Preparation of Novel Bimetallic and Trimetallic Species

Containing the

Cyclopentadienyliron Moiety

A Thesis

Submitted to the Faculty of Graduate Studies

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PREPARATION OF NOVEL BIMETALLIC AND TRIMETALLIC SPECIES
CONTAINING THE CYCLOPENTADIENYLIRON MOIETY

BY

SHELLY BERNARDIN

A Thesis/Practicum submitted to the Faculty of Graduate Studies of The University

of Manitoba in partial fulfillment of the requirements of the degree

of

MASTER OF SCIENCE

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Abstract

In light of the recently reported synthesis of oligomeric ethers containing the cyclopentadienyliron moiety, this work details three strategies towards the functionalization of these materials. These strategies focus on the incorporation of specific moieties due to their chemical behavior, as well as the incorporation of novel linkages, which would alter the tensile characteristics of the resulting oligomeric species.

Phenolphthalein was examined as an etheric bridge for bimetallic species due to the possibility of chemical modification of the lactone ring with a nucleophile. However, reaction with primary amines was found to cause an etheric cleavage reaction to occur, most likely through the formation of a tertiary carbocation intermediate. Interestingly, this reaction was found to be useful synthetically in the preparation of cyclopentadienyliron complexed anilines which may not be prepared via nucleophilic aromatic substitution of complexed chloroarenes or nitroarenes.

Etheric cleavage was also shown to occur in the presence of potassium permanganate, which caused the formation of a cyclopentadienyliron complexed phenol. This class of compounds has been synthesized previously only by nucleophilic displacement of a chlorine atom by the hydroxide ion. The resulting material is quite unstable, and decomposes over the course of a few days, even when stored at low temperature.

A third attempt to functionalize bimetallic analogues resulted in the successful formation of trimetallic and macrocyclic esters containing both ferrocene and cyclopentadienyliron moieties. Although it was hoped that these compounds would exhibit unique electrochemical behavior, the presence of strong electron withdrawing groups impeded the oxidation of the ferrocene moiety.

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List of Abbreviations

APT	attached proton test
ArC	aromatic carbon atom
ArH	aromatic proton
Cp	cyclopentadienyl
d	doublet
DCC	dicyclohexylcarbodiimide
dd	doublet of doublets
DMF	N,N-dimethylformamide
EPR	electron paramagnetic resonance spectroscopy
Fc	ferrocene
FcC	ferrocenyl carbon atom
FcH	ferrocenyl proton
HPLC	high performance liquid chromatography
J	coupling constant
m	multiplet
NMR	nuclear magnetic resonance
S_NAr	nucleophilic aromatic substitution
t	triplet

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1.0 Introduction

1.1. The Complexation of Metal Moieties to Arenes

The phenomenon now known as aromaticity has been recognized since the nineteenth century.[1] Since that time, the unique characteristics of materials exhibiting aromaticity have made the study of their reactivity an integral component of organic chemistry. Aromatic compounds are well known for their remarkable stability, which is thought to be due to their delocalized pi system.[2] As such, these compounds are electron rich, and are therefore quite susceptible to attack by electrophiles.

It is also this electron rich nature which makes these compounds suitable for use as ligands in organometallic complexes. Pi complexation of an aromatic compound to a metallic moiety may be initiated in a number of ways, such as through the use of heat, light, or by a chemical catalyst.[3] The coordination of a metal moiety to an aromatic compound has been shown to have a profound effect on the behavior of the aromatic component. These effects are summarized in **Figure 1.1**. Positive or negative charges located in the benzylic position of a complexed arene are stabilized by the presence of a metal moiety. This is proposed to occur via field effects. As well, the hydrogen substituents which are present on the complexed aromatic ring display an increase in acidity.[4] Due to the steric requirements of the often bulky metal moiety, the complexation of an arene can also require the attack of reagents at a specific face, which will affect the stereochemistry of the resulting product. This has been illustrated quite effectively by Meyer and Jaoen, where the chromium tricarbonyl moiety has been used to effect the synthesis of a chiral alcohol as shown in **Scheme 1.1**:[5]
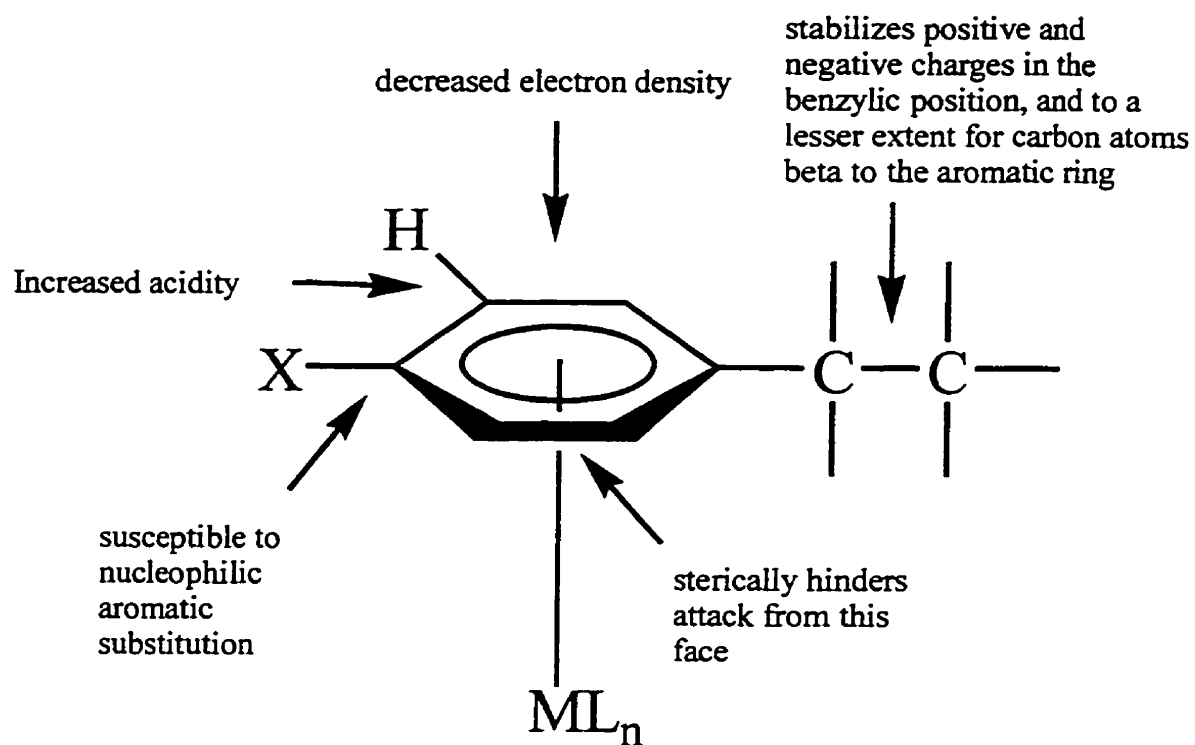
Figure 1.1: A summary of the effects on the reactivity of an arene when complexed to a metal moiety.
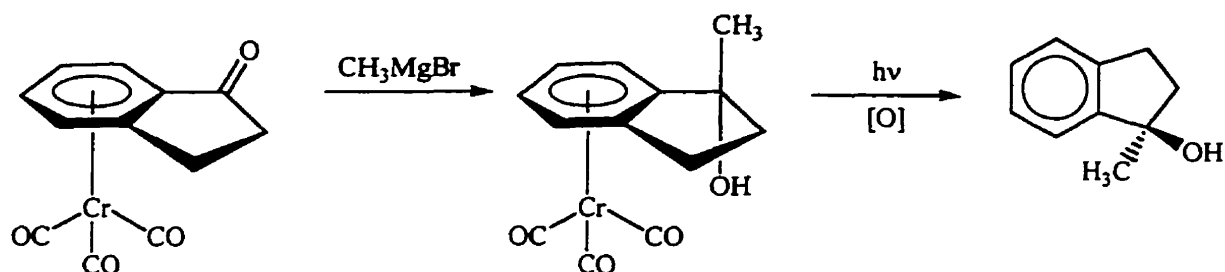
Scheme 1.1

However, to date, the primary focus of the literature has been on the decreased electron density exhibited by the aromatic ring upon complexation with a metal moiety. This allows arenes which are otherwise inert towards nucleophiles to undergo nucleophilic aromatic substitution.[4]

1.2. Metal Promoted Nucleophilic Aromatic Substitution

The lack of reactivity of aromatic compounds towards nucleophiles has been well documented, and may be attributed to their electron rich nature.[1] For this reason, nucleophilic aromatic substitution remains a largely unexplored synthetic reaction.[4] Traditional organic chemistry has focused on the promotion of nucleophilic aromatic substitution via the incorporation of electron withdrawing groups in the positions ortho and para to the leaving group. The nitro group is most typically used for this purpose, due to its strong electron withdrawing ability.[2] However, this methodology often requires the subsequent removal or transformation of the nitro group, which necessitates additional reaction steps under potentially harsh conditions. The inefficiency of these requirements has therefore limited the use of nucleophilic aromatic substitution as a synthetic tool.

However, many studies have shown that the π complexation of an arene to a metal moiety results in a polarity inversion, or ümpolung.[4] This causes the formerly nucleophilic

arene to become electrophilic, and thus susceptible to attack by a nucleophile. This behavior was first exploited by Whiting and Nichols, who used the complexation of the chromium tricarbonyl moiety to promote the reaction of the methoxy anion with the chlorobenzene complex:[6]
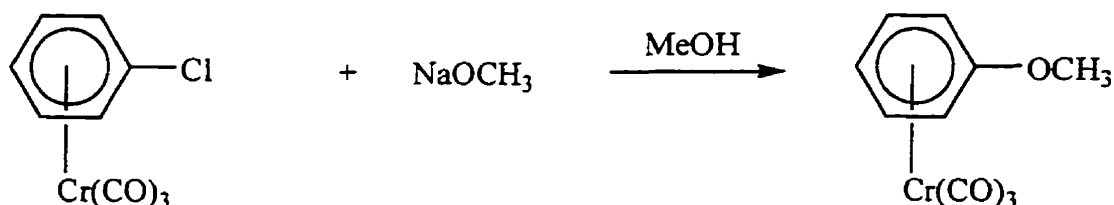
Scheme 1.2

For this methodology to be synthetically useful, several criteria must be met. First, the metal moiety must be a sufficiently strong electron withdrawing group, so as to allow nucleophilic aromatic substitution to occur under relatively mild reaction conditions. Second, the complexation reaction should occur efficiently. Starting materials should not be expensive, and must be commercially available. Finally, the arene itself must be easily recoverable. Typical methods of demetallation include photolysis, thermolysis or electrolysis.[7]

Many different metal moieties have been used as electron withdrawing groups to facilitate nucleophilic aromatic substitution. These include $Cr(CO)_3$, $Mn^+(CO)_3$ and Fe^+Cp (Cp=cyclopentadienyl). However, these metal moieties have different degrees of electron withdrawing capabilities. Knipe *et. al.* have found that these moieties, in order of increasing electron withdrawing ability are: $Cr(CO)_3$ < Fe^+Cp < $Mn^+(CO)_3$.[7,8] Experimental evidence has shown that the chromium tricarbonyl moiety has an electron withdrawing ability which is roughly equivalent to that of a nitro group in the para

position. In comparison, it has been estimated that the cyclopentadienyliron moiety has an electron withdrawing ability which is 10^5 times that of chromium tricarbonyl.[9]

Mechanistic studies focusing on the nucleophilic aromatic substitution of a complexed haloarene have also shown that the pathway through which the reaction occurs differs with the metal moiety that is used. Predictably, with a neutral metal species, such as chromium tricarbonyl, the first step involves the addition of the nucleophile at the carbon bearing the leaving group. This is the slow step. Following the formation of the Meisenheimer intermediate, there is a quick loss of the leaving group, resulting in the formation of the product. For cationic species, there is the potential for the formation of an ion pair, where the nucleophile is associated with the metal cation. Thus the two possible mechanisms may be represented by **Scheme 1.3**. Kinetic studies done by Knipe *et al.* support the formation of these ion pairs, although they have not been identified spectroscopically.[7] However, the rapid equilibrium exhibited by the cationic species does not result in a decrease in the overall rate of reaction, due to the overwhelmingly large effect of the positive charge in the stabilization of the transition state.

The cyclopentadienyliron moiety has several advantages over the other metallic moieties studied. Because the moiety is positively charged, it is a stronger electron withdrawing group than neutral metal moieties. The starting arene complexes are easily prepared from relatively inexpensive starting materials. Finally, the metal moiety is easily cleaved, through photolytic, thermolytic or electrolytic demetallation. Because of these advantages, the research presented in this body of work will focus on the cyclopentadienyliron moiety as the primary means to effect nucleophilic aromatic substitution.
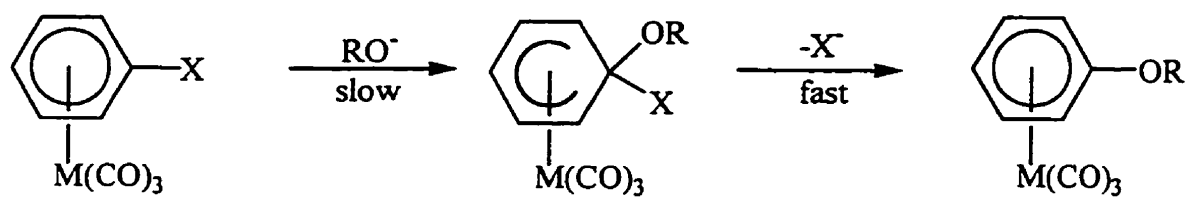
M = Cr, Mn

"Meisenheimer Intermediate"
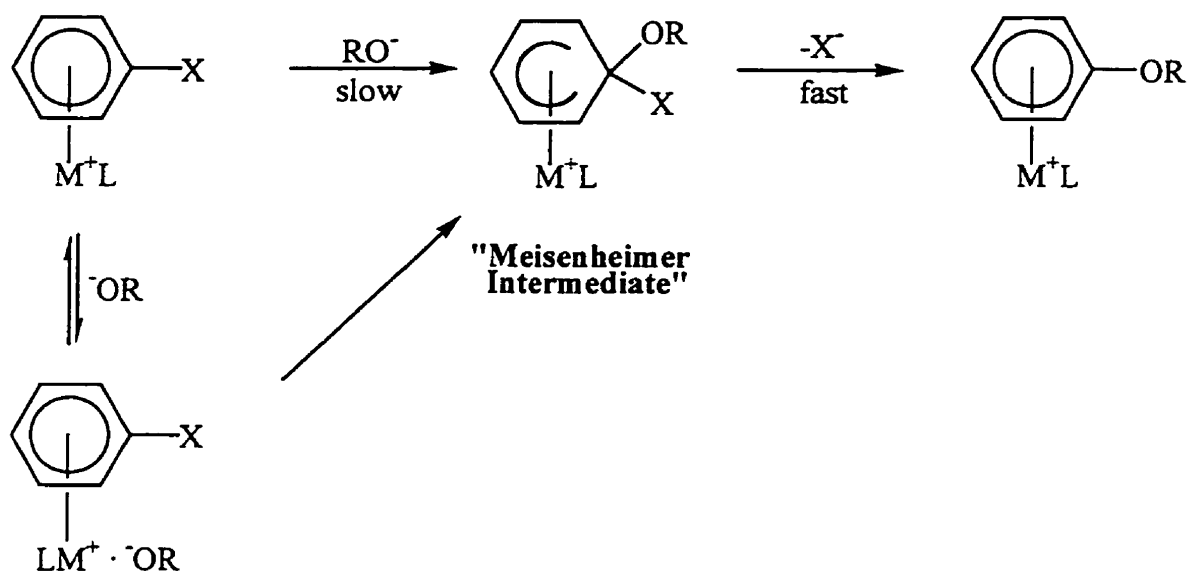
M	L
Mn	$(CO)_3$
Fe	Cp

Scheme 1.3

1.3. Preparation of Cyclopentadienyliron Complexes of Arenes via Ligand Exchange

The preparation of the first η^6-arene-η^5-cyclopentadienyliron complex was reported in 1957 by Coffield and his co-workers, who reacted cyclopentadienyliron dicarbonyl chloride with refluxing mesitylene in the presence of aluminum chloride. The complexed arene was isolated as its iodide salt (**Scheme 1.4**).[10]
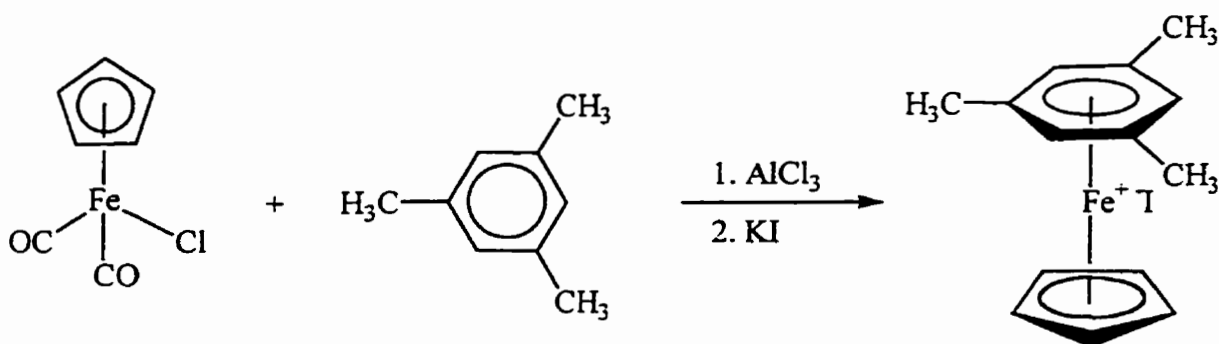
Scheme 1.4

However, the most efficient route yet presented for the synthesis of these aromatic complexes was reported by Nesmeyanov *et. al.*, who succeeded in the exchange of one cyclopentadienyl ligand of ferrocene with an arene.[11-13] The complexed arene formed in this reaction may be isolated as the tetrafluoroborate or ammonium hexafluorophosphate salt. This method requires the presence of a Lewis acid such as aluminum chloride to activate the arene towards reaction and prevent dehalogenation, as well as aluminum, which is present in order to prevent the oxidation of ferrocene to the ferrocenium state. This is shown in **Scheme 1.5**. Although early workers have suggested the use of an inert solvent, such as decalin, this is not required for arenes which exist as liquids at the reaction temperature.[14]
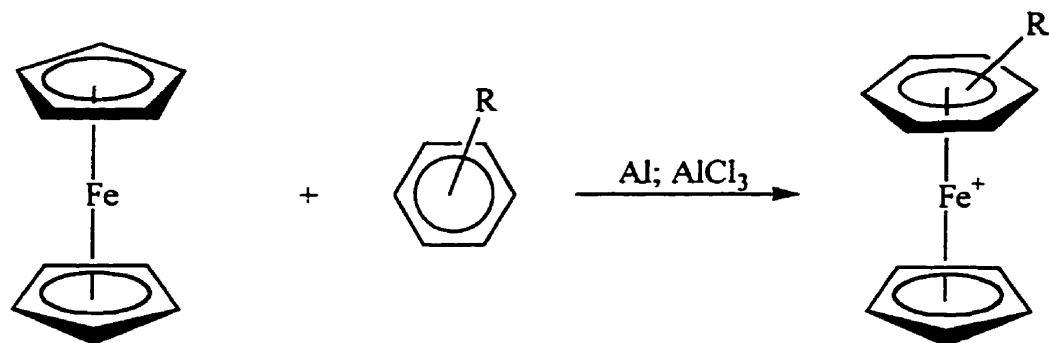
Scheme 1.5

Yields are typically in the range of 30 - 60%. If the substituted arene contains electron withdrawing substituents, longer reaction times and higher temperatures are required, which is accompanied by a decreased yield as compared to arenes containing electron releasing substituents.[11,12] It has been suggested that this effect is due to temporary complexation of aluminum chloride with the electron withdrawing group, which decreases the efficiency of the catalyst.[15]

Unfortunately, there are side reactions which accompany the exchange of the cyclopentadienyl ligand of ferrocene. A ferrocenophane may be isolated from the ligand exchange reaction mixture, and its formation may be rationalized upon consideration of the proposed mechanism for the reaction, as shown in **Scheme 1.6**.[16]

The reaction of ferrocene with a variety of different aromatic compounds has led to the synthesis of over sixty different cyclopentadienyliron complexes.[16] A number of different substituted benzenes have been successfully complexed to the cyclopentadienyliron moiety, as well as polyaromatic hydrocarbons (such as 9,10-dimethylanthracene)[17], and heterocycles (such as dibenzodioxin)[18,19]. In addition, ligand exchange has been found to occur intermolecularly,[20,21] and also may be used to form bimetallic species.[22] The wide range of cyclopentadienyliron complexes which have been prepared emphasizes the versatility of the ligand exchange reaction in which ferrocene acts as the substrate.
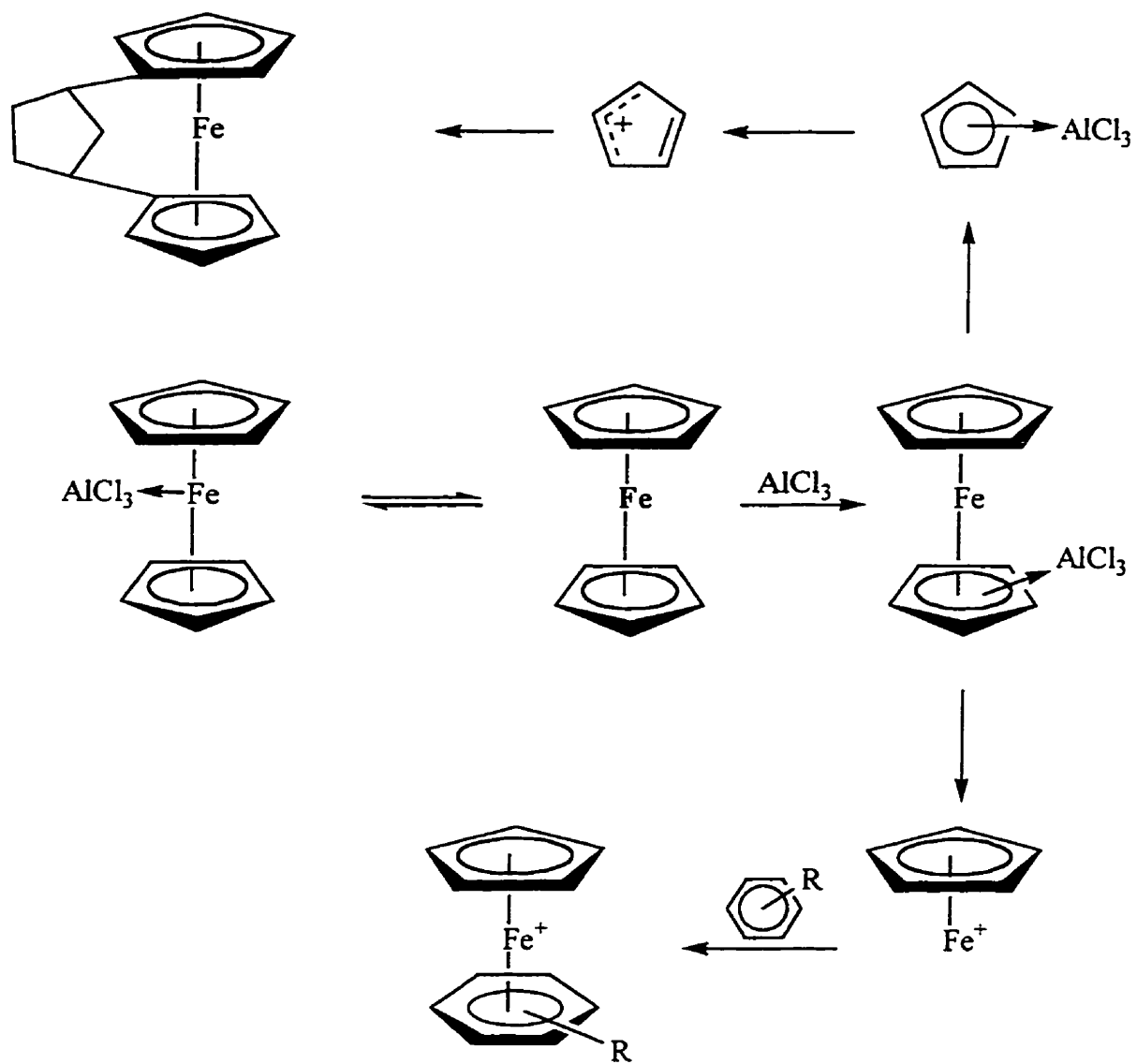
Scheme 1.6

1.4. Demetallation Procedures

The cyclopentadienyliron moiety may be easily cleaved to provide the purely aromatic compound, generally in good yield. This has been accomplished by several methods, including pyrolysis[23], photolysis[24] and electrolysis.[25]

Pyrolysis is a particularly harsh method to effect demetallation. It requires reaction temperatures typically over 200°C, as well as extremely low pressures.[26] Clearly, the organic compounds must prove quite robust in order to withstand such harsh conditions. Thus this procedure is generally reserved for compounds which prove particularly difficult to demetallate by other means. Electrolysis has also been used as a method for the removal of the cyclopentadienyliron moiety. Reduction is effected in the presence of a suitable nucleophile, such as P(OMe)$_3$. Once the one electron reduction of the eighteen electron complex to the neutral nineteen electron species occurs, the complex is susceptible to a ligand replacement reaction in which the arene is replaced by three P(OMe)$_3$ ligands.[25] This reaction has been found to have very high yields and short reaction times. However, there is the potential for side reactions if any of the substituents on the aromatic ring are susceptible to reduction.

When compared to these two methods, photolysis is often considered the method of choice for the demetallation of cyclopentadienyliron complexes. Its advantages include mild reaction conditions, particularly when compared to pyrolysis, short reaction times and high yields. First reported in 1970 by Nesmeyanov *et. al.*,[27,28] the mechanism of photolysis has since been investigated by several workers,[24,29-33] and is considered to be quite complex. It has been determined that there are two different possible products of photolysis when carried out in a polar and nucleophilic solvent such as acetonitrile.[30] These are illustrated in the following scheme:

$$[(arene)FeCp]^+$$

| |
hν | hν
-40°C | 20°C
+CH$_3$CN | +CH$_3$CN
-arene | -arene

$$[(CH_3CN)_3FeCp]^+ \xrightarrow{20°C} \text{½ } FeCp_2 + \text{½ } Fe(CH_3CN)_2$$
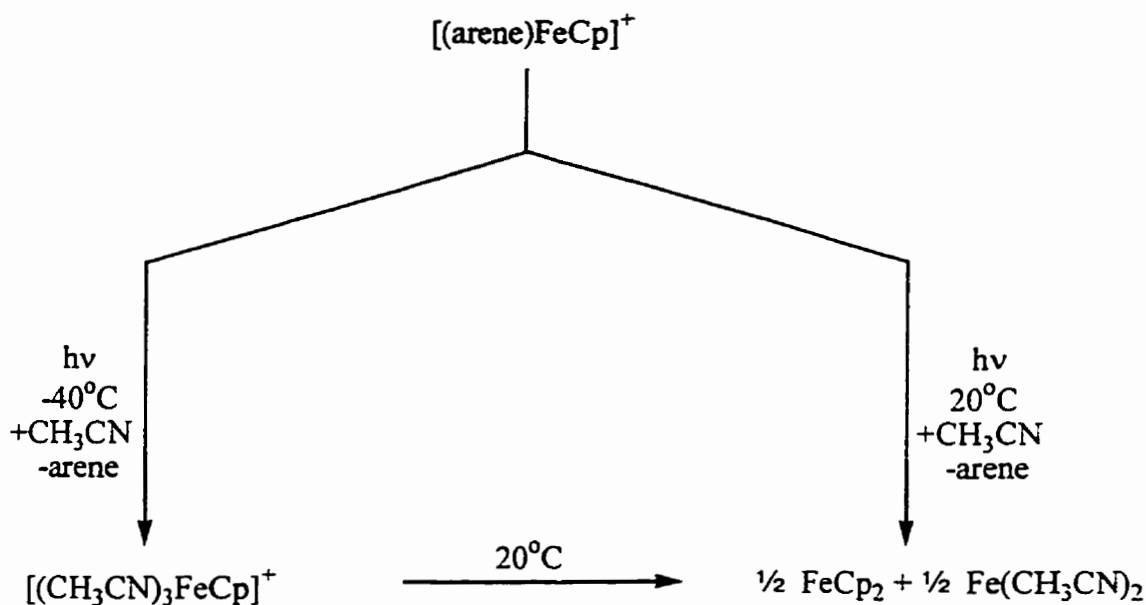
Scheme 1.7

At low temperature, the free arene is released and the iron cation forms a complex with the solvent molecules. At room temperature, ferrocene is evolved in addition to the complex salt.

It has been suggested that the absorption of light in the ligand field region of the spectrum causes the excitation of the complex to a triplet state.[24,31,32] In the presence of a nucleophile, which may be the solvent or an anion present in solution, three two electron donors will add to the complex, accompanied by the release of the arene. The resulting complex salt is inert towards further ligand exchange.

The medium in which photolysis takes place is therefore an important factor in the efficiency of this reaction. Strongly nucleophilic and polar solvents, such as acetonitrile, lead to an increased quantum yield, whereas apolar and weakly nucleophilic solvents, such as dichloromethane, result in a much lower quantum yield. Schrenk and co-workers found that, for the photolysis of η^6-p-xylene-η^5-cyclopentadienyliron(II), the quantum yields increased for different media according to the following order: $SbF_6^- \approx AsF_6 \approx CH_2Cl_2 <$

$PF_6^- \ll ClO_4^- \approx Br^- < BF_4^- < CF_3SO_3^- < CH_3CN < CH_3OH \approx$ propylene carbonate $\approx$ H_2O.[29]

A typical experimental procedure for photolytic demetallation involves the dissolution of the complex in an acetonitrile/dichloromethane mixture, followed by irradiation of this solution with a xenon lamp for four to six hours. The free arene must then be separated from the iron salts and ferrocene which are by-products of the reaction, and this may be done chromatographically, or through selective extraction. The yield of this reaction is quite high, often in excess of 80%.

1.5. Cyclopentadienyliron Promoted Nucleophilic Aromatic Substitution

Nesmeyanov and his co-workers first reported the use of the cyclopentadienyliron moiety for the activation of a complexed arene towards nucleophilic aromatic substitution in 1968. Since that time, there has been much attention focused on the use of this methodology for organic synthesis.[34-36] Chlorobenzene[37] and dichlorobenzene[38] complexes may be synthesized easily via the ligand exchange reaction of ferrocene. Aniline complexes may also be synthesized in this manner, and may be oxidized in the presence of hydrogen peroxide and trifluoroacetic acid to yield nitrobenzene cyclopentadienyliron compounds.[39] It has been shown that both halobenzene and nitrobenzene complexes may undergo nucleophilic aromatic substitution with various nucleophiles.[40-42] For example, the use of chloro- and nitrobenzene complexes has been documented in the synthesis of alkanoic acid esters, compounds which are well known in the pharmaceutical industry due to their anti-inflammatory properties.[43-45] In this synthetic route, a wide variety of alkanoic acids are prepared in good yield and under very mild reaction conditions, and thus this methodology represents a significant improvement over current industrial syntheses.[46,47] This reaction (**Scheme 1.8**) is shown below:

R= H
3-Me
4-Me

R' = Me
Et

R= 4-Et
4-^{i}Pr
4-Bu
4-^{t}Bu
4-^{s}Bu
3,4-Me$_2$
3,5-Me$_2$

R' = Me
Et
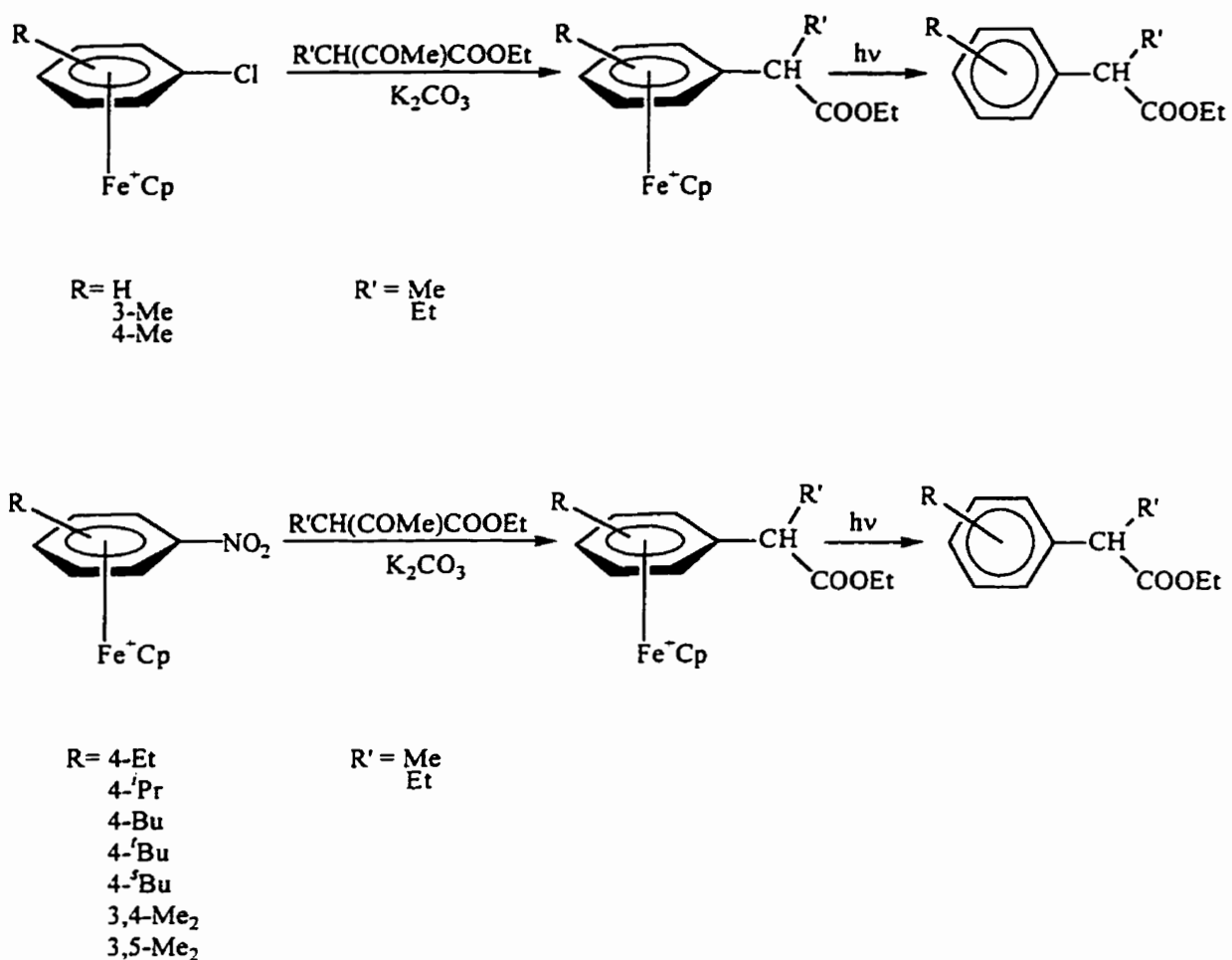
Scheme 1.8

As well, cyclopentadienyliron promoted nucleophilic aromatic substitution has been used for the synthesis of heterocyclic compounds, with the use of appropriate nucleophiles. This work, done by Sutherland and his co-workers, clearly demonstrates the flexibility of this methodology for the synthesis of various organic molecules (**Scheme 1.9**):[48,49]

X,Y = S, O, NH

R = H, Me
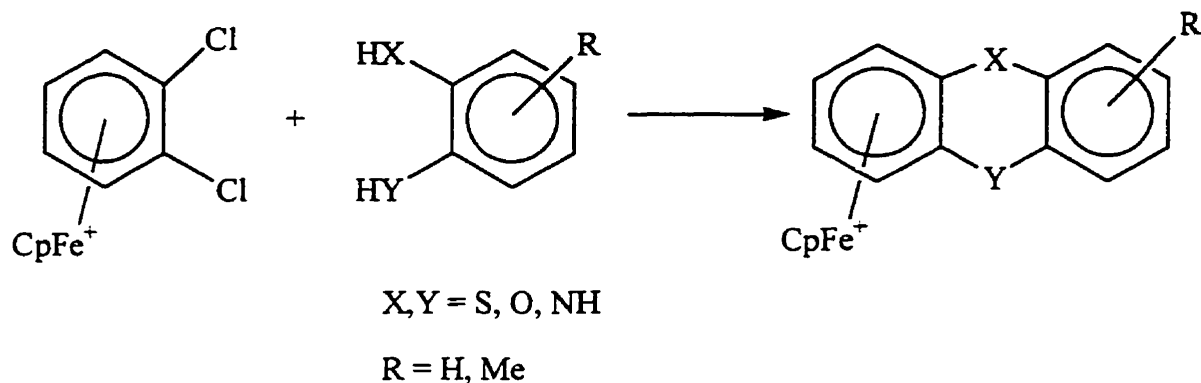
Scheme 1.9

Interestingly, the cyclopentadienyliron moiety has also allowed for the preparation of materials which may not be synthesized by purely organic methods. For example, Abd-El-Aziz *et. al.* were recently successful in the preparation of macrocyclic polyethers through stepwise nucleophilic aromatic substitution.[50] This methodology has allowed for the synthesis of both symmetrical and asymmetrical macrocycles, some of which may not be prepared by other means. This is illustrated in **Schemes 1.10** and **1.11**.

