2016

Syntheses and characterization of [4]Ferrocenophane

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Recommended Citation

Al-doori, Ahmed Sabah, "Syntheses and characterization of [4]Ferrocenophane" (2016). *Theses, Dissertations and Capstones.* Paper 1009.

SYNTHESES AND CHARACTERIZATION OF [4]FERROCENOPHANE

A thesis submitted to
the Graduate College of
Marshall University
In partial fulfillment of
the requirements for the degree of
Master of Science in
Chemistry
by
Ahmed Sabah Al-doori
Approved by
Dr. Michael Castellani, Committee Chairperson
Dr. John Hubbard
Dr. Robert Morgan

Marshall University
May 2016

DEDICATION

To the fragrant past and brightness of the future, my great homeland, Iraq;

To the river that never stops giving, my beloved mother;

To the big heart and motivation of my life, my dearest father;

To the symbol of sincerity and loyalty, my brothers and sisters;

To the joy of my life, my friends;

To those who illuminated my way, my teachers;

I dedicate this thesis

ACKNOWLEDGEMENTS

I would like to express my deepest gratitude to my advisor, Dr. Michael Castellani, for being so helpful and supportive throughout the duration of this project, and for all the time that he spent with me to get this project done. He was and will always be an inspiration for me as a chemist. I also would like to acknowledge the committee members of my thesis, Dr. John Hubbard and Dr. Robert Morgan, for all the help regarding my thesis problems. I would also like to thank my lab mates: Marwan Joudah, for his training and support; Benjamin Colman and Jordan Martinez, for sharing their previous experience on this project with me. Last, but not least, I would like to thank my sponsor, the Higher Committee for Education Development in Iraq, for giving me this opportunity to study abroad and have this amazing experience. Finally, I would like to thank Marshall University Department of Chemistry, for accepting me as a graduate student and allowing me to use their equipments and laboratories.

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ABSTRACT

Metallocenophanes are metallocenes in which the cyclopentadienyl ligands are connected by a molecular bridge. Recently, metallocenophanes have received increasing attention because of their structure, chemical reactivity, and potential use as building blocks for new materials. Even though metallocenophanes have been synthesized by different methods, the majority of these methods involved the use of iron with rare examples of other metals. Therefore, a new method was employed that in addition to making ferrocenophane, will allow us to synthesize metallocenophanes with V, Cr, Mn, Co, and Ni as central metals. This thesis reports the synthesis of [4]ferrocenophane via a “flytrap” route. The reaction of sodium cyclopentadienide with 1,4-dibromobutane afforded the ligand 1,4-bis(cyclopentadienyl)butane (86% yield of crude product). The ligand was deprotonated by butyllithium which after treating it with ferrous chloride afforded the final product as an orange solid in overall of (13% yield of crude product). The ^{1}H NMR confirmed the synthesis of [4]ferrocenophane. UV-Visible data analysis was used to confirm the parallel planar structure of the cyclopentadienyl rings in this compound.

CHAPTER ONE

INTRODUCTION

The Discovery of Metallocenes

A metallocene may be thought of as "sandwich complex," in which a metal lies between two parallel cyclopentadienyl ligands (Cp, Figure 1).

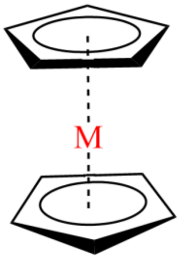


Figure 1: Metallocene structure

The first metallocene discovered was ferrocene in the early 1950's.[1] In an attempt to synthesize fulvalene, Kealy and Pauson reacted dicyclopentadienyl magnesium bromide (CpMgBr) with anhydrous iron (III) chloride. Sublimation of the resulting mixture yielded orange crystals with a formula of $C_{10}H_{10}Fe$.[1] Because of its unusual stability and special characteristics, the new iron compound attracted much attention. Kealy and Pauson's hypothesis was that the iron metal bonded to one carbon of each of the Cp rings ionically (Figure 2) as occurs in a Grignard reagent. [1]

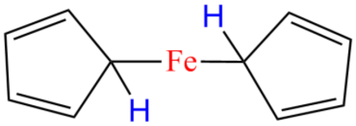


Figure 2: The iron compound structure proposed by Pauson and Kealy

Shortly after this, Wilkinson and Fischer separately proposed a 'sandwich structure' in which the iron metal is bound to all of the five carbon atoms of each of the Cp rings. Soon, the proposed structure was confirmed by the X-ray diffraction studies (Figure 3).[2,3,4] The name ferrocene was given to the new iron compound due to ferrocene possessing aromatic properties similar to those of benzene.[2]

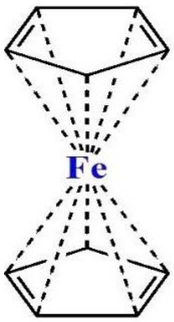
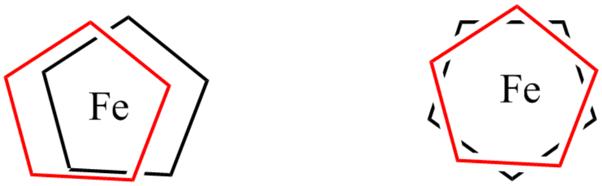


Figure 3: The ferrocene structure as it was proposed by Wilkinson and Woodward

Ferrocene is very symmetrical and can have two limiting conformations; eclipsed (D_{5h}) and staggered (D_{5d}) (Figure 4). The latter was found to be slightly more stable.[5]



Eclipsed (D_{5h})   Staggered (D_{5d})

Figure 4: Ferrocene conformational structures: eclipsed (D_{5h}), and staggered (D_{5d})

In addition to parallel Cp metallocenes, bent metallocenes have also been synthesized and found to be very interesting.[6] In these complexes, the Cp rings tilt from the parallel orientation of ferrocene (Figure 5).

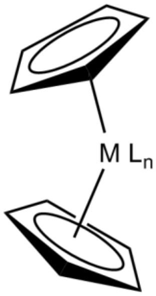


Figure 5: The structure of bent metallocenes

This tilt causes the orbitals of the Cp ligands to interact differently with the *d*-orbitals of the central metal than those in parallel metallocenes. Bent metallocenes can be prepared by bonding groups to the central metal in between the two Cp ligands or by connecting the two Cp rings with a short bridging group.[6] Crystallographic studies had shown that carbon bridges shorter than four carbon atoms leads to strained metallocenes.[7]

Ferrocene has many interesting properties. For example, it is highly stabile even at high temperatures and soluble in most organic solvents despite having metal-carbon bonds.[8] Therefore, ferrocene and its derivatives can be used in a variety of applications and conditions without the fear of breaking up the parent molecule.

Bonding in metallocenes

Metallocenes exhibit unusual stability and a unique structure.[8] Two approaches have been proposed to explain these interesting characteristics of metallocenes. The first approach was the 18 valence electron (18 VE) rule. The central metal has nine valence orbitals (one *s*, two *p*, and five *d*) which can accommodate 18 electrons. Some of these electrons come from the metal, and the rest are contributed from the ligands. The 18 electron rule is similar to that of the octet rule in which a complex achieves its highest stability if it possesses 18 electrons in its valence shell. In other words, these complexes have a closed shell structure which is isoelectronic with the noble gas in the period.

The second approach employs molecular orbital theory (MO) to explain the structure of metallocenes.[9] MO theory takes into consideration the interactions between the metal and ligand orbitals. Such interactions lead to the formation of bonding and anti-bonding orbitals. If there is little or no interaction between these orbitals, a non-bonding orbital is formed. In MO theory, if all the bonding orbitals are occupied, the complex is typically in its highest stability. This explains the high stability of ferrocene (18 VE). The π electrons in ferrocene are placed in both the bonding orbital (e_{1g}) and non bonding orbitals (a_{1g}), while the anti-bonding orbitals (e^{*}_{1g}) remain empty (Figure 6). Reducing the number of electrons in bonding orbitals, usually decreases the stability of the complex. This is simply because the bond between the metal and the ligand is weakened due to the extending of the distance between the metal and the ligand (Table 1). This explains the high reactivity of chromocene (16 VE) and vanadocene (15 VE).[10]

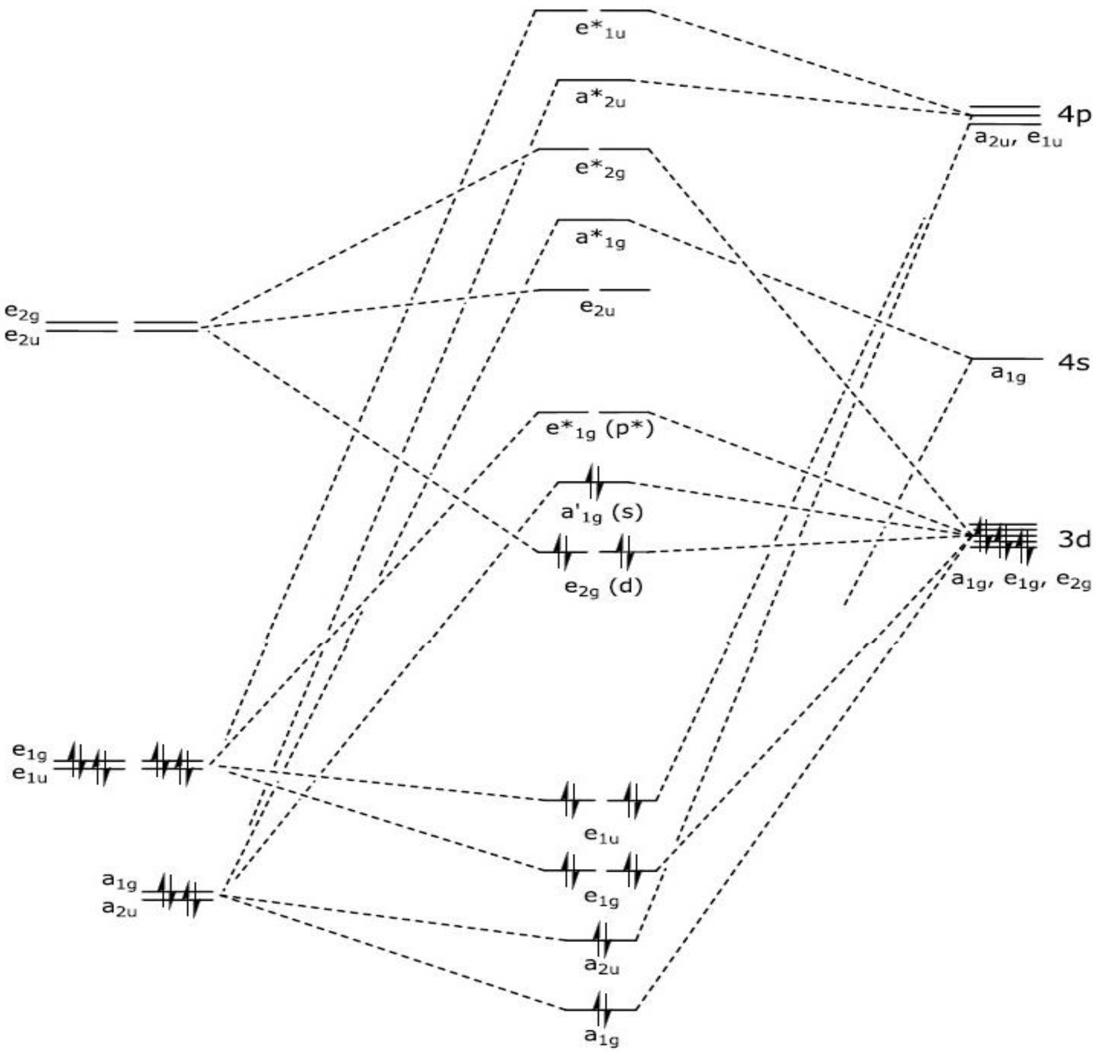


Figure 6: MO diagram for ferrocene (D_{5d})[10]

Similarly, complexes with more than 18 VE such as nickelocene 19 VE and cobaltocene 20 VE are less stable as well. The extra electrons placed in anti-bonding orbitals (e^{*}_{1g}) destabilize the complex.

M-Cp	Bond Length
V	2.27 Å
Cr	2.16 Å
Fe	2.05 Å
Co	2.12 Å
Ni	2.18 Å

Table 1: The M-Cp bond lengths in different metallocenes

Metallocenophanes

Metallocenophanes are metallocenes in which the two cyclopentadienyl ligands Cp are attached by an atomic or molecular bridge (Figure 7).

