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Selected Studies on Certain Iron Sandwich Complexes

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SELECTED STUDIES ON CERTAIN IRON SANDWICH
COMPLEXES

by

Mashitah M. Yusoff

A Thesis
Submitted to the
Faculty of The Graduate College
in partial fulfillment of the
requirements for the
Degree of Master of Arts
Department of Chemistry

Western Michigan University
Kalamazoo, Michigan
December 1991

I almost wish I hadn't gone down
that rabbit hole; and yet--and yet--
it's rather curious you know, this
sort of life!

Lewis Carroll
Alice in Wonderland

ACKNOWLEDGMENTS

The expert guidance of Prof. William Kelly for the duration of this project is gratefully acknowledged. Funding in the form of graduate teaching and research assistantships (1986-1989) from the Department of Chemistry and the College of Arts and Sciences at Western Michigan University (Kalamazoo), and a Malaysian Federal Teacher's Scholarship (1986-1987) are also acknowledged.

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This thesis is dedicated with love to my parents, Yusoff and Azizah.

Mashitah M. Yusoff

SELECTED STUDIES ON CERTAIN IRON SANDWICH COMPLEXES

Mashitah M. Yusoff, M.A.

Western Michigan University, 1991

In these studies, the synthesis of [2.3](1,3)cyclopentadiendo-paracyclophane was attempted. Like ferrocene and [2.2]paracyclophane, it is expected to exhibit transannular π -electronic interaction throughout its molecular structure and therefore, one dimensional semiconductivity.

The preparation of dialkylferrocenes had resulted in complex inseparable mixtures. Due to the fluxional nature of its intermediates, their conversion to stable Diels-Alder adducts would facilitate analysis. In this project, certain Diels-Alder adducts of *bis*-cyclopentadienyliron dicarbonyl intermediates were prepared for analysis.

Very few transition metal complexes of pyrrole are currently known. [2.2](2,5)Pyrroloparacyclophane was perceived to be stable especially as a part of an iron sandwich complex. The final phase of this project involves the attempted synthesis of the [2.2](2,5)pyrroloparacyclophane analogue of diazaferrocene.

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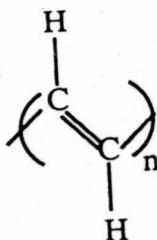
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CHAPTER I

ATTEMPTED SYNTHESIS OF [2.3](1,3)CYCLOPENTADIENDOPARACYCLOPHANE

Introduction

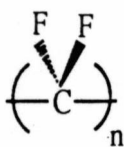
Published works on polymers such as polyacetylene 1 have generated considerable interest in conducting organic compounds.¹ The possibility of other conducting organic compounds like cyclophanes also have been recognized.²



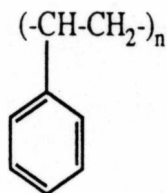
$n = \text{integer}$

1

Conductivity is expressed in $\text{ohms}^{-1} \text{cm}^{-1}$ ($\Omega^{-1} \text{cm}^{-1}$), the inverse of the unit of resistivity. Most organic solids are electrical insulators with typical conductance values of less than $10^{-10} \Omega^{-1} \text{cm}^{-1}$. Good insulators like Teflon 2 and polystyrene 3 have conductivities close to $10^{-18} \Omega^{-1} \text{cm}^{-1}$. Good conductors like copper and silver have conductance close to $10^6 \Omega^{-1} \text{cm}^{-1}$. Compound 1 has a conductance of approximately $147,000 \Omega^{-1} \text{cm}^{-1}$.³



2



3

Electricity flows by the movement of electrons. For material to carry electricity, some of the electrons must be free to move. In an extended network of conjugated bonds, the electron "moves" within and between discrete energy states called "bands." Each energy band has a finite capacity for electrons. The bands may also be empty. Electrons must have a certain energy to occupy a given band. In order to move from one band to another having a higher energy, the electron needs an energetic boost which can be achieved by feeding these electrons with bursts of energy from heat or light sources that can cause them to leap across the gap. Likewise, electron movement also requires a partially filled band. Therefore, conductance resembles a relay.

Compound 1 was first synthesized in 1955. In the early 1970s, another form of 1 was accidentally discovered which was later reported as the first conducting polymer. In 1981, the first battery with polymer electrodes was demonstrated. Six years later, conducting polymers matched the conductance of copper and in early 1988 the first rechargeable polyene battery was put on the market.⁴

Compound 1 is a highly conjugated polymer. Basically the removal of two electrons from its neutral *trans*-isomer forms a radical and cation pair (Figure 1).³ Combination of the radicals result in two cations. Each is shown as being localized but can be delocalized over several sites.

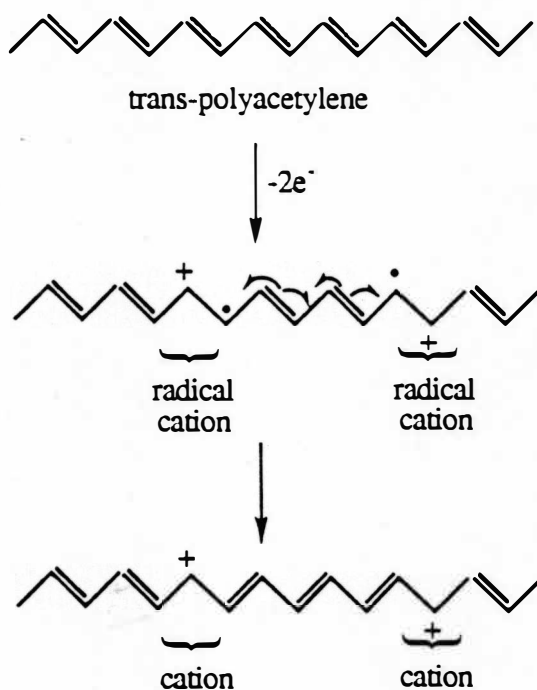
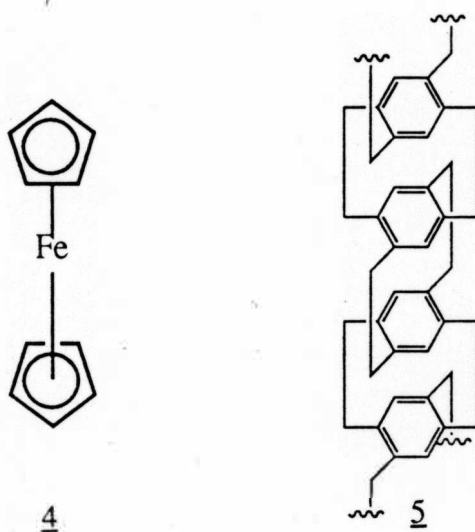
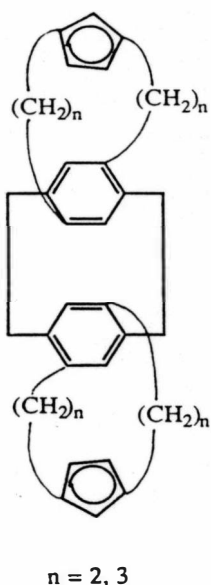


Figure 1. Conductivity of *Trans*-Polyacetylene.

Similarly ferrocene 4 and polydecker sandwich compounds such as 5, can exhibit transannular π -electronic interaction, between the layers and therefore, one-dimensional semiconductivity.

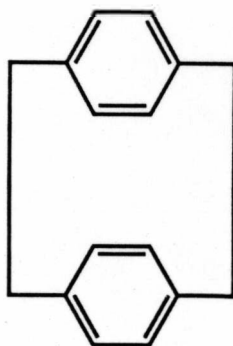


Multilayered cyclophanes with up to six layers have been synthesized which show considerable π -electron delocalization throughout the molecule.⁵ However, the preparation of a multilayered cyclophane, such as 6, has thus far proven elusive.



Cyclophanes

The cyclophane nomenclature was proposed by Cram to describe a certain class of bridged aromatic compounds.⁶ All ring systems containing at least one aromatic nucleus and one bridge, are termed "phane." For example, the "2's" in [2.2]paracyclophane 7 designate the number of carbon atoms in each bridge and "para" indicates that the bridges are para to each other in each aromatic nuclei. "Para" may also be written as "(1,4)." In comparison, the IUPAC nomenclature, although consistent for all compounds, becomes quite tedious for cyclophanes. For example, 7, would be known as tricyclo[8.2.2.2^{4,7}]hexadeca-4,6,10,12,13,15-hexane under this nomenclature.



1

Due to the shortness of the bridges, **1** and its analogs demonstrate large ring strain and conformational rigidity which makes them ideal models for the study of transannular π -electronic interactions (Figure 2).

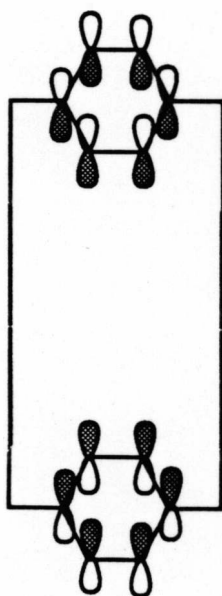
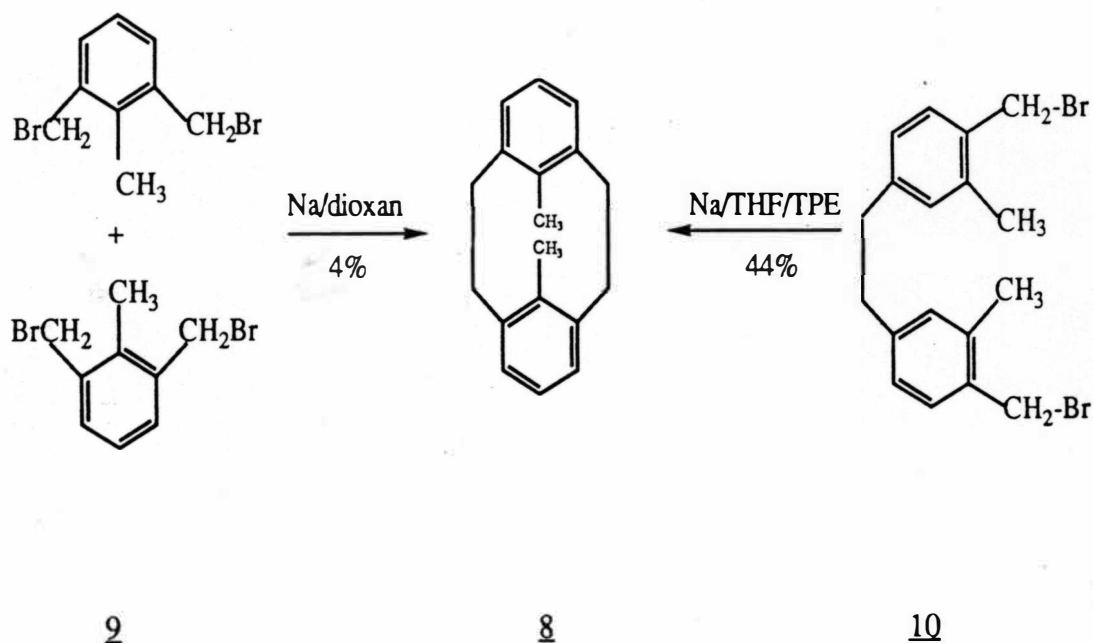


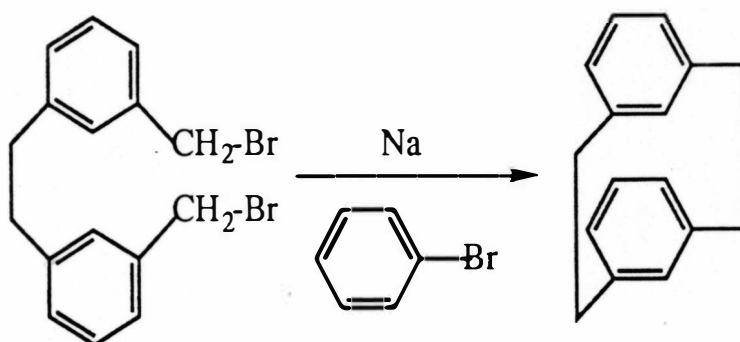
Figure 2. Transannular π -Electronic Interaction in [2.2]Paracyclophane.

The most successful method for the synthesis of [2.2]phanes is the Wurtz or coupling reaction.⁷ For example, in the synthesis of 8,16-dimethyl[2.2]-metacyclophane 8, reactive halogens 9 and 10, underwent ring-closure in the presence of finely divided metallic sodium as follows⁸



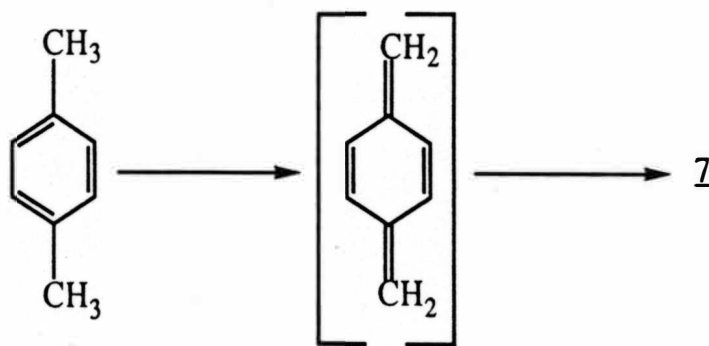
The original Wurtz reaction has since been improved. The yields obtained via the original method were low. Recently organometals such as phenyllithium and butyllithium have been used in place of sodium.

The first evidence of an attempt to prepare a [2.2]phane via the Wurtz reaction was made in 1899 where 1,3-bis-[bromomethyl]-benzene was reacted with excess sodium and molar amount of bromobenzene in water-free ether which resulted in varying yields of product.⁸ This product was later confirmed to be [2.2]metacyclophane, 11.⁹ Later improvement of this method using phenyllithium yielded 39% of 11.¹⁰



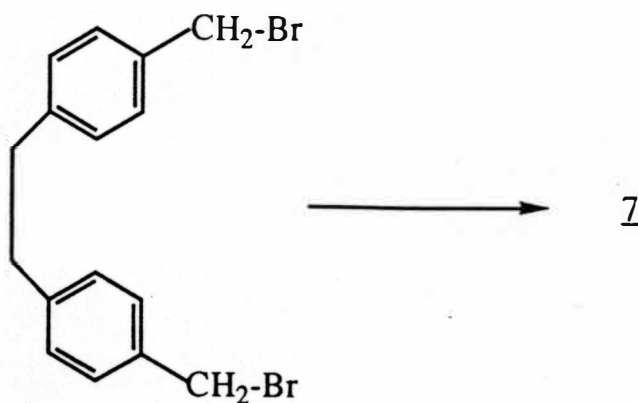
11

The first attempted synthesis of [m.n]paracyclophane was in 1933.¹¹ Brown and Farthing, in trying to isolate and polymerize *p*-xylene by cracking *p*-xylene 12, discovered trace amounts of 7.¹²



12

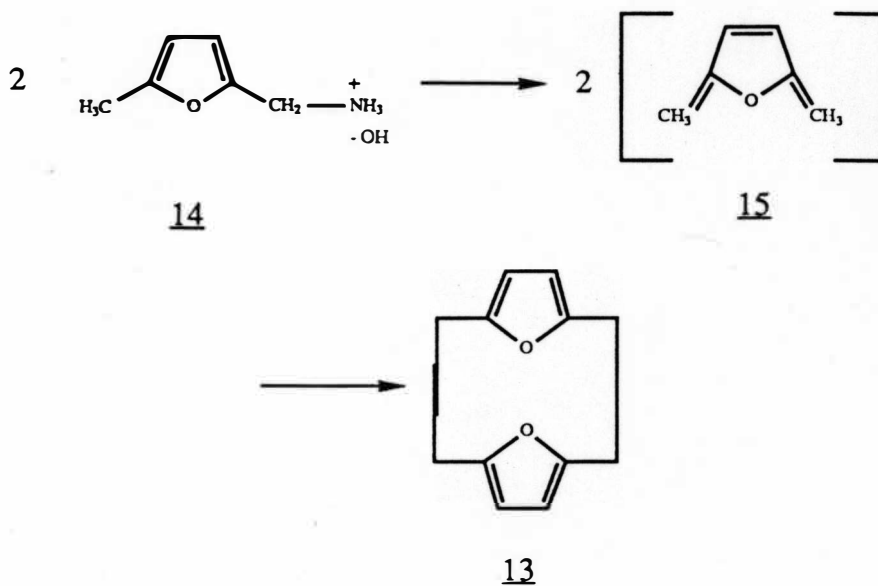
Cram and Steinberg isolated 7 in 2.1% yield via the intramolecular cyclization of 1,2-[bromomethyl]phenyl]-ethane using sodium.¹³



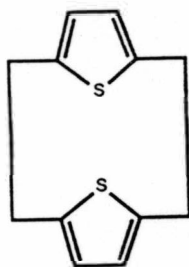
Preparation of Heterophanes

Cyclophanes containing heteroaromatic nuclei are called "heterophanes." The nuclei include for example, furan, pyrrole, thiophene, pyridine, pyridazine, and related five-membered rings.

