Communicating Research to the General Public

At the March 5, 2010 UW-Madison Chemistry Department Colloquium, Prof. Bassam Z. Shakhashiri, the director of the Wisconsin Initiative for Science Literacy (WISL), encouraged all UW-Madison chemistry Ph.D. candidates to include a chapter in their Ph.D. thesis communicating their research to non-specialists. The goal is to explain the candidate's scholarly research and its significance to a wider audience that includes family members, friends, civic groups, newspaper reporters, program officers at appropriate funding agencies, state legislators, and members of the U.S. Congress.

Nearly 100 Ph.D. degree recipients have successfully completed their theses and included such a chapter.

WISL encourages the inclusion of such chapters in all Ph.D. theses everywhere through the cooperation of Ph.D. candidates and their mentors. WISL is now offering additional awards of $250 for UW-Madison Ph.D. candidates in the sciences.

Wisconsin Initiative for Science Literacy

The dual mission of the Wisconsin Initiative for Science Literacy is to promote literacy in science, mathematics and technology among the general public and to attract future generations to careers in research, teaching and public service.

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An Exploration of the Redox Behavior and Higher Oxidation States of

Diruthenium Paddlewheel Complexes

by

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Chapter 1

Wisconsin Initiative for Science Literacy: Introduction for a General Audience

I often struggle to describe my thesis work to friends and family outside of chemistry. It feels very esoteric, and I often joke that I would need a weeklong lecture series to make sense of it all. Fortunately, that is not actually the case, and my research over the past several years can be described by considering a few key concepts I employ on a regular basis. I'll start this chapter off with a brief overview of my research goals, and then illustrate how the concepts of reaction intermediates, coordination compounds, and analytical methods explain what it is that I've done over the last five years.

The overarching goal of my work has been to prepare and study a diruthenium oxo compound. We'll build up to what this means over the course of this chapter, but suffice it to say that it has been a challenging project. In fact, the project is ongoing; it started with researchers before me and will continue after I graduate. In order to make progress toward this goal, I have repeatedly broken it down into smaller, simpler steps that I can accomplish to make incremental progress toward my ultimate goal.

The reason I was tasked with studying diruthenium oxo (pronounced "ox-oh ") compounds, and the reason I still find them so interesting after five years, is because they are unproven reaction intermediates. We'll talk about reaction intermediates shortly, but the "unproven" part is really important: researchers have repeatedly *proposed* diruthenium oxo compounds, but there is almost no published *evidence* to support their existence. This is what I have been working to resolve over the course of my thesis work.

1.1 Reaction intermediates.

At some point in your life, whether you remember it or not, you have surely seen a chemical equation. Chemical equations are fundamental tools for chemists and other scientists to describe a chemical reaction. On one side of an arrow, we list the starting chemicals, or reactants. On the other side of the arrow, we list all of the chemicals produced by the reaction, or products. Sometimes, we put annotations above or below the arrow to indicate some of the conditions under which the reaction took place. Scheme 1.1 lists several common chemical reactions that you may have encountered.

A) $2H_2 + O_2 \longrightarrow 2H_2O$

B) $2H_2O_2 \longrightarrow 2H_2O + O_2$

C) $C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O$

Scheme 1.1. Everyday chemical reactions. A) The reaction of hydrogen (H_2) and oxygen (O_2) to make water. This reaction can be done by igniting hydrogen in the presence of oxygen, or in a hydrogen fuel cell to generate electricity without making carbon dioxide. B) The decomposition of hydrogen peroxide (H_2O_2) into water (H_2O) and oxygen (O_2), which explains why bottles of hydrogen peroxide from the drug store have an expiration date. This reaction is harnessed in classic science demonstrations like "elephant toothpaste." C) Reaction of glucose ($C_6H_{12}O_6$) and oxygen (O_2) to produce carbon dioxide (CO_2) and water (H_2O). Your body is doing this right now to turn food into energy.

What a chemical equation doesn't tell you about a chemical reaction, however, is *how* it takes place. Consider the last reaction from Scheme 1.1: the combustion of glucose. If you take a sample of glucose, a white powder, and leave it in air, which is about 21% oxygen, nothing happens. But if you sprinkle that glucose into a flame, it burns, rapidly reacting with oxygen to form carbon dioxide and water. In your body, however, glucose undergoes the same *net* reaction - reacting with 6 molecules of oxygen to produce carbon dioxide, which you exhale, and water. Clearly, though, you don't have a combustion engine inside of your body. The reaction *mechanism*, or series of individual steps along the way from reactants to products, is different. When I took biology in high school, I was forced to memorize the Krebs cycle, also known as the citric acid cycle. The Krebs cycle is just one part of the mechanism by which your body converts glucose into carbon dioxide and water, and it involves several *intermediates*, or chemicals derived from the reagents that are not yet the products, as well as several other molecules, including enzymes, which act as *catalysts* to facilitate the reaction (remember, glucose and oxygen at room temperature don't do anything on their own).

