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# Electrochemical Synthesis of Organometallic Pi-Complexes

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## **Abstract**

Organometallic compounds have been known for over fifty years. However, synthesizing the basic metallocenes is at best a fairly long and complex process. Electrochemistry can often simplify complex reactions, so this experiment attempted to simplify the creation of organometallic pi-complexes using electrochemistry. Two iron electrodes were used in electrolysis at a fairly low current (5 mA) for extended periods of time to synthesize ferrocene in a dimethyl sulfoxide (DMSO) solution containing cyclopentadiene and an electrolyte, tetra-n-butylammonium hexafluorophosphate. Hexanes, hydrochloric acid, and anhydrous sodium sulfate were used to extract the ferrocene, which was subsequently purified through sublimation. The product was characterized positively as ferrocene through IR and UV-Vis spectrophotometry, thin layer chromatography (TLC), and melting point. Electrochemical synthesis and characterization of other known metallocenes is ongoing.

# Electrochemical Synthesis of Organometallic Pi-Complexes

## Introduction

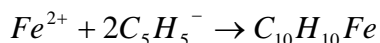
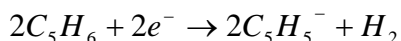
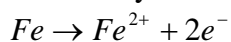
Organometallic chemistry is a branch of chemistry dealing with organometallic compounds, which are compounds that contain at least one carbon-metal bond. Because of the duality of these compounds, organometallic chemistry contains aspects of both inorganic and organic chemistry. Organometallic compounds are often used as catalysts, most notably in the processing of petroleum.

There is a specific group of organometallic compounds called the metallocenes, which consist of metal ions sandwiched between cyclopentadienyl rings. The first and most studied of the metallocenes is ferrocene, which was first discovered in 1951. Ferrocene is an iron II ion in between two cyclopentadienyl rings and has an orange color. It is the only metallocene that is air-stable, making it easier to study than the other metallocenes. Purification is quite simple, as ferrocene sublimates at a fairly low temperature.

Synthesis of the metallocenes, however, is not such a simple task. All of the conventional syntheses require creating the cyclopentadiene anion, cyclopentadienyl, from cyclopentadiene, then adding some form of the metal ion. For ferrocene, ferrous chloride (or ferric chloride reduced to ferrous chloride) is usually used. There are several difficulties with these procedures. They require several steps; none can be set up and left running. Not all the metal ions required to form the metallocene compounds are stable in the correct ionic state. In ferrocene syntheses, ferrous iron rapidly oxidizes to ferric iron, reducing yields if a reducing agent is not present. The many extra chemicals needed to work around the previous difficulties also complicate extraction of the product.

Electrochemical synthesis of metallocenes would simplify matters greatly. Electrochemistry can allow direct creation of a product in many syntheses without many intermediate products, and there is no reason to expect metallocenes to be any different. An electrochemical synthesis can be set up and left running. Other than the extraction, no other supervision of the reaction is needed. The ions needed are constantly formed at the anode, creating a virtually unlimited source of metal ions. Any excess ions are reduced and form on the cathode. Cyclopentadiene in solution forms its anion at the cathode. The only nonreactants in the reaction flask are the solvent and an electrolyte to carry a current. With less chemicals, extraction is also much easier. Despite the apparent simplicity of electrochemical synthesis, however, there are still many variables that could disrupt the reaction. To date, there is nothing in the literature on electrochemical synthesis of the metallocenes.

Ferrocene was chosen as the first compound to attempt to synthesize electrochemically because of its stability in air. The reactions are as follows:



## Procedure

### Materials

#### *Equipment*

- 250 mL boiling flask (round bottom flask)
- Fractionating column
- Steel wool
- Condenser (West condenser)
- 3-way thermometer adapter
- Thermometer
- Power supply and matching wires with alligator clips
- Rubber septa with holes (for the wires)
- Three-neck 500 mL round bottom flask
- Matching cap or septum with a syringe
- Magnetic stirring rod
- Hot plate / magnetic stirrer
- Crystallizing dish or large waterproof container
- Buchner or Hirsch Funnel
- Filtration flask
- Vacuum line

#### *Chemicals*

Dicyclopentadiene was cracked to form cyclopentadiene. Electrodes used were platinum, iron, and nickel (wire or foil). Solvents were chosen based on the solubility of cyclopentadiene in them, so all were organic or had organic characteristics. A particularly effective solvent was dimethyl sulfoxide (DMSO). Others that were used include acetone, acetonitrile, methanol, toluene, and tetrahydrofuran. Electrolytes were also chosen based on solubility. The main electrolyte used was tetra-*n*-butylammonium hexafluorophosphate, although tetraethylammonium perchlorate was occasionally used. Other chemicals included iron (II) chloride tetrahydrate (ferrous chloride), hydrochloric acid, and hexanes. Sources of nitrogen gas and crushed ice will also be needed.

