SOAR Research – Faculty Proposal – Summer, 2014

Synthesis, Isolation and Characterization of Orientational Isomers of Rhodium Complexes

Faculty: Stephen Dunham, Ph.D., and Shari U. Dunham, Ph.D., Associate Professors of Chemistry

Student: Caroline Bartulovich

Project Start Date: May 27, 2014
Length of Project: 10 weeks

Description of the project
Synthesis, Isolation, and Characterization of Orientational Isomers of Rhodium Complexes

The biological activity of many anticancer compounds can be attributed to their binding interactions with deoxyribonucleic acid (DNA). We are particularly interested in transition metal compounds that bind DNA. Our research with a series of rhodium (Rh) compounds has shown that isomers of rhodium complexes can be isolated and they have unique binding reactions with DNA. Our goals in this project are to first make and isolate these rhodium compounds with specific orientational isomerism. Once isolated, these rhodium isomers will be characterized by their reactions with asymmetric compounds, and also by growing single crystals of rhodium compounds for x-ray diffraction.

Previous Work on Experiment Design
A spring 2013 honors project by Jacob Donchez ('13) explored the synthesis, isolation, and characterization of several new Rh compounds. These compounds are isomers because they have the same number of atoms (molecular formula), but uniquely different chemical and spectroscopic properties. We believe that these Rh compounds are orientational isomers of each other, but we do not have enough unique data to assign a specific orientation to each compound because symmetry makes each half of the molecule identical to the other half.

Synthesis and Isolation of Orientational Isomers
The first goal of the project is to repeat the previous synthesis and isolation of the Rh isomers (Donchez '13). The synthesis has been followed by high performance liquid chromatography (HPLC) as each compound in the reaction mixture gave a unique peak in the HPLC chromatogram (Donchez '13). HPLC also provided a method for purifying Rh isomers as they elute from the HPLC column at unique times.

Characterization from Symmetry Breaking Reactions
One experimental goal for this summer will be to react the purified Rh isomers with asymmetric compounds. When the asymmetric compound forms new bonds with a Rh isomer, the symmetry that relates the two halves of the Rh compound will be broken to

generate unique nuclear magnetic resonance (NMR) spectra of the resulting asymmetric Rh compound. Spectroscopic data for the asymmetric Rh compounds can then be used to infer the structure of the symmetrical Rh orientational isomer.

Growing Crystals
Another experimental goal for this summer will be to grow single crystals of one or more Rh orientational isomers. Crystallization can occur when a solution containing the Rh compound of interest is slowly infused with another solvent that lowers the Rh compound solubility until crystals form. When crystals have a consistent orientation of the Rh compound in the solid state, a single-crystal, they will diffract x-rays to reveal the location of the atoms that makeup that compound. In order to grow crystals, many variables need to be systematically explored including solvent mixtures, initial concentration of Rh isomer, temperature, and solvent infusion methods.

Roles and responsibilities

- A project director (Shari or Stephen Dunham) will be available to train Caroline on the use of instrumentation, Rh compound synthesis reactions, data analysis in excel, and visual representation of results in Microsoft Word or Powerpoint.
- Caroline will prepare and present at daily meetings (~15-30 min) with project directors (Shari and/or Stephen Dunham)
- Caroline will maintain a research laboratory notebook that will include regular and complete entries. The laboratory notebook will have an updated table of contents at the beginning. Entries should be dated, clearly written and organized, and made at least daily with details of ideas for experiments, planning of experiments, clear reference to location and organization of electronic data for each experiment, and a summary of results from each experiment. Project directors will look at Caroline's notebook periodically and provide informal feedback throughout the summer. The notebook will be submitted to the project directors upon completion of the Summer Research.
- Throughout the summer, Caroline will prepare a summary figure for each set of experiments (with detailed figure caption!) to clearly illustrate the results of each experiment. These summary figures will be submitted electronically to the project directors before completion of the Summer Research.
- Caroline may consider continuing this research as an honors project or independent study during the 2014-2015 academic year, so a final report/poster may not be required at the end of the summer but instead by the end of her research experience and in time for the Annual Student Scholarship and Creative Endeavors Day in spring of 2015.

