

Microscale Preparation of Ferrocene¹

Introduction

The delocalized π -electron systems of aromatic molecules can overlap with d orbitals on metal ions to form d - π metal-ligand bonds. This gives rise to an interesting class of coordination complexes that are commonly referred to as "sandwich compounds" or "half-sandwich" compounds, so named because the metal ion lies parallel to both π -rings or facial to a single π -cloud of the aromatic ligand, respectively. The first example of this kind of complex was $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}$, bis(cyclopentadienyl)iron(II), commonly known as ferrocene. The symbol η before the ligand formula, pronounced "eta", describes the *hapticity* of the cyclopentadienyl ligand, i.e. the number of carbon atoms of the ligand bound to the metal atom. For example, $\eta^5\text{-C}_5\text{H}_5$ is pronounced "eta-5 cyclopentadienyl". As the systematic name suggests, the compound is formed between two C_5H_5^- cyclopentadienyl ions, each with its six-electron aromatic system bound to a single Fe^{2+} ion. The two rings may assume various orientations between fully eclipsed (D_{5h}) and fully staggered (D_{5d}) conformations (Fig. 1). The staggered configuration is more stable, but the barrier to rotation is less than 4 kJ mol^{-1} . In the crystalline solid, where intermolecular energies are of the same or greater magnitude than the barrier, molecules of different orientations are randomly distributed throughout the structure. Regardless of orientation, the basic sandwich structure is remarkably stable. The compound is highly stable and soluble in most organic solvents. Noteworthy, ferrocene undergoes facile electrophilic aromatic substitution reactions even more readily than benzene.

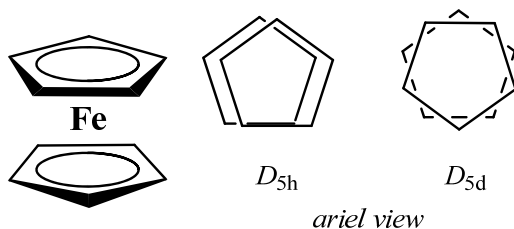
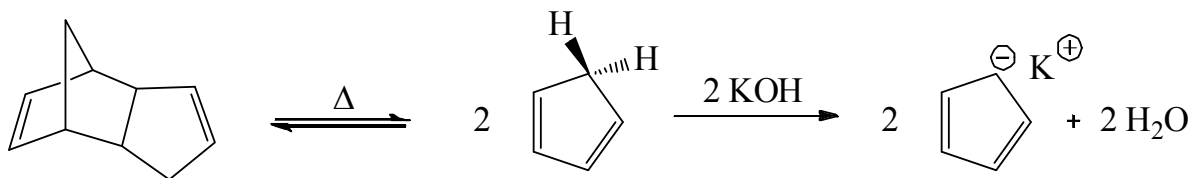


Figure 1.

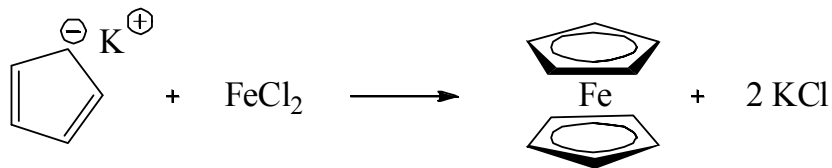
In this experiment we will prepare ferrocene under an inert (N_2) atmosphere. The starting material cyclopentadiene will be prepared in advance by a retro-Diels-Alder reaction via distillation of the dicyclopentadiene precursor. The burgundy-colored cyclopentadienyl ion will then be prepared by reaction with KOH in 1,2-dimethoxyethane as solvent (Scheme 1).



Scheme 1.

¹Adapted from Kenneth L. Williamson, *Macroscale and Microscale Organic Experiments*, D. C. Heath, Lexington, Mass., 1989, pp. 331 - 333.

A solution of FeCl_2 in dimethylsulfoxide is slowly added to the solution containing C_5H_5^- ions, resulting in formation of the pale orange ferrocene product. An inert atmosphere must be maintained throughout the preparation to prevent oxidation of Fe^{2+} to Fe^{3+} , which would prevent product formation. The crude product will be purified by sublimation to yield orange crystals.



Scheme 2.

Procedure

Cyclopentadiene should be prepared by the thermal cracking of dicyclopentadiene shortly before it is to be used. If necessary, the freshly prepared cyclopentadiene can be stored for several hours on dry ice ($-78\text{ }^\circ\text{C}$) to inhibit the slow dimerization that occurs at room temperature. The cracking is accomplished by slowly distilling dicyclopentadiene through a fractionating column, collecting only that material that collects between 42.5 and $44.0\text{ }^\circ\text{C}$. (cyclopentadiene boils at $42.5\text{ }^\circ\text{C}$, and dicyclopentadiene boils at $170\text{ }^\circ\text{C}$.) Sufficient quantity of cyclopentadiene will be prepared for your use prior to the laboratory session.