### Methods

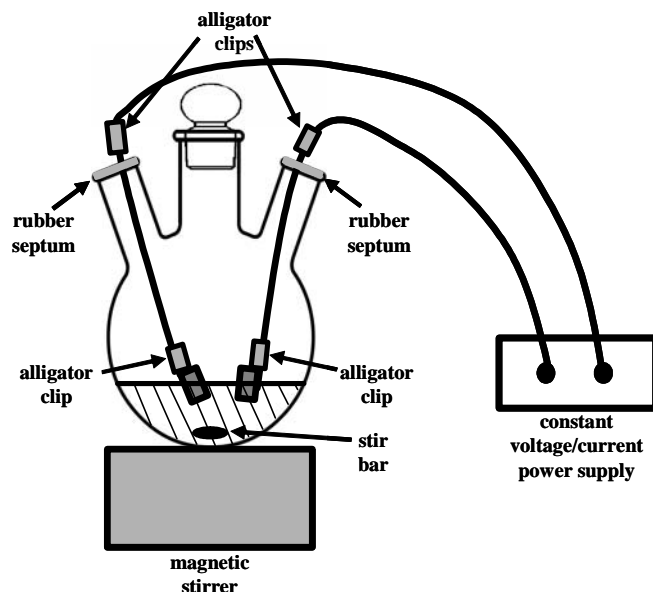
#### *Preparation of Cyclopentadiene*

Cyclopentadiene dimerizes to form dicyclopentadiene, so dicyclopentadiene needed to be cracked to form cyclopentadiene prior to usage. A fractional distillation setup with a thermometer was used for the cracking. Although keeping the collection vessel at a low temperature (dry ice temperature is best) helps slow the dimerization process, it was not done in this experiment. Dicyclopentadiene was poured into the heating flask along with an ample amount of boiling stones. Since dicyclopentadiene is a solid at room temperature, its container was warmed before use. The heating flask was heated until the dicyclopentadiene started bubbling and the temperature in the vapor column reached 40°C. Colorless and transparent cyclopentadiene started dripping into the collection vessel around that time. After that, the temperature in the vapor column

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was kept at 40°C for the remainder of the distillation. Ideally, fresh cyclopentadiene should be distilled for each experiment. However, cyclopentadiene can be kept in a freezer to significantly slow dimerization if needed, so each batch of cyclopentadiene was stored in a freezer and used for several trials.

### *Electrochemical Synthesis*



The equipment needed for electrochemical reactions is fairly simple. A power supply capable of constant voltage/current operations with its matching wires and a three-necked flask are the only essential pieces of equipment. A magnetic stirrer/hot plate and a magnetic stir bar are highly helpful in maintaining solution consistency, and a crystallizing dish or other waterproof container is helpful in keeping the reaction cool via a water or ice bath. All the above mentioned equipment was used in all of the later trials.

The solvent, electrolyte, and magnetic stir bar were added first into the flask. The magnetic stirrer was switched on to help dissolve the electrolyte. The two metal electrodes were then inserted through the two side necks of the flask and sealed with their septa. The cyclopentadiene was added last to lower the amount of dimerization. After all the reactants were in the flask, nitrogen gas was bubbled through the solution for a few minutes. The middle neck was immediately sealed with a cap or a vented septum (with a syringe) once the nitrogen line is removed. The power supply was set to maintain either a constant current or voltage, and the reaction was started.

### *Ferrocene Synthesis*

Successful ferrocene synthesis was obtained twice using the following parameters. 100 mL of dimethyl sulfoxide (DMSO) was used as the solvent, and about 0.28 g of tetra-n-butylammonium hexafluorophosphate was used as the electrolyte. The amount of cyclopentadiene used in both successful syntheses was 1.2 g (1.5 mL). A cap was used instead of a vented septum to seal because the amount of hydrogen gas produced was negligible. The current was kept constant at 5 mA, while the voltage varied from 20 V to 25 V. The two reactions that were successful were run for 405 minutes and 24 hours.

### *Product Extraction*

One of the more difficult parts of syntheses is extracting and isolating a specific product. The problem with using DMSO as a solvent is its high boiling point; it is

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extremely difficult to evaporate. A procedure was developed to isolate organometallic pi-complexes from the overall product in DMSO.

