

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.

Over 20 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 chemistry Ph.D. candidates.



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.

UW-Madison Department of Chemistry
1101 University Avenue
Madison, WI 53706-1396
Contact: Prof. Bassam Z. Shakhashiri
bassam@chem.wisc.edu
www.scifun.org

May 2014

Bimetallic Reactive Intermediates Containing Late Transition Metals

by

Amanda R. Corcos

A dissertation submitted in partial fulfillment of
the requirements for the degree of

Doctor of Philosophy

(Chemistry)

at the

University of Wisconsin–Madison

2016

Date of final oral examination: March 3, 2016.

Final Oral Committee:

John F. Berry, Professor, Chemistry

Thomas C. Brunold, Professor, Chemistry

Clark R. Landis, Professor, Chemistry

Jennifer M. Schomaker, Associate Professor, Chemistry

Shannon S. Stahl, Professor, Chemistry

Chapter 1

Wisconsin Initiative for Science Literacy: Introduction for a General Audience.

1.1 Chemistry.

You may have taken a general chemistry class in high school or even college. What are some of the things you remember? Perhaps using a Bunsen burner or a hot plate? Watching a reaction change color? One of the things I best remember was when my high school chemistry teacher splashed three clear, colorless liquids on a blackboard and asked us to identify them. The acetone quickly evaporated, the ethanol caught fire when lit with a match, and the water did neither of these things. I was interested and excited that we could differentiate seemingly identical compounds based on their physical properties. This is the very essence of chemistry, of studying the properties and composition of different compounds and correlating them to physical and electronic structure. Chemistry is used to describe the world around us, and it often acts as a “bridge” between the natural sciences, including biology and physics.¹

1.2 Inorganic Chemistry.

There are many subdivisions of chemistry, and maybe you know of some: organic chemistry, theoretical chemistry, nuclear chemistry, biochemistry, and inorganic chemistry, to name a few. Many people are familiar with organic chemistry, as it is a required course to attend medical school and is often associated with the pharmaceutical industry, which designs and prepares drugs to treat disease. If you have not heard of organic chemistry, you most certainly have interacted with organic matter, like medicine and food. The term “inorganic”, if you look at

its etymology, should then describe any and all things that are not organic. Inorganic chemistry is most often associated with the materials we use in technology, like batteries, cell phones, and cars – things that are not “natural” but are “man-made”. This, however, is misleading. Salt, sand, minerals, gemstones, gas, and water are all “natural” and are not organic – they are inorganic!

Many inorganic complexes contain a metal, and these are most often a transition metal. The transition metals occupy a significant amount of space on the periodic table (Figure 1.1). You may have heard of some of these transition metals, like iron or zinc, as they are biologically important – iron is in your blood and zinc is an antioxidant that helps your immune system. There is also a wide range in the number of transition metal atoms that we can use at any one time. For example, an inorganic complex may consist of a single titanium atom supported by many ligands (described in the next section), or it can consist of a surface of thousands of titanium atoms bound together with only oxygen atoms. There are also many more options, including using multiple different metals.

