the formation of a half-sandwich organometallic (right) from Fe(Np)$_2$(TMEDA).](image)

Next, we will treat our half-sandwich alkyl organometallics with a bifunctional imidazolyl phosphine ligand to produce our desired catalytic system. (Fig. 24) We also intend
to get crystal structures of the mono-alkyl half-sandwich complexes and fully characterize them using NMR. If this system is active to olefin metathesis it will simultaneously decrease the costs of polymer production and pharmaceutical synthesis, while also allowing for more environmentally friendly industrial practices.

![Figure 24: A schematic for the synthesis of the proposed half-sandwich metathesis catalyst. A bifunctional ligand is shown above the reaction arrow and the catalyst is shown on the right side of the reaction equation.](image)

**Part II: Iron Oxide Nanocluster: Fe₉O₆(Np)₆(TMEDA)₃**

**Background**

Nanomaterials often exhibit properties that differ significantly from those of their bulk counterparts. For example, bulk gold is close-packed, with its atoms packed as closely together as possible, and its color is ... you guessed it ... gold. (Fig. 25) Gold nanoparticles with diameters on the scale of visible light exhibit optical properties that are much different than the bulk. As nanoparticles are brought to the same size as light’s wavelength (~400 – 700 nm), they undergo a strong absorbance at the wavelength in a process known as surface plasmon resonance, whereby the electrons in the particle polarize to generate a dipole across the particle. With this absorbance, gold nanoparticles can be synthesized in all colors. These particles are still similar to bulk material in that their atoms are close packed. (Fig. 26)
As one ventures further into the nano-regime, more outlandish properties come into play, and one begins to observe properties like superatomic orbitals and sphere-shaped (not close-packed) particles. I’ve become very interested in a class of compounds known as magic number nanoclusters. Nanoparticles smaller than the visible range, ones with only a few hundred atoms or less, are stabilized at monodisperse sizes with a specific number of atoms. This specific number of atoms is termed a “magic number”, and at this size, interesting electronic and structural properties are observed. I first became interested in these compounds when I stumbled upon Au$_{25}$ clusters while I was taking a course on nanotechnology with the honors program.\textsuperscript{27} (Fig. 27)
After discovering the clusters shown above, I investigated this class of compounds further and performed a literature research project on them. Magic number clusters are stabilized by a protective ligand framework (Fig. 28, left), and they exhibit a metal core that often has a cage-like structure. (Fig. 28, right) Electrons can delocalize throughout the cores of these clusters to establish electron orbitals that are delocalized over a set of atoms. The cage structure of the magic number cores gives them a net spherical shape, which makes these delocalized orbitals look like jumbo-sized analogues to atomic orbitals, and so they are termed superatomic orbitals.$^{28,29}$ (Fig. 29)
Magic Number Iron Oxide

In the midst of my literature review on magic number clusters, and as I became motivated to someday work with them, I inadvertently synthesized one, Fe$_9$O$_6$(Np)$_6$(TMEDA)$_3$. I had been synthesizing a batch of Fe(Np)$_2$(TMEDA) on the Schlenk line, when I accidently let a very small amount of air into my reaction vessel. Low valent iron complexes, such as Fe(Np)$_2$(TMEDA), are sensitive to oxygen and will readily oxidize in the presence of air. I then began looking around for literature evidence for magic number iron oxide clusters, and I found a group from Japan that was conducting theoretical studies on these compounds back in the years 1999 and 2000. The group performed an experiment where they placed an iron rod inside of a mass spectrometer, and in a time-synchronized manner they pulsed the rod with a spray of electrons then they pulse the flying iron particles with an oxygen spray. In the resulting mass spectrum they observed what they proposed were magic number iron oxide particles, Fe$_9$O$_6$ and Fe$_{13}$O$_8$. (Fig. 30) With these masses in hand, the
group performed quantum chemical calculations to optimize structures for the iron oxide clusters. (Fig. 31)

Figure 30: Mass spectral data that was reported by Sun et al. in the year 2000 suggesting the presence of magic iron oxides, nickel oxides, and cobalt oxides, $M_9O_6$ and $M_{13}O_8$.\textsuperscript{30}

Figure 31: The computationally optimized structures of $Fe_9O_6$ (left) and $Fe_{13}O_8$ (right).\textsuperscript{30,31}
Our discovery of this cluster stands as the most surprising and exciting moment in my research career, and I still remember that day very clearly. We had been trying to collect a structure for Fe(Np)$_2$(TMEDA) from the batch that I had let a trace amount of air into on the X-ray diffractometer. Using a microscope, Dr. Hulley was sifting through a mixture of clear, glassy, amorphous crystals of Fe(Np)$_2$(TMEDA), which he didn’t expect to diffract well because of their shape. Suddenly, Dr. Hulley let out a distinctive “Oooo”, as he discovered a brown rhombohedron that stood out among its amorphous partners. He scooped this crystal up and threw it on the X-ray diffractometer. Later on that afternoon, we were both surprised by our results. (Fig. 32) The cluster features two different iron environments: six tri-coordinate iron (II) atoms bound to two oxygen and one neopentyl on the top and bottom, and three tetrahedral iron (II) atoms bound to two oxygen and one TMEDA. The cluster features an Fe$_9$O$_6$ core with a roughly 0.7 nm void in the middle of it and it is bound by a total of six neopentyl ligands and three TMEDA ligands.

