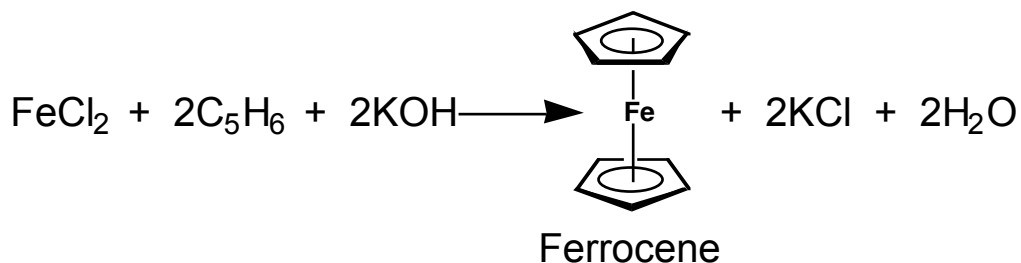


EXPERIMENT C

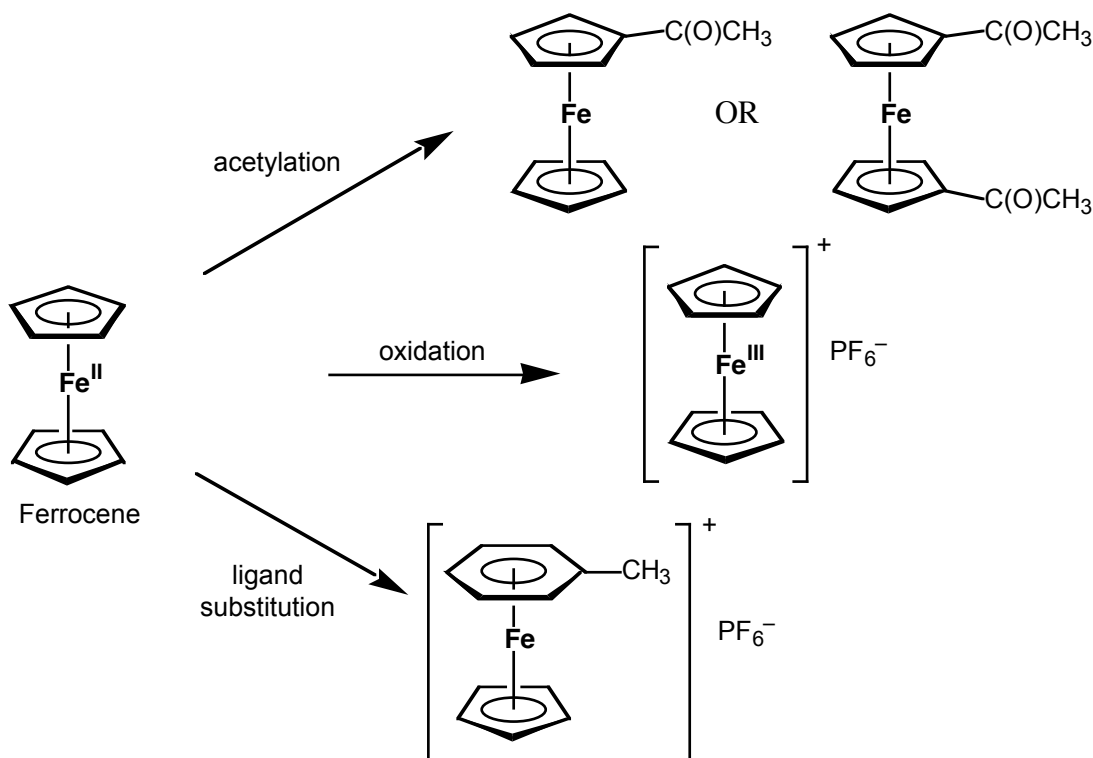
ORGANOMETALLIC CHEMISTRY

Reactions of bis(cyclopentadienyl)iron(II), ferrocene.

Bis(cyclopentadienyl)iron(II) or ferrocene was one of the first transition metal organometallic compounds to be prepared. The structure is shown below and consists of an Fe(II) center bonded to two η^5 -cyclopentadienyl (Cp) ligands. This type of complex is often referred to as a sandwich compound, and when the carbon based ligands are η^5 -cyclopentadienyl groups the complexes are referred to as metallocenes, MCp_2 . RuCp_2 , $[\text{CoCp}_2]^+$, and NiCp_2 are some examples of other metallocenes that have been synthesized and characterized.



In this experiment you will purify reagent grade ferrocene by sublimation and perform three reactions; (1) acetylation with acetic anhydride; (2) oxidation to the ferrocenium ion, $[\text{FeCp}_2]^+$; and (3) substitution of a cyclopentadienyl ligand with toluene.



**ALL MANIPULATIONS MUST BE CARRIED OUT IN A FUMEHOOD.
PROTECTIVE EYEGLASSES AND GLOVES MUST BE WORN.**

Session 1

1. Acetylation of Ferrocene.

Place 1.5 g of ferrocene (either sublimed or from the reagent bottle) in a small Erlenmeyer flask with 5 mL of acetic anhydride and add 1 mL of 85% phosphoric acid. Stopper the flask with a CaCl_2 drying tube and heat for 20 min. on a steam bath. Pour the mixture into 20 g of ice and when melted, neutralize the solution with solid NaHCO_3 until CO_2 evolution ceases. Cool the mixture for 30 min. in ice and suction filter the product, wash with water and air dry for 15 min. The product you have made is a mixture and will be purified using column chromatography in Session 2.

