

## Experiment VII.1

### Photochemical and Electrochemical Studies of an Organometallic Sandwich Compound

A landmark chemical event occurred in 1951 when the independent discovery of ferrocene, Figure 1, was reported by two groups. The first group proposed a  $\sigma$ -bonded structure,<sup>2</sup> and the following year the correct  $\pi$ -bonded structure was advanced.<sup>3</sup> Soon after, Fischer and Wilkinson independently reported the isoelectronic cobalt(III) compound.<sup>4</sup> The dynamic fluxional behavior of this family of "sandwich" compounds and their benzene-like electrophilic substitution reactions stimulated academic research in this area. Fischer and Wilkinson were awarded the Nobel prize for their work in 1973.

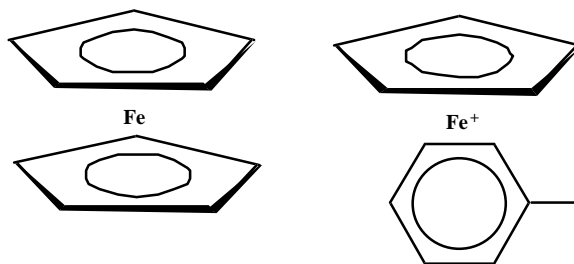


Figure 1.

You have previously prepared ferrocene, in the Advanced Organic Laboratory, and have discussed its fascinating fluxional behavior. In this laboratory, you will build on this knowledge and prepare a different iron(II) sandwich compound,  $[\text{CpFe}(\text{tol})]\text{PF}_6$ , where Cp is  $\eta^5\text{-C}_5\text{H}_5$  and tol is  $\eta^6\text{-toluene}$ . In the early 1970's Russian workers discovered that this compound undergoes a variety of interesting photochemical reactions.<sup>5</sup> Specifically, they noted that when  $[\text{CpFe}(\text{tol})]^+$  is photolyzed in acetonitrile equal concentrations of ferrocene and  $[\text{Fe}(\text{CH}_3\text{CN})_6]^{2+}$  are obtained in high yield. At low temperature the purple photo-intermediate  $[\text{CpFe}(\text{CH}_3\text{CN})_3]^+$  could be characterized. If the photolysis is performed in the presence of added ligands, L, then substituted complexes of the type  $[\text{CpFe}(\text{CH}_3\text{CN})_{3-n}(\text{L})_n]^+$  can be isolated. When chelating ligands such as phenanthroline (phen) are present the tris chelated species,  $\text{Fe}(\text{phen})_3^{2+}$  is formed quantitatively. All the photochemical reactions are summarized in Figure 2.

Because all the species in Figure 2 are redox active, the course of the reactions can be monitored by electrochemical techniques. Electrochemistry, in particular cyclic voltammetry, is a very useful tool for characterization of inorganic compounds and for

elucidating the mechanism of photochemical processes. The fundamental aspects of cyclic voltammetry will be discussed in the recitation period and are available through outside reading.<sup>6</sup>

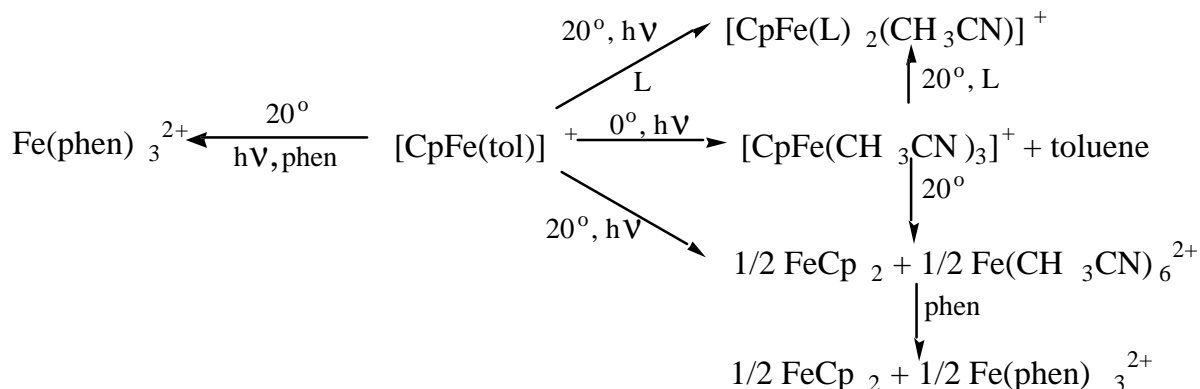


Figure 2.

### Hazards

**Acetonitrile** (CAS No. 75-05-8): Acetonitrile is harmful if swallowed, inhaled, or adsorbed through the skin. Overexposure has caused reproductive disorders in laboratory animals. ORL-RAT LD50: 2730 mg/kg.

**Diethyl ether** (CAS No. 60-29-7): Diethyl ether is an extremely flammable solvent. Exposure to moisture tends to form peroxides, which may be explosive. The solvent is a potent narcotic. ORL-MAN LDLo: 260 mg/kg. ORL-RAT LD50: 1215 mg/kg.

**Hexane** (CAS No. 110-54-3): Hexane is harmful if swallowed, inhaled, or absorbed through the skin. It is a flammable liquid. ORL-RAT LD50: 28,710 mg/kg.

