

The Synthesis of Ruthenocene⁻ - A Methodology Appropriate for the Inorganic Undergraduate Curriculum

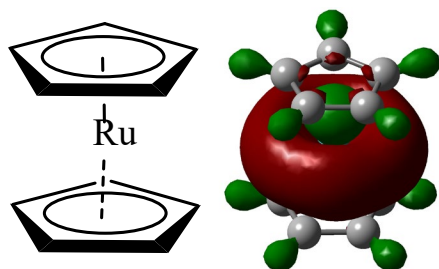
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ABSTRACT

The discovery of ferrocene, $\text{Fe}(\text{C}_5\text{H}_5)_2$, in the 1950's sparked the development of organometallic chemistry including metallocene compounds. Shortly after the isolation of ferrocene, the analogous ruthenium and osmium compounds were discovered. The preparation of ferrocene is common in undergraduate inorganic laboratory courses, but an appropriate undergraduate synthesis of ruthenocene, $\text{Ru}(\text{C}_5\text{H}_5)_2$, is lacking. Herein we describe a convenient synthesis of $\text{Ru}(\text{C}_5\text{H}_5)_2$ for the undergraduate teaching laboratory. This microscale reaction incorporates elements of green chemistry and introduces students to an air sensitive reaction with sublimation as a purification method. Students explore the characterization of ruthenocene, through experimental and computational approaches.

GRAPHICAL ABSTRACT



KEYWORDS

Audience: Upper-Division Undergraduate

Domain: Inorganic Chemistry, Laboratory Instruction

Pedagogy: Hands-on Learning/Manipulatives

Topics: Coordination Compounds, Computational Chemistry, Green Chemistry, Microscale Lab, Organometallics, Spectroscopy

INTRODUCTION

The beginning of modern organometallic chemistry can be traced to 1951 with the discovery of ferrocene, $\text{Fe}(\text{C}_5\text{H}_5)_2$, the first metallocene complex.^{1,2} Interest in sandwich complexes grew rapidly with over 100 publications dealing with metal cyclopentadienyl complexes by 1956.³ These compounds were initially proposed as reducing agents, antioxidants, catalysts, paint pigments, as well as additives to prevent knocking in fuels and to promote smokeless combustion.³ More recently, metallocene complexes have found a greater importance in the fields of biological and medicinal chemistry, catalysis, non-linear optics and supramolecular chemistry.⁴ The importance of the discovery of ferrocene and related sandwich compounds, such as ruthenocene, to the field of organometallic chemistry is illustrated by the awarding of the 1973 Nobel Prize in Chemistry to Fischer and Wilkinson for their work on these complexes.⁵

Ruthenocene, $\text{Ru}(\text{C}_5\text{H}_5)_2$, which adopts a similar sandwich structure to the isoelectronic ferrocene, was first discovered in 1952.^{6,7} The initial 1950's structural determination found an eclipsed⁷ and staggered^{8,9} configurations for ruthenocene and ferrocene (see Figure 1). The structural difference resulted from the decreased steric interaction of the cyclopentadienyl rings in ruthenocene due to the larger ionic radius of Ru. Further work in the 1970's and 80's resulted in the isolation of the eclipsed structure of ferrocene.¹⁰⁻¹²

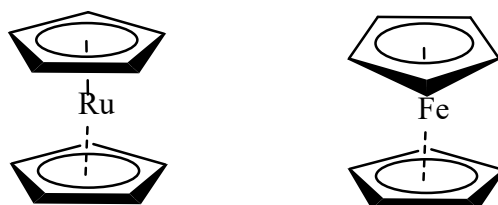


Figure 1. Structure of $\text{Ru}(\text{C}_5\text{H}_5)_2$ and $\text{Fe}(\text{C}_5\text{H}_5)_2$

Due to the significance of these complexes, ferrocene has become a fixture of undergraduate inorganic laboratory courses,¹³ while the analogous ruthenocene has not. A reason is the perceived prohibitive cost to make ruthenocene based on the price of RuCl_3 (25 mg: ~ \$655)¹⁴ versus FeCl_2 (25 mg: ~\$110).¹⁵ Although the exact cost per student to run either reaction depends on the supplier and the amount of chemicals procured, an analysis of the price of all reactants illustrated that the cost different between the two reactions is not large. The total cost of chemicals per student to produce

ferrocene¹⁶ is between ~ \$1.00 to \$2.50 while it is ~\$5.00 to \$6.00 (USD) for the ruthenocene reaction. (This excludes the cost of C₅H₅⁻ which is used equally in both reactions. The cost analysis was also based on the same molar amount of the starting metal chloride). The lower-than-expected difference is due to the increased solvent cost in the ferrocene reaction compared to the solvents used in the ruthenocene reaction. This counters the increased price of using RuCl₃ over FeCl₂ (See Supporting Material for the cost break down).