The DMSO solution is poured into a 500 mL extraction funnel, and a flask is placed underneath. 40 mL of hexanes are added to the funnel, and the flask is capped and shaken well, with regular release of gas using the stopcock. Bubbles or foam may form from the DMSO and hexanes. The hexanes layer may not even be visible at first. The foam should mostly subside ten or twenty minutes. Some color should transfer into the hexanes layer. The DMSO (bottom) layer is drained along with any remaining foam, while the hexanes (top) layer is poured out into a separate flask. The drained DMSO solution is then put back into the funnel, and the wash with hexanes is repeated three more times, for a total of four washes. In the final wash, wait as long as possible for the foam to completely subside. If some foam remains, keep in with the hexanes solution.

The hexanes solution is then put into the funnel and washed with 40 mL of 1M HCl two times. The HCl is drained off after each wash, and the hexanes solution is kept in the funnel. After the HCl washes, anhydrous sodium sulfate is added to rid the hexanes of any remaining water. The hexanes will easily evaporate in an evaporating dish or a beaker, leaving the metallocene.

### *Product Characterization*

The resulting product may be characterized in a number of ways. The cleaned hexanes solution may be used for thin layer chromatography (TLC) to determine purity and give a rough characterization of the product. TLC works best if a known sample of the product is dissolved in hexanes and run alongside the product for comparison. The cleaned solution can also be used in visible and IR spectrophotometers to determine the spectrum of the product. Mass spec and melting point determination can also be used to reinforce characterization of the product.

## Results

Trial Summary Chart

	Electrodes: black, red (1)	Electrolyte (2)	Solvent (3)	Cpd? (4)	Other (5)	Environment (6)	Voltage/ Current (7)
T1	Pt-w, Fe-f	TBA HFP	DMSO	Yes	N/A	Air, capped	300 V
T2	Pt-w, Fe-w	TBA HFP	Acetone	Yes	N/A	N <sub>2</sub> , constant	50 mA
T3	Pt-w, Fe-w	TBA HFP	Acetonitrile	Yes	N/A	N <sub>2</sub> , capped	50 mA
T4	Pt-w, Fe-w	TBA HFP	DMSO	Yes	N/A	N <sub>2</sub> , vented	50 mA
T5	Pt-w, Fe-w	TBA HFP	DMSO	Yes	N/A	N <sub>2</sub> , vented	
T6	Pt-w, Fe-w	TBA HFP	Methanol	Yes	Hxy HCl	N <sub>2</sub> , bubbled	10 mA
T7	Pt-w, Fe-w	TBA HFP	DMSO	Yes	N/A	N <sub>2</sub> , vented	10 mA
T8	Pt-w, Pt-w	TBA HFP	DMSO	Yes	FeCl <sub>2</sub> ·4H <sub>2</sub> O	N <sub>2</sub> , capped	10, 140 mA
T9	Pt-w, Pt-w	TEA ClO <sub>4</sub>	DMSO	Yes	FeCl <sub>2</sub> ·4H <sub>2</sub> O	N <sub>2</sub> , capped	50 mA, 300 V
T10	Pt-w, Pt-w	TBA HFP TEA ClO <sub>4</sub>	Toluene Methanol	Yes	FeCl <sub>2</sub> ·4H <sub>2</sub> O	N <sub>2</sub> , capped	50 mA
T11	Pt-w, Pt-w	TBA HFP	DMSO	Yes	FeCl <sub>2</sub> ·4H <sub>2</sub> O	N <sub>2</sub> , vented	50 mA
T12	Pt-w, Fe-w	TBA HFP	DMSO	Yes	N/A	N <sub>2</sub> , vented	50 mA
T13	Pt-w, Fe-f	TBA HFP	THF	Yes	N/A	N <sub>2</sub> , capped	300 V
EF	Pt-w, Pt-w	TBA HFP	DMSO	No	Ferrocene	N <sub>2</sub> , sealed	
T14	Fe-w, Fe-w	TBA HFP	DMSO	Yes	N/A	N <sub>2</sub> , sealed	5 mA
T15	Fe-w, Fe-w	TBA HFP	DMSO	Yes	N/A	N <sub>2</sub> , sealed	5 mA
N1	Ni-w, Ni-w	TBA HFP	DMSO	Yes	N/A	N <sub>2</sub> , sealed	5 mA

Notes:

- (1) "w" means wire was used, "f" means foil was used
- (2) TBA HFP: tetra-n-butylammonium hexafluorophosphate  
TEA ClO<sub>4</sub>: tetraethylammonium perchlorate
- (3) DMSO: dimethyl sulfoxide  
THF: tetrahydrofuran
- (4) Indicates whether or not cyclopentadiene was present in the electrolysis
- (5) N/A: no other chemicals present in electrolysis  
Hxy HCl: hydroxylamine hydrochloride
- (6) Capped: sealed using appropriate cap  
Constant: constantly pumped gas  
Sealed: sealed using septum  
Vented: sealed using septum with small syringe inserted  
Bubbled: constant bubbling of gas in solution
- (7) Values given are the constant set in the electrolysis. If two values are given, the constant changed during the reaction.