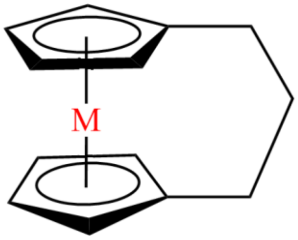


Figure 7: Metallocenophane structure

The first bridged ferrocene (ferrocenophane) was prepared shortly after the discovery of ferrocene.[11] Ferrocenophanes are the most studied complexes among all of metallocenophanes. Research has shown that the two Cp ligands cannot connect with a one atom carbon bridge because of the strain that would be generated. However, cyclopentadienyl rings have been prepared with two or more bridging atoms.[12] Strained metallocenophanes can undergo ring-opening polymerization and yield high molecular weight polymers (Figure 8).[13]

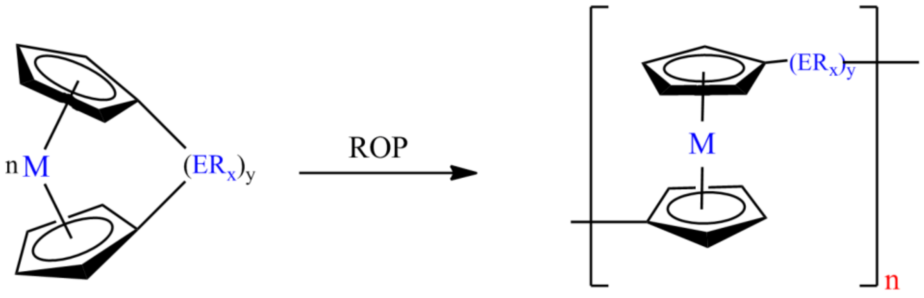
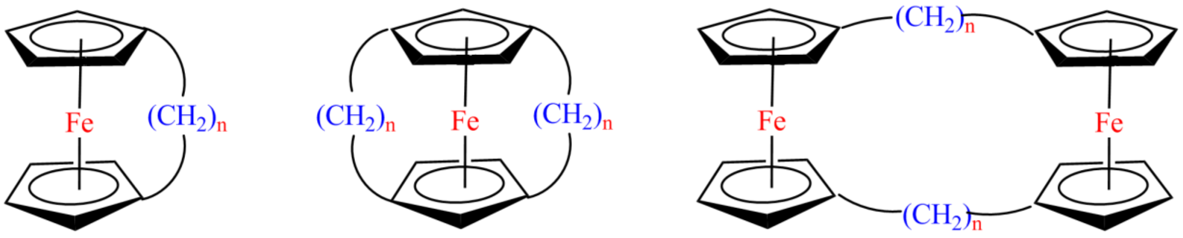


Figure 8: Ring-opening polymerization of metallocenophanes

Ferrocenophanes can be grouped into two major classes. The first class includes mononuclear ferrocenophane in which one or more bridging units are introduced. Based on the number of the bridges, mononuclear ferrocenophanes can be divided into two subgroups: single bridge ferrocenophanes ([m]) and multiply-bridged ferrocenophanes ([m]^n).

The second class is defined as multinuclear ferrocenophanes ([m^n]) in which ferrocene units are connected by one or multiple bridges (Figure 9).[9]



[m]ferrocenophanes [m]^{n}ferrocenophanes [m^n]ferrocenophanes

Figure 9: Ferrocenophane structures

Syntheses of Metallocenophanes

Metallocenophanes have been prepared via a variety of different synthetic routes. The most common methods that were found useful in the synthesis of different metallocenophanes include:

Salt-Metathesis Route (metallocene lithiation): This method involves the deprotonation of the parent metallocene, allowing it to react with a dihalide compound which serves as a bridging unit, between the two Cp rings. Usually, this method is utilized when preparing strained metallocenophanes.

In 1975, Osborne and co-workers utilized this method to prepare the first [1]ferrocenophane with a silicon bridge (Figure 10).[14] The parent ferrocene was deprotonated in the presence of tetramethylethylenediamine (TMEDA) and the resulting compound (dilithioferrocene.tmeda) was reacted with dichlorodimethylsilane (Me_2SiCl_2) to afford [1]ferrocenophane. Similarly, distanna[2]ferrocenophane (**1996**) and trithia-bridged ferrocenophane were successfully synthesized.[15,16] In addition, different metallocenophanes with [1],[2], and [3] bridging units were successfully synthesized as well.[17]

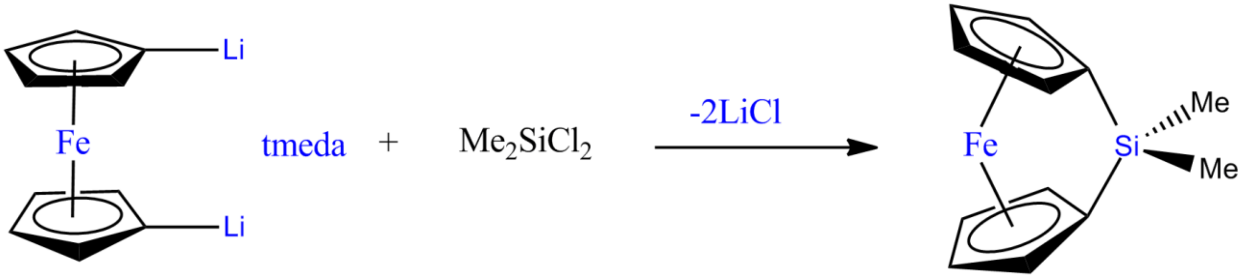


Figure 10: Synthesis of the first [1]ferrocenophane

Ring-closing Metathesis Route: This method is considered one of the most important methods of preparing metallocenophanes. Here, 1,1-dialkylmetallocene is transformed into [m]metallocenophane using 3 mol-% of the Grubbs' catalyst $RuCl_2$-(CHPh)(PCy_3)$_2$. This method is commonly used when synthesizing metallocenophanes with four, six, and eight bridging units. In 2002, Ogasawara and co-workers reported the preparation of [4]ferrocenophane.[18] Similarly, Buchowicz and co-workers reported the preparation of [4]nickelocenophane.[19] Figure 11 shows the general pathway of preparing [4]metallocenophane.

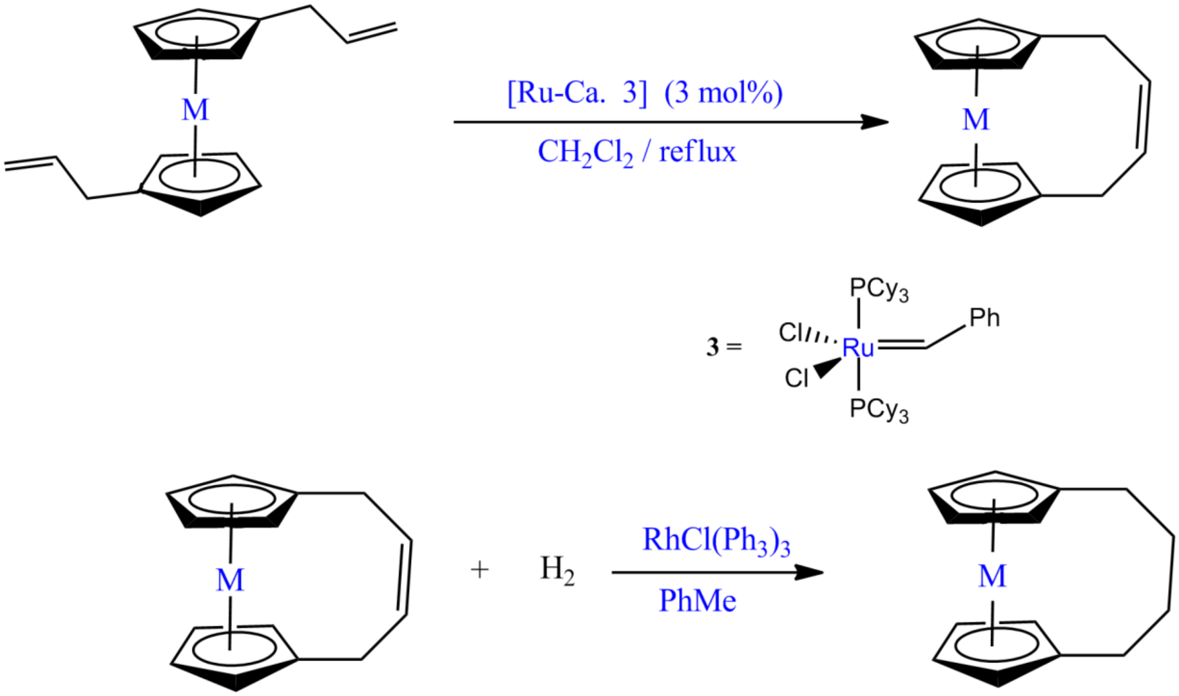


Figure 11: Synthesis of [4]metallocenophane via ring-closing metathesis route[18,19]

Fly-trap Route: This method was first proposed by Lüttringhaus and Kullick in 1960.[20] Ferrocenophanes with 3, 4, and 5 hydrocarbon bridges were prepared by this route. In addition, wide variety of metallocenophanes were successfully synthesized via the same method. In 2008, Mayer, *et al*. reported the synthesis of first [2]cobaltocenophane, and [3]cobaltocenophane in 8% and 9% yields, respectively.[21] Generally, the mechanism of the reaction includes the formation of the ligand (bis-cyclopentadienyl alkane) from the reaction of sodium cyclopentadienide with a dibromoalkane, and then the ligand is doubly deprotonated and allowed to react with a metal salt (MX_2) to give an [m]metallocenophane as a final product.

Figure 12 shows the general pathway of preparing a generic metallocenophane via the fly-trap route.

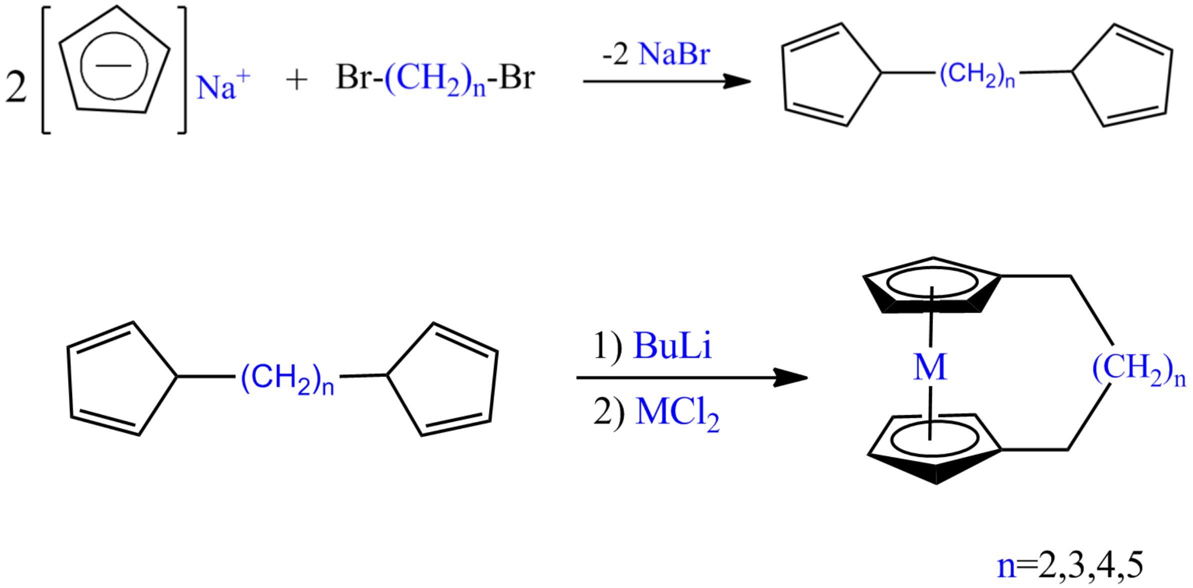


Figure 12: Metallocenophanes Synthesis via the fly-trap Route

The Effects of the Tilt Angle (α) in Metallocenophanes

The introduction of bridging units to metallocenes has a very interesting effect on the resulting metallocenophanes and the tilt angle that would be generated (α, Figure 13).

