

# Microscale Preparation of Ferrocene<sup>1</sup>

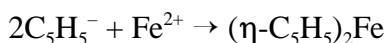
## Introduction

The delocalized  $\pi$ -electron systems of aromatic molecules can overlap with  $d$  orbitals on metal ions to form ligand-metal bonds. This gives rise to an interesting class of coordination complexes that are commonly referred to as "sandwich compounds", so named because the metal ion lies between the parallel rings of the aromatic molecules. The first example of this kind of complex was  $(\eta\text{-C}_5\text{H}_5)_2\text{Fe}$ , bis(cyclopentadienyl) iron(II), which is usually called ferrocene.<sup>2</sup> As the systematic name suggests, the compound is formed between two ligand  $\text{C}_5\text{H}_5^-$  ions, each with its six-electron aromatic system, bonded to an  $\text{Fe}^{2+}$  ion. The two rings may assume various orientations between fully eclipsed ( $D_{5h}$ ) and fully staggered ( $D_{5d}$ ). The staggered configuration is more stable, but the barrier to rotation is less than 20 kJ/mol. 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, and ferrocene undergoes ring substitution reactions even more readily than benzene. The compound is soluble in many organic solvents and is stable up to 500 °C.

In this experiment we will prepare ferrocene under an inert ( $\text{N}_2$ ) atmosphere. The burgundy-colored pentadienyl ion is formed first by reaction with KOH in solvent 1,2-dimethoxyethane:



A solution of  $\text{FeCl}_2$  in dimethylsulfoxide is slowly added to the solution containing  $\text{C}_5\text{H}_5^-$  ions, resulting in formation of ferrocene:



An inert atmosphere must be maintained throughout the preparation to prevent oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ , which would prevent product formation. Once obtained, the crude product will be purified by sublimation to yield shiny golden-orange crystals.

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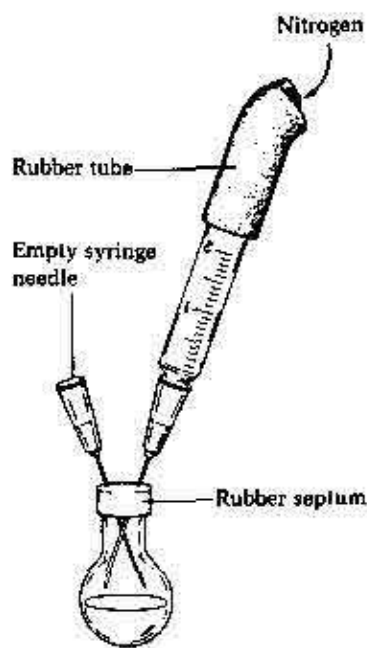
<sup>1</sup>Adapted from Kenneth L. Williamson, *Macroscale and Microscale Organic Experiments*, D. C. Heath, Lexington, Mass., 1989, pp. 331 - 333.

<sup>2</sup>The symbol  $\eta$  is now used in the formula for this and other sandwich compounds to indicate that all carbon atoms of the ring are bonded to the metal atom.

## 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 may have been prepared for you immediately prior to the laboratory session.]

Using a mortar and pestle, grind approximately  $1\text{ g}$  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  $0.75\text{ g}$  of finely powdered KOH to a  $5\text{-mL}$  short-necked, round-bottomed flask, followed by  $1.25\text{ mL}$  of dimethoxyethane. Cap the flask with a septum and pass nitrogen into the flask or, better, through the solution for about  $2\text{ min}$ . This is done by connecting a tank of nitrogen via a rubber tube to a  $22$  gauge needle and adjusting the nitrogen flow to a few milliliters per minute. 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  $18$  gauge needle through the septum of the flask as an outlet and then inset the  $22$  gauge nitrogen inlet. (See figure below.) 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.

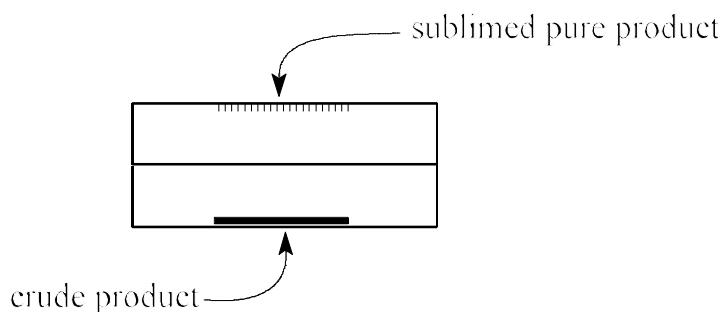


To a 13 x 100 mm reaction tube (test tube) add 0.35 g of finely powdered green  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  and 1.5 mL of dimethyl sulfoxide (DMSO). Cap the tube with a rubber septum, insert an empty 18 gauge needle through the septum and pass nitrogen into the tube for about 2 min to 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 glass syringe, inject 0.300 mL of freshly prepared cyclopentadiene into the flask containing the KOH. Do not grasp the body of the syringe, because the heat of your hand will cause the cyclopentadiene to volatilize. Shake the flask vigorously and note the color change as the potassium cyclopentadienide is formed. After several minutes the color should change to a deep burgundy (not a pale pink). After waiting about 5 min for the anion to form, pierce the septum with an empty needle for pressure relief and inject the  $\text{FeCl}_2$ -DMSO solution from the reaction tube in six 0.25-mL portions over a 10-min period. Between injections remove both needles from the septum and shake the flask vigorously. After all of the  $\text{FeCl}_2$ -DMSO solution has been added, rinse the reaction tube with 0.25 mL more DMSO and add this to the flask. Continue to shake the solution for about 15 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 all the excess potassium hydroxide. Collect the crystalline orange ferrocene 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 with purifying the ferrocene by sublimation. *Record the weight of your crude product.*

Ferrocene sublimates 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 the other same-size half Petri dish over the first half dish (see below).



Continue warming the crude product *gently* on the hot plate as pure product sublimes 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.

In a test tube, dissolve a few crystals of ferrocene in approximately 10 mL of  $\text{CCl}_4$ . In a separate test tube, dissolve a few crystals of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (or any other soluble Fe(III) salt) in approximately 10 mL of water. Observe the color of each solution. Then, add the  $\text{Fe}^{3+}(\text{aq})$  solution to the test tube containing the ferrocene solution. Stopper and shake. Let the two layers separate and observe the colors. Explain your observations, giving a balanced chemical equation for the reaction that occurs. Is this consistent with a +2 oxidation state for iron in ferrocene? Explain.

Take the infrared spectrum of ferrocene. Characteristic absorption bands in  $\text{cm}^{-1}$  and their relative intensities are 170 (m), 478 (s), 492 (s), 782 (w), 811 (s), 834 (w), 1002 (s), 1051 (w), 1108 (s), 1188 (w), 1411 (s), 1620 (m), 1650 (m), 1684 (m), 1720 (m), 1758 (m), 3085 (s). The complete interpretation of the spectrum has been given by E. R. Lippincott and R. D. Nelson, *Spectrochim. Acta* **1958**, *10*, 307.

### Laboratory Report

1. Submit your sample, clearly labeled with the names of all group members participating in the preparation.
2. Submit your infrared spectrum.
3. 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, and explanation of the reaction that occurs between ferrocene and  $\text{Fe}^{3+}(\text{aq})$ .