Q1. What is the mechanism for the acetylation ?

2. Oxidation of Ferrocene.

Place 0.5 g of ferrocene (either sublimed or from the reagent bottle) in a small Schlenk flask and add 2 mL of acetone and 8 mL of distilled water. Weigh 0.55 g of anhydrous FeCl_3 quickly and add to the solution. Stir under a nitrogen atmosphere for 30 mins. Prepare a solution of NH_4PF_6 in water (0.5 g in 5 mL) and add this to the reaction mixture. Cool in ice for 20 mins and filter off the product in air. Wash with ice cold water and air dry. Weigh your product and report a yield. Record an IR spectrum of your product as a KBr pellet.

Q2. Why is the color of the product so different?

Session 2

1. Purification of Products from the Acetylation of Ferrocene.

Place about 75 g of alumina in a short chromatography column and cover this with about one centimeter of purified sand. Flush the column with CH_2Cl_2 in order to wet the support. Dissolve your crude solid in about 20 mL of CH_2Cl_2 and add this solution to the top of the wet support. Allow the material to be absorbed by the column and flush with CH_2Cl_2 , (do not let the support go dry). Collect the first orange band that elutes and evaporate it to dryness either on a rotary evaporator or on the vacuum line. After the first band has eluted flush the column with acetone to elute the second darker orange band from the column, and evaporate this to dryness also. The second product will initially be an oil following evaporation of the solvent. Add 5 mL of diethyl ether to this oil and stir, followed by evaporation of the ether in vacuo. The product should now be a solid. Wash the solid with 5 mL of hexane and cool in ice for 10 mins. Collect the orange solid by suction filtration and dry in air. Get an IR spectrum (KBr pellet) of the **first** product (NO NMR needed!), and IR (KBr pellet), ^1H and ^{13}C NMR (CDCl_3) spectra as well as a GCMS of the **second** solid. You must determine what both products are from their spectroscopic data and determine the yield.

For comparison, also measure the IR spectrum of ferrocene as a KBr pellet, obtain ^1H and ^{13}C NMR spectra in CDCl_3 and run a GC-MS.

Q3. Explain in detail why one of the compounds elutes from the column first and the other one later.

Q4. Propose a reason for the difference in color of the two products.

2. Cyclic Voltammetry of Ferrocene and its acetylation products.

Cyclic voltammetry is a technique used to measure the redox properties of substances. The sample (ca. 1 mM) is dissolved in dichloromethane (ca. 15 mL) containing a supporting electrolyte (tetrabutylammonium hexafluorophosphate, ca. 0.1 M) in an electrochemical cell. A cyclic voltammogram is obtained by measuring the current flow through the solution at varying voltages. Peaks are observed at particular voltages and indicate oxidation or reduction of species at those voltages. Run spectra of the ferrocene precursor and the **second** acetylation product.

Q. Compare the CV plots for the two species and discuss them also in context with the preparative oxidation of ferrocene performed in session 1.

Session 3 (START IMMEDIATELY SO THAT YOU WILL FINISH IN TIME)

Substitution of a Cyclopentadienyl Ligand in Ferrocene by Toluene.

Make sure you have all the following apparatus before you start; 200 mL Schlenk flask; condenser; T- or stopcock adapter; tygon tubing; bubbler filled with paraffin oil. Place 10 g of anhydrous AlCl_3 in a 200 mL Schlenk flask (weigh this out very quickly and carefully, it is toxic and reacts with moisture to release HCl! DO NOT SNIFF IT!) and pump on the solid for 10 mins. Fill the flask with N_2 and under a positive pressure of nitrogen add 2.8 g of ferrocene and 0.7 g of Al powder (20 mesh or finer). Now add 50 mL of toluene and a stir bar, and make sure the solution is vigorously stirred with a heating mantle under the flask. Attach a condenser and heat the solution to reflux for 90 min. with a positive pressure of N_2 over it (NOT THROUGH IT!). While the solution is refluxing, prepare the NH_4PF_6 solution as described below[§] and get all the apparatus ready for the next steps.

Cool the flask to room temperature and carefully place it in an ice bath. VERY SLOWLY add 50 mL of ice-cold distilled water, and make sure the mixture is well stirred and mixed; all clumps of silvery material should be broken up to allow all the reactants to hydrolyze. Filter off the silvery aluminum gently by suction through a filter paper and separate the aqueous and toluene layers in a separatory funnel. Discard the toluene layer and further extract the aqueous layer twice with 10 mL portions of toluene until the color of the toluene is very pale yellow. Filter the aqueous fraction containing the product by gravity through a filter paper directly into the NH_4PF_6 [§] solution with some stirring. Allow the precipitate to stand for 10 mins in an ice bath. Filter the solid off by suction and dry under vacuum in a flask on the vacuum line. Weigh the product and record a percentage yield based on ferrocene. Obtain IR (KBr pellet), ^1H and ^{13}C NMR (d^6 -acetone) spectra of your product. A copy of the ^{31}P NMR (d^6 -acetone) spectrum of this product is available on the course website. Do not forget to assign this spectrum as well as those you obtained.

[§]Prepare a solution of ammonium hexafluorophosphate by dissolving 4 g in 30 mL of water.

Q. Propose a possible mechanism for this reaction!