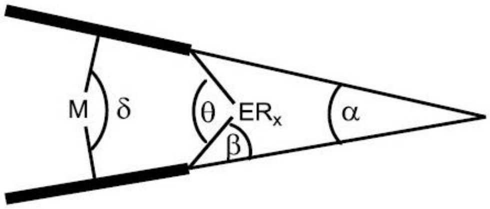


Figure 13: The geometrical parameters (α, β, δ) depictions of metallocenophanes[10]

The size of the angle (α) is caused mainly by two factors: the size of the metal and the elements comprising the bridging units.[10] Large metals push the ligands away from each other which increases the tilt angle while small metals decrease the distance between the two Cp ligands which result in smaller tilt angle. In addition, the size of the bridging elements can affect the tilt angle in different ways. If two complexes consist of the same central metal, but different bridging units, this would result in metallocenophanes with shorter bridges producing larger tilt angles while metallocenophanes with longer bridges causing smaller tilt angles. Table 2 shows the effect of the increased radius of bridging elements on the tilt angles. For example, [1]ferrocenophane with a boron bridge shows the largest tilt angle which is consistent with its small atomic radius (87 ppm).

E	Radius/ppm	α[˚]
B	87	32.4
S	88	31.1
p	98	26.7
Si	111	20.8

Table 2: Tilt angles of [1]ferrocenophane with different bridging elements

Tilted structures are not necessarily strained.[9] According to Green, the *d*-electron configuration of the central metal can influence the (α) angle of [m]metallocene. The parallel structures in metallocenes are the result of electrons not occupying the anti-bonding orbitals, which minimize electron- electron repulsion. If none of these forces is present, there is no inherent weakening of the metal ring bonding upon the tilt angle.[22] To elaborate on this, Green has shown that when comparing the calculated energy of ferocene (Fe(II), d^6) with the hypothetical triplet zirconocene [Cp_2Zr] (Zr(II), d^2), the energy varies with the tilt angle (Figure 14). In ferrocene, all of the orbitals in the HUMO level are occupied. As a result, the energy of the complex is raised above the ring bending. Therefore, the two Cp rings in ferrocene prefer to be parallel planar. Zirconocene on the other hand, shows no energy variations when the tilt angle changes. Based on these results, with two or fewer *d* electrons, metallocenophanes could be strain free even if very short bridges are introduced.[22]

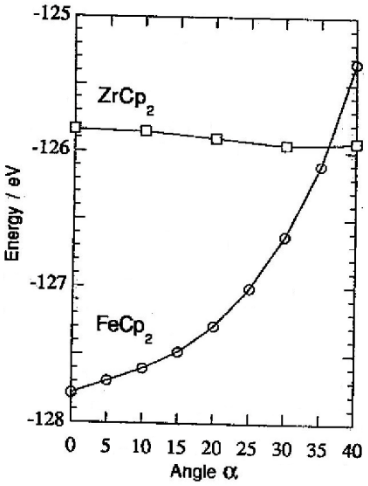


Figure 14: Variation of the total energy of (Cp_2Fe) and triplet (Cp_2Zr) as tilt angle increases.[22]

Project Goals

Over the past 50 years, ferrocenophanes have been prepared by different synthetic routes. However, there have been rare examples of applying these methods on different metals other than iron. For instance, in 2007, Buchowicz and co-workers reported the synthesis of [4]nickelocenophane via ring-closing metathesis route.[19] Generally, these methods work quite well with iron, but poorly with other metals. In 1986, Bitterwolf reported the synthesis of bridge substituted [4]ferrocenophane. The reaction steps are shown in Figure 15.[23]

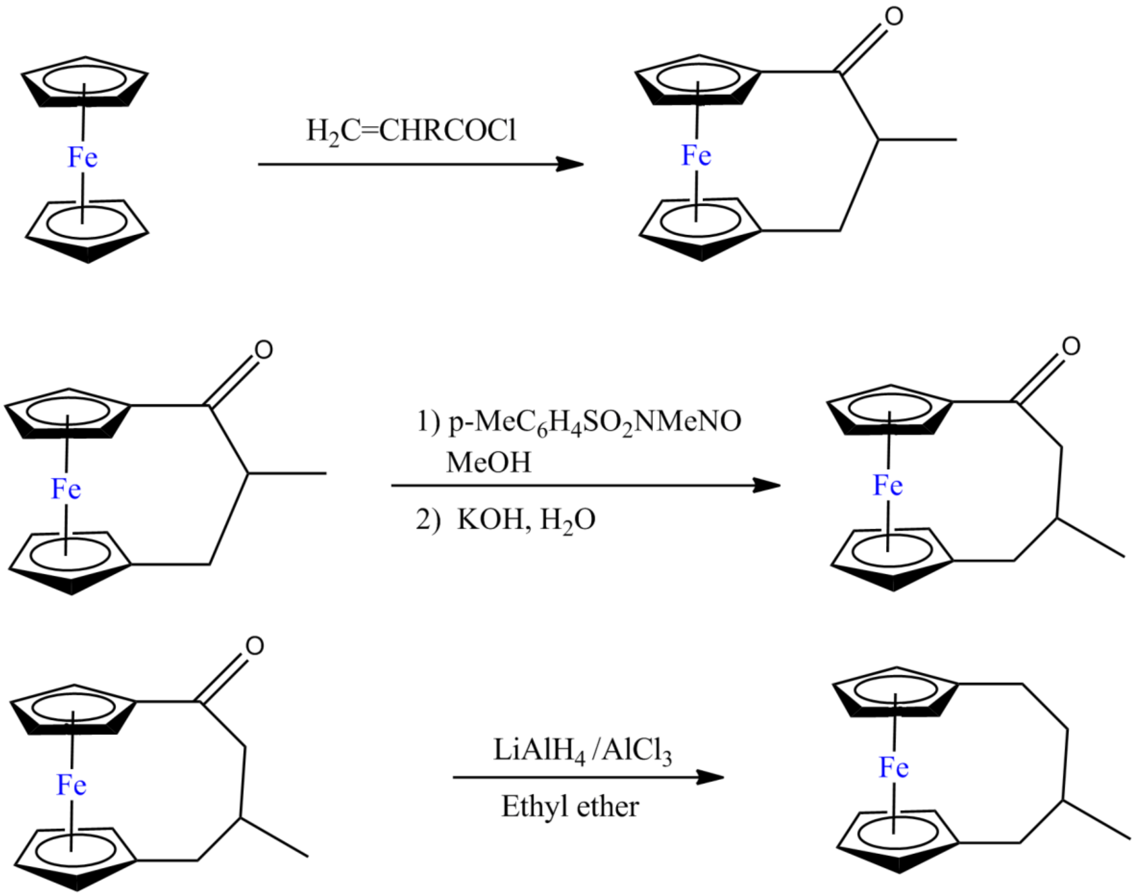


Figure 15: Synthesis of bridge substituted [4]ferrocenophane

In other reported ferrocenophanes, similar methods have been employed.[24,25] In those methods, ferrocene often was used to make ferrocenophanes and the reason is related to its closed shell structure of ferrocene (18 VE). However, when other metallocenes are utilized, specifically open shell complexes, the reaction takes different pathways. Instead of making metallocenophanes, the central metal becomes an active site which leads to the reaction between the reagents and the metal instead of the Cp rings. To overcome this problem, we propose the use of the flytrap route. When utilizing this method, active metals could be involved in the synthesis of different metallocenophanes. The flytrap method was first reported by Lüttringhaus and Kullick in 1960. They made [3], [4], and [5]ferrocenophane. However, the yields were extremely low (*vide infra*). In this project, we seek to utilize the same route with a modification of the original procedure of Lüttringhaus and Kullick, hoping to increase the overall yield and fully characterize the [4]ferrocnenophane, and then apply it to more active metals. The general pathway of the reaction is shown below (Figure 16).

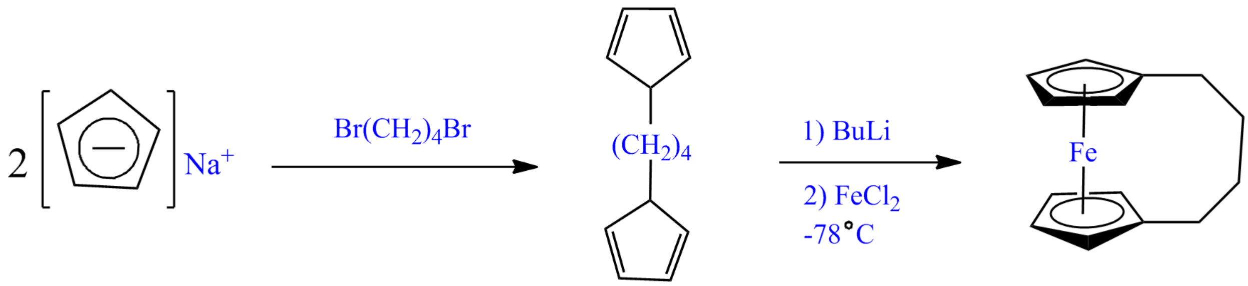


Figure 16: Synthesis of [4]ferrocenophane via fly-trap route

CHAPTER TWO

EXPERIMENTAL SECTION

General Data

All air and moisture sensitive compounds were handled under a nitrogen atmosphere using standard Schlenk techniques unless otherwise stated. Solids were handled under argon in a Vacuum Atmospheres glovebox equipped with an HE-493 dri-train. Hexane was degassed by bubbling nitrogen through it. Tetrahydrofuran (THF) was distilled from potassium/benzophenone ketyl under nitrogen. Butyllithium (Aldrich), 1,4-dibromobutane (ACROS), dicyclopentadiene (ACROS), iron powder (Aldrich), iron(III) chloride (ACROS) and anhydrous iron(II) chloride (Strem) were used as received. NMR spectra were obtained on a Bruker AVANCE III 400 MHz instrument.

Preparation of $[(C_5H_4)(CH_2)_4[(C_5H_4)]Fe$

Preparation of sodium cyclopentadienide, $Na(C_5H_5)$: This procedure is a modification of a previously published paper.[26] Dicyclopentadiene (88.7 g, 671 mmol) was placed into a 500 mL Schlenk flask. Sodium metal (2.5g, 109 mmol) was added to the flask, and the system was charged with nitrogen. The reaction mixture was heated to reflux at 160 ºC for 9 hours. After cooling to room temperature, the resulting solid was filtered through a fritted funnel and washed with hexane (20 mL) three times. The resulting white solid was dried *in vacuo* to yield 9.2 g (96%).

Preparation of 1,4-bis(1,3-cyclopentadienyl)butane, $(C_5H_5)(CH_2)_4(C_5H_5)$: Two equivalents of sodium cyclopentadienide (5.2 g, 29.5 mmol) were placed into a three-neck round bottom flask equipped with a magnetic stir bar, a reflux condenser, a N_2 inlet, and dropwise addition funnel. Tetrahydrofuran (60 mL) was added to the flask via the addition funnel, and the resulting brown mixture stirred for 10 min. Then, 1,4-dibromobutane (6.33 g, 29.3 mmol) was added dropwise to the stirred mixture to afford a creamy yellow solution that was then heated to reflux for 5 h. After cooling to room temperature, the solvent was removed *in vacuo*, leaving a light yellow solid. The solid was extracted with hexane (60 mL) and filtered via Buchner funnel in the air. The yellow liquid was cooled to (– 10 ºC) overnight. The solvent was removed, and the resulting dark yellow oil was filtered through a 1 in layer of silica gel. The hexane was removed *in vacuo* to afford 4.71 g (86%) of 1,4-bis(cyclopentadienyl)butane as a golden oil.

