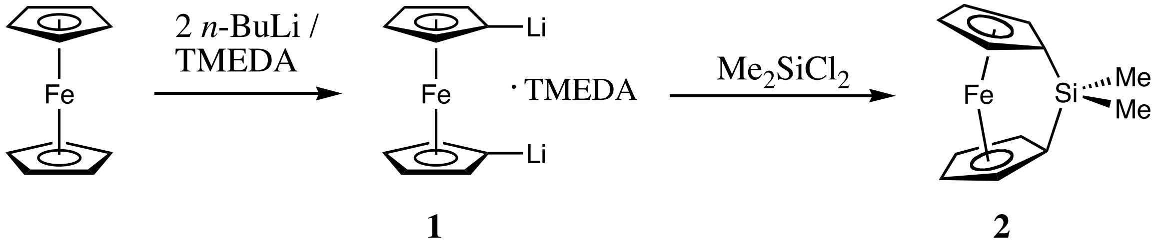
EXPERIMENT F
ORGANOMETALLIC POLYMER CHEMISTRY

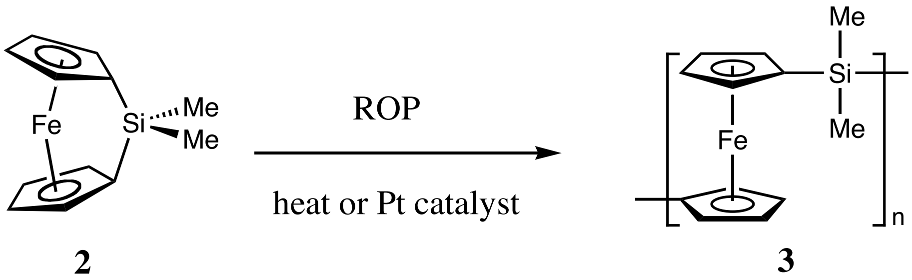
Synthesis Of A Ferrocene-Based Polymer Via Ring-Opening Polymerization

This experiment has a number of parts. You will synthesize a strained ferrocene derivative via lithiation of ferrocene followed by treatment with dichlorodimethylsilane. This product will be purified by sublimation, characterized and polymerized to a high molecular weight poly(ferrocenylsilane), an organometallic polymer. Two polymerizations, both examples of Ring-Opening Polymerization (ROP), will be used. First, half of the product will be thermally polymerized; second the remaining monomer will be polymerized using a Pt catalyst. Finally you will test some simple properties of films of the polymeric material. For recent books and reviews on Inorganic Polymers see refs.1 and 2.

INTRODUCTION.

The first step involves the lithiation of ferrocene (to give **1**) using two equivalents of n-butyllithium in the presence of tetramethylethylenediamine (TMEDA), which facilitates the reaction through break-up of the less reactive aggregated structures by coordinating to lithium and enhancement of the ionic character of the lithium carbon bonds. Reaction of **1** with dichlorodimethylsilane yields the red, crystalline [1]ferrocenophane **2**.[3] This species has a strained structure in which the cyclopentadienyl ligands are tilted with respect to one another by around 21°,[4] and the strain energy of **2** has been measured to be 80 kJ mol^{-1}.[5] In contrast to **2**, ferrocene has cyclopentadienyl ligands that are parallel to one another. The monomer (**1**) can be isolated as a red-orange crystalline solid or alternatively subjected to ROP directly. Transition-metal-catalyzed polymerization of unpurified **2** to yield the amber-colored poly(ferrocenylsilane) **3** can be performed at 50-80 °C over 2 - 24 h in solution by the addition of very small amounts of a Pt catalyst. The polymer **3** can be isolated by precipitation from toluene or THF into a non-solvent such as hexanes and can be cast into free-standing films again from toluene or THF. Following drying, characterization of the poly(ferrocenylsilane) **3** can be achieved by ^{1}H NMR spectroscopy. The iron centers of **3** can be readily oxidized by dipping a film of the material into a solution of iodine in hexanes; this leads to a blue coloration as the material is electrochromic. Reduction of the oxidized films to the neutral amber state can be achieved by dipping the film into a solution of a reducing agent such as methanolic hydrazine. Cyclic voltammetry gives insight into one of the most interesting characteristics of these polymers, the fact that two reversible oxidation waves are detected as the iron centers are redox coupled (oxidation of one center makes the neighboring iron centers more difficult to oxidize due to Fe•••Fe interactions).[4,5]