The cyclopentadienyliron moiety has also recently been reported to facilitate the one step synthesis of a variety of poly(aromatic ethers) and thioethers via nucleophilic aromatic substitution.[51] Poly(aromatic ethers) and thioethers are tremendously important in manufacturing industries as thermoplastics. This unique synthetic methodology methodology has the advantage that the resulting metallated polymers are quite soluble in a variety of organic solvents, including dichloromethane and N,N-dimethylformamide (DMF). As well, the reaction conditions required are quite mild. The synthesis of these compounds is illustrated in **Scheme 1.12**.
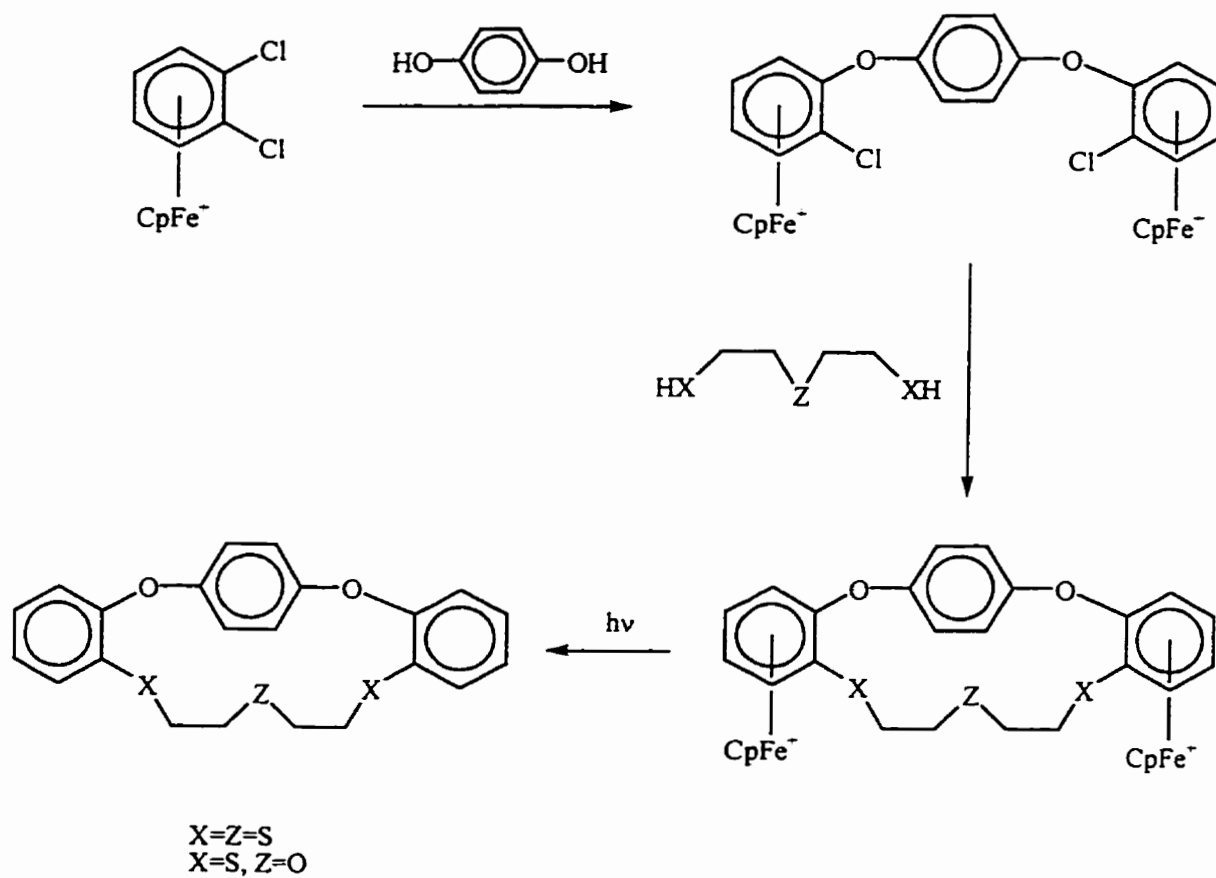
Scheme 1.10
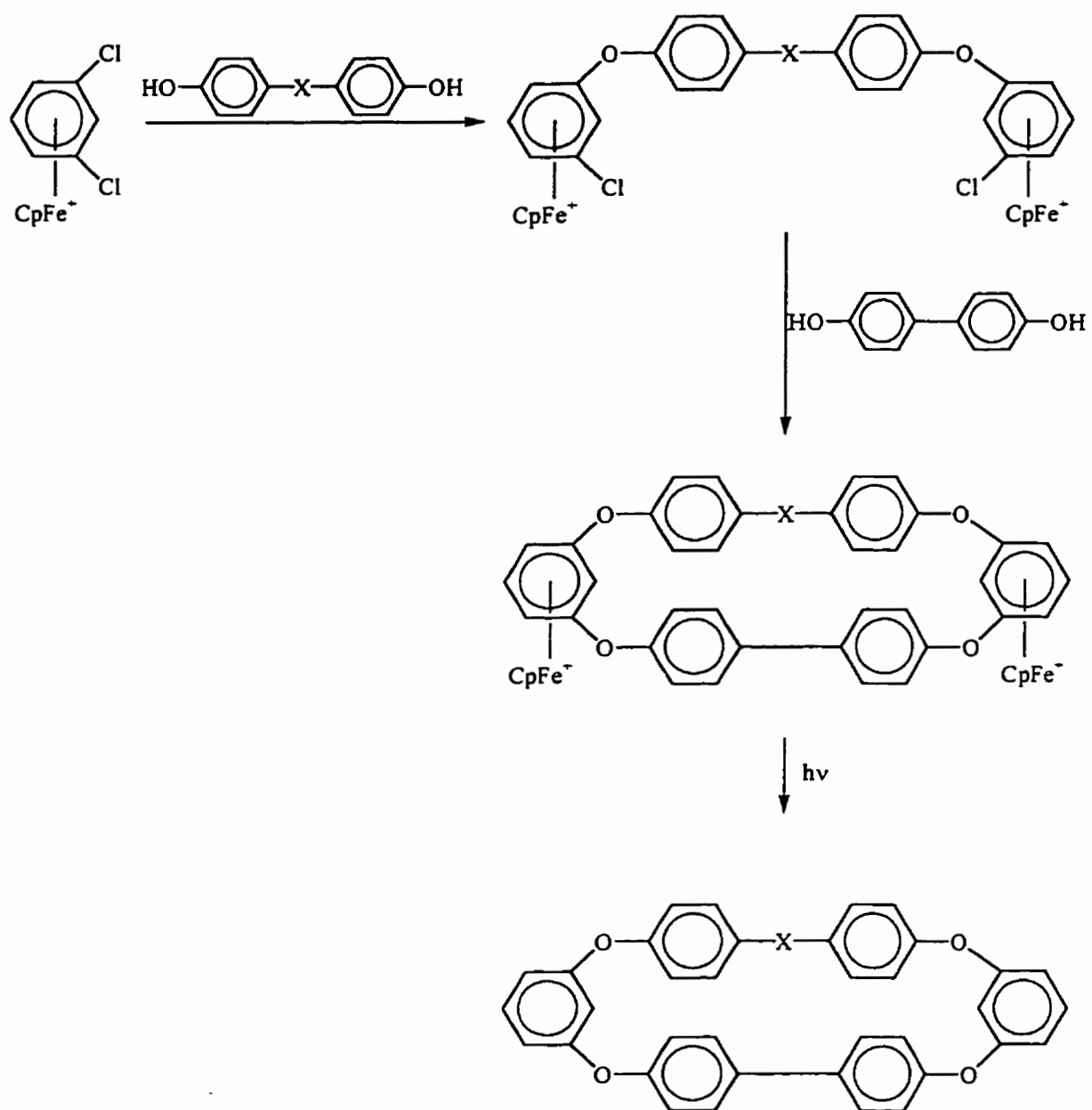
X = direct bond or CMe$_2$

Scheme 1.11

16

X	Y
S	$(CH_2)_4$
S	$(CH_2)_6$
S	$(CH_2)_8$
S	—⬡—S—⬡—
O	—⬡—C(CH_3)(CH_3)—⬡—
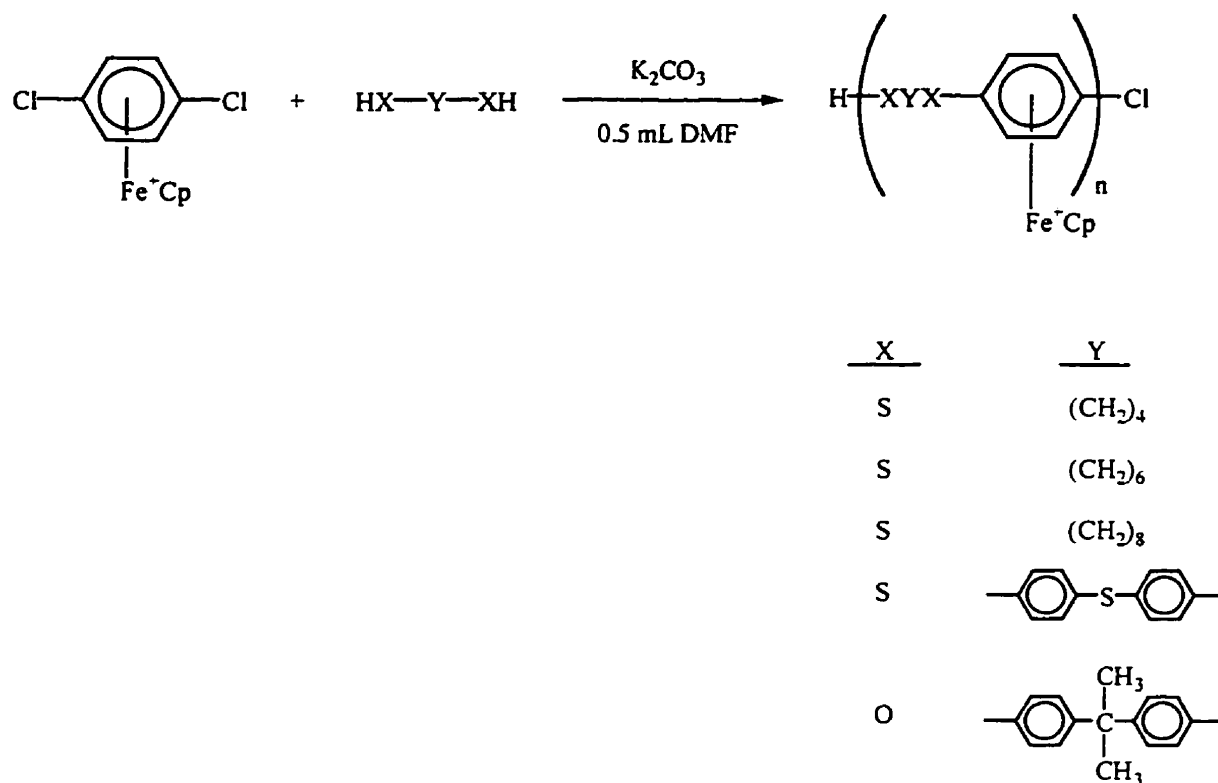
Scheme 1.12

Finally, Abd-El-Aziz and co-workers have employed the stepwise nucleophilic aromatic substitution of cyclopentadienyliron complexed arenes for the synthesis of oligomeric poly(aromatic ethers).[52] This methodology for the synthesis of high molecular weight compounds has the advantage of control over the molecular weight which is obtained, and thus permits the ability to engineer the properties of the corresponding material. As well, different linkages or functional groups may be introduced at any step during the synthesis, also allowing for the controlled design of polymeric materials in order to exhibit any desirable properties. This is shown in **Scheme 1.13**:

where n = 33
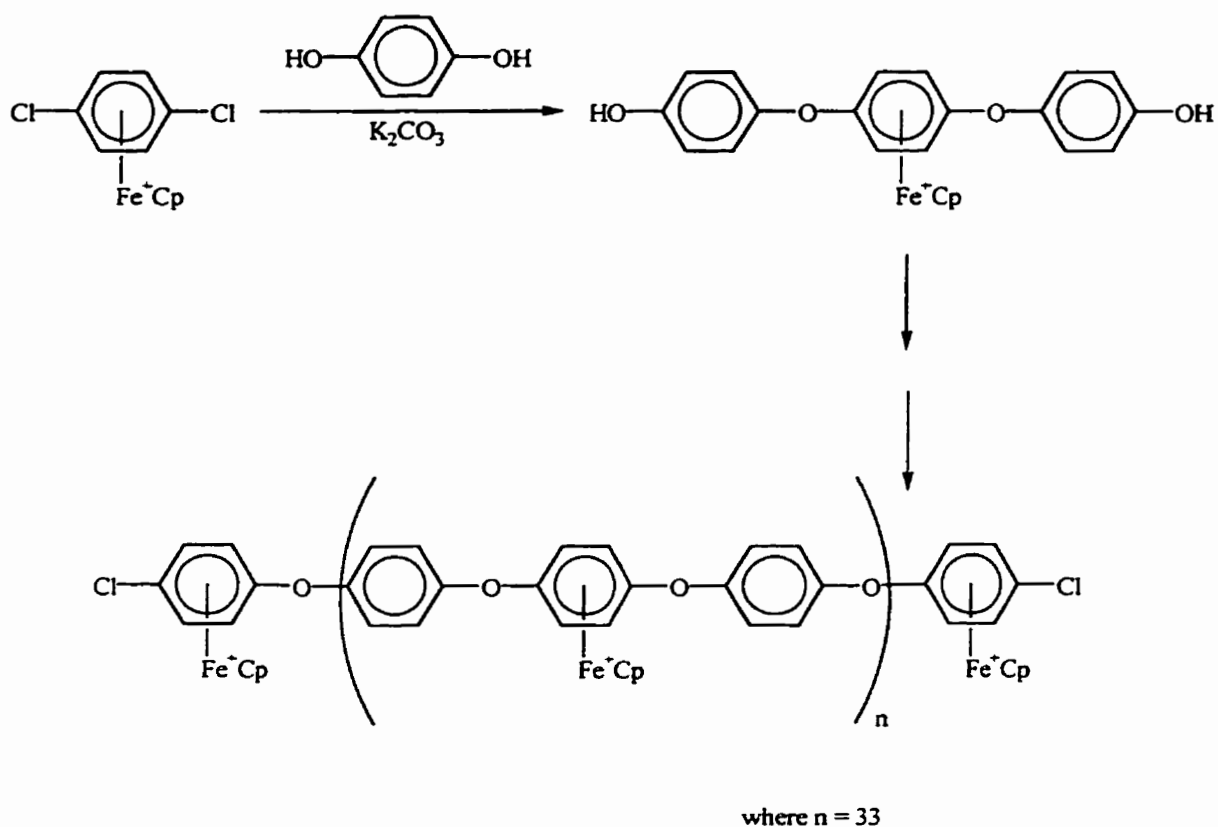
Scheme 1.13

Although Abd-El-Aziz and co-workers limited their oligomers to chains containing thirty-five metals pendant to the backbone of the chain, there is every indication that extension of this work to higher molecular weight materials should be possible. Thus this method provides the potential for a great degree of flexibility in the molecular weight and properties of poly(aromatic ethers) which may be obtained.

Interestingly, oxidation of cyclopentadienyliron complexes of arenes with strong oxidizing agents does not lead to the formation of dicationic species. η^6-Benzene-η^5-cyclopentadienyliron(II) hexafluorophosphate remains unreacted after reflux with CrO_3 in H_2SO_4, or with H_2O_2 in NaOH.[53] Fortunately, functional groups which are located on the aromatic ring do not display a similar resistance to chemical oxidation.

Nesmeyanov and his co-workers were successful in effecting the oxidation of both η^6-tolyl-η^5-cyclopentadienyliron(II) and η^6-p-chlorotolyl-η^5-cyclopentadienyliron(II) salts with potassium permanganate (**Scheme 1.14**).[53-55] This reaction is analogous to the long known organic reaction, where arenes with alkyl side chains are oxidized to the carboxylic acid.[1] The acid functionality may be further reacted in the presence of an amine to form an amide.[54]
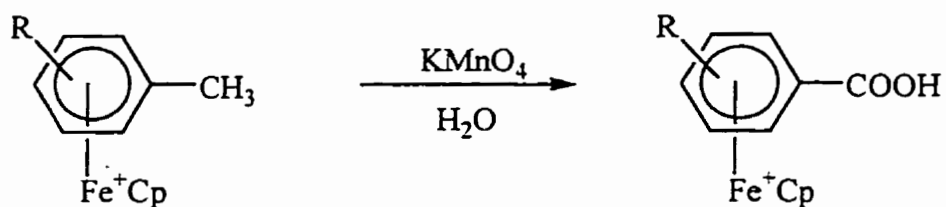
Scheme 1.14

This reaction further demonstrates the variety of starting materials which may be synthesized containing the cyclopentadienyliron moiety. The fact that the resulting complexed acid will react in the presence of an amine to form an amide suggests that the

reactivity of the cyclopentadienyliron complexed acid is similar to that of purely organic carboxylic acids, and that complexes containing ester or amide linkages may be synthesized via this methodology.

1.7. Spectroscopic Characterization of Cyclopentadienyliron Complexes

Cyclopentadienyliron complexes are routinely characterized via spectroscopic methods.[56] Nuclear magnetic resonance, or NMR, is one of the most common methods of structure determination which is used, due to the ease of interpretation of the resulting spectra.[57]

There have been many studies of both the ^{1}H and ^{13}C NMR spectra of arene complexes of the cyclopentadienyliron moiety, and several obvious trends have been observed. First, there is a very noticeable upfield shift which occurs for the arene residues upon complexation to a metal moiety. These shifts are observed in both the ^{1}H and ^{13}C NMR spectra.[58,59] There have been many theories as to the origin of this upfield shift. These include metal to ligand π^* back donation, ligand σ to metal donation, ligand π to metal donation and anisotropy of the neighbouring metal atom.[60] Experimental work and *ab initio* calculations have shown that there is not one effect which can be used to explain the magnitude of the upfield shift. Most likely, all of these factors contribute to this shift in differing amounts.[61]

Characteristically, the cyclopentadienyl ion resonance also appears shifted downfield in both ^{1}H and ^{13}C NMR spectra from its position in ferrocene. For the η^6-benzene-η^5-cyclopentadienyliron(II) complex, this shift is 0.89 ppm for the ^{1}H NMR spectrum. Nesmeyanov *et. al.* have suggested that this shift is due to the presence of a

positive charge on the iron atom, which is partially delocalized on the cyclopentadienyl ring.[58] This causes the ring to become deshielded, and thus absorb at higher frequency.

A third interesting feature of the NMR spectra of cyclopentadienyliron complexes of arenes is the downfield location of the resonances of the quaternary carbons. Some of these resonances may be shifted as far as 80 ppm downfield of their protonated counterparts. This may be easily explained by the resonance structures which are possible for a substituted arene complex:[60]
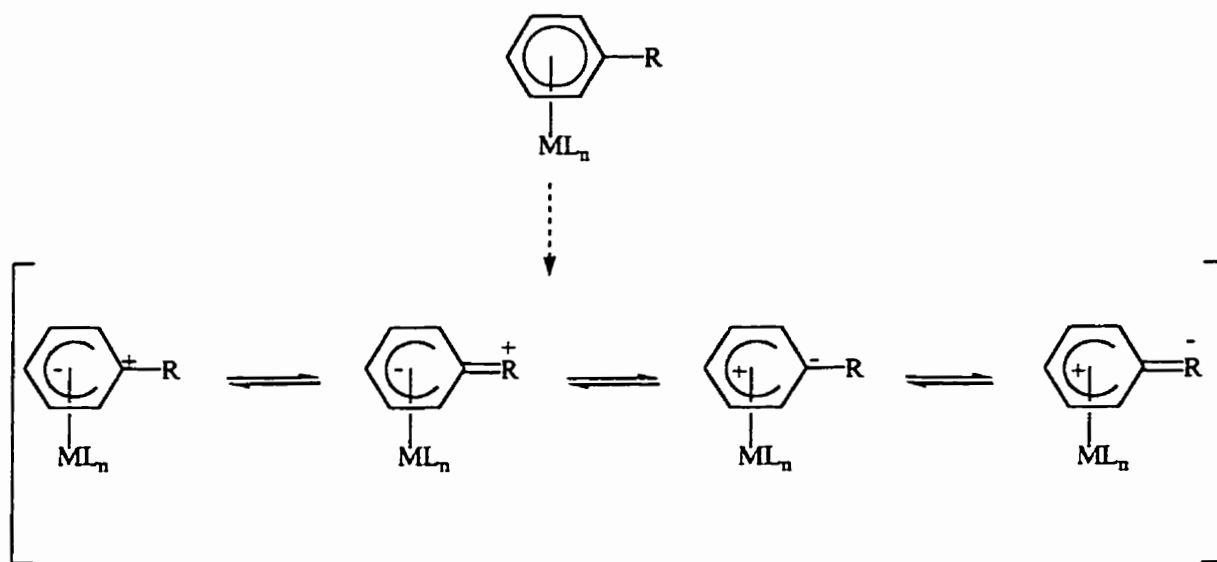
Figure 1.2: Possible resonance forms for cyclopentadienyliron complexes of substituted arenes.

In these structures, there is a possibility of either a positive or a negative charge being carried on the aromatic ring. Almost certainly, the resonance structures with the negative charge delocalized throughout the ring will exhibit an increased stability, as the excess electron density may be delocalized by the metal atom as well. This stabilization of these

resonance forms causes the carbon bearing the substituent to be deshielded, and thus this carbon resonance is shifted far downfield. In corollary, the carbon atom para to the substituent should, by this explanation, be the most shielded, and thus should be found the most upfield. This also has been experimentally observed.[60]

1.8. Scope of the Present Work

With the recently reported ability to synthesize poly(aromatic ethers) in a stepwise fashion, it has become apparent that the incorporation of different linkages and functional groups will be required in order to achieve control over the characteristics which the resulting material will possess.[45] To this end, this study has focused on the incorporation of very specific functional groups, in the hopes that these moieties will affect properties such as the mechanical strength and flexibility of the material.

To accomplish this goal, bimetallic compounds were used as models, for several reasons. Bimetallic species are easily synthesized, generally in one step.[62,63] As well, because they are simpler analogues of the oligomeric materials, their ^1H and ^{13}C NMR spectra are much more easily interpreted. The present work focuses on three different strategies for the preparation of novel bimetallic species. Phenolphthalein, due to its lactone ring, is examined as an etheric bridge. As well, the synthesis of diacid species is examined in order to introduce ester or amide linkages into bimetallic species. The third study focuses on the incorporation of ferrocene moieties into cyclopentadienyliron bimetallic complexes, in order to study the electrochemical behavior of the mixed-valence species.

2.0 Cleavage of Cyclopentadienyliron-Complexed Ethers

2.1. Introduction

2.1.1. Phenolphthalein as a Nucleophile

Phenolphthalein is a commonly used indicator for acid/base titrations.[64] The characteristic brilliant purple colour which is exhibited in basic conditions may be easily understood by considering the chemistry of phenolphthalein in solution (**Figure 2.1**). Under acidic conditions, phenolphthalein is colourless. However, when the pH is raised to above 8, the lactone ring is opened, causing the formation of a tertiary carbocation.[65] This cation is resonance stabilized, as illustrated in the figure. It is this species which is responsible for the colour of phenolphthalein in basic solution.[66] Over time, hydroxide ions may attack the carbocation, resulting in the formation of the colourless carboxylate species also depicted in **Figure 2.1**.

Phenolphthalein is also interesting as a potential bridge for bimetallic complexes due to its structure. Phenolphthalein contains two phenolic groups, which act as excellent nucleophiles in the presence of a weak base, such as potassium carbonate. As well, phenolphthalein contains a lactone ring, which is a potential site for the functionalization of bimetallic species.

pH ≤8

colourless

pH >8

purple

OH⁻

colourless
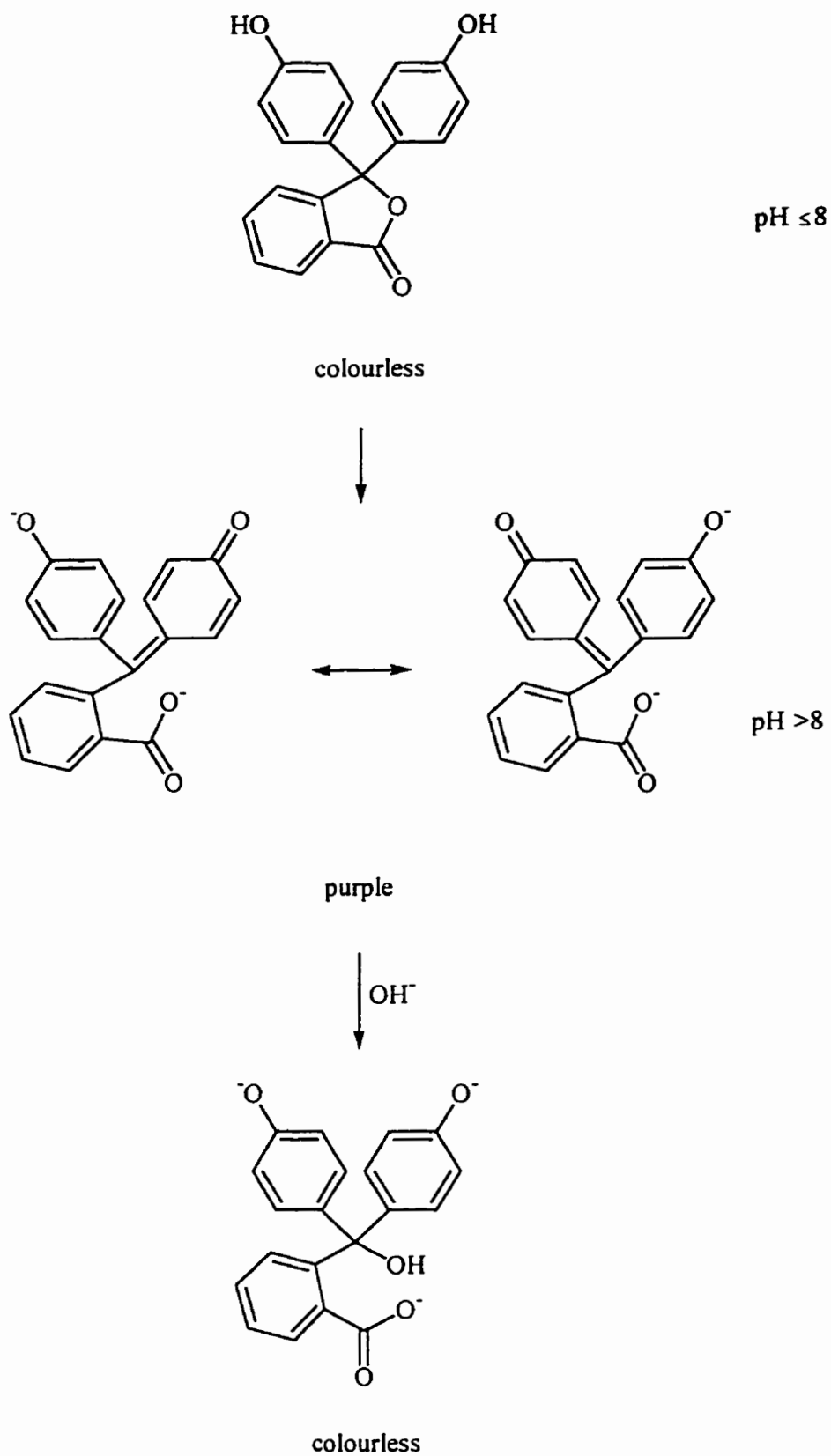
Figure 2.1: The resonance forms of phenolphthalein in acidic and basic solution.

Phenolphthalein was used as a nucleophile by Abd-El-Aziz and de Denus, who reacted it with the dichloroarene complex shown in the following scheme (**Scheme 2.1**).[67]
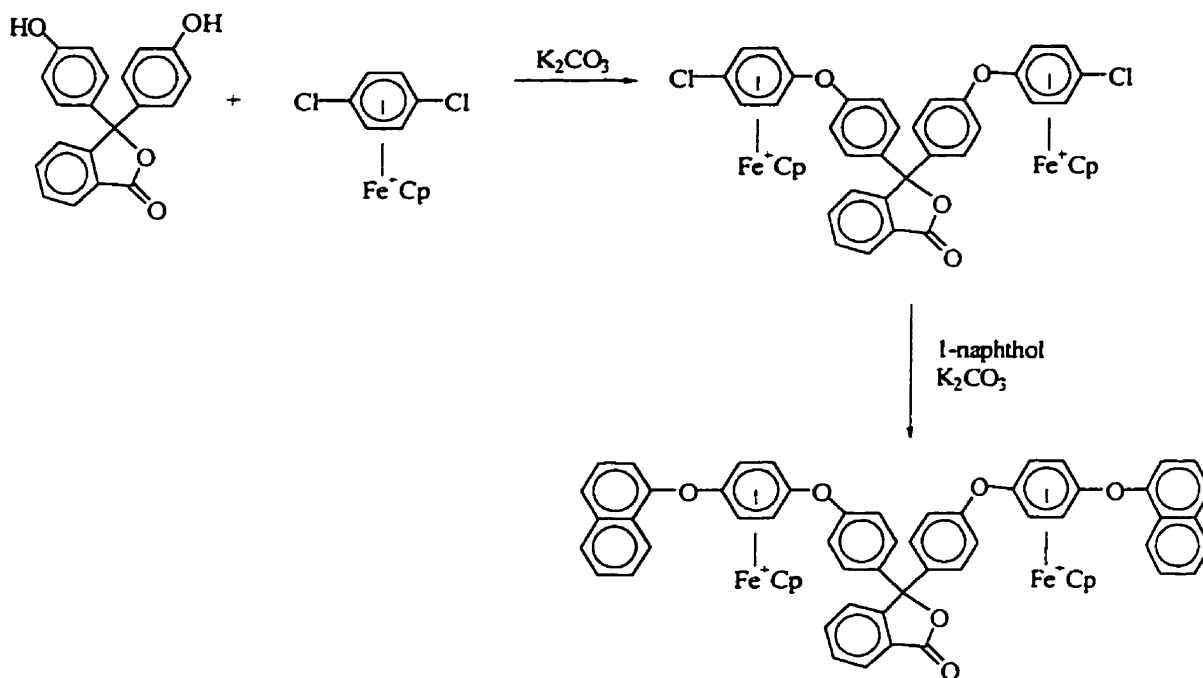
Scheme 2.1

After a capping reaction with 1-naphthol, these bimetallic species were demetallated, and subsequently polymerized via the Scholl reaction to prepare higher molecular weight species, as described in **Scheme 2.2**. Phenolphthalein was incorporated into these polyether chains specifically due to the presence of the lactone ring. If successful, functionalization of the lactone could allow for the formation of crosslinks between poly(aromatic ether) chains, resulting in the construction of a network polymer. Therefore the present work focuses on the reactivity of the phenolphthalein moiety.
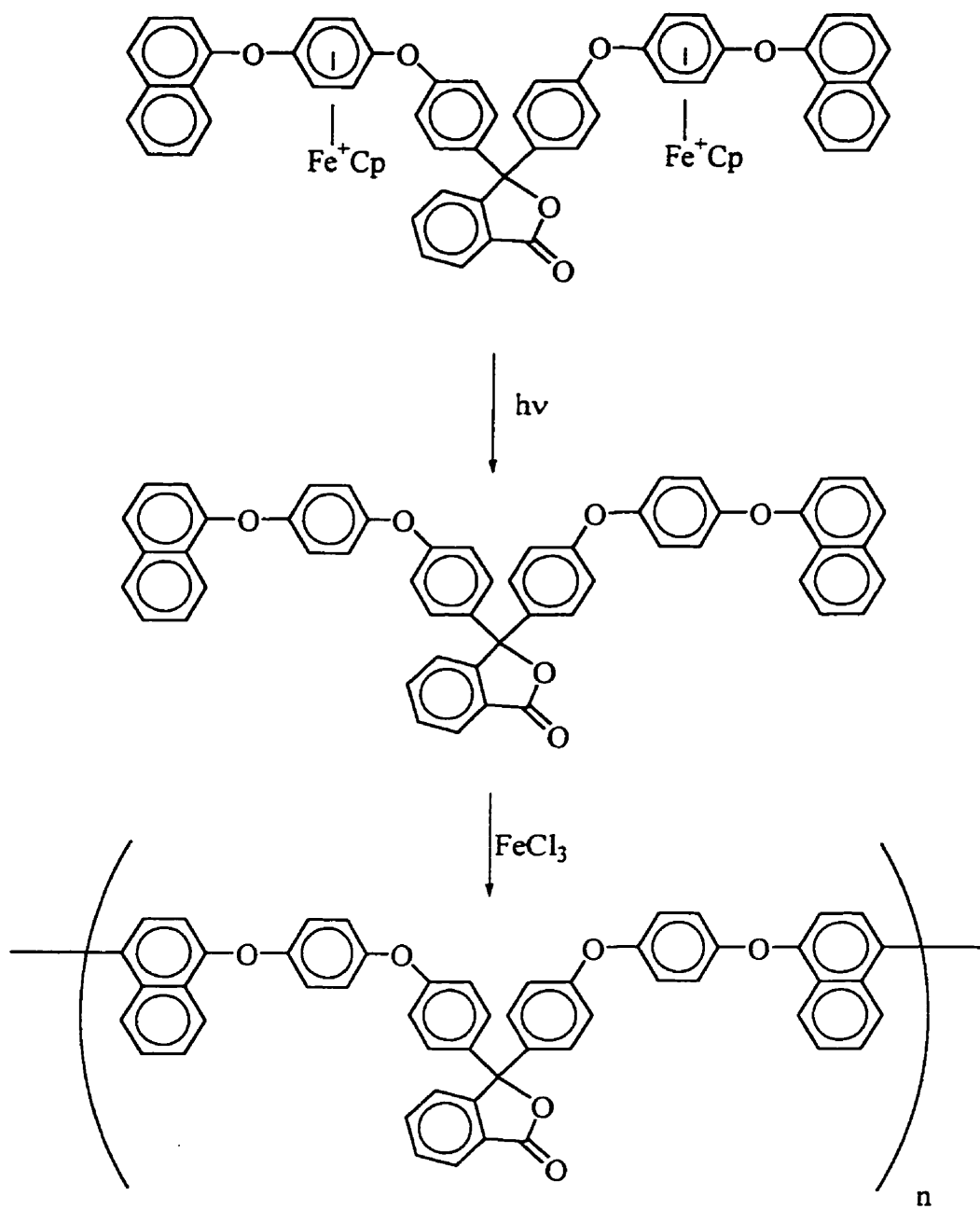
Scheme 2.2

2.1.2 Lactone Ring Opening

Lactones are cyclic esters, and thus exhibit a reactivity quite similar to their acyclic analogues. This is illustrated in **Figure 2.2**. Nucleophiles such as amines or halide ions may attack the electropositive carbon atom bound to the oxygen atom of the backbone, resulting in the cleavage of the cycle. This causes the formation of an acyclic carboxylate.[68]
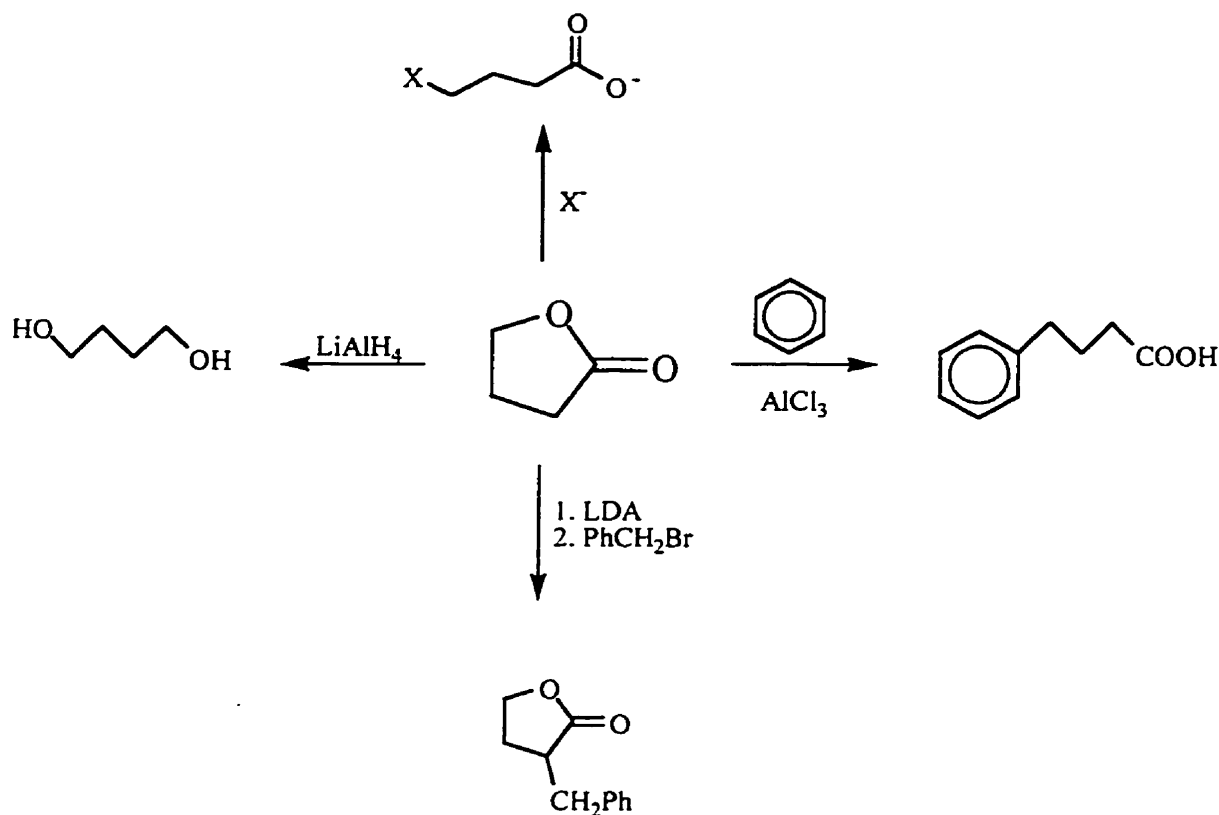
Figure 2.2: A summary of the reactivity of lactones

In devising an attempt to cleave the lactone ring of the phenolphthalein moiety in the bimetallic species, it was decided that the preliminary focus would be on nucleophilic attack by an amine. This methodology offered several advantages. Amines are excellent

nucleophiles, and do not require strongly basic conditions in order to increase their nucleophilicity. As well, there are a wide variety of commercially available amines and diamines. In this way, it was hoped that an efficient method for crosslinking phenolphthalein-containing polyethers could be developed.