Several different approaches to produce ruthenocene have been published,^{17,18} including the use of a Grignard reagent,⁶ the reduction of Ru(III) (from RuCl₃) to Ru(II) via Zn¹⁹⁻²⁴ or Ru,²⁵ and the reaction of NaC₅H₅ with Ru₂(OCOC₃H₇)₄.²⁶ None of the published methods have focused on a methodology appropriate for an undergraduate experiment. To introduce undergraduate students to the synthesis of ruthenocene, a laboratory experiment was developed which utilized the reduction of Ru(III) in Ru to Ru(II) by Zn in the presence of C₅H₆ to produce ruthenocene. It was designed to be included in our third-year inorganic laboratory course (Chem 336: Advanced Inorganic Chemistry Laboratory), which provides students with a hands-on investigation of many of the topics presented in the connected lecture course (Chem 332: The Chemistry of Transition Metals) and the prerequisite second year inorganic lecture and laboratory courses (Chem 230: Inorganic Chemistry and Chem 236W: Inorganic Chemistry Laboratory).²⁷ This reaction is designed to be completed in one laboratory period (4 hrs.) with the aim to develop the laboratory techniques standard to many inorganic syntheses, such as the manipulation of an oxygen sensitive reaction. This experiment builds upon many of the skills already acquired by students including the setup and completion of a reaction, initial determination of purity via melting point (mp) and the interpretation of Infrared (IR), and Nuclear Magnetic Resonance (NMR) spectra.

LEARNING OBJECTIVES

The synthesis of the product in this experiment builds upon basic laboratory techniques such as measuring volumes and masses, stirring, filtration and crystallization that the students learned in previous chemistry laboratory courses. Students are introduced to oxygen sensitive reactions and the use of sublimation as a purification method. The analysis conducted in this experiment expands on

the students' previous knowledge of IR, NMR and Mass spectroscopy (MS). On top of synthetic approaches, the Gaussian²⁸ calculation of the ruthenocene complex was introduced to allow students to have an understanding and comparison between theoretical and experimental chemistry. By using GaussView 5.0,²⁹ students visualize the molecular motions of the complex and how they relate to the IR signals. The degeneracy within the complex, with regards to the NMR spectra, is highlighted in these calculations. Students are also provided a glimpse of the complexity of the molecular orbitals involved in the bonding of ruthenocene. Environmental awareness is also examined as students are asked to review this process through the lens of green chemistry.

The main learning objectives for this experiment include:

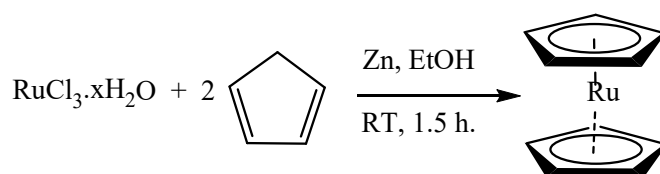
1. Performing an air-sensitive reaction.
2. Purification via sublimation.
3. Experimentally examine ruthenocene via IR, NMR, MS and melting point.
4. Computationally examine ruthenocene via IR and NMR spectroscopy, as well as generate molecular orbitals involved in bonding.
5. Introduce green chemistry through the examination of this reaction through the lens of the 12 principles of green chemistry.

EXPERIMENTAL

Procedure

In a 50 mL round bottom flask, 95% ethanol is deoxygenated by bubbling with N₂ gas, followed by the addition of a stir bar, RuCl₃, Zn dust and the cyclopentadiene, which was prepared by the laboratory technician and stored in the freezer to minimize dimerizing.³⁰ The round bottom flask is then capped with an inlet tube to maintain an N₂ atmosphere in the reaction container.²⁰ The solution is stirred at room temperature for 1.5 hours. At the start of the reaction a blue hue may appear in the black/dark brown reaction solution. The blue hue has been attributed to the formation of mixed oxidation state ruthenium chloride complexes.^{19,24,31} The solvent is removed on rotary evaporator, and the brown crude product transferred onto a Petri dish bottom in preparation for purification of the ruthenocene product by sublimation (Scheme 1).