The 1,6-Hoffman elimination method has found widespread use in the syntheses of [2.2]phanes. Winberg, Fawcett, Mochel, and Theobald used this method to prepare the very first reported [2.2]heterophane, 13.¹⁴



Pyrolysis of the quaternary ammonium hydroxide 14, generated the intermediate 2,5-dimethylene-2,5-dihydrofuran, 15 (stable at -78°C). When heated to reflux in absolute ethanol, [2.2](2,5)furanophane, 13, was obtained in 73% yield.¹³ Similarly, [2.2](2,5)thiophenophane 16 was obtained in 19% by azeotropic removal of water from an analogous reaction.¹⁴

16

Cram, Montgomery, and Knox obtained 7; [2.2](2,5)furanopara-cyclophane, 17; and 13 in 23%, 12% and 9% yields respectively via the crossbreeding 1,6 to 1,6 cycloaddition reaction (Figure 3).¹⁵

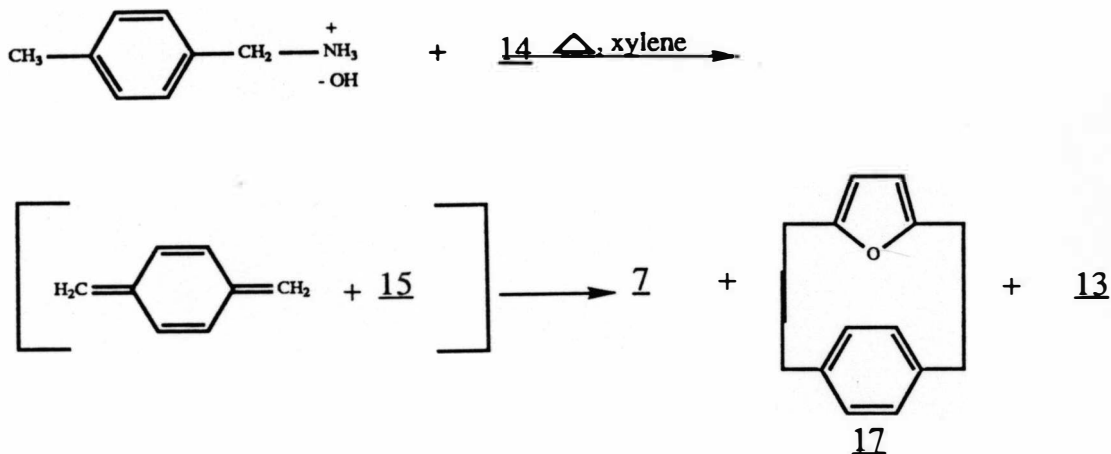
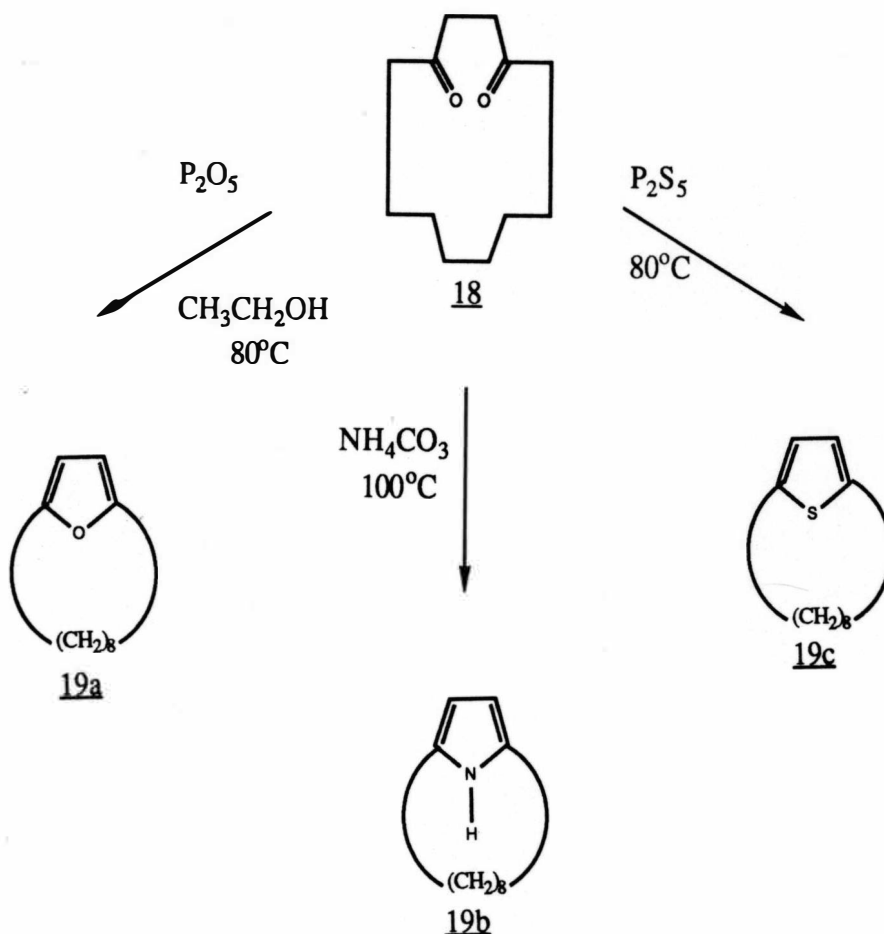


Figure 3. Synthesis of Phanes Via the 1,6 to 1,6 Cycloaddition Reaction.

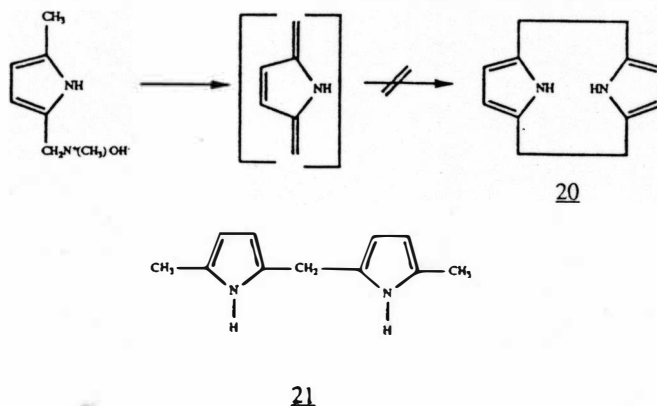
Pyrolysis of equimolecular amounts of *p*-xylyltrimethyl ammonium hydroxide in xylene and 5-methylfurfuryltrimethyl ammonium hydroxide, generated the intermediates 1,4-dimethylenexylene and 2,5-dimethylene-2,5-dihydrofuran, which are stable at -78°C .¹⁶

The work of Nozaki, Koyama, and Mori¹⁶ and later Keehn, Rosenfield, and Haley¹⁷ mainly paved the way for utilizing the Paal-Knorr synthesis of five-membered heterocyclic ring compounds in preparing heterophanes incorporating the pyrrole and thio-moiety.

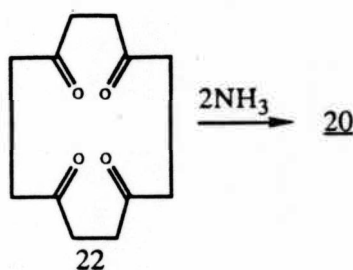
Nozaki et al. prepared [8](2,5)furanophane 19a, [8](2,5)pyrrolophane 19b, and [8](2,5)-thiophenophane 19c from cyclododeca-1,4-dione 18.¹⁶



The attempted synthesis of [2.2](2,5)pyrrolophane 20 by 1,6-Hofmann elimination proved unsuccessful and led only to dipyrromethanes 21.



Synthesis of 20 was eventually accomplished using the Paal-Knorr cyclization of 3,6-diketo[8]paracyclophane 22.¹⁷



Quod erat demonstrandum

Although the preparation of 6 has so far been fruitless, it is highly likely that 6 can be easily isolated as a moiety incorporated into an iron sandwich complex structure such as 4. π -Electron delocalization in such systems with its alternating organic and inorganic "monomers" is expected to be extensive. Mixed valence organometalocene polymers such as polyvinylferrocene has been found to be semiconducting when oxidized to approximately 50% Fe(III).¹⁸

Research Objective

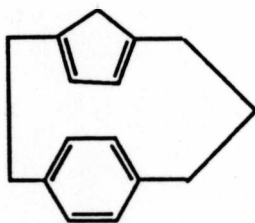
Ferrocene 4 and [2.2]paracyclophane 7 are the most thoroughly investigated double-layer molecules in organometallic and organic chemistry. It was proposed that these two prototypes might be linked with each other so as to form multilayered systems having the general structure 23 in which inorganic and organic elements alternate.¹⁹



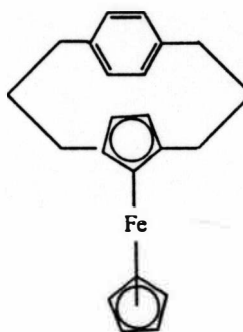
23

The electrochemical behavior of oligomers and polymers of this type is of particular interest as several authors have asserted that multinuclear complexes derived from 4 may function as "electron reservoirs," thereby storing or transferring electrons either stoichiometrically or catalytically.²⁰

The carbanions derived from [2.3](1,3)cyclopentadiendoparacyclophane 24 are considered to be particularly well-suited as the organic structural components for the aforementioned system.



24



25

Although 6 has not been synthesized previously, a structurally similar [3.3](1,3)ferrocenophane 25 has been prepared through a high-dilution condensation of 1,3-diformylbenzene and 1,3-diacetylferrocene.²¹

The goal of this research then is the preparation of 24. First, the crossbreeding reaction method as reported by Cram, et al. for 17¹⁵ and modified by Whitesides, Pawson, and Cope²² was duplicated. This reaction proceeded by way of 1,6-Hoffman elimination (Figure 3). (*Vita supra*)

Figure 4 was envisioned for the synthetic route toward 24.

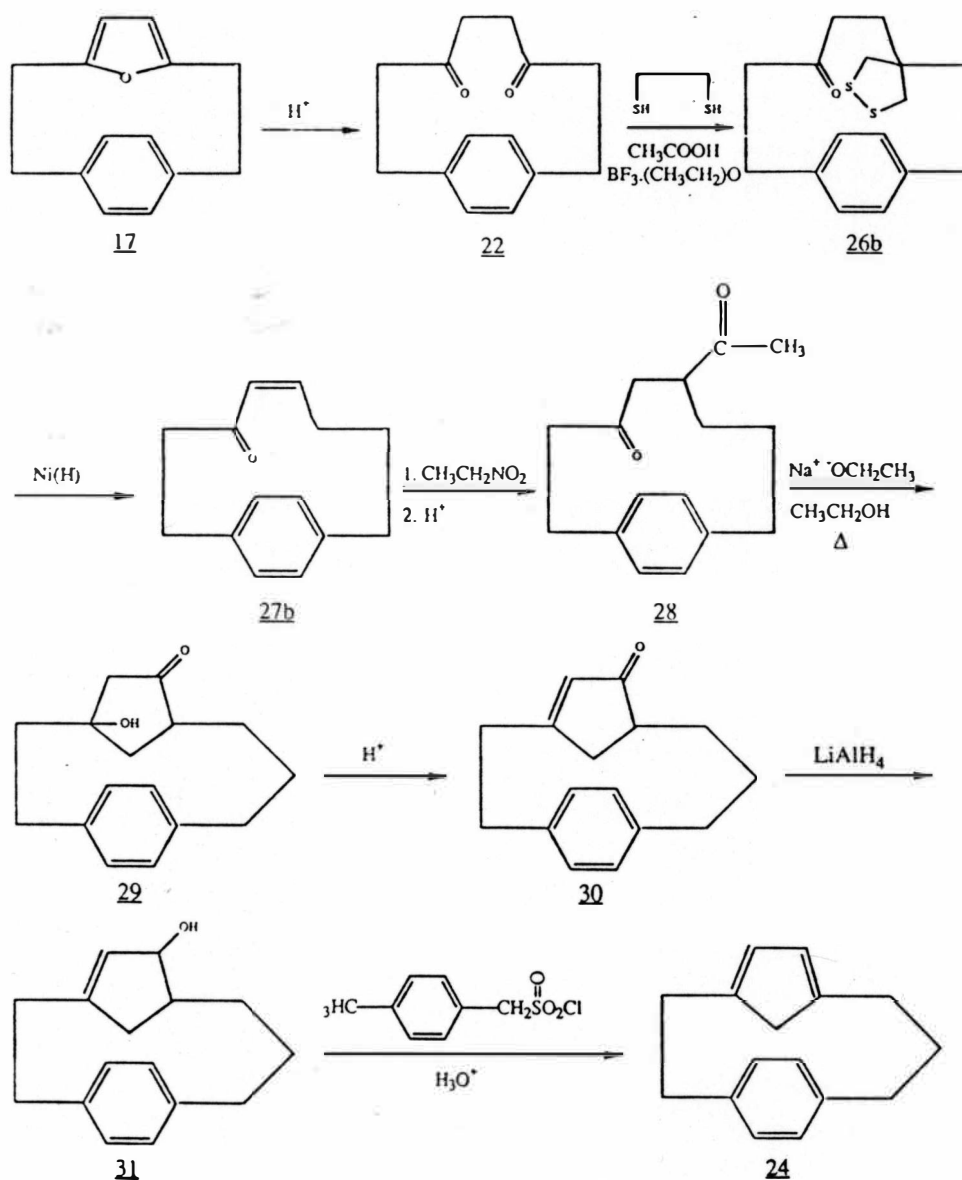


Figure 4. Proposed Synthesis of [2.3](1,3)cyclopentadiendoparacyclophane.

According to Cram et al., [2.2](2,5)furanoparacyclophane 17 was to undergo acid hydrolysis to yield 3,6-diketo[8]paracyclophane 22. Treatment of 22 with 1 mole of ethanedithiol in an acetic acid-boron trifluoride etherate would result in a mixture of which the monoethanedithioketal 26b would be isolated. Then, desulfurization of 26 with W-2 Raney nickel should generate a mixture of which 3-keto-4-[8]paracyclophene 27b would be the compound of interest.¹⁶

Based on the work of Nozaki 27b would then be subjected to a Michael addition reaction followed by a Nef reaction to give the diketone 28.¹⁷ The latter would then undergo condensation in the presence of sodium ethanoate in warm ethanol to form 29. In acid, 24 would be hydrolyzed to 30 and upon reduction with lithium aluminum hydride, would form the alcohol 31. Introduction of tosylate ion using p-toluenesulfonic acid for example, would then be routine as tosylate is a good leaving group and following dehydration, would easily give the desired product 24. [Refer to Appendix A for mechanism of this synthesis.]

Eventual introduction of a cyclopentadiene unit into the paracyclophane will enable construction of a ferrocene-like sandwich complex 32 (Figure 5).

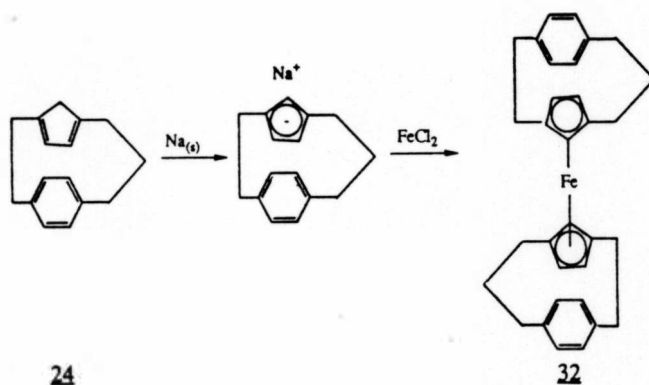


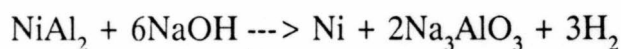
Figure 5. Construction of [2.3](1,3)Cyclopentadiendoparacyclophane Iron Sandwich Complex.

Discussion

The initial preparation of the monoethanedithioketal, 26b proceeded smoothly and in 14% overall yield. However the first encounter with a major difficulty in our proposed synthesis appeared at the desulfurization step involving W-2 Raney nickel. According to Cram et al.¹⁵ the yields for 27a and 27b were 26% and 30% respectively.

However, actual yield was very low (<0.01%) such that analysis of final product was difficult. Infrared spectra in chloroform showed two carbonyl stretches: 1710 cm⁻¹ for 27b and 1695 cm⁻¹ for 27a. The difference in R_f values for these two compounds was 0.01 which implied that separation was nearly impossible under normal conditions.

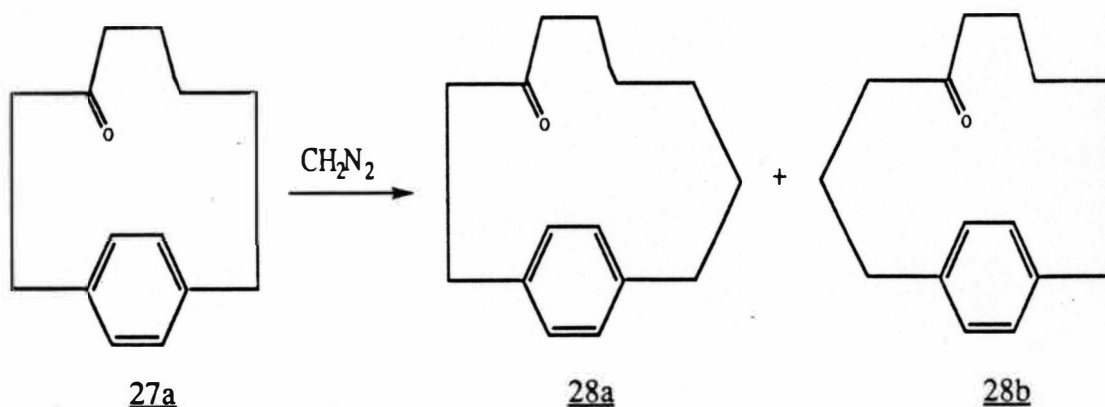
W-2 Raney nickel used in the above reaction was obtained commercially and deactivated. In another trial, W-2 Raney nickel was prepared from nickel-aluminum alloy (NiAl₂)²³.



There was no improvement in yield using this later batch of W-2 Raney nickel.