2.2 Results and Discussion

2.2.1 Preparation of Starting Materials

In order to determine whether the lactone ring of the phenolphthalein moiety could be successfully opened, a number of bimetallic species containing the phenolphthalein moiety were prepared via nucleophilic aromatic substitution (**Scheme 2.3**). The reaction conditions for the preparation of all of the bimetallics are very similar, requiring the presence of potassium carbonate to deprotonate the nucleophile, and DMF as a solvent. The identity of the starting materials was confirmed by both ^{1}H and ^{13}C NMR, as illustrated in **Tables 2.1 and 2.2**.

The ^{1}H and ^{13}C NMR spectra for all of the bimetallic complexes are quite similar, and are thus easily interpreted. As a representative example, the NMR spectra of compound **2.1** will be discussed, as illustrated in **Figures 2.3** and **2.4**. Protons on the cyclopentadienyl ring resonate at 5.25 ppm, giving rise to a singlet. The complexed aromatic protons appear as a multiplet at 6.41 ppm, and integrate for 10 hydrogen atoms. A doublet of doublets may be observed further downfield. This corresponds to the protons on the two aromatic rings of the phenolphthalein moiety which are bound to the etheric linkages. Finally, two multiplets may be seen at 7.78 and 7.97 ppm. These correspond to the protons of the aromatic ring which is fused to the five-membered lactone.
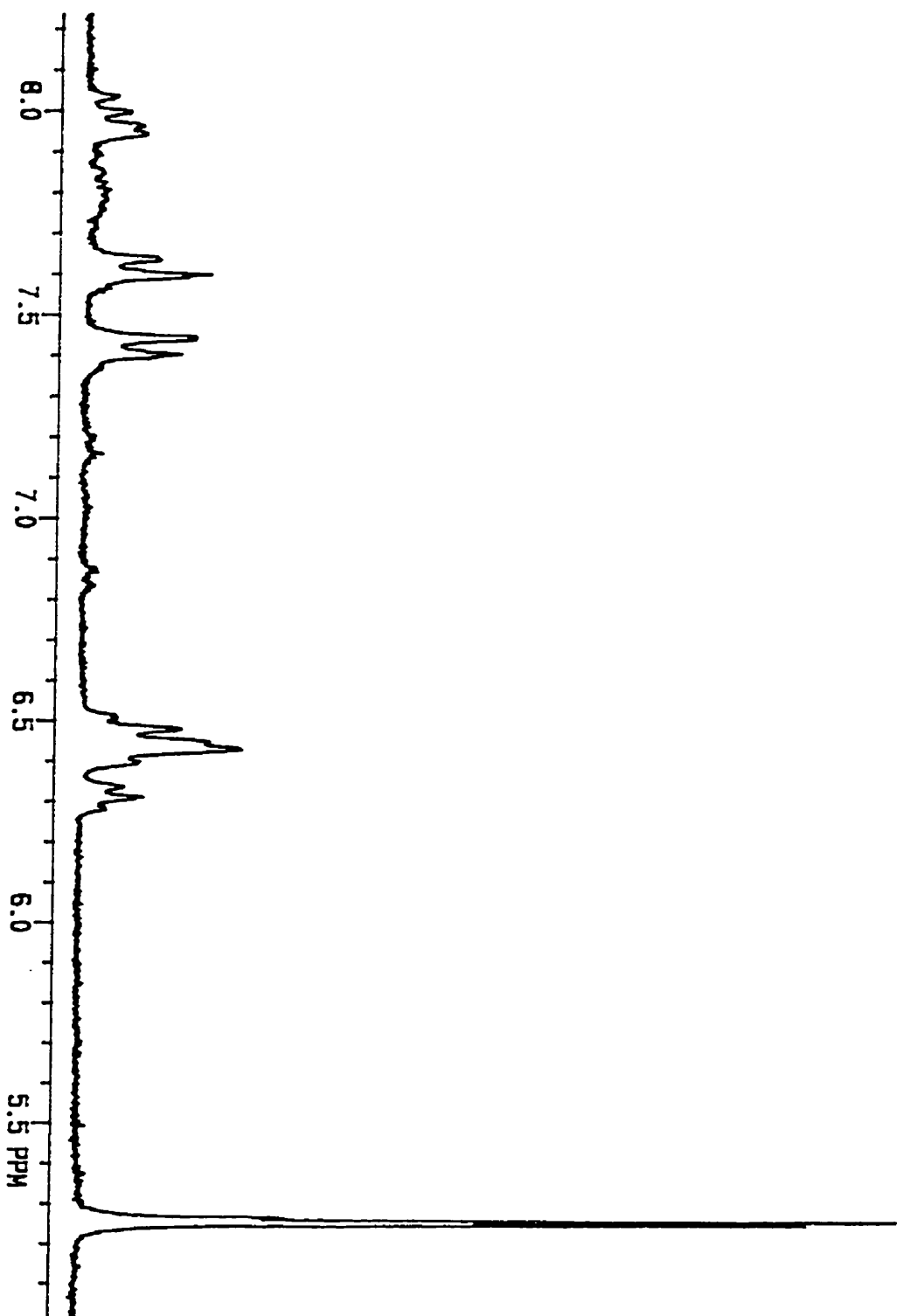
Figure 2.3: ^{1}H NMR spectrum of complex 2.1
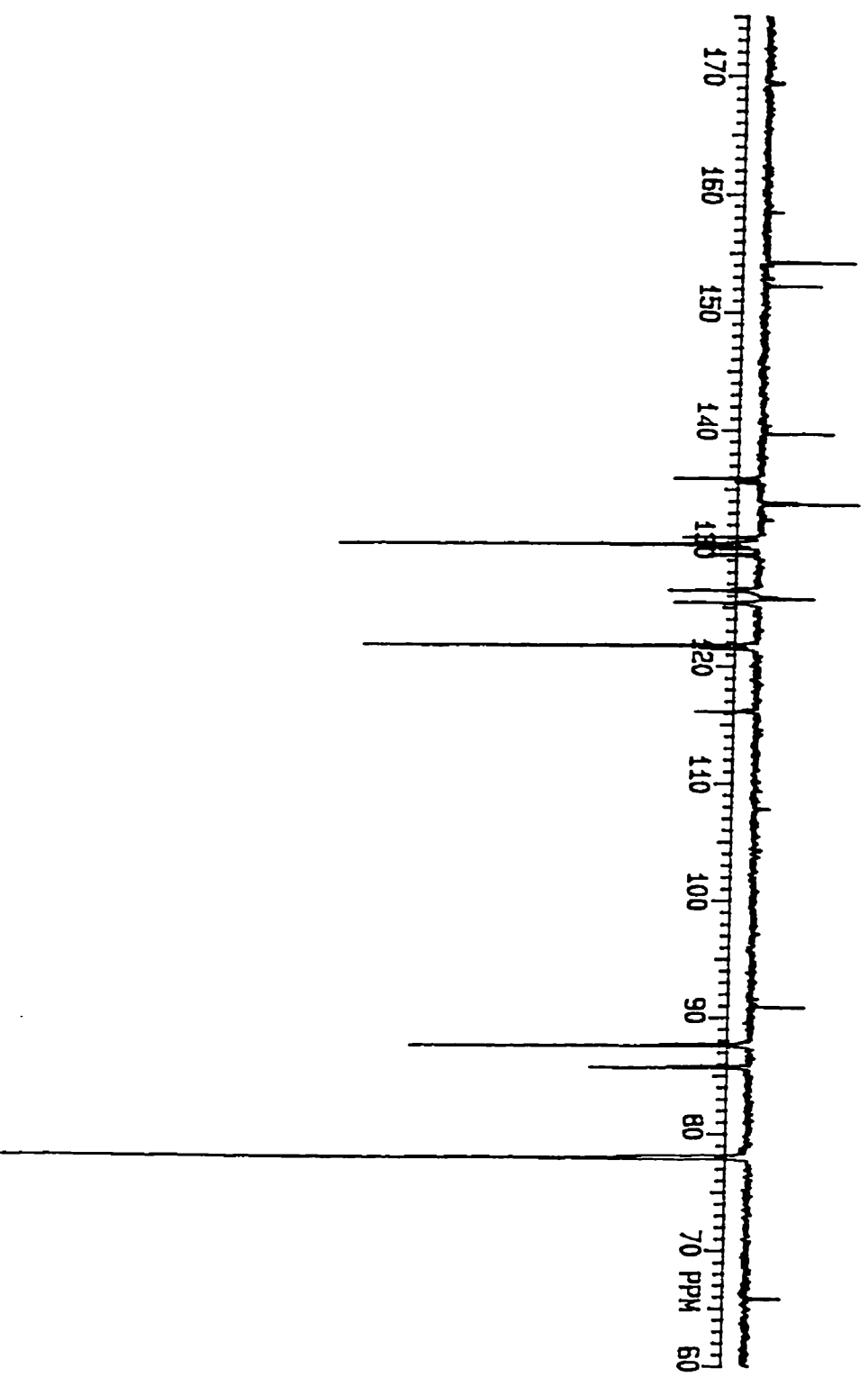
Figure 2.4: 13C NMR spectrum of complex **2.1**

The ^{13}C NMR spectrum is easily interpreted as well. The five equivalent carbons of the cyclopentadienyl ring resonate at 78.19 ppm. Complexed aromatic carbons resonate at 85.94 ppm (for the carbon atom para to the ether bridge) and 87.84 ppm (both meta and ortho). At 90.96 ppm, the aliphatic quaternary carbon of the phenolphthalein moiety gives rise to a single peak, which is followed by a peak appearing at 121.83 ppm, which may be attributed to the four uncomplexed carbon atoms meta to the phenoxy bridge. The corresponding four atoms which are ortho to the etheric bridge resonate at 130.44 ppm. Four other peaks are found at 125.55, 126.55, 131.01 and 131.98 ppm, and may be attributed to the resonance of carbon atoms of the uncomplexed aromatic ring which is fused to the lactone. Four quaternary carbons give rise to peaks at 133.86, 139.76, 152.25 and 154.27 ppm, where the two upfield peaks correspond to the carbon atoms bound to the aliphatic quaternary carbon, and the two downfield peaks may be attributed to the carbon atoms bound to the etheric bridge and the carbonyl group of the lactone. Finally, the peak appearing the furthest downfield, at 169.30 ppm, may be attributed to the carbonyl carbon.

R =	H	2.1
	2-CH$_3$	2.2
	4-CH$_3$	2.3
	4-Cl	2.4
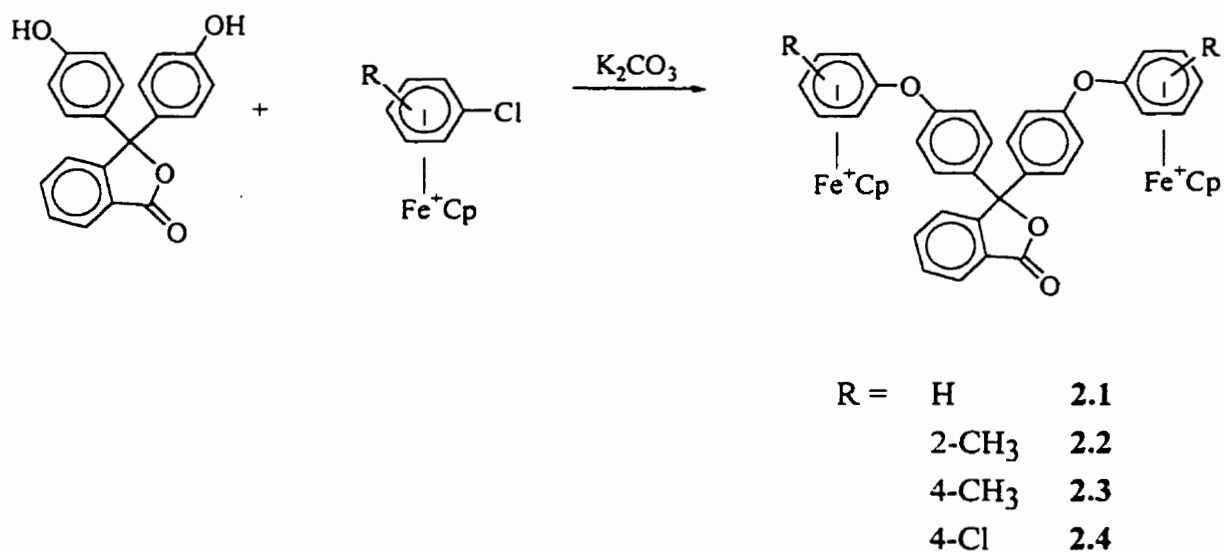
Scheme 2.3

Table 2.1: ^1H NMR data for complexes **2.1** to **2.4**.

δ (ppm), in acetone-d_6					
Complex	Yield (%)	Cp (10H)	Complexed ArH	Uncomplexed ArH	Other
2.1	94	5.25	6.41 (m, 10H)	7.52 (dd, J 8.7, 8H) 7.78 (m, 1H) 7.97 (m, 3H)	
2.2	97	5.19	6.23 (m, 6H) 6.55 (d, J 6.2, 2H)	7.49 (dd, J 8.9, 8H) 7.78 (m, 1H) 7.95 (m, 3H)	2.62 (s, 6H, CH_3)
2.3	93	5.21	6.36 (m, 8H)	7.50 (dd, J 8.0, 8H) 7.80 (m, 1H) 8.01 (m, 3H)	2.49 (s, 6H, CH_3)
2.4	93	5.37	6.52 (d, J 6.3, 4H) 6.80 (d, J 6.6, 4H)	7.51 (dd, J 8.5, 8H) 7.77 (m, 1H) 7.94 (m, 3H)	

Note: Coupling constants are reported in hertz.

Table 2.2: ^{13}C NMR data for complexes 2.1 to 2.4

δ (ppm), in acetone-d_6					
Complex	Cp	Complexed ArC	Uncomplexed ArC	Aliphatic Quaternary	Other
2.1	78.19	85.94, 87.84, 125.77*	121.83, 125.55, 126.55, 130.44, 131.01, 133.86*, 135.98, 139.76*, 152.25*, 154.27*	90.96*	169.30 (CO)
2.2	78.32	77.54, 85.31, 86.04, 89.62, 94.31*, 125.73*	121.20, 125.44, 126.48, 130.29, 130.92, 135.89*, 135.89, 139.34*, 152.27*, 154.88*	91.00*	16.18 (CH$_3$) 169.33 (CO)
2.3	78.65	77.50, 87.94, 101.60*, 125.78*	121.68, 125.58, 126.52, 130.40, 130.98, 132.73*, 135.96, 139.60*, 152.25*, 154.49*	90.93*	20.00 (CH$_3$) 169.25 (CO)
2.4	80.60	77.56, 87.91, 105.07*, 125.91*	121.82, 125.57, 126.62, 130.57, 131.07, 133.43*, 136.00, 140.13*, 152.28*, 154.28*	90.95*	169.28 (CO)

Note: * denotes a quaternary carbon.

2.2.2. Reaction of Phenolphthalein-Containing Bis(cyclopentadienyliron) Ethers with Primary Amines

Once the preparation of the starting materials was successfully completed, complex **2.1** was selected to be reacted with n-butylamine in an attempt to open the lactone ring, as is shown in **Scheme 2.4**. However, upon analysis of the reaction product, it became clear that the desired carboxylic acid was not obtained. The product was a red/orange oil which was characteristic of complexed anilines previously prepared via nucleophilic aromatic substitution.[42] Additionally, the ^{1}H NMR spectrum showed the disappearance of all uncomplexed aromatic resonances, as well as an upfield shift of the peaks corresponding to the remaining protons, consistent with the incorporation of an electron-donating functionality onto the complexed ring. This is illustrated in **Figure 2.5**.
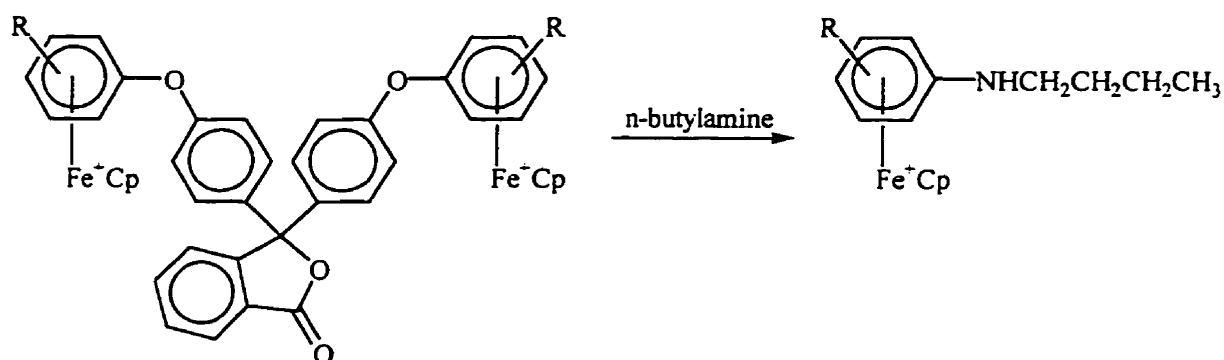
R =	H	2.1	2.5
	2-CH$_3$	2.2	2.6
	4-CH$_3$	2.3	2.7
	4-Cl	2.4	2.8

Scheme 2.4
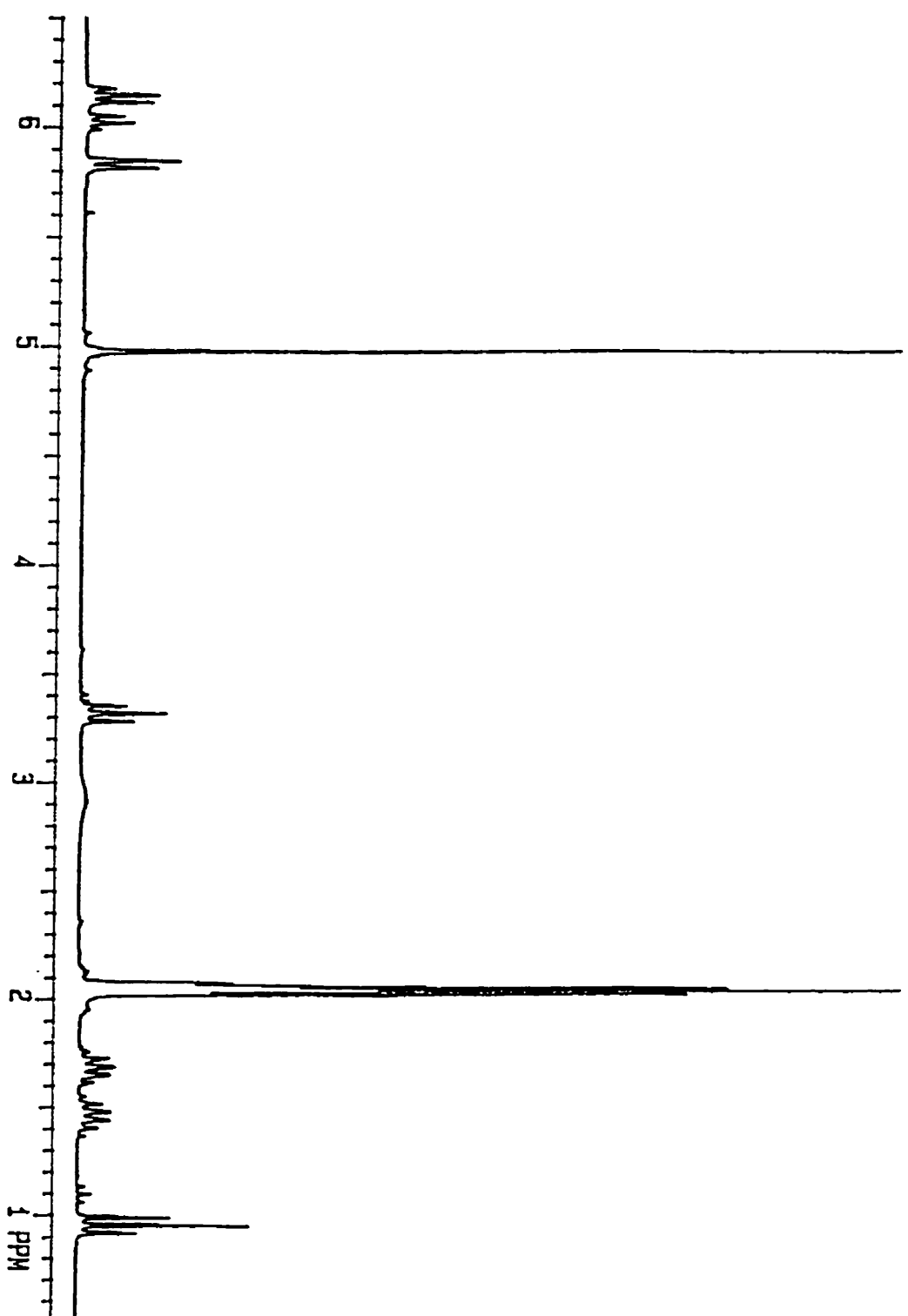
Figure 2.5: ^{1}H NMR spectrum of complex **2.5**
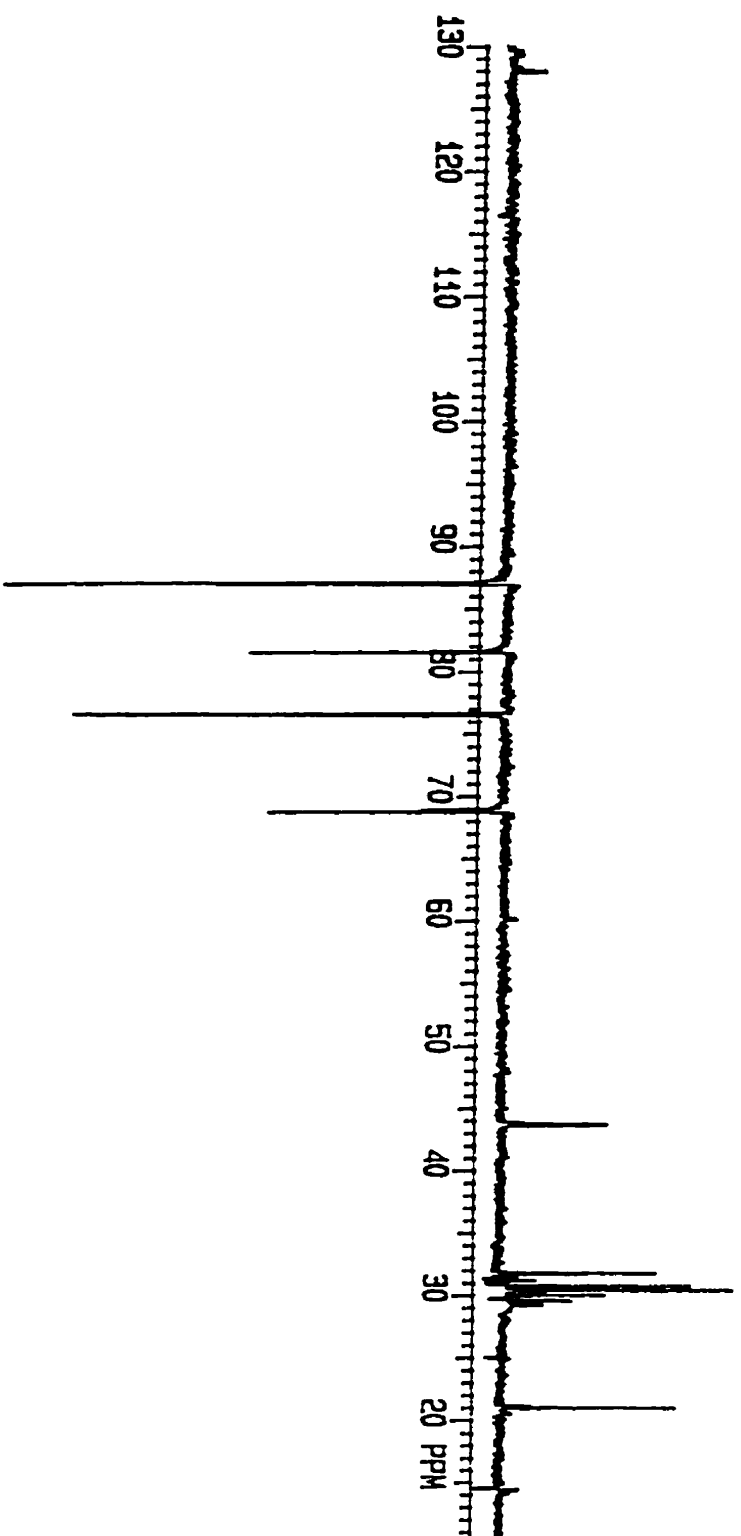
Figure 2.6: ^{13}C NMR spectrum of complex 2.5

^{13}C NMR spectroscopy, as shown in **Figure 2.6** also indicates that the product obtained is not an amide, but is in fact, a complexed aniline. Again, the characteristic upfield shifts of both the cyclopentadienyl resonances and the complexed aromatic carbons may be observed.

In order to understand this unexpected result, phenolphthalein-containing bimetallics **2.2** to **2.4** were also reacted with n-butylamine. This is shown in **Scheme 2.4**. Both ^1H and ^{13}C NMR spectra were obtained for the reaction products, and this data is summarized in **Tables 2.3** and **2.4**. It may be seen that these compounds have very similar spectra. As an example, complex **2.5** will be discussed in more detail. The complexed aromatic protons give rise to peaks at 6.04 (for the proton para to the amine group), 6.16 (for the two protons meta to the substituent), and 5.84 ppm (for the two protons ortho). These peaks also exhibit the expected splitting patterns. As well, the peaks in the aliphatic region of the spectrum at 3.34, 1.70, 1.48 and 0.97 ppm indicate that the amine has in fact been incorporated into the complex. The NH peak has not been identified, but is likely obscured by the complexed aromatic peaks which appear in the same region where the broad singlet would be expected.

The ^{13}C NMR peaks may also be easily assigned to specific carbon atoms. The peak appearing at 68.81 ppm is due to the resonance of the carbon atom para to the substituent. Peaks at 81.58 and 87.04 ppm may be assigned to the two carbon atoms ortho and meta to the substituent, respectively. The quaternary carbon gives rise to a peak at 128.00 ppm. As well, the peaks in the aliphatic region, at 43.78, 31.80, 21.08 and 14.01 are due to the three CH_2 groups and one CH_3 group of the N-butyl substituent, respectively.

Table 2.3: ^{1}H NMR data for complexes 2.5 to 2.7

δ (ppm), in acetone-d_6				
Complex	Yield (%)	Cp (5H)	Complexed ArH	Other
2.5	69	4.99	5.84 (d, J 6.7, 2H)	0.97 (t, J 7.2, 3H, CH$_3$)
			6.04 (t, J 5.8, 1H)	1.48 (sextet, J 7.4, 2H, CH$_2$)
			6.16 (t, J 6.2, 2H)	1.70 (quintet, J 7.0, 2H, CH$_2$)
				3.34 (quartet, J 6.4, 2H, CH$_2$)
2.6	63	4.89	5.88 (m, 2H)	0.96 (t, J 7.2, 3H, CH$_3$)
			6.13 (m, 2H)	1.49 (sextet, J 7.4, 2H, CH$_2$)
				1.73 (quintet, J 7.4, 2H, CH$_2$)
				2.41 (s, 3H, CH$_3$)
				3.40 (quartet, J 7.2, 2H, CH$_2$)
				5.58 (br.s, 1H, NH)
2.7	66	4.93	5.77 (d, J 7.0, 2H)	0.95 (t, J 7.1, 3H, CH$_3$)
			6.07 (d, J 7.0, 2H)	1.45 (sextet, J 7.6, 2H, CH$_2$)
				1.66 (quintet, J 7.8, 2H, CH$_2$)
				2.41 (s, 3H, CH$_3$)
				3.30 (m, 2H, CH$_2$)
				5.90 (br. s, NH)

Note: Coupling constants are given in hertz.

Table 2.4: ^{13}C NMR Data for Complexes **2.5** to **2.7**.

δ (ppm), in acetone-d₆			
Complex	Cp	Complexed ArC	Other
2.5	76.98	68.81, 81.58, 87.04, 128.00*	14.01 (CH_3), 21.08 (CH_2), 31.80 (CH_2), 43.78 (CH_2)
2.6	76.45	65.99, 80.22, 83.25*, 85.09, 88.75, 126.32*	17.72 (CH_3), 20.66 (CH_2), 31.35 (CH_2), 43.55 (CH_2)
2.7	76.62	67.68, 86.81, 96.36*, 126.35*	13.97 (CH_3), 19.64 (CH_3), 20.61 (CH_2), 31.38 (CH_2), 43.48 (CH_2)

Note: * denotes a quaternary carbon.

Interestingly, complex **2.2** has a methyl group in the position ortho to the etheric bridge. It was thought that the presence of this group might influence the reaction, due to steric effects. However, it may be seen from the NMR data and **Figures 2.7** and **2.8** that the aniline complex was obtained cleanly and in good yield upon reaction of **2.2** with n-butylamine. Thus, a methyl group in this position does not seem to affect the progress of the reaction.

Also of interest is the result obtained when n-butylamine is reacted with complex **2.4**, a phenolphthalein-containing bimetallic species with chlorine atoms in the positions para to the etheric bridge. In this complex, there are two possible sites of reaction. First, the amine may act as a nucleophile to displace the chlorine atom. As well, it is possible for
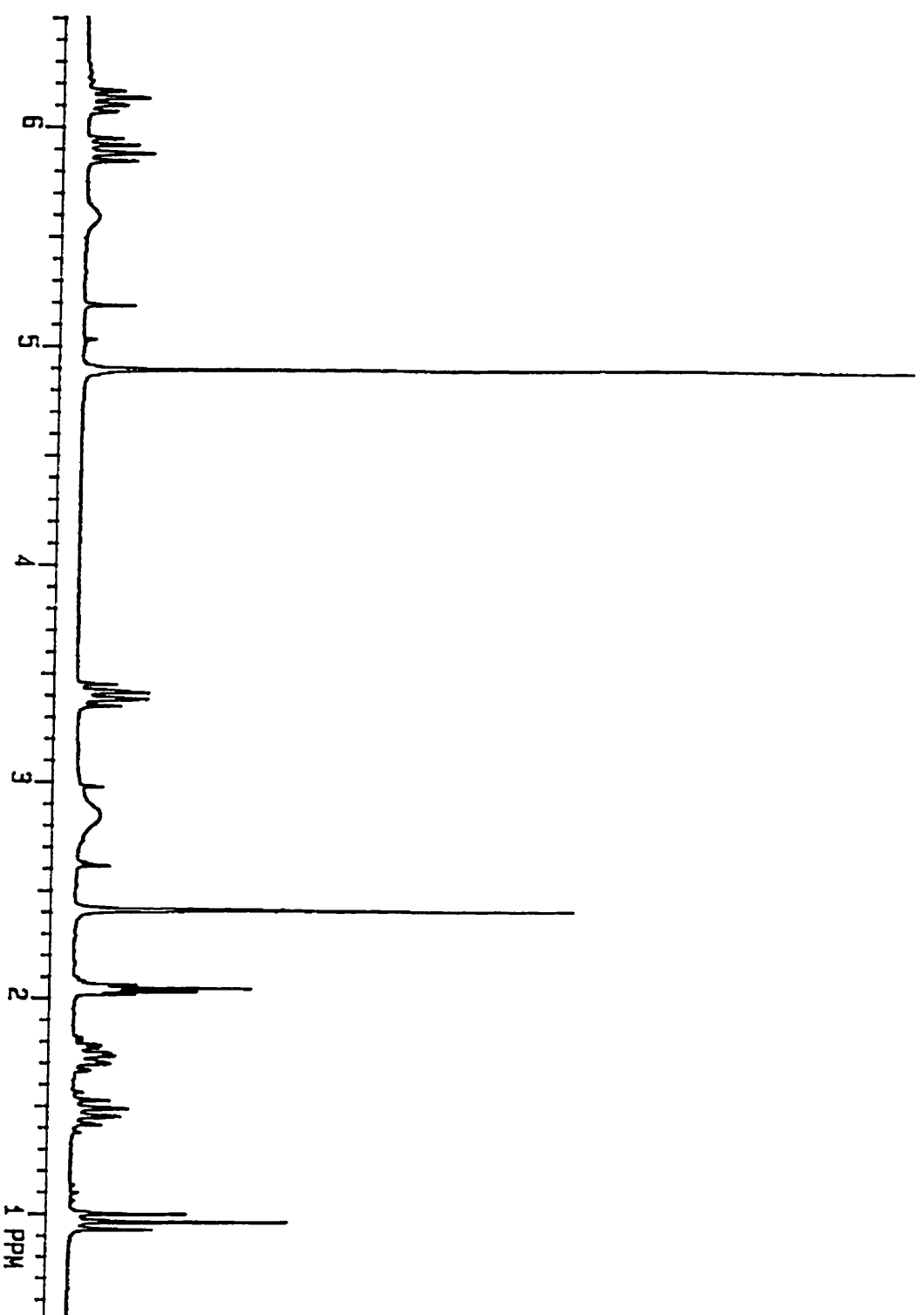
Figure 2.7: ^{1}H NMR spectrum of complex **2.6**, which contains a methyl group ortho to the N-n-butylamine functionality
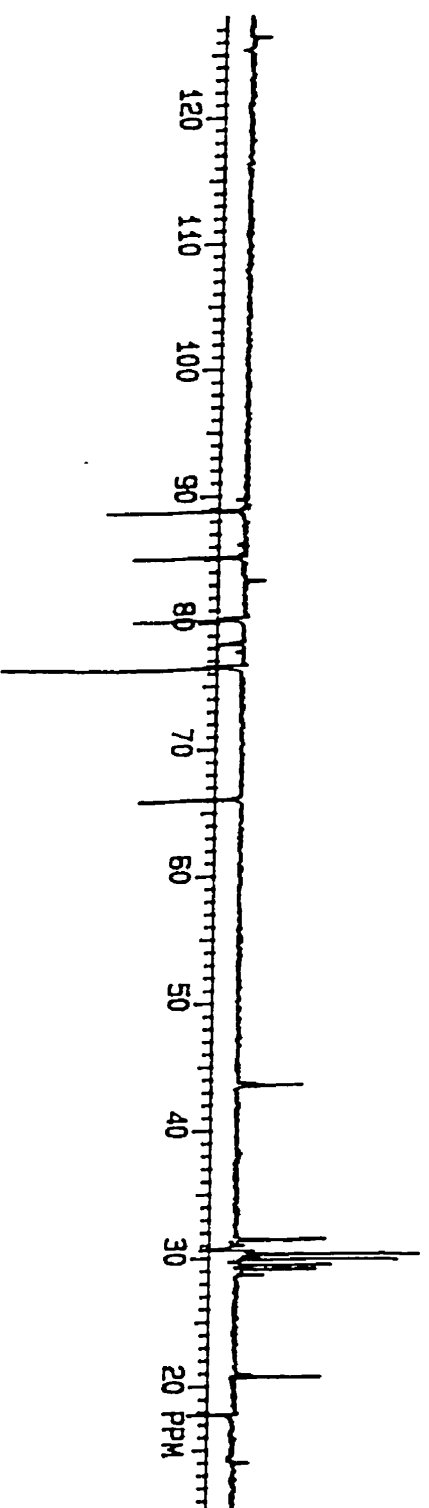
Figure 2.8: 13C NMR spectrum of complex **2.6**, which contains a methyl group ortho to the N-n-butylamine functionality.

the amine to substitute at the etheric bridge, resulting in cleavage. However, even in the presence of an excess of amine, it should not be possible to generate the phenylenediamine derivative, which would arise from reaction occurring at both sites. This result is predicted by the work of Abd-El-Aziz and co-workers, which involves the preparation of N-substituted phenylenediamines via nucleophilic aromatic substitution.[69,70] It was found that, regardless of the amount of amine present in the reaction mixture, it was impossible to synthesize phenylenediamine complexes via nucleophilic aromatic substitution unless the reaction was carried out in an acidic medium. This was explained as being due to the formation of a zwitterionic species,[71] as shown in **Figure 2.9**. In this species, a negative charge is carried on the aromatic ring, and this increase in electron density prevents any further reaction with the incoming nucleophile. The addition of a small amount of glacial acetic acid suppresses deprotonation, and thus allows disubstitution to occur.
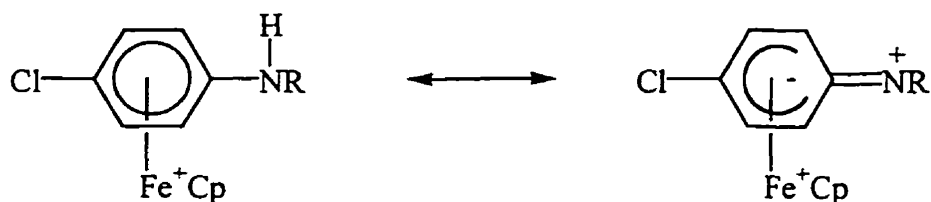
Figure 2.9: The formation of a zwitterion by deprotonation of the amine group.