Most early syntheses of ferrocene-backbone polymers gave very low molecular weight products.[2,4] This is a result of the condensation routes used to prepare the materials where an exact 1:1 reaction stoichiometry of difunctional reactants, a necessary condition for the production of high molecular weights, was very difficult to achieve. Poly(ferrocenylsilane) **3** can be made via a condensation polymerization of dilithioferrocene•TMEDA with Me_2SiCl_2 in polar solvents such as THF,[6] however the molecular weight of the product is extremely low ($M_n <$ 2,000) which means that the chains are not long enough to take advantage of the processability characteristics of high molecular weight polymers. When pure **2** is used, the ROP route provides molecular weights of up to 4,000,000. This is an example of a chain growth type of polymerization, which leads to high molecular weight polymers much more readily than polycondensation, a step-growth route. It is noteworthy that this type of ROP route can be applied to a wide range of strained ferrocenophanes and other strained organometallic monomers.[4,7,8]

This experiment illustrates a combination of organometallic and polymer chemistry and illustrates a useful principle of polymer synthesis; that chain-growth polymerizations provide easy access to high molecular weight polymers compared to polycondensations.

Experimental Procedure

Note that this first part of session 1 needs to be performed at the end of the previous session !

Session 1a *Dilithiation of Ferrocene: Synthesis of **1**.*

NOTE: *n*-Butyllithium and dilithioferrocene are flammable in air and are very air sensitive. This will test your experimental expertise, the more air or water you let into the flask the poorer your yield will be. ABSOLUTELY <u>ALL</u> ASPECTS OF THIS EXPERIMENT <u>MUST</u> BE DONE IN A HOOD!

Weigh 6.0 g (32.6 mmol) of ferrocene and place it in a dry 24/40 200 mL Schlenk flask. The flask should be pre-dried in a hot (120-150°C) oven for at least 30 mins prior to use. Add 100 mL of hexanes (reagent grade) to the flask from a measuring cylinder followed by 4.5 mL of TMEDA from a plastic 10 mL disposable syringe (STENCH!!) (All disposable syringes should be placed in the syringe waste bucket!). Add a stir bar and flush the flask with nitrogen gas for 5 min and then place a rubber septum in the 24/40 joint. Using a 30 mL disposable syringe and a 12” (#16) syringe needle measure out 26 mL of a 2.5 M butyllithium solution in hexanes and add it quickly to the flask through the septum. The syringe needle should now be rinsed immediately with *tert*-butanol to destroy unreacted *n*-BuLi in order to prevent clogging of the needle. The reaction is now left stirring until the next lab period. Close the stopcock and ensure that the flask is sealed under a N_2 atmosphere. During this time, the initially cloudy orange solution turns clear red prior to the precipitation of orange dilithioferrocene.

Q. What is the soluble red-colored intermediate?

Session 1b *Synthesis of the Silaferrocenophane **2**.*

Under a flow of N_2 replace the septum on the flask with a small addition funnel and purge the system with nitrogen gas for 5 mins, do not purge too vigorously as this will evaporate the solvent **(CARE! flakes of dilithioferrocene may blow out of the flask and will ignite on contact with air, make sure no flammable materials e.g. paper, solvents are close to the vessel when the septum is removed)** Prepare a solution of dichlorodimethylsilane (4.5 mL) in hexanes (30 mL) and quickly place it in the addition funnel, then put the septum in the top of the funnel. Do not leave the dichlorodimethylsilane solution standing in air for an extended period, it will react with moisture and the reaction stoichiometry will be incorrect.

Q. What are the products of this hydrolysis and how will an imbalance in the stoichiometry affect your preparation of the monomer?

Cool the reaction flask to at least -10 ˚C using an ice/salt bath, (be sure the flask and its contents are adequately cooled to this temperature).