When we study a chemical reaction mechanism and the intermediates involved, we learn far more than we could from just studying the reactants and products. Different mechanisms for metabolizing glucose explain why yeast can generate alcohol when fermenting for bread or beer, but you don't become inebriated when you work out. As chemists, we seek to understand reaction mechanisms both as a fundamental pillar of knowledge, and for the practical benefits that come from such knowledge. If we know how a reaction works, perhaps we can apply that mechanism to a different set of reactants, generating new products. This is routinely done in pharmaceutical work to design and prepare new potential drugs. I also mentioned catalysts earlier, which are molecules that facilitate a chemical reaction, but are not used up in the process. Think of slicing tomatoes in your kitchen: the whole tomato is the reactant, the slices are the products, and the knife is the catalyst that makes the process happen. A huge aspect of chemistry is discovering and studying new catalysts so that we can control chemical reactions.

Often, a catalyst molecule will temporarily react with a reactant, forming an intermediate that undergoes further chemical transformations to form the product while giving back the catalyst. The diruthenium oxo compounds that I mentioned earlier are proposed intermediates in a variety of chemical reactions, often as catalytic intermediates (those intermediates formed by a catalyst).

If we can verify that diruthenium oxo compounds are indeed intermediates in these reactions, or if we can disprove that, we will significantly advance our understanding of these reaction mechanisms. With that knowledge, we can work to design new catalysts or establish new mechanisms for preparing valuable products, such as those relevant for pharmaceuticals or renewable energy. Given that the study of a single type of reaction intermediate is the focus of my entire PhD work, you might guess that it isn't as straightforward as it may seem on paper. Studying highly reactive compounds requires creativity, hard work, and a wide variety of analytical techniques. We'll learn about some of the techniques I use in my research in section 1.3.

1.2 Coordination compounds.

Chemists organize compounds into several different categories. Coordination compounds make up a diverse subset of molecules (discrete collections of atoms that can be written down with a formula like those in Scheme 1.1) that also contain individual metal atoms. The portions of the molecule that bind to the metal atoms are known as ligands. This motif is how you have iron in your blood; it's not little flecks of iron metal, but individual atoms incorporated as part of hemoglobin protein molecules. Most frequently, coordination compounds contain a single transition metal atom (transition metals are the ones in the big middle chunk of the periodic table, Figure 1.1).