Preparation of $Li_2[(C_5H_4)(CH_2)_4(C_5H_4)]$: Under nitrogen, $(C_5H_4)(CH_2)_4(C_5H_4)$ (1.8 g, 9.6 mmol) was placed in a 250 mL Schlenk flask equipped with a stir bar and a rubber septum. Hexane (40 mL) was added to the flask via a syringe. The solution was stirred for 10 min., then cooled in a liquid nitrogen/acetone bath to -78 ºC for 15 min. Butyllithum (2.5 M, 5.54 g, 86.5 mmol) was added dropwise via syringe to the flask. The mixture was stirred for 10 min., warmed to ambient temperature, and stirred for two hours. After 30 min., a white solid began to precipitate. After two hours, the resulting white solid was isolated via filtration and dried *in vacuo* and kept in the glovebox. Yield: 1.45 g (76%)

Preparation of $[(C_5H_4)(CH_2)_4[(C_5H_4)]Fe$: The deprotonated ligand $Li_2 [(C_5H_4)(CH_2)_4(C_5H_4)]$ (0.5 g, 2.5 mmol) was placed into a round bottom flask equipped with a rubber septum and a magnetic stir bar. Anhydrous iron(II) chloride (0.32 g, 2.5 mmol) was placed into another Schlenk flask that was equipped with a rubber septum and a magnetic stir bar. Tetrahydrofuran (THF) (20 mL) was added to each of the flasks. Both solutions were stirred for 15 min, then cooled to -78 ºC. The iron(II) chloride suspension was added to the

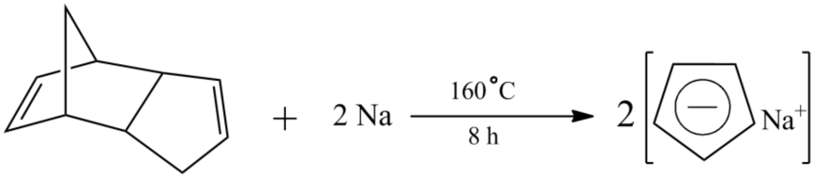
Li_2 [(C_5H_4)(CH_2)$_4$[(C_5H_4)] via cannula. The mixture turned dark orange and was stirred for 15 min. at -78 ºC. After warming to room temperature, the solution turned black after an hour. The solution was stirred for 16 h.

The solvent was removed *in vacuo*, leaving a viscous black solid. The solid was extracted with 60 mL hexane at 60 ºC for 30 min and filtered to produce an orange liquid. The orange liquid was concentrated by removing half of the hexane *in vacuo*. The resulting concentrated dark orange liquid was stored in a refrigerator (-10 ºC) overnight, and 0.08 g (13%) of [(C_5H_4)(CH_2)$_4$(C_5H_4)]Fe precipitated as an orange solid. NMR (C_6D_6) 1H: δ 1.6 (d, CH_2), 2.3 (s, CH_2), 3.98 (d, Cp-Cp).

CHAPTER THREE

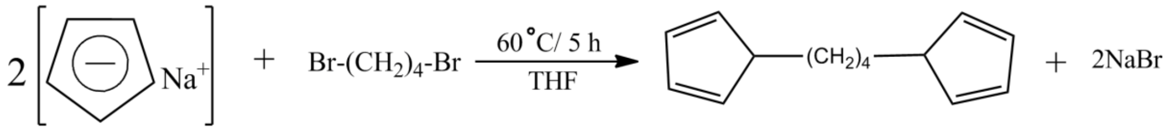
RESULTS AND DISCUSSION

Synthesis of sodium cyclopentadienide: This compound was prepared in a minor modification of the procedure that was previously reported by *Panda et al*.[26] Dicyclopentadiene and sodium metal were used as a starting materials. After approximately 6 hours at reflux, the reaction was incomplete and sodium particles were still seen in the reaction mixture. However, allowing the reaction to extend to 9 hours afforded sodium cyclopentadienide as a white solid in overall yield of 96%.



(1)

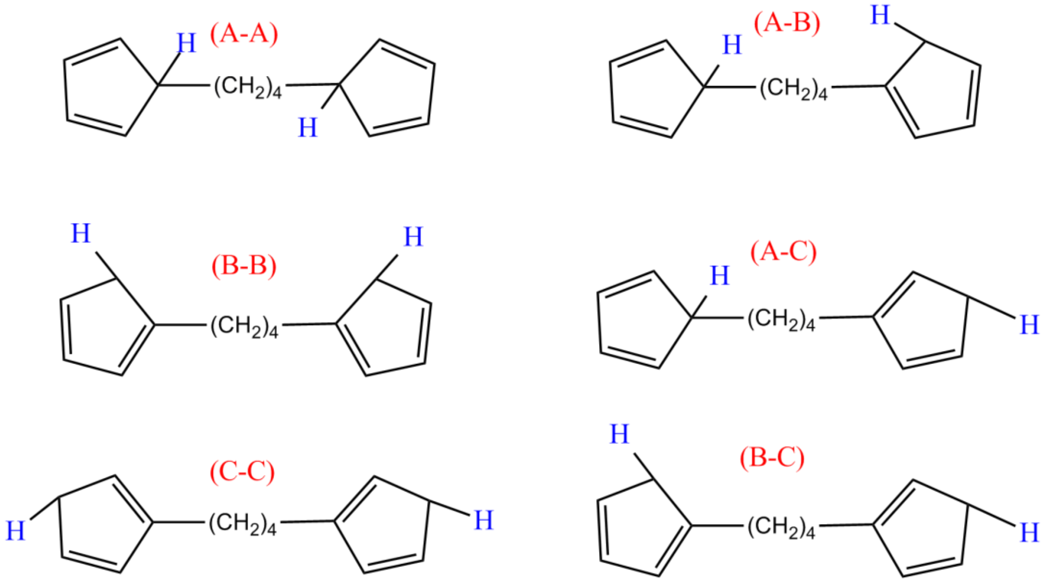
Synthesis of 1,4-bis(dicyclopentadienyl)butane: This compound was also obtained by modifying a previous procedure.[27] Sodium cyclopentadienide reacted with 1,4-dibromobutane, to give a yellow-orange oil. After the product was purified by filtering the yellow oil through a 1 inch layer of silica gel and removing the solvent *in vacuo*, a golden oil was obtained in overall yield of 86%. This yield assumes the total mass of product is the expected product. As will be shown, the material is not pure and the actual yield is lower, possibly by a significant amount.



(2)

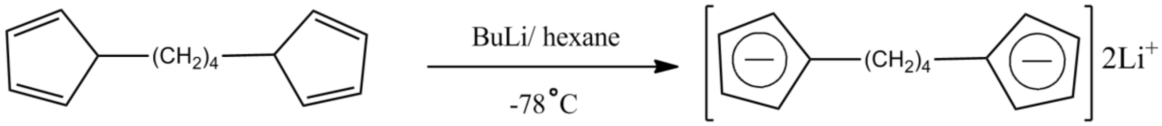
The ligand was characterized by ^{1}H NMR spectroscopy (Figure 22 in the Appendix). However, it was not fully interpreted due to the complexity of the spectrum. The protons on the Cp rings should display two doublets near (6-6.5 ppm). What was observed was more complex.

In addition, the protons of the carbon chain should generate two triplets, but the aliphatic region of the NMR (0.8-3 ppm) was much more complex than this. One explanation for the complexity of the spectra is that the ligand is expected to have six isomers (Scheme 1).[27]

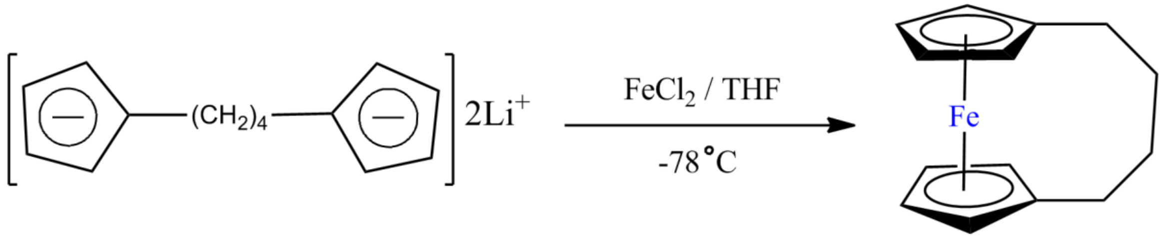


Scheme I: The Six Isomers of 1,4-bis(dicyclopentadienyl)butane

The deprotonation of the ligand was achieved in a cold bath (acetone/liquid nitrogen -78 ºC), using n-butyllithium with hexane as the solvent. The resulting compound was obtained as a white solid. The overall yield was 76% of the expected mass.

 (3)

Synthesis of [4]ferrocenophane: This compound was obtained by following a procedure reported earlier by Luttringhaus *et al.*[20] The deprotonated ligand was reacted with ferrous chloride in THF at (-78 ºC) to afford [4]ferrocenophane as an orange solid in an apparent overall yield of 13%.



(4)

Surprisingly, when attempting to sublime the orange solid, it liquefied as the temperature approached 100 ºC.

^{1}H NMR spectroscopy confirmed the synthesis of [4]ferrocenophane (Figure 23 in the Appendix). This spectrum will be interpreted based on a hypothesis proposed by Rinehart *et al*.[28] In tilted ferrocenophanes, it is suggested that the α-protons of the Cp rings are closer to iron atom than the β-protons (Figure 17). As a result, α-protons would experience greater shielding than the β-protons. This effect would cause a small splitting of the Cp protons. Figure 24 in the Appendix shows a spectrum of [3]ferrocenophane with the cyclopentadienyl proton splitting pattern.

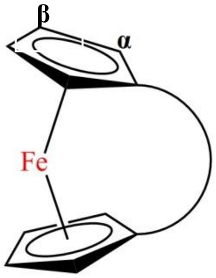


Figure 17: The location of α and β protons in ferrocenophanes

Using a similar approach, the ^{1}H NMR spectrum of [4]ferrocenophane shows three signals. The first appeared at *ca*. 4 ppm. This signal was assigned for the protons of the Cp rings. The absence of large splitting of the ring's protons indicates that the two Cp rings are no longer tilted. However, the minor splitting of the Cp rings proton resonance can be explained by either steric compression or anisotropy effects that can be attributed to the CH_2-CH_2 bonds. The second and third signals appeared at (1- 3 ppm) and were assigned to the methylene groups of the carbon bridging units.

UV-VISIBLE SPECTROSCOPY

The UV/Visible spectrum of [4]ferrocenophane will be interpreted based on the UV/Visible spectra of ferrocene and tilted ferrocenophanes that have been reported previously.[17] As was discussed earlier, a hexane solution of ferrocene is amber in color. The UV/Visible spectrum of ferrocene shows two weak bands at (325 nm and 440 nm). Previous studies have assigned the 325 nm band in ferrocene to the absorption of the Cp rings, while the 440 nm band has been attributed to a pure 3d-3d transition.[29,30]

The two Cp rings shift from their parallel orientation when short bridges are introduced. The previously reported [1]ferrocenophanes have extremely strained structures. When a short bridge is connecting the two Cp rings such as in [1]ferrocenophane, the *d*-orbitals rearrange to adapt to the new molecular geometry. This means that the non-bonding orbitals on the iron metal have to be orthogonal (Figure 18). This tilt causes the energy levels of the *d*-orbitals to be shifted from their original place in which the (a_1') HOMO is raised while LUMO level is lowered in energy.[17]

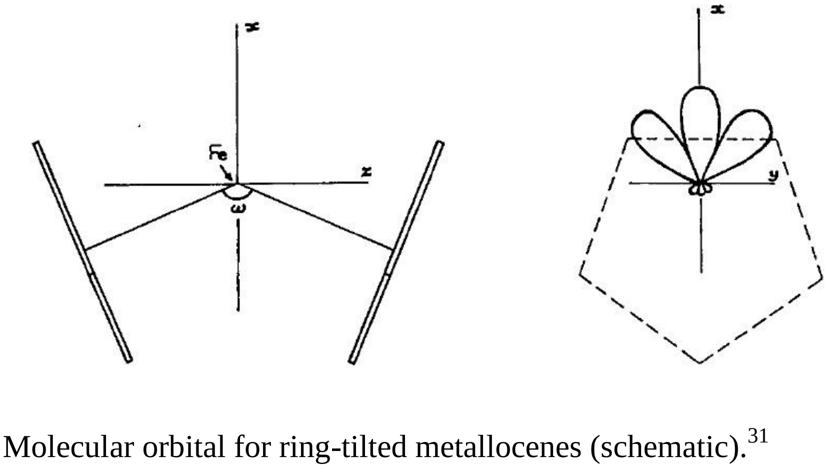
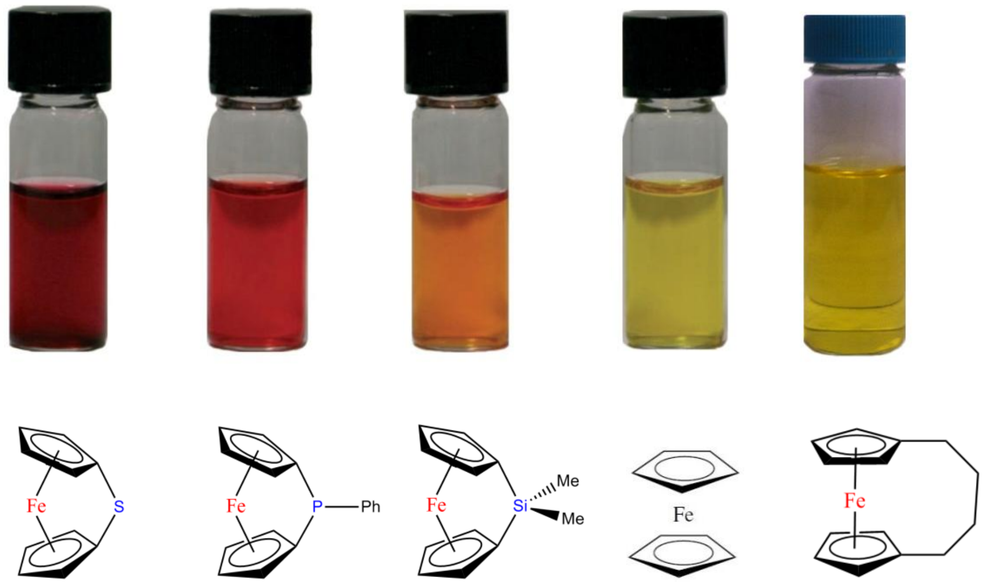


Figure 18: Molecular orbital for ring-tilted metallocenes (schematic).[31]

As the two Cp rings move away from the parallel structure of ferrocene, the wavelength shifts to longer wavelength than the 440 nm of ferrocene. The preparation of [1]ferrocenophane with different bridging units such silicon, phosphorus, and sulfur showed long wavelength absorption (Figure 19).