![Figure 32: Two views of the crystal structure of Fe$_9$O$_6$(Np)$_6$(TMEDA)$_3$, which we obtained while working with Fe(Np)$_2$(TMEDA). Colors orange, red, blue, and gray correspond to iron, oxygen, nitrogen, and carbon, respectively. Hydrogen are omitted from this image for clarity.](image)
After the initial discovery, Dr. Hulley requested that I try and synthesize the cluster again. After months of permutation and reiteration, performing experiment after experiment, we slowly discovered how to maximize our yields of this curious compound. First, we needed to discover what the source of oxygen was, and we discovered water didn’t work and oxygen did. After identifying gaseous O\textsubscript{2} as our oxygen source, we began working with pure compressed-O\textsubscript{2}, which we added to a stirring solution of Fe(Np)\textsubscript{2}(TMEDA) in toluene. We continued attempting the synthesis with pure O\textsubscript{2} for a month or two, but could not obtain the crystalline material we wanted, and so we went back to using air and immediately got the desired product. The reason that O\textsubscript{2} from air works and pure O\textsubscript{2} doesn’t is most likely because in air the O\textsubscript{2} is much more dilute than it would be in pure form, and addition of pure air over-oxidizes the material beyond the desired Fe\textsubscript{9}O\textsubscript{6} form. We also discovered that the synthesis does not work in pentane, and we have only obtained the cluster when it is synthesized in toluene. We now add 4.5 equivalents of O\textsubscript{2} in air to a concentrated, stirring solution with 9.0 equivalents of Fe(Np)\textsubscript{2}(TMEDA) in 1.25 mL of toluene through a series of stepwise additions using a gas-addition bulb. (Fig. 33)

Initially, I crystallized the cluster out of concentrated pentane solutions obtained after filtration of the reaction mixture. This method of crystallization was troublesome in that both the product and starting material co-crystallized together. Eventually, I discovered that the cluster crystallized very well onto clean glass surfaces from dilute solutions of pentane, and later we discovered that it even crystallized out of dilute toluene solutions. Once the distinctly rhombohedral crystalline material is obtained, it is very difficult to get back into solution, and it quickly begins to crash back out of solution. (Fig. 34)
Figure 33: (left) A reaction schematic for our current approach to synthesizing Fe₉O₆(Np)₆(TMEDA)₃. (right) The standard glassware used for the reaction. It consists of a 2.0 mL round bottom flask, connected to a 11.20 mL gas-addition bulb with Teflon valves, that is further connected to the Schlenk line.

Figure 34: A microscope image of the box-shaped crystals of Fe₉O₆(Np)₆(TMEDA)₃
The cluster is has precisely 183 atoms, and in its crystalline form has an asymmetric unit with the formula Fe$_2$O(Np)(TMEDA)$_{1/2}$. (Fig. 35) The lattice cell is rhombohedral, and each one contains three clusters (one corner and two inside) and three voids (two inside and one accounted at the edges of the lattice cell). The cluster can be broken up into a protective ligand sphere and a Fe$_9$O$_6$ core. (Fig. 36)
With a protocol developed so that we can synthesize Fe₉O₆ more consistently, we have begun characterizing this compound using solution-phase NMR spectroscopy and various magnetic measurements. We employed the Evans Method to determine the solution-phase magnetic moment of the compound. To accomplish this, we dissolved a specific amount of the cluster in D₈-Toluene, and then placed that solution in an NMR tube with a non-interaction D₈-Toluene capillary. This provided a system where some solvent is able to interact with the cluster, and some is not. The solvent peaks in the resultant NMR spectrum exhibit a shift that results from this interaction, and this shift can be used to calculate the spin-only magnetic moment of the cluster. Using this method, we calculated a spin-only magnetic moment of 7.3 Bohr Magnetons within the temperature range of – 40 °C to 40 °C. (Fig. 37)
After determining the cluster’s solution-phase magnetic behavior, we collaborated with the Tang Group in UW’s Department of Physics to determine the solid state magnetic behavior. The Tang Group uses a physical properties measurement system (PPMS) to conduct high-sensitivity measurements on solid-state samples. We have obtained strange results with their measurements, whereby two solid-state samples produce different magnetic results. A fresh sample of crystalline material was noted to have behavior similar to a spin glass, which is a so-called frustrated magnet that occurs in compounds with a triangular arrangement of atoms.\textsuperscript{33,34} (Fig. 38, top) Below a certain critical temperature, in our case at about 100 Kelvin, the electrons in a spin glass become frustrated and take on a random alignment. An old sample of this material is noted to have different magnetic...
properties that appear to be similar to those of a simple paramagnet. (Fig. 38, bottom) Dr. Hulley believes that this may be the results the breakdown of the crystalline structure via a slow loss of pentane that is trapped in the voids of the crystal. We recently realized that this cluster also crystallizes with toluene in the voids, which has a much lower vapor pressure than pentane, which may allow for long-term storage. As such, we plan to repeat our magnetic measurements with crystals that we have grown from toluene to check whether we once again observe spin glass behavior.

Figure 38: (top) Magnetic moment measurements for a crystalline sample that resemble spin-glass behavior. (bottom) Magnetic moment measurements made for an old sample that behaved as a paramagnet. Temperatures are varied from 300 K to 4 K.
We plan to continue our studies of the paramagnetic behavior of the Fe₉O₆ cluster, and we plan to investigate its utility in designing solid-state materials and metal organic frameworks. It has been awesome to work with this compound and slowly learn more about it. We hope to publish these results in the coming year, which will serve as my first scientific publication, and we will soon submit a composition of matter patent on this compound. Although I will be starting my Ph.D. the Fall of 2017 at a separate institution, the Hulley Group plans to continue its work with this cluster, and I am excited to see what sort of applications they find for it.

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Works Cited


