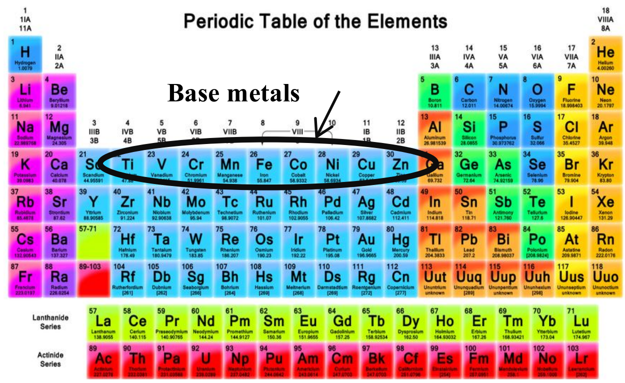
Background, Relevance, and Significance

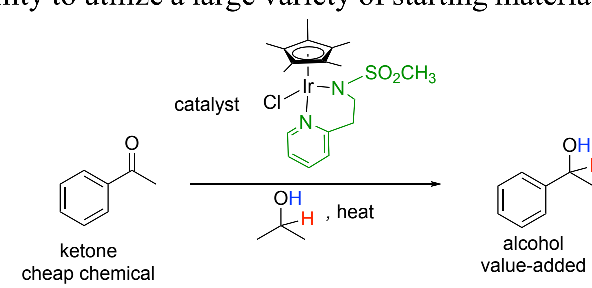
My scholarly work is focused on the development of more energy efficient means to produce chemicals using catalysis. Nearly all chemicals we use daily are produced using at least one catalytic reaction. A catalyst is a species added to a chemical reaction in a small amount that speeds up the reaction. The catalyst provides a lower energy pathway to go from starting material to product; thus, making the overall reaction less energy intensive and more economical. Catalysts are essential for the selective, efficient, and sustainable synthesis of a variety of widely used commodity and specialty chemicals, including acetic acid (vinegar) and aldehydes that are used in the flavor and fragrance industry. A familiar catalyst is the catalytic converter in a car that reduces the toxicity of its emissions. *Therefore, it is of interest to conduct research to improve the production of our supply of chemicals so that they are more cost-efficient to the consumer and produced using more responsible means.* This happens first by improving the catalysts available to make chemicals.

Figure 1. Periodic table of the elements. http://0.tqn.com/y/chemistry/1/S/D/d/1/PeriodicTableWallpaper.jpg



This project describes the preparation of new sustainable catalysts to produce chemical products more efficiently and cost-effectively. Specifically, we are interested in exploring the reactivity of iron (Fe) and cobalt (Co) catalysts, where Co and Fe are elements from the periodic table (**Figure 1**). Currently, there is great interest in academia and industry in the rational development of first row transition metal complexes that catalyze reactions traditionally performed by second and third row metals. The first row transition metals, also called base metals, are generally less expensive as they are more abundant in the Earth's crust and more readily mined. For example, iron ($0.07/g) and cobalt ($0.21/g) are substantially cheaper than palladium (Pd) ($30/g), iridium (Ir) ($31/g), and rhodium (Rh) ($37/g), which are traditionally present in catalysts for different reactions. In addition, iron is considered much less toxic and more environmentally benign when compared to other transition metals, making it of interest to pharmaceutical industries, where trace metal contamination is a real concern in the synthesis of drug molecules. However, even though iron and cobalt remain cheaper to use in catalysis, these metals are not widely used in industry. The reason for this is due to a lack of an understanding of how base metal catalysts operate in catalytic reactions. In addition, challenges exist in terms of selectivity and the ability to utilize a large variety of starting materials.

Previous chemistry developed in my group includes the discovery of air- and moisture-tolerant iridium (Ir) catalysts to transform compounds called ketones and aldehydes (carbon-oxygen double bond containing molecules) to alcohols (carbon-oxygen single bond containing molecules, **Scheme 1**).[1,2] This fundamental chemical transformation, taking an aldehyde or ketone to an alcohol, is called a reduction reaction and it involves the addition of hydrogen across the carbon-oxygen double bond of the ketone or aldehyde to yield the reduced product called an alcohol. The overall reduction is



Scheme 1. Transfer hydrogenation catalyzed by Ir.

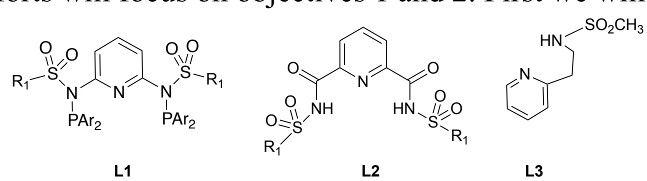
evidenced by reducing the number of bonds between carbon and oxygen. Catalytic reduction reactions are extremely important to the pharmaceutical and fine chemical industry, as the alcohol products, serve as building blocks to drug molecules, fragrances, and other relevant consumer products. In most instances, reduction reactions utilize expensive iridium or rhodium catalysts. Unfortunately, iridium is not abundant in the Earth's crust; it is one of the nine least abundant metals, making it expensive for catalytic chemistry. Thus, if we find alternate cheaper metal catalysts that are more robust, tolerant to air and moisture, and easily synthesized we would be able to significantly advance this field. Therefore, we are proposing to evaluate the synthesis of novel iron and cobalt catalysts attached to similar ligands, where ligand is defined as a small molecule, ion or atom attached to the metal center, that we used with iridium to explore catalytic reduction chemistry (**Scheme 1**). The ligand is identified in green in **Scheme 1**. *The purpose of our work is to develop base metal catalysts for reduction reactions and improve the technologies available for industrially and pharmaceutically relevant transformations. We will approach this by changing the metal in our catalyst from iridium to more abundant and cheaper cobalt and iron.*

Proposed Research

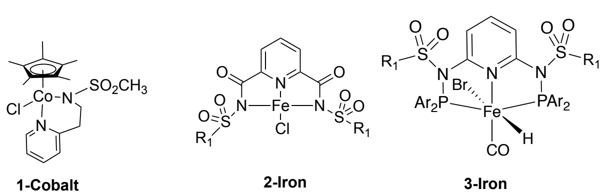
We have **four main objectives** to this work that will be completed during the SOSA period.