Solution #1. Using a mortar and pestle, grind approximately 1 g of KOH pellets to a powder. *Wear eye protection, use rubber or plastic gloves, and keep the work area free of spilled KOH.* In case of skin or eye contact, flush with copious quantities of water. Potassium hydroxide is very hygroscopic, so this process should be accomplished as quickly as possible to minimize contact with moist air. Quickly add 0.75 g of finely powdered KOH to a 5-mL short-necked, round-bottomed flask, followed by 1.25 mL of dimethoxyethane. Cap the flask with a septum and pass nitrogen into the flask or, better, through the solution for about 2 min. This is done by connecting a tank of nitrogen via a rubber tube to a 20 gauge needle and adjusting the nitrogen flow. Test the flow rate by bubbling it under a liquid such as acetone or extra dimethoxyethane. Once the nitrogen flow has been regulated, insert an empty 20 gauge needle through the septum of the flask as an outlet and then inset the 20 gauge nitrogen inlet (Fig. 2). Shake the flask vigorously to dislodge the solid KOH from the bottom of the flask while passing in nitrogen. This shaking will help to dissolve the solid and will also serve to saturate the solution with nitrogen.

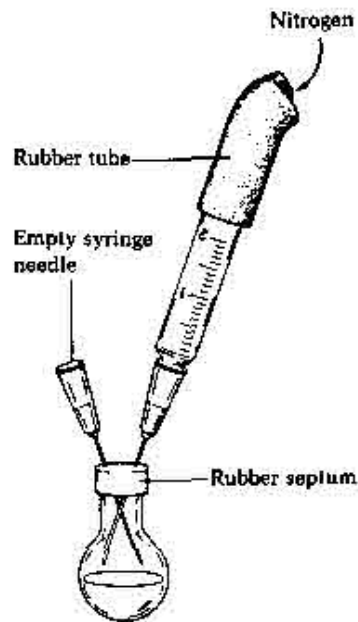


Figure 2.

Solution #2. To a 13 x 100-mm test tube add 0.35 g of finely powdered green $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and 1.5 mL of dimethyl sulfoxide. Cap the tube with a rubber septum, insert an empty 20 gauge needle through the septum and pass nitrogen into the tube for about 2 min to displace the oxygen present. Remove the needles and then shake the vial vigorously to dissolve all of the iron chloride. This can be a slow process, and some warming may be needed to speed dissolving.

Using an accurate syringe, inject 0.30 mL of freshly prepared cyclopentadiene into the flask containing the KOH. Shake the flask vigorously and after 5 minutes the color should change to a deep burgundy (not a pale pink). Next pierce the septum with an empty needle for pressure relief and immediately inject 0.20 mL of the FeCl_2 -DMSO solution. Immediately remove both needles from the septum and shake the flask vigorously for 2 min. Repeat this addition/shaking procedure another 5 times. Finally, after all of the FeCl_2 -DMSO solution has been added, rinse the reaction tube with 0.20 mL of DMSO and add this to the flask. Continue to shake the solution for about 10 min to complete the reaction. To isolate the crude ferrocene, pour the dark slurry into a mixture of 4.5 mL of 6 M HCl solution and 5 g of ice in a 30-mL beaker. Stir the contents of the beaker thoroughly to dissolve and neutralize the excess potassium hydroxide. Collect the orange ferrocene product on a Hirsch funnel, wash the crystals well with water, press out excess water, squeeze the product between sheets of filter paper to complete the drying, and then proceed *record the weight of your crude product.*

Ferrocene sublimes nicely at atmospheric pressure; vacuum sublimation is usually not needed. To sublime the ferrocene, obtain two same-type halves of a small Petri dish (i.e., two tops or two bottoms). Spread out your product in one of the Petri dish halves, and warm the crude product *gently* on a hot plate at its lowest setting for a few minutes to remove the last traces of moisture from the ferrocene. Then invert a same-size half Petri dish over the first half dish (Fig. 3).

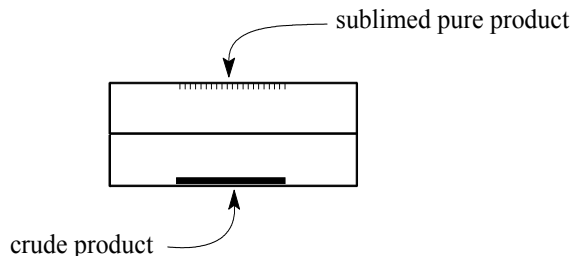


Figure 3.

Continue warming the crude product *gently* on the hot plate as pure product sublims on the inverted cover. The most common cause of product loss at this stage is overheating, with resulting scorching of the product. When sublimation is complete, transfer the pure product to a tared stoppered vial, determine the weight of sublimed product, and calculate the percent yield. Determine the melting point in a sealed (preferably evacuated) capillary tube, since the product

sublimes at the melting point. The melting point of pure ferrocene should be 173-174 °C.

Qualitative analysis. In a test tube, dissolve 2-3 crystals of ferrocene in approximately 3 mL of CCl₄. Transfer the solution back to the test tube, add 2-3 crystals of (NH₄)₂Ce(NO₃)₆, stopper and shake vigorously, maintaining the test tube under the fume hood at all times. Note any color changes and record the UV-vis spectrum. Explain your observations, giving a balanced chemical equation for the reaction that occurs.

Laboratory Report

1. Submit your sample, clearly labeled with the names of all group members participating in the preparation.
2. Your written report should include yield and percent yield of both crude and purified products, the melting point of the sublimed product, brief descriptions of any departures from the recommended synthetic procedure.
3. Give a fully balanced chemical equation for the reaction that occurs between ferrocene and (NH₄)₂Ce(NO₃)₆.
4. UV-vis spectra will be converted to text files and emailed to individual students. Spectra should be overlaid in MS Excel and their lowest energy absorptions normalized for comparison. Give adequate interpretation of differences in the UV-vis spectrum before and after reaction.