

An Introduction to Aromatic Organometallic Syntheses: Ferrocene

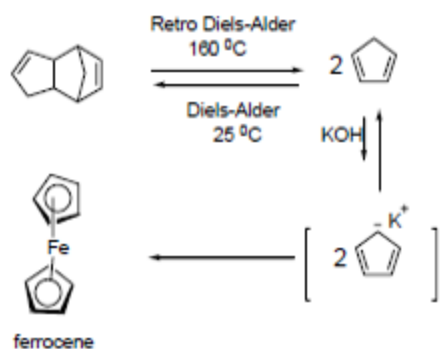
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ABSTRACT

Aromatic organometallic compounds have played an important role in organic synthesis. Organometallic compounds containing transition metals are of particular interest because of the involvement of d orbitals in bonding, coordination complex formation, and interactions with aromatic electron systems. Ferrocene was synthesized using an established procedure, as outlined in Scheme 1.



Scheme 1 – Synthetic Scheme for production of ferrocene
From INTRODUCTION TO ADVANCED SYNTHESIS, CHEM
4330/6330, Lab Manual, Fall 2026 Edition, Georgia State University

Cyclopentadiene was obtained by cracking dicyclopentadiene and then treated with a strong base to generate the cyclopentadienyl anion. The anion subsequently reacted with an iron (II) salt ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) to produce ferrocene. The product was isolated and purified by sublimation, after which its melting point was determined, and its identity and purity were evaluated using proton nuclear magnetic resonance (^1H NMR) and carbon-13 nuclear magnetic resonance (^{13}C NMR) spectroscopy. The measured melting point was close to the literature value, and both NMR spectra exhibited a single product signal, consistent with the spectroscopic characteristics of ferrocene. The purified yield projected a mass of 2.1 g, based on crude mass and the purification of a small sample. The corresponding projected percent yield was 34% of total theoretical product.

Ferrocene derivatives exhibit a diverse range of properties that make them valuable in several areas of research, including medicinal chemistry, catalysis, industrial applications, fuel additives, and optoelectronic materials. These varied applications continue to motivate research into ferrocene and its derivatives.

Keywords: Organometallic; ferrocene; cracking; sublimation.

1.0 INTRODUCTION

Organometallic compounds are generally defined as compounds containing at least one direct chemical bond between a carbon atom and a metal atom. The metals involved may include alkali metals, alkaline earth metals, and transition metals. Broader definitions may also encompass compounds containing bonds between carbon and certain metalloids, such as boron or silicon, although their classification as organometallic compounds depends on the definition used.

Organometallic reagents have long played an important role in organic synthesis, serving as sources of carbon-based groups for the formation of new carbon–carbon bonds. Their use dates back nearly two centuries, with organometallic chemistry subsequently expanding to include a wide range of reagents, such as organolithium compounds, Gilman reagents (organocuprates), and metal alkoxides.

Of most interest in this paper are metallocenes, compounds with two negatively charged aromatic rings sandwiching a transition metal ion. Some of the more well-known examples include cobaltocene, nickelocene, titanocene dichloride (an unconventional metallocene), and the compound synthesized in this experiment, ferrocene. These compounds exhibit distinctive bonding, due to the delocalized π -electron system of the cyclopentadienyl ligand, forming what is referred to as a η^5 bond, more accurately, η^5 denoting coordination hapticity. The η^5

bonding is simultaneously from the transition metal ion and all 5 carbons of the cyclopentadiene ring.¹

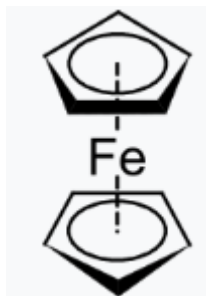


Figure 1 Ferrocene structure (public domain, Wikipedia)

The structure and bonding in ferrocene were worked on and published in the early 1950's by Ernst Fischer and Reinhard Jira. Quoting their paper "With three π -electron pairs from each of the parallel aromatic cyclopentadiene anions, the central Fe^{II} ion achieves six octahedrally arranged, coordinative covalencies and thus obtains the krypton configuration".² Hans Jaffé, in 1953, and Leslie Orgel / Christopher Longuet-Higgins, in 1954, quantified how the Fe 3d orbitals (such as 3d π and 3d δ) symmetry-match and overlap with the π -orbitals of the cyclopentadienyl rings, explaining its extraordinary stability.³ The iron's 3d orbitals interacting with the π electrons of the aromatic rings, satisfy the 18-electron rule for stable transition metal complexes.^{4,5} The η^5 -3d orbital bonding (more accurately η^5 -3d, 4s, and 4p [iron]) was backed up with computational work done in 1976, by P. S. Bagus, U. I. Walgren, and J. Almlof.⁶