### Reactions of Note

Coarse brown particles forming: T2, T3

Stringy and sticky products forming: T6

No color change: T13

Electrolyzing ferrocene: EF

Successful Syntheses of Ferrocene: T14, T15

Selected Trial Summaries

*T1*

Black electrode: Platinum wire                      Red electrode: Iron foil  
Electrolyte: tetra-n-butylammonium hexafluorophosphate, 0.1435 g  
Solvent: dimethyl sulfoxide (DMSO), 100 mL  
Cyclopentadiene: 1.7 g  
Environment: air, sealed with cap; ice bath after 20 minutes  
Voltage: 300 V, constant                      Current: around 42 mA

The color quickly began turning gold and continually grows more intense with time. The flask also began warming at an alarming rate, so the flask was placed into an ice bath 20 minutes into the reaction without stopping the current. Unfortunately, DMSO freezes at slightly below room temperature, so most of the solution froze, unbeknownst to the researcher. At 120 minutes, the reaction was shut off, and the frozen solution was noticed. The DMSO was melted by raising it to room temperature. The resulting mixture appeared dark brown. A solution of 90 mL 6M HCl and about 100 g of crushed ice was prepared, and the result of the reaction was added to the acid solution. The mixture turned dark green, with some brownish particles on top. It was filtered using a Butener funnel and qualitative filter paper, but only some dark brown stains that were impossible to isolate remained in the filter paper.

*T2*

Black electrode: Platinum wire                      Red electrode: Iron wire  
Electrolyte: tetra-n-butylammonium hexafluorophosphate, 0.0981 g  
Solvent: acetone, 160 mL  
Cyclopentadiene: 11.06 g  
Environment: nitrogen gas, constant purging; ice bath  
Voltage: 126 V, went up                      Current: 50 mA, constant

The color turned gold very quickly. However, coarse brown particles started appearing and swirling around in solution. The liquid level dropped significantly over the course of the reaction. Because of the dropping liquid level, the power supply was shut off at 135 minutes. The mixture was first filtered through qualitative filter paper, which caught a dark brown cakelike substance that dried and broke up. Crushing and attempting to sublime the substance was not successful, so the substance was not ferrocene. The filtrate was filtered through hardened filter paper twice, leaving brown and orange powder. Sublimation also didn't work for the powder.

*T3*

Black electrode: Platinum wire                      Red electrode: Iron wire  
Electrolyte: tetra-n-butylammonium hexafluorophosphate, 0.1091 g  
Solvent: acetonitrile, 100 mL  
Cyclopentadiene: 11.15 g  
Environment: nitrogen gas, sealed with cap; water bath  
Voltage: 85 V                      Current: 50 mA, constant

The solution turned cloudy when cyclopentadiene was added to the solvent/electrolyte. After 5 minutes, the cap popped off, presumably because of the

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hydrogen gas generated at the platinum electrode. It was quickly dried and replaced. Brownish particles like the ones in T2 quickly began appearing, so the reaction was stopped at 9 minutes.

### T4

Black electrode: Platinum wire                      Red electrode: Iron wire  
Electrolyte: tetra-n-butylammonium hexafluorophosphate, 0.0992 g  
Solvent: dimethyl sulfoxide (DMSO), 100 mL  
Cyclopentadiene: 10.44 g  
Environment: nitrogen gas, sealed with vented septum; water bath  
Voltage: 300 V to 232 V                      Current: 41 mA to 50 mA (constant)

The solution starts turning olive green, and eventually turns dark green and finally to dark brown. The power was shut off at 125 minutes, and the iron electrode was blackened.

### T5

Black electrode: Platinum wire                      Red electrode: Iron wire  
Electrolyte: tetra-n-butylammonium hexafluorophosphate, 0.1042 g  
Solvent: dimethyl sulfoxide (DMSO), 99 mL  
Cyclopentadiene: 14.31 g  
Environment: nitrogen gas, sealed with vented septum; water bath  
Voltage: unknown                      Current: probably constant 10 mA

After 15 minutes, the reaction was stopped. The color was very dark green or brown, and it appeared stable.