Scheme 1. Synthesis of Ruthenocene



The Petri dish is placed on a hot plate and capped with the Petri dish cover. An ice filled beaker is placed on the cover (Figure 2). At 70 °C the product slowly starts to collect on the Petri dish cover via sublimation, with rapid collection at 105 °C. Ruthenocene is collected as fine, white crystals: yield 120.0 mg (68%); mp 199-200 °C; ^1H NMR (500 MHz, CDCl_3) δ = 4.56 (s); ^{13}C NMR (125 MHz, CDCl_3) δ = 70.15 (s); MS (ESI-Single quad) m/z 231.9 (M+).

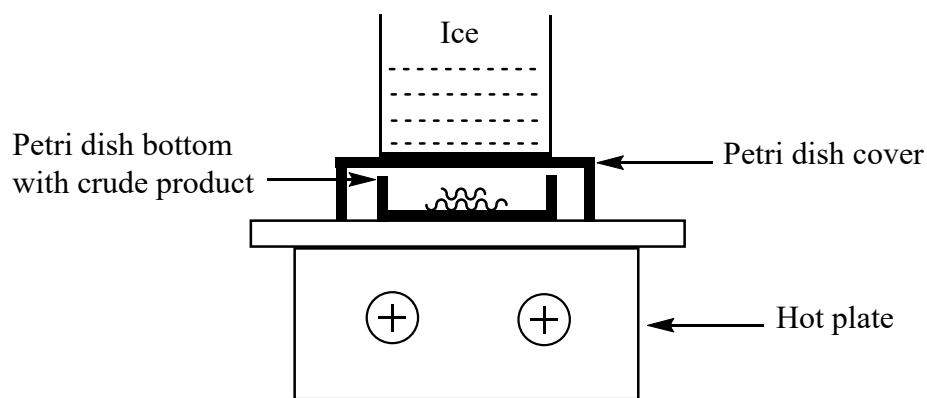


Figure 2: Ruthenocene sublimation set-up.

HAZARDS

Eye protection, laboratory coat and gloves should always be worn. All laboratory work should be done in a fume hood. All materials should be handled and disposed of based on the information provided in their safety data sheets. The hazard for each material includes: acetone (flammable, irritant)³², cyclopentadiene (flammable, irritant, environmental hazard, strong odor)³³, ethanol (flammable)³⁴, nitrogen (compressed gas)³⁵, ruthenium (III) chloride (irritant, corrosive)³⁶, zinc dust (flammable, environmental hazard)³⁷. Nitrogen gas should only be used by an individual familiar with the proper use of a compressed gas and compressed gas cylinders.³⁸

RESULTS AND DISCUSSIONS

This experiment allows students to investigate related metallocene complexes containing either first or second row transition metal. Although ferrocene and ruthenocene are similar, they do have different properties,³⁹ including the chemistry to produce them. The ferrocene reaction¹⁶ at its basic form is a ligand replacement reaction, where the chlorine atoms on Fe are replaced by $C_5H_5^-$ which was made in situ from the decomposition of C_5H_6 . The ruthenocene procedure has an added oxidation-reduction reaction, which is not seen in the ferrocene reaction. In the ruthenocene reaction, all reactants are made in situ, that is the initial Ru(III) complex and C_5H_6 do not react, rather they both undergo a reaction (to Ru(II) (via Zn) and $C_5H_5^-$) to produce intermediates which react to give the product. This does not occur in the ferrocene procedure.

Including the ruthenocene reaction into the undergraduate chemistry curriculum allows for a greater variety of how these two complexes can be used. Although the cost to make ruthenocene is greater than for ferrocene, the difference is not prohibitive. To help reduce the cost, the two reactions (ferrocene and ruthenocene) can be alternated between semesters, where students make one of the complexes but are given samples from the surplus of the other complex made the semester before. The surplus ruthenocene could also be used in subsequent semesters as a reagent to further explore the chemistry of ruthenocene.^{22,40,41} Given the 10x increase in the cost of ruthenocene versus the metal chloride,⁴² it is cost prohibitive for students to explore the chemistry of ruthenocene without first making it.

