Microscale Preparation of Ferrocene[1]

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 (η^5-$C_5H_5)_2$Fe, or 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, η^5-C_5H_5 is pronounced "eta-5 cyclopentadienyl". As the systematic name suggests, the compound is formed between two $C_5H_5^-$ cycopentadienyl ions, each with its six-electron aromatic ring 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}. For example, only a single proton resonance is observed in its ^{1}H NMR spectrum. 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.
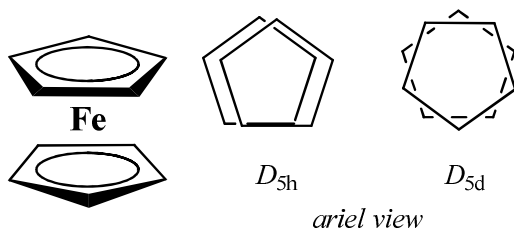

Figure 1.

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).
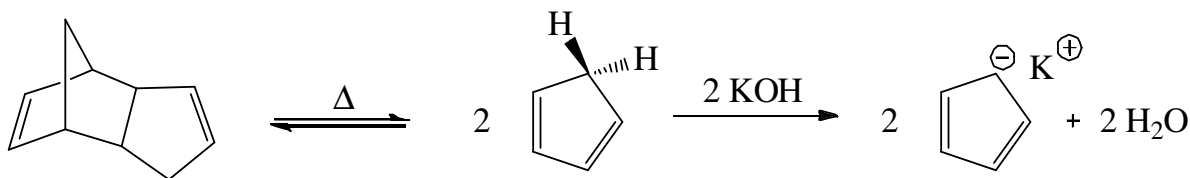
Scheme 1.

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[1] Adapted 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.
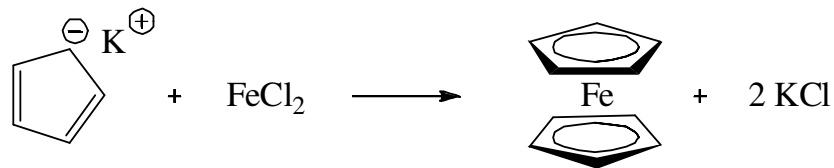
Scheme 2.

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 ^{o}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 ^{o}C. (cyclopentadiene boils at 42.5 ^{o}C, and dicyclopentadiene boils at 170 ^{o}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 hydroscopic, 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 dimethyoxyethane. Cap the flask with a septum and pass nitrogen into the flask or, better, through the solution for about 1-2 min. This is done by connecting a nitrogen source via a rubber tube to a 20 gauge needle and also inserting an independent syrine to maintain atmospheric pressure while adjusting the nitrogen flow. [Hint: Test the flow rate by bubbling it under a liquid such as acetone or extra dimethoxyethane prior to insertion into your reaction]. 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
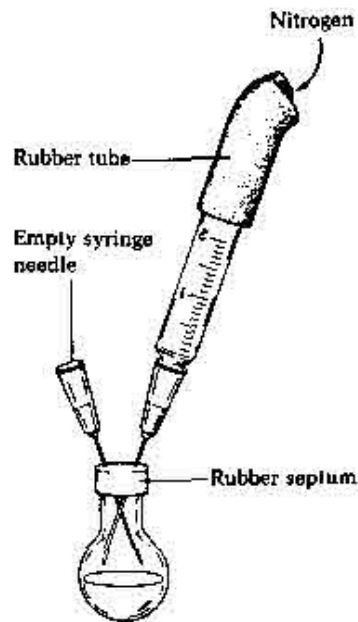

Figure 2.

passing in nitrogen. This shaking will help to dissolve the solid and will also serve to saturate the solution with nitrogen. After 1-2 min purging remove both needles and set the flask aside

Solution #2. To a test tube add 0.35 g of finely powdered green $FeCl_2\cdot 4H_2O$ and 2 mL of dimethyl sulfoxide. Immediately 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 gentle warming may be needed to speed dissolving (I emphasize gentle heating as this is a sealed vessel).

Using an accurate syringe, inject 0.30 mL of freshly prepared cyclopentadiene into the 5-ml round bottomed 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 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 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 small Petri dishes. Spread out your product in one of the Petri dishes 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 second Petri dish over the first dish with some ice placed on top to cool and help condense the gas phase ferrocene   (Fig.   3).
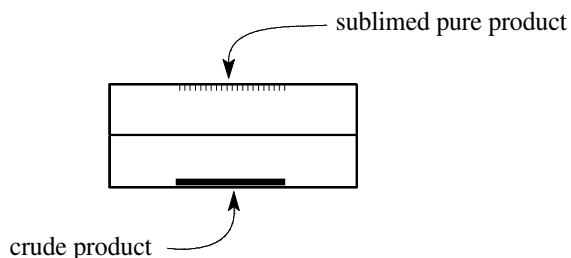

Figure 3.

