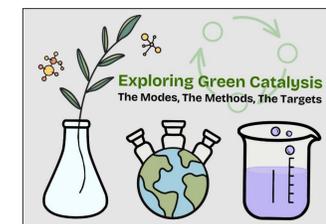


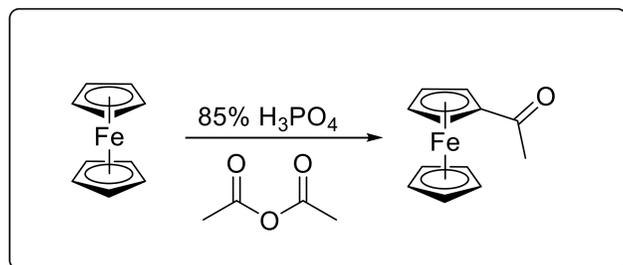
Activity 1 Print Files

Activity 1 – Our Role: Exploring individuals' roles in developing sustainable alternatives.

Activity 1: It's Not Easy Being Green



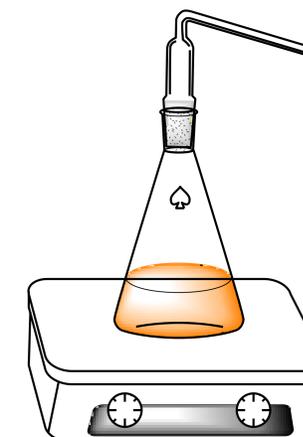
1 The Experiment



Students will complete a **Friedel-Crafts Reaction**

1. Acetic anhydride, ferrocene, and catalytic phosphoric acid are mixed and warmed
2. The reaction is poured over ice and filtered to isolate
3. TLC is done to determine the best solvent system for their column
4. Column chromatography is used before characterizing by m.p. and IR

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2 The Stakeholders

Who are the stakeholders?

1. Suzie Synthesis is an undergraduate student completing this experiment.
2. Freddie Friedel is a graduate student teaching assistant.
3. Gabriel Green is a lab technician for the undergraduate labs.
4. Professor Penelope Phenol is the faculty member/Lab Director.
5. Pierre Proline is a Health and Safety Officer for his university.

What is your definition of **sustainable** and **green chemistry**? How long have you had this definition? Do you think it can change? How does this align with definitions from the Canadian Society for Chemistry/American Chemical Society?

1. What sustainability concerns most directly impact your **stakeholder**?
2. Which of your suggested changes can your **stakeholder** reasonably contribute to?
3. How do the perspectives of other **stakeholders** affect the changes you prioritize?

1. What are the “non-sustainable” elements of this experiment?
2. What changes would you make to make the experiment procedure itself more sustainable?
3. What changes would you make to make the experimental space itself more sustainable?
4. What changes would you made beyond the experiment procedure and space in the interest of sustainability?



Persona 1: Undergraduate Student (Suzie Synthesis)

Suzie Synthesis is a third-year student registered in the third-year inorganic laboratory course. Suzie is an avid hiker on the weekend and loves nature. She is really excited about majoring in chemistry and is considering graduate school. She is a first-generation university student so she is still learning about how to navigate conversations with her teaching assistants and professors.



Persona 2: Teaching Assistant (Freddie Friedel)

Freddie Friedel is a second-year graduate student focused on catalyst development who is in his second semester teaching the inorganic laboratory course. Freddie is still struggling with the work-load associated with graduate school but he really cares about his teaching and the students. Freddie thinks he wants to pursue an academic career and is looking for the opportunity to learn how to write a grant application.



Persona 3: Lab Technician (Gabriel Green)

Gabriel is in the first year of their role in serving as the technician for the second-, third-, and fourth-year inorganic chemistry labs. Gabriel is a recent graduate of the school they are now working as a technician at where they had a combined major in Chemistry and Earth Science. Gabriel has a lot of ideas about how to modernize the inorganic laboratories based on their undergraduate experience, but they aren't sure who to talk to about these ideas.



Persona 4: Faculty Member/Lab Director (Professor Penelope Phenol)

Professor Phenol has been working at her institution for eight years and has been in charge of the inorganic chemistry laboratories for the last two years. Penelope has a heavy teaching load, splitting her time between the inorganic chemistry labs and teaching a section of general chemistry in both the first and second semester. Penelope can mentor undergraduate students for their undergraduate theses and has done so the last three years. The inorganic laboratory curriculum Penelope is currently teaching hasn't been updated in 12 years.