λ_{max} (nm):	*504*	*498*	*478*	*440*	*432*
α (˚) :	*31.1*	*26.7*	*20.8*	*0*	*1*

Figure 19: Color shifts and λ_{max} (nm) absorption of different tilted ferrocenophanes

The explanation of the peak position shifts from 325 nm band has been attributed to symmetry factors since the 325 nm band represents the absorption of the Cp rings. In other words, the increased tilt angles of the three [1]ferrocenophanes cause a decrease in the HOMO-LUMO gap of the *d* orbitals. Consequently, the energy is lowered which leads to a red shift.[17]

The UV-Visible spectrum of [4]ferrocenophane shows two weak bands (Figure 20). The first band appeared at 326 nm, while the second band occurred at 432 nm. Both bands have been marked as symmetry forbidden electronic transitions (N-Q).[29] As expected, the spectrum of [4]ferrocenophane shows significant similarity to the parent ferrocene . They both have the same color shift which can be attributed to the HUMO-LUMO gap differences. As the tilt angle decreases, the HUMO-LUMO gap increases, leading to higher energy and therefore to a yellow shift. Since both compounds have the same color shifts and similar λ_{max} absorption, this suggest that the two Cp ligands in [4]ferrocenophane are parallel.

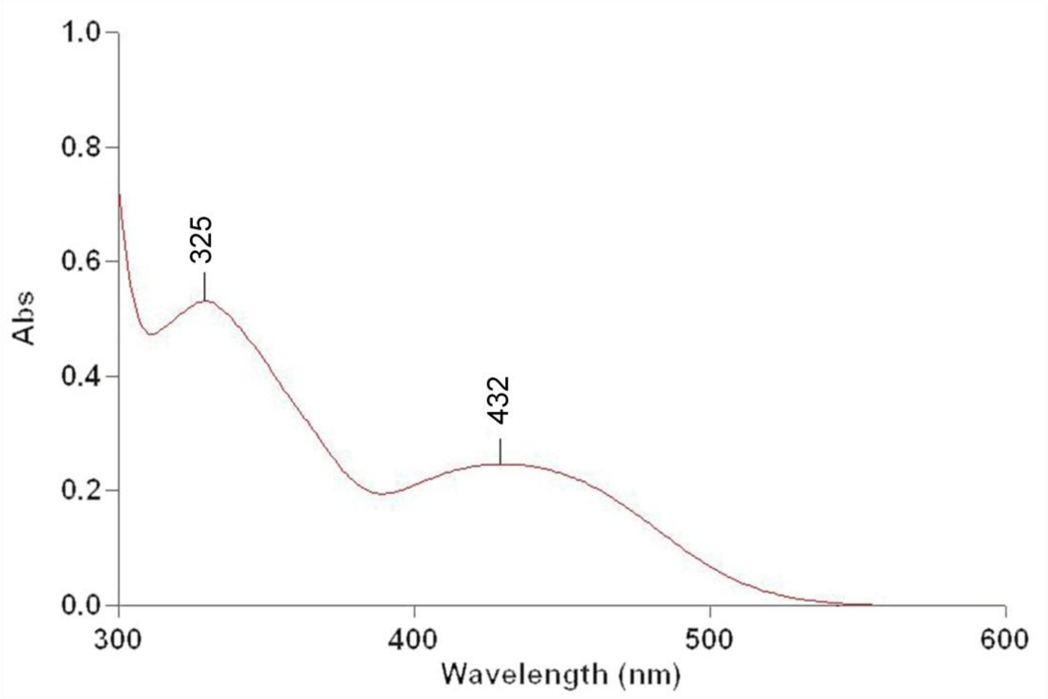
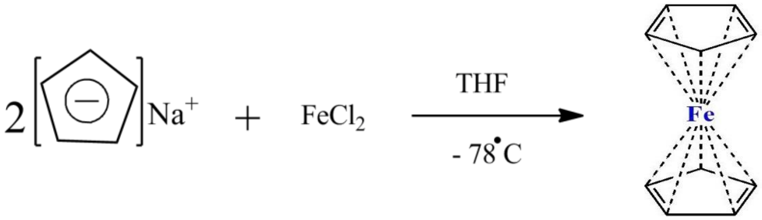


Figure 20: The UV-VIS spectrum of [4]ferrocenophane in hexane

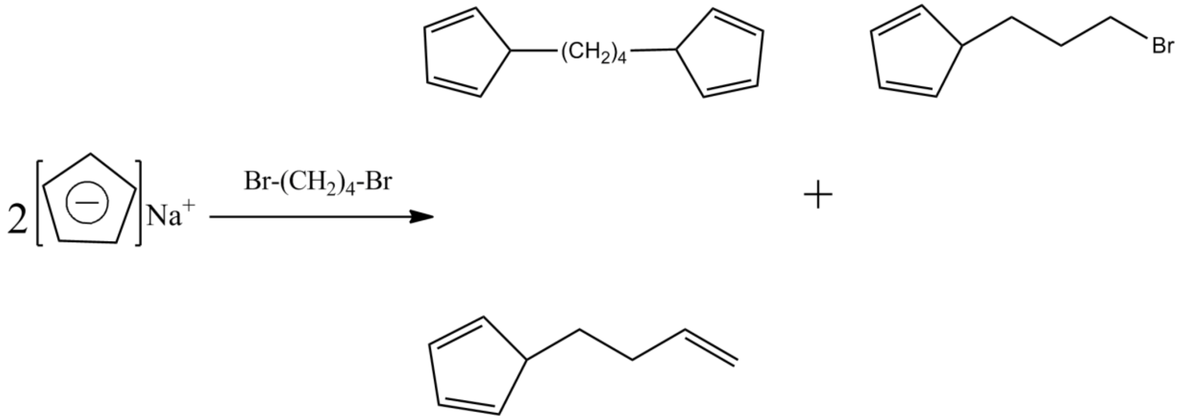
Low Yield Investigations

When this project was begun, the aim was to reproduce, and then improve upon, Lüttringhaus and Kullick's work which involved the synthesis of [m]ferrocenophanes. In 1960, they were the first to synthesize [m]ferrocenophanes following a method called "flytrap route". However, the yields were extremely low. For instance, ferrocenophane with [3], [4], and [5] carbon bridging units were prepared in 2.5%, 0.053%, 0.025% respectively. Our group wanted to improve the yields by modifying the original procedure. Over the past six years, many attempts have been made to make ferrocenophanes. Wilson was able to make [4]octamethylferrocenophane in a crystalline form, but in overall yield of 2 %.[32] Later, Joudah appeared to succeed to increasing the yield, but without purification.[33] The product was never isolated in above trace amounts as a solid, which clearly indicated the presence of impurities. Finally, in the current attempts to synthesize [4]ferrocenophane, the same problems were encountered: low yield and lack of purification. In the next discussion, possible factors that could have affected the reaction steps will be investigated.

The first step involved the preparation of sodium cyclopentadiende. The compound was obtained as white solid with no purification. The compound was air-sensitive which made it difficult to characterize. However, the compound was identified and shown to be sodium cyclopentadienide by reacting it with ferrous chloride, which afforded ferrocene in a high yield, suggesting the material is highly pure.

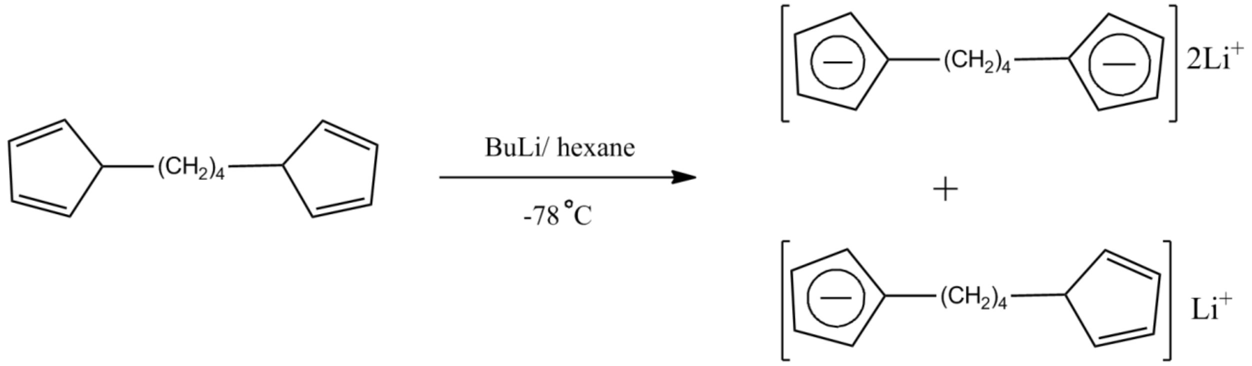


The second step involved the preparation of 1,4-bis(dicyclopentadienyl)butane. The ligand was obtained as a golden oil. However, the ligand could not be purified further. Besides the six isomers that the ligand is expected to have, other products might have also been mixed with the ligand as it is shown below:



Usually such a mixture can be identified through spectroscopic methods. Unfortunately, the ^{1}H NMR spectrum of the ligand was very complex and it was not possible to determine which materials were present in the mixture. All of the expected products have similar structures so there will be considerable overlap in the ^{1}H NMR. For example, vinyl proton exists in all of the different products. Therefore, it would not be possible to distinguish one from the other. If the ligand was pure, the ^{1}H NMR should look similar to that shown in Figure 25 in the Appendix.

The third step involved the deprotonation of the ligand which yielded a white solid. After the deprotonation, all of the six isomers of the ligand are transformed to only one anion. However, the other expected products from the previous reaction could also be deprontonated or reacted with each other. Unfortunately, it was extremely difficult to know if this occurred. In addition, it was not possible to know if one of the Cp ring was deprotonated or both of them.



The final step involved the preparation of [4]ferrocenophane. However, other compounds could be made in this reaction as well (Figure 21).