The stability and unique character of ferrocene make it useful in many areas. Given its unique electronic and structural properties, ferrocene has found applications in a wide range of fields, such as performance enhancing and emission reducing fuel additives; electrochemical sensors; organic reaction catalysts; and medicinal chemistry in the development of a wide range of drugs.^{7,8}

The synthesis of ferrocene described in this paper relies on the activation of cyclopentadiene using a strong base, potassium hydroxide (KOH). The unusual acidity of the methylene hydrogens on the sp^3 -hybridized carbon of cyclopentadiene stems from the high stability of its conjugate base. Deprotonation yields the aromatic cyclopentadienyl anion, which satisfies Hückel's rule with $[4n+2]$ π electron system. This resonance and aromatic stabilization gives cyclopentadiene a remarkably low pK_a of about 16.^{9,10}

This experiment explores the synthesis of ferrocene, utilizing cyclopentadiene, freshly cracked from dicyclopentadiene and activated with potassium hydroxide, then reacted with ferrous chloride under inert gas conditions. Exposure to oxygen can promote oxidation of Fe(II) and degradation of cyclopentadiene, and cyclopentadiene can also undergo polymerization. Therefore, all manipulations must be conducted under an inert atmosphere.



Equation 1 Synthesis of ferrocene from cyclopentadiene and ferrous chloride

For an inert atmosphere, previous syntheses of ferrocene often used a Schlenk technique, involving glassware that introduced and removed a steady flow of inert gas. A simpler setup uses a flask fitted with a septum, through which inert gas is introduced using a gas line and needle, with a plain syringe needle for inert gas exhaust.¹¹

The objective of this experiment was to explore the basic synthesis, including its methods and protocols. This forms a starting point for an investigation into the use of differing reagents, conditions, and techniques for future ferrocene and ferrocene related syntheses.

2.0 RESULTS AND DISCUSSION

A 1,2-dimethoxyethane/KOH solution was added, dropwise to a DMSO and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ solution, in an inert atmosphere, and allowed to react. After reaction completion, it was poured into an acidic ice bath, then filtered and dried to get the crude product.

Ferrocene has a relatively low vapor pressure, 340 Pa (100 °C), but high enough to allow sublimation of the crude product without decomposition.^{12,13} The figure below shows a general setup for sublimation. This experiment used a petri dish, heated with a hotplate, with the lid cooled by a beaker of ice and water.

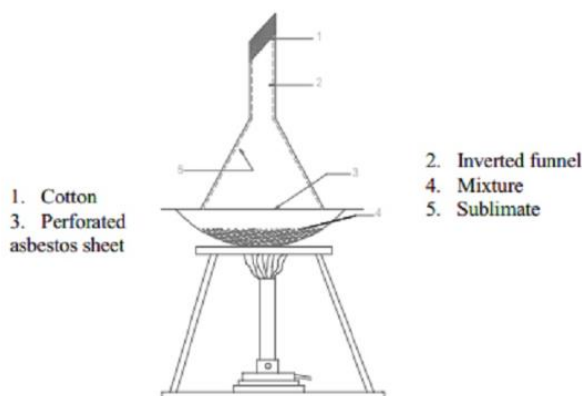


Figure 2 Sublimation purification Obtained from 11th 12th std standard Class Organic Inorganic Physical Chemistry Higher secondary school College Notes, https://www.brainkart.com/article/Sublimation---Purification-of-Organic-compounds_2799

The crude product was obtained in 3.79 g (61% crude yield). Sublimation of a 704 mg portion of the crude material afforded 391 mg of purified product, corresponding to a crude-to-purified recovery of approximately 56%. Assuming the same recovery for the entire crude batch, the estimated purified product mass was 2.1 g, corresponding to an estimated overall yield of 34%. This value is a projection based on partial purification rather than a directly measured yield for the complete batch. The purified results projection is found in Table S1, in the Supplemental Information section.