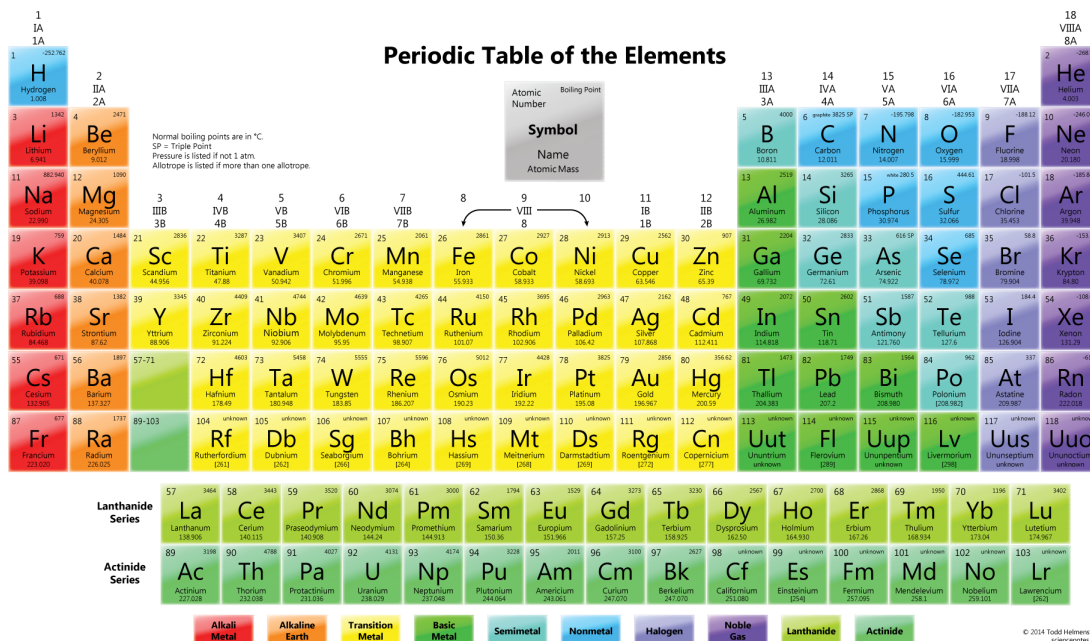


Figure 1.1 Periodic table of the elements.² Transition metals are yellow.

1.3 Design and Synthesis of New Compounds.

In the laboratory we use an assortment of metals depending on the goal we are trying to achieve. We can also “customize” them for our specific purpose by altering their oxidation state and the ligands that support them. The oxidation state of a metal indicates how many electrons it has, and it represents the number of electrons that metal can still gain or lose. Ligands are ions or molecules that bind to the metal center. They are usually made of carbon and hydrogen atoms, and can often include nitrogen, oxygen, and other atoms. A ligand is like the skeleton of a building: it is part of the framework that supports the larger structure and affects its design, use, and utility. For example, Figure 1.2 shows multiple test tubes, each filled with a colored solution. Each solution contains ruthenium: the color difference is due to the different supporting ligands and subsequent oxidation state of each metal center.

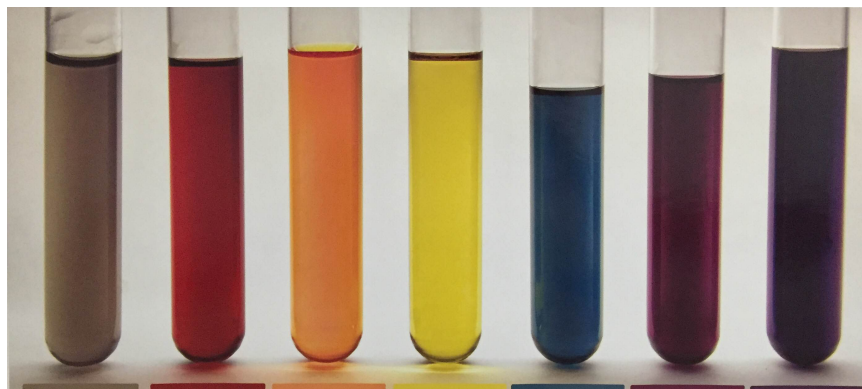


Figure 1.2 Photograph of different ruthenium complexes in solution. The color of any metal-based complex can change based on the metal’s oxidation state and its supporting ligands.

Designing and synthesizing a new compound in the lab is very much like buying a new car. There are many important questions to ask, including but not limited to: Why are you buying a new car? What were the limitations of the previous car? Were there any positive aspects of your old car you would like the new one to have? Is a car commercially available or do you need

to custom order it? And, significantly, how much is a new car going to *cost*? All of these questions must also be asked and answered when designing a new compound, which I have had the opportunity to do many times in my research project. Most often I use the same metal, but I change the number and type of ligands that support it.

There are many different ways to synthesize compounds, and the method I use to make them depends on their properties. Sometimes we can simply dissolve two reagents in solution and stir them together to form a new complex. Other times we are required to heat the reaction to form the new complex. If a complex is air- or water-sensitive, then we prepare and store them in an oxygen-free, dry environment like a glovebox. Many of the compounds I study are extremely sensitive to oxygen and water, and some are also temperature-sensitive! Storing these samples requires liquid nitrogen, which, at 77 K (-196 °C or -321 °F), freezes or suspends the samples so they no longer react or decompose on their own.