**Methylene chloride** (CAS No. 67-63-0): Methylene chloride (dichloromethane) is harmful if swallowed, inhaled, or absorbed through the skin. It is a possible carcinogen. ORL-HMN LDLo: 357 mg/kg. ORL-RAT LD50: 1600 mg/kg.

**Toluene** (CAS No. 108-88-3): Toluene is a flammable liquid. ORL-HMN LDLo: 50 mg/kg. ORL-RAT LD50: 5000 mg/kg.

### Experimental Procedure.

#### A. Synthesis and Purification of $[\text{CpFe}(\text{tol})]\text{PF}_6$

Begin by placing 1.25 g of ferrocene, 0.25 g aluminum powder, a stir bar, and 2.5 g of aluminum chloride in a side-arm round bottom flask equipped with an addition funnel. Evacuate any purge three times with inert gas. Add 20 mL of argon saturated

toluene and 0.12 mL of argon saturated water with stirring. Reflux this mixture for two hours under argon.

Prepare 50 mL of a water-ice mixture. After the toluene solution has refluxed for two hours, carefully (with gloves) add it to the water-ice mixture with stirring. Transfer as much solid as possible from the side-arm flask to the Erlenmeyer. Any resulting chunks should be broken up with a glass rod. The resulting mixture is then transferred to a separatory funnel.

In the separatory funnel, the yellow or yellow-green aqueous layer containing the product is separated from the organic layer. The aqueous layer contains a mixture of species including the desired product. Add to this mixture 0.13 g of ascorbic acid to reduce any ferricinium ion,  $[\text{Fe}(\text{Cp})_2]^+$ , to ferrocene. Extract this solution three times with 25-mL portions of hexane to remove the ferrocene and then slowly suction filter to remove the remaining aluminum metal.

Prepare a solution of 1 g of  $\text{NH}_4\text{PF}_6$  in 5 mL of water and add this gradually to the filtrate with stirring to form a yellow precipitate of crude  $[\text{CpFe}(\text{tol})]\text{PF}_6$ . Stir for three minutes. If the mother liquor is still quite yellow, add more  $\text{NH}_4\text{PF}_6$ . Stir for about ten minutes and suction filter the crude product.

The product is purified by allowing a  $\text{CH}_2\text{Cl}_2$  solution of the iron salt to pass through a short column of alumina. The teaching assistant will help you prepare the alumina column. Wrap aluminum foil around the column before adding the crude product to minimize room light exposure. The volume of eluted solution is reduced to about 3 mL, and the yellow micro-crystalline product is precipitated with about 10 mL of diethyl ether. Weigh the product and store it until next week.

### B. Electrochemistry and Photochemistry of $[\text{CpFe}(\text{tol})]\text{PF}_6$

Begin today's experiment by making cyclic voltammetry (CV) measurements with ferrocene. This will allow you to familiarize yourself with the instrumentation and techniques used in electrochemical studies. Prepare a mM ferrocene solution in 0.1 M tetra-n-butylammonium hexafluorophosphate (TBAH) in acetonitrile. A three electrode arrangement with a glassy-carbon working electrode, a platinum-wire auxiliary electrode and a  $\text{Ag}/\text{AgNO}_3$  reference electrode will be employed. Obtain cyclic voltammograms from -0.50 to +1.00 V vs  $\text{Ag}/\text{Ag}^+$  at 20, 50, 100 and 200 mV/s. From this data construct a table containing  $E_{1/2}$ , the peak currents, the ratio of the two currents  $i_{pa}/i_{pr}$ , and the peak separation as a function of scan rate. Record a good quality CV at 200 mV/s. Also plot  $i_p$  vs  $(\text{scan rate})^{1/2}$ .

Now prepare a 20 mL solution  $\sim 10^{-5}$  M [CpFe(tol)]PF<sub>6</sub> in 0.1 M TBAH in acetonitrile. If your material is pure you should observe no electrochemistry over this range. Purge the solution with argon and extend the negative potential limit -1.30 V. Record a good quality CV at 200 mV/s.

Place this solution in front of a white light source for ten minutes and record the CV. If a large amount of starting material is still present, continue the photolysis for another fifteen minutes. When essentially no [CpFe(tol)]PF<sub>6</sub> is observed record a quality CV at 200 mV/s.

Add 14.0 mg of 1,10 phenanthroline (phen) to the photolyzed solution with stirring. Allow the reaction to proceed for at least five minutes. Now record the CV from -0.500 to +1.800 V at 200 mV/s. Measure the area under any waves observed. Bubble argon through the solution and extend the negative limit to -1.80 V. Record the CV carefully once. This will reduce the Fe(II) by two electrons and deposit a passivating elemental iron film on the electrode surface. If you do not produce a quality CV on the first attempt: 1) turn the potentiostat to stand-by; 2) remove the working electrode and wipe the iron film away with an acetone-soaked tissue; and 3) replace the electrode and try again.

## References

1. This experiment is adapted from: 1) Szafran, Z.; Pike, R.M.; Singh, M.M. "Microscale Inorganic Chemistry: A Comprehensive Laboratory Experience", **1991**, John Wiley & Sons, New York, NY, pg 235; and 2) Boyd, D.C.; Johnson, B.J.; Mann, K.R. *J. Chem. Ed.* **1992**, *69*, A315.
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