NMR analysis was performed on the sample to confirm successful synthesis and evaluate purity. In the ^1H NMR and ^{13}C NMR spectra can be found in Figure S1 and S2 of the Supplementary Information section. In the ^1H NMR scan, residual solvent peaks were observed: a small trace water signal appeared at 1.527 ppm, and a residual CDCl_3 t peak appeared at 7.255 ppm (literature: 7.26 ppm). The ferrocene moiety exhibited a sharp, intense singlet at 4.024 ppm, which closely aligns with the expected value of 4.17 ppm.^{14,15}

The ^{13}C NMR scan showed a single singlet at 68.65 ppm, characteristic of ferrocene. A strong triplet signal appeared at 77.05 ppm (average of two sources). This appears at where CDCl_3 solvent is expected and had a ^{13}C - ^2H J coupling constant of 32 Hz, at the upper range of the solvents expected coupling constant value.^{16,17,18} The melting point of the purified product had a value of 167-169 °C, which is lower than the 172.5 °C literature value.¹⁹ The absence of unexplained signals in the ^1H and ^{13}C NMR spectra, combined with a narrow melting point range of 3 °C, no obvious major impurities in the product.

Due to its unique combination of thermal stability and aromaticity, ferrocene remains a versatile scaffold for applications in functional dyes, pharmaceuticals, and materials science.

3.0 EXPERIMENTAL

3.1 Chemicals

The chemicals used in this experiment were: potassium hydroxide- certified ACS pellets, Fisher Scientific, New Jersey, CAS # 1310-58-3; iron (II) chloride tetrahydrate – 99+%, Acros Organics, New Jersey, CAS# 13478-10-9; methyl sulfoxide – 99.7% pure, Acros Organics, New Jersey, CAS# 67-68-5; 1,2-dimethoxyethane (ethylene glycol dimethyl ether) – 99+%, Acros Organics, New Jersey (or Implex Int'l Inc. , Wood Dale, IL), CAS# 110-71-4; nitrogen – ultra high purity-pure, AirGas, 259 Radnor-Chester Rd, Ste 100, Radnor, PA 19087-5283,

CAS# 7727-37-9; cyclopentadiene – prepared from dicyclopentadiene, 95%, stabilized w/100-200 ppm 4-tert-butylcatechol, Acros Organics, New Jersey, CAS# 77-73-6; and hydrochloric acid, 6 M – prepared from conc. HCl, 37%, Sigma Aldrich, St. Louis, MO, CAS# 7647-01-0.

3.2 Equipment

The equipment used included rotary evaporator, Bruker NMR, Bruker Avance 400 MHz, manufactured by Bruker BioSpin, 40 Manning Road, Billerica, MA 01821; UV; and a Waters Xevo G2_XS mass spectrometer, Waters Corporation, 34 Maple Street, Milford, MA 01757.

3.3 Procedures

Glassware that was to contain reactants was dried in an oven at 100 °C. To a flask, ground iron (II) chloride tetrahydrate was added (6.53 g), to which dimethyl sulfoxide was added (25 mL), sealed with a septum, and flushed with dry nitrogen. In another flask, ground potassium hydroxide was added, 1,2-dimethoxyethane (30.4 mL) was added, sealed with a septum, and the flask flushed with nitrogen, then stirring was started for each flask.

To the flask containing KOH and 1,2-dimethoxyethane (glyme) freshly prepared cyclopentadiene (5.5 mL) was added, dropwise, *via* syringe, to the stirring mixture. The dicyclopentadiene had been cracked to produce cyclopentadiene, previous to this experiment. Fifteen minutes after the last of the cyclopentadiene was added, a syringe was used to add the iron chloride/DMSO solution (25 mL), dropwise, to the stirring KOH/glyme/cyclopentadiene solution (60 mL). Once all the iron chloride solution had been added, it remained stirring for an additional thirty mins.

The reaction solution was then removed and slowly poured into an ice and 6N HCl solution. It formed an orange precipitate, which after mixing for 5 minutes, was vacuum filtered, and

rinsed with excess water/HCl solution, then distilled water. The vacuum was allowed to keep drawing air through the precipitate for an extra five mins to help dry some of the water. The residue was then transferred to a watch glass and placed in a drawer to dry for a week. The dried crude weight was 3.79 g, a crude yield of 61%. It was yellow, beige in color. Reactant details are in Table 1.

Table 1 – Reactants

RMF = relative mole factor - integer

Reactants	RMF	MW (g/mol)	Molarity (mols)	mass (g)	volume (mL)	density (g/mL)
<i>dicyclopentadiene</i>	1	132.2				
cyclopentadiene	2	66.1	0.067	4.41	5.5	0.802
FeCl ₂ ·4H ₂ O	1	198.8	0.033	6.60		
KOH		56.11	0.535	30.00		
1,2-dimethoxyethane		62.07	1.113	52.10	60	0.8683
DMSO		78.13	0.291	27.51	25	1.1004

Of the dried sample, 704 mg was transferred into a weighed petri dish, then the dish with lid, was placed on a hot plate as it approached 80 °C, the temperature dial was eased back to keep the temperature from rising. After 1.5 hours, the petri dish was removed and allowed to cool. The purified fraction weighed 391 mg, for a yield of 56% crude to purified. Extrapolating this to the full synthesis, if the total amount had been purified to the same percentage, the purified yield would be 2.1 g, a 34% yield overall. A 50 mg sample was sent for analysis using ¹H NMR and ¹³C NMR. The melting point was determined to be 167-169 °C.