1.4 Spectroscopy.

After we design and synthesize a new compound, we need to prove that we did in fact generate the intended complex. If we do not confirm the identity of the complex, if we assume it to be “A” but it is really “X”, then we will misinterpret all of the resulting data and mis-assign the properties of the complex. It is a little bit like the old prank where someone replaces the salt in a salt-shaker with sugar: both white powders look the same, but if you use sugar to flavor your food instead of the intended salt, then the food will taste will terrible. So how can you tell the difference between the white powder of sugar and salt? You can taste it – you know that salt is bitter and sugar is sweet, so whichever flavor you taste will tell you what the powder is. Tasting complexes, however, is NOT an option in the laboratory. I repeat: DO NOT TASTE reagents in

the lab!! The vast majority of chemicals we work with are highly toxic and therefore poisonous, if not also carcinogenic. How, then, do we tell compounds apart? How to do we study their properties? We can observe how the compound interacts with electromagnetic radiation. This is called spectroscopy, and it is critical to use multiple different methods of spectroscopy to investigate new compounds.

Some of the most common methods of spectroscopy include nuclear magnetic resonance (NMR), electron paramagnetic resonance (EPR), infrared (IR), resonance Raman, and ultra violet and visible absorption (UV-Vis), and X-ray crystallography (XRD). NMR is extremely powerful, for it provides information about the connectivity of atoms by using radio frequencies to excite specific nuclei. One of the limitations of NMR is that the molecules under study, for the most part, need to be diamagnetic, meaning that they must have an even, paired number of electrons. EPR is similar to NMR, but it is used to investigate paramagnetic complexes, which are species with unpaired electrons. IR and resonance Raman provide information about the vibrational stretches and connectivity of atoms. XRD utilizes X-ray beams that are then diffracted by the atoms in the complex under study. It is one of the most powerful techniques, for with it we can attain a 3-D image of the molecule and determine the bond lengths, angles, and charge of the complex. XRD is limited in scope, however, for it can only be used with single crystals – powders and liquids cannot be studied – and it only provides information about that one crystal, not the bulk sample of material. It is important to recognize that each technique has its strengths and weakness, and only after using multiple techniques can we get a more-complete picture of the molecules under study.

1.5 Overview of My Thesis Work.

So far I have given you a few clues about my research: I modify the oxidation state and supporting ligands on inorganic compounds which are often air-, water-, and temperature sensitive, and I use some very specific spectroscopies to investigate and characterize them. Let's get into the nitty-gritty now.

While I worked on many projects, the vast majority of my research centered on studying discrete complexes that had a metal-metal bond and a metal-ligand multiple bond (Figure 1.3). These types of complexes have been identified as reactive intermediates in catalytic cycles to make new bonds with carbon, nitrogen, and oxygen. Why do we care about a reactive intermediate? We care because, for a long time, the relevant species were only postulated – there was no proof. If we can characterize these species and show that they are mechanistically relevant to catalysis, then we can better optimize the catalytic cycle to be more efficient, cost-effective, and potentially broaden the applicability of the cycle.

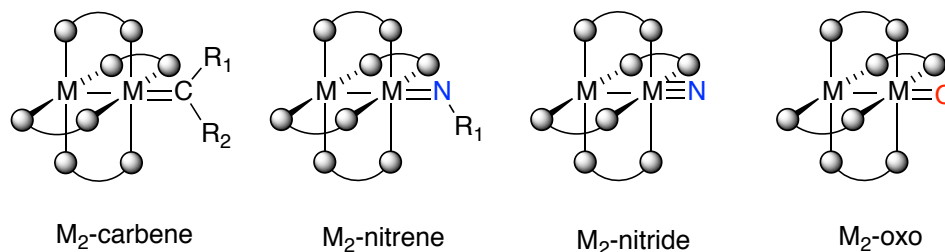


Figure 1.3 Proposed bimetallic complexes with a metal-metal, metal-ligand multiple bond.