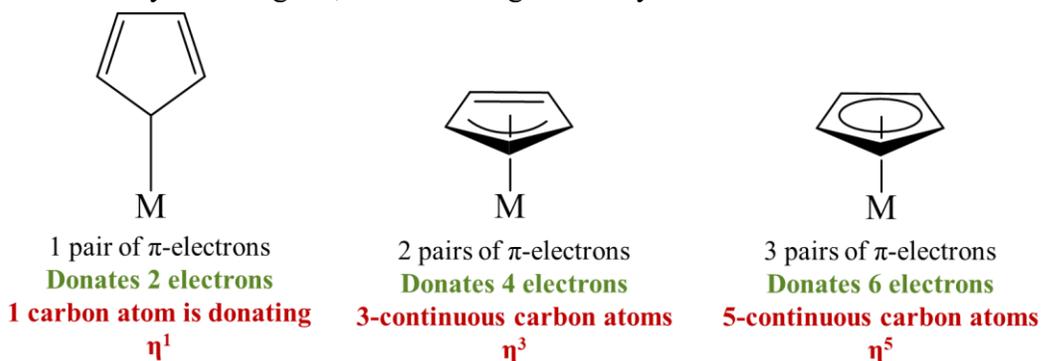
Persona 5: Health and Safety Personal (Pierre Proline)

Pierre has been working at his university in health and safety for 14 years where he supports all STEM fields. Pierre really likes collaborating with faculty and students in the undergraduate and graduate labs and has taken initiatives to update the signage in the first-year labs in the last year. As a student, Pierre didn't take any classes that discussed green chemistry, but he has been reading about it in *Chemistry and Engineering News*.

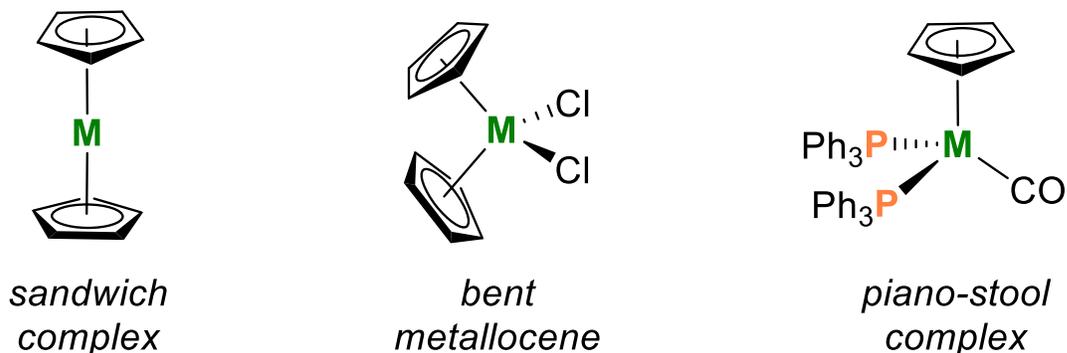
Experiment 3

Synthesis of Acetylcyclopentadienyl(cyclopentadienyl)iron(II)

Cyclopentadienyl (Cp) ligands have become ubiquitous organometallic chemistry. Cyclopentadienyl ligands are able to bond to an array of transition metal centers through their π -system resulting in firmly bound ligands, inert to most nucleophiles and electrophiles, although not strong oxidants. The inert nature of Cp ligands makes them reliable spectator ligands, meaning they do not engage in further chemistry with the metal or incoming substrates, allowing for a wide range of catalytic transformations. Functionalization of Cp ligands can be tailored to increase the steric bulk (cone angle) or electron donicity of the ligand, in turn tuning reactivity at the metal.



The hapticity of Cp ligands can be either η^1 , η^3 , or η^5 allowing the ligand to accommodate a range of oxidation states. A “ring slip” refers to when the Cp ligand changes hapticity from η^5 to η^1 or η^3 in order to allow for additional chemistry at the metal, creating a vacant site where a substrate can bind. Metallocene complexes, also referred to as sandwich complexes, feature a metal bound to two Cp ligands (Cp_2M). When the Cp ligands are arranged to the side of the metal ($\text{Cp}_2\text{M-L}$) the complex is called a bent metallocene. Similarly, complexes featuring a single Cp ligand (CpML_n) are referred to as piano-stool complexes.