3.4 Product Characterization

1. bis(η⁵-cyclopentadienyl)iron, yellow, transparent, flat crystals, yield 2.1 g, projected percent yield 34%; MP 167-169 °C; ¹H NMR (400 MHz, CDCl₃) δ/ppm 4.024 (10H, s); ¹³C {²H}-NMR 100 MHz, CDCl₃) δ/ppm 68.65.

4.0 CONCLUSIONS

The synthesis of ferrocene proceeded without significant experimental difficulties. The thermal decomposition of dicyclopentadiene to generate cyclopentadiene was completed before the experiment. The crude product precipitated as a yellow solid, consistent with the expected appearance of ferrocene. The crude yield was 61%, whereas the purified yield was estimated to be 34% based on the purification of a small portion of the crude product. Because the purified yield was extrapolated from a partial purification, further experiments would be needed to establish the yield obtained through purification of the entire crude product.

The synthesis followed an established synthetic route under relatively mild conditions, although an inert atmosphere was required. These conditions suggest that the protocol may be adaptable to substituted cyclopentadienes; however, potential complications include the formation of isomeric mixtures, changes in reactivity associated with substituent electronic effects, and reduced air stability for certain derivatives. These possibilities would require experimental evaluation. Post-synthetic functionalization of ferrocene may offer an alternative approach when direct synthesis from substituted cyclopentadienes presents difficulties.

Future work should focus on improving the isolated yield, evaluating safer reagents, and simplifying the experimental procedure. Another objective is to investigate whether the thermal decomposition of dicyclopentadiene can be integrated into the synthesis, potentially eliminating the need to prepare cyclopentadiene in a separate step. These modifications could improve the efficiency and practicality of the overall procedure.

5.0 REFERENCES

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6.0 SUPPLEMENTAL INFORMATION

6.1 Formulas

6.2 Significant Figures

Significant figures used were the significant figures of the raw data plus one, for all calculation results.

6.3 Raw Data

Available on request.

6.4 Tables, Graphs, and Plots

Table S1 – Product yields: theoretical and actual/projected

Product	RMF	MW	mols	Theoretical		Actual (crude)		Projected (purified)	
				pred mass (g)	density (g/mL)	mass (g)	% yield	mass est (g)	% yield est
Ferrocene	1	186.0	0.033	6.21	1.107	3.8	61%	2.1	34%