When complex **2.4** is reacted with n-butylamine, it is evident that there are multiple products which result. The ^{1}H NMR spectrum obtained from the product mixture indicates the presence of at least two different complexed anilines, as evidenced both by the number and location of the cyclopentadienyl resonances (**Figure 2.10**). There is no unreacted starting material present, which may be confirmed by the absence of a cyclopentadienyl peak at 5.25 ppm. However, the absence of a singlet in the complexed
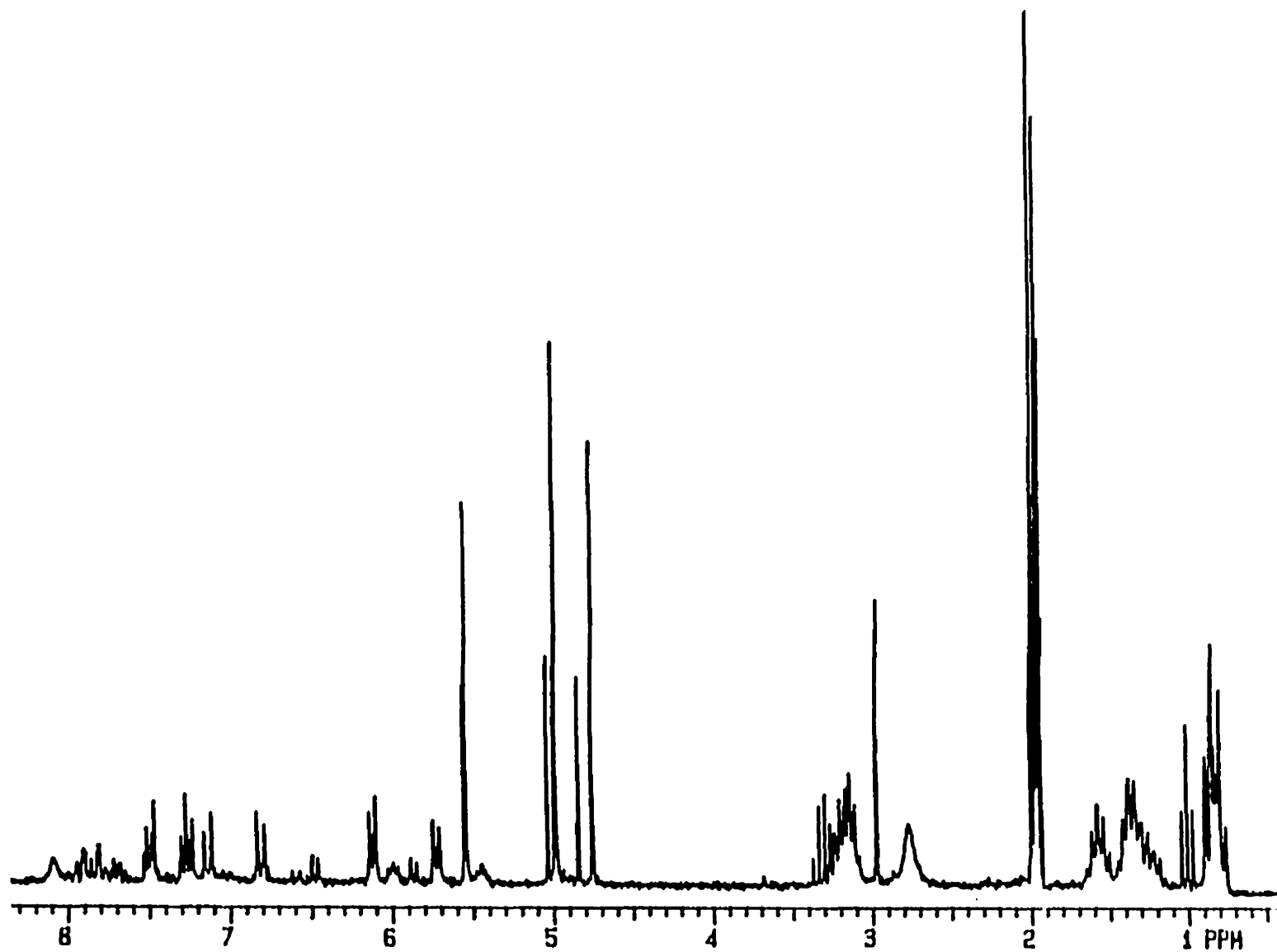
Figure 2.10: ^{1}H NMR spectrum of the product of the reaction of compound **2.4** and n-butylamine.

aromatic region of the spectrum (5.5 ppm to 6.2 ppm), which would correspond to the diamine species, adds further evidence for the formation of the zwitterionic species shown in **Figure 2.9**.

In addition, this study correlates well with the work reported by Abd-El-Aziz and his co-workers, in which n-butylamine was reacted with a cyclopentadienyliron-complexed arene containing both nitro and chlorine substituents as potential leaving groups.[69] These two groups differ quite substantially in their ability to act as leaving groups, just as the positively charged ether should differ from the chlorine group. Interestingly, Abd-El-Aziz found that sufficiently strong bases, such as primary amines, attack exclusively at the chlorine atom if it is ortho to the nitro group. This may be explained by the decrease in electron density at the carbon bearing the chlorine group, due both to the electron withdrawing effect of the chlorine group and by the inductive and resonance effects of the nitro group in the ortho position. However, when the nitro group is in the para position, a mixture of products result, indicating attack at both carbons bearing leaving groups. Thus this work, in which the chlorine atoms are para to etheric bridge and a mixture of products is obtained, is complementary to that reported by Abd-El-Aziz.

The next study focused on the characteristics of nucleophiles which would cause etheric bond cleavage. Phenol or thiol based nucleophiles did not cause any cleavage of the etheric bond at all; in fact, no observable reaction occurred. As well, when the reaction was attempted with a secondary amine, such as dipropylamine, again, no etheric cleavage reaction resulted. This could not be attributed to a difference in the strength of the nucleophile; both primary and secondary amines have very similar pK_a's.[1] In order to determine whether a steric factor involving the amine could be interfering with the cleavage reaction, a sterically hindered primary amine, t-butylamine, was utilized. Again, in this instance, the cleavage reaction did not occur. Thus, it seems quite likely that there is, in fact, a steric requirement for the nucleophile.

In order to fully understand the properties of nucleophiles capable of causing etheric bond cleavage, nitrogen-containing nucleophiles weaker than primary amines were reacted with complex **2.1**. Aniline, which has a pK_a known to be considerably lower than primary and secondary amines, did not give any cleavage product. In fact, no observable reaction occurred when complex **2.1** was reacted with aniline. Because the NH_2 group is quite unhindered in aniline, it may be suspected that this result is due directly to the decreased basicity of aniline as compared to primary amines. Thus pK_a, along with steric effects, play an important role in the determination of whether a nucleophile is able to cause etheric bond cleavage.

Interestingly, a variety of different primary amines in which the NH_2 group is not hindered caused the cleavage of etheric bonds when reacted with complex **2.1**. These are illustrated in **Scheme 2.5**, along with the ^1H and ^{13}C NMR spectral data of their resulting complexed anilines (**Tables 2.5** and **2.6**). Compound **2.9** may be considered a representative example of these compounds, and its ^1H and ^{13}C NMR spectra are shown in **Figures 2.11** and **2.12** respectively.

2.1	R' = $CH_2C_6H_5$	**2.9**
	$(CH_2)_2NH_2$	**2.10**
	$(CH_2)_4NH_2$	**2.11**
	$(CH_2)_6NH_2$	**2.12**
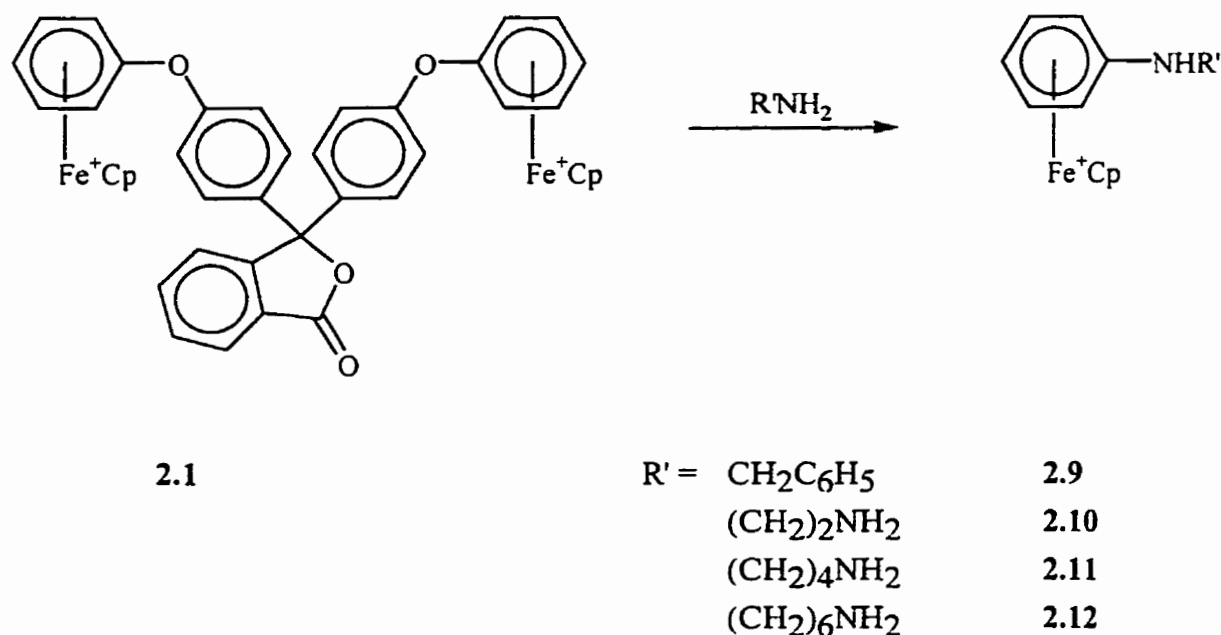
Scheme 2.5

45
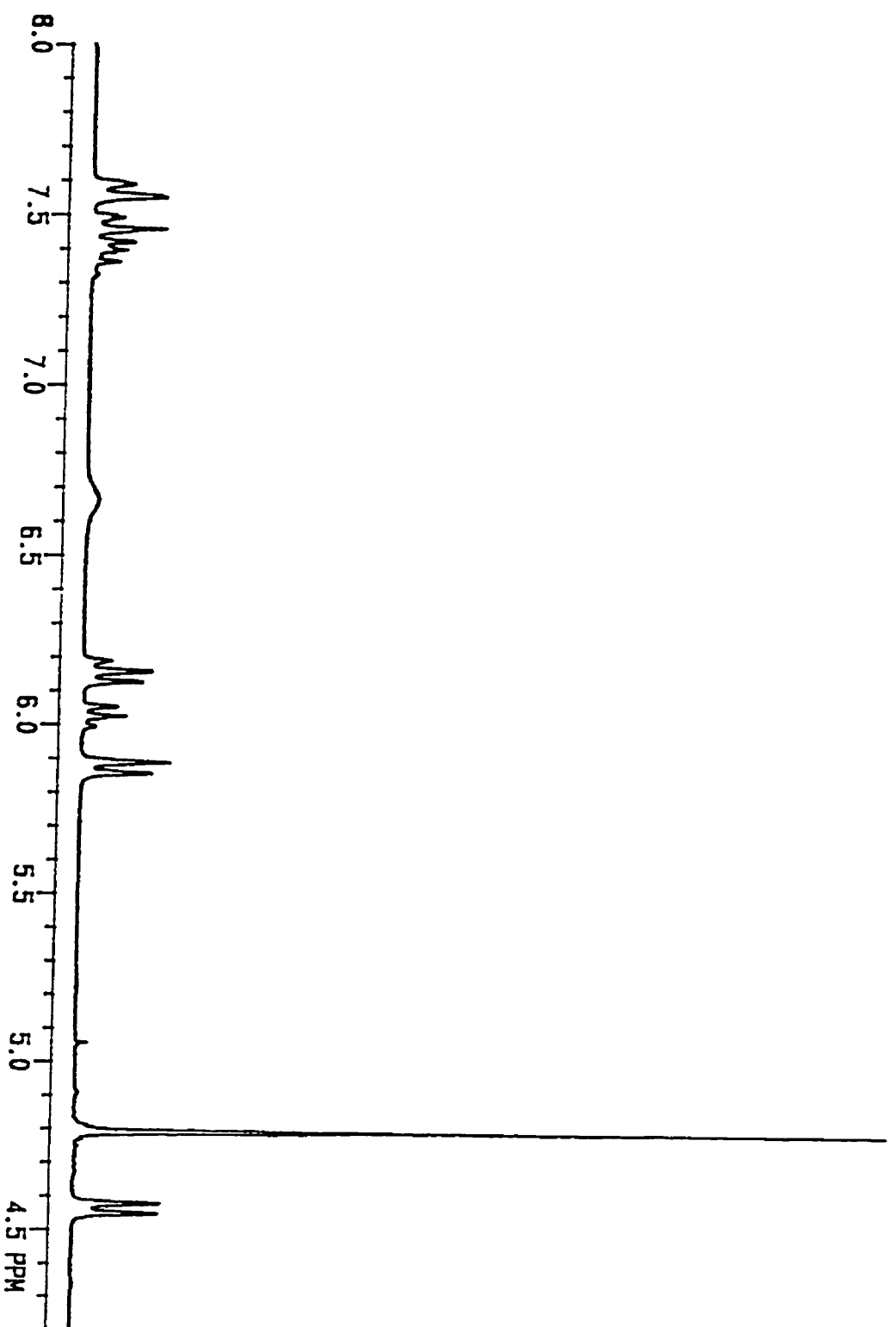
Figure 2.11: ^{1}H NMR spectrum of complex 2.9
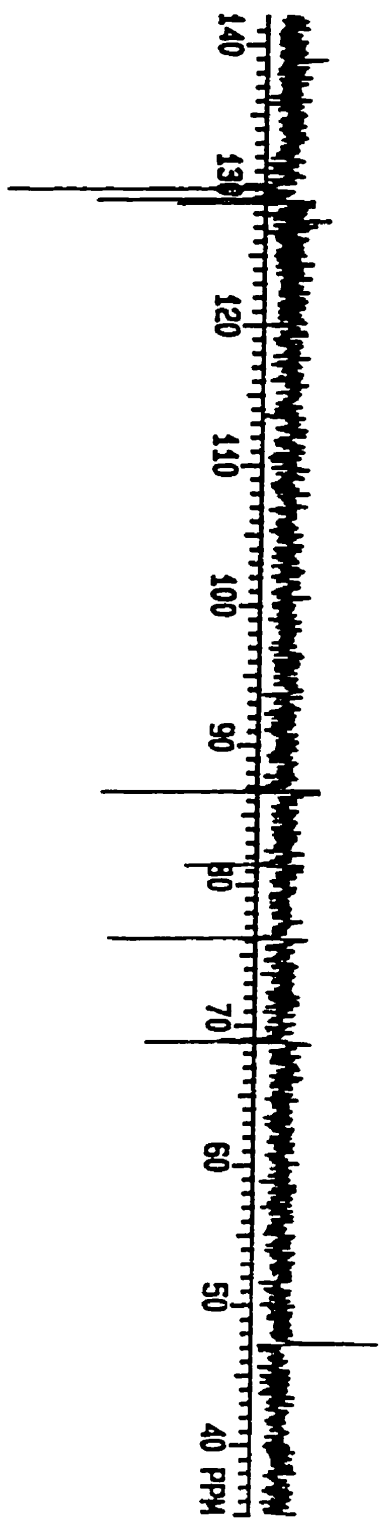
Figure 2.12: 13C NMR spectrum of complex 2.9.

The ^{1}H NMR spectrum of compound 2.9 may be easily analyzed. The doublet appearing at 4.56 ppm is representative of the benzylic CH_2 group, which is coupled with the NH group immediately adjacent to it. Further downfield, the cyclopentadienyl resonance is seen as a singlet at 4.80 ppm. A doublet appearing at 5.88 ppm may be attributed to the two protons ortho to the amino substituent, and the triplets at 6.03 ppm and 6.17 ppm may be attributed to the proton para and two protons meta, respectively. A broad singlet appears at 6.80 ppm, which is the result of the resonance of the NH proton. At 7.45 ppm, a multiplet integrating to 5 protons appears due to the uncomplexed aromatic protons present in the complex.

^{13}C NMR data may also be interpreted quite simply. The peak appearing at 47.21 ppm is attributable to the benzylic CH_2 group, while that appearing at 76.18 ppm is due to the five equivalent carbons of the cyclopentadienyl ring. Peaks appearing at 68.84, 81.39 and 86.66 ppm are due to the carbons ortho, para and meta to the substituent, respectively. A complexed quaternary carbon resonance appears at 127.41 ppm. Uncomplexed carbon atoms give rise to peaks at 128.70, 128.91 and 129.73 ppm, and may be assigned to the protons ortho, meta and para to the CH_2 group, respectively. Finally, an uncomplexed quaternary carbon gives rise to a peak at 138.86 ppm.

Table 2.5: ^{1}H NMR data for complexes **2.9** to **2.12**

			δ (ppm), in acetone-d_6	
Complex	Yield (%)	Cp (5H)	Complexed ArH	Other
2.9	68	4.80	5.88 (d, J 6.1, 2H)	4.56 (d, J 6.1, 2H, CH$_2$)
			6.03 (t, J 5.7, 1H)	6.80 (br.s, NH$_2$)
			6.17 (t, J 6.3, 2H)	7.45 (m, 5H, uncomplexed ArH)
2.10	32	4.97	5.87 (d, J 6.7, 2H)	3.48 (m, 6H, 2 CH$_2$, NH$_2$)
			5.99 (t, J 5.7, 1H)	
			6.12 (t, J 6.4, 2H)	
2.11	54	5.00	5.85 (d, J 6.6, 2H)	1.79 (m, 4H, 2CH$_2$)
			6.04 (t, J 5.6, 1H)	2.82 (m, 4H, CH$_2$, NH$_2$)
			6.17 (t, J 6.5, 2H)	3.37 (m, 2H, CH$_2$)
2.12	68	4.99	5.85 (d, J 6.2, 2H)	1.60 (m, 10H, 4CH$_2$, NH$_2$)
			6.03 (t, J 5.7, 1H)	3.19 (m, 2H, CH$_2$)
			6.16 (t, J 6.3, 2H)	3.34 (m, 2H, CH$_2$)

Note: Coupling constants are given in hertz.

Table 2.6: ^{13}C NMR data for complexes 2.9 to 2.12.

Complex	Cp	Complexed ArC	Other
2.9	76.18	68.84, 81.39, 86.66, 127.41*	47.21 (CH$_2$), 128.70, 128.91, 129.73, 138.86* (uncomplexed ArC)
2.10	76.14	68.64, 81.12, 86.54, 127.12*	44.15 (CH$_2$), 50.17 (CH$_2$)
2.11	76.14	68.17, 81.07, 86.60, 127.64*	27.19 (CH$_2$), 42.90 (CH$_2$), 43.45 (CH$_2$), 51.03 (CH$_2$)
2.12	75.71	67.93, 80.71, 86.18, 127.06*	26.76, 27.03, 31.08, 37.54, 43.04, 51.13 (CH$_2$)

Note: * denotes a quaternary carbon

The yields obtained for the etheric cleavage reaction are quite good, typically on the order of 65 to 70%. The calculated yield is based on obtaining two moles of the complexed aniline for every one mole of bimetallic reacted. This stoichiometry was immediately evident, as these numbers are in excess of 50%. For the preparation of compounds 2.10, 2.11 and 2.12, an obvious trend develops when examining the yield that is obtained. The N-ethylenediamineaniline complex has the lowest yield, and has the smallest aliphatic bridge between the two amino groups. It is also the most soluble in water, and thus more product was likely lost in the workup procedure, as detailed in the

experimental section. However, as the aliphatic bridge between the two amino groups increases, solubility of the complexed aniline product in water is decreased, and thus it was possible to isolate a greater percentage of the compound.

It is also interesting to note that of the series of diamines which were used as nucleophiles, only ethylenediamine has been successfully used in the preparation of complexed anilines via nucleophilic aromatic substitution. Compounds **2.11** and **2.12** have not been synthesized by this method, and thus this unique etheric cleavage reaction represents the only viable route thus far reported for their preparation.

Another interesting result was obtained upon the reaction of tyramine with complex **2.1**, as shown in **Scheme 2.6**. The product in this example clearly shows that only strong nucleophiles are capable of initiating the etheric cleavage reaction, as reaction in the presence of potassium carbonate caused the formation of only one product. This single product was formed by the nucleophilic attack of the amine group, and not the phenoxide. The most likely explanation for this result involves the pKa's of each of the nucleophilic groups. A phenol has a lower pK_a than a primary amine, and thus is not as strong a nucleophile.[1] Unfortunately, due to the extreme solubility of the complex in water, any remaining DMF had to be removed via vacuum distillation, and this caused spontaneous demetallation due to the high temperatures that were required. Therefore the complexed aniline could not be isolated, although the ^{1}H and ^{13}C NMR spectra for the demetallated species were recorded, and are illustrated in **Figures 2.13** and **2.14** as well as **Tables 2.7** and **2.8**.
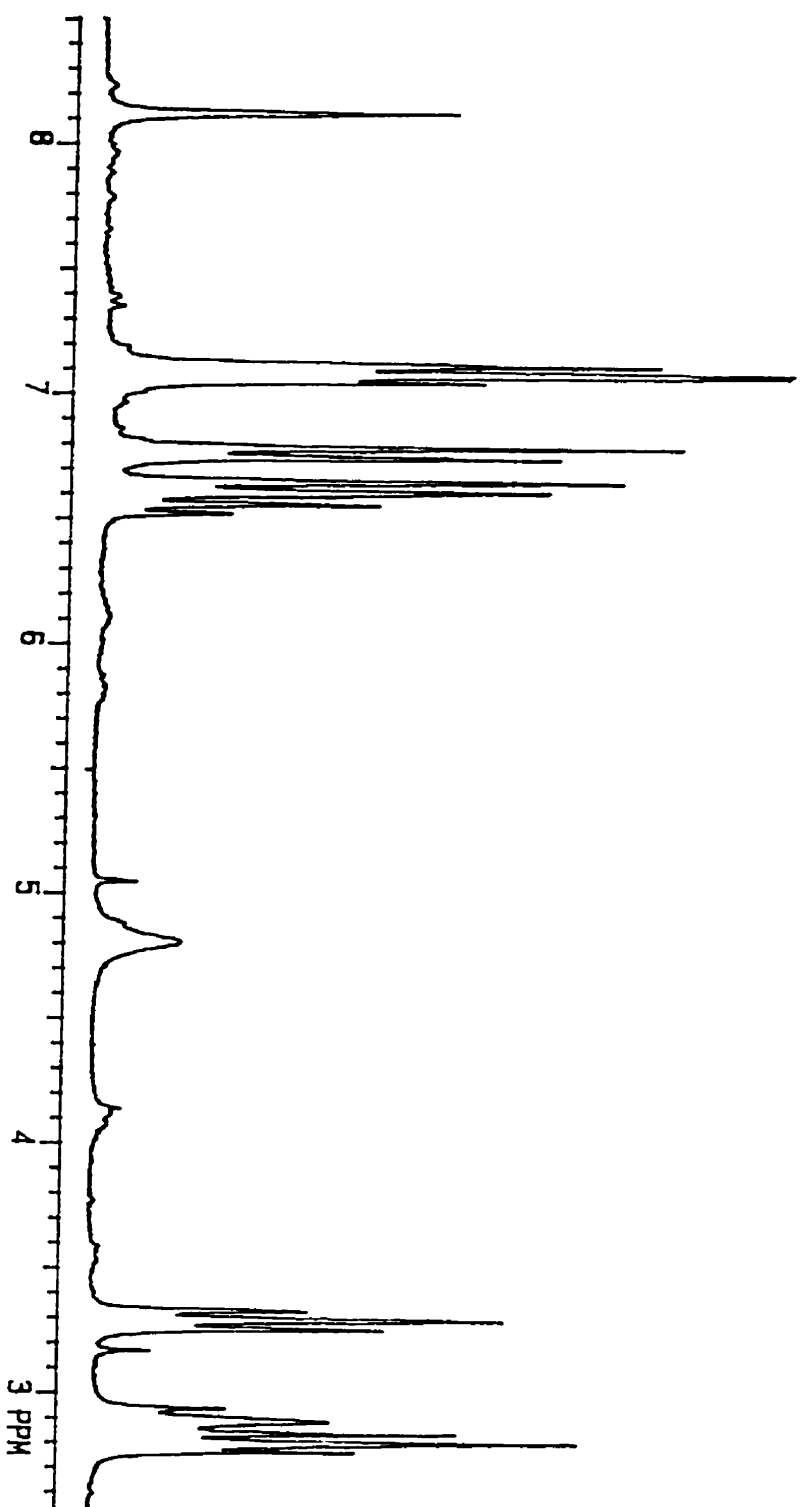
Figure 2.13: ^1H NMR Spectrum of the demetallated compound **2.13**
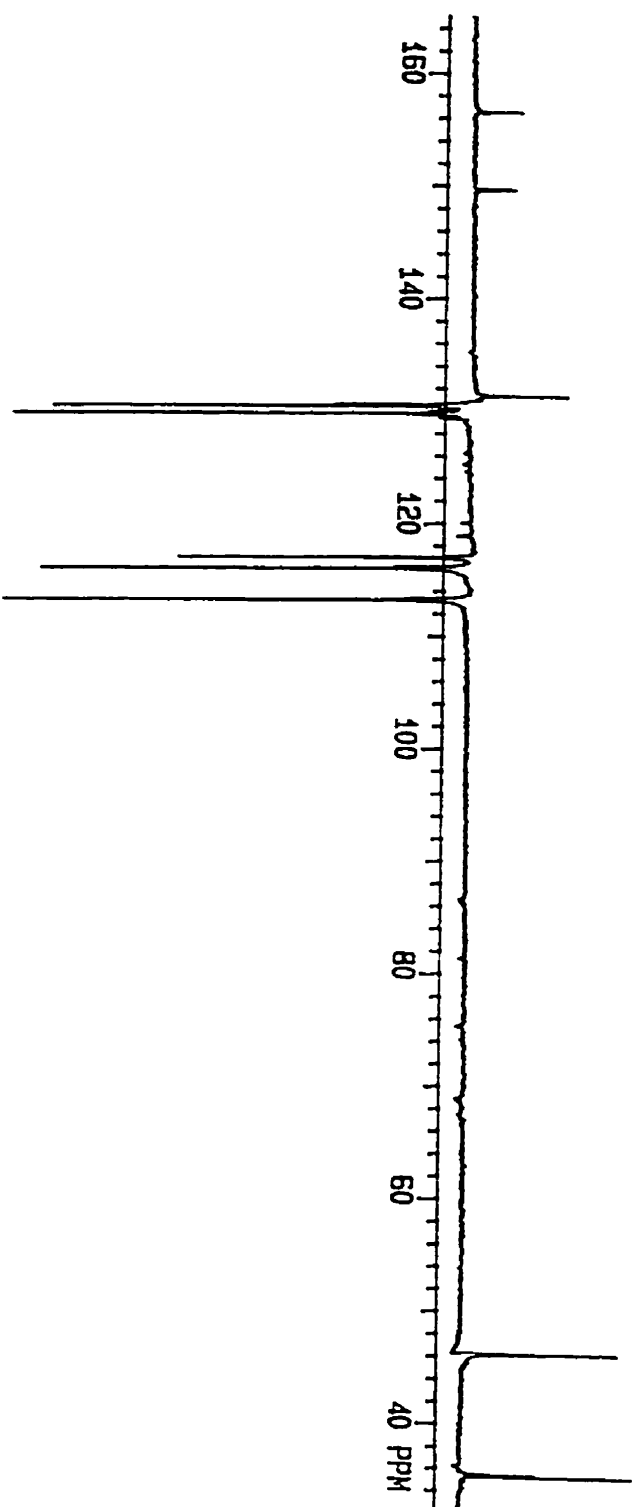
Figure 2.14: ^{13}C NMR Spectrum of the demetallated compound **2.13**
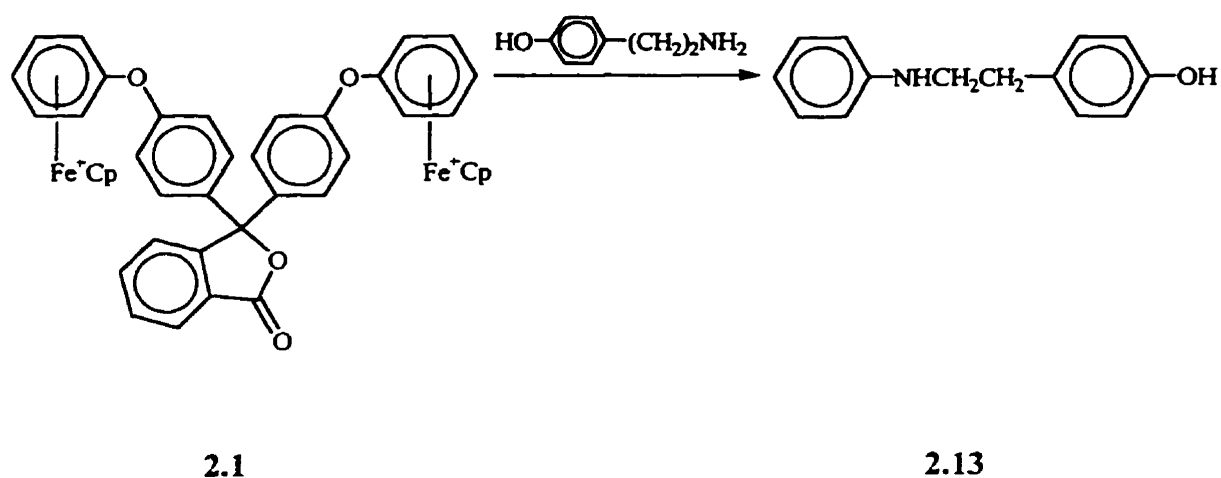
Scheme 2.6

Table 2.7: The ^{1}H NMR spectral data for compound **2.13**.

		δ (ppm), in acetone-d_6	
Complex	Yield (%)	Aromatic Protons	Other
2.13	45	6.64 (m, 3H)	3.29 (t, J 7.4, 2H, CH$_2$)
		6.76 (d, J 8.4, 2H)	2.79 (m, 2H, CH$_2$)
		7.08 (m, 4H)	4.80 (br.s, 1H, NH)
			8.12 (s, 1H, ArOH)

Note: Coupling constants are given in hertz.

Table 2.8: The ^{13}C NMR data for complex **2.13**.

δ (ppm), in acetone-d$_6$		
Complex	Aromatic Carbons	Other
2.13	113.22, 116.00, 116.99, 129.75, 130.45, 131.35*, 149.69*, 156.59*	35.31 (CH$_2$), 46.15 (CH$_2$)

Note: * denotes a quaternary carbon.

From the information obtained from the previously discussed study of the various factors which influence the reaction, a possible mechanism may be proposed. This is illustrated in **Scheme 2.7**. In this mechanism, the initial step is the opening of the lactone ring, which occurs quite readily due to the basic reaction environment. The tertiary carbocation which is formed in this step is extensively resonance stabilized, and is further stabilized by solvation in a polar solvent, such as DMF. The various resonance structures which are possible leave a positive charge on the oxygen atom of the etheric bridge, making the ether moiety an excellent leaving group in the presence of a nucleophile, such as n-butylamine. The presence of the cyclopentadienyliron moiety on the complexed ring helps to facilitate nucleophilic aromatic substitution to take place, and thus is necessary for the etheric reaction to occur. Attack may occur at either complexed ring, and thus the products are the two moles of complexed aniline and one mole of phenolphthalein.
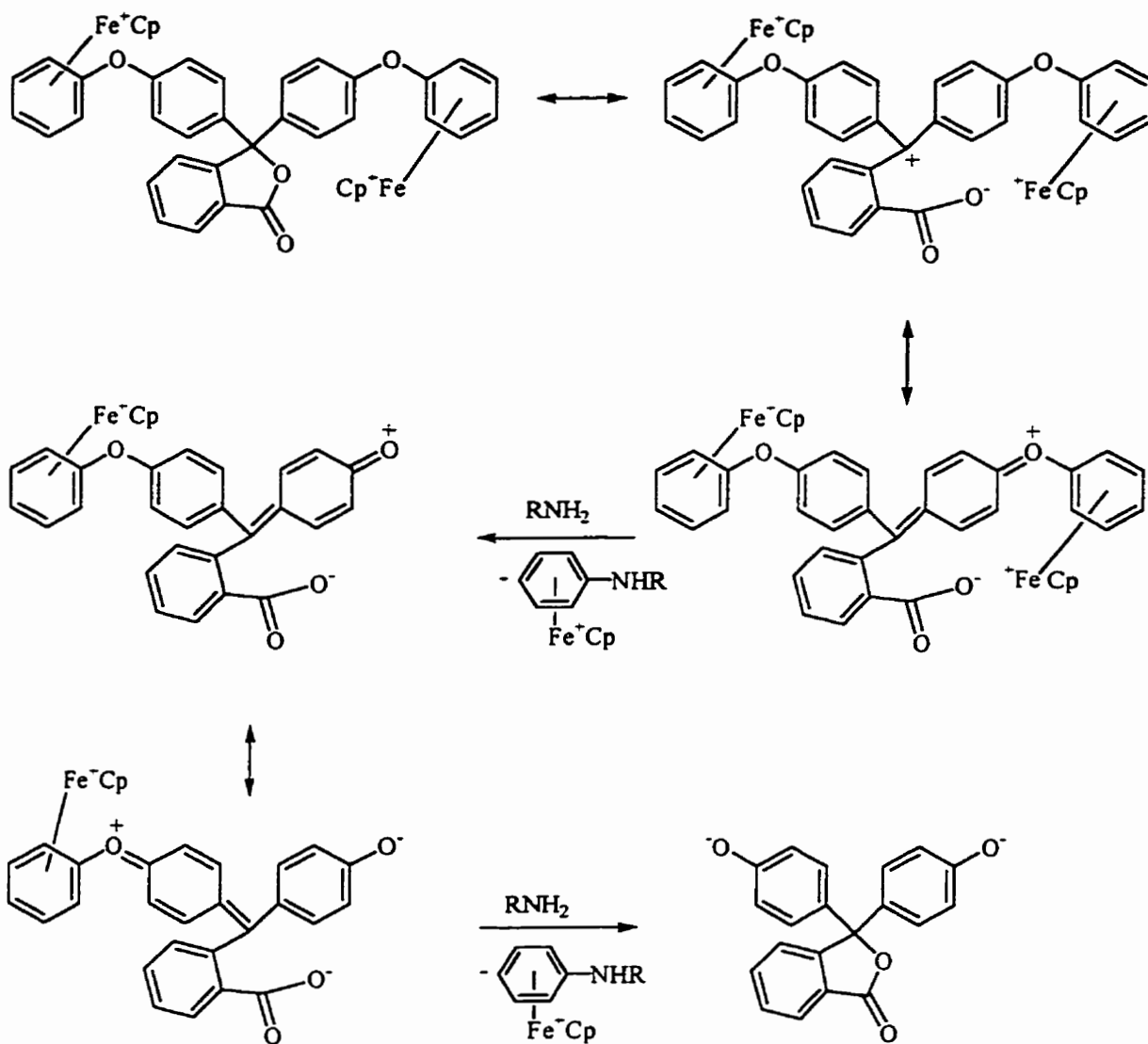
Scheme 2.7

The presence of phenolphthalein as a by-product of the reaction is immediately evident upon the addition of a slight amount of base to the reaction mixture. The resulting bright red colour is characteristic of phenolphthalein's ability to change colour in the presence of a basic solution.