### T6

Black electrode: Platinum wire                      Red electrode: Iron wire  
Electrolyte: tetra-n-butylammonium hexafluorophosphate, 0.1918 g  
Solvent: methanol, 100 mL  
Cyclopentadiene: 8.63 g  
Environment: nitrogen gas, constant bubbling through solution; water bath  
Voltage: 2-3 V                      Current: 10 mA (constant)

The solution turned cloudy when cyclopentadiene was added to the solvent/electrolyte. As the reaction proceeded, something stringy and white began forming on the bottom of the flask. The reaction was run for 45 minutes, during which the solution began turning transparent and gained a slight orange hue. As the solution was exposed to air, it kept getting more orange. The stringy substance formed was quite sticky, and it did not dissolve in water. Acetone slowly dissolved the substance.

### T7

Black electrode: Platinum wire                      Red electrode: Iron wire  
Electrolyte: tetra-n-butylammonium hexafluorophosphate, 0.0992 g  
Solvent: dimethyl sulfoxide (DMSO), 100 mL  
Cyclopentadiene: 10.44 g  
Environment: nitrogen gas, sealed with vented septum; water bath  
Voltage: 190 V, then 300 V (constant)                      Current: 10 mA (constant)



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The reaction was first run at a constant current of 10 mA. During that time, the solution turned olive green. After that, the reaction was run at a constant voltage of 300 V for 10 minutes. The solution turned orange in that period. The UV-Vis spectrum of the solution was taken every 10 minutes into the reaction. The peak absorbance seemed to shift, but it is most likely because one peak grows and begins covering up another one.

### T8

Black electrode: Platinum wire                      Red electrode: Platinum wire  
Electrolyte: tetra-n-butylammonium hexafluorophosphate, 0.23 g  
Solvent: dimethyl sulfoxide (DMSO), 81 mL  
Cyclopentadiene: 5.16 g  
Other chemicals: Iron II chloride tetrahydrate, 3.5598 g in 21 mL DMSO  
Environment: nitrogen gas, bubbled then sealed with vented septum; water bath  
Voltage: 100 V, drops after FeCl<sub>2</sub> added    Current: 10 mA to 140 mA (constant)

The reaction was run with two platinum electrodes. The intent was to try to generate cyclopentadienyl electrochemically, and then add the iron 2+ ion manually like in traditional syntheses. The ferrous chloride solution was added 20 minutes into the reaction. By then, the solution had taken on a faint orange hue. After the ferrous chloride was added, the solution turned green. At 60 minutes, the current was raised to a constant of 140 mA. This caused the solution to begin turning gold, and something black began collecting on the platinum electrode. The reaction was stopped at 70 minutes.

### T9

Black electrode: Platinum wire                      Red electrode: Platinum wire  
Electrolyte: tetraethylammonium perchlorate, 0.23 g  
Solvent: dimethyl sulfoxide (DMSO), 80 mL  
Cyclopentadiene: 5.36 g  
Other chemicals: Iron II chloride tetrahydrate, 3.3892 g in 20 mL DMSO  
Environment: nitrogen gas, bubbled then sealed with vented septum; water bath  
Voltage: 155 V to 300 V                      Current: 50 mA (constant)

The reaction was run with two platinum electrodes. The intent was to try to generate cyclopentadienyl electrochemically, and then add the iron 2+ ion manually like in traditional syntheses. The cathode (black) broke 23 minutes into the reaction, causing the reaction to stop. The ferrous chloride solution was added over 5 minutes, causing the solution to quickly turn dark green. The solution was stirred for 20 minutes, but no precipitate formed. The result was added to 50 mL of 6M HCl and 50 g of crushed ice, causing the solution to turn tallow and a large layer of whitish particles to form on top. A filtration caught particles similar to the ones in T1.

### T10

Black electrode: Platinum wire                      Red electrode: Platinum wire  
Electrolytes: tetra-n-butylammonium hexafluorophosphate, 0.3122 g  
                  tetraethylammonium perchlorate, 0.3227 g  
Solvents: toluene, 80 mL; methanol, 63 mL  
Cyclopentadiene: 10.4 g  
Other chemicals: Iron II chloride tetrahydrate, 4.0606 g in 21 mL DMSO

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Environment: nitrogen gas, bubbled then sealed with septum; ice bath at 10 minutes

Voltage: 227 V to 163 V to 290 V after ice bath      Current: 50 mA (constant)

The tetrabutylammonium was not soluble in toluene, but was partially soluble when methanol was added. The tetraethylammonium was not soluble in the mixture. When methanol was added, the solution turned cloudy, but began clearing up when the electrolysis started. The black electrode lets off a constant and thick stream of bubbles, but there is no apparent color change. The electrolysis was stopped at 270 minutes, and the ferrous chloride solution was added over 40 minutes. There was no apparent change in the solution, besides a color change to the color of the ferrous chloride solution, a slight gold.