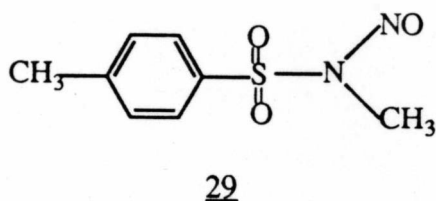
Chain Extension of Ketones

In a separate trial to experiment with chain extension of ketones, 27a was subjected to diazomethane (CH₂N₂) to generate 3-keto[9]paracyclophane, 28a, and 4-keto[8]paracyclophane, 28b.



Since **27a** prefers carbon addition on the longer keto bridge to avoid steric constraints, **28a** is therefore expected to be the predominant product. The mechanism of such methylene unit insertion into a single bond is not clearly understood but is possibly a free radical process.²⁴

Diazomethane was prepared fresh from N-methyl-N-nitroso-p-toluene-sulfonamide **29** (or Diazald, which was obtained from Aldrich) in a mini-Diazald generator as described by Black.²⁵



First, the diazomethane was tested on some 4-heptanone for reactivity. Result: 100% conversion to 4-octanone.

Next, **26b** was desulfurized with commercial, deactivated W-2 Raney nickel to generate **27a**. The product was an inseparable mixture. Treatment with diazomethane without separation would result in another complex mixture. It is possible that a slight warming of the reaction mixture that took place initially may have contributed to the formation of **27b**.

Conclusion

The methods of Cram et al.¹⁵ in desulfurization of 26b using W-2 Raney nickel were irreproducible. Thus the remaining route toward 24 could not be realized. A special mention must be made regarding the Raney nickel reagent used for desulfurization: it can lead to side reactions involving reduction, oxidation, rearrangement, or condensation.²³

Experimental Section

Infrared spectra were taken on a Beckman Acculab infrared spectrophotometer. Nuclear magnetic resonance spectra were obtained on the IBM-NR/200AF.

Column chromatography was done with Woehlm neutral alumina Activity I. Plates used in thin layer chromatography were EM Science Pre-coated TLC Plates Silica Gel 60 F-254. Compounds were located by ultraviolet rays or spotting in an iodine chamber.

[2.2](2,5)Furanoparacyclophane was generated in this laboratory via the method of Cram et al.¹⁵ as modified by Whitesides et al.²² Raney nickel catalyst (analogous to Raney 28 or W-2) was obtained from Aldrich.

Solvents used in the reactions and developing the chromatograms were distilled. Dioxane and acetone were distilled from CaH_2 and stored over molecular sieves (3\AA).

Melting points were determined on the Thomas Hoover Uni-Melt capillary melting point apparatus and were uncorrected.

3,6-Diketo[8]paracyclophane, 22

A solution of 4.65g (0.023 mole) of 17, 27 mL of water, 54 mL of glacial acetic acid, and 1.5 mL of 10% sulfuric acid was refluxed for 18 hours. The solution was cooled, poured into 500 mL of water, and extracted with three 50-mL portions of dichloromethane. The organic layer was washed with water, saturated sodium bicarbonate solution, then saturated sodium chloride solution, and was dried. Removal of the solvent yielded 5.00 g of yellow solid which was crystallized from 95% ethanol to give 4.32 g (87%, lit. 82%) of colorless crystalline 22, mp 154.5-155.0°C [lit.¹⁵ 154.0-154.5]. IR (CHCl₃): ν , cm⁻¹ (C=O) 1715 [lit.¹⁵ 1705]. NMR (CDCl₃) δ , ppm: 1.78 (s, 4H) 2.70 (b, 4H) 2.75 (b, 8H) 7.10 (s, benzylic)

Monoethanedithioketal, 26b

A solution of 3.00 g (0.014 mole) of 22 in 120 mL of glacial acetic acid was treated with a solution of 1.33 g (0.014 mole) of ethanedithiol in 66 mL of glacial acetic acid, and to the resulting solution was added 0.6 mL of boron trifluoride etherate. The reaction mixture was sealed tightly and allowed to stand for 2 days at 25°C. the reaction mixture was poured in 500 mL of water, the mixture was extracted with three 150-mL portions of dichloromethane, and the combined organic layers were washed with water, saturated sodium bicarbonate, and saturated sodium chloride solution. The solution was dried over anhydrous magnesium sulfate and evaporated, and the residue taken up in a

minimum amount of benzene and subjected to alumina column chromatography. Elution with 10% ether-90% pentane yielded 0.45 g (16%, lit.¹⁵ 67%) of the bisethanedithioketal 26a, which when recrystallized from ethanol gave mp 139-140°C [lit.¹⁵ 139.0-139.5)

Elution of the column with 50% ether-50% pentane produced 2.66 g (67%, lit.¹⁵ 67%) of the monoethanedithioketal 26b, which when recrystallized from ethanol gave mp 157-158°C [lit. 157-157.50°C]. IR (CHCl₃): ν , cm⁻¹ (C=O) 1715 [lit.¹⁵ 1707]. NMR (CDCl₃) δ , ppm: 2.28 (b, 2H) 2.50 (t, 2H) 3.02 (b, 2H) 3.13 (t, 2H) 3.39 (s, 4H) 7.25-7.45 (b, benzylic)

Elution of the column with pure ether produced 0.33g of starting material.

3-Keto-4-[8]paracyclophene, 27b

To a solution of 1.75g (0.006 mole) of 26b in 100 mL of dioxane was added 17.5 g of W-2 Raney nickel which had been deactivated by refluxing it in dry acetone for 2 hours. The mixture was refluxed for 10 hours, cooled, and filtered, and the solvent was removed *in vacuo*. The product, a brown-yellow oil, was diluted with pentane and subjected to alumina column chromatography. Elution of the column with 10% ether-90% pentane and evaporation *in vacuo* gave a yellow oil. Crystallization effected from hexane yielded 0.006g (0.50%) of yellow solid, mp 52.0-56.0°C [lit.¹⁵ 56.0-57.0 - 27b and 69.0 for 27a]. IR (CHCl₃): ν , cm⁻¹ (C=O) 1695 [lit.¹⁵ 1687 - 27b], 1710 [lit. 1709 - 27a]

Ether eluted approximately 1 g of starting material. Further purification was not possible.

3-Keto[8]paracyclophane, 27a

To a solution of 1.75 g (0.006 mole) of 26b in 100 mL of acetone was added 17.5 g of W-2 Raney nickel which had been deactivated by refluxing it in dry acetone for 2 hours. The mixture was stirred for 1 hour at room temperature, filtered, and the solvent removed *in vacuo*. Crystallization was effected on the brownish-yellow oil obtained with hexane to yield 0.90 g (74.3%, lit.¹⁵ 80%) of yellow solid, mp 63.5-66.5°C [lit.¹⁵ 69.0]. Infrared (CHCl₃) gave carbonyl stretches at 1705 cm⁻¹ and 1605 cm⁻¹. NMR (CDCl₃) δ , ppm: 2.50 (t, 2H) 2.80 (t, 2H) 3.10 (t, 2H) 5.10 (m, olefinic) 7.30 (s, benzylic).

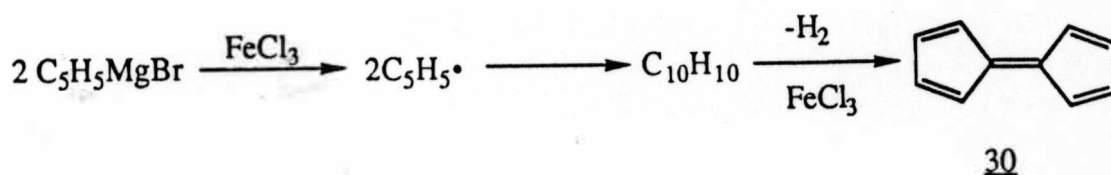
Ether eluted approximately 0.4 g of starting material.

CHAPTER II

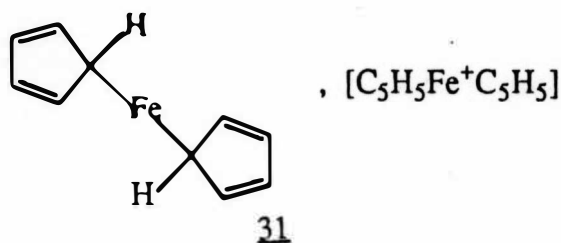
PREPARATION OF DIELS-ALDER ADDUCTS OF CERTAIN BIS-CYCLOPENTADIENYLIRON DICARBONYL INTERMEDIATES

Introduction

In 1951, Kealy and Pauson, while attempting to synthesize fulvalene 30, obtained the highly stable ferrocene instead.²⁶



The following structure 31 was originally proposed for ferrocene.



Research activity intensified when two independent groups discovered ferrocene's unusual *pi*-bonded structure. Fischer proposed the "double-cone structure" (Figure 6) based on X-ray structural analysis and observations of diamagnetism and chemical behavior.²⁷

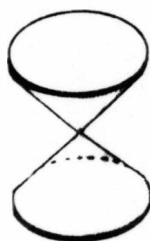


Figure 6. Fischer's "Double-cone Structure" of Ferrocene.

Wilkinson independently proposed the "sandwich structure" (Figure 7) based on infrared spectroscopy, observations of diamagnetism, and zero dipole moment.²⁸

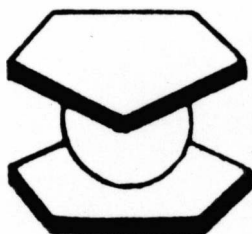
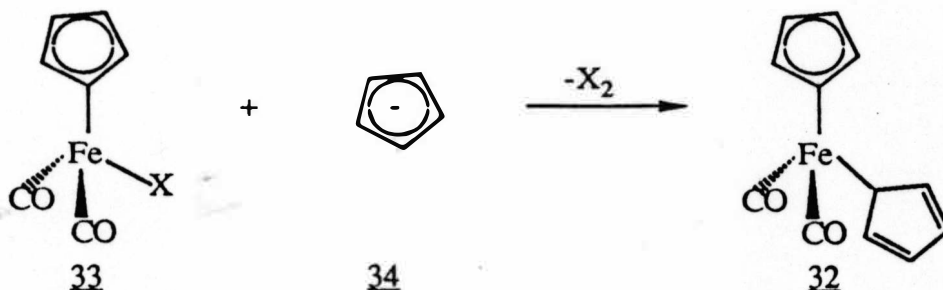


Figure 7. Wilkinson's "Sandwich Structure" of Ferrocene.

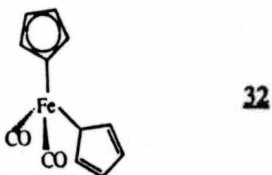
The International Union of Pure and Applied Chemistry (IUPAC) has recommended a special nomenclature for complexes containing unsaturated hydrocarbons(ligands) coordinated to metal. In π -complexes, at least two carbons of the ligand are bonded to the metal. However, since the exact nature of the bonding (i.e., either the π - or the σ -) is often uncertain, it is more precise to indicate the atoms bonded to the metal atom. According to the IUPAC, when all the unsaturated carbon atoms are coordinated to the metal, the name

of the ligand is preceded by " η -" (the Greek symbol pronounced "eta," meaning "hapto"). The number of coordinated ligands is additionally indicated by a numerical right superscript. When only one ligand atom is bonded to the metal atom, the prefix " η^1 -" (indicating σ -bonded) is used. For example, the following structure, 32, is $\eta^5\text{-C}_5\text{H}_5\text{Fe(CO)}_2 \eta^1\text{-C}_5\text{H}_5$ (commonly abbreviated "Fp Cp").

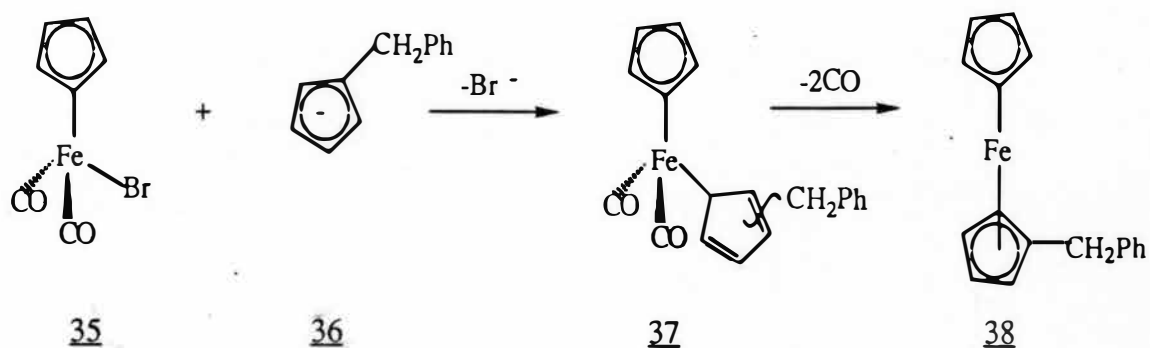


Every carbon in each cyclopentadiene ring capping the iron, is sp^2 hybridized and has a p orbital capable of overlapping to give a cyclic π system parallel above and below the ring which in turn overlap with the empty d orbitals of the metal iron.

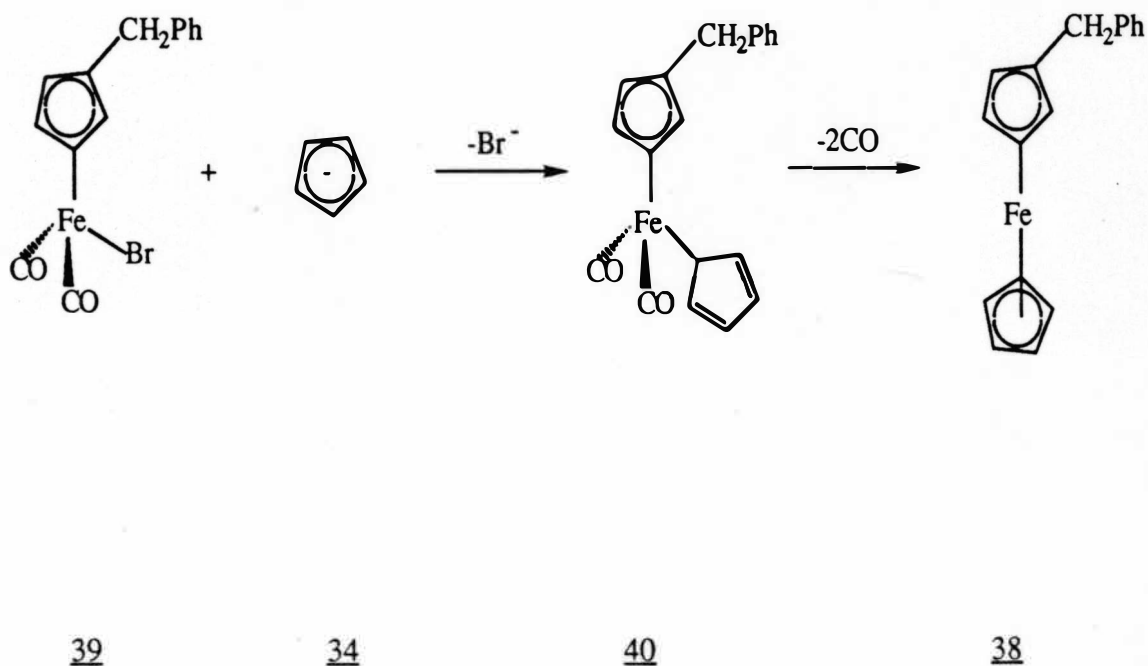
In 1956, Piper and Wilkinson reported the preparation of ferrocene from the reaction of η^5 -cyclopentadienyliron dicarbonyl halide (commonly abbreviated FpX) 33 and cyclopentadienide anion (commonly abbreviated Cp-) 34, which proceeded via the *bis*-cyclopentadienyliron dicarbonyl intermediate, 32.²⁹ In this intermediate, one cyclopentadienyl cap is π -bonded while the other is σ .



In the same year, Hallam and Pauson³⁰ described the preparation of benzylferrocene 38 from the reaction of FpBr and the anion of benzyl cyclopentadiene.