1. Prepare and characterize new ligands with similar architectures to those investigated in the iridium catalysts
2. Coordinate the ligands to iron and cobalt and characterize the metal catalysts
3. Develop catalytic methods to investigate the iron and cobalt catalysts in reductions
4. Evaluate mechanism of reduction reaction to improve catalyst design

During year 1 of the funding period, our efforts will focus on objectives 1 and 2. First we will develop a library of ligands **L1-L3** (**Scheme 2**) that are similar in structure to those that we have previously reported (**Scheme 1**). The R1 and Ar groups can be readily modified to tune the properties of the ligand using procedures found in the chemical literature. In my Spring 2017 CHE452 course, we prepared many variants of **L2** and **L3** and developed new procedures to make them. We are using this style of ligand because we know that when they are coordinated to iridium they exhibit reduction catalysis. Thus, we propose a similar finding should be obtained for the iron and cobalt catalysts since they are nearby on the periodic table. Once the ligands are synthesized and characterized, we will move to objective 2 and coordinate the ligands to cobalt and iron. Some catalysts of interest are shown in **Scheme 3**. We will utilize well-known literature methods for ligand complexation to the metal center. During my 2017-2018 year-long sabbatical at Princeton, I am learning the techniques used to synthesize iron and cobalt complexes so that I can bring them back to TCNJ. In order to verify that we have the proposed catalysts we will utilize a suit of techniques for characterization. We will use NMR, IR, and X-ray available at TCNJ to characterize the catalysts. In addition, I will have access to additional instrumentation at Princeton to characterize the catalysts, if necessary, due to collaborations I am making while on sabbatical. At the end of year 1 of the funding period, I will summarize our findings and begin to identify plausible catalytic conditions.



Scheme 2. Ligand library.



Scheme 3. Iron and cobalt catalysts.

During year 2, our primary focus will be on catalyst optimization and substrate screening. I will conduct these studies in collaboration with my research students. Specifically, we will optimize the catalyst amount, solvent, reaction time, and need for additive. Once suitable conditions are identified, the substrate scope will be expanded to see the tolerance of our catalysts. Most recently we have started a collaboration with Professor Dan Mindiola at UPenn. We will utilize the high throughput catalysis screening facility located at Penn to aid in speedy catalyst optimization. My lab will also concomitantly study the mechanism of the reductions using our new cobalt and iron catalysts to identify plausible intermediates to improve catalyst design.

I plan to utilize the 3FWH release in the spring semesters which will allow me to interpret the collected data during the fall semesters and write up the findings in two manuscripts. I will also utilize student collaborators to help conduct the experiments proposed in this project to complete the work within a two-year period. In addition, I will present the results obtained in collaboration with my students at chemistry-based meetings, typically held in the spring. The results obtained during year 1 will be used as the basis of an external grant to the National Science Foundation (NSF).

Year 1: Fall 2018-Spring 2019	Year 2: Fall 2019-Spring 2020
Synthesize ligands, coordinate to Co & Fe, develop catalysis Spring 2019: present results at a chemistry meeting, write up experimental section	Optimize catalytic conditions for reduction reactions Fall 2019: Write proposal to NSF Spring 2020: present results at a chemistry meeting, complete and submit manuscript(s)

Expected Outcomes, Global Significance, and Dissemination of Results

The execution of research in catalytic chemistry is aimed at developing efficient methodology that could replace environmentally unfriendly practices, as a strategy toward the effective and sustainable preparation of chemicals. *The research that I will conduct during this SOSA period is of broad interest to the community, as it provides a sustainable means using base metal catalysts to produce chemicals traditionally prepared using less sustainable, more toxic, and expensive catalysts.* This work will allow me to engage in a complementary area of research and incorporate new tools and techniques that I learned while on my sabbatical. The transformative results to be obtained through my research plan will significantly add to the general chemical literature. This research will be published in impactful peer-reviewed journals, presented at local and national meetings, and support a grant application, where the broader community will evaluate the science.

Teaching and mentoring students to conduct experiments advances discovery while positively impacting students' education. Another initiative of mine is to provide students with a unique learning experience and to have them contribute to the scientific community through the preparation, characterization, and catalytic studies of organometallic catalysts. Students will also present results at campus functions, group meetings, and chemical society meetings. Research in my group will enable students to correlate material learned in chemistry classes and labs with novel, hands-on experimentation, while moving my research agenda forward. I plan to continue to incorporate my research projects into the classroom to provide *all* students with a unique research experience. These skills are important for all students to learn and they enable the preparation of the next generation of scientists for meaningful chemistry-based careers.

Dissemination of Results

• Students and I will present research results at local meetings and at national American Chemical Society meetings in spring 2019 and 2020. I will present at a high-profile conference in 2020.
• Results will support the submission of a grant to the National Science Foundation in fall 2019.
• Manuscripts will be prepared for submission to *Organometallics* and *ACS Catalysis*.

References

1. Townsend, T.; Kirby, C.; Ruff, A.; O'Connor, A. R. *J. Organomet. Chem.* **2017**, *843*, 7-13
2. Ruff, A.; Kirby, C.; Chan, B. C.; O'Connor, A. R. *Organometallics* **2016**, *35*, 327-335.