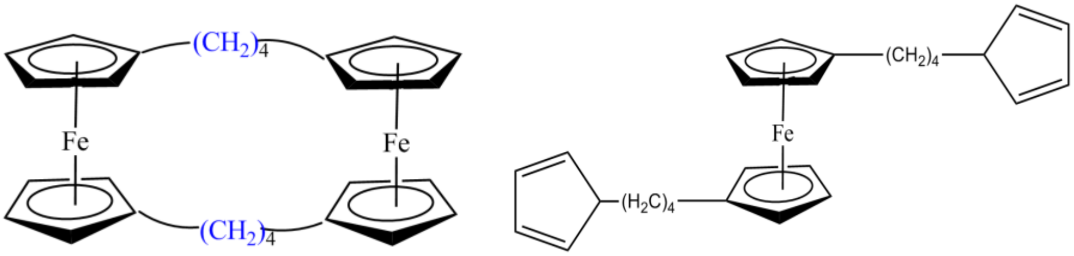


Figure 21: The different compounds that could be mixed with the [4]ferrocenohane

The reaction of the deprotonated ligand with the ferrous chloride resulted in a viscous black solid that, when extracted with hexane, gave a yellow solution. Numerous attempts were made to obtain [4]ferrocenophane in a solid form from this solution. Removing the solvent afforded a very thin, sticky, orange film that would not sublime or be purified further. However, removing half of the solvent, and storing the solution in a refrigerator (-10 ºC) overnight afforded an orange solid as a precipitate. The solid was shown to be [4]ferrocenophane by ^{1}H NMR spectroscopy (Figure 23 in the Appendix). Unfortunately, sublimation of the resulting solid produced a sticky liquid. Furthermore, the ^{1}H NMR spectrum of the initial solution was very complex and suggested that other compounds could also be present in the solid (Figure 26 in the Appendix).

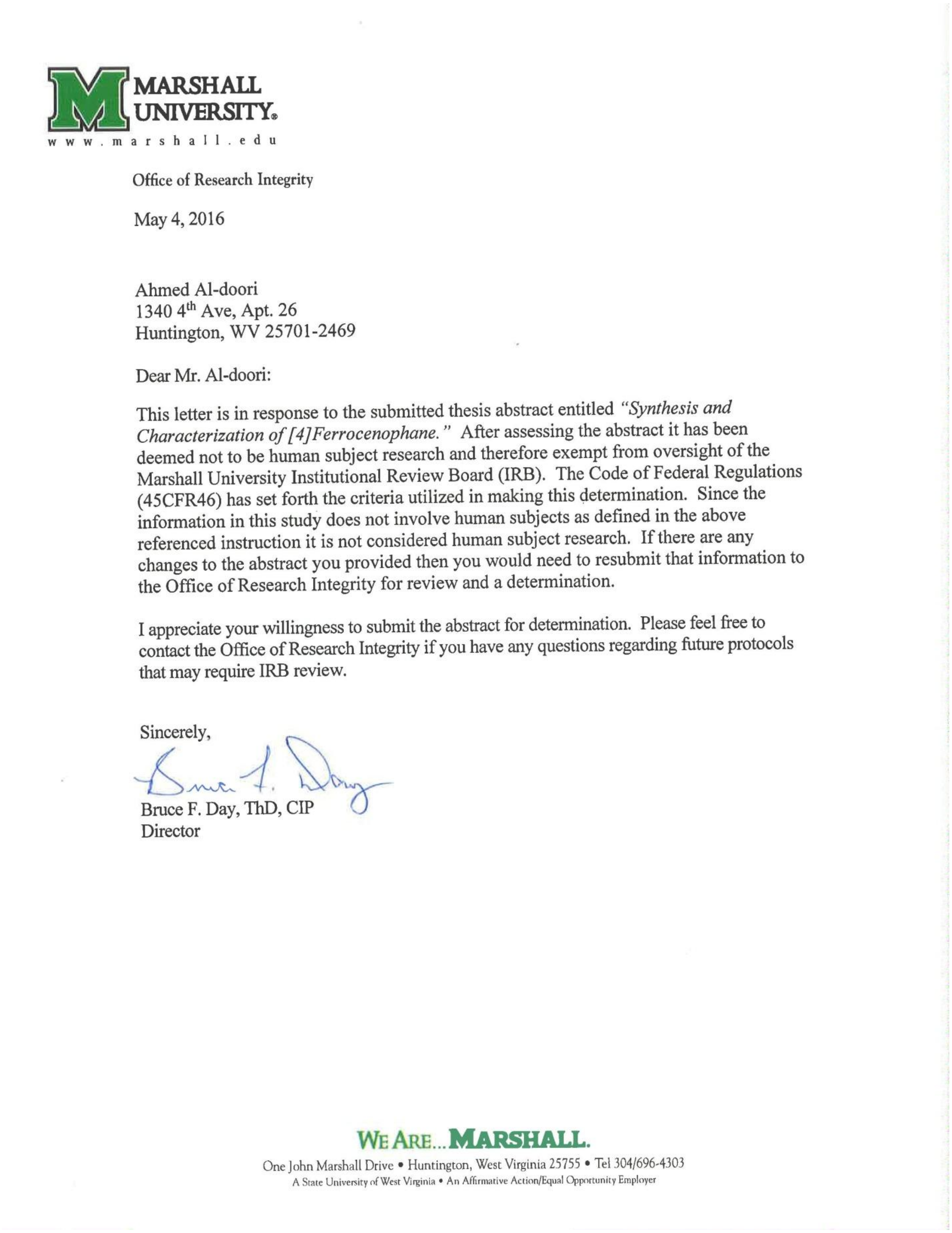
The initial solution was separated in a column chromatography, three bands were isolated, but only two bands were obtained (Figure 27 and 28 in the Appendix). Unfortunately, the two bands could not be identified. However, the fact that those two bands were isolated from the solution confirms the existence of other impurities in the solid which can contribute to minimizing the overall yield.

CHAPTER FOUR

CONCLUSIONS

In this project, [4]ferrocenophane was prepared by following a procedure similar to that of Luttringhaus. This method involved employing a short series of simple reactions and inexpensive chemical materials. The Iigand 1,4-bis(cyclopentadienyl)butane was obtained from the reaction between sodium cyclopentadienide and 1,4-dibromobutane. The ligand then was doubly deprotonated with butyllithium and when treated with ferrous chloride, [4]ferrocenophane was obtained in 13% apparent yield. ^{1}H NMR and UV-Visible spectroscopy have confirmed the synthesis of this compound. In addition, identity of this compound was verified through the ^{1}H NMR and UV-Visible data analysis. Moreover, spectroscopic data analysis of previously reported [1]ferrocenophanes supports the parallel structure of [4]ferrocenophane through the comparison of both the tilted angles and color shifts. The UV-Visible spectrum of [4]ferrocenophane showed two weak bands (326 and 432 nm) similar to that of ferrocene. Even though [4]ferrocenophane was synthesized, the spectroscopic measurements suggest that “flytrap route” was not ideal for making this compound. While it seems likely that this work has improved on Lüttringhaus and Kullick’s 0.053% yield, it is also clear that the inability to purify this material simply makes this route of doubtful usefulness. Also, even if the material obtained here was mostly pure, the yield would still be less than 10%, which is of questionable value.

APPENDIX



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Office of Research Integrity

May 4, 2016

Ahmed Al-doori
1340 4th Ave, Apt. 26
Huntington, WV 25701-2469

Dear Mr. Al-doori:

This letter is in response to the submitted thesis abstract entitled *"Synthesis and Characterization of [4]Ferrocenophane."* After assessing the abstract it has been deemed not to be human subject research and therefore exempt from oversight of the Marshall University Institutional Review Board (IRB). The Code of Federal Regulations (45CFR46) has set forth the criteria utilized in making this determination. Since the information in this study does not involve human subjects as defined in the above referenced instruction it is not considered human subject research. If there are any changes to the abstract you provided then you would need to resubmit that information to the Office of Research Integrity for review and a determination.

I appreciate your willingness to submit the abstract for determination. Please feel free to contact the Office of Research Integrity if you have any questions regarding future protocols that may require IRB review.

Sincerely,

Bruce F. Day

Bruce F. Day, ThD, CIP
Director

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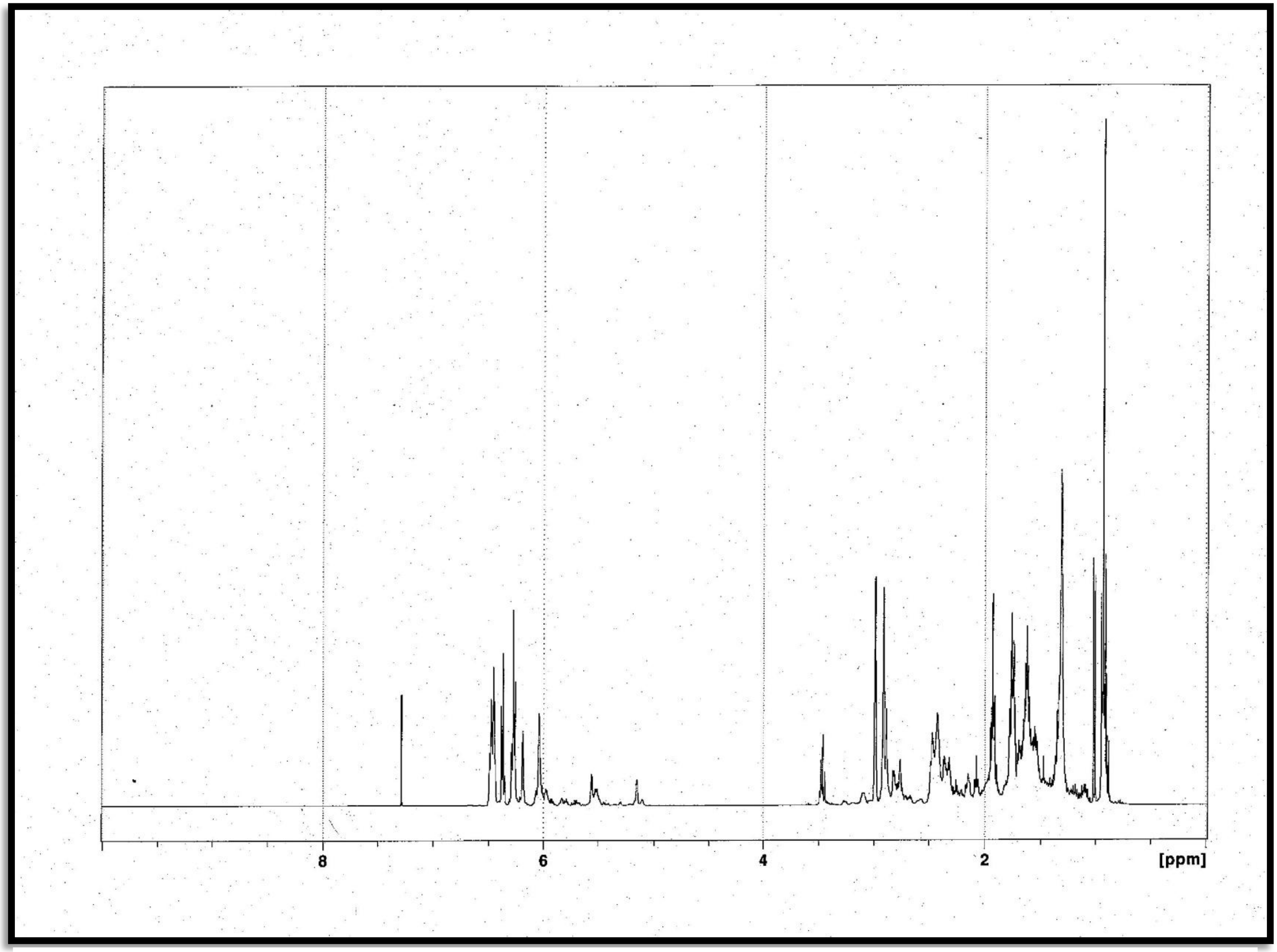