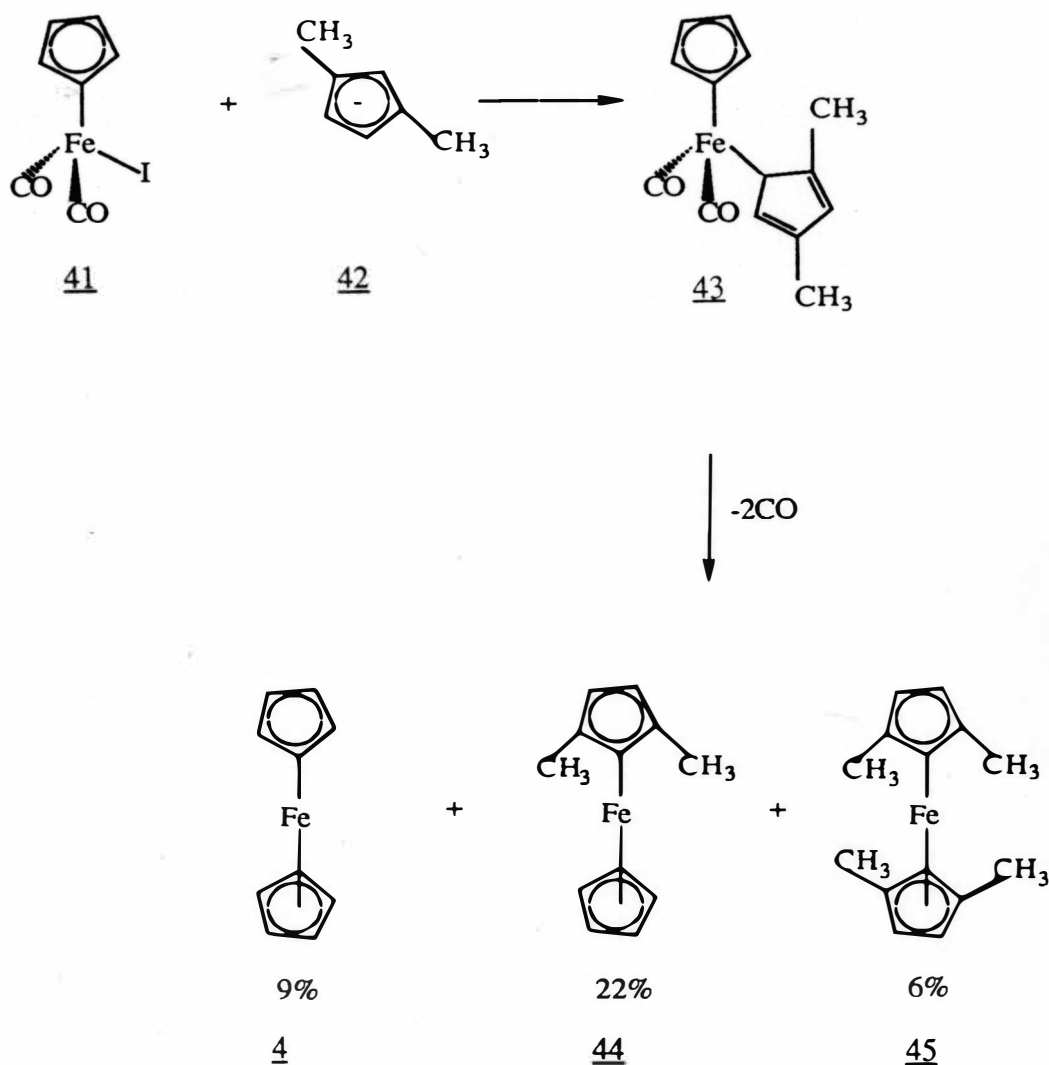


The inverse of this reaction was also reported in the paper. In the reaction, 38 was prepared by the reaction of benzylcyclopentadienyliron dicarbonyl bromide and 34. Bis-cyclopentadienyliron dicarbonyl complex was isolated as the intermediate in both reactions.³¹

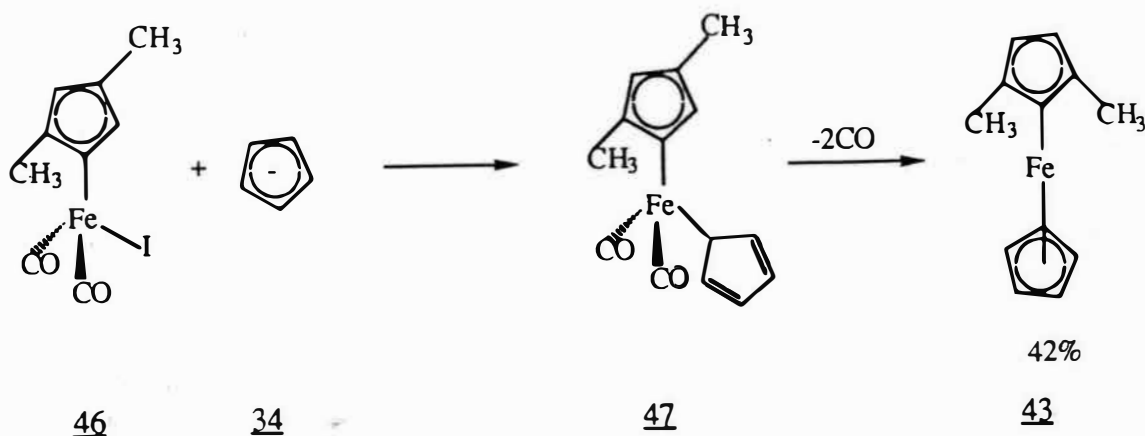


The usual preparation of dialkylferrocenes involves repeated substitutions and difficult separation of regioisomers.³² Kelly et al.,³³ in attempting to prepare 1,3-dimethylferrocene, uncontaminated by the 1,1'- and 1,2-regioisomers, employed the reaction described by Hallam and Pauson.³⁰

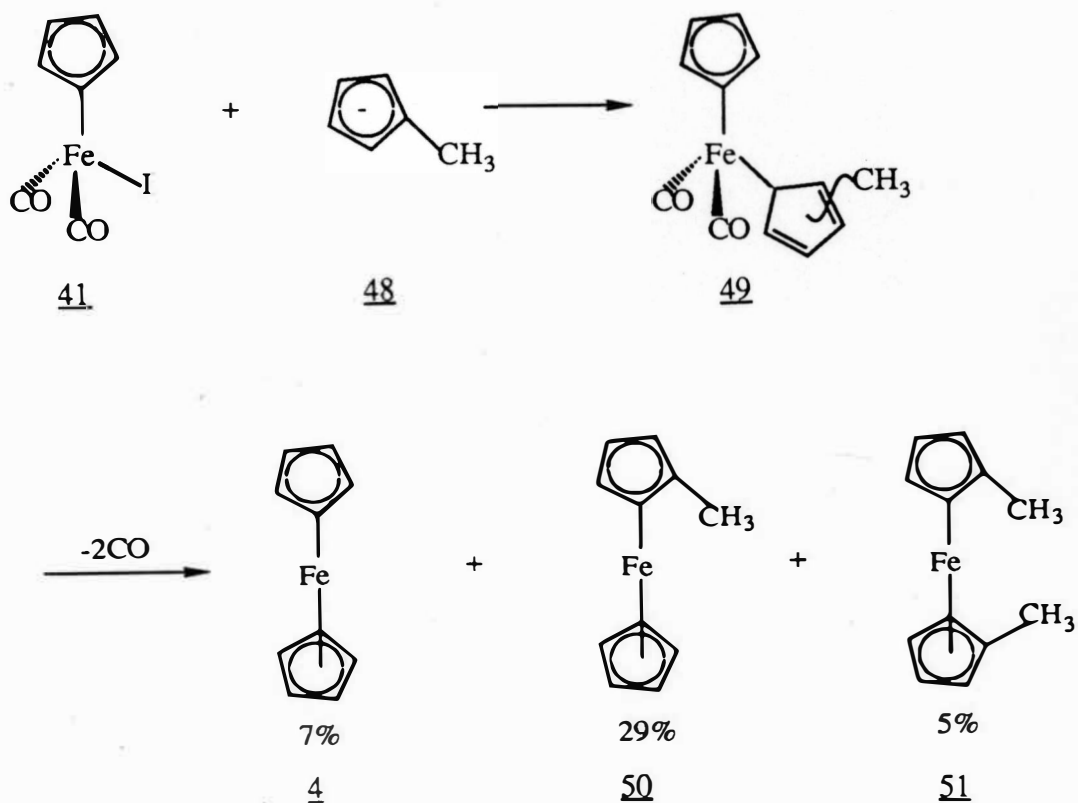
FpI, 41, was treated with potassium 1,3-dimethylcyclopentadienide, 42, generating an unexpected mixture of ferrocenes. In addition to the desired 1,3-dimethylferrocene 44, ferrocene 4, and 1,1', 3,3'-tetramethylferrocene 46 were



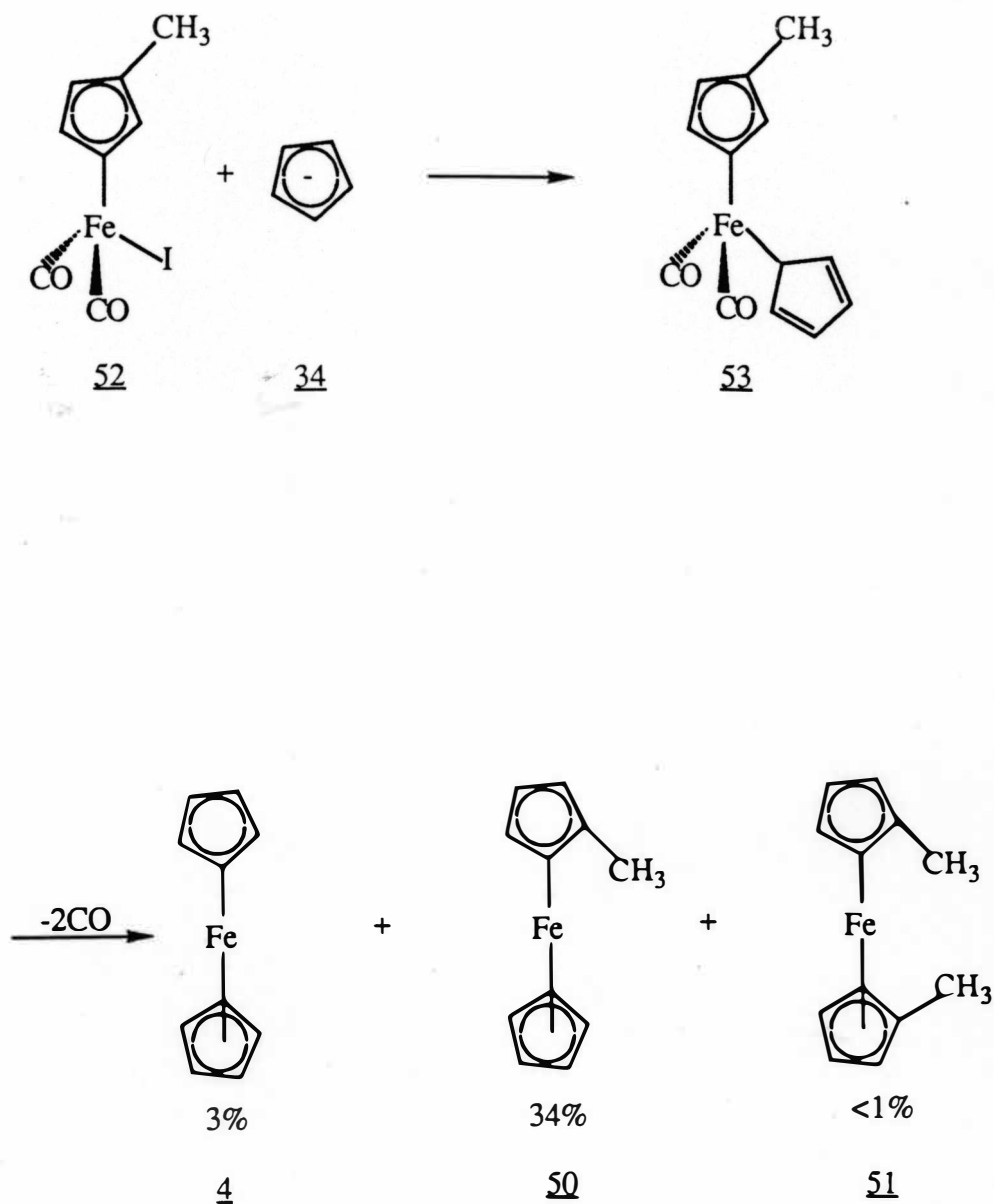
When the inverse of the reaction was taken, a mixture of product was obtained with a very large percentage of the desired 1,3-regioisomer, 44.



Similarly, when 41, reacted with the anion of methylcyclopentadienide 48, a mixture of ferrocenes was observed.



When MeFpI , 52, was reacted with 34, which was the reverse of the above reaction, a mixture of ferrocenes was observed in smaller amounts.



Kelly et al.³⁴ have proposed the following mechanism to explain the nature of the *bis*-cyclopentadienyliron dicarbonyl complex intermediate (Figure 8).

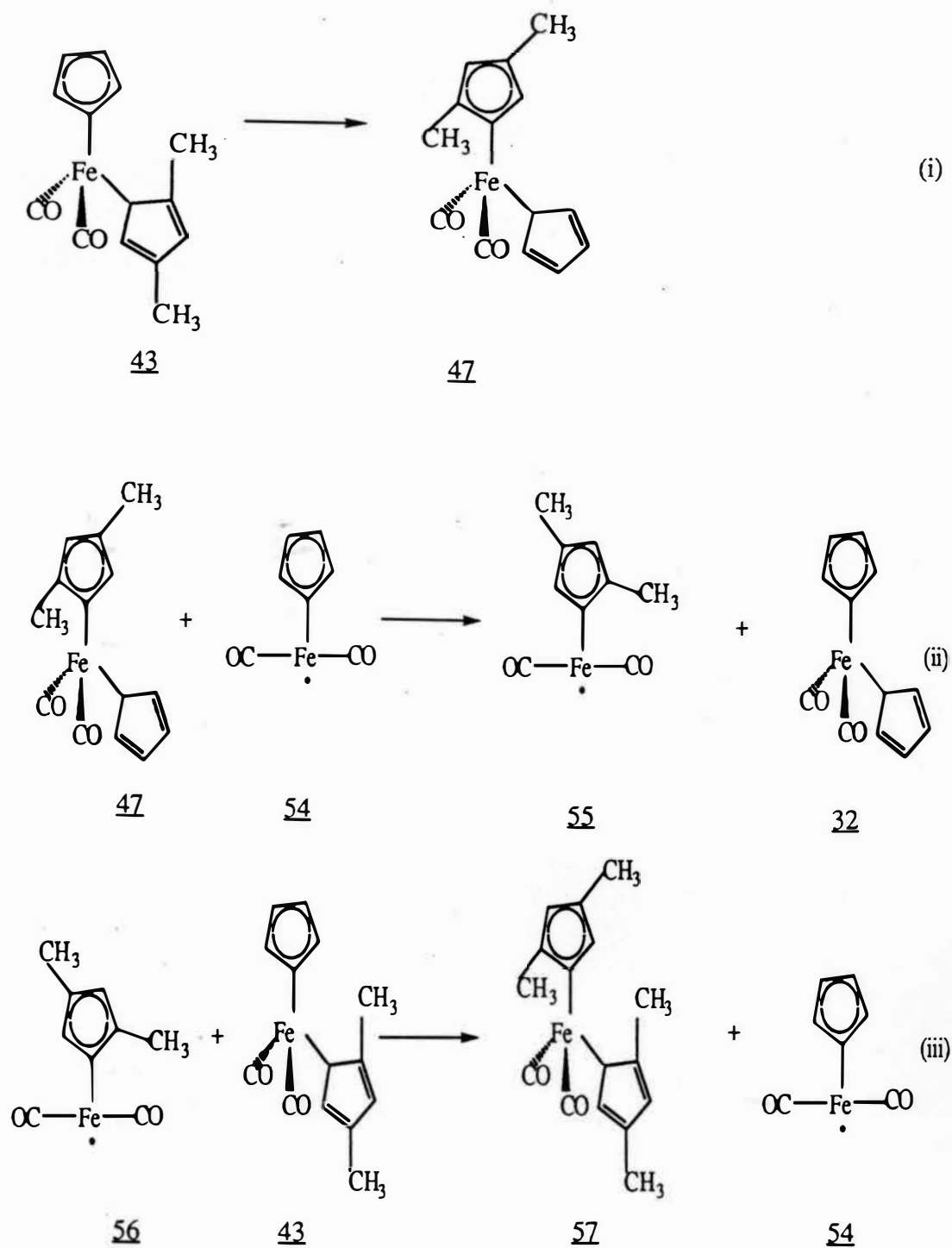


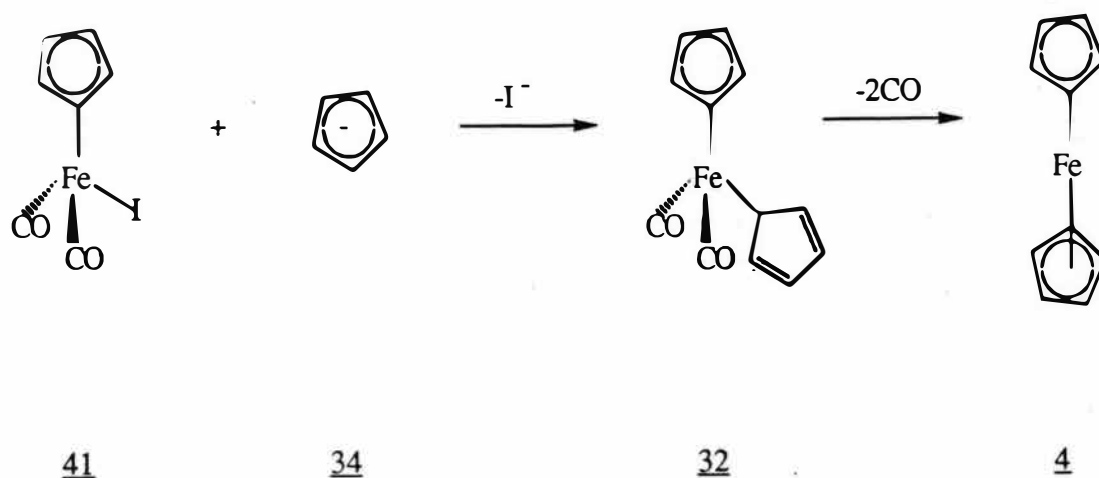
Figure 8. The Proposed Mechanism for the Nature of 1,3-Dimethylbis-cyclopentadienyliron Dicarbonyl Intermediate.

Compound 43 undergoes a π - σ ring interchange giving the complex 47. Substitution of the 17-electron iron moiety 54 via a homolytic displacement on the η^1 -Cp ring of 47 results in the formation of 32 and a new 17-electron iron species 55. Species 55 then substitutes on the η^1 -Cp of 43, resulting in the formation of 57. Subsequent decomposition of 32, 43, 47, and 57 then result in formation of the observed ferrocene mixture.

