The Microscale Synthesis of Ferrocene: Techniques

**Distillation of Cyclopentadiene**

-Dicyclopentadiene
Thermal cracking of dicyclopentadiene is used to obtain fresh cyclopentadiene (Cp) required for the synthesis of ferrocene. Using a simple distillation set-up, like that described by Woolins¹, add 2-3mL dicyclopentadiene to 1mL mineral oil (or silicone oil) in the reaction flask. Dicyclopentadiene is solid at room temperature and has a very strong odor; heat the reagent bottle to ~35°C using a sand bath in the fume hood until 2-3mL of liquid can be obtained. Be aware that dicyclopentadiene will solidify very quickly when cooled, much like wax. Warm glassware used to transport and distribute dicyclopentadiene to prevent solidification, which results in loss of reagent and smelly clean up.

-Distillation
Woolins suggests heating of the reaction vessel using a sand bath; this was found to be an ineffective method of controlling the temperature in the distillation flask. Instead, suspend the flask above a hot plate; alternatively, an oil bath may be used. The system must be flushed with nitrogen to create inert atmosphere conditions. To do this, use the Schlenk line- once the system has been sufficiently flushed, reduce nitrogen flow to a trickle. A very strong flow of the cold nitrogen into your reaction flask will lower the temperature in the flask and prevent the thermal cracking of dicyclopentadiene. The vacuum line out should also be set very low, as it could cause negative pressure in the system and lower the boiling point of the reactants. With these factors taken into consideration, set heat source to half power and allow the flask time to heat. If needed, increase heat in small increments or move flask closer to heat source until vapors in the flask become visible or begin to reflux. At this point, the nitrogen flow can be closed off while leaving the vacuum line slightly open. This will allow the vapors to travel up to the condenser and begin to distill without being cooled by the nitrogen flow. The thermometer at the distillation head should read between 40°C and 50°C, the boiling point of cyclopentadiene. Keep in mind that increasing the temperature too fast or raising the temperature too high will result in the vaporization of dicyclopentadiene, causing fuzzy white crystals to form in the receiving flask. If this happens, the distillation must be repeated. Once the cyclopentadiene (which should remain a liquid in the chilled receiving flask) begins to distill, no other adjustments need to be made to the set-up.
The Synthesis of Ferrocene

-Forming the Cyclopentadiene Salt
While the distillation of cyclopentadiene is taking place, a solution composed of 1.5g KOH and 2.5mL monoglyme can be prepared under inert atmosphere. Many procedures suggest the use of ethylene glycol as a solvent; this is NOT advisable, as ethylene glycol forms an extremely viscous solution when combined with cyclopentadiene. This solution is so viscous that stirring with a stir bar is impossible and a reaction cannot take place. The KOH must be ground in a mortar and pestle because it will usually come in the form of pellets or chips. Because KOH is very hygroscopic, grind the pellets or chips quickly and add to the monoglyme immediately. This addition results in an exothermic reaction, heating the solution. This solution must be cooled before the freshly distilled cyclopentadiene is added, as heat may cause cyclopentadiene to dimerize back into dicyclopentadiene. With the solution sufficiently cooled, add 600microliters of fresh cyclopentadiene to the flask. To do this while still maintaining inert atmospheric conditions, ensure that the flow of nitrogen out of the flask goes against the opening from which the cyclopentadiene is being added. The resulting solution may be brown, rose colored, black, or beige.

-Addition of Iron Chloride
Another solution, again under inert atmosphere, can be prepared from 750mg FeCl₂·H₂O in 2mL DMSO and added dropwise to the cyclopentadiene salt solution over 30 minutes. A color change may be observed here. Stir this solution for 15-20mins after all of the iron chloride solution has been added; the solution no longer has to be under inert atmosphere at this point. Prepare a mixture of 10g of ice and 8mL of 6M HCl and add it to the solution while continuing stirring, resulting in a green color change. Filter the resulting solution using vacuum filtration, saving the stir bar as it may be coated in the sticky product. Wash the solid with 5mL portions of water until the filtrate reads neutral using pH paper. Allow product to air dry for characterization.

-Purification
If required, the product can be sublimed to remove impurities. Remove as much of the solid product as possible from the stir bar and filter paper. Dissolve the remaining product from the filter paper and stir bar in methylene chloride, and then boil off the solvent to isolate the extracted product. Sublimate the solid by heating it to ~90°C in a beaker with a chilled watch glass covering the mouth of the beaker. Do not heat the beaker to above 100°C, as it may cause decomposition. Bright orange crystals should form on the watch glass, purified ferrocene.