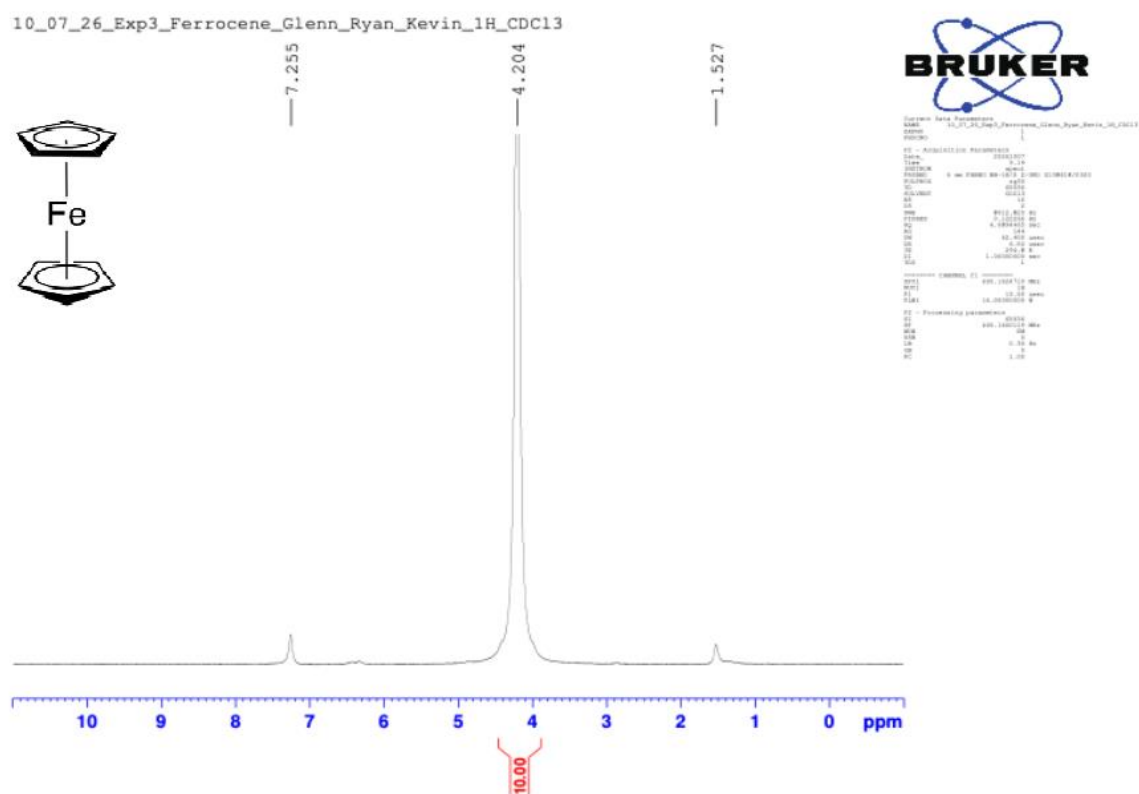
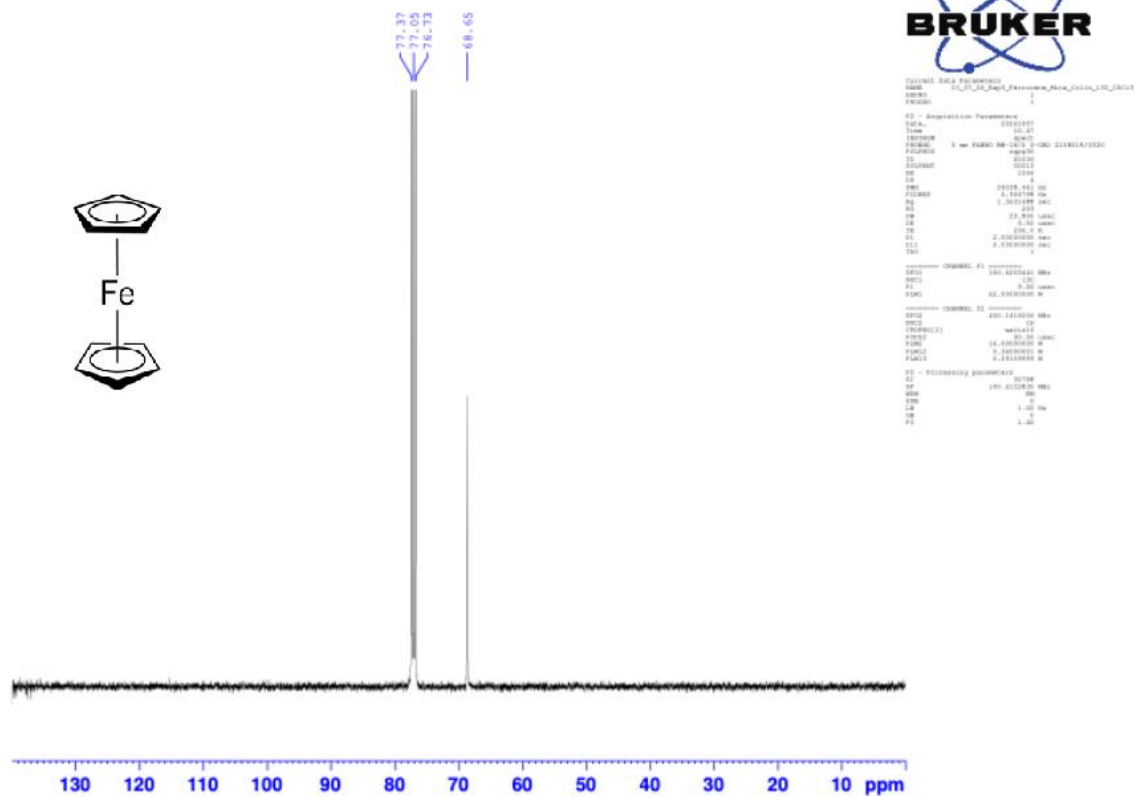


Figure S1 – ^1H NMR of the synthesized ferrocene product

Figure S2 – ^{13}C NMR of ferrocene