In this experiment, you will perform a Friedel-Crafts acylation reaction, purify the target compound by column chromatography, and learn how to use a rotatory evaporator to isolate a compound from solution. In the first week, you will perform a reaction between

ferrocene and acetic anhydride. In the second week, you will use thin-layer chromatography to determine the number of products from the reaction, and to determine a suitable solvent for separating the mixture by column chromatography. Based on IR spectroscopy and melting point determination, you will identify your product and assess its purity.

Recommended Reading:

1. Housecroft, C.E. and Sharpe, A.G. Inorganic Chemistry, 4th Ed.
 - Chapter 3: Section 3.7 Vibrational spectroscopy, pages 79 – 82.
 - Chapter 4: Section 4.6 Infrared and Raman spectroscopy, pages 98 – 102.
 - Chapter 24: Section 24.13 Complexes containing η^5 -cyclopentadienyl ligands, pages 924 – 930.
2. Crabtree, R. H. The Organometallic Chemistry of Transition Metals, 6th Ed.
 - Chapter 5: Section 5.4 Cyclopentadienyl Complexes, pages 147 – 150.
3. Clayden, J., Greeves, N., and Warren, S. Organic Chemistry, 2nd Ed.
 - Chapter 21: A closer look at Friedel-Crafts chemistry, pages 492 – 494.
4. Thin Layer Chromatography (TLC) and Recrystallization – Two Solvents
Technique overviews and videos: <https://www.chem.ualberta.ca/~orglabtutorials/>.
5. Rotary Evaporator Tutorial: <https://sites.google.com/ualberta.ca/inorganic-chemistry-labs/online-resources/techniques-video-library/using-a-rotovap?authuser=0>.
6. Column Chromatography Tutorial:
<https://www.youtube.com/watch?v=Fy1duyp3IY>.
7. IR Spectroscopy Tutorial: <https://sites.google.com/ualberta.ca/inorganic-chemistry-labs/online-resources/spectroscopy-tutorial?authuser=0>.

SAFETY NOTES			
CHEMICALS	PICTOGRAMS	HAZARD	PRECAUTIONS
ferrocene		<p>Flammable solid. Harmful if swallowed or inhaled.</p> <p>May damage fertility or the unborn child.</p> <p>May cause damage to organ through prolonged or repeated exposure if inhaled.</p> <p>Very toxic to aquatic life with long lasting effects.</p>	<p>Avoid contact and inhalation.</p> <p>Wear gloves</p>
acetic anhydride		<p>Flammable liquid and vapor.</p> <p>Harmful if swallowed.</p> <p>Causes severe skin burns and eye damage.</p> <p>Fatal if inhaled.</p>	<p>Avoid contact and inhalation.</p> <p>Wear gloves and use in fumehood.</p> <p>Keep away from sources of ignition.</p>
85% phosphoric acid		<p>May be corrosive to metals.</p> <p>Harmful if swallowed.</p> <p>Causes severe skin burns and eye damage.</p>	<p>Avoid contact and inhalation.</p> <p>Wear gloves and use in fumehood.</p>
sodium hydrogen carbonate	None	Not a hazardous substance or mixture.	

hexanes		<p>Highly flammable liquid and vapor.</p> <p>May be fatal if swallowed and enters airways.</p> <p>Causes skin irritations. May cause drowsiness or dizziness.</p> <p>Suspected of damaging fertility or the unborn child.</p> <p>May cause damage to organs through prolonged or repeated exposure if inhaled.</p> <p>Toxic to aquatic life with long lasting effects.</p>	<p>Avoid contact and inhalation.</p> <p>Wear gloves.</p> <p>Keep away from sources of ignition.</p> <p>Use in fumehood.</p>
petroleum ether		<p>Extremely flammable liquid and vapor.</p> <p>May be fatal if swallowed and enters airways.</p> <p>Causes skin irritation.</p> <p>May cause drowsiness or dizziness; genetic defects or cancer.</p>	
ethyl acetate		<p>Highly flammable liquid and vapor.</p> <p>Causes serious eye irritation.</p> <p>May cause drowsiness or dizziness.</p>	
dichloromethane		<p>Causes skin and serious eye irritation.</p> <p>May cause drowsiness or dizziness.</p> <p>Suspected of causing cancer.</p>	<p>Avoid contact and inhalation.</p> <p>Wear gloves.</p> <p>Use in fumehood.</p>
silica gel	None	<p>Not a hazardous substance or mixture.</p>	<p>Avoid inhalation.</p>