This etheric cleavage reaction is quite unique. There are very few methods in traditional organic chemistry whereby an etheric bond may be broken. Most methods require harsh reaction conditions (such as heating in concentrated HI)[1], and even these are unable to cleave diaryl ethers. However, this cleavage reaction may occur only for phenolphthalein-containing cyclopentadienyliron complexes. The extensive delocalization of the pi bonds in the phenolphthalein moiety stabilizes the positive charge created upon the opening of the lactone ring. Also, as described in the previous chapter, the cyclopentadienyliron moiety facilitates the nucleophilic aromatic substitution step when a primary amine is present.

It may already be seen that this methodology is useful synthetically. Complexes **2.11** and **2.12** have not yet been synthesized by any other method. As well, it is hoped that this technique may be useful for the synthesis of nonsymmetric complexes containing an amine functionality as well. This would be possible if the chloroarene bimetallic **2.4** is reacted with one desired nucleophile, and then subjected to the etheric cleavage reaction. Nonsymmetric complexes are quite difficult to synthesize, and thus this etheric cleavage reaction represents a novel route to the synthesis of these compounds.

2.2.3 Photolytic Demetallation of Cyclopentadienyliron-Complexed Anilines

As reported by Abd-El-Aziz and his co-workers, a complexed aniline may be liberated from the cyclopentadienyliron moiety through photolysis.[70] This was performed in an acetonitrile/dichloromethane mixture, in the presence of light emitted by a xenon lamp, as illustrated in **Scheme 2.8**.

2.5	R=	H	R'=	(CH$_2$)$_3$CH$_3$	2.14
2.6		2-CH$_3$		(CH$_2$)$_3$CH$_3$	2.15
2.7		4-CH$_3$		(CH$_2$)$_3$CH$_3$	2.16
2.9		H		CH$_2$C$_6$H$_5$	2.17
2.11		H		(CH$_2$)$_4$NH$_2$	2.18
2.12		H		(CH$_2$)$_6$NH$_2$	2.19
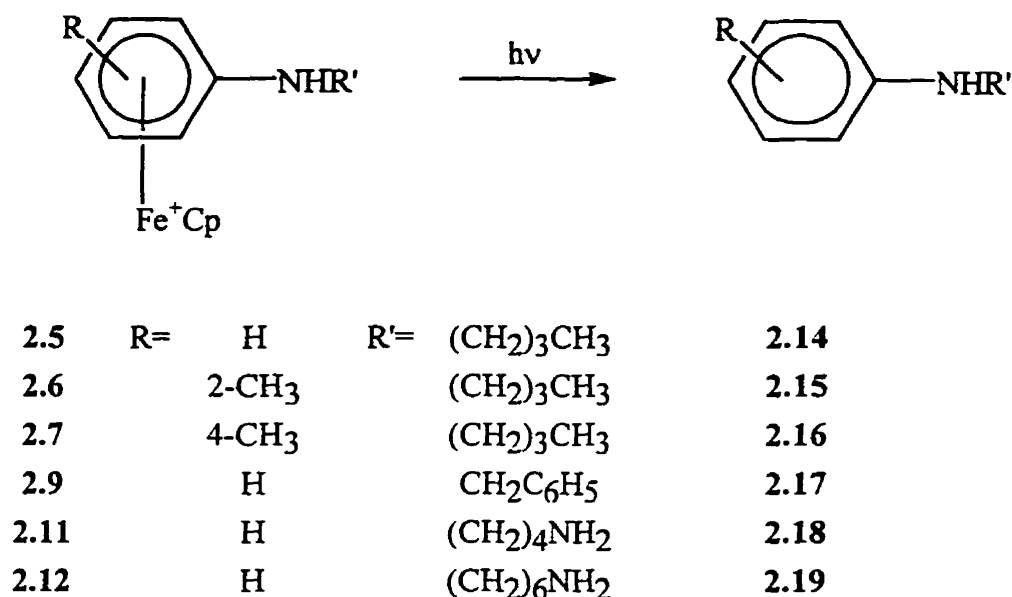
Scheme 2.8

As with the metallated species, both ^{1}H and ^{13}C NMR studies were performed in order to confirm the identities of the uncomplexed anilines. These are shown in **Tables 2.9** and **2.10**.

Demetallation afforded the uncomplexed anilines in good yield, with few impurities. This may be illustrated in **Figures 2.15** and **2.16**, which show the ^{1}H and ^{13}C NMR spectra for the demetallated compound **2.14**. In **Figure 2.15**, a triplet may be seen at 0.93 ppm, corresponding to the methyl group of the compound. Peaks at 1.46, 1.68 and 3.29 ppm are all due to CH$_2$ groups, and exhibit the expected splitting patterns. At 7.10 ppm, there is a multiplet, which corresponds to the aromatic protons. This integrates to five hydrogen atoms, which is consistent with the proposed structure.

Looking at the ^{13}C NMR spectrum, it may be seen that it is easily assigned as well. The carbon atom of the methyl group resonates at 13.69 ppm, and is followed by three CH$_2$ groups giving rise to peaks appearing at 19.95, 29.99 and 47.37 ppm, respectively. At 116.25 ppm, a peak exists which may be attributed to the carbon atoms
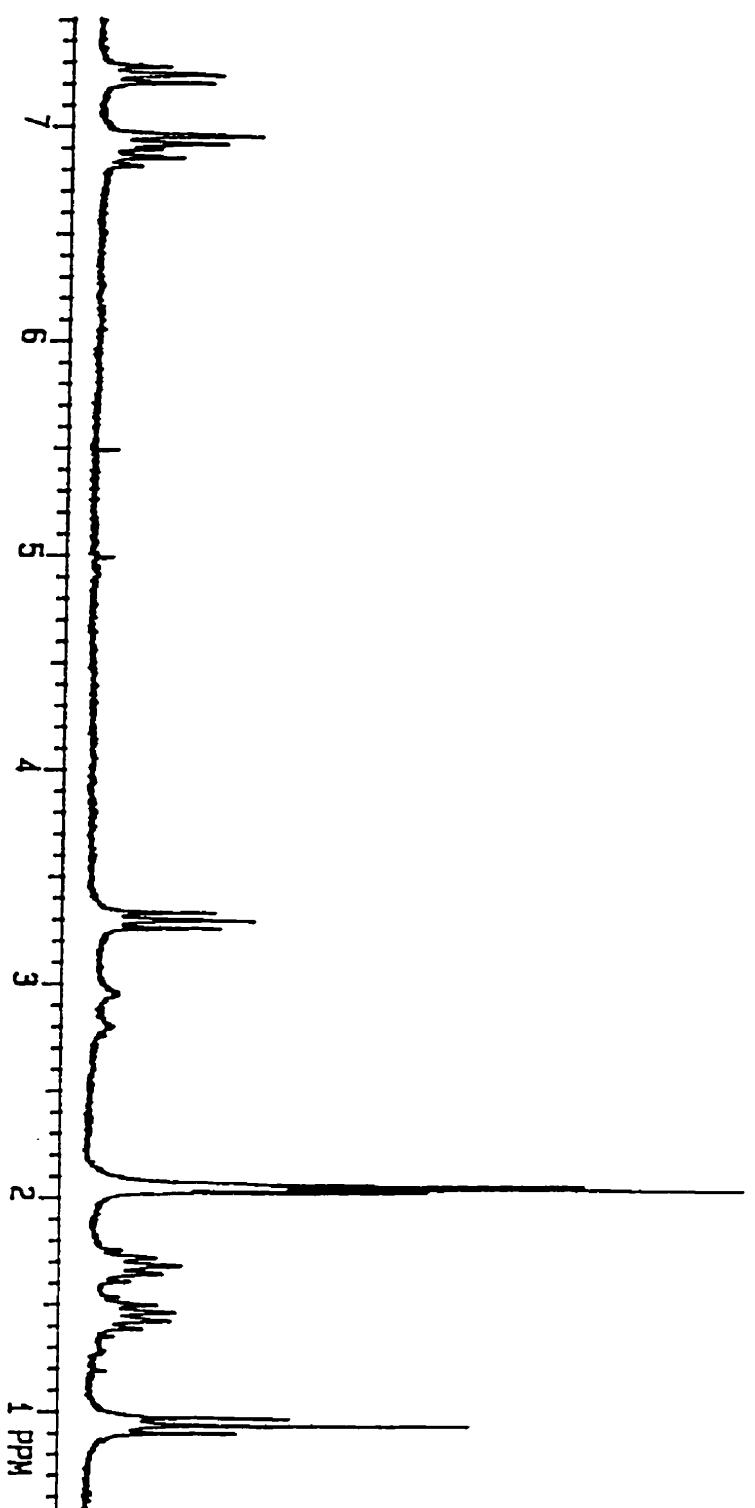
Figure 2.15: ¹H NMR spectrum of **2.14**, successfully demetallated via photolysis.
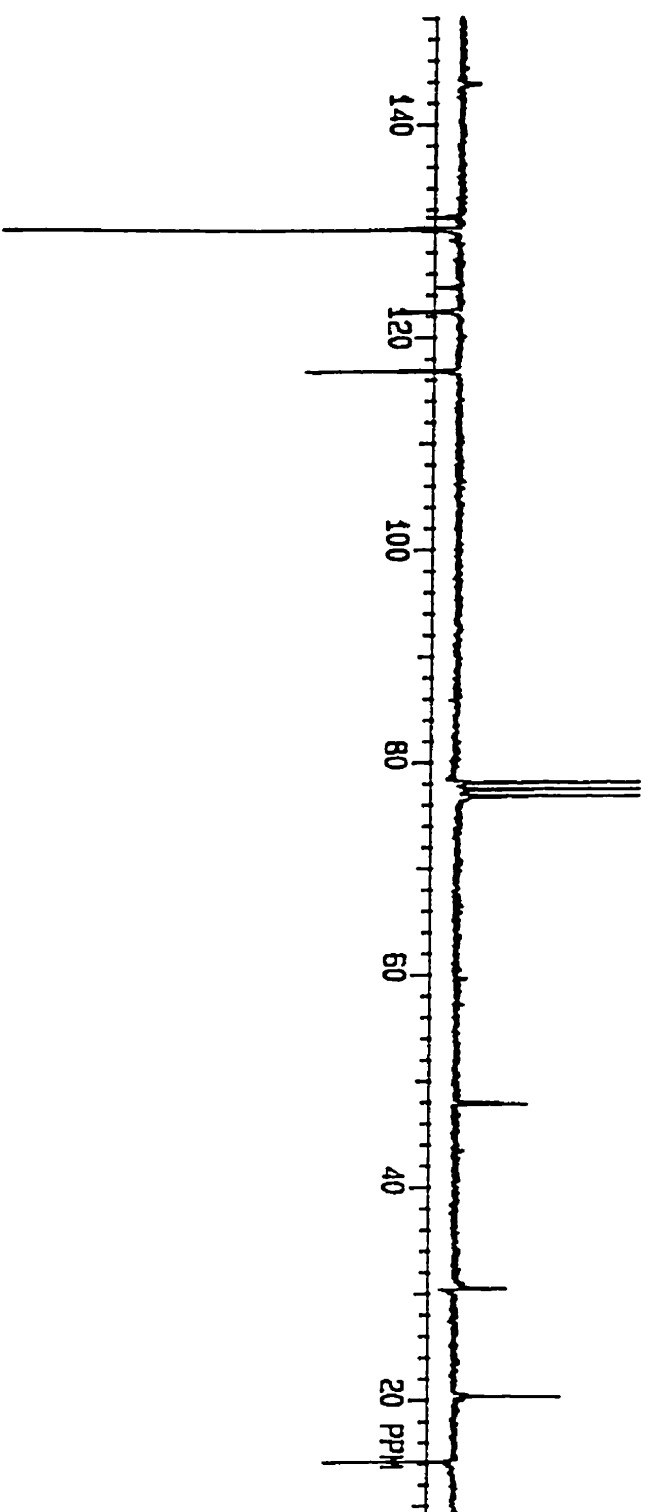
Figure 2.16: ^{1}H NMR spectrum of **2.14**, successfully demetallated via photolysis.

ortho to the amino substituent. Peaks at 121.89 and 129.67 ppm may be attributed to the para carbon atom and meta carbon atoms, respectively. Finally, the quaternary carbon gives rise to a peak at 143.39 ppm.

Demetallation via photolysis was successful for all of the complexed anilines which were prepared, with the exception of compound **2.10**. Unfortunately, due to the low yields which were consistently obtained for the synthesis of this compound, an amount sufficient for photolysis was not achieved. Although photolytic demetallation is successful on a microscale level or smaller, the method of recovery limits the amounts which may be used. Particularly for monometallic species, the metal moiety may represent more than half of the molecular weight of a complex. Therefore, such a small amount of organic material may prove difficult to extract from a chromatograhic column. Attempts to increase the scale of the reaction resulted instead in a decreased overall yield. However, this compound, unlike complexes **2.11** and **2.12**, may be synthesized by cyclopentadienyliron-promoted nucleophilic aromatic substitution, and thus the etheric cleavage reaction does not represent an efficient method for its preparation.

Table 2.9: ^{1}H NMR data for the demetallated compounds **2.14** to **2.19**.

Compound	Yield (%)	ArH	Other
		δ (ppm), in CDCl$_3$	
2.14	69	7.10 (m, 5H)	0.93 (t, J 7.1, 3H, CH$_3$)
			1.46 (sextet, J 7.4, 2H, CH$_2$)
			1.68 (quintet, J 7.5, 2H, CH$_2$)
			3.29 (t, J 7.3, 2H, CH$_2$)
2.15	74	7.13 (m, 4H)	0.94 (t, J 7.3, 3H, CH$_3$)
			1.45 (sextet, J 7.3, 2H, CH$_2$)
			1.71 (quintet, J 7.4, 2H, CH$_2$)
			2.32 (s, 3H, CH$_3$)
			3.32 (t, J 7.5, 2H, CH$_2$)
			4.32 (br.s, NH)
2.16	75	7.08 (d, J 8.3, 2H)	0.91 (t, J 7.3, 3H, CH$_3$)
		7.20 (d, J 7.9, 2H)	1.38 (sextet, J 7.4, 2H, CH$_2$)
			1.62 (m, 2H, CH$_2$)
			2.34 (s, 3H, CH$_3$)
			5.51 (br.s, 1H, NH)
2.17	52	6.67 (m, 3H)	4.39 (s, 2H, CH$_2$)
		7.23 (m, 7H)	
2.18	43	6.67 (m, 3H)	0.92 (m, 2H, CH$_2$)
		7.18 (m, 2H)	1.33 (m, 4H, CH$_2$ and NH$_2$)
			1.75 (m, 2H, CH$_2$)
			3.18 (br. s, 2H, CH$_2$)
			4.23 (br. s, 1H, NH)
2.19	45	6.57 (m, 3H)	1.51 (m, 6H, 3 CH$_2$)
		7.07 (t, J 7.3, 2H)	1.86 (m, 2H, CH$_2$)
			3.05 (m, 4H, CH$_2$ and NH$_2$)
			3.35 (m, 2H, CH$_2$)
			3.94 (t, J 7.1, NH)

Note: Coupling constants are in hertz.

Table 2.10: ^{13}C NMR spectral data for compounds **2.14** to **2.19**.

	δ (ppm), in CDCl₃	
Compound	ArC	Other
2.14≠	116.25, 121.89, 129.67, 143.39*	13.69 (CH₃), 19.95 (CH₂), 29.99 (CH₂), 47.37 (CH₂)
2.15	125.73, 127.65*, 127.86, 128.70, 131.68, 137.22	13.48 (CH₃), 16.73 (CH₃), 19.71 (CH₂), 28.61 (CH₂), 50.25 (CH₂)
2.16	120.37, 131.62, 136.55*, 136.60*	14.46 (CH₃), 20.58 (CH₂), 21.83 (CH₃), 29.37 (CH₂), 52.15 (CH₂)
2.17	113.17, 117.91, 127.29, 127.58, 128.62, 129.27, 139.08*, 147.66*	48.62 (CH₂Ar)
2.18	113.31, 117.88, 129.27, 132.92*	68.67 (CH₂), 44.26 (CH₂), 30.85 (CH₂), 24.23 (CH₂)
2.19	114.08, 118.55, 130.23, 148.88*	44.99 (CH₂), 39.06 (CH₂), 30.09 (CH₂), 27.39 (CH₂), 27.13 (CH₂), 26.55 (CH₂)

Note: * denotes a quaternary carbon.

≠ run in acetone-d₆

2.2.4 Etheric Cleavage in the Presence of Potassium Permanganate

Nesmeyanov and his co-workers have reported the oxidation of complexed tolyls to carboxylic acids in the presence of potassium permanganate.[53-55] The ability to effect this oxidation results in the potential to form bimetallic esters and amides, which should exhibit properties which are unique from those displayed by ethers, thioethers and amines. Although Nesmeyanov has been successful in the preparation of a monometallic amide and ester,[54,72] there has been no report of the formation of bimetallic species containing ester or amide linkages.

Attempts to synthesize the diacid chloride from the cyclopentadienyliron complex of terephthalic acid have thus far failed, due to the presence of such strong electron withdrawing groups on the ring. Therefore, the monometallic species shown in **Scheme 2.9** was prepared, which did not contain tolyl groups which were complexed to metal moieties. It was expected that this species would be easily oxidized; from the dicarboxylic acid, conversion to the acid chloride was anticipated to be quite straightforward.
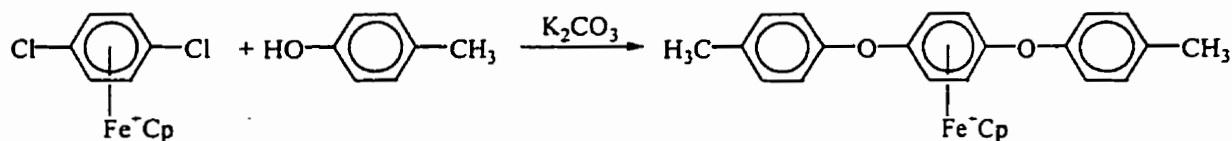
2.20

Scheme 2.9

Oxidation of compound **2.20** was carried out in the presence of potassium permanganate in refluxing H_2O, under reaction conditions similar to those reported by

Nesmeyanov. However, although a single product was isolated, it clearly did not contain a carboxylic acid functionality.

Examination of the ^{1}H NMR spectrum which was obtained for the product showed the continuing presence of a methyl group, and the absence of the characteristic acid proton at 10-12 ppm. As well, the ratio of uncomplexed protons to cyclopentadienyl protons decreased by half. This is illustrated by the ^{1}H and ^{13}C NMR spectra for the starting complex **2.20**, as shown in **Figures 2.17** and **2.18**, which may be compared to those of product **2.21**, which may be seen in **Figures 2.19** and **2.20**. A tabular comparison of these two materials may be seen in **Tables 2.11** and **2.12**.

2.20

2.21
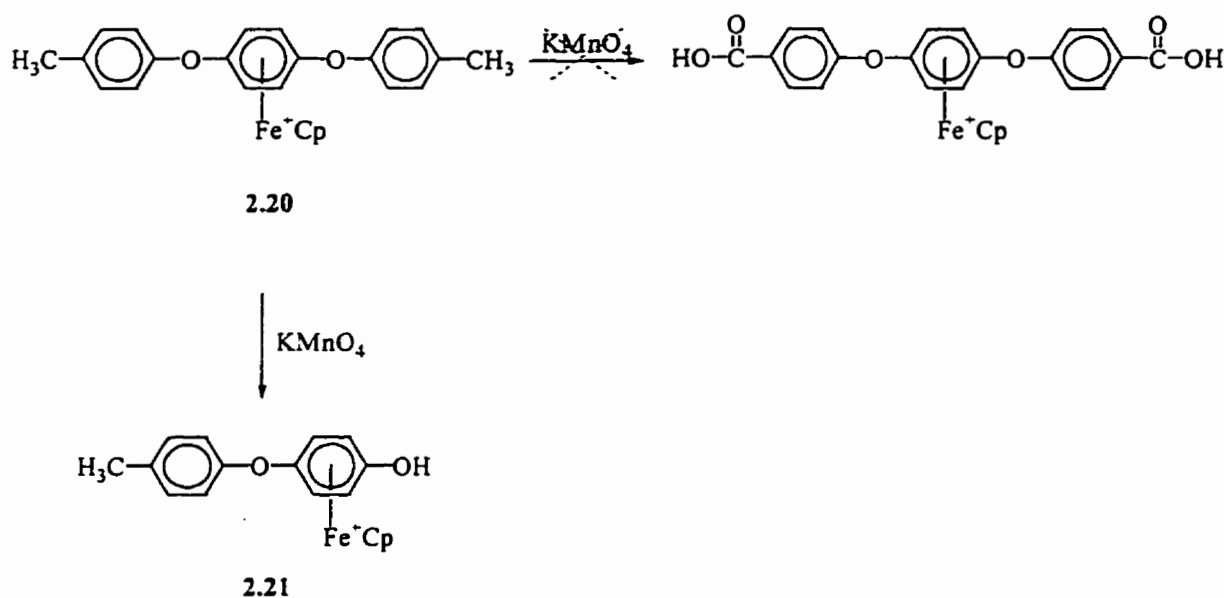
Scheme 2.10
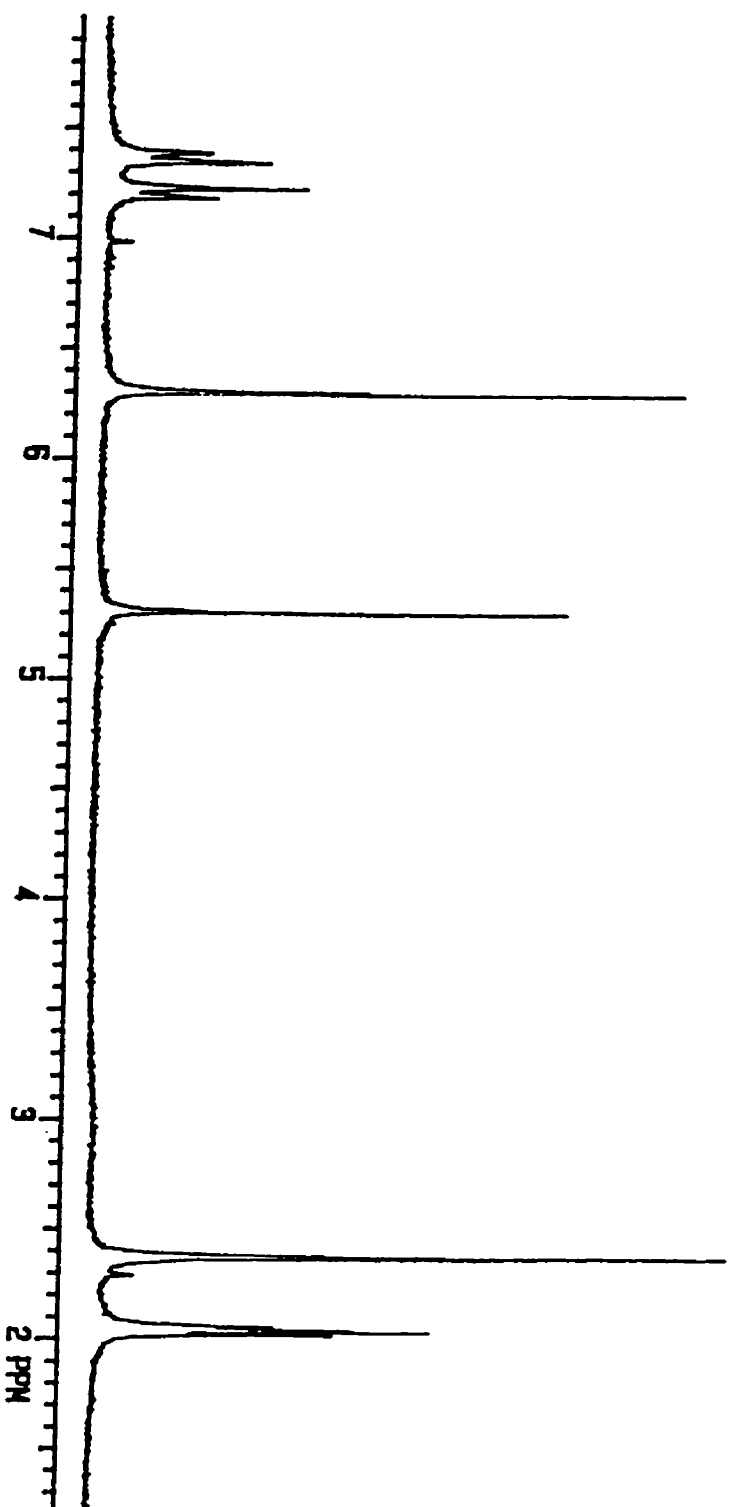
Figure 2.17: ^{1}H NMR spectrum of starting complex 2.20.
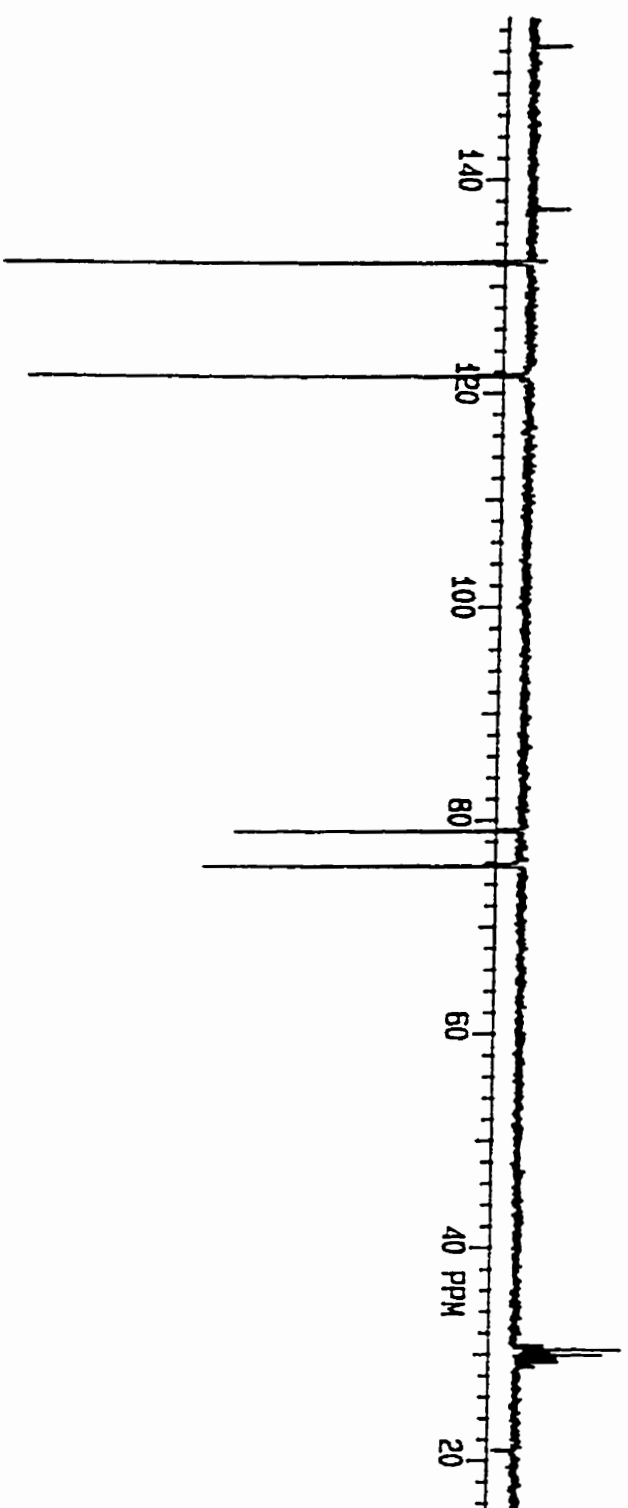
Figure 2.18: ^{13}C NMR spectrum of complex 2.20.
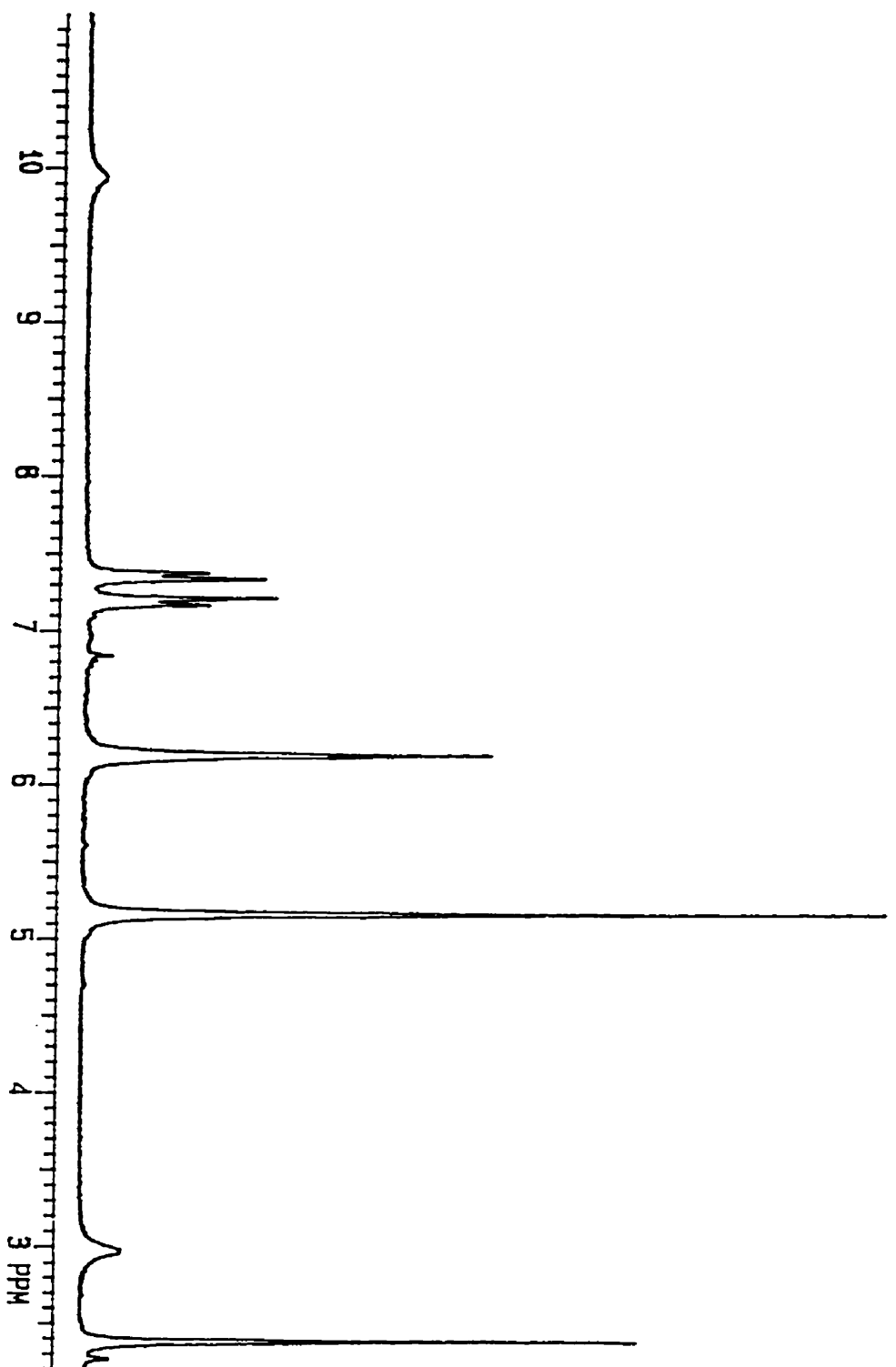
Figure 2.19: ¹H NMR spectrum of etheric cleavage product 2.21.
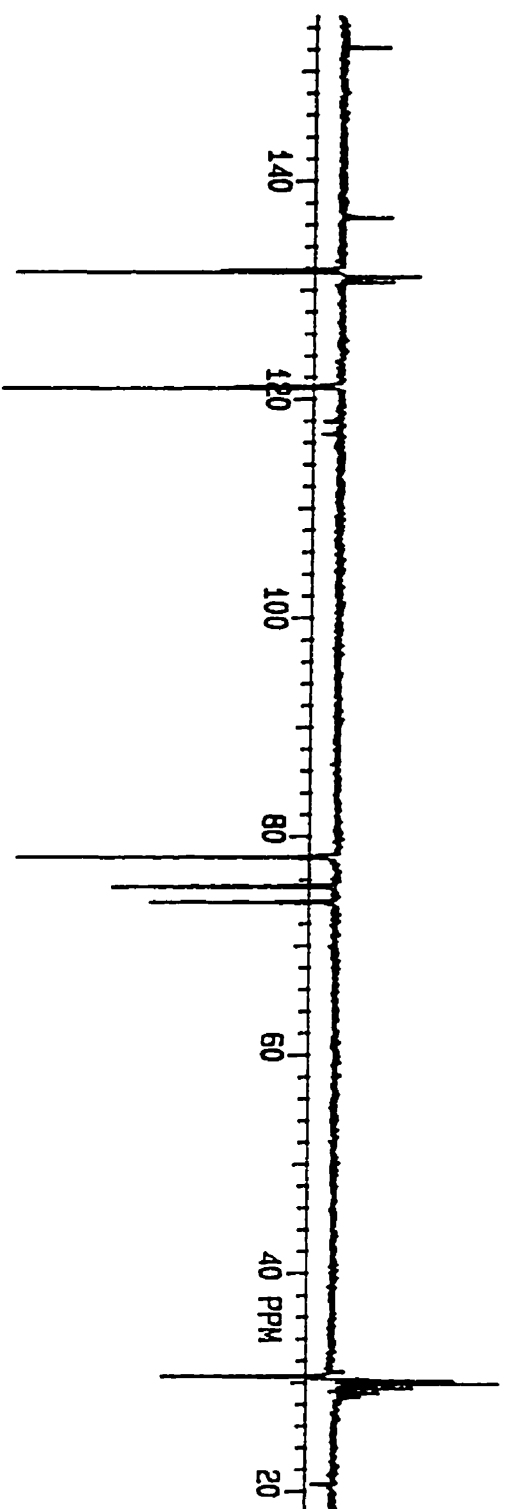
Figure 2.20: 13C NMR spectrum of etheric cleavage product 2.21.

Table 2.11: ^{1}H NMR Spectral Data for Complexes **2.20** and **2.21**

δ (ppm), in acetone-d$_6$					
Complex	Yield (%)	Cp	Complexed ArH	Uncomplexed ArH	Other
2.20	96	5.30	6.30 (s, 4H)	7.21 (d, 4H, J 8.4) 7.36 (d, 4H, J 8.1)	2.38 (s, 6H, CH$_3$)
2.21	26	5.15	6.18 (s, 4H)	7.18 (d, 2H, J 8.4) 7.35 (d, 2H, J 8.4)	2.37 (s, 3H, CH$_3$) 9.91 (s,1H, ArOH)

Note: Coupling constants are in hertz.

Table 2.12: ^{13}C NMR Spectral Data for Complexes **2.20** and **2.21**.

δ (ppm), in acetone-d$_6$				
Complex	Cp	Complexed ArC	Uncomplexed ArC	Other
2.20	78.96	75.63, 137.28*	121.52, 132.19, 152.41*	20.98 (CH$_3$)
2.21	78.02	73.96, 75.41, 130.74*, 131.11*	121.08, 131.73, 136.62*, 152.15*	20.64 (CH$_3$)

Note: * denotes a quaternary carbon.

In the ^1H NMR spectrum, a signal is seen at 2.37 ppm which corresponds to the protons of the methyl group. The cyclopentadienyl ring protons give rise to a peak at 5.15 ppm, which is a chemical shift characteristic of complexed ethers, and itself has a relative integration of 5 protons. The complexed aromatic protons giving rise to a peak at 6.18 ppm have a relative integration of four protons, and the uncomplexed protons whose resonances appear as doublets at 7.18 ppm and 7.35 ppm also integrate to four hydrogen atoms. Finally, a peak which may be assigned as due to a phenolic proton may be seen at 9.91 ppm. From this information, it seems reasonable to hypothesize that, again under these conditions, an etheric cleavage reaction has taken place.

The ^{13}C NMR spectrum provides further evidence that etheric cleavage has occurred. The methyl group gives rise to a peak at 20.64 ppm, which is followed by two peaks occurring at 73.96 and 75.41 ppm, due to the complexed aromatic carbon atoms. The five equivalent carbon atoms of the cyclopentadienyl ring resonate at 78.02 ppm. Two complexed quaternary carbons give rise to peaks at 130.74 and 131.11 ppm. The uncomplexed aromatic carbons resonate at 121.08 and 131.73 ppm, corresponding to the carbons which are ortho to the ether bridge and methyl group, respectively. Finally, there are also two uncomplexed quaternary carbons resonances appearing at 136.62 (carbon atom bound to the methyl group) and 152.15 ppm (carbon atom bound to the phenoxy bridge).