Project Timetable

- Weeks 1-3: Setup Rh synthesis reactions and learn to operate various instruments: HPLC for Rh isomer isolation, NMR, and MALDI-MS for Rh compound characterization.
- Weeks 4-8: Carry out reactions of purified Rh isomers with asymmetric compounds to characterize Rh isomers by NMR spectroscopy. Setup

crystallization trials for growing single crystals of Rh isomers for x-ray diffraction.

- Weeks 9-10: Perform any required replicate experiments and write final paper.

Summary of benefits

Student engagement in discipline-appropriate scholarly research. Caroline will be engaged in synthetic inorganic laboratory research that includes reading and summarizing primary literature, planning and performing experiments that require the use of several new instrumental methods, and collecting/analyzing/organizing significant amounts of electronic data. In addition, she will prepare and receive feedback on various visual representations of experimental results (preparing figures in a format appropriate for publication in a Chemistry journal). The Drs. Dunham will work with Caroline to prepare a scientific poster for presentation of this work at a local and possibly a national conference. Caroline has had previous summer research experience in the Department of Chemistry (with Dr. Carl Salter). This project is significantly different because it will allow her to explore details of synthetic chemistry and instrumental analysis that she did not encounter in her previous SOAR project.

Impact on faculty, campus community, and discipline. Caroline's work on this project will contribute to the discipline of inorganic chemistry by characterizing the structures of several new Rh compounds. None of the compounds that she will work on have been published. This project will benefit the Drs. Dunham by building upon work of two former research students (Donchez & Kuperavage Summer 2011, Donchez Honors '12-'13) and completing the characterization needed for understanding how structures of Rh compounds relates to DNA binding kinetics. Her results will be an important part of future publication of these compounds in a peer reviewed Chemistry journal. By presenting her research during the summer to the SOAR group, and as a poster at Moravian Scholarship and Performance Day in April 2015, and perhaps participate in Moravian College Honors program in '14-'15 academic year, Caroline's work will impact the campus community at Moravian by exposing others to beauty and complexity of inorganic chemistry research.

Budget Items

- $500.00 to offset part of the costs for reagents required for synthesis and characterization.
    - diRhodium trifluoroacetate, 1 g $ 358
    - Methanol, HPLC Grade, 8 L $ 236

Total $ 594

Dirhodium trifluoroacetate is a commercial starting material required for the synthesis of the orientational isomers. It is a consumable specialized reagent so there are no standard supplies of this compound available in the department of Chemistry at Moravian College.

HPLC grade Methanol is required for the HPLC purification of the orientational isomers. The solvent is consumed in the process of purifying compounds by HPLC and there is a limited supply of this solvent in the department of Chemistry.

Synthesis, Isolation and Characterization of Orientational Isomers of Rhodium Complexes

Caroline Bartulovich, Chemistry, Class of 2015
Dr. Shari Dunham and Dr. Stephen Dunham
Requesting On-Campus Housing

A major reason that I choose to attend Moravian was because of the numerous opportunities they have for undergraduate research. By participating in this SOAR project I would gain much needed experience doing original scientific research. Up until this point in my scientific career I have been handed a lab manual and told step by step directions on how to accomplish something. One thing that I find incredibly exciting about participating in a SOAR project is the responsibility I will have and the fact that I will be held accountable to the findings that stem from this project. There will be no answer sheet and if something does not go as planned then my advisors and myself will have to work together to figure it out and make the appropriate adjustments. In a meeting that I had with Dr. Stephen Dunham to discuss this project, he told me that I will be using equipment that I will also be using next semester in my Instrumental Analysis class. By participating in this project I will be getting a head start using the equipment that I will not only be using in my Instrumental Analysis but also when I go into industry. I would be very interested in using my previous knowledge from my classes and of certain equipment for different and more complex chemical reactions. Also, by participating in this SOAR project I hope to gain a clearer picture as to what I would like to do after graduation from Moravian. Although I believe that I want to go straight into industry, by participating in this undergraduate research, I may find that I would like to pursue graduate school or a career in research.

Results from this project if conclusively shown could possibly be published in a journal such as the *Journal* of *Inorganic Chemistry.* This could be something very good for both myself and Moravian College. Having my name on a publication in the actual field of known chemical research could be a definite professional benefit for me when I am searching for a job in chemistry. This project could also potentially turn into an independent research project or an honors project that I would complete during my senior year at Moravian College.