The hypothesis of Kelly et al. coincides with Cotton's view. According to the latter,³⁵ η^1 -Cp compounds were the first group of organometallic compounds for which fluxional behavior was observed. At room temperature, the solution nmr spectrum of η^5 -CpFe(CO)₂ η^1 -Cp showed two singlets. Upon cooling, the resonance due to the σ -bonded Cp group split into triplets, while the peak of the η^5 -group remained unaffected. The site change process occurring in the system was said to be undergoing a 1,2-shift of the iron atom around the σ -bonded ring. Therefore, in order to facilitate manipulation and spectroscopic identification, it was perceived to be easier to convert such intermediates into more stable complexes.

Research Objective

The well-known reaction of FpI 5 and Cp- 2 results in the formation of the intermediate in which one Cp ligand is π -bonded to the iron, the other is σ -bonded. The intermediate 32 readily decomposes with a loss of carbon monoxide through a thermal or photochemical process.³⁶

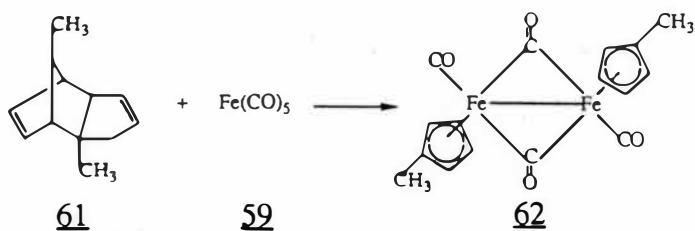
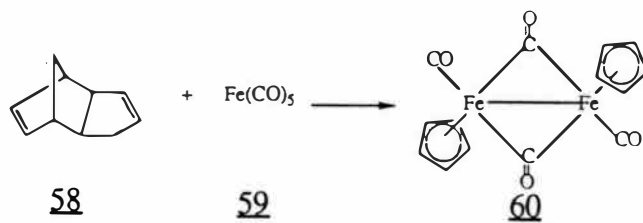


Kelly et al. had noted a surprising product distribution in his group's attempts to prepare 1,3-dimethylferrocene.³³ Similarly, a mixture of ferrocenes was observed in the reaction of 41 with 48, as well as the inverse of the reaction.

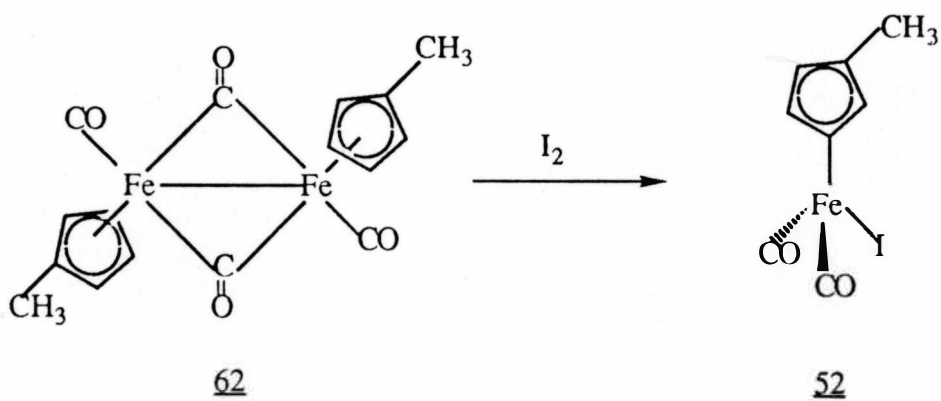
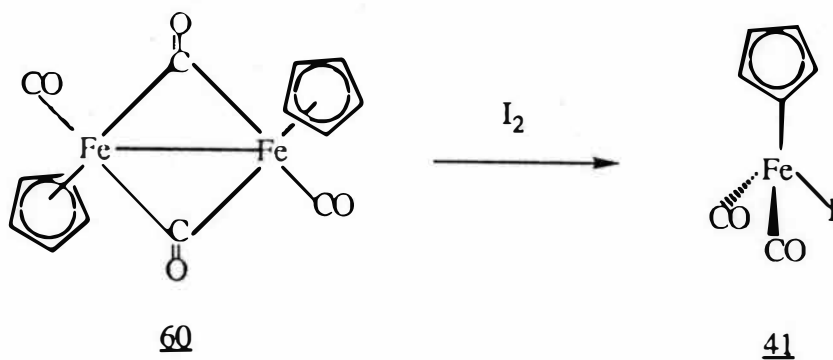
The *bis*-cyclopentadienyliron dicarbonyl intermediates can be isolated by chromatography and in theory, identified by a variety of techniques. Several researchers have shown that the η^1 -Cp ring of *bis*-cyclopentadienyliron dicarbonyl intermediates reacts with a variety of dienophiles to yield stable cycloadducts.^{37,38}

In this project, the synthesis of Diels-Alder adducts of 32, 49, and 53 will be attempted with the following dienophiles: (a) maleic anhydride, (b) dimethyl-acetylene dicarboxylate(DMAD), and, (c) tetracyanoethylene (TCNE).

First, *bis*-cyclopentadienyldiiron dicarbonyl tetracarbonyl, 60, and the *bis*-methylcyclopentadienyldiiron tetracarbonyl, 62, were prepared by treating cyclopentadienyl dimer, 58, and dimethylcyclopentadienyl dimer, 61, respectively with iron pentacarbonyl in a 1:6.5 mixture.^{30,39}



Then, FpI and MeFpI were generated by oxidative cleavage of the dimers.³⁰



The *bis*-cyclopentadienyliron intermediates 32, 49, and 53, were formed via Figure 9.³⁰

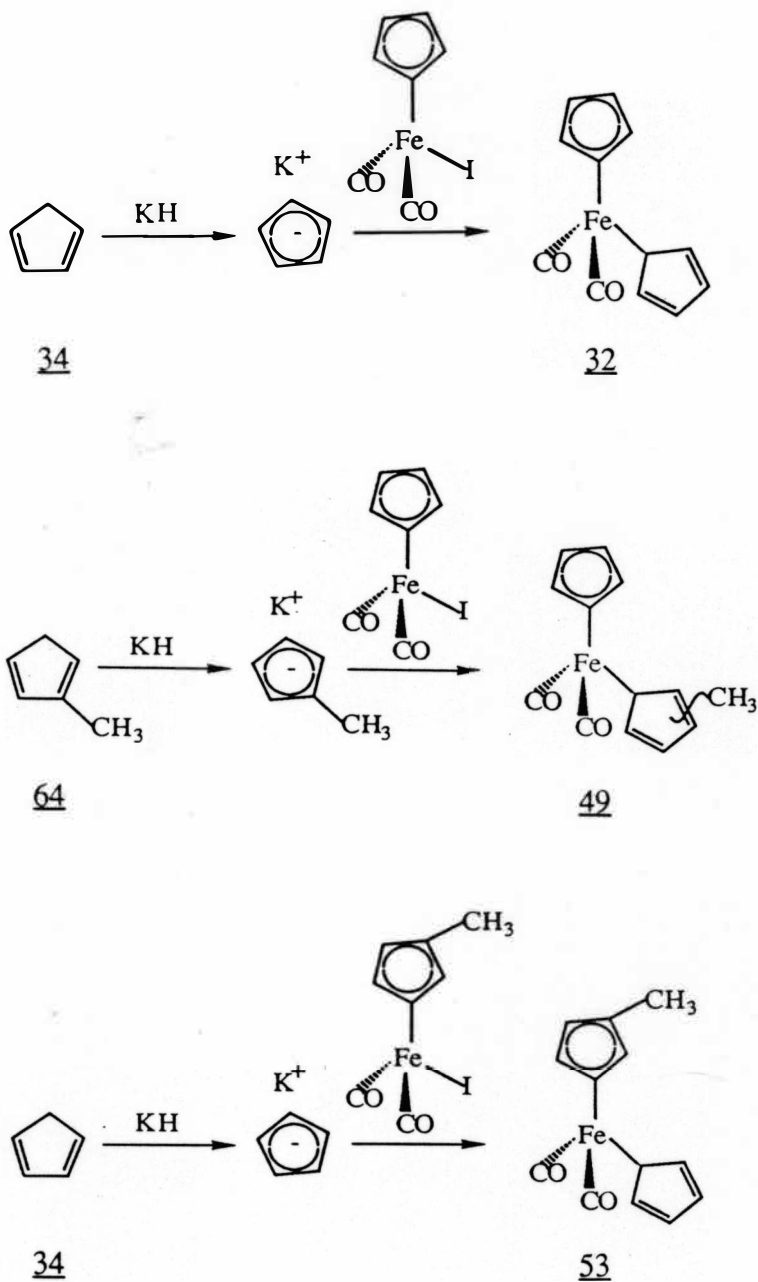
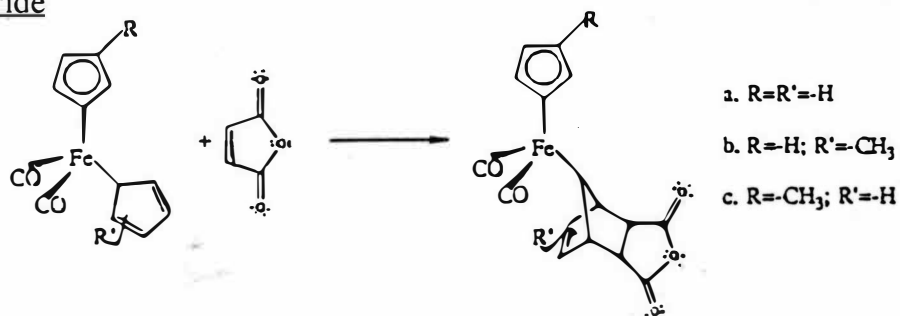


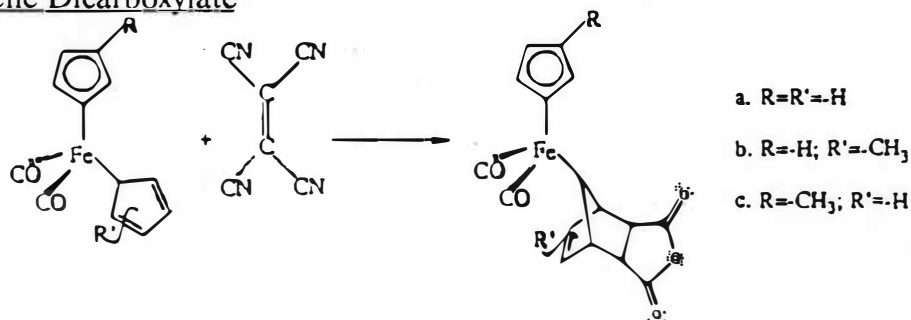
Figure 9. Formation of *Bis*-Cyclopentadienyliron Dicarbonyl Intermediates.

Thereafter, the intermediates 32, 49, and 53 were treated with the dienophiles as outlined in Figure 10 below.^{33,37,40} [Refer to Appendix B for the reaction mechanisms to Figure 10.]

Reaction of *Bis*-Cyclopentadienyliron Dicarbonyl Intermediate With Maleic Anhydride



Reaction of *Bis*-Cyclopentadienyliron Dicarboxylate Intermediate With Dimethylacetylene Dicarboxylate



Reaction of *Bis*-Cyclopentadienyliron Dicarboxylate Intermediate With Tetra-cyanoethylene

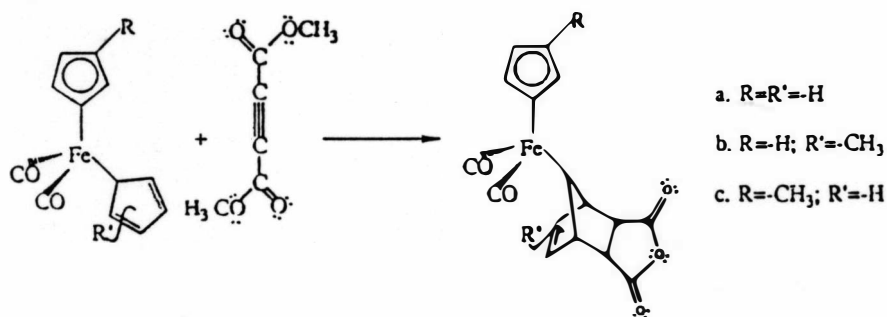


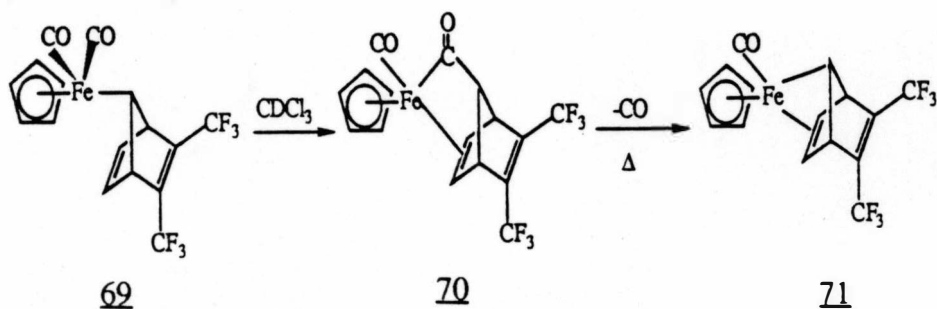
Figure 10. Reaction of *Bis*-Cyclopentadienyliron Dicarboxylate Intermediates With Selected Dienophiles.

Analysis of the Diels-Alder adducts should indicate the trend by which the *bis*-cyclopentadienyliron dicarbonyl intermediates would tend to follow.

Discussion

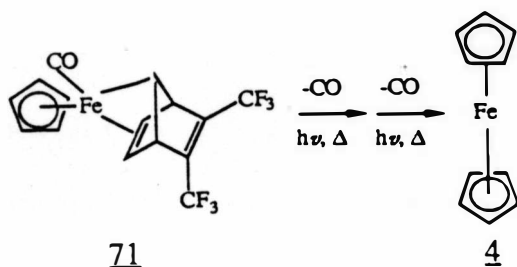
Various trials to prepare Diels-Alder adducts of the described *bis*-Cp intermediates were met with successive failures in the ability to analyze the product mixtures by nuclear magnetic resonance as well as low-resolution mass-spectra techniques. In both analyses, the adducts tended to form inseparable complexes or decomposed upon exposure to deuterated chloroform or on the gas chromatography column.

Williams and Wojcicki⁴¹ had observed the formation of the isomer 71 when 69 was stored in CDCl_3 .



This was especially true for the DMAD and TCNE adducts.

Further decomposition to ferrocene, 4, can be expected by prolonged heat and light exposure.

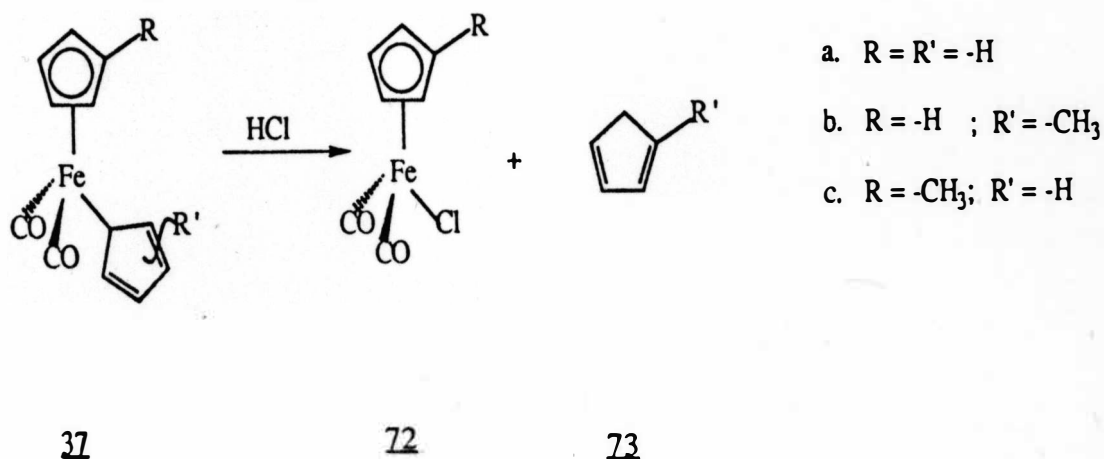


The maleic anhydride adducts were slightly more practical. The melting point determinations indicated that the adducts were fairly pure except for 66. The impurity in the latter could very well be due to the presence of another isomer.

The isolation of the *bis*-Cp intermediates was successful to the extent that some crystals were afforded enabling melting point and infrared determination, as well as for use in further reactions. However, the intermediates were also susceptible to decomposition in CDCl_3 , on the gas chromatography column, and over a short period of time during refrigeration.

Acid-hydrolyzed *Bis*-Cp Intermediates

In separate trials, 0.015 g portions of the *bis*-Cp intermediates were subjected to acid hydrolysis using 20 mL portions of degassed 20% hydrochloric acid under a nitrogen atmosphere³⁰ as described.



The cyclopentadienyliron dicarbonyl chloride was isolated as 0.001 g of blackish solid, 72a, mp $81.0\text{--}83.0^\circ\text{C}$ [lit.⁴¹ $84\text{--}87$] in a sealed tube. Methyl

cyclopentadienyliron dicarbonyl chloride, 72c, was isolated as 0.001 g of blackish solid, mp 23.0-25.5°C. The melting point for 72b (a black solid) could not be determined accurately due to a low yield. The accompanying viscous light yellow solution when analyzed gave bp 39.0-40.5°C [lit.⁴¹ 40] for 72a and 73c. The boiling point for 73b could not be obtained due to its high viscosity and especially low yield.