Figure 22: ^{1}H NMR spectrum of 1,4-bis(cyclopentadienyl)butane in $CDCl_3$

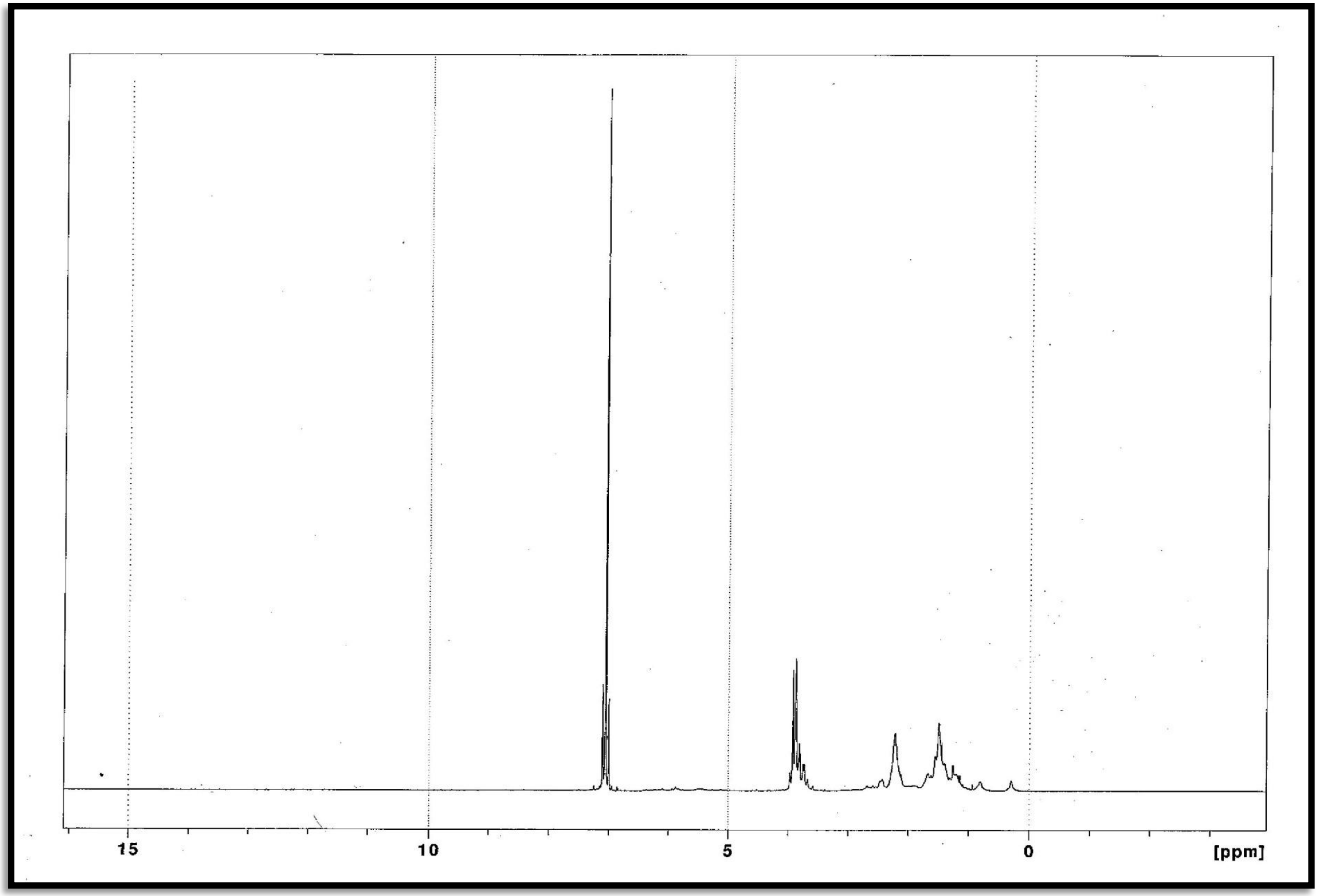

Figure 23: ^{1}H NMR spectrum of [4]ferrocenophane in d_6-benzene

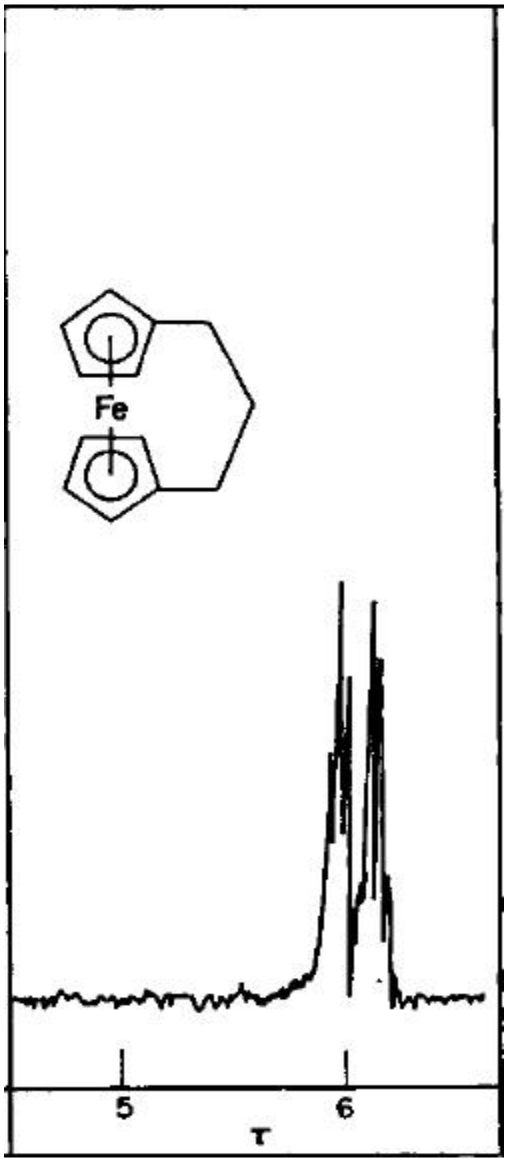

Figure 24: ^{1}H NMR spectrum of [3]ferrocenophane in d_6-benzene [7]

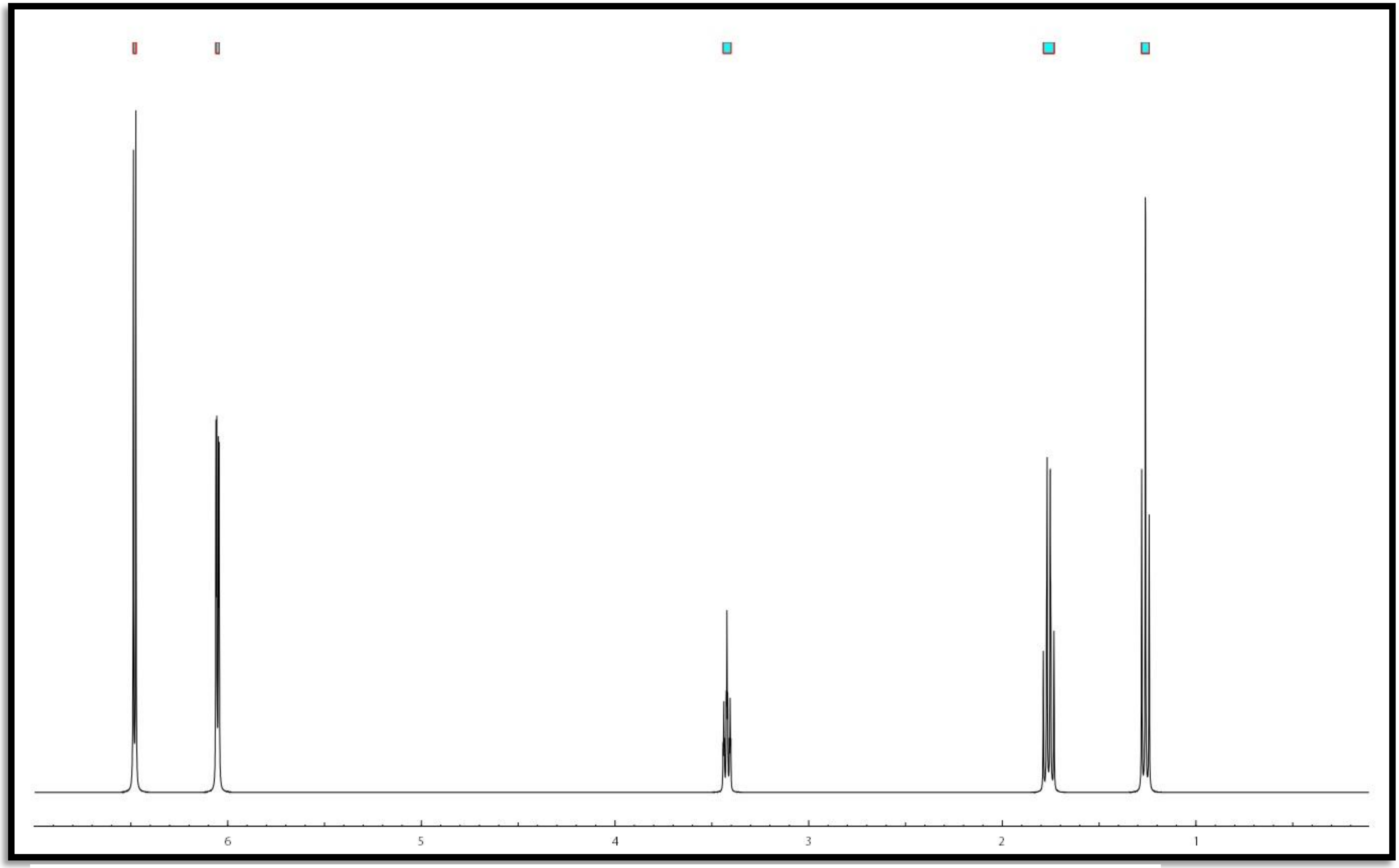

Figure 25: Hypothetical ^{1}H NMR spectrum of 1,4-bis(cyclopentadienyl)butane

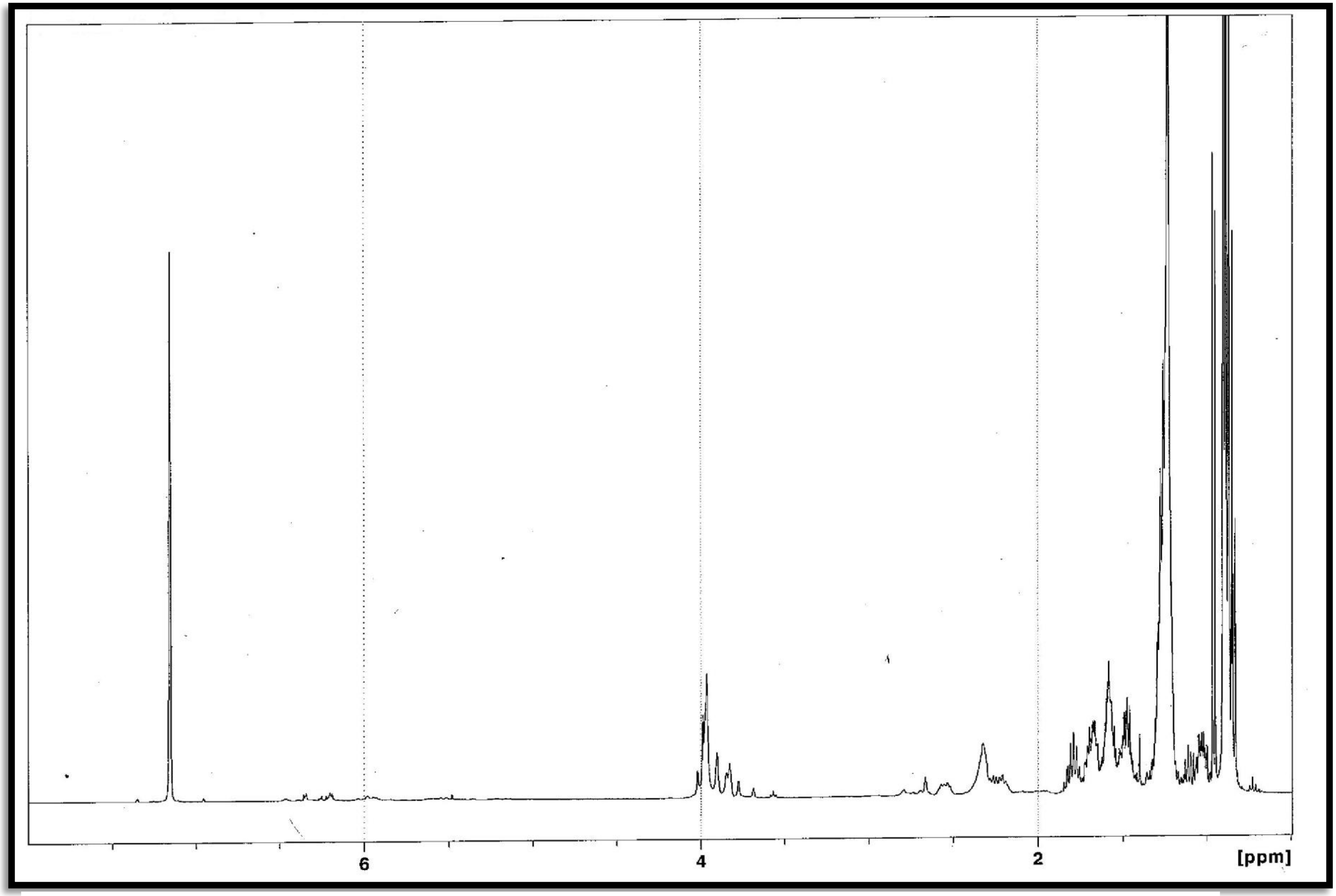

Figure 26: ^{1}H NMR spectrum of the initial mixture of [4]ferrocenophane in $CDCl_3$