Q. Why does the ice/salt bath get cold? And why is it so important to control the temperature in this experiment?

Slowly add the dichlorodimethylsilane solution dropwise to the orange precipitate over a period of about 20 mins with stirring. Continue stirring the reaction at 0 ˚C for ca. 30 min, then allow the flask to warm to room temperature and stir for at least another 30 min. The resulting solution should be red after allowing the LiCl precipitate to settle. Prepare a dry 100 mL Schlenk flask with a stir bar and septum and fill it with N_2 by repeated evacuations and refills with N_2. The flask **MUST** have the 24/40 ground glass opening and should fit the sublimation finger in your kit (smaller size). Transfer the red solution into the 100 mL flask by cannula, a TA will explain how to do this. **DO NOT EXPOSE THE RED SOLUTION TO AIR!** Carefully remove the solvent on the vacuum line and dry under vacuum for 30 min. The flask may now be left under N_2 in the freezer until the next session.

Session 2 *Isolation of the Silaferrocenophane* ***2*** *by sublimation.*

Attach the flask to the Schlenk line and evacuate and refill at least three times, finishing with nitrogen in the flask. Be sure to check that the nitrogen supply is turned on and that the line has dry nitrogen in it before you begin. Under a flow of nitrogen, replace the septum in the 100 mL flask with a water-cooled sublimation finger and heat the flask under vacuum at ca. 50 ˚C for 15-20 min (use an appropriate amount of grease for the joint; it should turn smoothly). An orange film should appear on the cold finger, this is unreacted ferrocene. Admit N_2 to the flask, remove the finger and wash the ferrocene into a small beaker using hexanes. Dry the cold finger with a clean tissue and replace it in the flask. (If you have time, it helps to do this twice or three times to remove all the ferrocene). Continue heating at ca. 80 ˚C under high vacuum for 2 h. Note: care should be taken not to heat the sublimation flask above 90 ˚C as this may melt **2** and cause thermally-induced ROP of **2** to occur. Red crystals of the ferrocenophane **2** should form on the finger over time. Allow the flask to cool, and carefully blow all the water out of the cold finger using compressed air. Rinse with acetone and then blow out the acetone using compressed air and ensure the flask is under vacuum. Do not shake the flask. Carefully transport the flask to the dry box, with a clean small beaker, two clean dry 25 mL Schlenk flasks with septa (one of which should contain a micro stir bar), two small sample vials and a clean dry NMR tube with cap. In the dry box, very carefully weigh and transfer your product to the small flasks for thermal and metal-catalyzed polymerizations. The best way to do this is to scrape off the red crystals into the pre-weighed beaker and then transfer the sample to the flasks. Weigh ca. 1 g of monomer into each flask, noting the exact mass of monomer in each and the total mass (if you have less than 2 g of monomer, divide it equally between the two flasks). Leave the remainder of your monomer in a labeled vial the glove box. In addition, place about 20 mg of monomer in the vial and prepare an NMR sample in C_6D_6 (benzene-d^6), (PREPARE THE NMR SAMPLE IMMEDIATELY BEFORE OBTAINING THE SPECTRUM; COORDINATE THIS WITH THE NMR TECHNICIAN). Obtain ^{1}H and ^{13}C NMR spectra of **2**. The ^{29}Si NMR spectrum of **2** (Fspectrum1.pdf) is available online and should also be assigned. The thermal and metal-catalyzed polymerizations of **2** should be performed in the next session.

Session 3 Platinum-catalyzed *and thermal* ROP of the [1]Silaferrocenophane **2**;
Synthesis of the Poly(ferrocenylsilane) **3**.

1. *Pt-catalyzed ROP of **2**.* Add 10 mL of dry, degassed toluene to the red crystalline monomer **2** in the flask with the stir bar and, using a pipette, add 1 drop of the platinum catalyst provided (do not add more than one drop, but make sure that some catalyst is added to the solution). Stir the solution vigorously at r.t. until the end of the period, during which time the red suspension should fade to an orange-amber color At the end of the period the TA will take the flask and continue to stir it until the next lab period, when you will work up the resulting polymer.