Experimental Section

Infrared spectra were taken on a Beckman Acculab infrared spectrophotometer. Nuclear magnetic resonance spectra were obtained on the IBM-NR/200 AF.

Alumina chromatography was performed with Aldrich Alumina, activated, neutral, Brockmann standard grade ~ 150 mesh converted to Activity III with distilled water (6%). Plates used in thin layer chromatography were EM Science Pre-coated TLC Plates Silica Gel 60F-254. Compounds were located by ultraviolet rays or spotting in an iodine chamber.

Potassium hydride was obtained from Aldrich in a 35% dispersion in mineral oil and was washed with pentane and dried before use.

Solvents used in the reactions and developing the chromatograms were distilled. THF was dried over potassium hydroxide and distilled from sodium under nitrogen.

Melting points were determined on the Thomas Hoover Uni-Melt capillary melting point apparatus and were uncorrected. Boiling points were uncorrected.

In some instances, literature data were unavailable for comparison due to current reference limitations.

Bis-cyclopentadienyldiiron tetracarbonyl, 60

A three-necked flask equipped with a condenser, thermometer, and inlet for admission of N_2 was flushed with a rapid stream of N_2 for 10 minutes. Iron pentacarbonyl (29.39 g, 0.15 mol) and cyclopentadiene dimer 22 (129.57 g, 0.98 mol) were placed in the flask and stirred at 135°C for 12 hours. Upon cooling, the mixture was again flushed with a rapid stream of N_2 . A black slurry was obtained which was washed with cold pentane to yield 23.0 g (43.3%) of dark red powder 23. MP $190.5\text{--}192^\circ\text{C}$ (dec). IR (CHCl_3): ν , cm^{-1} (C=O) 2010, 1960.

Bis-methylcyclopentadienyldiiron tetracarbonyl, 62

A Parr bomb was flushed with CO_2 and charged with iron pentacarbonyl (14.60 g, 0.07 mol) and methylcyclopentadiene dimer (72.90 g, 0.46 mol). The mixture was heated at 135°C and under 100 psi pressure for 2 days. The dark red slurry obtained was washed with cold pentane yielding 6.40 g (23.5%) of dark red crystalline solid, 25. MP $114\text{--}115^\circ\text{C}$. IR (CHCl_3): ν , cm^{-1} (C=O) 2000, 1950.

Cyclopentadienyliron dicarbonyl iodide, 41

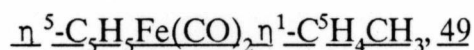
A mixture of cyclopentadienyliron dicarbonyl dimer 60 (50 g, 0.14 mol), iodine (50g), and 250 mL of CHCl_3 was refluxed for 30 minutes. After cooling

to room temperature, the mixture was extracted with a solution of sodium thiosulfate pentahydrate (100 g) in water (400 mL). The black organic portion was filtered over a coarse sintered glass crucible and filtrate evaporated to dryness. Black crystalline solid of 5 (62.80 g, 73.2%) was obtained. MP 117-118.5°C [lit.^{41 42}]. IR (CHCl₂): ν , cm⁻¹ (C=O) 1990, 2040.



A three-necked flask equipped with inlet for admission of N₂ and rubber septa was flushed with N₂ for 10 minutes, and charged with KH (0.85 g, 0.02 mol) and THF (50 mL). Cyclopentadiene (1.45 g, 10% excess) was added to the stirring mixture at room temperature. FpI 41 (6.10 g) was added when all the KH was reacted. The reaction was stopped after 30 minutes and slurry filtered through a coarse sintered glass crucible. The filtrate was concentrated *in vacuo* and residue taken up in benzene. Column chromatography (pentane) yielded an orange yellow band 8 (0.89 g) followed by a dark red oil which was recrystallized in a pentane-benzene mixture to yield reddish-orange crystals 32 (0.15 g, 3% yield). MP 33-34°C, IR (CHCl₂): ν , cm⁻¹ (C=O) 2010, 1945.

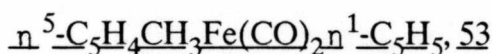
Diethyl ether eluted 5.06 g of 60.



A three-necked flask equipped with inlet for admission of N₂ and rubber septa was flushed with N₂ for 10 minutes, and charged with KH (0.80 g, 0.02 mol) and THF (50 mL). Methylcyclopentadiene (2.05 g, 0.03 mol) was added to the stirring mixture at room temperature. Compound 41 (6.08 g) was added

when all the KH had reacted. The reaction was stopped after 30 minutes and slurry filtered through a coarse sintered glass crucible. The filtrate was concentrated *in vacuo* and residue taken up in benzene. Column chromatography (pentane) yielded a reddish-orange solid (0.95 g) consisting of an inseparable mixture of ferrocenes, followed by a dark red band. Removal of solvent gave a red oil which was recrystallized in a pentane-benzene mixture to yield dark red crystals 14 (0.44 g, 10% yield). MP < 19°C. IR (CHCl₂): ν , cm⁻¹ (C=O) 2010, 1940 [lit.³⁹ 2011, 1960].

Diethyl ether eluted 6.30 g of black polymeric mixture.



A three-necked flask equipped with inlet for admission of N₂ and rubber septa was flushed with N₂ for 10 minutes, and charged with KH (1.94 g, 0.05 mol) and THF (50 mL). Cyclopentadiene (3.64 g, 0.06 mol) was added to the stirring mixture at room temperature. MeFpI (5.00 g) was added when all the KH had reacted. The reaction was stopped after 20 minutes and slurry filtered through a coarse sintered glass crucible. The filtrate was concentrated *in vacuo* and residue taken up in benzene. Column chromatography (pentane) yielded an orange solid (0.73 g) consisting of an inseparable mixture of ferrocenes, followed by a dark red oil which was recrystallized in a pentane-benzene mixture to yield dark red crystals 52 (0.26 g, 2% yield). MP 25-26°C. IR (CHCl₂): ν , cm⁻¹ (C=O) 2010, 1940.

Diethyl ether eluted 6.95 g of black polymeric mixture.

Reaction of Compound 32 With Maleic Anhydride

A two-necked flask equipped with an inlet for admission of N_2 and rubber septum was charged with 32 (0.08 g, 0.0003 mol) and $CHCl_2$ (10 mL). Maleic anhydride (0.03 g, 0.0003 mole) was added to the dark red solution and it immediately turned yellow. The solution was left to stir overnight at room temperature. A minimal amount of diethyl ether was added to the reaction mixture to precipitate yellow needles 64a (0.01 g, 9.8%), IR ($CHCl_2$): ν , cm^{-1} (C=O) 2010, 1955, 1769.

Reaction of Compound 49 With Maleic Anhydride

A two-necked flask equipped with an inlet for admission of N_2 and rubber septum was charged with 49 (0.22 g, 0.001 mol) and $CHCl_2$ (10 mL). Maleic anhydride (0.09 g, 0.001 mole) was added to the dark red solution and it immediately turned yellow. The solution was left to stir overnight at room temperature. A minimal amount of diethyl ether was added to the reaction mixture to precipitate yellow needles 64b (0.01 g, 28.3%), mp 136-140°C, IR ($CHCl_2$): ν , cm^{-1} (C=O) 2010, 1955, 1770.

Reaction of Compound 53 With Maleic Anhydride

A two-necked flask equipped with an inlet for admission of N_2 and rubber septum was charged with 18 (0.26 g, 0.001 mol) and $CHCl_2$ (10 mL). Maleic anhydride (0.09 g, 0.001 mole) was added to the dark red solution and it

immediately turned yellow. The solution was left to stir overnight at room temperature. A minimal amount of diethyl ether was added to the reaction mixture to precipitate yellow needles 64c (0.01 g, 28.3%), mp 124-125°C, IR (CHCl₂): ν , cm⁻¹ (C=O) 2010, 1955, 1775.

Reaction of Compound 32 With DMAD

A two-necked flask equipped with an inlet for admission of N₂ and rubber septum was charged with 32 (0.08 g, 0.0003 mol) and CHCl₂ (10 mL). After 20 minutes, DMAD (0.04 g, 0.0003 mole) was added and the solution left to stir overnight at room temperature. The product was subjected to column chromatography. Pentane eluted DMAD (0.01 g) followed by a light brown band which gave a solid 66a (0.02 g, 17.3%), IR (CHCl₂): ν , cm⁻¹ (C=O) 2000, 1945, 1715 (C=C) 1630 [lit.³⁹ 2007, 1951, 1729, 1709].

Reaction of Compound 49 With DMAD

A two-necked flask equipped with an inlet for admission of N₂ and rubber septum was charged with 49 (0.22 g, 0.001 mol) and CHCl₂ (10 mL). After 20 minutes, DMAD (0.13 g, 0.001 mole) was added and the solution left to stir overnight at room temperature. The product was subjected to column chromatography. Pentane eluted DMAD (0.04 g) followed by a light brown solid 66b (0.07 g, 17.6%, lit. 87%), IR (CHCl₂): ν cm⁻¹ (C=O) 2010, 1940, 1720 (C=C) 1630 [lit.³⁹ 2006, 1949, 1726, 1706].

Reaction of Compound 53 With DMAD

A two-necked flask equipped with an inlet for admission of N_2 and rubber septum was charged with 18 (0.26 g, 0.001 mol) and $CHCl_2$ (10 mL). After 20 minutes, DMAD (0.13 g, 0.001 mole) was added and the solution left to stir overnight at room temperature. The product was subjected to column chromatography. Pentane eluted DMAD (0.06 g) followed by a light brown band 66c (0.1 g, 25.1%), IR ($CHCl_2$): ν , cm^{-1} (C=O) 2010, 1940, 1725 (C=C) 1640.

Reaction of Compound 32 With TCNE

A two-necked flask equipped with an inlet for admission of N_2 and rubber septum was charged with 32 (0.18 g, 0.001 mol) and $CHCl_2$ (20 mL). After 30 minutes, TCNE (0.09 g, 0.0001 mole) was added and the solution left to stir overnight at room temperature. The mixture was concentrated *in vacuo* and precipitation effected by cold hexane. A yellow green solid, TCNE (0.05 g) was recovered. The mother liquor was reduced to a black solid 68a (0.13 g, 35.2%), mp 108-109°C [lit.³⁶ 108], IR ($CHCl_2$): ν , cm^{-1} (C=N) 2245, 2230, 1725 (C=O) 2035, 1975 [lit.³⁹ (KBr) 2015, 1960].

Reaction of Compound 49 With TCNE

A two-necked flask equipped with an inlet for admission of N_2 and rubber septum was charged with 49 (0.37 g, 0.0014 mol) and $CHCl_2$ (20 mL). After

30 minutes, TCNE (0.16 g, 0.0014 mole) was added and the solution left to stir overnight at room temperature. The mixture was concentrated *in vacuo* and precipitation effected with cold hexane. A yellow green solid, TCNE (0.08 g) was obtained. The mother liquor was reduced to a greenish solid, 68b (0.06 g, 11.1%), IR (CHCl_2): ν , cm^{-1} (C=N) 2255, 2220 (C=O) 2020, 1965.

Reaction of Compound 63 With TCNE

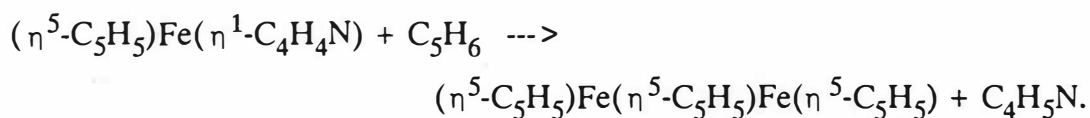
A two-necked flask equipped with an inlet for admission of N_2 and rubber septum was charged with 63 (0.65 g, 0.003 mol) and CHCl_2 (20 mL). After 30 minutes, TCNE (0.35 g, 0.003 mole) was added and the solution left to stir overnight at room temperature. The mixture was concentrated *in vacuo* and precipitation effected by cold hexane. Minute amounts of yellow-green specks were obtained. Analysis was not possible.

CHAPTER III

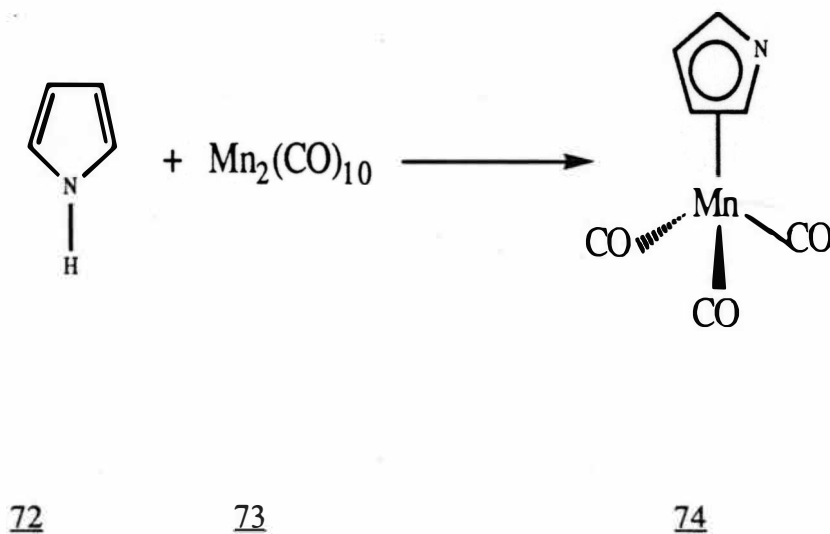
ATTEMPTED SYNTHESIS OF THE [2.2](2,5)PYRROLOPARACYCLOPHANE ANALOGUE OF DIAZAFERROCENE

Introduction

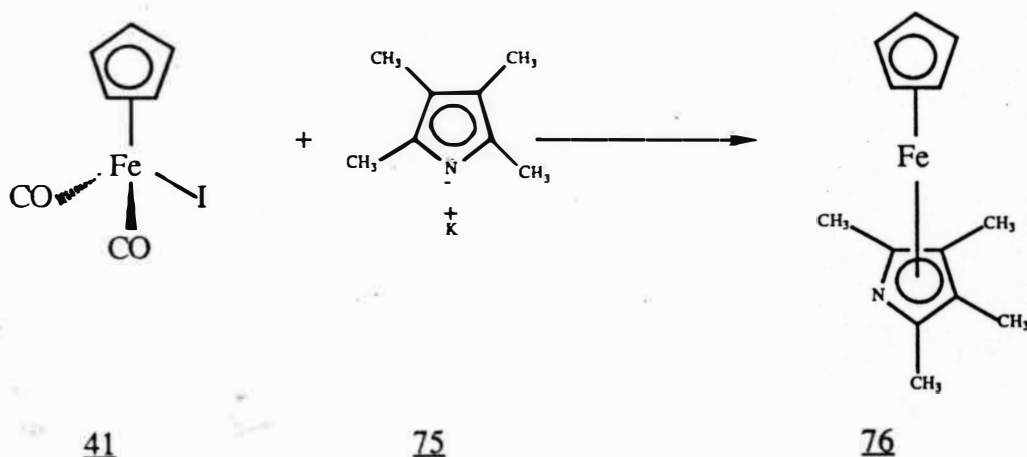
The stability of diazoferrocenes and their nitrogen-rich analogues have raised questions for over 20 years. The work of Seel and Sperber⁴³ for instance, concluded that



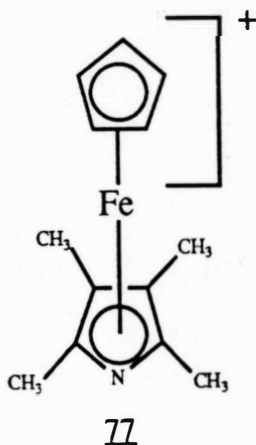
Earlier, the work of Joshi, Pauson, Qazi, and Stubbs⁴⁴ involving the preparation of pyrrolylmanganesetricarbonyl 74 from dimanganesedecacarbonyl 73 and pyrrole 72 was extended to include the preparation of azaferrocene 76.⁴⁵



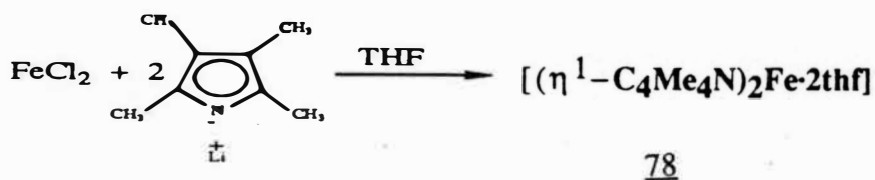
This proceeded via the reaction of dicarbonylcyclopentadienyliron iodide 41 with the pyrrolylpotassium 75



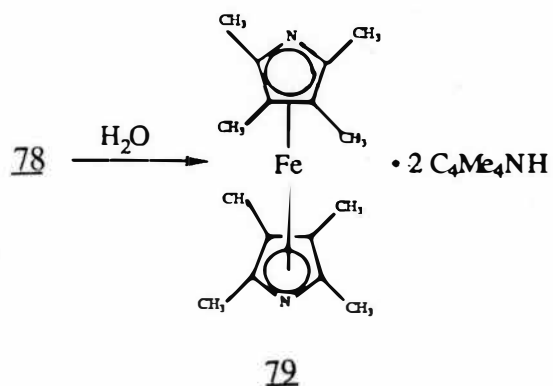
Recently, Kuhn, Horn, Boese, and Augart synthesized the azaferrocene complex, 77⁴⁶.