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 pre-weighed glass vial, determine the weight of sublimed product, and calculate the percent yield. Determine the melting point in the fume hood (remember ferrocene will sublime upon heating).   The   melting   point   of   pure   ferrocene   should   be   173-174 ^{o}C.

Qualitative analysis. In a test tube, dissolve 2-3 crystals of ferrocene in approximately 3 mL of ethanol. Using this stock solution record a UV-vis absorption spectrum of your product using ethanol as a blank (ideally you want to observe an optical density of ~ 0.5 at 440 nm). Add 1-2 drops of 0.1 M aqueous ceric(IV) ammonium nitrate $(NH_4)_2Ce(NO_3)_6$ and mix the solution thoroughly using a pipette. Note any color changes and record the UV-vis spectrum again. 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. In the introduction give a full account of the Dewar-Chatt-Duncanson model for π-bonding in organometallic systems.

4. Give a fully balanced chemical equation for the reaction that occurs between ferrocene and $(NH_4)_2Ce(NO_3)_6$.

5. UV-vis spectra will be converted to text files and emailed to individual students. Spectra should be overlayed in MS Excel or an equivalent software following the instructions given below. Give adequate interpretation of differences in the UV-vis spectrum before and after reaction.

Processing UV-vis electronic absorption spectra:
These instructions allow for plotting the molar extinction coefficients for ferrocene and the ferricinium cation for direct comparison of both species. By overlaying plots of ferrocene and ferrocinium vs molar extinction coefficient we can make two important observations
  1. the wavelengths at which both samples absorb.
  2. how efficient each complex is at absorbing light across the UV-visible spectrum

A standard plot of just wavelength (X-axis) vs absorbance (Y-axis) will not allow comparison of how effectively each system can absorb light. As you might imagine such a comparison is critical when comparing dyes for photochemical applications.

Some basic stepwise instructions:

- Correct for baseline errors; as both samples do not absorb at 800 nm please correct both Fc and Fc+ data sets such that the absorption value at 800 nm = 0. This will require adding (or subtracting) a single value to (or from) the entire data set, e.g. if the Fc data reads an absorbance of 0.017 at 800 nm subtract 0.017 from that entire column of data. Once both sets of data have been corrected this will allow an accurate comparison of absorption maxima for both spectra once overlayed.
- Plot both sets of data overlayed on the same graph using Absorption vs. Wavelength.
- Set the wavelength range from 300 – 800 nm and adjust the absorption axis accordingly for a clear presentation of data.
- The molar extinction coefficient of ferrocene in ethanol at 440 nm = 90 M^{-1} cm^{-1}
  Remember Beer's law: "a = e.c.l"
  where a = absorption (no units); e= molar extinction coefficient (M^{-1} cm^{-1}); c = concentration (M); l = path length of cuvette (typically 1 cm). Rearrange Beers law to solve for the concentration of ferrocene in your first sample prior to oxidation: "c = a/e.l"
  (read "a" from the plot at 440 nm; e = 90 M^{-1} cm^{-1} at 440 nm; path length of the cuvette is 1 cm; now solve for "c"). Assuming that
  1. The volume of aqueous $(NH_4)_2Ce(NO_3)_6$ added to the solution was negligible
  2. Complete oxidation of ferrocene to ferricinium
     Then the concentration of ferricinium = concentration of ferrocene calculated above. Again using Beers law "a=e.c.l" solve "e" for ferricinium by reading its absorption maximum from the Absorption vs. Wavelength plot ; "e=a/c.l"

Finally, replot both sets of data but this time instead of Absorption vs. Wavelength plot as Molar Extinction Coefficient vs. Wavelength.
Remember from Beer's law that "e= a/c.l" and that each data set you have is in terms of absorption. Thus, we need to divide each data set by "c.l" (actually as "l = 1 cm" we need simply divide by the sample concentration calculated above). From this plot we can now compare how efficient each complex is at absorbing light across the UV-visible spectrum.

[Note: to understand units of "e" rearrange Beer's law such that "e = a/c.l" ; as "a" has no units the default units for "e" are the product of inverse concentration (M^{-1}) and inverse length (cm^{-1})]