### T11

Black electrode: Platinum wire                      Red electrode: Platinum wire

Electrolyte: tetra-n-butylammonium hexafluorophosphate, 0.2277 g

Solvent: dimethyl sulfoxide (DMSO), 80 mL

Cyclopentadiene: 6.1 g

Other chemicals: Iron II chloride tetrahydrate, 2.0703 g in 20 mL DMSO

Environment: nitrogen gas, bubbled then sealed with vented septum; water bath

Voltage: 219 V to 168 V                      Current: 50 mA (constant)

This reaction was conducted identically to T9, with only a change of electrolyte. Each time the black electrode broke, it was replaced. Once the fourth wire broke at about 110 minutes, the reaction was stopped. The ferrous chloride was added the next day.

### T12

Black electrode: Platinum wire                      Red electrode: Iron wire

Electrolyte: tetra-n-butylammonium hexafluorophosphate, 0.2271 g

Solvent: dimethyl sulfoxide (DMSO), 100 mL

Cyclopentadiene: 6.4 g

Environment: nitrogen gas, bubbled then sealed with vented septum; water bath

Voltage: 189 V to 153 V                      Current: 50 mA (constant)

This reaction was left running overnight. Unfortunately, the iron electrode broke during that time. It lasted at least 2 hours and 41 minutes, and no more than 18 hours, 31 minutes. The color changed from tan to a deep orange in the first two hours, and was dark brown by the next day.

### T13

Black electrode: Platinum wire                      Red electrode: Iron foil

Electrolyte: tetra-n-butylammonium hexafluorophosphate, 0.4809 g

Solvent: tetrahydrofuran, 100 mL

Cyclopentadiene: 1.6 g (2 mL)

Environment: nitrogen gas, bubbled then sealed with cap; water bath

Voltage: 300 V                      Current: 15 to 11 mA

Large bubbles began forming on the iron electrode. Where they popped, blue-green spots appeared. An orange precipitate formed on the platinum electrode. Eventually, transparent and colorless goo formed on the iron electrode, and the orange

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precipitate from the platinum electrode fell off into the solution. At the end of the reaction, the platinum electrode was coated with something black, most likely iron.

### T14

Black electrode: Iron wire

Red electrode: Iron wire

Electrolyte: tetra-n-butylammonium hexafluorophosphate, 0.2816 g

Solvent: dimethyl sulfoxide (DMSO), 100 mL

Cyclopentadiene: 1.2 g (1.5 mL)

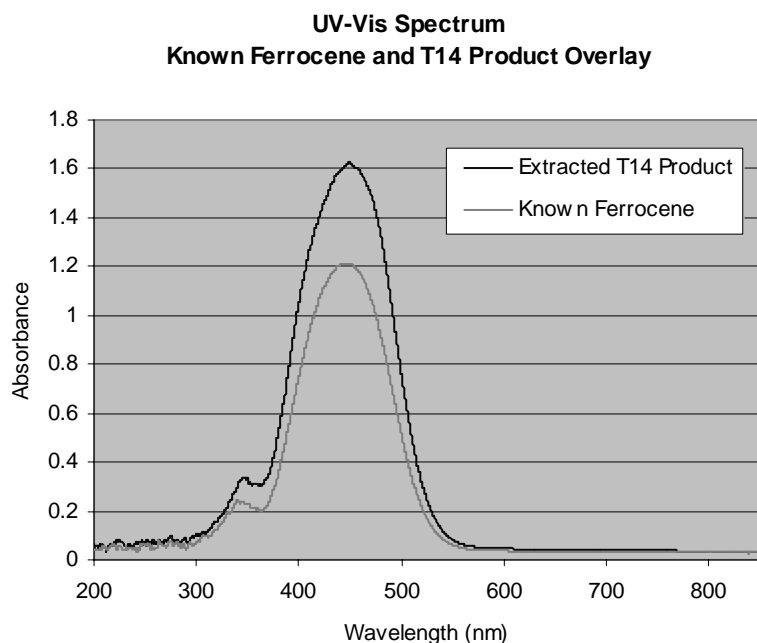
Environment: nitrogen gas, bubbled and sealed with septum; water bath