SAFETY NOTES	
DISPOSAL	<ul style="list-style-type: none"> - dispose of aqueous washes in the metal ion aqueous waste container in the lab. - dispose of any waste organic solvents (chromatography washes) in the non-halogenated waste bottle in the fumehood. - dispose of waste dichloromethane in the halogenated waste bottle in the fumehood. - dispose of waste silica gel in the “silica gel waste” bottle located in the fumehood. - dispose of any other waste inorganic solids in the chem 3740 solid waste bottle in the fumehood.
EQUIPMENT	<ul style="list-style-type: none"> - see Appendix A for <i>Instructions for Using Bottle Top Dispensettes</i>. - clamp the filter flask to a stand - see Appendix B for <i>Procedure for Filtration</i>. - the use of the rotary evaporator will be demonstrated to you by the lab instructor. It operates under reduced pressure and a shield should be placed in front of it during use. Turn off the water to the condenser when finished. - see Appendix E for <i>Instructions for Determining Melting Points</i>.

I. Week One. Synthesis and Isolation of Crude $\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_4\text{COCH}_3)$

Perform in a fumehood.

Add 1 mL of 85% phosphoric acid dropwise to a stirring mixture of 1.73 g of ferrocene and 8.2 mL of acetic anhydride in a small Erlenmeyer flask. Use a CaCl_2 drying tube to protect the solution. The reaction is heated in a boiling water bath for 10 minutes, and then the mixture is poured onto approximately 20 g of ice in a large beaker. After the ice has melted, NaHCO_3 is added until CO_2 no longer forms, and the solution is neutral. The solution is cooled in an ice bath for 30 minutes and the product is allowed to precipitate. The solid is isolated by vacuum filtration and washed with water until the washings are pale orange. The crude solid is dried in air for 15 minutes before being isolated from the vacuum filtration apparatus.

II. Week Two. Purification of $\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_4\text{COCH}_3)$ by Chromatography

Run a thin layer chromatograph (TLC) of the crude product in 95:5 petroleum ether: dichloromethane and determine the retention factor (R_f) of each species. Set-up a vacuum filtration flask. Load a 25 mL filter frit halfway with silica. Dissolve your sample in < 1 mL of dichloromethane and load onto the surface of the silica using a pipette. Pull a gentle vacuum until the sample is absorbed. Using 100 mL of eluent (see ratio above) run a flash column by pulling the solvent through the silica. Transfer the first 100 mL of a round bottom flask. Using a clean vacuum filtration flask, switch the eluent to 20 mL of pure dichloromethane. Transfer this solution to a second, round bottom flask. Isolate the products from each flask as solids by rotary evaporation of the eluted solutions. Obtain infrared spectra of the two compounds, and their melting points. Calculate the percent recovery and percent yield of $\text{Fe}(\text{C}_5\text{H}_5)_2$ and $\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_4\text{COCH}_3)$, respectively. Determine the melting point of each sample and collect an IR spectrum (KBr pellet).

Troubleshooting: If your product is forming an oil rather than the desired solid, add approximately 2 mL of hexane to the oil and stir vigorously. This helps to remove the “sticky” dichloromethane allowing your product to precipitate.

Troubleshooting: If the rotovap is not completely removing the solvent, or when you pull the flask off of the rotovap the product solubilizes, empty the solvent trap and the bump trap and return the flask to the rotovap. NOTE: Be careful heating your sample to remove the solvent, consider the melting point of the product.

Questions. Answer the following questions in the results/discussion section of your formal report.

1. What is the role and purpose of phosphoric acid? (1 mark)
2. What is the mechanism for the formation of acetylferrocene according to the reagents used in this experiment? (4 marks)
3. Why was sodium bicarbonate added at the end? (2 marks)
4. What is the point group symmetry of ferrocene and acetylferrocene? (2 marks)
5. If you were to form *bis*(acetylcyclopentadienyl iron(II)), what would be the *two* possible symmetries? How might you identify each isomer using IR spectroscopy? (See Experiment 2 for an overview of determining IR spectral features using symmetry elements). (2 marks)
6. In what order did $\text{Fe}(\text{C}_5\text{H}_5)_2$ and $\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_4\text{COCH}_3)$ elute? Why? (4 marks)