In order to more fully understand the extent of this reaction, the bimetallic analogue of compound **2.20** was prepared, according to **Scheme 2.11**. Once this was accomplished, compound **2.22** was subjected to the same oxidative conditions as complex **2.20**. Again, compound **2.21**, the etheric cleavage product, was obtained. This was verified by both ^1H and ^{13}C NMR spectroscopy, which corresponded exactly with the spectra obtained for the product of **Scheme 2.10**.
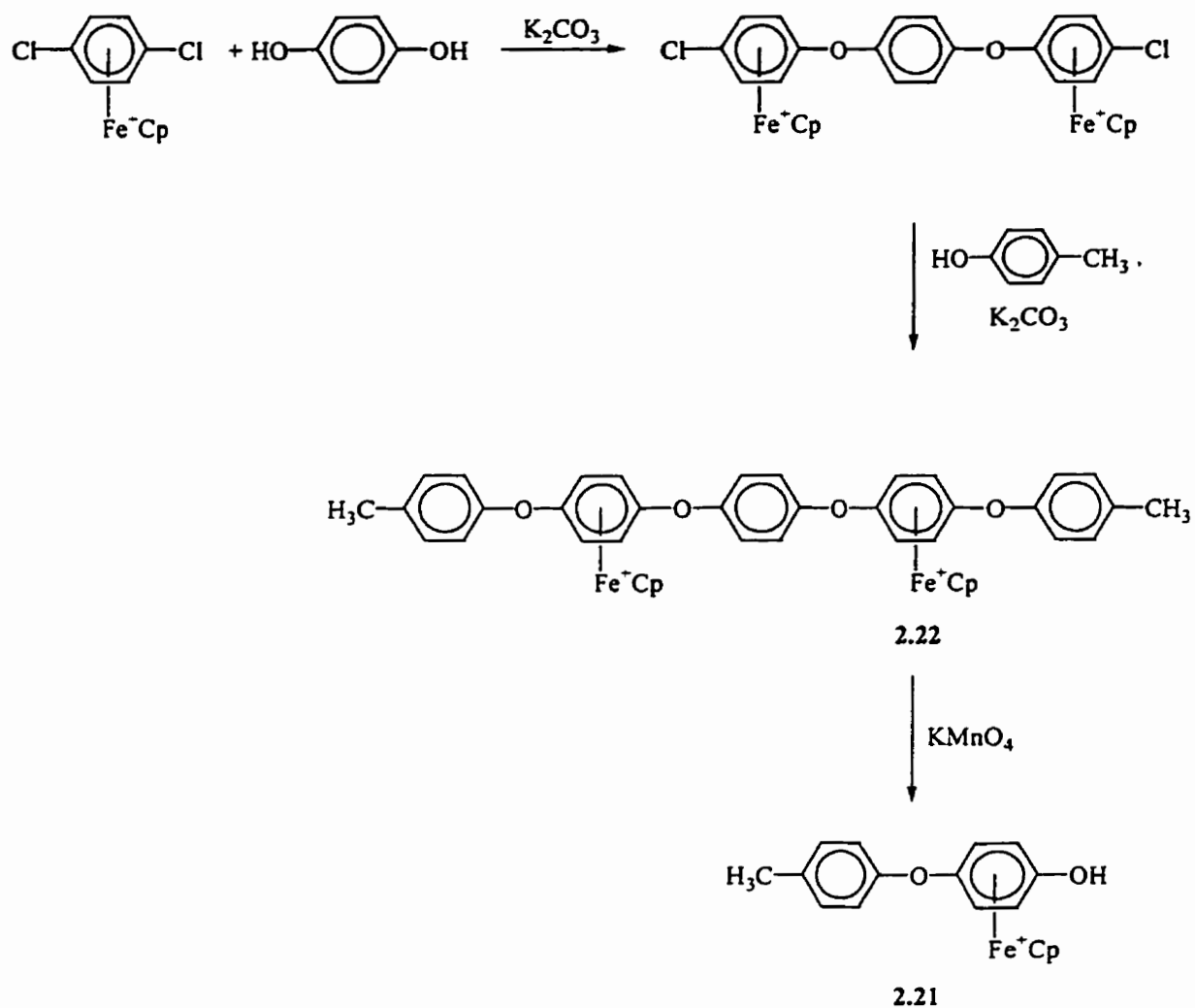
Scheme 2.11

We were also interested in determining whether any sort of cleavage reaction would occur when the monometallic species **2.23** was reacted in the presence of potassium permanganate. Its synthesis was quite straightforward, as shown in **Scheme 2.12**. When compound **2.23** was reacted with potassium permanganate, the carboxylic acid was obtained. No cleavage reaction occurred. Therefore, it may be hypothesized that in order for the etheric cleavage reaction to occur, there must be two etheric linkages

on the complexed aromatic ring. ^{1}H and ^{13}C NMR data may be found in **Tables 2.13** and **2.14**.
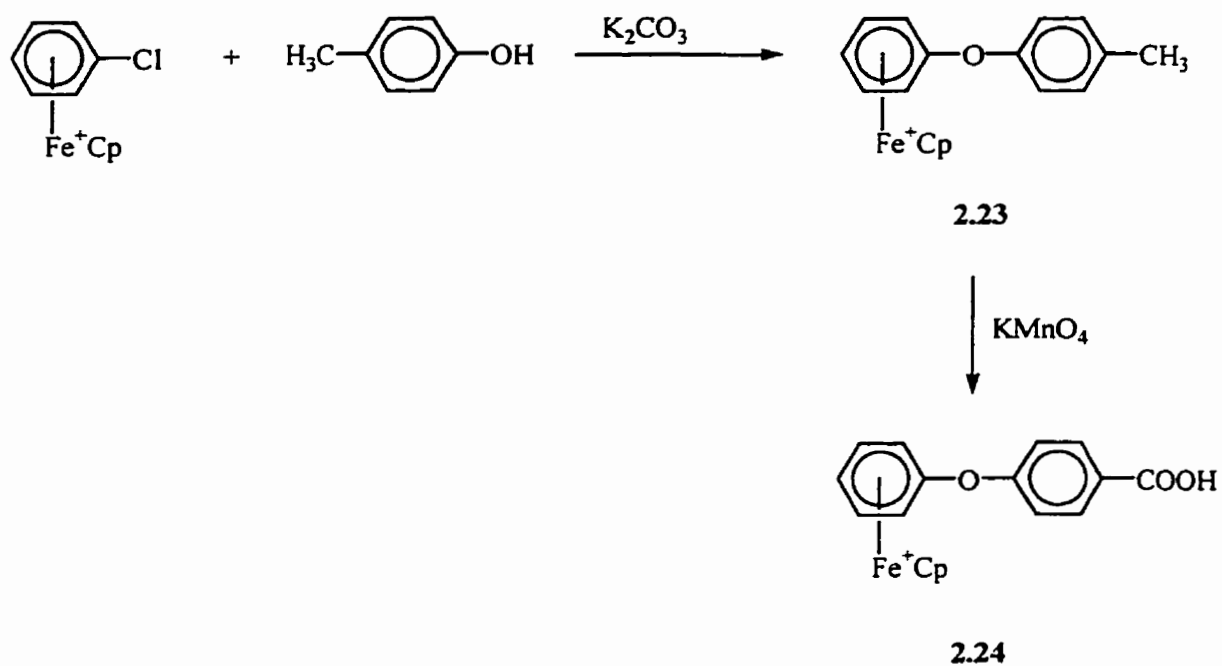
Scheme 2.12

Table 2.13: ^{1}H NMR spectral data for complexes **2.23** and **2.24**

δ (ppm), in acetone-d$_6$					
Complex	Yield (%)	Cp	Complexed ArH	Uncomplexed ArH	Other
2.23	83	5.25	6.35 (m, 3H) 6.46 (m, 2H)	7.32 (dd, J 8.4, 4H)	2.39 (s, 3H, CH$_3$)
2.24	45	5.12	6.23 (m, 5H)	6.91 (d, J 8.8, 2H) 7.91 (d, J 8.8, 2H)	

Note: Coupling constants are in hertz.

Table 2.14: ^{13}C NMR spectral data for complexes **2.23** and **2.24**.

δ (ppm), in acetone-d$_6$				
Complex	Cp	Complexed ArC	Uncomplexed ArC	Other
2.23	77.88	77.24, 85.49, 87.60, 134.71*	121.54, 131.58, 137.12*, 151.56*	20.80 (CH$_3$)
2.24	77.39	76.70, 84.029, 122.34*	115.90, 132.62, 134.18*, 160.17*	167.71 (CO)

Note: * denotes a quaternary carbon.

The strong downfield shift of the signals due to the uncomplexed aromatic protons in the ^{1}H NMR spectrum gives good evidence that the acid has indeed been formed. It may be noticed that the signals of the protons which are adjacent to the acid functionality are shifted the most, from 7.32 ppm to 7.91 ppm. As well, the ^{13}C NMR spectrum supports the assigned structure, particularly with the dramatic downfield shift of the resonance of the quaternary carbon bound to the acid group (from 151.56 to 160.17 ppm).

Decomposition of polynuclear aromatics in the presence of potassium permanganate has been reported previously.[73] However, it is quite rare for a single product to be isolated. In this case, it is possible to speculate a mechanism whereby the etheric bond is cleaved by the permanganate ion:
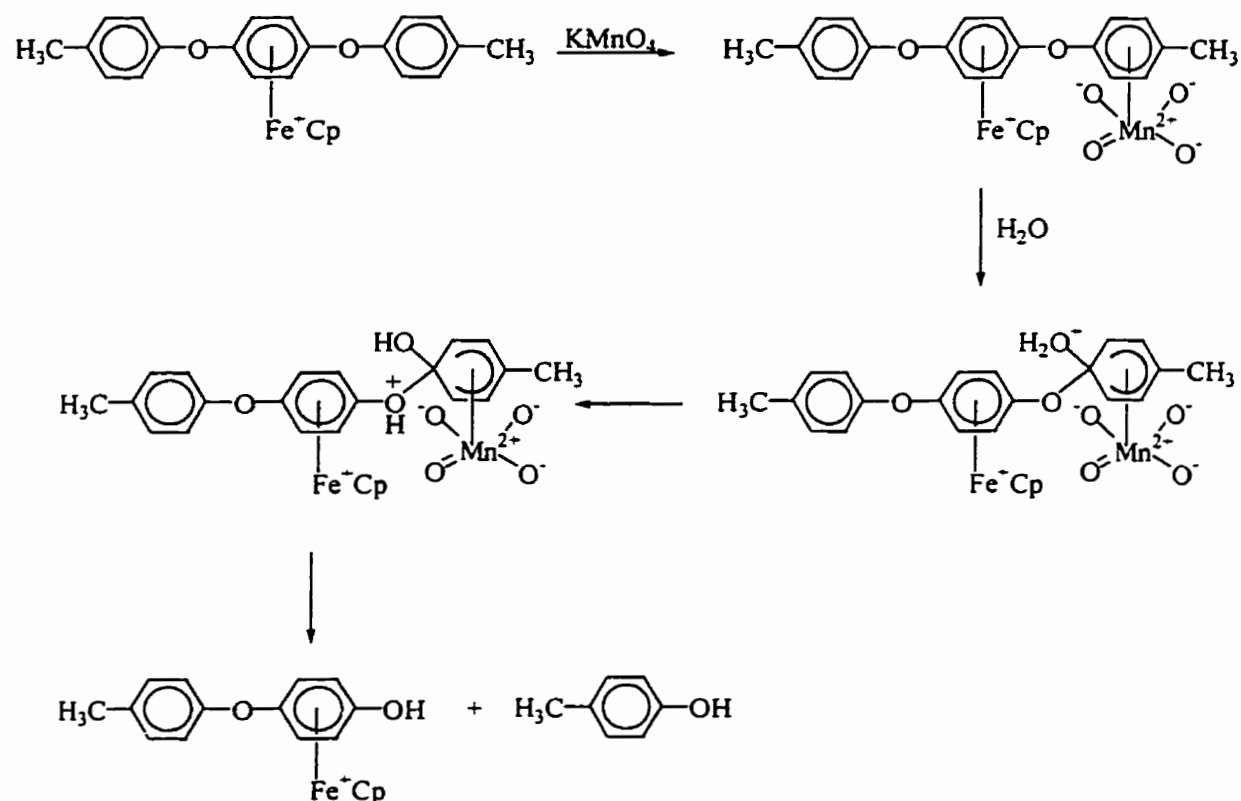
Scheme 2.13

In this mechanism, the first step involves the coordination of the manganese atom to the electron rich aromatic ring. This is hypothesized to be the initial step in the oxidation of toluenes.[74] The presence of the metal moiety helps to draw electron density away from the aromatic ring, and leaves it susceptible to nucleophilic attack; in this case, attack by the water which is present as a solvent. The etheric group then becomes a good leaving group, after protonation at the oxygen atom. Once this group has left, the acidic conditions required by the workup procedure result in the protonation of the phenol and the isolation of the product.

Compound 2.21 is novel in that it has not been synthesized previously by any other synthetic route. Although several workers have attempted to exchange one cyclopentadienyl ring of ferrocene with a phenolic compound, as yet this reaction has not been possible. Indeed, compound 2.21 is quite unstable, and decomposes within a few days, even when stored at -30°C. There has been some success in the literature in the preparation of cyclopentadienyliron complexed phenol and thiophenol via nucleophilic aromatic substitution of η^6-chlorobenzene-η^5-cyclopentadienyliron(II) hexafluorophosphate with hydroxide or hydrogen sulfide ion.[75] These complexes was found to be quite unreactive as nucleophiles, which would be expected due to the strong electron withdrawing effect of the metal moiety.

2.3 Conclusion

Through the investigation of the reaction of phenolphthalein-containing bimetallics with amines, it has been determined that these compounds may undergo an etheric cleavage reaction which results in the formation of cyclopentadienyliron complexed anilines. This unique reaction provides the first ever synthesis of complexes 2.11 and 2.12, which may not be synthesized by nucleophilic aromatic substitution. As well, this methodology could potentially be useful for the synthesis of complexes containing two

distinct functional groups, provided that the original bimetallic species is functionalized prior to the etheric cleavage reaction. Thus this represents a unique route to the synthesis of nonsymmetrical cyclopentadienyliron complexes.

As well, the unusual etheric cleavage reaction which occurs in the presence of potassium permanganate also results in the first ever synthesis of compound **2.21**. It is proposed that the permanganate ion complexes with the tolyl group, which then leaves the etheric group susceptible to nucleophilic attack by water, which is present as the solvent.

In general, etheric bonds are difficult to cleave. The presence of two aryl groups adjacent to the oxygen makes this bond even stronger. Thus this work represents a unique class of reactions which may ultimately be useful synthetically.

2.4 Experimental

2.4.1 General Methods

^{1}H and ^{13}C NMR were recorded at 200 MHz and 50 MHz, respectively, on a Varian Gemini 200 NMR spectrometer. ^{13}C NMR spectra were run with APT (attached proton test), which allowed for the distinction between quaternary and methylene carbon atoms from methyl and methine carbon atoms. Chemical shifts were calculated from peaks due to the residual protons in the deuterated solvents; acetone-d_6 was referenced to 2.04 ppm (^{1}H NMR) and 29.8 ppm (^{13}C NMR), while CDCl$_3$ was referenced to 7.26 ppm (^{1}H NMR) and 77.0 ppm (^{13}C NMR).

2.4.2 Starting Materials

Phenolphthalein, p-cresol, potassium permanganate, potassium carbonate, ammonium hexafluorophosphate and the various amines and chlorobenzenes utilized are all commercially available (Aldrich) and were used without purification. The solvents that were used were HPLC grade, and were used as received, without further purification.

2.4.3 Preparation of the Chloroarene Cyclopentadienyliron Complexes

The chlorobenzene cyclopentadienyliron complexes which were used were all synthesized by the previously reported ligand exchange reaction.[11-13,38] 150 mmol of ferrocene was placed in a three-necked round bottom flask, along with 300 mmol of aluminum chloride, 150 mmol of aluminum powder and 275 mmol of the desired chloroarene complex. The flask was equipped with a thermometer and adapter, and the contents were heated to 135°C under nitrogen. After five hours, the mixture was hydrolyzed in an ice/water mixture, and filtered over sand. Washing the aqueous phase with three 50 mL aliquots of petroleum ether, and subsequent addition of 75 mmol of ammonium hexafluorophosphate afforded a yellow/green precipitate, which was extracted out of solution by dichloromethane. Evaporation of the organic solvent to concentration results in a dark green solution, which yields a green/yellow precipitate upon the addition of ether. This may be collected with a Buchner funnel and dried to give the starting cyclopentadienyliron species.

2.4.4 Preparation of Phenolphthalein-Containing Bimetallic Species (2.1 - 2.4)

2 mmol of the starting chlorobenzene cyclopentadienyliron complex was placed in a 50 mL round bottom flask along with 1 mmol of phenolphthalein and 2.5 mmol of potassium carbonate. 10 mL of DMF was added as a solvent, and the mixture was stirred for sixteen hours over nitrogen. After this time, the reaction mixture was poured into 10% HCl (by volume), and a concentrated solution of ammonium hexafluorophosphate was added. The resulting yellow precipitate was collected in a glass crucible and washed liberally with water. After this was completed, the precipitate was rinsed with two 30 mL aliquots of ether.

2.4.5 Etheric Cleavage Reactions with Phenolphthalein-Containing Ethers (2.5 - 2.12)

1 mmol of the starting bimetallic complex, along with 8 mmol of the primary amine were placed in a 25 mL round bottom flask in 5 mL of DMF. The mixture was heated to 80°C and stirred under nitrogen for sixteen hours. After this time the flask was allowed to cool to room temperature, and the contents were poured into a dilute NaOH solution. The mixture then turned a bright pink. The complex was exhaustively extracted from the water layer with dichloromethane, and then washed with the dilute NaOH solution until the bright pink colour was no longer evident. The organic layer was then dried over magnesium sulfate, filtered, and the solvent removed by rotary evaporation. If, after this time, there was still a significant amount of DMF remaining in the product, this was removed via vacuum distillation. Once all DMF was removed, the product was rinsed liberally with ether and dried, leaving an orange oil.

2.4.6 Reaction of 2.1 with Tyramine (2.13)

1 mmol of complex **2.1**, along with 8 mmol of tyramine and 0.7 mmol of K_2CO_3 were placed in a 25 mL round bottom flask, and dissolved in 5 mL of DMF. The mixture was heated to 60°C and allowed to stir under nitrogen for 16 hours. The workup proceeded as above.

2.4.7 Photolytic Demetallation (2.14 - 2.19)

The complex was dissolved in dichloromethane and transferred to a Pyrex photolysis tube. Acetonitrile was added so that the solvent mixture was 3:1 dichloromethane to acetonitrile. The solution was then placed near a xenon lamp, and allowed to be irradiated for eight hours. After this time, the contents of the photolysis tube were evaporated under reduced pressure to concentration, and introduced to a silica gel column (60 - 100 mesh). Elution with hexane resulted in the collection of a fraction composed entirely of ferrocene. Subsequent elution with a 10% ethyl acetate 90% ether solution resulted in collection of the demetallated aniline.

2.4.8 Preparation of Compound 2.20

2.20 mmol of p-cresol was placed in a 50 mL round bottom flask equipped with a stir bar. Also added was 1 mmol of η^6-1,4-dichlorobenzene-η^5-cyclopentadienyliron(II) hexafluorophosphate, and 2.5 mmol of potassium carbonate. These solids were dissolved in 10 mL of DMF, and allowed to react for sixteen hours while stirring under a nitrogen atmosphere. After this time, the mixture was poured into a 10% (by volume) HCl solution, followed by the addition of a concentrated solution of ammonium hexafluorophosphate. The resulting yellow precipitate was collected in a crucible, and

washed generously with water. After this was finished, washing with two aliquots of ether left a pale yellow powder.

2.4.9 Permanganate Ion Cleavage of Cyclopentadienyliron-Complexed Ethers (2.21)

10 mmol of potassium permanganate along with 1 mmol of the complex were combined in a 100 mL round bottom flask along with 50 mL of distilled water. The mixture was allowed to reflux for 24 hours. After this time, the flask was cooled to room temperature, and oxalic acid was added until effervescence ceased. Upon completion of the addition of oxalic acid, the reaction mixture changed colour from black, to purple to orange/yellow. The excess oxalic acid was removed by suction filtration, and the filtrate was acidified with concentrated HCl to a pH of 1. After this, a concentrated solution of ammonium hexafluorophosphate was added, and the aqueous layer was extracted with nitromethane. The organic layer was dried over magnesium sulfate, which was removed by gravity filtration. Rotary evaporation of the solvent left a yellow solid.

3.0 The Preparation of Ferrocene-Containing Cyclopentadienyliron Complexes

3.1 Introduction

3.1.1 The Ferrocene Molecule

Ever since its accidental discovery in 1951 by Pauson and co-workers, ferrocene has remained one of the most studied organometallic compounds.[76] Dubbed a "sandwich complex" because of its structure, ferrocene consists of two cyclopentadienyl rings located in planes above and below an iron atom, which is in the (II) oxidation state. This unique structure is illustrated below:
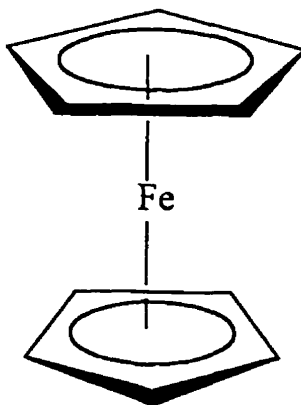
Figure 3.1: The ferrocene molecule.

Ferrocene exhibits a chemistry which is very closely related to that of aromatic compounds. For example, ferrocene is capable of undergoing classical Friedel-Crafts alkylation and acylation in the presence of a Lewis acid.[77] Therefore the chemistry of

ferrocene is well understood and quite diverse.[78,79] This is illustrated in **Figure 3.3**, which features several examples of typical reactions involving ferrocene.
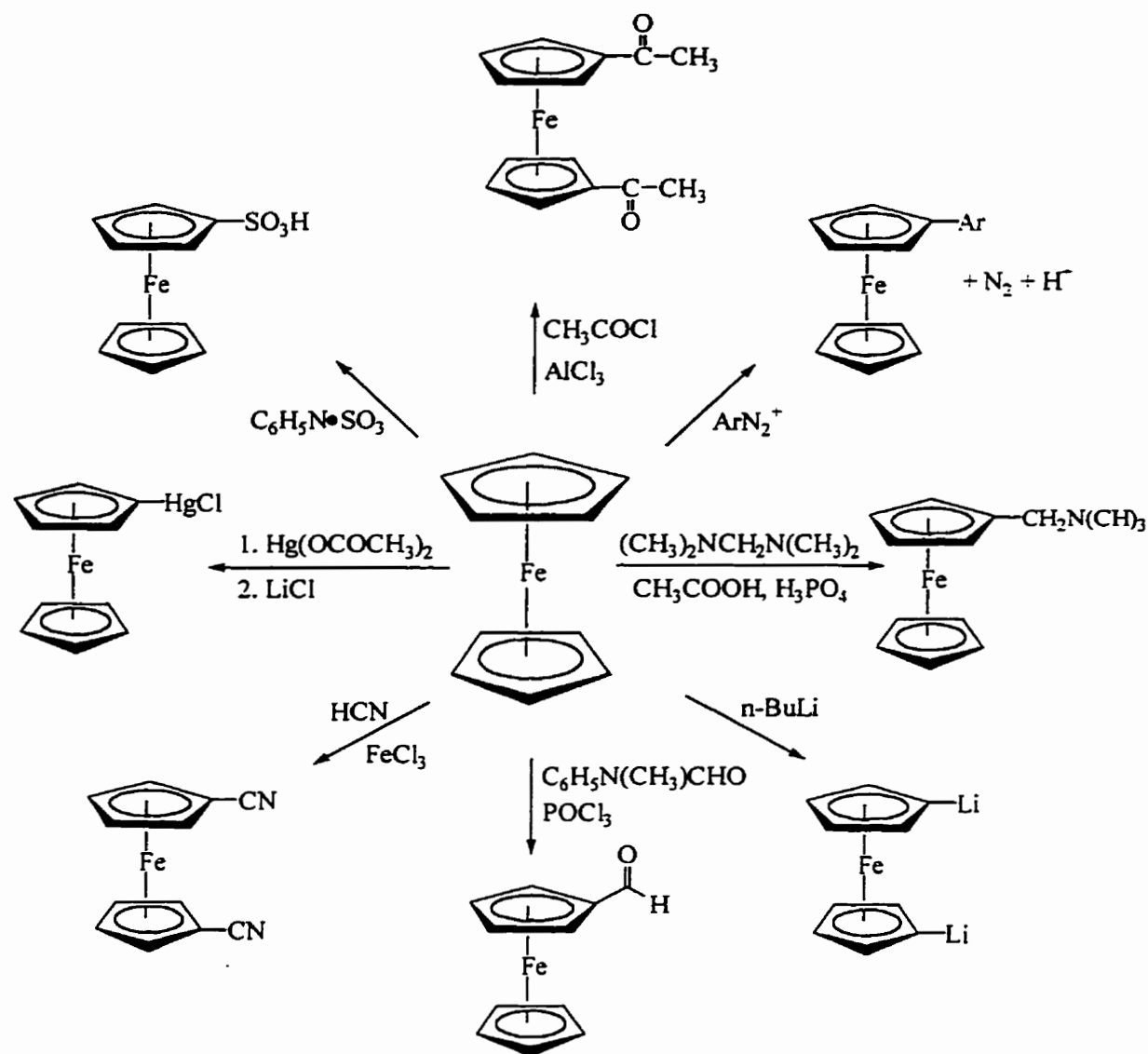
Figure 3.2: The reactivity of ferrocene.

Ferrocene is also known to be an electron rich species. Because of this fact, ferrocene may be easily oxidized to the ferrocenium state, either by chemical means (for

example, by reaction with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, or DDQ) or via electrolysis. Cyclic voltammetry studies have shown that the oxidation of ferrocene is reversible, and occurs at 0.31 V, versus a saturated calomel electrode in acetonitrile.[80] In fact, this oxidation reaction is so reproducible that it is commonly used as a reference for cyclic voltammetry studies.[81]

Several workers have studied the electrochemical behavior of a variety of substituted ferrocenes.[82-85] From this work, a general trend has been observed. Electron donating substituents allow ferrocenes to be oxidized at much lower potentials than electron withdrawing substituents. This may be illustrated by a very simple example. Hydroxyferrocene and aminoferrocene are quite sensitive to air, and in its presence are oxidized rapidly. However, 1,1'-diacetylferrocene is much more resistant towards oxidation, and even $FeCl_3$ is an insufficiently strong oxidizing agent to cause its reaction, although $FeCl_3$ easily oxidizes unsubstituted ferrocene.[82]

The ease and reproducibility with which ferrocene may be oxidized has led to its use in a variety of potentiometric applications. For example, several workers are currently using ferrocene to synthesize biosensors.[86-88] Because of the ability to manipulate ferrocene via well understood organic reactions, ferrocene may be easily coupled to enzymes. For example, Badia and her co-workers were successful in functionalizing glucose oxidase with ferrocene, through the coupling of lysine residues with ferrocenecarboxylic acid.[86] Glucose oxidase requires FAD as a co-factor for the oxidation of glucose, which is reduced during the course of the reaction to FADH. The ferrocene moieties, when oxidized to the ferrocenium species, may act as oxidizing agents to convert FADH back to its original state. By voltammetry, the amount of ferrocene in its reduced, neutral state may be monitored, which is directly proportional to the amount of FADH which is oxidized back to FAD. This, in turn, allows for the determination of the original amount of glucose in solution. Therefore, this method represents a unique,

reagentless technique for the determination of glucose concentrations. This may be extrapolated for use with biologically relevant samples, such as blood.

Ferrocene has also been shown to be tremendously stable at high temperatures.[89] This property, along with its novel electrochemical behavior has resulted in the incorporation of this sandwich complex into a variety of polymeric materials. These include ferrocene-containing polyesters and amides,[90,91] polyvinylferrocenes,[92] ferrocene-containing polyurethanes, polysilyls and polysiloxanyls.[93-95] Some of these polymeric materials have been found to be stable to UV radiation; thus they are used in materials such as paint, to minimize degradation upon exposure to such energetic radiation. As well, some exhibit a toughness which permits their use as heat shields for space flight.[92] Thus the development of these types of materials is extremely relevant technologically.

3.1.2 Electrochemical Behavior of Cyclopentadienyliron Complexes

In contrast to ferrocene, arene complexes containing the cyclopentadienyliron moiety do not undergo oxidation. In fact, these complexes are, in general, quite electron deficient. However, as may be expected, many of these complexes have been shown to be capable of undergoing reduction.[96,97]
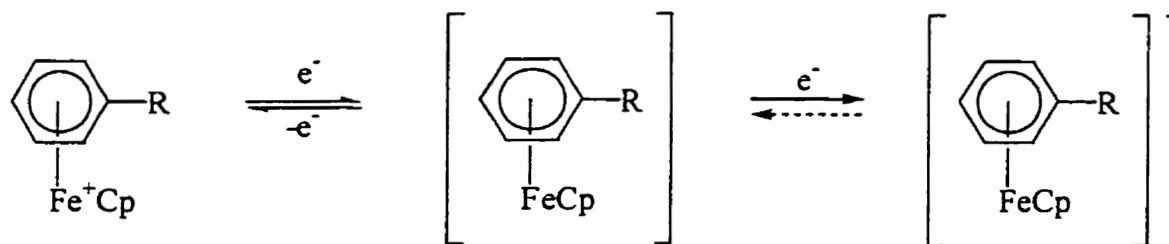
Scheme 3.1

As illustrated in **Scheme 3.1**, cyclopentadienyliron complexes of arenes may accept one electron to become the neutral nineteen electron species. This reduction is typically reversible. Subsequently, another electron may be accepted in order to form the twenty electron complex. The stability of this negatively charged complex depends on the nature of the substituents located on either the arene or cyclopentadienyl ring.

Just as for ferrocene derivatives, the nature of the substituent on the arene ring has a profound effect on the reduction potential of the complex. Electron donating substituents generally cause a shift in the $E_{1/2}$ to more negative potentials, whereas electron withdrawing substituents have an opposite effect. Functional groups also have a marked effect on the stability of the resulting products. Electron withdrawing substituents act to stabilize the electron rich nineteen or twenty electron species. As well, the presence of bulky substituents helps to deter the dimerization of nineteen electron radicals.[98]

Nineteen electron complexes have been characterized by EPR, since these complexes contain an unpaired electron. EPR has been run on the monoreduced cyclopentadienyliron complexes of fluorobenzene and tetramethylthiophene, as well as benzene, naphthalene, phenanthrene, pyrene and triphenylene.[99,100] Interestingly, EPR studies of the complexes of perylene and coronene, which contain more than four aromatic rings, show that the extra electron is delocalized almost entirely on the ligand. This is not observed for polyaromatic ligands containing fewer than four rings.

Astruc has suggested that the nineteen electron species which are formed upon the one electron reduction of cyclopentadienyliron complexes of arenes may act as electron reservoirs for the reduction of organic species. Indeed, he has already shown that the nineteen electron complex η^6-hexamethylbenzene-η^5-cyclopentadienyliron(I) may be used to reduce tetracyanoquinodimethane, phenazine and bifluorenylidene.[98]

Bimetallic cyclopentadienyliron complexes may also be subjected to two successive two-electron reductions, although their behavior depends substantially on the nature of the bridge between the metal centres. Abd-El-Aziz and co-workers probed the

reduction behavior of both cyclopentadienyliron complexed diethers and dithioethers via cyclic voltammetry.[101] They found that, when the bridging atom was oxygen, there was no communication between adjacent metal centres; this was indicated by the presence of one distinct $E_{1/2}$ for the formation of the nineteen electron species, and another for the formation of the twenty electron species. When the bridge was a sulfur atom, there was communication between the iron atoms. This was shown by two different $E_{1/2}$ potentials corresponding to each metal atom for the formation of the nineteen electron species. This duality was also shown for the formation of the highly unstable twenty electron species.

3.1.3 Electron Hopping in Mixed Valence Species

Kaufman and Cowan were the first workers to synthesize a mixed valence bimetallic species containing both a ferrocene and a ferrocenium moiety.[102] When examining the properties of biferrocene Fe(II)Fe(III) picrate, they determined that the conductivity of this species was six orders of magnitude higher than either biferrocene or biferrocene Fe(III)Fe(III) dipicrate. IR spectra indicated peaks attributable to ferrocene, the ferrocenium moiety, and the picrate anion, as well as a unique peak which could not be ascribed to any of the previous species.[103,104]

The substantial increase in conductivity of the mixed valence species may be attributed to a phenomenon known as "electron hopping". This model suggests that it is the transfer of one electron from an electron rich moiety to an electron poor moiety which results in the transfer of electric charge.[105,106] Thus, in the presence of a current, one electron is transferred from the ferrocene moiety to the ferrocenium moiety, causing a reversal of their original states. Although this seems quite unusual, there have been some instances in which ferrocene has acted as an electron donor. For example, in the report published by Cowie *et. al.*, a dative bond is formed between a palladium atom and the iron

atom of a ferrocene moiety.[107] Thus the iron atom of ferrocene is a documented electron donor.

Pittman and co-worker have extended the initial work by Kaufman and Cowan into the area of ferrocene-containing polymers. Polyvinylferrocene, polyferrocenylene and polyethynylferrocene are all polymers which have insulating properties. However, when Pittman reacted these polymers with less than an equivalent of an oxidizing agent (such as DDQ, iodine or tetracyanoquinodimethane), the measured degree of conductivity rose six to eight orders of magnitude.[108] The use of less than a full equivalent of oxidizing agent allowed the oxidation of only some of the ferrocene moieties, and thus the mixed valence polymer was formed. In the presence of an electric current, "electron hopping" was allowed to occur from the unoxidized ferrocene moieties to adjacent ferrocenium moieties. In this way, charge is carried throughout the entire polymer.

3.1.4 Scope of the Present Work

Ferrocene is a well documented electron donor, due to its electron rich nature. Arene complexes of the cyclopentadienyliron moiety, however, are electron poor, and as such are excellent electron acceptors. The combination of these two moieties may provide unique materials which may act as both electron reservoirs and electron acceptors.

Ferrocene has been previously incorporated into molecules containing the cyclopentadienyliron moiety. This was accomplished by Astruc and co-workers, who prepared dendrimers containing a central arene complexed to a cyclopentadienyliron moiety as the core.[109] Emanating from the central core were phenolic groups, which were reacted with ferrocenoyl chloride in the presence of thallium (I) ethoxide. Thus the neutral ferrocene species and the positively charged cyclopentadienyliron moiety were bound together via an ester linkage, as shown in **Figure 3.3**. Astruc found that the ferrocene subunits underwent a one electron oxidation, as would be expected. The

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ferrocene units were far enough away from each other so as to prevent communication; all of the ferrocene units underwent oxidation at the same potential. The cyclopentadienyliron moieties underwent one reversible one electron reduction to form the nineteen electron species; however, upon more negative potentials, the complexes underwent a subsequent irreversible one electron reduction to form the unstable twenty electron complex.[109] However, no conductivity measurements were made for these materials.
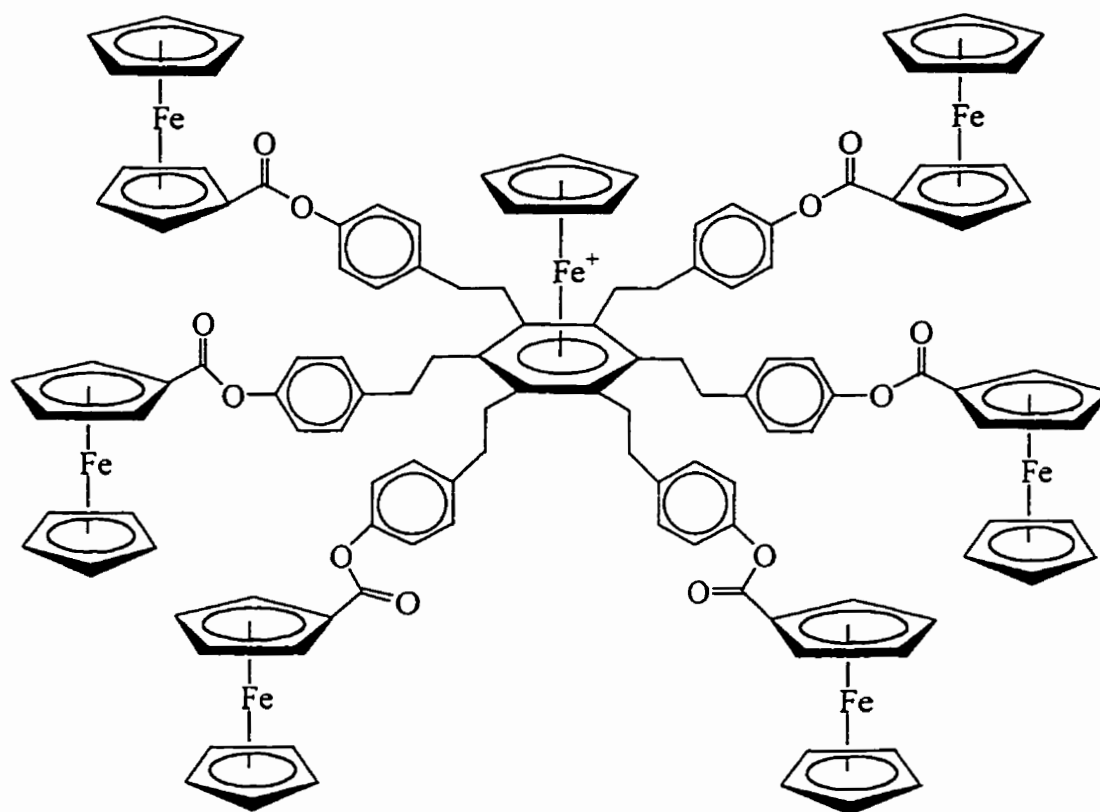
Figure 3.3:   An example of a polyester containing both ferrocene and
cyclopentadienyliron moieties.

