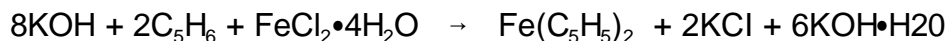




The Preparation of Ferrocene¹

[Bis(cyclopentadienyl)iron(II)]



Total time required: 1 day (or 5 hours if product dried *in vacuo*)
Actual working time: 4 hours

Preliminary study assignment: J. Birmingham, *Synthesis of Cyclopentadiene Metal Compounds*, Adv. Organometallic Chem., 2, 365, **1965**; G. E. Coates, M. L. H. Green, and K. Wade, *Organometallic Compounds*, Vol. 2, Methuen and Co., Ltd., London, **1968**, pp. 90-115; W. L. Jolly, *Inorg. Chem.*, **1967**, 6, 1435, and other standard texts.

Reagents required:

- 120 ml of 1,2-dimethoxyethane
- About 45 g of KOH pellets (protected from moisture)
- 8 ml of cyclopentadiene - obtained from the thermal cracking of dicyclopentadiene (3a,4,7,7a-tetrahydro-4,7-methanoindene)
- 9.5g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$
- 50 ml of dimethyl sulfoxide (DMSO)
- 60 ml of concentrated aqueous HCl
- About 140 g of ice
- Cylinder of nitrogen

Special apparatus required:

- Fractional distillation apparatus
- 300 ml three-necked (standard taper joints) round bottomed flask
- Magnetic stirrer and large stirring bar
- 100 ml dropping funnel, standard taper, pressure-equalizing
- T-tube Mineral oil bubbler
- Pyrex Petri dish with cover, 150 x 20 mm

Procedure:

The potassium hydroxide pellets are quickly ground with a mortar and pestle until the largest particles are less than 0.5 mm in diameter. Because it is very difficult to pulverize a large quantity of potassium hydroxide at one time, the pulverization should be carried out in batches of 15 g or less. It is important to minimize the exposure of the KOH powder to the atmosphere; therefore it is stored in a tightly capped tared bottle.

The cyclopentadiene is prepared by the thermal cracking of dicyclopentadiene. Dicyclopentadiene is slowly distilled through a fractionating column, collecting only that material which refluxes below 44° (cyclopentadiene boils at 42.5°, and dicyclopentadiene at 170°). If several students plan to prepare cyclopentadiene, it is advised that they cooperate in this step and distill at least 50 ml of dicyclopentadiene from a flask having a capacity twice the volume of the dicyclopentadiene. The receiving flask should be mounted in a beaker of ice. The freshly distilled cyclopentadiene must be used within 2 or 3 hours, or stored in the freezer compartment of the refrigerator for about two weeks, because slow dimerization occurs at room temperature.

¹Adapted from W. L. Jolly, *The Synthesis and Characterization of Inorganic Compounds*, 2nd Edition, Prentice-Hall, Inc., Englewood Cliffs, NJ, **1970**.

The magnetic stirring bar, 120 ml of 1,2-dimethoxyethane, and 35 g of powdered potassium hydroxide are placed in the three-necked flask. One side neck is stoppered and the other is connected to the T-tube mercury bubbler and the nitrogen cylinder. While the mixture is slowly stirred and the flask is being flushed with a stream of nitrogen, 8.0 ml of cyclopentadiene is added. The main neck is then fitted with the dropping funnel. After about 99 percent of the air has been flushed from the flask, a solution of 9.5 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ in 50 ml of dimethyl sulfoxide is placed in the dropping funnel. The mixture is stirred vigorously. After about 10 minutes, the drop-by-drop addition of the iron(II) chloride solution is begun. The rate of addition is adjusted so that the entire solution is added in 45 minutes. Then the dropping funnel stopcock is closed and vigorous stirring is continued for a further 30 minutes. Finally, the nitrogen flow is stopped, and the mixture is added to a mixture of 130 ml of 6M HCl and about 140 g of crushed ice. Some of the resulting slurry may be used to rinse the reaction flask. The slurry is stirred for about 15 minutes, and the precipitate is collected on a sintered glass funnel and washed with four 25-ml portions of water. The moist solid is spread out on a large watch glass and dried in the air overnight. The yield is about 8 g of ferrocene. This product should be quite satisfactory as an intermediate for subsequent syntheses. An extremely pure product can be obtained by sublimation. Purify about 2.0 g which is to be used for the characterization. Use the original product for the other parts of this experiment. The material to be sublimed is placed in the inverted cover of a Petri dish so that none of the material is within 2 mm of the side wall of the cover. The Petri dish itself (the smaller of the pair) is inverted and placed in the cover, and the apparatus is then placed on a hot plate. The hot plate is gradually warmed up until the top surface of the apparatus is almost too hot to touch. After 4 to 10 hours, the ferrocene should be completely sublimed onto the upper glass surface and should be completely separated from the small amount of residue on the bottom by a gap of several millimeters. If any of the ferrocene crystals are touching the residue, the temperature of the hot plate should be increased, and more time allowed for complete sublimation. The yield is about 8.0 g of ferrocene, melting at 173-174°.

Characterization:

The infrared spectrum of ferrocene may be determined by using either solutions in carbon tetrachloride and carbon disulfide or a KBr pellet. Absorption bands are observed at the following frequencies (in cm^{-1}): 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). A complete interpretation of the spectrum has been given by Lippincott and Nelson.²

The ultraviolet spectrum in ethanol or hexane shows maxima at 325 nm ($\epsilon=50$) and 440 nm ($\epsilon=87$), and rising short-wavelength absorption ($\epsilon=5250$ at 225 nm).

The ^1H and ^{13}C NMR spectra should be measured and the mass spectrum can be obtained.

²Lippincott, E. R.; Nelson, R. D., *Spectrochimica Acta*, **10**, 307, 1958.