

Communicating Research to the General Public

At the March 5, 2010 UW-Madison Chemistry Department Colloquium, the director of the Wisconsin Initiative for Science Literacy (WISL) encouraged all Ph.D. chemistry 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, state legislators, and members of the U.S. Congress.

Ten Ph.D. degree recipients have successfully completed their theses and included such a chapter, less than a year after the program was first announced; each was awarded \$500.

WISL will continue to encourage Ph.D. chemistry students to share the joy of their discoveries with non-specialists and also will assist in the public dissemination of these scholarly contributions. WISL is now seeking funding for additional awards.



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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**New Diruthenium Nitrido Compounds
and Intra- and Intermolecular Reactivity with Aryl C–H Bonds**

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CHAPTER 1.

WISCONSIN INITIATIVE FOR SCIENCE LITERACY: INTRODUCTION FOR A GENERAL AUDIENCE.

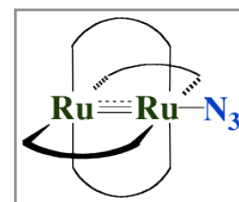
1.1. Chemistry in Everyday Life. Every moment of every day, from the food we eat to the air we breathe, from bioaccumulation on our teeth to the toothpaste we use to remove it, from the bacteria that make us sick to the pharmaceuticals and nutrients that help us return our bodies to a healthier state: Chemistry is an indisputable and mammoth presence in our lives! For the ability to produce improved food products, control contaminants in our environment, understand our bodies as biological systems, and provide ingredients for healthier living, we all owe a debt of gratitude to chemistry and the art of chemical transformations.

Chemical transformations, or reactions, involve a change in substances involved, and a change in energy. If a substantial energy contribution is required for a certain reaction to occur, that reaction is much less likely to progress as desired. One of the common goals of chemists is to understand the energetic change involved in reactions and to find ways of lowering the energy necessary for desirable reactions to proceed. Take for example any of the modern pharmaceuticals in your medicine cabinet: Years of chemical research optimizing the synthesis of the active ingredient occurred prior to any testing or trials, and this optimization was a relentless search for the easiest way to produce the desired ingredient while minimizing the costs of time, money, and overall energy.

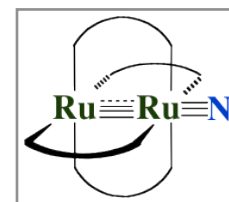
1.2. A Little Aid Goes a Long Way. In our everyday lives, employing an assistant tends to decrease the amount of energy we need we expend... if we choose our help wisely. Chemical reactions can function in much the same way: introducing a good assistant, or a catalyst, can help the reaction proceed more quickly and efficiently than if the catalyst was not present. Sometimes

new and better results are achieved with assistance, just like new and more efficient reactions can sometimes proceed in the presence of this aid. In many cases, catalysts in chemical reactions simply consist of a new place for a transfer of atoms and/or electrons to take place, such as a metal center.

1.3. Metal Centers as Reaction Sites. The chemistry presented in this work focuses on a special kind of metal center where chemical reactions can take place. We have two positively charged ruthenium (Ru) metal ions bound to each other surrounded by four ligands, or organic carbon-based groups of atoms, with electrons that can be used to hold the metal atoms in place in a four-fold paddlewheel shape. On either end of the axis of this paddlewheel, much like on a rotating axle, there can be an exposed ruthenium “hub cap” where a chemical transformation, or reaction, might occur. We will explore reactions where a chloride ion (Cl⁻) on one of these ruthenium centers is exchanged with a negatively-charged azide ion, N₃⁻.



1.4. Energetically-Favorable N₂ Loss. Once the azide is bound to the ruthenium center, interesting chemistry can occur. Much like the azide compounds present in automobile air bags, when a little energy is added, N₂ or nitrogen gas (the same as what comprises ~78% of the air we breathe) is very rapidly released. The stability of the triply-bonded N₂ molecule results in this particular product being very favorable from an energetic standpoint. In the case of our diruthenium azide compounds, when even a small energy is added by way of heat or light, N₂ can be released leaving behind the diruthenium paddlewheel with one nitrogen atom remaining attached that can form a triple bond to the Ru atom. Depending upon what ligands are bridging



between the two ruthenium centers, they might be pulling electrons out and away from the Ru–Ru≡N axis to result in a reactive and electron-seeking nitrogen atom, now called a nitride, making that N atom less likely to stay bound exclusively to that ruthenium center and more likely to interact (or react) with something else, and maybe transfer to another separate atom or molecule entirely. Conversely, if the bridging ligands are pushing electron density *into* the Ru–Ru≡N axis, the N atom is not as desperate to seek out other sources of electrons and may not transfer away from the ruthenium core as readily. Understanding how we might tune the reactivity of these nitrides has led to interesting results in our studies.