In this study, the primary goal was the incorporation of both of the ferrocene subunit and the cyclopentadienyliron moiety into a single molecule. The behavior of these comounds would then be probed via cyclic voltammetry.

3.2 Results and Discussion

3.2.1 Preparation of Amides

There are many examples in the literature of the formation of ferrocene-containing amides via condensation reactions.[90,91,110] Using this methodology, there are two possible approaches. In the first, a ferrocene-containing acid chloride may be reacted with a suitable amine. An alternative approach involves the use of an aminoferrocene to react with an appropriate acid chloride. Although there are several aminoferrocene derivatives known, many of them are susceptible to degradation in air.[111] As well, our inability to synthesize the acid chloride of the terephthalic acid complex compelled us to explore the first synthetic route.

1,1'-Ferrocenedicarbonyl chloride may be easily synthesized in three steps; these are illustrated in **Scheme 3.1**.

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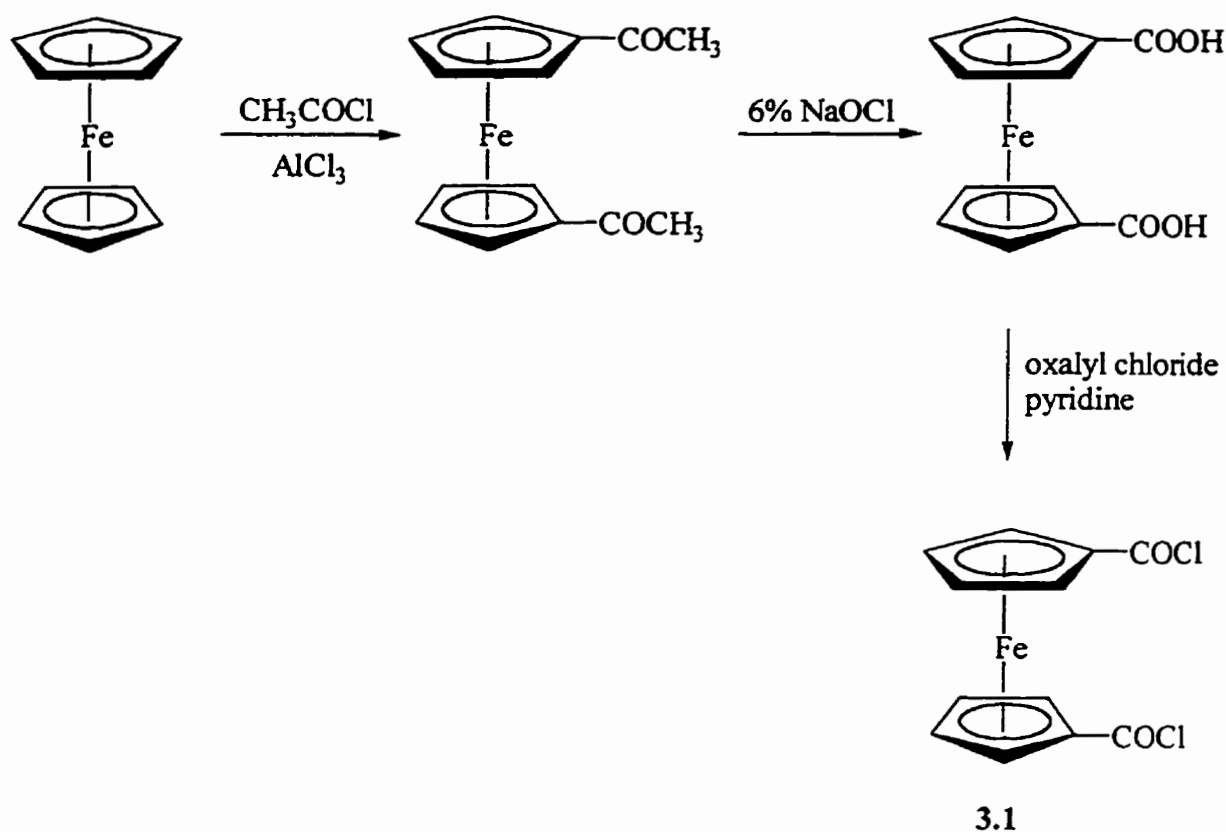
Scheme 3.1

This synthetic strategy was chosen in an attempt to minimize the synthesis of monoacylated derivatives, which could potentially cause side reactions in later steps.

The diacetylation of ferrocene was carried out via the method of Rosenblum and Woodward.[112] 1,1'-Diacetylferrocene was precipitated out selectively with cyclohexane, which left all other reaction products in solution. Oxidation of the diacetyl derivative, followed by the formation of the diacid chloride has been well documented by Knobloch and Rauscher, who utilized compound **3.1** in order to synthesize polyamides and polyesters via condensation reactions.[113]

Once compound **3.1** was obtained, and its identity verified using both ^{1}H and ^{13}C NMR, 1,1'-ferrocenedicarbonyl chloride was reacted with η^6-aniline-η^5-cyclopentadienyliron (prepared by ligand exchange), with pyridine as a catalyst. The

resulting product clearly contained an amide linkage, but did not exhibit the characteristic cyclopentadienyl peak in either the ^1H or ^{13}C NMR spectrum. This is illustrated in **Scheme 3.2**.
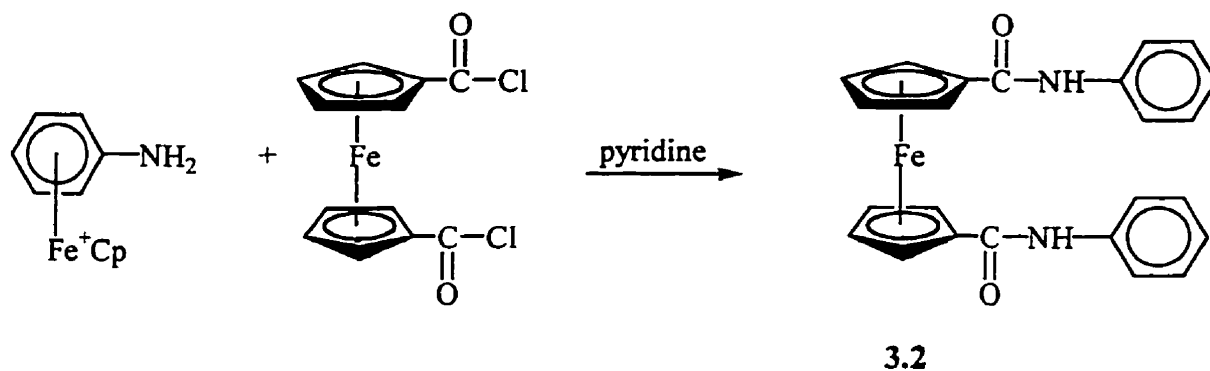
Scheme 3.2

The NMR spectra, which may be seen in **Figures 3.4** and **3.5**, with the data summarized in **Tables 3.1** and **3.2**, suggest that spontaneous demetallation has occurred. This is interesting, because the reaction was not carried out at high temperatures, or under harsh conditions. In order to confirm that the demetallated product was indeed the material obtained, 1,1'-ferrocenedicarbonyl chloride was reacted with uncomplexed aniline, again in the presence of pyridine, under identical reaction conditions. When the ^1H NMR spectrum was obtained for the resulting compound, it was found that it was identical to that obtained for the reaction with the complexed aniline. Therefore, attempts to form amides containing both ferrocene and cyclopentadienyliron moieties were abandoned.
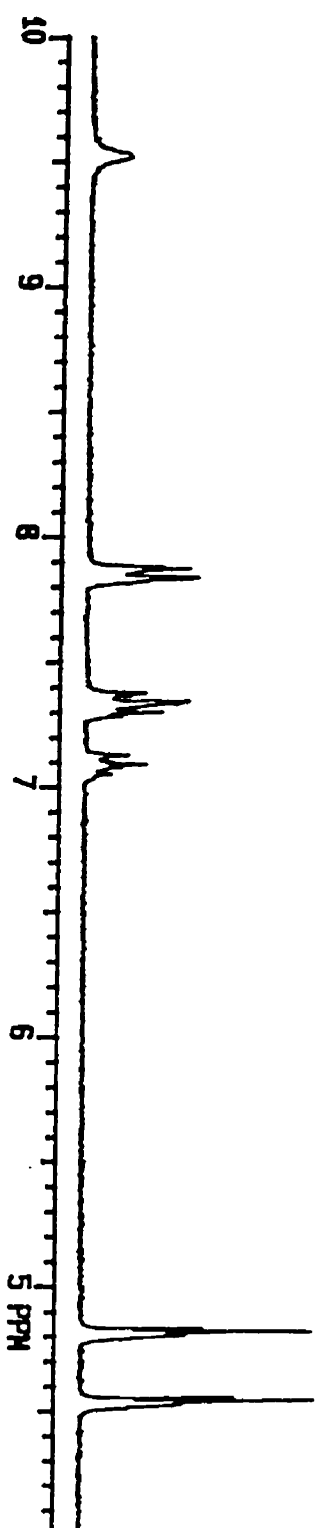
Figure 3.4: ^1H NMR spectrum of ferrocene-containing amide 3.2.
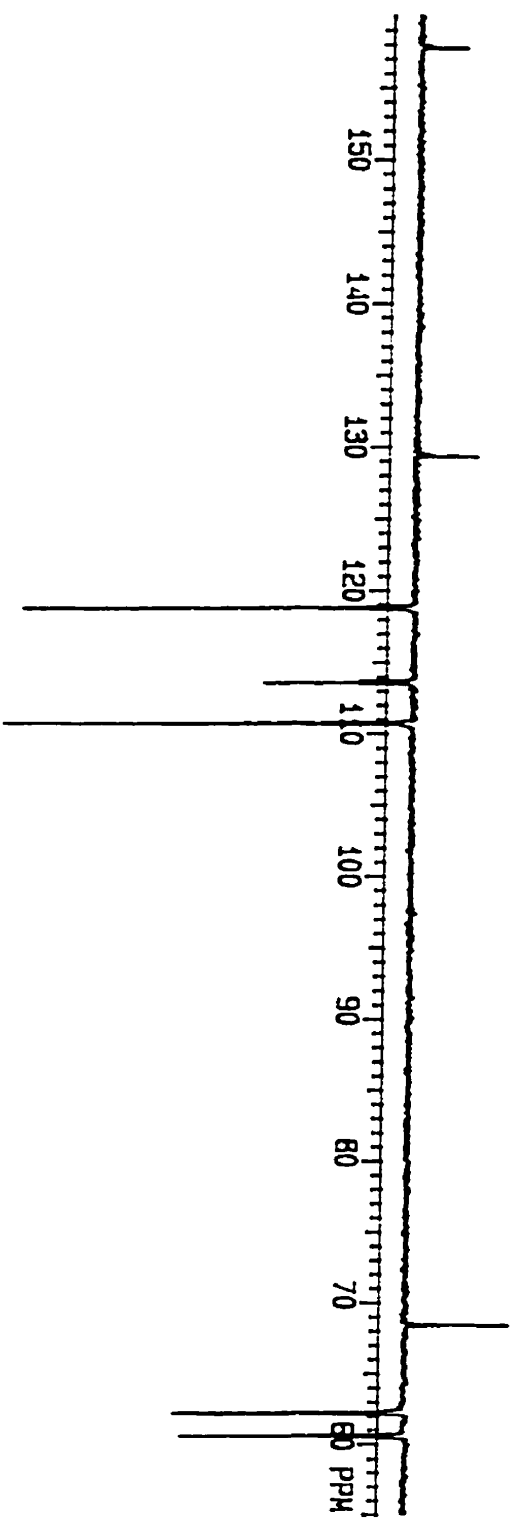
Figure 3.5: 13C NMR spectrum of ferrocene-containing amide **3.2**.

Table 3.1: ^{1}H NMR spectral data for complexes **3.1** and **3.2**.

δ (ppm), in acetone-d$_6$				
Complex	Yield (%)	Ferrocene (FcH)	Uncomplexed ArH	Other
3.1	88	4.95 (m, 4H) 5.10 (m, 4H)		
3.2	67	4.54 (m, 4H) 4.82 (m, 4H)	7.09 (t, J 6.2, 2H) 7.34 (t, J 7.8, 4H) 7.86 (d, J 7.5, 4H)	9.52 (br.s, 1H, NH)

Note: Coupling constants are in hertz.

Table 3.2: ^{13}C NMR spectral data for complexes **3.1** and **3.2**

δ (ppm), in acetone-d$_6$		
Complex	Uncomplexed ArC	Other
3.1		75.19 (FcC), 77.15 (FcC), 78.17* (FcC), 168.54 (CO)
3.2	110.71, 113.60, 119.77, 129.40*	60.54 (FcC), 62.17 (FcC), 68.42* (FcC), 157.80 (CO)

Note: * denotes a quaternary carbon.

3.2.2 Preparation of Esters

Esters are closely related to amides, and may be synthesized using similar methods. Thus, due to the spontaneous demetallation which was observed in our attempts to form amides, our focus shifted to the preparation of esters using the same ferrocene-containing starting material.

Reports of the ligand exchange of alcohols are scarce,[16,75] and for this reason, a complexed alcohol was synthesized by nucleophilic aromatic substitution. An advantage of this methodology is that the alcohol group is not attached directly to a complexed ring, which would decrease its nucleophilicity. As well, this eliminates any steric crowding between the two metal centres, which may have been responsible for the spontaneous demetallation of **3.2**.

4-Hydroxybenzyl alcohol was chosen as a nucleophile to react with η^6-chlorobenzene-η^5-cyclopentadienyliron(II) hexafluorophosphate, due to the presence of the phenol group, which acts as an excellent nucleophile, and the presence of a benzylic alcohol, which is very reactive towards esterification reactions.[1] Interestingly, only substitution by the phenolic group was observed, due to the strength of the base that was used. Potassium carbonate is sufficiently mild to deprotonate only the phenolic protons, leaving the benzylic alcohol intact. The benzylic alcohol functionality is therefore not a strong nucleophile, and lacks the ability to displace the chlorine atom of the complex. This is illustrated in **Scheme 3.3**.
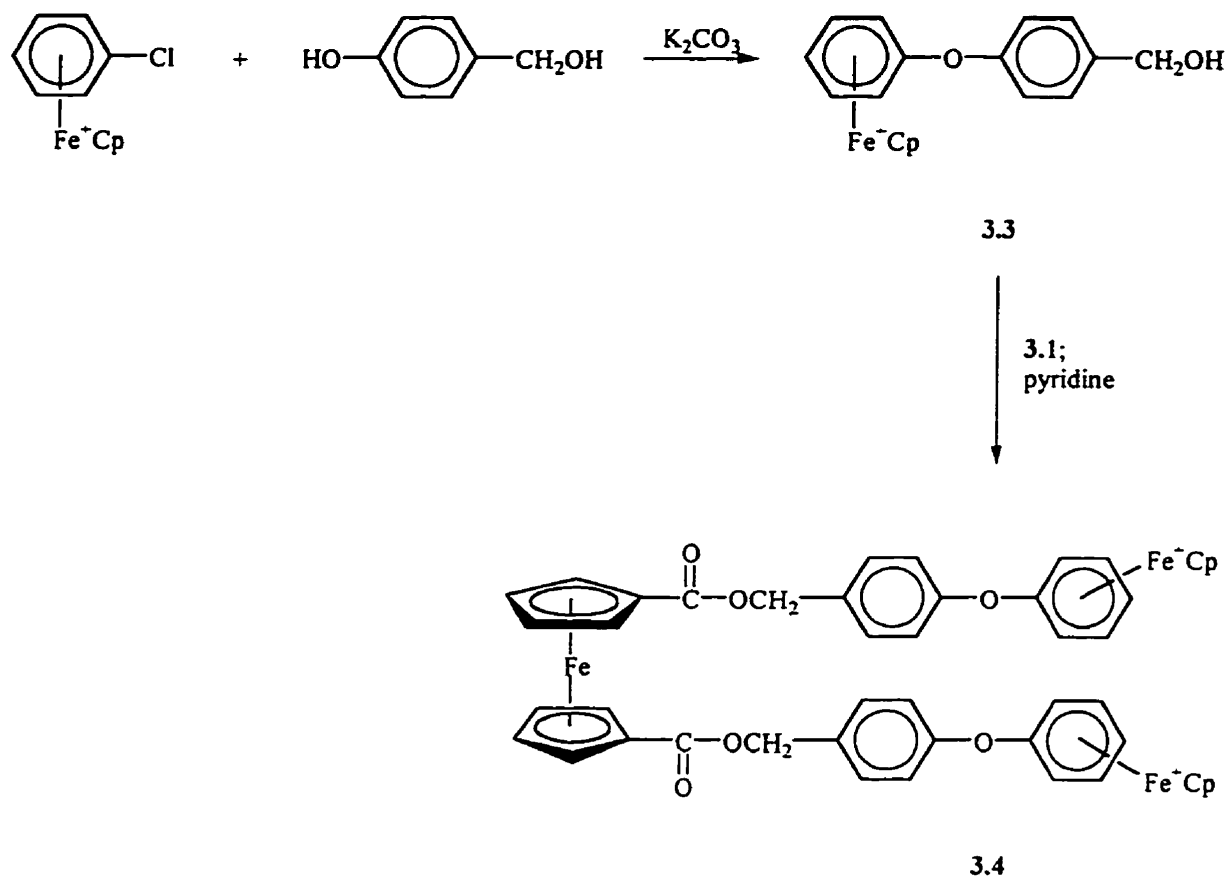
Scheme 3.3

Reaction of the complexed alcohol with the diacid chloride resulted in the preparation of the trimetallic ester. This was isolated as a light orange powder, intermediate between the characteristic deep orange of ferrocene and bright yellow of cyclopentadienyliron complexes.

Characterization of the alcohol-functionalized cyclopentadienyliron complex, along with the trimetallic ester, was accomplished through the use of ^1H and ^{13}C NMR. This may be illustrated in **Figures 3.6** through **3.9**. As well, this data is summarized in **Tables 3.3** and **3.4**.
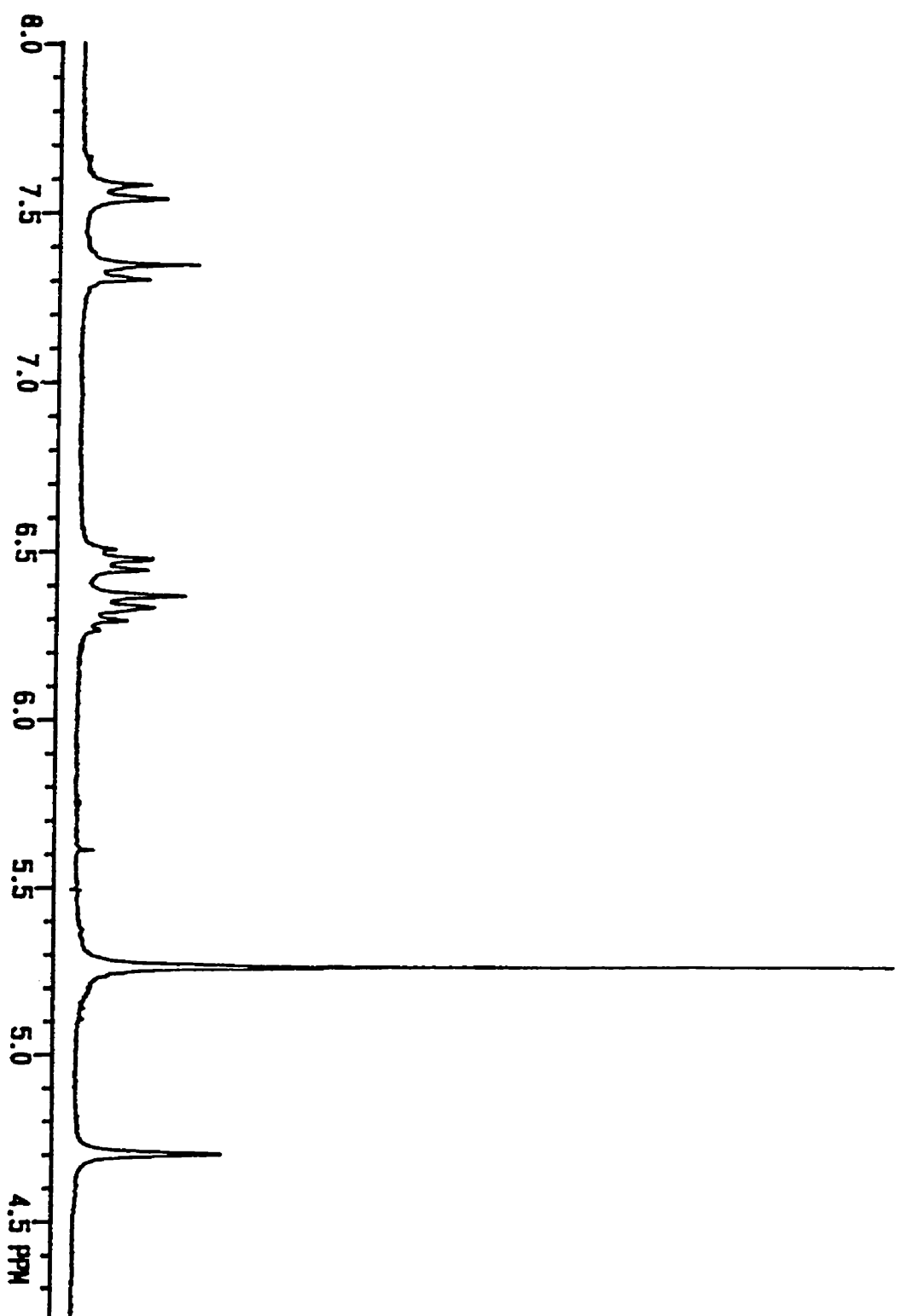
Figure 3.6: ^{1}H NMR spectrum of starting material 3.3.
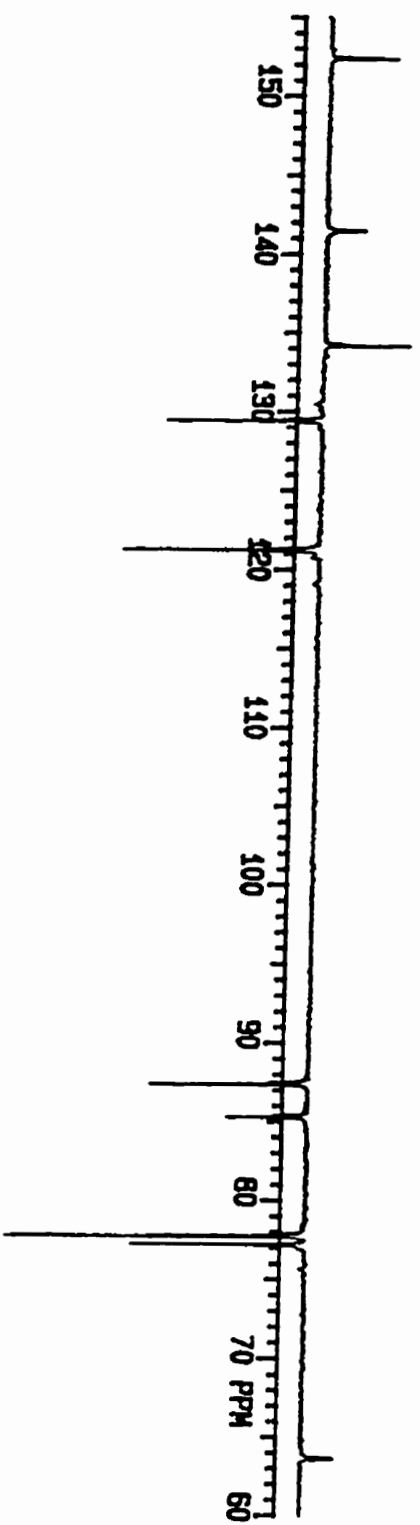
Figure 3.7: 13C NMR spectrum of starting material **3.3**.
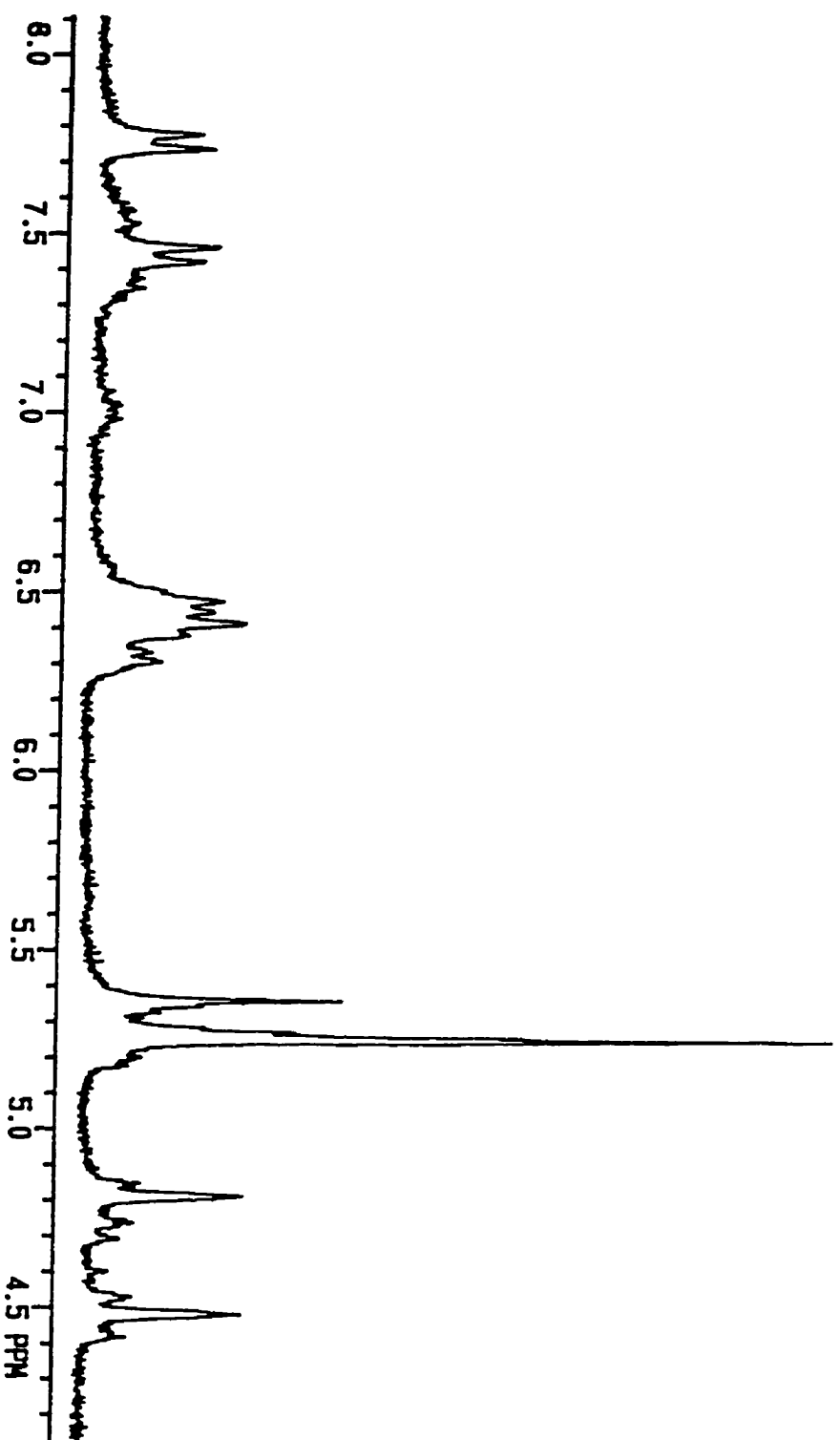
Figure 3.8: ^{1}H NMR spectrum of diester 3.4.
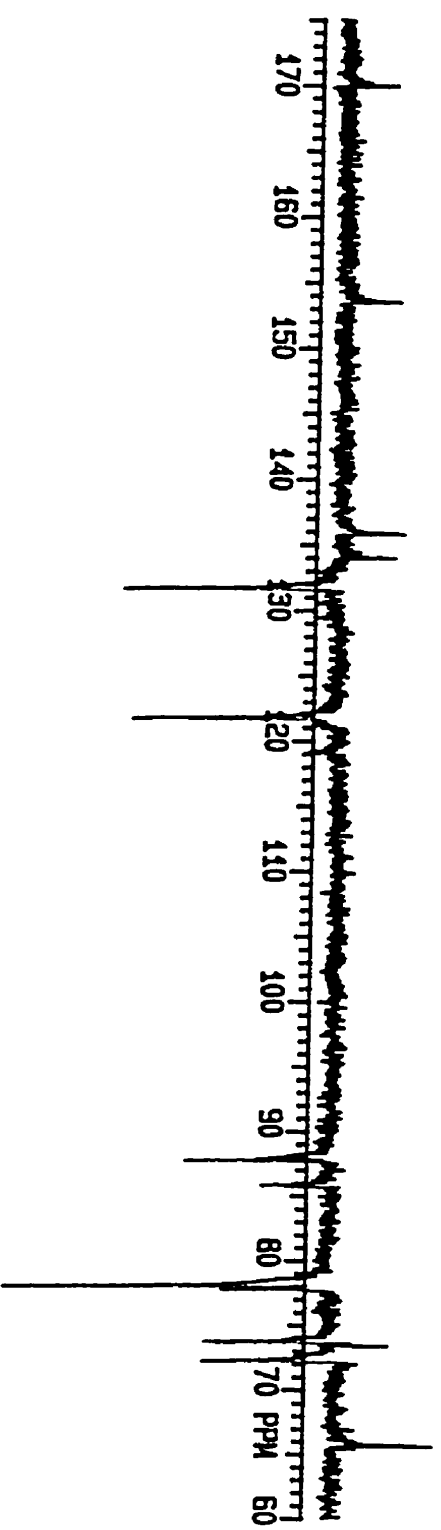
Figure 3.9: 13C NMR spectrum of diester 3.4.

Table 3.3: ^{1}H NMR spectral data for complexes **3.3** and **3.4**.

	δ (ppm), in acetone-d_6				
Complex	Yield (%)	Cp	Complexed ArH	Uncomplexed ArH	Other
3.3	83	5.26	6.36 (m, 10H)	7.32 (d, J 8.4, 2H) 7.56 (d, J 8.7, 2H)	4.70 (s, 2H, CH$_2$)
3.4	62	5.25	6.47 (m, 10H)	7.44 (d, J 7.8, 2H) 7.75 (d, J 8.3, 2H)	4.48 (m, 4H, FcH) 4.81 (m, 4H, FcH) 5.36 (s, 2H, CH$_2$)

Note: Coupling constants are in hertz.

Table 3.4: ^{13}C NMR spectral data for complexes **3.3** and **3.4**.

	δ (ppm), in acetone-d_6			
Complex	Cp	Complexed ArC	Uncomplexed ArC	Other
3.3	77.72	77.21, 85.34, 87.40, 134.24*	121.23, 129.44, 141.51*, 152.40*	63.65 (CH$_2$)
3.4	78.05	77.73, 85.81, 87.77, 133.99*	121.71, 131.63, 135.84*, 153.57*	65.66 (CH$_2$), 72.19 (FcC), 73.51* (FcC), 73.70 (FcC), 170.00 (CO)

Note: * denotes a quaternary carbon

Several changes in the NMR spectrum may be seen upon esterification of compound 3.3 with 1,1'-ferrocenedicarbonyl chloride. The first is a downfield shift of the CH_2 group, which appears at 5.36 ppm in the ester, as compared to 4.70 ppm in the starting complex. There is also a significant downfield shift for the uncomplexed aromatic protons, which are also quite close to the ester linkage. The complexed protons, being quite far from the ester linkage, experience only slight changes in their chemical shifts. The protons arising from the ferrocene nucleus appear at 4.48 and 4.81 ppm, which is a significant upfield shift from the diacid chloride starting material. This is again consistent with what would be expected upon esterification.

The same general trend is found in the ^{13}C NMR spectrum. Again, there is a downfield shift in the resonance attributed to the CH_2 group, from 63.65 to 65.66 ppm. The uncomplexed aromatic carbons show a similar shift. The cyclopentadienyl resonance, as well as the complexed carbons are at positions very similar to the starting material. This is due to the fact that they are quite far removed from the ester linkage. Again, the ferrocene resonances at 72.19 and 73.51 ppm are shifted upfield from 1,1'-ferrocenedicarbonyl chloride, the starting material.