The specific systems I studied use two ruthenium atoms bound to one another and supported by four equatorial ligands which form a paddlewheel-type structure (Figure 1.4). The two equatorial ligands I used are named “chp” and “ap”, and they both bind to the Ru_2 core in a (4,0) geometry. This means that, for chp, all of the O atoms of the ligand bind to one ruthenium

atom while all of the N atoms bind to the other ruthenium. The ap ligand has two nitrogen atoms which can bind to the ruthenium core, but they have different properties: one nitrogen atom is in a ring while the other is not. Here, all of the N atoms of the ring bind to one ruthenium atom, while the N atom not in the ring binds to the other. By using these ligands I can block one end of the ruthenium unit while leaving the other end free and available to form the metal-ligand bond mentioned previously.

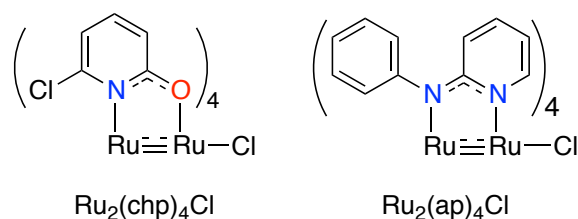


Figure 1.4 Drawings of diruthenium complexes with equatorially-bound chp and ap ligands.

After synthesizing these complexes I can then systematically change the axial ligand to be a nitride “N” atom or oxo “O” atom precursor, like azide or nitrate, respectively, or I can switch to have an ion that does not bind to the diruthenium core. I can then either expose these complexes to light to break specific bonds, or I can use a chemical oxidant that will transfer a single atom to the available diruthenium axial site. For example, Figure 1.5 shows a diruthenium azide complex I made from a chloride precursor ($\text{Ru}_2(\text{chp})_4\text{Cl}$) from Figure 1.4), and after I expose it to light in a frozen matrix, then the N=N bond breaks and I am left with (and can investigate!) the diruthenium nitride species, which now has a metal-metal bond and a metal-ligand multiple bond.

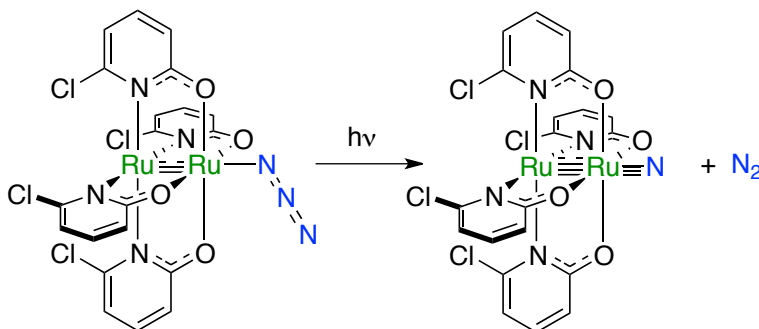


Figure 1.5 Formation of diruthenium nitride from diruthenium azide.

Once generated, these complexes (with a metal-metal bond and a metal-ligand bond) are extremely reactive. Remember when I said I have to store some of them in liquid nitrogen? If I warm these complexes even to $-78\text{ }^{\circ}\text{C}$ (from being frozen at $-196\text{ }^{\circ}\text{C}$) then they react and can no longer be studied. And this helps explain the limited number of spectroscopies I can use to probe and characterize these sensitive materials, for some spectroscopies are solution-phase measurements (UV-Vis), some require solid-state crystalline materials (XRD), and some require diamagnetic materials (NMR). The reactive intermediates I study do not meet any of these requirements, so I often use EPR, resonance Raman, and I collaborate with scientists who have access to other non-standard spectroscopies that are housed at national labs. Thank you, government funding (especially the National Science Foundation and Department of Energy) !

I hope that I've shown you that chemistry, and inorganic chemistry in particular, is exciting, accessible, and relevant. Thank you for reading!

References.

- (1) Brown, T. L.; Lemay, H. E.; Bursten, B. E.; Lemay, H. *Chemistry: The Central Science*. Prentice Hall. 8th ed. 2000.
- (2) <http://sciencenotes.org/printable-periodic-table/>