1.5. Desperate Reactions. In this dissertation, we first explore rather reactive Ru–Ru≡N compounds, where the N atom is fairly loosely bound and reacts readily with the closest source of electrons it can find: a carbon-hydrogen bond attached to the bridging ligand, even when the closest C–H bond is not the best source of electrons. In the presence of solvents and other molecules, the nitride selectively reacts with the ligand C–H bond, forming a new carbon-nitrogen bond. This reactivity is introduced in Chapter 3 and explored in much greater depth, invoking computational models and analysis, in Chapter 4.

Although the intramolecular reactivity of these nitrides is very interesting, the reaction is not reversible once the N atom inserts into the C–H bond to form the amine. One of the goals of adding a catalyst to facilitate a reaction is to only have to add a very small amount, as opposed to adding more and more of that which should make the reaction proceed easier. At some point, the costs will outweigh the benefits of the reaction and the assistant will no longer be effective. And so, as chemists seeking long lasting assistance and minimal costs, we would like to introduce a reaction center in which a chemical transformation occurs, after which the original conditions

would be reset so that the transformation can occur again. In our system, this would require that the N_3^- anion coordinate to the Ru–Ru axis, N_2 be extruded to leave behind the Ru–Ru \equiv N compound, the N atom react with a bond in such a way that it abandons the ruthenium center entirely so that the next N_3^- anion can coordinate to the recently vacated axis and the cycle can continue. This describes a manner in which our Ru–Ru paddlewheel species could become involved in catalytic amination of a substrate.

1.6. Harnessing Reactivity. Two primary methods were explored to encourage intermolecular reactivity in our diruthenium nitride systems: Eliminating the proximal C–H bonds of the ligands into which the nitride could insert, and also physically blocking one of the two ruthenium active sites to prevent intermolecular aggregation of the diruthenium azide molecules. This is discussed further in Chapter 6 of this work. We employ the ligand, 2-chloro-6-hydroxypyridinate (“chp”), which accomplishes both of these methods at once as the azide compound formed (1) has no bonds proximal to the nitride and so intramolecular insertion reaction pathways are shut down, and (2) has one of the two ruthenium centers completely blocked by steric crowding of chloride arms on each of the four ligands, keeping the diruthenium nitride molecules from interacting with one another. As a result, if the nitride were successfully formed with this compound, the N atom would either be forced to react with a secondary compound, or would not be sufficiently reactive and could possibly be isolated as a nitride species. Either of these results would be considered very interesting.

Ultimately, we have found that this diruthenium azide species bridged with four chp ligands could be excited by heat or light in a solution of benzene resulting in the insertion of the N atom into a benzene C–H bond, producing isolable aniline, discussed further in Chapter 5 of

this work. This $\text{Ru}_2(\text{chp})_4\text{N}_3$ -based aniline synthesis provides great insight into manipulation of nitrido compounds, into the utility of axial coordination of a secondary ruthenium center, as well as a foundation for catalytic studies further expanding the utility and effect of this specific twig on its branch of the chemistry tree.

I have found over the years that explaining my work to a non-scientific audience, which happens to be the composition of 99.99% of the population at large, is one of the more challenging aspects of my daily life as a chemist. This becomes even more startling when one considers that I have a great deal more experience than the average chemist when it comes to explanations as a direct result from my immersion in the teaching culture and study of pedagogy and most recently andragogy as they relate to the learning processes involved in chemistry. This ability to decompose research, or any technical topic, into its most critical essence is (or should be) one of the highest priority goals for myself and my colleagues. Sadly, the more I interact with scientists and my colleagues in general, I am finding that their own understanding of their research theories and practice trump their ability to relay what they know, even on a broad and most elementary scale, to others. This has disturbed me for a long time and although I have struggled to keep these ideas of broad audience communication at the forefront of my own understanding of my work, I am very excited for the opportunity to bring this freshly minted Ph.D. degree and my teaching experience, along with all of my own energy, to my position as chemistry department teaching faculty at the University of Minnesota. There will be an adjustment period rectifying the immersion into Gophers fans and my Bucky allegiance, but I am excited beyond words for the opportunity to work at this level to expose students, colleagues,

and the public to the excitement of chemistry, and to help them recognize the beauty of chemistry and science in their own daily lives!

Thank you to all of my family, friends, and students over the years that have helped to keep me fluent in the language of science, and dynamic in my comprehension and application of techniques to impart amazing aspects of the world around us to everyone!

I leave you with somewhat cohesive images, revisiting the concept of paddlewheel type structure and axial reactivity, and a little fun with my love of the river: Something so seemingly calm can simply pass by anything and everything along its path, or it can dramatically sculpt a landscape leaving an aftermath forever changed. My goal is to inspire the world around me and not just simply pass along my merry way but instead dramatically sculpt both my own path and the aftermath I leave behind!



So, as you sit with this dissertation in your hands, I thank you for helping make this a reality...

And of course... On Wisconsin!