Voltage: 25 V

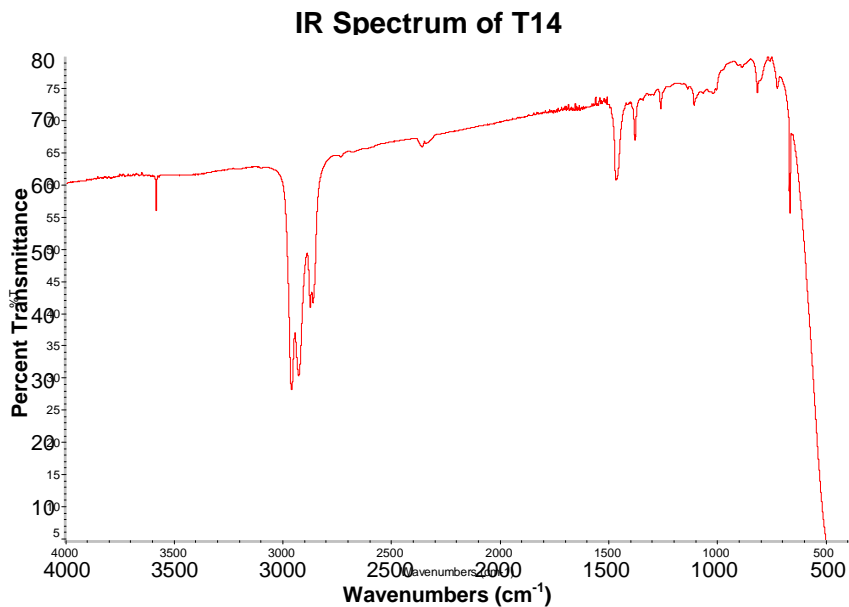
Current: 5 mA (constant)

The reaction was run for 24 hours, periodically taking UV-Vis spectra of the solution. Solution color changed from yellow to very dark orange at the end of the reaction. The copper alligator clip for the black electrode was blackened, but the iron electrode appeared clean. The copper alligator clip for the red electrode was clean, but the iron electrode below the solution was slightly blackened. Product extraction was performed on the solution with four (4) 40-mL hexane washes, two (2) 40-mL 1M HCl washes, and a purge with anhydrous sodium sulfate. No further attempt was made to purify this sample before characterization.

A thin layer chromatography (TLC) in a 1:1 toluene/hexanes (by volume) solution of the purified product was run alongside a solution of known ferrocene in hexanes. The yellow spots advanced at the same rate, fairly close to the line of liquid. A picture was taken after the toluene/hexanes solution dried off the plate but before the yellow spots vanished from the plate through sublimation.



A solution of known and purified ferrocene in hexanes was prepared. The UV-Vis spectrum of the known ferrocene solution and the spectrum of the T14 product in hexanes were compared. The comparison is shown in the overlay chart to the left. Their spectra are exactly the same; both have large peaks in absorbance at about 450 nm and smaller ones at about 350 nm.



IR spectra of the known ferrocene solution and the T14 product in hexanes were also taken and compared. There were four distinctive peaks in the T14 spectrum that weren't in the spectrum of known ferrocene; one at a wavenumber of about 1250

$\text{cm}^{-1}$ , and three between wavenumbers of  $2800 \text{ cm}^{-1}$  and  $3000 \text{ cm}^{-1}$ . However, the group of three peaks is present in a known spectrum of ferrocene from the Aldrich Catalog of FT-IR Spectra. The peaks of the T14 spectrum match the peaks of the known ferrocene in every other way. There are distinctive peaks at wavenumbers of 800, 100, and  $1100 \text{ cm}^{-1}$ , and three smaller ones at wavenumbers around  $1900 \text{ cm}^{-1}$ . Since no attempt at purification of the product was made before characterization, some contaminants might have remained. Irregardless, there is enough correlation in the spectra to conclude that ferrocene was produced.

### T15

Black electrode: Iron wire

Red electrode: Iron wire

Electrolyte: tetra-n-butylammonium hexafluorophosphate, 0.2754 g

Solvent: dimethyl sulfoxide (DMSO), 100 mL

Cyclopentadiene: 1.2 g (1.5 mL)

Environment: nitrogen gas, bubbled and sealed with septum; water bath

Voltage: 20 V

Current: 5 mA (constant)

The reaction was run for 405 minutes, periodically taking UV-Vis spectra of the solution. Otherwise, the reaction proceeded exactly like T14, up to and including the washes.

The resulting hexanes solution was allowed to dry. The remaining product was placed into a sublimation apparatus and heated to about  $60^\circ\text{C}$ . Orange crystals formed on the cold finger over a period of 7 hours. The crystals, weighing 0.0098 g, were collected, and some was used in a melting point determination alongside a known sample of ferrocene. The synthesized ferrocene melted at  $172\text{-}174^\circ\text{C}$ , while the known sample melted at  $171\text{-}173^\circ\text{C}$ . The two are close enough to conclude that they are the same compound, namely ferrocene.