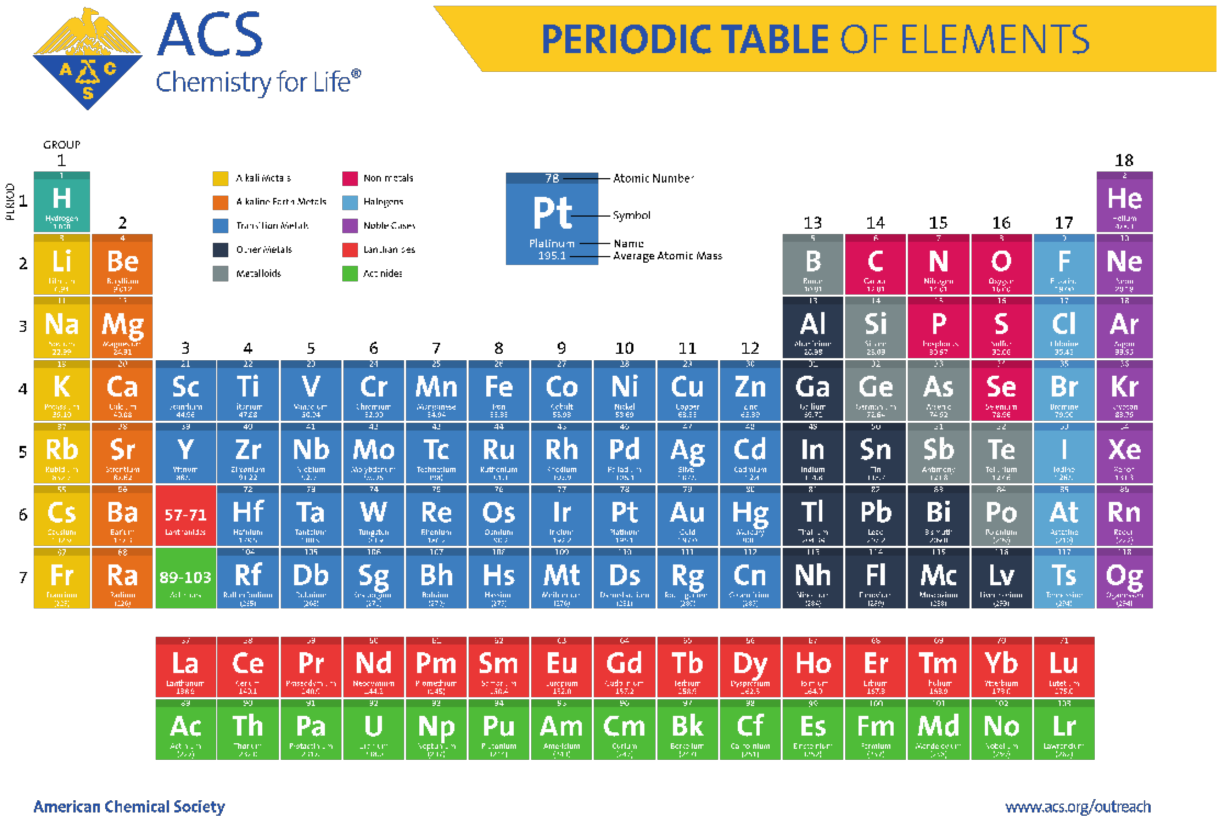

Figure 1.1 *The periodic table of the elements, with transition metals in dark blue. Ruthenium, the transition metal I work with, is right in the middle, in group 8, period 5. Image from the American Chemical Society, https://www.acs.org/content/acs/en/education/whatischemistry/periodictable.html accessed Nov. 23, 2011.*

The presence of a metal imparts all sorts of interesting properties on coordination compounds, and the wide variety of metals available for making coordination compounds means that this field of chemistry has an incredible list of applications in addition to the wide variety of naturally occurring coordination compounds in biology. Cisplatin, a common chemotherapy medication, is a simple coordination compound containing platinum (group 10, period 6); many extraction processes for refining metals from ores rely on the formation of coordination compounds of those metals; and a whole host of coordination compounds are employed as catalysts to facilitate all manners of chemical reactions, from drug synthesis to plastic manufacturing.

With this definition, we can now break down what I mean when I say that I study diruthenium oxo compounds. Starting with diruthenium, this simply means two ruthenium atoms are present in the molecule. Oxo refers to oxygen, and more specifically describes an oxygen atom bound to a metal atom and nothing else. Beyond two ruthenium atoms and an oxygen atom, the compounds I study are commonly known as paddlewheel complexes due to the general shape: the two ruthenium atoms are bound together like an axle, and there are four ligands arranged like the fins of a paddleboat's paddlewheel. You can see this in Figure 1.2. With the particular ligands I use, only one side of the diruthenium axis is available to bind to another element. When the X, which is used to indicate a variety of possible ligands, is an oxygen atom, we have a diruthenium oxo paddlewheel complex.

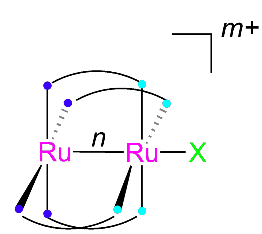

Figure 1.2 *Schematic drawing of a diruthenium paddlewheel complex. Imagine the axle through the Ru–Ru–X axis. The connected blue dots represent the bridging ligands, which look like the fans of a paddlewheel. My work in this thesis involves changing the charge of the complex (m^+), the Ru–Ru bond order (n), as well as the identity of the ligands, both X, the axial ligand, and the blue dots, which represent the equatorial ligands.*

1.3 Techniques I use in my research.

Trying to prepare and study reactive intermediates can be extremely difficult. Since the goal is to study something reactive, the trick is to keep it from reacting long enough to study it. While many of the compounds that I have synthesized are indefinitely stable, many others are unstable, decomposing in minutes even when chilled with dry ice to –78 °C. Over the course of my studies, I have had the opportunity to learn and use a wide variety of fascinating instruments and techniques, and I would like to share a few of my favorites here.

Single-Crystal X-Ray Diffraction. I hope you are familiar with Rosalind Franklin, who was an X-ray crystallographer involved in determining the structure of DNA. In the time since Franklin's work, X-ray crystallography has come a long way. Today, analysis of the diffraction pattern of X-rays from a small crystal, often less than 1 mm in any dimension, provides enough information to determine the identity of and distance between each atom in a molecule. To achieve this, crystals must be carefully grown in the lab; the large crystals of minerals that may come to mind are actually made up of many crystals in different orientations, all growing into each other. Once high-quality single-crystals are obtained, they can be mounted inside an X-ray diffractometer. After the diffractometer is closed, the crystal is exposed to a tightly focused beam of X-ray irradiation and a digital detector records the intensity and location of diffracted X-rays around the crystal. Computer software then allows us to model this diffraction pattern, determining the identity and arrangement of the atoms that make up the crystal. The instruments available in the Department of Chemistry at UW-Madison are able to achieve length measurements of chemical bonds, which are often 1-2 Å (Å is the symbol for angstrom, a unit of distance equal to 10^{-10} m, or one ten-billionth of a meter), with a precision greater than 0.01 Å, or 0.000000000001 m. While this technique is excellent for many compounds, some of my research compounds are too reactive to grow crystals suitable for X-ray diffraction.