2. *Thermal ROP of the [1]Ferrocenophane* ***2.*** Heat the other flask containing **2** under N_2 in an oil bath up to 140 °C. **Gradually increase the temperature** and observe the reaction, and be sure to heat to this temperature. The material melts (ca. 75 °C) and may change color from red to orange. The melt then becomes highly viscous and immobile as polymerization proceeds, 30 mins to 1 hour. Once the melt is immobile, allow the flask to cool and dissolve polymer **3** in THF (some gentle heating may be required). Add the solution dropwise by pipette to a beaker of hexanes (200 mL) with rapid stirring. The solution should be added slowly dropwise to the edge of the vortex of the vigorously stirred non-solvent. An orange precipitate of polymer should form. Continue stirring for 10 mins and then filter off the polymer on a filter paper. Obtain an ^{1}H NMR spectrum of this polymer sample ($CDCl_3$) and submit a sample in THF to the TA for Gel Permeation Chromatography (GPC)*. Be sure to run the NMR sample shortly after it has been prepared as the sample will slowly oxidize and broaden the NMR spectrum. Some samples may be cloudy, this is alright but may cause broadening of the signals. Also prepare a sample for thermogravimetric analysis (TGA).

If you have time, try to cast the film of this polymer before you leave so that the solvent evaporates between sessions. If not cast the film at the very beginning of the next session. The ^{29}Si NMR spectrum of **3** is available online and should also be assigned, (Fspectrum2.pdf).

Casting of Films of ***3****.* Free-standing amber films of **3** can be cast on glass in a small Petri dish by thinly spreading a concentrated solution in THF or toluene (ca. 0.5 g of **3** in 10 mL of solvent) and allowing the solvent to evaporate (over 2 - 24 h, or days). The film is best removed from the glass dish using a razor blade or a sharp knife.

* GPC gives an estimate of the molecular weight distribution in the polymer sample.

Session 4 *Purification of the Poly(ferrocenylsilane)* ***3****. Casting and Oxidation of Films of* ***3****.*

1. *Purification of* ***3****.* Add the solution from the Pt-catalyzed polymerization dropwise by pipette to a beaker of hexanes (200 mL) with rapid stirring. The solution should be added slowly dropwise to the edge of the vortex of the vigorously stirred non-solvent. An orange precipitate of polymer should form. Continue stirring for 10 mins and then filter off the polymer on a filter paper (the clear red solution left over contains unreacted ferrocenophane **2**, ferrocene, and possibly some oligomeric material and can be discarded). Redissolve the crude polymer in a *minimum* amount of THF, and reprecipitate into hexanes (200 ml). Filter off the polymer again, wash with hexanes (20 mL) and suck air through the orange powder for 10 mins to dry it. The cyclic voltammogram of the polymer should be measured as described in lab E, and should be discussed in your

report (compare with the result for ferrocene itself!). Also record a ^{1}H and ^{13}C NMR spectrum of your polymer in $CDCl_3$. Submit a sample to the TA for GPC and compare the GPC data of the polymers prepared by different methods. Lower molecular weight samples may have the appearance of a fine powder, whereas higher molecular weight polymers appear more rubbery and compressible. This polymer also should be processible and you can cast films (sometimes it is easier to use the polymer from the Pt-catalyzed polymerization for film formation).
Compare the ^{1}H NMR spectrum and the GPC results to those of the polymer obtained in the thermal reaction. Generally, the lower the purity of ***2****, the easier thermal ROP will take place and the lower the molecular weight of the product* ***3****.*

2. *Oxidation and Reduction of Films of* ***3.*** The amber films can be oxidized by dipping into a hexane solution of iodine. The blue-black films should be washed with hexanes from a wash bottle (care is needed as oxidation makes the polymer films much more brittle), to remove excess iodine. The films change color as a result of oxidation of the Fe^{II} sites to Fe^{III}. Reduction back to the amber form can be achieved by dipping the films in a solution of hydrazine in methanol. Submit samples of your films, both oxidized and reduced, with your lab report.
Q: How many Fe sites are oxidized by iodine? How does this correspond to your CV results?

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