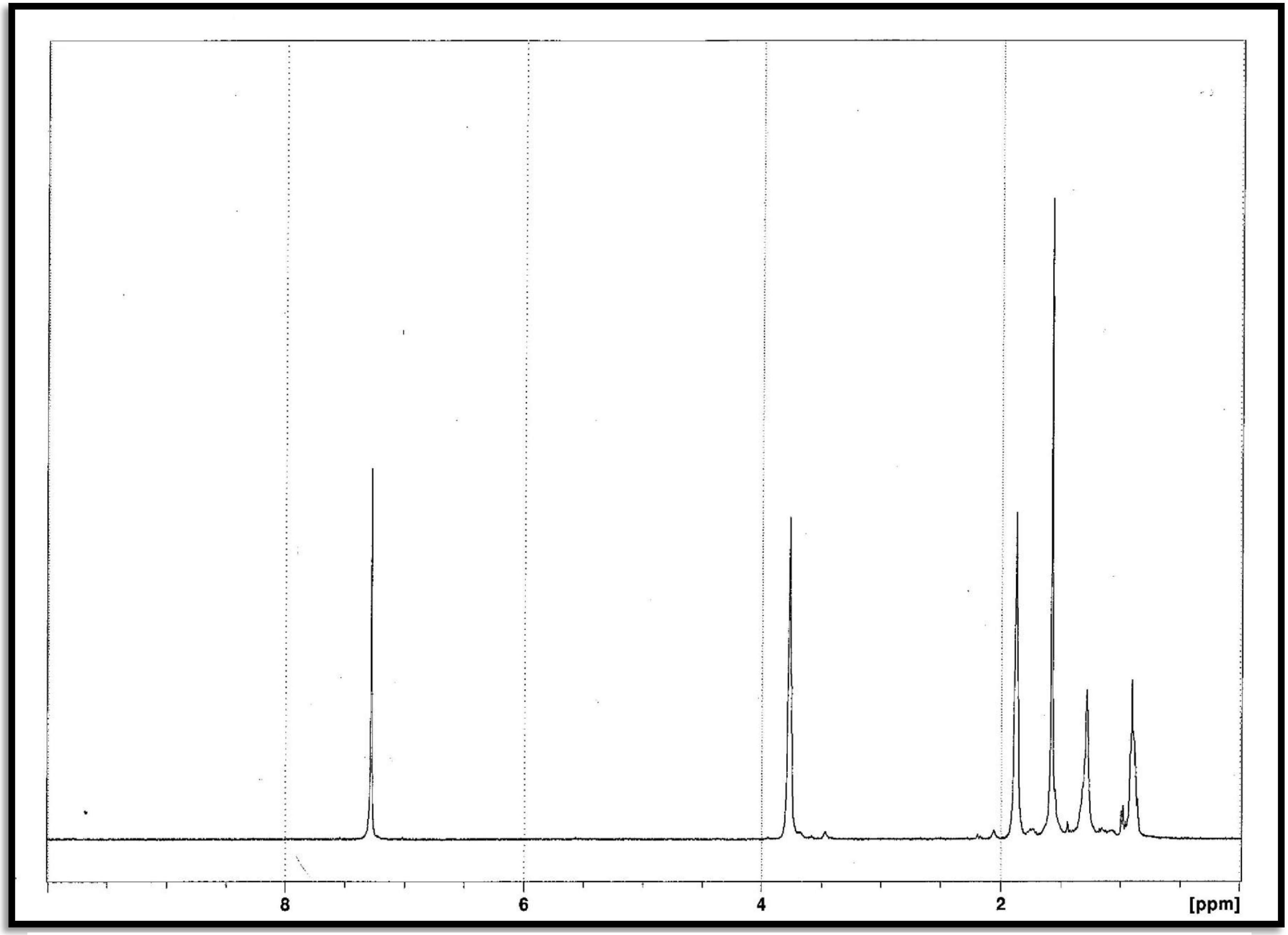

Figure 27: ^{1}H NMR spectrum of the first isolated band of [4]ferrocenophane mixture in d_6-benzene

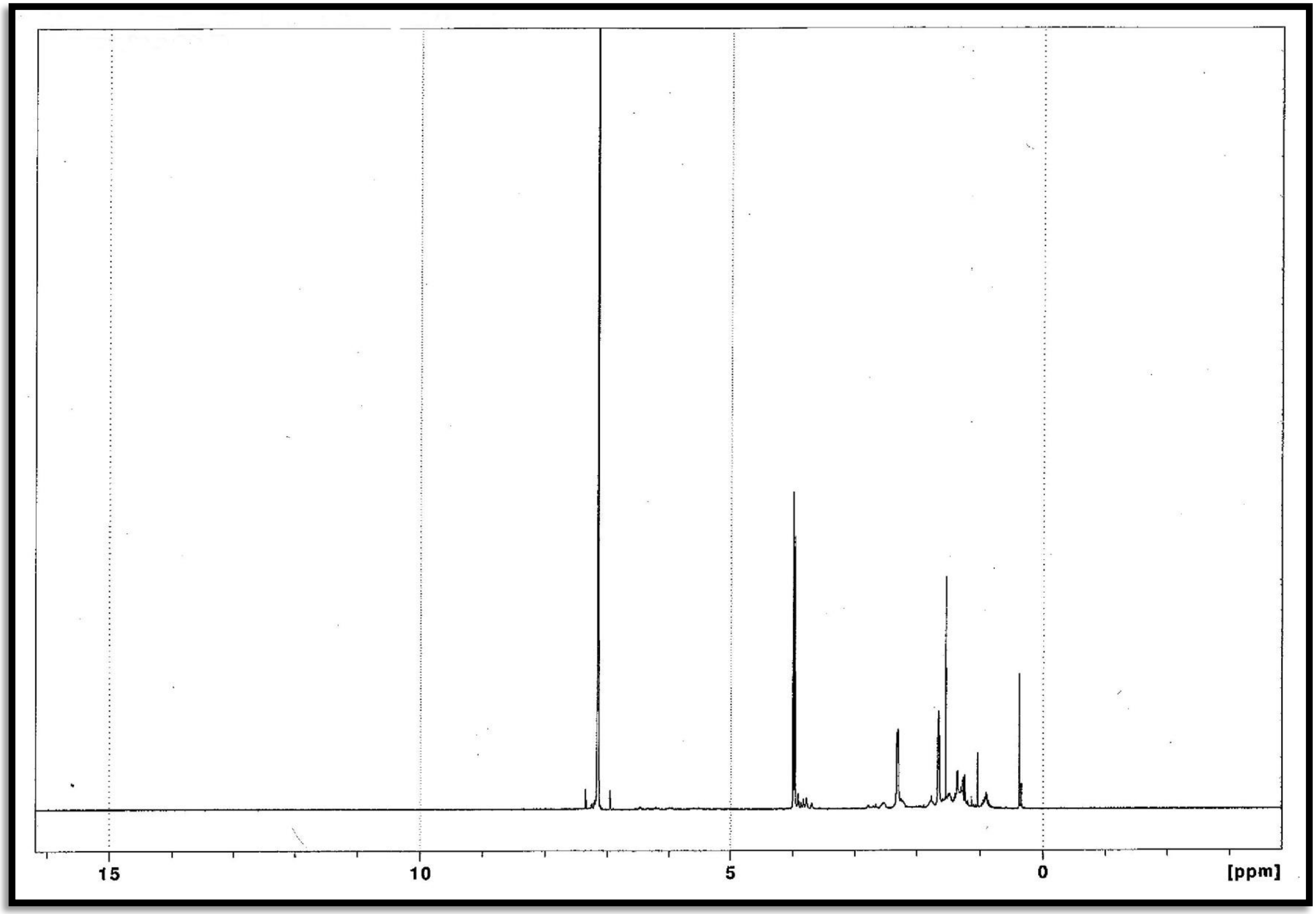

Figure 28: ^{1}H NMR spectrum of the second isolated band of [4]ferrocenophane mixture in d_6-benzene

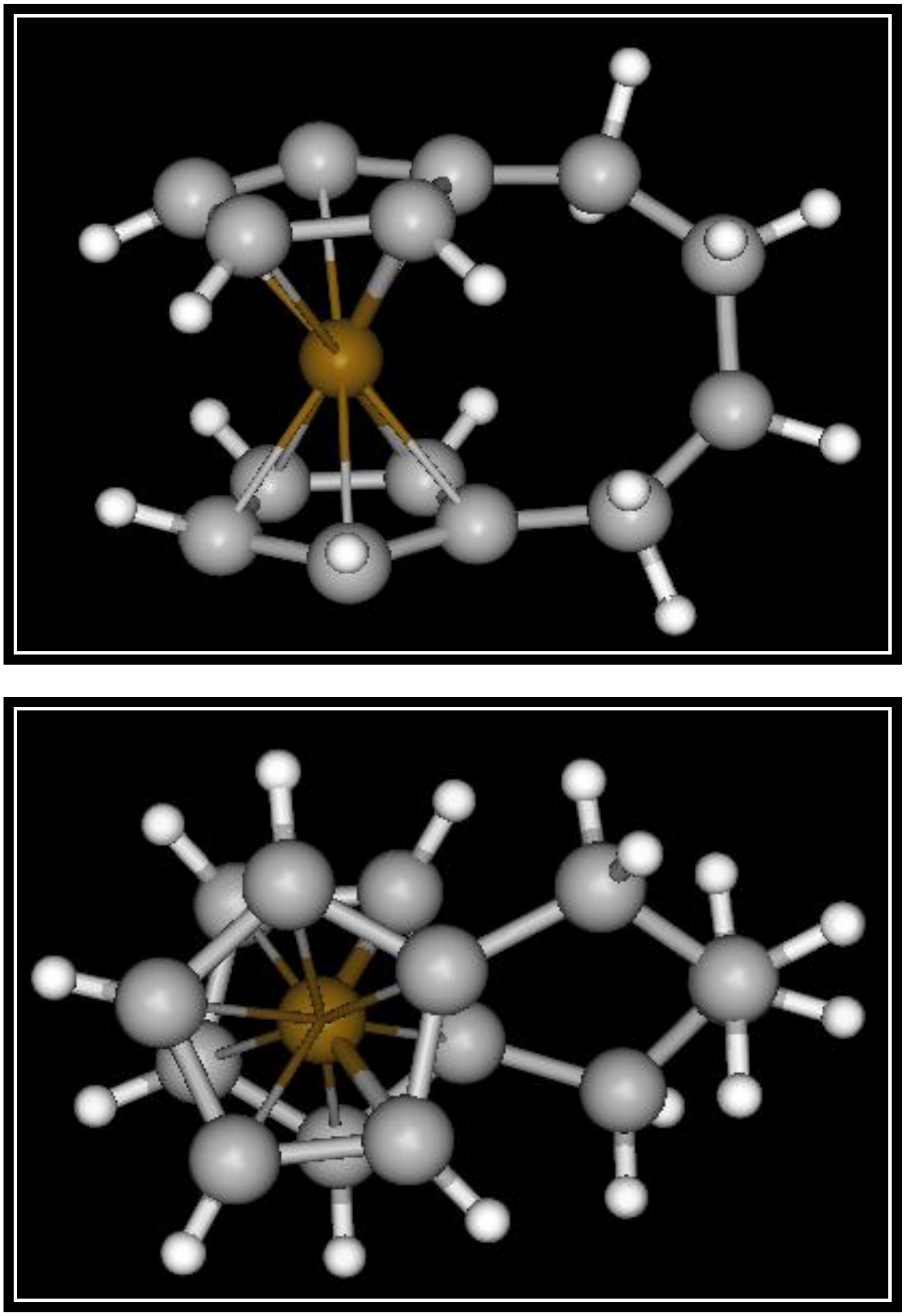

Figure 29: The 3D structure of [4]ferrocenophane.[33]

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