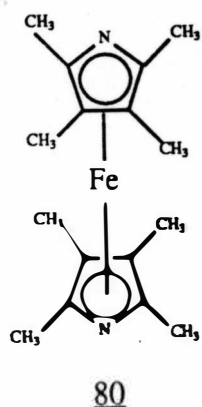
Encouraged by the demonstrated stability of 77, Kuhn et al. then attempted the synthesis of $[(\eta^5\text{-C}_4\text{Me}_4\text{N})_2\text{Fe}]$, a diazaferrocene.⁴⁷ However, this led only to the complex, 78,



which decomposed to 79 in the presence of traces of water.



The complex 79 was also unstable in solution at room temperature, decomposing within a few hours with the liberation of THF. 1,1'-Diazaferrocene, 80 was not detected.



Research Objective

Whereas the stability of 1,1'-diazaferrocene is still questionable^{43,45} the synthesis of [2.2](2,5)pyrroloparacyclophane analogue of diazaferrocene, 81, based on the stability of the paracyclophane moiety was pursued.

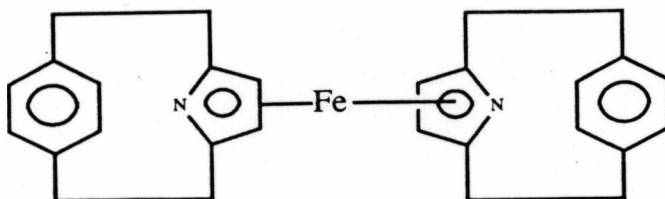
81

Figure 11 illustrates the proposed route toward the formation of 81.

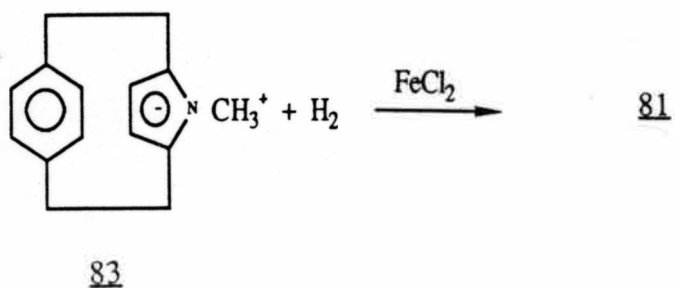
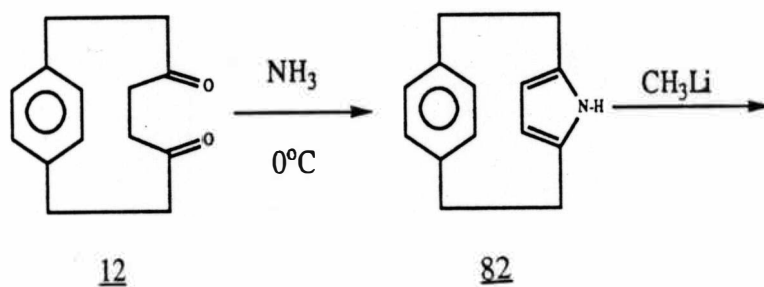


Figure 11. Proposed Synthetic Route Toward the [2.2](2,5)Pyrroloparacyclophane Analogue of Diazaferrocene.

First, [2.2](2,5)pyrroloparacyclophane, 82, was synthesized from 3,6-diketo[8]paracyclophane, 12, via the Paal-Knorr cyclization according to the method developed by Keehn, Rosenfield, and Haley.⁴⁷ Compound 13 was then treated with methyllithium to generate its anion. Reaction of the anion 83 with anhydrous iron (II) chloride will be expected to yield the [2.2](2,5)pyrroloparacyclophane analogue of diazaferrocene, 81.

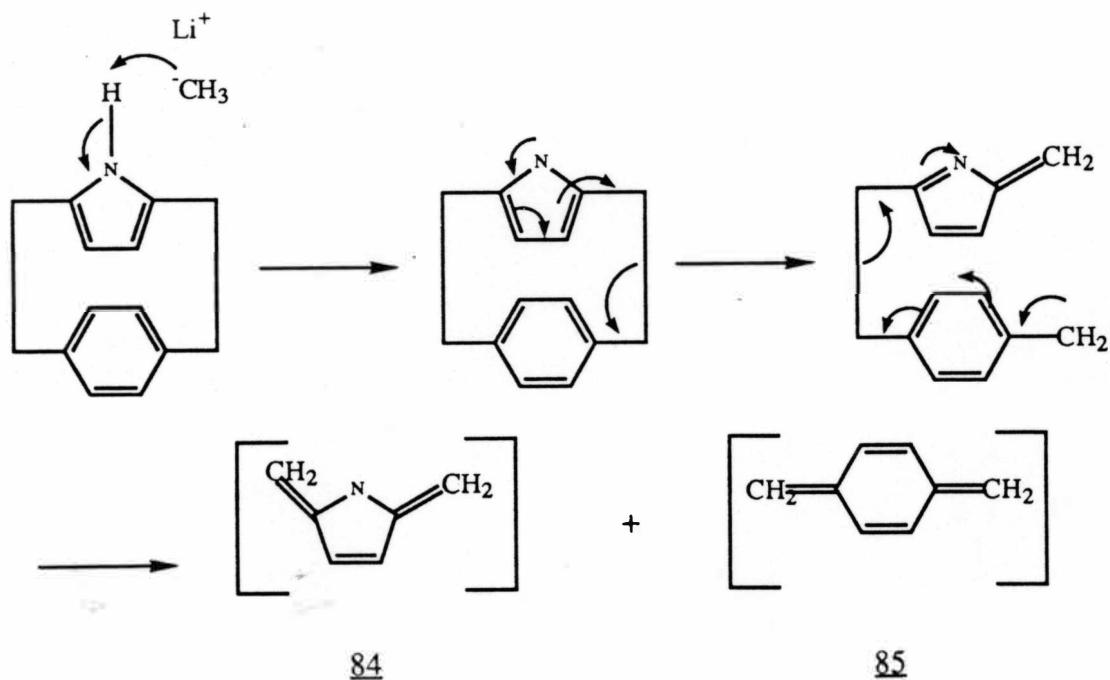
The final product, if extended into a longer polymer, was expected to retain transannular π -electronic interaction throughout the molecule. On top of proving the stability of 1,1'-diazaferrocene, this appears as an interesting prospect indeed.

Discussion

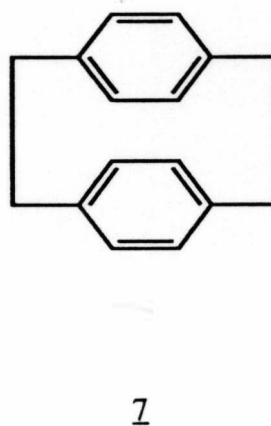
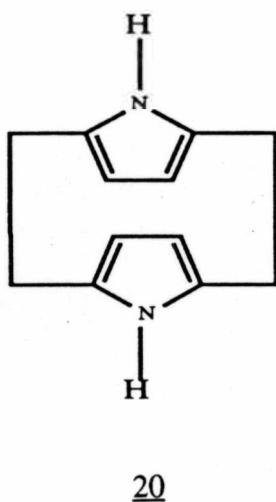
Very few transition metal complexes of pyrrole are known. The attempted synthesis of a [2.2](2,5)pyrroloparacyclophane analogue of diazaferrocene, 81, seeks to explore the stability of such a diazaferrocene as well as its electrochemical behavior.

In this synthesis, 83 was generated via the Paal-Knorr cyclization of 3,6-diketo[8]paracyclophane and then treated with fresh iron (II) chloride. Compound 81 was not isolated.

The first part of the synthesis of final product involved a base (CH_3Li)-catalyzed attack on the acidic hydrogen of the pyrrole moiety to generate the intermediates 2,5-dimethylene-2,5-dihydropyrrole, 84, and 1,4-dimethylenexylene, 85.

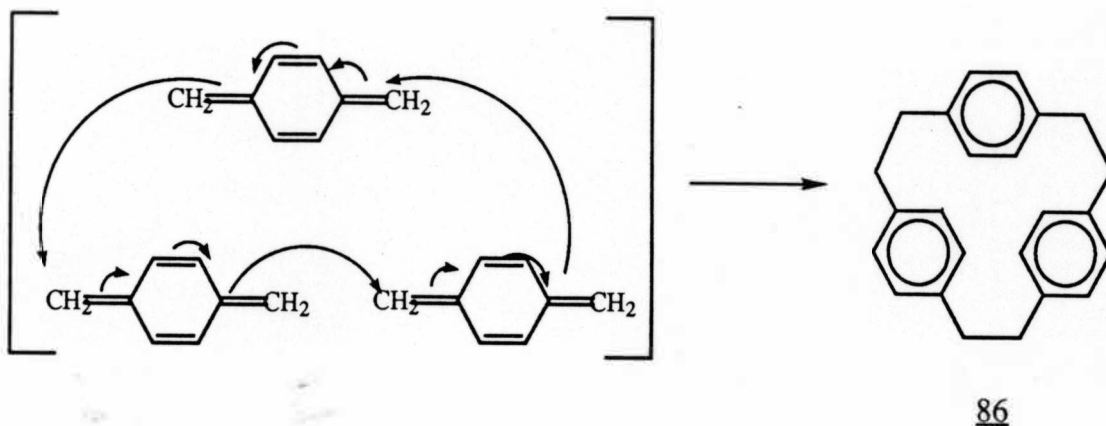


1,6 to 1,6 cycloaddition reaction would then result in the formation of [2.2]pyrrolophane, 20 and [2.2]paracyclophane, 7.

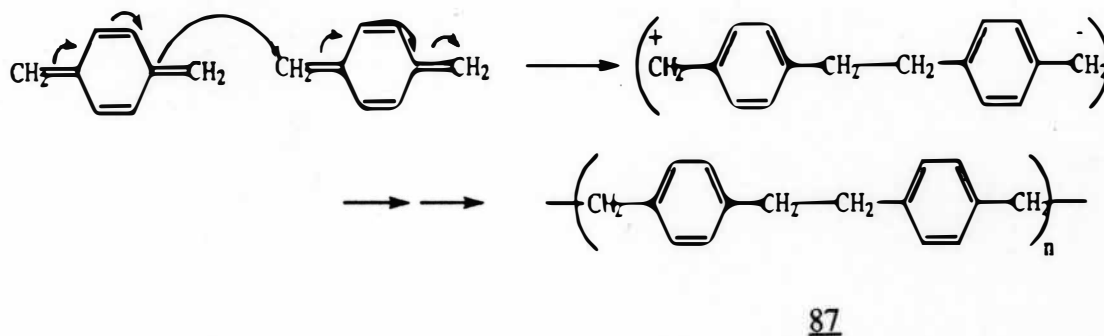


However, these were not the only products. Spectral and chemical analysis indicated 7 and an uncharacterized polymeric mass. The latter may be made up of several types of dimers and polymers. In addition to the formation

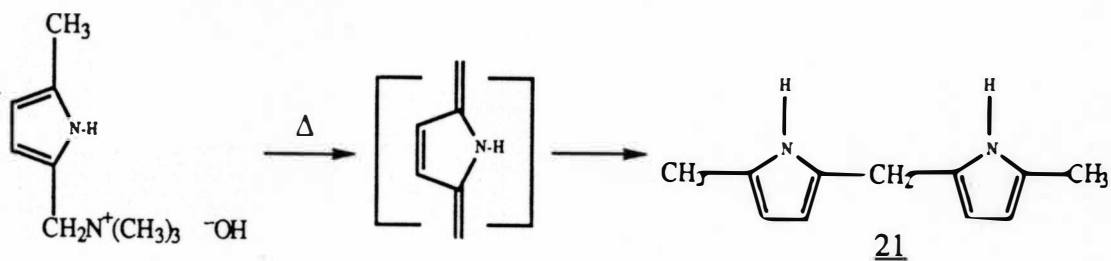
of 7, 85 could also undergo cycloaddition reaction to form [2.2.2]paracyclophane, 86,



as well as a free-radical initiated process to form polyxylene, 87.

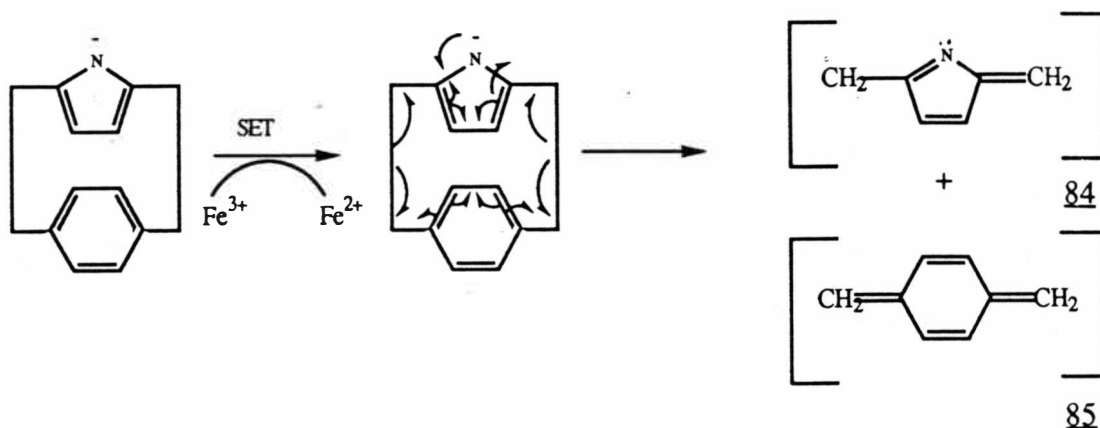


Compound 84 can also undergo reactions to form dimers and polymers. Keehn et al.,⁴⁷ for example, have found that pyrolysis of the quaternary ammonium hydroxide salt of pyrrole did not form [2.2]pyrrolophane as anticipated but instead, dipyrlylmethane, 21.



A control experiment involving the generation of the [2.2]pyrrolo-paracyclophane anion was quenched with water. The result was a stunning 100% recovery of the starting material. This strongly indicated that a free radical type process must have occurred during treatment with iron (II) chloride.

In addition, 83 can also undergo an iron (II) chloride catalyzed homolysis to form the intermediates 84 and 85, which can in turn undergo coupling reactions and further polymerize.



Kuhn et al.,⁴⁵ had been encouraged by the stable tetramethylpyrrole and utilized it to attempt the isolation of 1,1'-diazaferrrocene. Similarly, 83 used in this project was perceived to be a highly suitable candidate for the formation of 81 due to its stability arising from extensive π -electron delocalization. The size of the metal atom also contributes to the potential stability of a sandwich complex.

Experimental Section

Infrared spectra were taken on a Beckman Acculab infrared spectrophotometer. Nuclear Magnetic Resonance spectra were obtained on the

IBM-NR/200 AF spectrophotometer. Gas chromatograph/low resolution spectra were done on the Hewlett Packard 590 with a HP-5970 series Mass Selective Detector.

Alumina chromatography was performed with Aldrich Alumina, activated, neutral, Brockmann standard grade ~ 150 mesh converted to Activity III with distilled water (6%). Plates used in thin layer chromatography were EM Science Pre-coated TLC Plates Silica Gel 60F-254. Compounds were located by ultraviolet rays or spotting in an iodine chamber.

Methylolithium was obtained from Aldrich as a 1.4M solution in diethyl ether and used directly. Ferrous chloride was freshly prepared by the method outlined in Organic Synthesis Collective Volume IV.

Solvents used in the reactions and developing the chromatograms were distilled. THF was dried over potassium hydroxide and distilled from sodium under nitrogen.

Melting points were determined on the Thomas Hoover Uni-Melt capillary melting point apparatus and were uncorrected.

[2.2](2,5)Pyrroloparacyclophane, 83

A three-necked flask, equipped with a condenser, rubber septum, and glass stopper, was charged with glacial acetic acid (50 ml, purged with N₂ for 15 min.) and 3,6-diketo[8]paracyclophane 22 (0.70 g, 0.003 mmol). The flask was wrapped in aluminum foil to exclude light and heated under nitrogen in an oil bath (80°C) for 10 minutes. Precondensed liquid ammonia was bled into the mixture via a cannular placed through the rubber septum and the N₂ inlet at the

top of the condenser was replaced with a drying tube (Drierite). The ammonia was allowed to bubble into the heated and stirred solution for 30 minutes. By this time, the mixture had usually solidified. It was cooled in ice and made basic (pH 10) with ammonium hydroxide (concentrated). The light-yellow solution was extracted with CHCl_3 (4 x 25 ml). The organic layer was washed several times with water until the wash was neutral and dried over anhydrous sodium sulfate. Removal of solvent *in vacuo* yielded a yellow-white solid. This was purified by chromatography on silica gel (elution with CHCl_3). Recrystallization from hexane afforded silky white needles of 83 (0.47 g, 80%, lit.⁴⁷ 55%): mp 195.0-196.5°C (lit. 197-198); NMR (CDCl_3) δ , ppm: 6.7 (4H), 5.45 (d, 2H), 5.0 (broad s, 1H), 2.6 (m, 8H); IR (CHCl_3) ν , cm^{-1} : 3400 (N-H).

[2.2](2,5)Pyrroloparacyclophane Analogue of Diazaferrocene, 81

Into a three-necked flask fitted with an inlet for admission of N_2 , condenser, and rubber septum, was placed 15 ml of dry THF and 0.20 g (197.30 g/mol, 0.001 mol) of 13. This mixture was stirred at -78°C until all of 9 dissolved. Methyllithium (0.75 ml, 0.00105 mol) was then added to the brown mixture and gradually brought to room temperature.