### N1

Black electrode: Nickel wire

Red electrode: Nickel wire

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Electrolyte: tetra-n-butylammonium hexafluorophosphate, 0.2780 g

Solvent: dimethyl sulfoxide (DMSO), 100 mL

Cyclopentadiene: 1.2 g (1.5 mL)

Environment: nitrogen gas, bubbled and sealed with septum; water bath

Voltage: 19 V

Current: 5 mA (constant)

This was the only attempted synthesis of a metallocene other than ferrocene. The solution starts looking green at about 20 minutes, and eventually turns an olive green color. Product extraction was performed on the solution with four (4) 40-mL hexane washes, two (2) 40-mL 1M HCl washes, and a purge with anhydrous sodium sulfate. The resulting olive green solution was evaporated under vacuum in two separate centrifuge tubes. The next day, one was completely evaporated, leaving a yellowish brown residue behind. The other solution was not evaporated. IR and UV-Vis spectra were taken. The IR spectra was similar to the nickelocene spectra from the Aldrich Catalog of IR Spectra

## Conclusions

Dimethyl sulfoxide (DMSO) is not a very common solvent, but it appears to work well for these electrochemical syntheses. When acetone (T2) and acetonitrile (T3) were used, coarse brown particles quickly began appearing, and the solution level dropped significantly over time, indication that acetone and acetonitrile are unsuitable for these reactions. Acetonitrile (T3) and methanol (T6) solutions turn cloudy when cyclopentadiene is added, but they clear up as the reaction progresses. Toluene (T10) simply does not dissolve the electrolytes used, even when combined with methanol. There was also no apparent color change when toluene/methanol was used. Tetrahydrofuran (T13) causes something that appears to be a film to appear on the iron anode. DMSO was the only solvent tested that did not produce strange results. Ideally, DMSO should have been dried of all water, but no special care was taken to dry any of the solvents for these reactions.

Tetra-*n*-butylammonium hexafluorophosphate was the main electrolyte used. It produces current to voltage ratios of 1 mA to 4 V or 5 V in DMSO. Tetraethylammonium perchlorate was occasionally used, but not alone often enough to determine its effectiveness as an electrolyte.

Nitrogen gas was bubbled through solution to get rid of any air inside the reaction flask for most of the reactions. Some metal ions or products may not be stable in air, so the reaction is conducted under nitrogen as a safeguard.

Using two platinum electrodes to generate the cyclopentadiene anion before adding the metal as a salt is not viable because the black electrode constantly and consistently breaks, at least at high currents (T9, T11). Using a platinum cathode and a metal anode may not work long-term, since the iron electrode in T12 broke sometime between 3 and 18 hours (left overnight). Two of the same metal electrodes seems to work well, since an iron-iron reaction ran for 24 hours straight, albeit at a low current (T14). The iron-iron combination also produced a solution from which ferrocene was extracted.

All successful reactions were run at a constant current of 5 mA. However, since the extraction process was not developed until later in the experiment, the initial trials at higher currents may have produced their intended products. Time constraints prevented retesting at higher currents.

Extraction of the metallocene product through hexanes and HCl wash and with anhydrous sodium sulfate works fairly well. Some metallocenes are not air-stable, however, so some difficulty did arise in keeping those compounds in an air-free environment during extraction. Since only organic compounds are soluble in hexanes, any excess metal ions will remain in the DMSO. Tetra-*n*-butylammonium hexafluorophosphate is also not soluble in hexanes.

A TLC against a known sample of the metallocene is a quick method of determining the product and the effectiveness of the extraction. IR and UV-Vis spectra can definitively characterize the product, and checking the melting point reinforces that characterization.

Electrochemical synthesis of metallocenes is entirely possible. The main benefit over conventional syntheses is the simplicity of electrochemical reactions. With the extraction process developed, synthesis and isolation of metallocenes becomes much

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easier. However, the yields from the syntheses were fairly low. The low current at which the successful reactions were run would take over a day to in theory synthesize even a gram of product. One of the problems of using DMSO as a solvent is its high freezing point; cyclopentadiene will eventually dimerize if not kept very cold, limiting the time a reaction can be run for. However, DMSO will freeze if the reaction put inside an ice bath, much less a dry ice bath. The extraction process, although successful, has not been optimized for maximum yield. Future research could focus on synthesis and characterization of other metallocenes. Work also needs to be done on improving the synthesis and extraction processes to improve yields. Although the door to electrochemical syntheses of organometallic pi-complexes has been opened, there is still much to explore.

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