Electron Paramagnetic Resonance (EPR) Spectroscopy. It may surprise you to learn that individual electrons behave like little tiny bar magnets. While the explanation for this behavior is quantum mechanical in nature, the result is pretty straightforward: an individual electron acts like an exceedingly small yet powerful magnet. In most molecules, though, there is an even number of electrons and they pair up so that each electron cancels out the magnetic field of its partner electron. With coordination compounds, however, the metal atom can support one or more unpaired electrons, giving the compound magnetic behavior, known as paramagnetism. In EPR spectroscopy, we exploit these unpaired electrons by placing a paramagnetic sample in a strong magnetic field. We can then expose the sample to microwave radiation (the same as your kitchen microwave, Wi-Fi, or 5G cellular). This can cause the electron's magnetic field to flip between being aligned with the strong applied field to being aligned against it. By measuring the strength of the applied magnetic field and the frequency where the electron flips, we can learn about the number of unpaired electrons as well as the shape and distribution of the paramagnetic compound's magnetic field. Many compounds have very low sensitivity for EPR, so we run the experiments at very low temperatures (around 10 K, or –263 °C / –442 °F). This is also beneficial for extremely reactive compounds, as the low temperature prevents decomposition. Therefore, this technique is suitable for many paramagnetic compounds, whether they are stable or not.

SQUID Magnetometry.

Another technique for measuring paramagnetic compounds is SQUID magnetometry. SQUID is an acronym standing for Superconducting QUantum Interference Device, which ultimately just means that the device uses very low temperature (around 4 K, –269 °C, –452 °F) superconducting components to detect the magnetic field of paramagnetic materials. A typical SQUID magnetometer is designed to operate over a wide temperature range, cooling the sample from room temperature down all the way to 2 K, just a few degrees above absolute zero. (Absolute zero is the lowest possible temperature, –459.67 °F. At absolute zero, there is no heat energy left in a material.) By measuring the magnetic properties of a sample over a wide range of temperatures and in different strengths of magnetic fields applied by the magnetometer, we can gain insight into the nature of the unpaired electrons in the compound. The biggest drawback to SQUID magnetometry, however, is that it measures the average of the entire sample, so you need a very pure sample. This makes it very difficult to collect data for reactive compounds, which may decompose as you attempt to purify them.

Since I have mentioned two methods for studying magnetism, it is important to discuss why we need multiple techniques for this. EPR generally works for coordination compounds only if they have an odd number of unpaired electrons, while SQUID magnetometry works for any number of unpaired electrons. As I mentioned above, however, EPR is more suitable for highly reactive compounds where you cannot isolate a large, pure sample for SQUID. Moreover, the specific information you can obtain from each technique is a bit different. SQUID is particularly effective for measuring properties such as coupling (when different magnetic systems, either in different parts of a molecule or between neighboring molecules interact) and zero-field splitting (a particular favorite of mine where multiple magnetic states have different energies due to the quirks of how unpaired electrons interact with each other quantum mechanically). EPR, on the other hand, can give very precise measurements of how strongly the unpaired electrons interact with a magnetic field. This is measured with a *g*-value, and how it differs from 2.0 (the value for a free electron, or an electron that is not a part of a molecule) can tell us a lot about the arrangement of all the electrons in the molecule. SQUID magnetometry can provide estimates of *g*-values, and

EPR can give approximate measures of coupling and zero-field splitting, but when possible, collecting both types of measurements allows for the most accurate description of what is going on with a compound's unpaired electrons.

1.4 What comes next?

Over the last five years, I have learned a wide variety of synthetic (making things), analytical (studying the things that I made), and computational (using computer models to predict measurable properties) techniques in order to address a highly specific question: are diruthenium oxo compounds actually the reactive intermediates in the reactions where they are predicted to be? While I don't have a definitive answer to this question, I have made significant advances in our understanding of this class of compound. However, it is time for me to hand that question to other researchers, as I will be taking the skills and knowledge I've accumulated at UW-Madison to Georgia Tech, where I will be working as a postdoctoral researcher for Prof. La Pierre. I will apply what I know to a new class of compounds: coordination compounds containing f-block metals (the f-block consists of the lanthanides and actinides and is often drawn below the rest of the table, Figure 1.1.). F-block coordination compounds can have fascinating magnetic and electronic properties, and I look forward to diving deep into the subject while also mentoring the PhD students who will soon be writing theses of their own.