In general, the adoption of second row transitional metals in the inorganic laboratory curriculum lags the first-row examples, including the ruthenium-based experiments. A search of this journal's database for "Laboratory Experiments" containing the term "Ruthenium" yielded only 23 results.⁴³ Of these, 11 mentioned ruthenium in the Introduction of the article, but ruthenium was not part of the experiments, and 7 experiments made use of a purchased ruthenium complex, either as a catalysts or a reagent. Over an 11-year span (2011- 2022) this journal published only 6 experiments making a

ruthenium-based coordination complex, thus illustrating the need for more examples such as the experiment presented.

We designed this experiment with an effort to incorporate elements of the 12 principles of green chemistry.⁴⁴ Ethanol was used as the reaction solvent; the scale of the reaction was decreased to limit the amount of excess product generated as well as the purification step via extraction or chromatography followed by re-crystallization was replaced by sublimation. This was done to decrease the amount of solvent used and make use of electrical devices as our electricity is renewable. The green chemistry ideals introduced in this experiment were also examined by the students through the laboratory formal report. Initially students had to summarize the green chemistry principles of which many had not been previously exposed to. They then compared a published method to make ruthenocene²³ to the method undertaken in their experiment. Students were asked to compare the two methods. Based on the 12 principles of green chemistry they were to decide which method is a greener process and to state why, by indicating which of the principles was adopted. All students (50 students over two semesters) found this new method to be the “greener” process with the two most common reasons being the decrease in waste generated and the use of safer solvents. This portion of the formal report allowed the student to examine two reactions from the viewpoint of green chemistry and make a decision on which method is “greener”, a skill that students should apply to all reactions to reduce waste. (See Supporting Material for the green chemistry analysis results.)

This experiment, including IR and melting point analysis, was completed by all students in 3.5 hours, thus within one laboratory period (4 hrs.). Students were provided with the NMR and MS data and completed the computational analysis outside of the laboratory period. Each of our students, from two semesters (50 students total) performed all aspects of the experiment individually. The results of this experiment were summarized in a formal laboratory report submitted by the students. Our formal reports are graded on two aspects, (1) an assessment of their writing skills, which builds upon prior writing knowledge⁴⁵, (2) the correct interpretation of the data with respect to the chemistry.

Through this experiment students investigated ruthenocene, a complex containing a η^5 bound ligand, both experimentally and computationally via Gaussian²⁸ and GaussView 5.0.²⁹ The symmetry of this complex was explored through an examination of the ¹H and ¹³C NMR spectra, both resulting in

the expected singlet.¹⁸ Computational analysis using Gaussian and GaussView 5.0, allowed students to visualize the degeneracy within ruthenocene, resulting in the observed NMR spectra. Students were able to further practice their characterization skills through the assignment of the IR spectrum of ruthenocene. The motion associated with the signals observed in the IR spectrum,²⁰ were illustrated by the animated vibrations shown in GaussView 5.0. Students also used the Gaussian calculations to generate various molecule orbitals found in ruthenocene. The use of the Gaussian calculation in this experiment was not to predict the peak location in the NMR or IR spectra rather to generate a similar spectra that could be used to help assign the peaks and provide a visual interpretation of the data, thus highlighting the strength of computational methods, even a basic calculation as was conducted.

Our students were able to complete this portion of the experiment as they all previously completed an introductory assignment on the use of Gaussian/GaussView 5.0 to predict the IR and NMR data as well as the molecular orbital diagram of coordination complexes. The assignment introduced them to calculations and briefly explored the limitations. (A thorough discussion of calculation approaches and limitations were left for more advanced courses.) The limitation of the calculations were evident in the student data where the experimental and calculated values were similar but not exact (see Table 1).

Table 1. Experimental vs. Gaussian Computational Data

IR ^a (cm ⁻¹)							
Expt.	3083	1404	1099	1001	863	805	444
Calc.	3274	1439	1115	1019	-	804	422
NMR	¹ H (ppm)		¹³ C{ ¹ H} (ppm)				
Expt.	4.56		70.15				
Calc.	3.76		66.08				

^a Only medium to very strong peaks included.