This was transferred with a cannular into a three-necked flask fitted with an inlet for admission of N_2 and rubber septa, previously charged with FeCl_2 (0.13 g, 0.001 mol). The mixture was left to stir under N_2 overnight protected from light. The solvent was removed *in vacuo* and residue eluted in benzene. Column chromatography yielded a yellowish band in pentane. Recrystallization from hexane afforded a white solid [2.2]paracyclophane (0.10 g, 48%); 285.5-

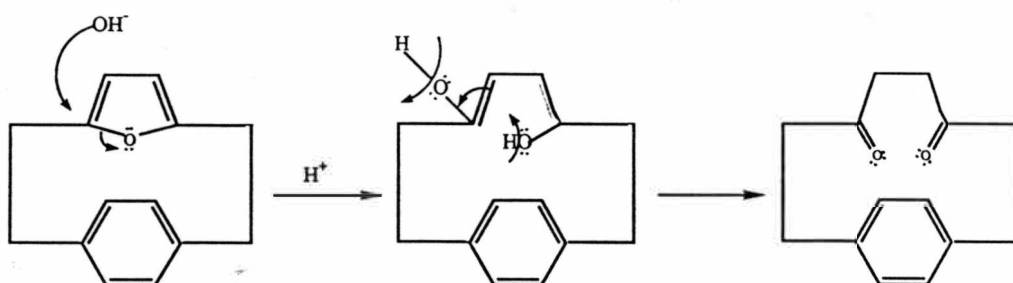
286.0°C; NMR (CDCl_3) δ , ppm: 6.5 (s, aromatic), 3.1 (s, benzylic); Low resolution-MS: (m/e) 429 (M^+) 186, 121, 56 (Fe).

A pentane-benzene mixture eluted approximately 0.1 g of uncharacterized polymeric mass.

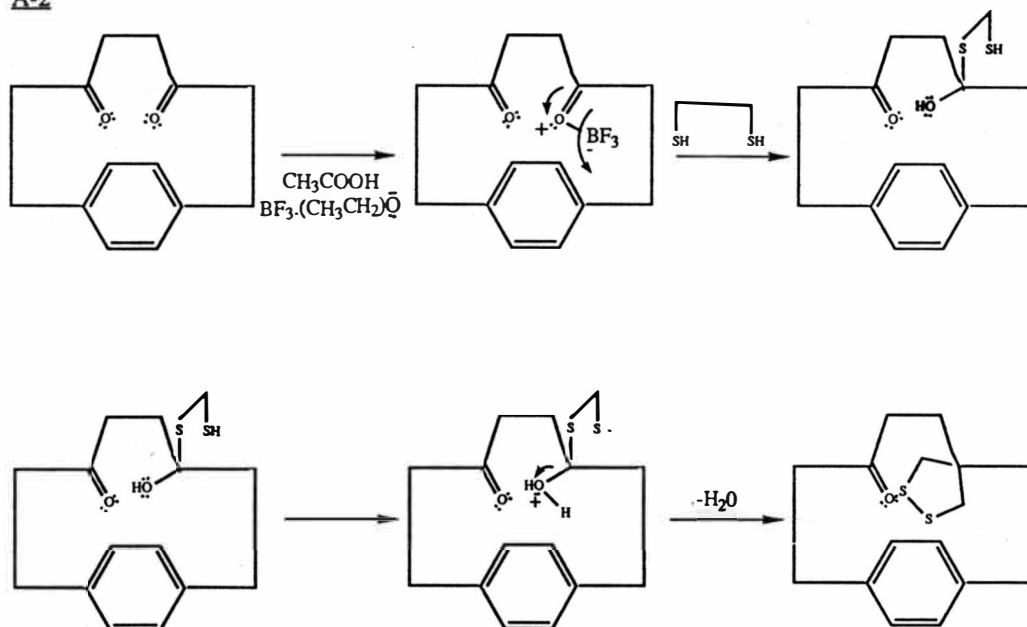
APPENDICES

Appendix A
Mechanism for the Designed Synthesis of [2.3](1,3)
Cyclopentadiendoparacyclophane

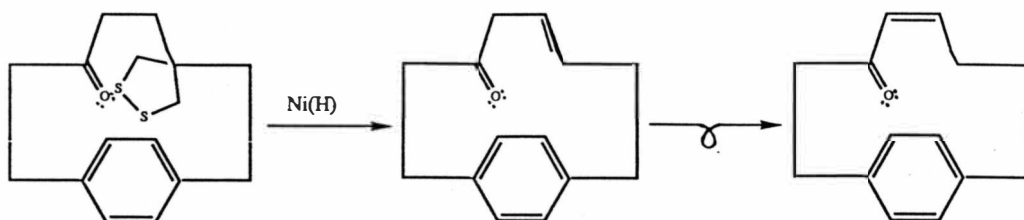
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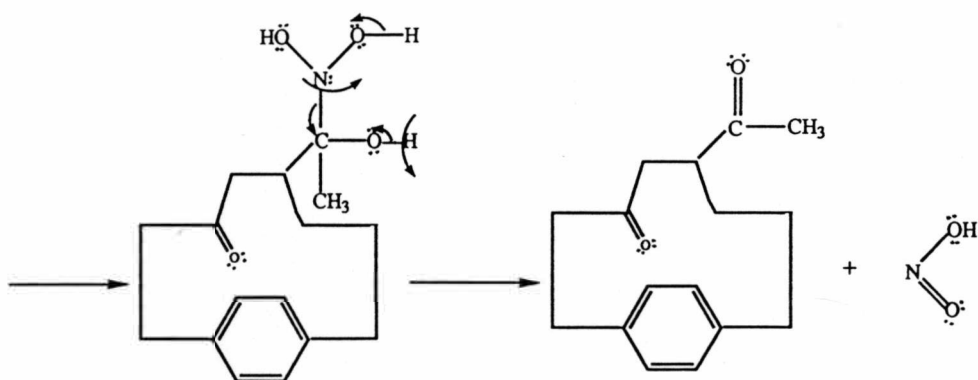
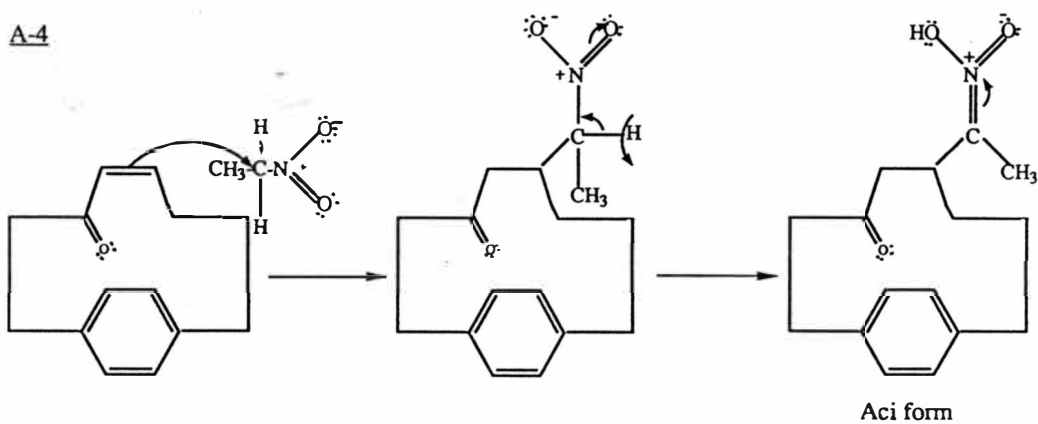
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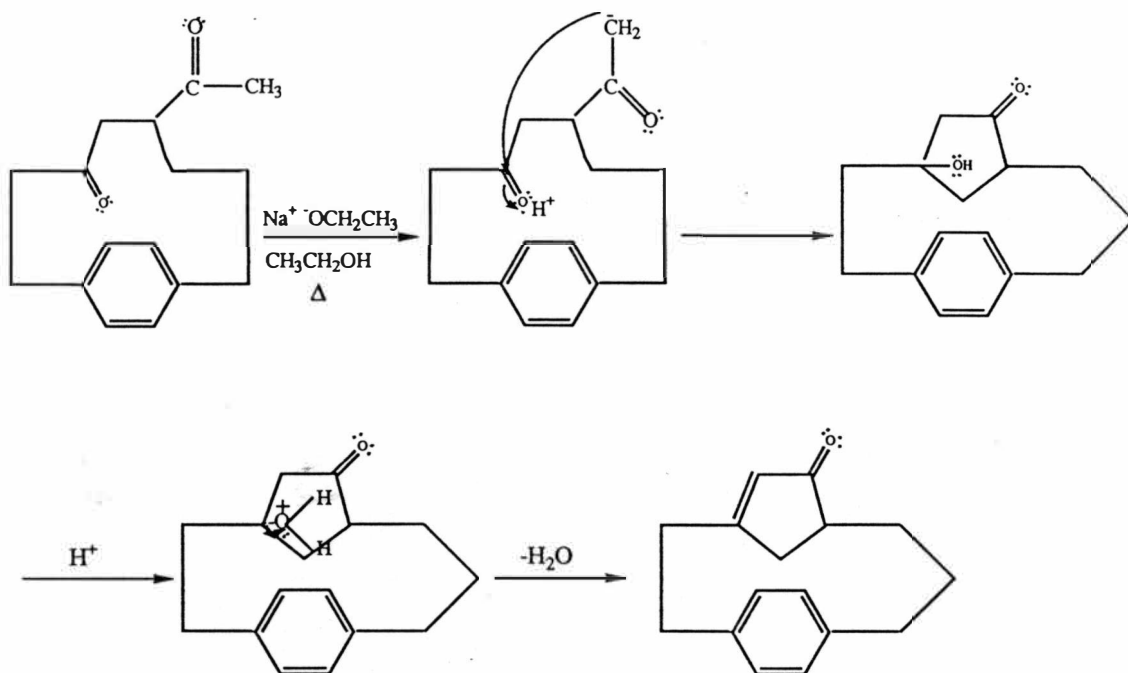
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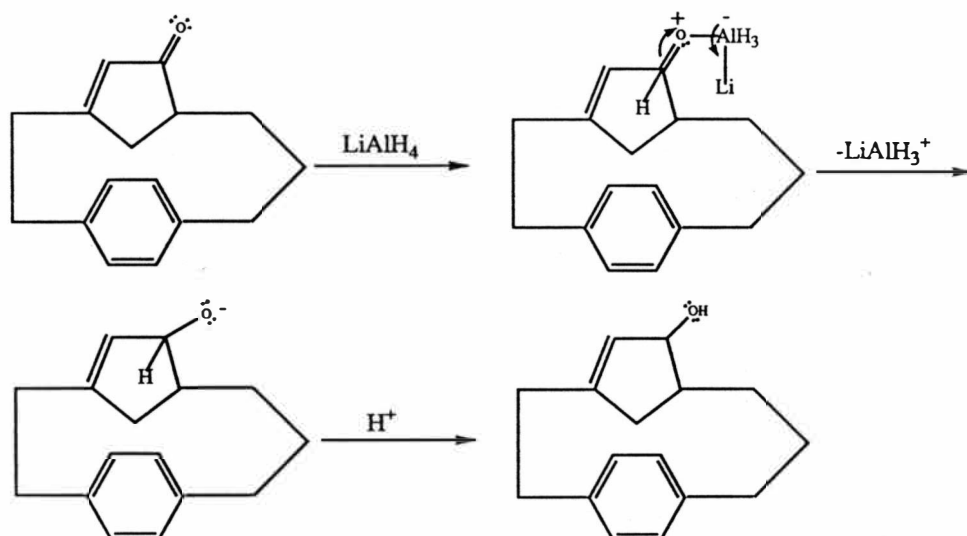
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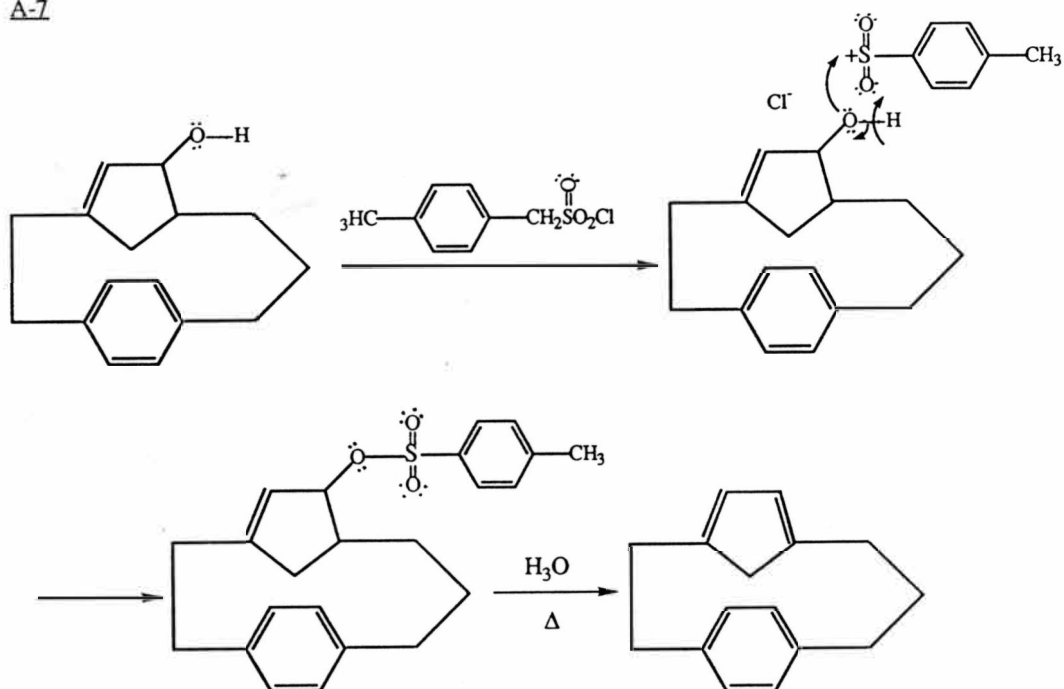
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A-6

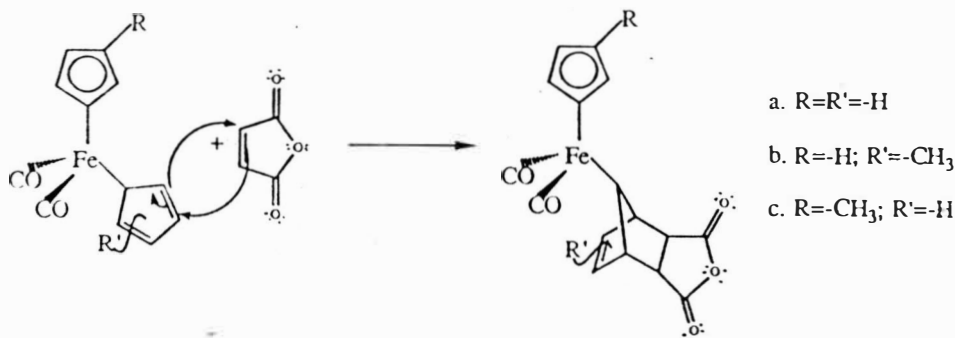
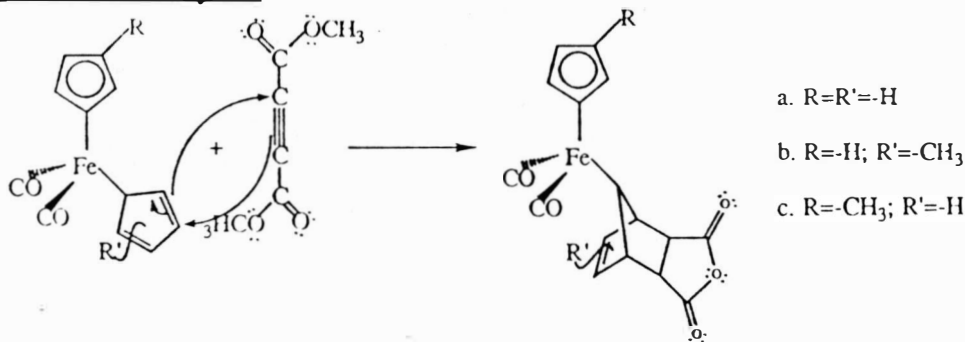
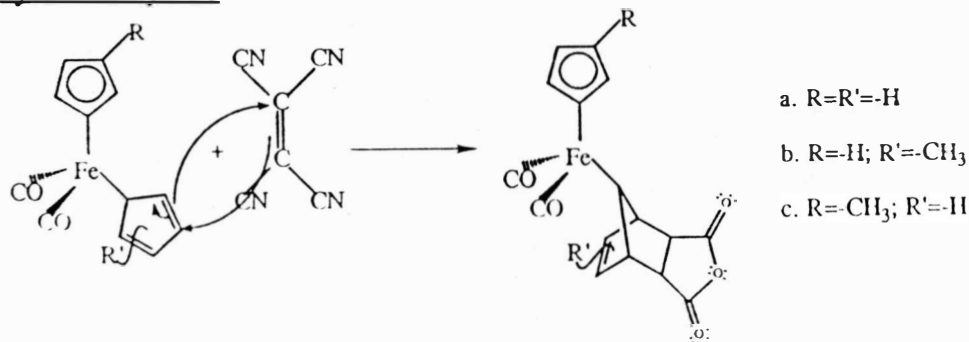


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Appendix B

Mechanism for the Diels-Alder Addition of Certain *Bis*- Cyclopentadienyliron Dicarbonyl Intermediates With Selected Dienophiles

B-IReaction of Bis-cyclopentadienyliron dicarbonyl Intermediate with Maleic AnhydrideB-IIReaction of Bis-cyclopentadienyliron dicarbonyl Intermediate with Dimethylacetylene DicarboxylateB-IIIReaction of Bis-cyclopentadienyliron dicarbonyl Intermediate with Tetracyanomethylene

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