Our students have access to the Gaussian/GaussView programs on campus and through a university license they can also download the programs onto their personal computers, thus they can complete this exercise at home as part of the formal report. The Gaussian and GaussView 5.0 programs can be cost prohibitive. There are free alternative programs that can be used such as the ORCA⁴⁶ and Avogadro⁴⁷ programs. Due to our access to GaussView 5.0 and Gaussian we did not investigate the use of alternative programs.

Students also examined the complex via MS and melting point. The MS showed signals due to ruthenocene and decomposition products, but also highlights the ruthenocene isotope pattern which is dominated by the Ru isotope pattern.⁴⁸ The melting point determination of ruthenocene is different than the standard process as the melting point (199-200 °C) is higher than the sublimation temperature. Some students noticed this and questioned if the melting point could be determined. Others failed to realize it and questioning why the amount of material used in the melting point determination was decreasing with no melting occurring and product collected higher up the melting point tube (See Supporting Material for all the spectra).

All students were able to successfully complete this air sensitive reaction. For many it was their first experience purifying a product via sublimation. Through the formal laboratory report students summarized their results, thus providing a means to measure the success of our learning objectives. For the presentation of the experimental data in formal laboratory report student achieved an average mark of 74%, with the common mistakes due the labeling of one of the spectra, interpretation of the data, or missing analysis. Students achieved an average grade of 88% on the computational work section of the report, with a higher grade for the green chemistry analysis of the reaction. An analysis of all the formal laboratory reports did not show a specific question in the report that causes issues with all students.

The student opinion of the experiment was investigated through a student feedback survey based on a ranking using a five-point Likert scale “Strongly Disagree/Decrease” to “Strongly Agree/Increase”⁴⁹ (Table 2).

Table 2. Student Feedback

For the following two statements, rate your level of agreement:	Means Score (N = 40) ^a
I found the ruthenocene topics to be interesting.	4.37 ^b
The examination of the NMR and IR spectrum of ruthenocene through GaussView 5/Gaussian improved my understanding of the experimental NMR and IR spectrum.	4.18 ^b
Your ruthenocene product will be given to an SFU graduate student to be used in his/her research project. Knowing this, does your opinion of the experiment increase or decrease?	4.17 ^c

^a N=40 out of 50 students in the course over two semesters

^b Likert rating scale: strongly agree = 5; agree = 4; neutral = 3; disagree = 2; strongly disagree = 1.

^c Likert rating scale: strongly increases = 5; increases = 4; neutral = 3; decreases = 2; strongly decreases = 1.

Analysis of the student feedback (Table 2) showed that students enjoyed this experiment and found the topic interesting, with all students either strongly agreeing or agreeing to the statement “I found the ruthenocene topics to be interesting.” Their opinion of the experiment further increased when informed through the survey that their products would be used by graduate students in the completion of their graduate studies. This result was not surprising given that students wish to incorporate aspects of green chemistry into their experiments, such as the reduction of waste generated through producing a product that can be used further. Students also felt that their understanding of the IR and NMR spectra of ruthenocene improved through the analysis of these spectra using Gaussian and GaussView 5.0. The most common response when asked “What specific aspect of the ruthenocene experiment did you like?” was the use of sublimation to collect the pure product. This was a technique that students had not previously encountered, thus fulfilling the aim of this experiment to expand the student’s experimental skill set. (See Supporting Material for all comments.)

CONCLUSION

Through this experiment, the synthesis of ruthenocene can be brought into the inorganic undergraduate curriculum, with a method that will allow students to easily generate the product within a typical laboratory period. This experiment introduces students to techniques that many have not been previously exposed too, such as purification through sublimation, with a product yield that allows for the characterization of the product.

With this experiment, the analysis of $M(C_5H_5)_2$ complexes in the undergraduate curriculum is no longer limited to ferrocene as we introduced a convenient method to make the related ruthenocene complex.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI:

10.1021/acs.jchemed.XXXXXXX. [ACS will fill this in.] Example brief descriptions with file formats indicated are shown below; customize for your material.

Supporting Material_Instructions (PDF)

Supporting Material_Students (PDF)

Gaussian_Calculation_Log_Output_File_NMR (PDF)

Gaussian_Calculation_Log_Output_File_Opt&Freq (PDF)

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