In an attempt to further extend this methodology, the diether complex was prepared and reacted with the ferrocene-containing diacid chloride. This is shown in Scheme 3.4. The ^{1}H and ^{13}C NMR data collected for complexes 3.5 and 3.6 are shown in Figures 3.10 through 3.13, with the corresponding data summarized in Tables 3.5 and 3.6.
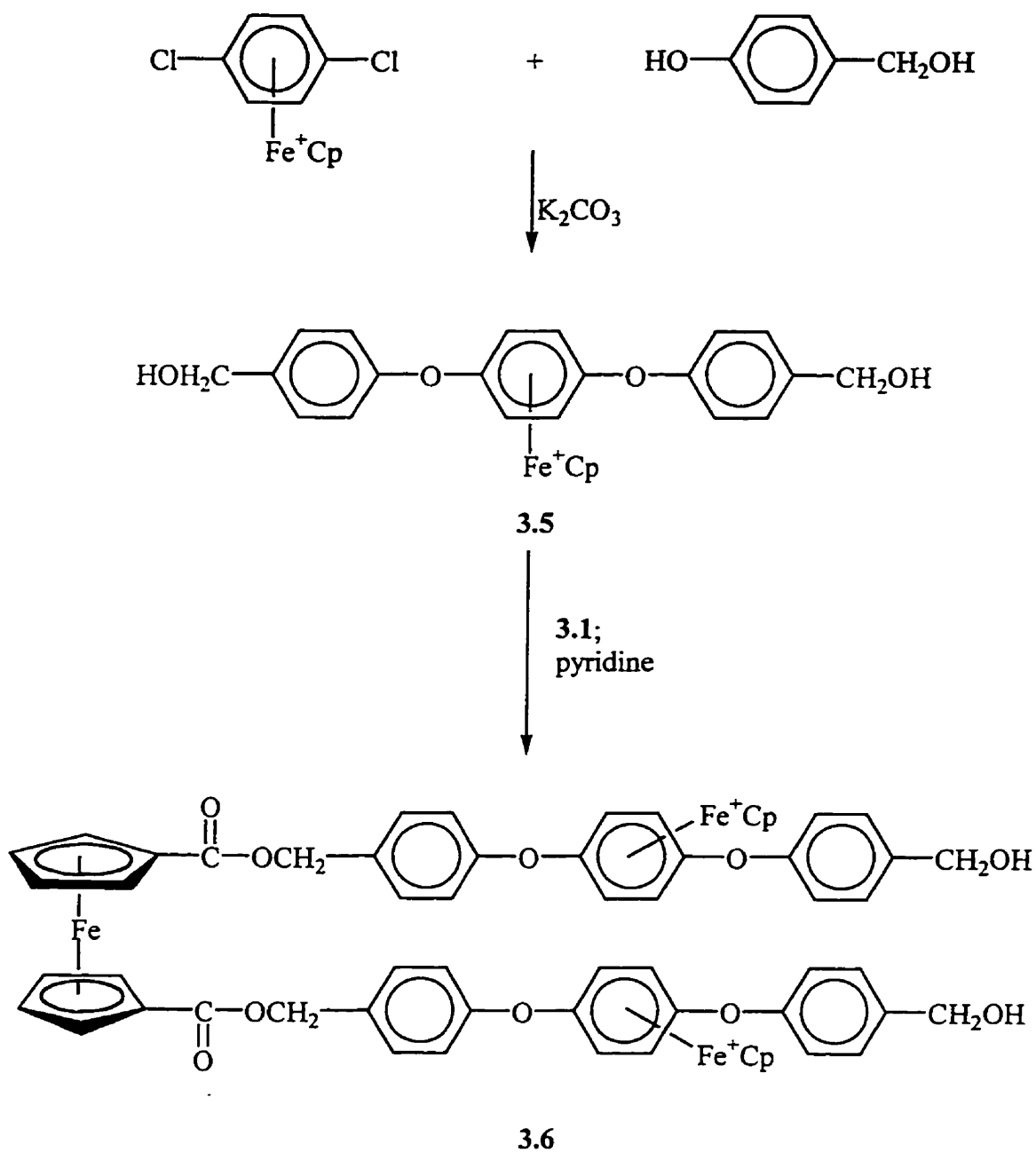
Scheme 3.4
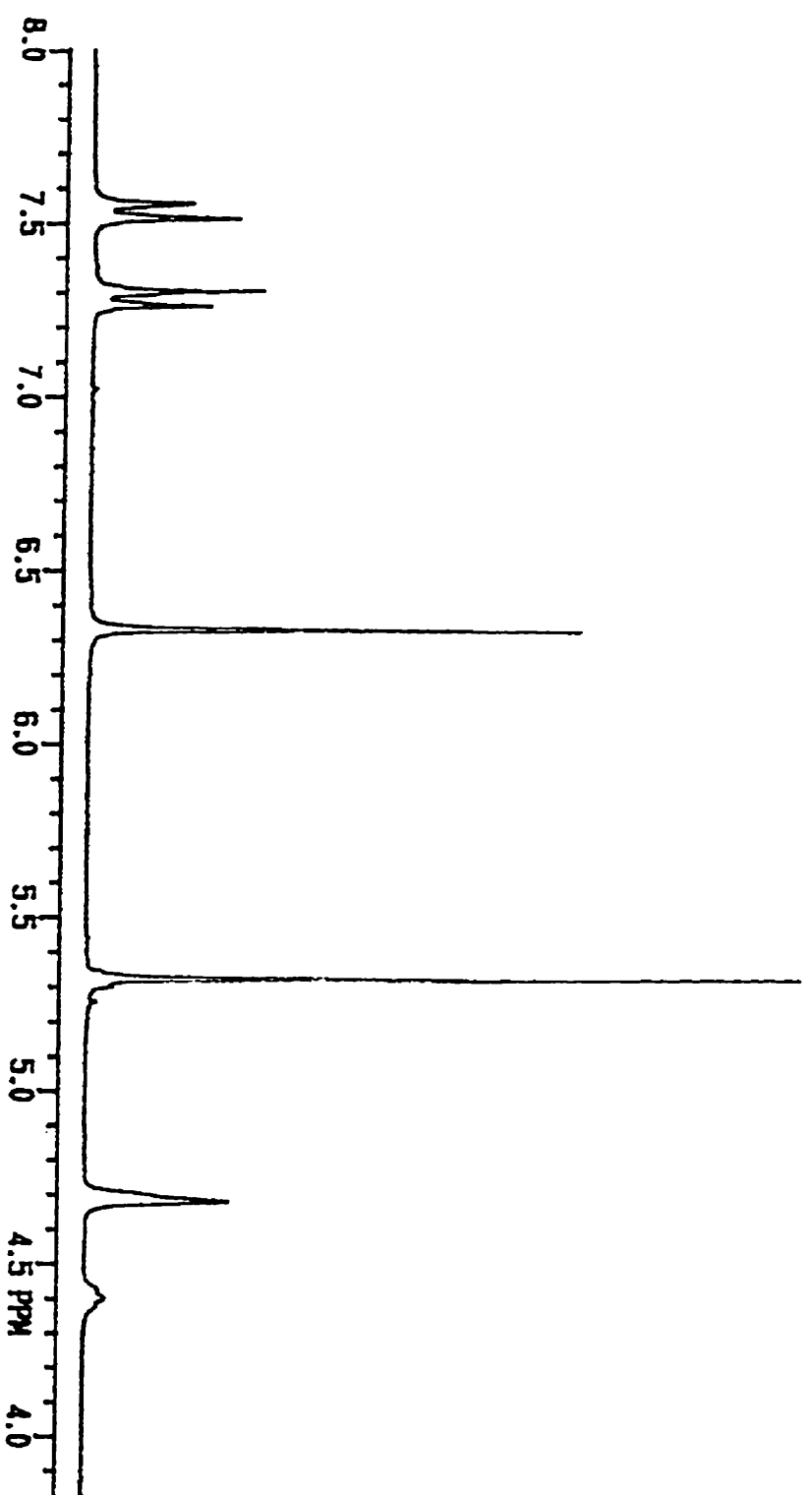
Figure 3.10: ^{1}H NMR spectrum of starting complex 3.5.
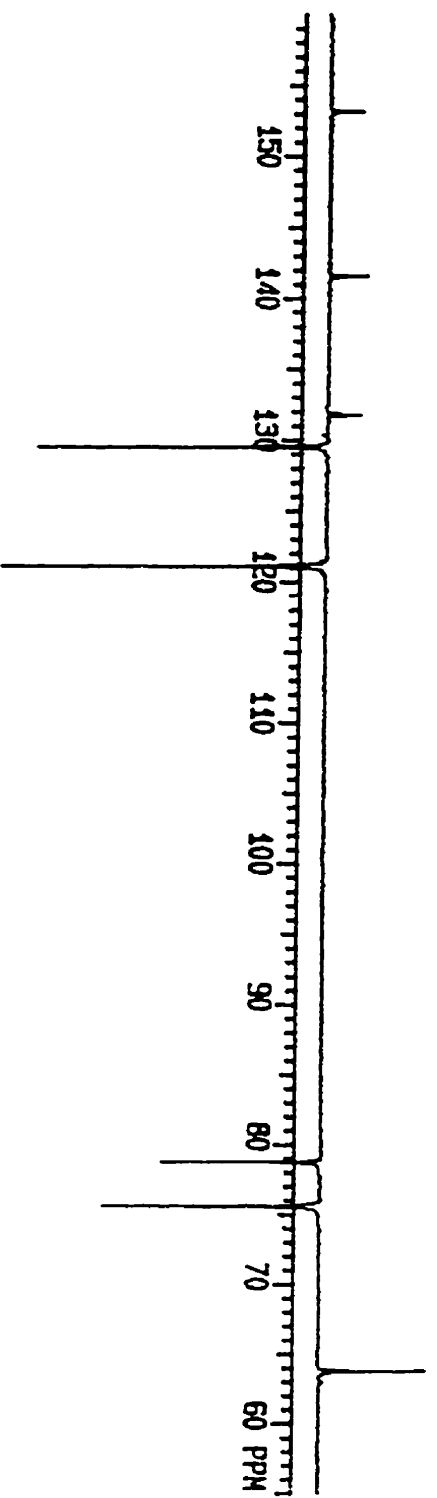
Figure 3.11: ^{13}C NMR spectrum of starting complex 3.5.
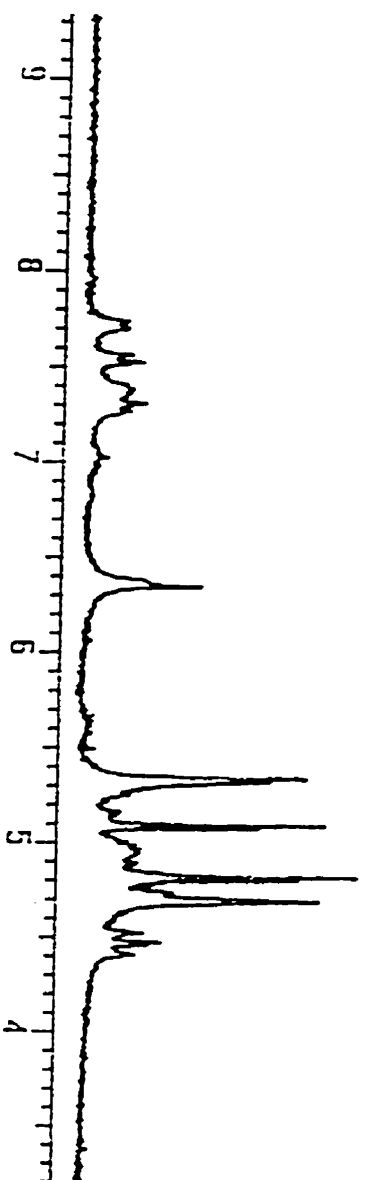
Figure 3.12: ^{1}H NMR spectrum of diester 3.6.
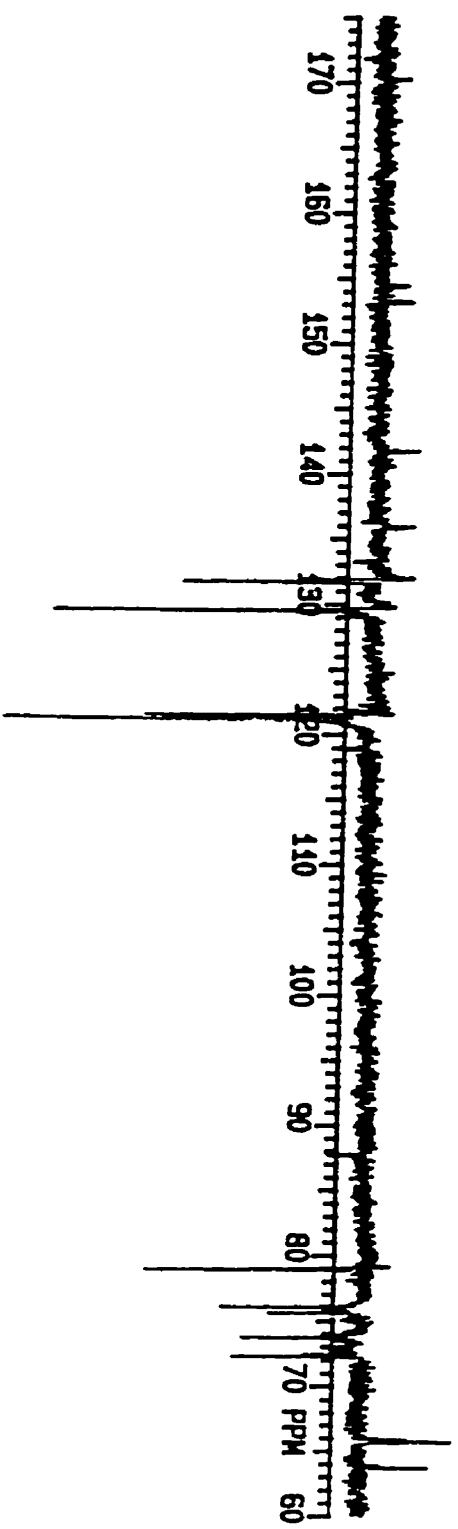
Figure 3.13: 13C NMR spectrum of diester 3.6.

Table 3.5: ^{1}H NMR data for complexes **3.5** and **3.6**

δ (ppm), in acetone-d_6					
Complex	Yield (%)	Cp	Complexed ArH	Uncomplexed ArH	Other
3.5	87	5.32	6.33 (s, 4H)	7.41 (dd, J 8.7, 8H)	4.40 (t, J 5.0, 1H, OH) 4.68 (s, 2H, CH_2)
3.6	49	5.33	6.34 (s, 8H)	7.72 (m, 4H) 7.54 (d, J 8.3, 4H) 7.29 (m, 8H)	4.46 (m, OH) 4.69 (CH_2) 4.81 (FcH) 5.08 (FcH) 5.29 (CH_2)

Note: Coupling constants are reported in hertz.

Table 3.6: ^{13}C NMR data for complexes 3.5 and 3.6

Complex	Cp	Complexed ArC	Uncomplexed ArC	Other
		δ (ppm), in acetone-d$_6$		
3.5	75.59	78.76, 131.83*	121.11, 129.53, 141.58*, 153.17*	63.77 (CH$_2$)
3.6	75.67	74.97, 78.92, 131.96*, 135.94*	121.16, 121.45, 129.57, 131.72, 141.74*, 153.18*, 154.41*	63.77 (CH$_2$), 65.78 (CH$_2$), 73.60 (FcC), 74.97 (FcC), 170.18 (CO)

Note: * denotes a quaternary carbon.

Upon obtaining this trimetallic ester which contained two terminal benzyl alcohol groups, we were interested in attempting to close the cycle, to form a macrocyclic trimetallic species. This was done by the reaction of another equivalent of 1,1'-ferrocenedicarbonyl chloride, again with pyridine as a catalyst in refluxing dichloromethane. This is shown in **Scheme 3.5**. The product which was isolated was difficult to characterize via ^1H NMR, due to the presence of what appeared to be multiple products, as shown in **Figure 3.14**. However, the ^{13}C NMR (**Figure 3.15**) clearly shows a symmetry about the molecule, with a single CH$_2$ peak appearing at 65.80 ppm, and only three uncomplexed aromatic carbons. This conflicting evidence may be explained by the formation of a closed ring, where the orientations of the pendant iron moieties are "locked" into place. Thus, the ^1H NMR spectrum shows the presence of two isomers, one where the iron moieties are cis to each other and another where they are trans.

Figure 3.14: ^{1}H NMR spectrum of macrocycle 3.7.
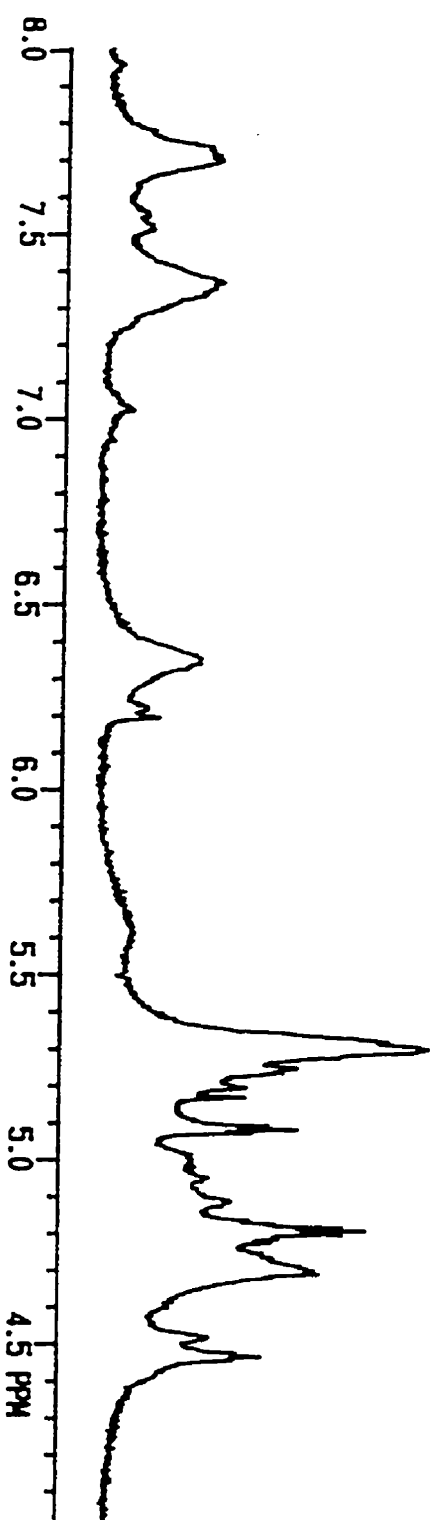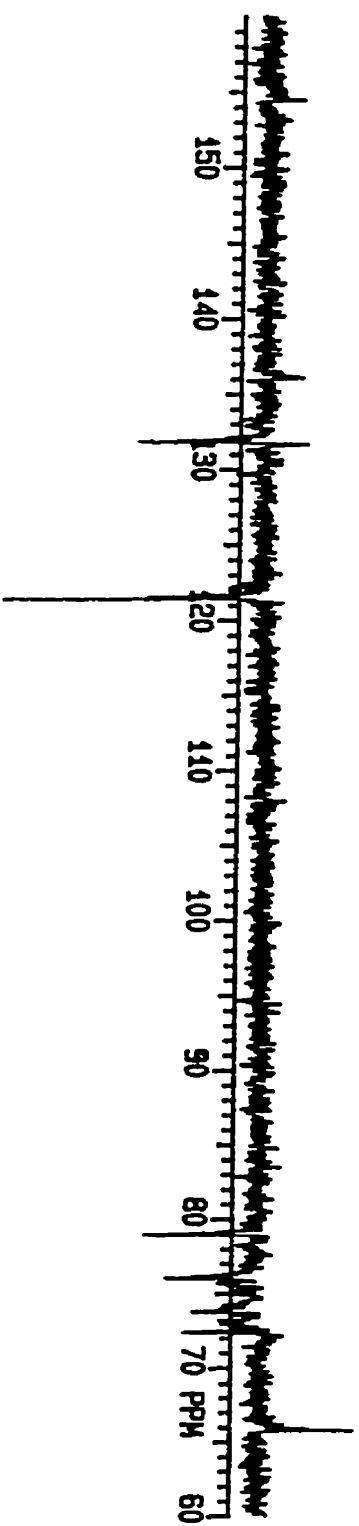
Figure 3.15: 13C NMR spectrum of macrocycle 3.7.

3.6

3.1
pyridine

3.7
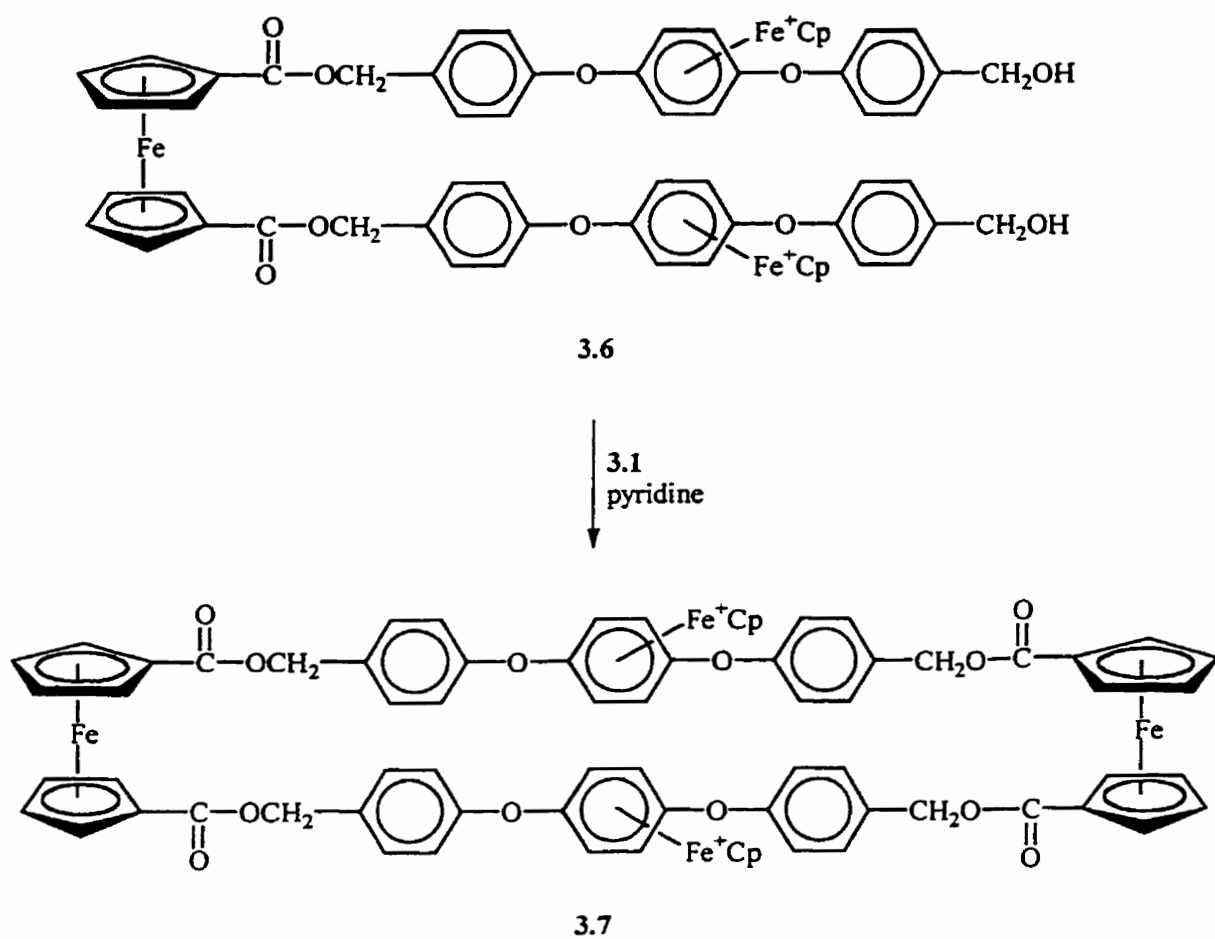
Scheme 3.5

The ^{13}C NMR spectral data, illustrating the symmetry of the molecule, may be seen in **Table 3.7**.

Table 3.7: ^{13}C NMR spectral data for complex 3.7.

δ (ppm), in acetone-d_6				
Complex	2Cp	Complexed ArC	Uncomplexed ArC	Other
3.7	79.03	76.13, 131.66*	121.49, 131.88, 136.05*, 154.46*	65.78 (CH_2), 72.43 (FcC), 73.79 (FcC)

Note: * denotes a quaternary carbon.

As of yet, the yield for this macrocycle has been extremely low (16%), thus precluding any attempts to photolyze this material. However, once this is accomplished, the ^1H NMR spectrum of the macrocycle should be much more straightforward, due to the presence of only one geometrical isomer.

Interestingly, when cyclic voltammetry was used in order to probe the behavior of these compounds in the presence of a potential, two one electron reductions were obvious, due to the two one-electron successive reductions of the cyclopentadienyliron moiety. However, no oxidation of the ferrocene moiety was observed. Indeed, a similar lack of oxidation was observed for the starting material, 1,1'-ferrocenedicarbonyl chloride. From this information, it may be presumed that this is due to the presence of two strong electron withdrawing substituents on the cyclopentadienyl rings of ferrocene. These groups act to impede oxidation by the reduction of electron density throughout the ring system.[82]

3.2.3 Coupling Using Dicyclohexylcarbodiimide

The resistance of the prepared trimetallic esters to oxidation indicated that our synthetic strategy had to be altered. 1,1'-Ferrocenedicarbonyl chloride could not be used as the starting material to form amides and esters, due to the close proximity of the electron withdrawing carbonyl group to the ferrocene nucleus. 1,1'-Ferrocenediacetic acid features a carboxylic acid functionality separated from the nucleus by one methylene unit; however, although the synthesis of the diacid chloride has been reported once in the literature, we have experienced difficulty in the reproduction of this work.[114] Indeed, except for this one isolated report, there has been no mention of the preparation or use of 1,1'-ferrocenediacetyl chloride. Additionally, we have been unable to synthesize acid chlorides from benzoic acids complexed to the cyclopentadienyliron moiety, due to the presence of strong electron withdrawing groups on the ring. Therefore, our attention shifted to the use of coupling reagents.

Dicyclohexylcarbodiimide, or DCC, is one of the most popular coupling agents, due both to its efficiency and the ease of its use.[115] DCC is known to form esters and amides in high yields, often at room temperature.[116] As well, DCC is quite insoluble in common solvents such as dichloromethane and diethyl ether, which makes the isolation of the reaction products quite straightforward. Due to these advantages, DCC is commonly used in peptide synthesis,[1] and in the preparation of phenolic esters, which are quite difficult to prepare by other methods.[116]

In order to determine whether DCC could act as a coupling agent between η^6-(benzoic acid)-η^5-cyclopentadienyliron(II) hexafluorophosphate and an alcohol, benzyl alcohol and the complex (prepared via the procedure reported by Nesmeyanov *et. al.*)[53] were combined, as shown in **Scheme 3.6**.
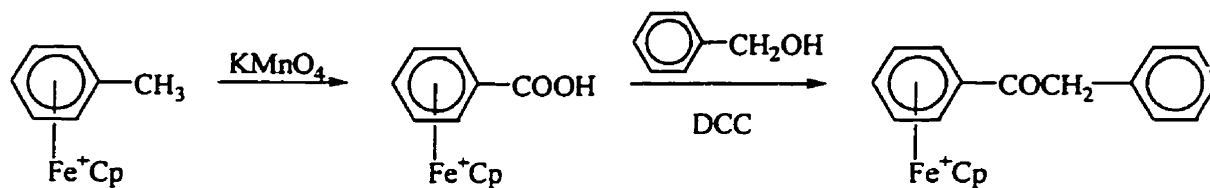
3.8

Scheme 3.6

^{1}H and ^{13}C NMR data were collected for the resulting complex **3.8**, and these spectra are illustrated in **Figures 3.16** and **3.17**. The numerical data from these figures is summarized in **Tables 3.8** and **3.9**.

Table 3.8: ^{1}H NMR spectral data for complex **3.8**.

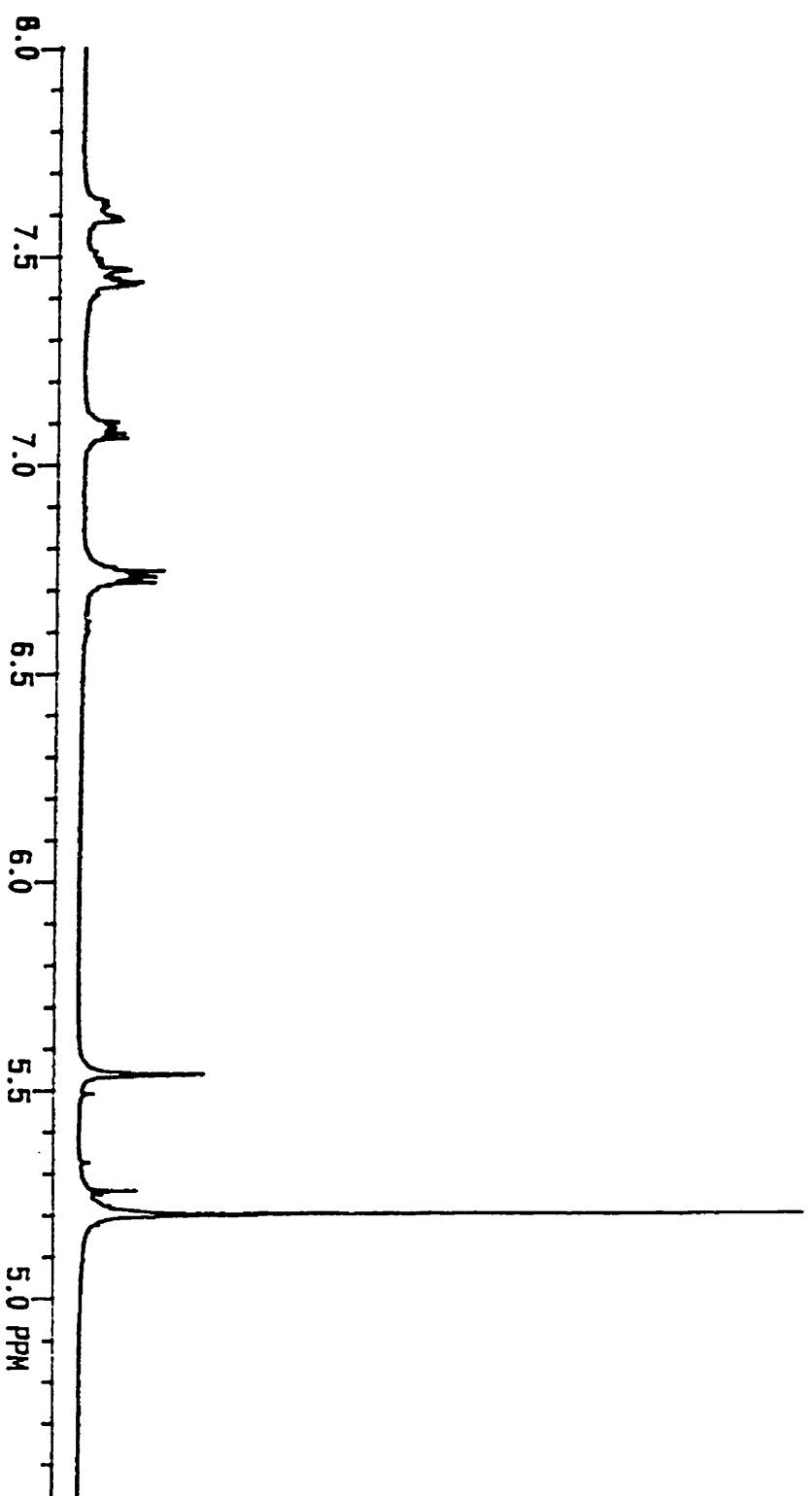| δ (ppm), in acetone-d_6				
Complex	Yield (%)	Complexed ArH	Uncomplexed ArH	Other
3.8	28	6.73 (m, 3H) 7.08 (m, 2H)	7.45 (m, 3H) 7.61 (m, 2H)	5.20 (s, 5H, Cp) 4.54 (s, 2H, CH$_2$)

Note: Coupling constants are in hertz.
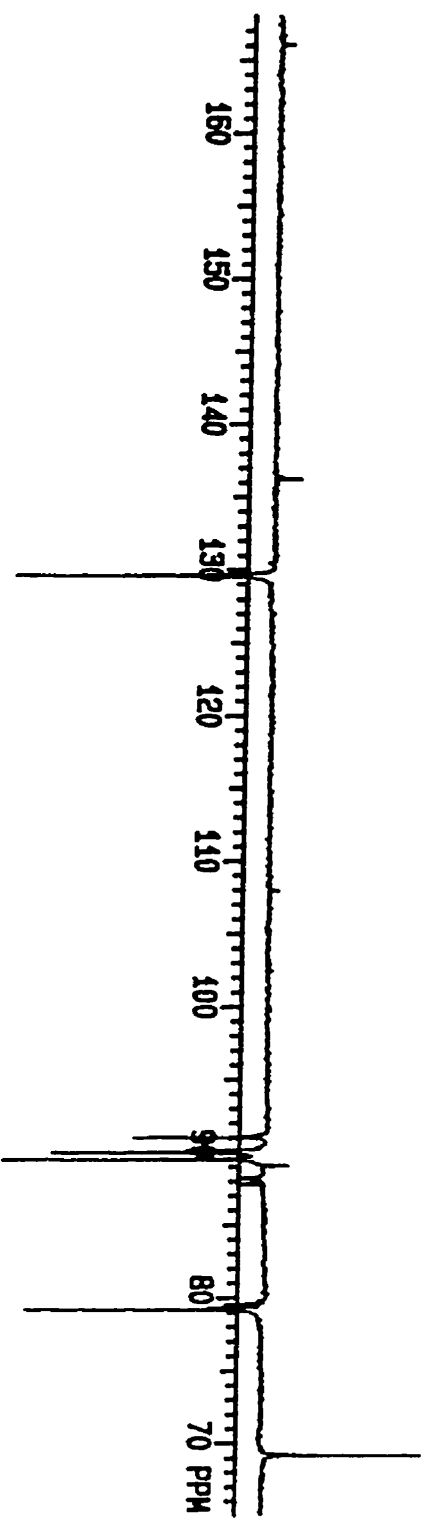
Figure 3.16: ^{1}H NMR spectrum of ester 3.8.

Figure 3.17: 13C NMR spectrum of ester 3.8.

Table 3.9: ^{13}C NMR spectral data for complex **3.8.**

δ (ppm), in acetone-d_6			
Complex	Complexed ArC	Uncomplexed ArC	Other
3.8	89.04*, 89.48, 90.03, 91.01	129.55, 129.61, 136.27*	69.19 (CH_2) 79.20 (Cp) 166.00 (CO)

Note: * denotes a quaternary carbon.

The downfield shift of the resonance of the CH_2 group indicates that esterification has taken place. It may be seen that the location of the peak due to the CH_2 group in both the ^1H and ^{13}C NMR spectra is in a very similar location in complexes **3.4, 3.6, 3.7** and **3.8**. As well, the presence of the resonance for the carbonyl group at 166.00 ppm is quite obvious in the ^{13}C NMR spectrum. The uncomplexed carbons and protons also exhibit a downfield shift from their positions in benzyl alcohol.

Attempts to synthesize esters from ferrocenyl diols have thus far been unsuccessful. Ferrocenes containing hydroxyl groups alpha to the cyclopentadienyl ring suffer from the α-metallocenylcarbonium ion effect, in which a positive charge is stabilized by the presence of the electron rich cyclopentadienyl ring.[117,118] It is also thought that these alcohols may be quite sterically hindered due to the close proximity of the ferrocene nucleus. Thus these compounds are quite unreactive towards esterification. We have also attempted to react 1,1'-bis(β-hydroxyethyl)ferrocene, which was synthesized according to the method reported by Gonsalves and his co-workers,[91] with the complexed acid. In this compound, the two hydroxyl groups are separated from the ferrocene nucleus by an

additional methylene unit, in an attempt to minimize the α-metallocenylcarbonium ion effect. However, here again we find little evidence of reaction, due to decomposition of the ferrocene-containing diol.

However, the preparation of cyclopentadienyliron complexed esters via coupling with DCC is interesting in its own right, even if it did not allow for the incorporation of ferrocene subunits. Although the ethyl ester of the complexed carboxylic acid has been synthesized by reflux in an acidified ethanol solution,[72] coupling via DCC does not require the evaporation of the alcohol after the reaction has taken place. Thus esters of high boiling alcohols, such as benzyl alcohol, may be prepared under mild conditions.

3.3 Conclusion

From the previous discussion, it may be seen that it is possible to synthesize trimetallic species containing both the cyclopentadienyliron moiety and ferrocene. However, in order for ferrocene to exhibit oxidative behavior, the ferrocene nucleus must remain electron rich. The presence of electron withdrawing groups on the cyclopentadienyl rings acts to decrease electron density, and thus inhibits the oxidation of the ferrocene moiety. However, this synthetic strategy may be used to design unique materials, such as the closed macrocycle 3.7.

One major hindrance to the preparation of amides and esters containing the cyclopentadienyliron moiety is that it is difficult to synthesize acid chlorides from complexed acids due to the electron withdrawing ability of the metal moiety. This may be overcome, however, through the use of a coupling agent such as dicyclohexylcarbodiimide (DCC). DCC may be used to synthesize esters from η^6-(benzoic acid)-η^5-cyclopentadienyliron(II) hexafluorophosphate without requiring acid catalysis or a large excess of alcohol. Therefore, this methodology may allow for the synthesis of a variety of

different metallated compounds containing ester linkages, which may be combined with previously established methodology for the synthesis of amines, ethers and thioethers.

3.4 Experimental

3.4.1 General Methods

The general experimental methods are as described previously in Section 2.4.1.

3.4.2 Starting Materials

Pyridine, 4-hydroxybenzyl alcohol, benzyl alcohol, dicyclohexylcarbodiimide (DCC) and ferrocene are all commercially available (Aldrich) and were used without further purification. As well, N,N-dimethylformamide and dichloromethane were used as solvents (HPLC grade) and were also not purified further. Ligand exchange materials were synthesized as discussed previously.

3.4.3 Preparation of Compound **3.2**

0.25 mmol of the complexed aniline was placed in a 25 mL round bottom flask. The complex was then dissolved in 10 mL of dichloromethane, and 0.5 mmol of both 1,1'-ferrocenedicarboxylic acid and potassium carbonate was added. The mixture was then allowed to reflux for thirty minutes, under a nitrogen atmosphere. The reaction mixture, changed in colour from dark brown to light orange, was then allowed to cool to room temperature, and was added to a 10% HCl (by volume) solution. A concentrated solution of ammonium hexafluorophosphate was then added. The aqueous phase was then extracted with dichloromethane until the extracted layer was quite pale in colour. The

organic phase was washed once with the dilute acid solution, and then dried over anhydrous magnesium sulfate. Gravity filtration, followed by evaporation under reduced pressure left an orange oil, which was washed liberally with diethyl ether.

3.4.4 Preparation of Complex 3.3

1 mmol of the starting complex was placed in a 50 mL round bottom flask along with 1.2 mmol of 4-hydroxybenzyl alcohol and 1.5 mmol of potassium carbonate. The mixture was dissolved in 10 mL of DMF and stirred under nitrogen for sixteen hours. After this time, the mixture was poured into approximately 20 mL of a 10% HCl (by volume) solution. This was followed by the addition of a concentrated solution of ammonium hexafluorophosphate. The aqueous layer was extracted several times with dichloromethane, until it was no longer a brilliant yellow. The organic phase was then washed liberally with water, dried over anhydrous magnesium sulfate, and gravity filtered. Evaporation of the solvent under reduced pressure resulted in a brown oil.

3.4.5 Preparation of Complex 3.5

1 mmol of complex along with 2.4 mmol of 4-hydroxybenzyl alcohol and 2.5 mmol of potassium carbonate were combined in a 50 mL round bottom flask. The contents were dissolved in 10 mL of DMF, and allowed to stir under nitrogen for sixteen hours. After this time, the mixture was poured into a 10% HCl solution, followed by the addition of a concentrated ammonium hexafluorophosphate solution. Extraction of the aqueous phase with dichloromethane left a brown organic phase and a faintly yellow aqueous phase. Extensive washing of the organic phase with water helped to remove any DMF remaining from the reaction mixture. Finally, the organic phase was dried over anhydrous

magnesium sulfate, and gravity filtered. Evaporation of the solvent under reduced pressure resulted in the formation of a brown oil, which was redissolved in a minimal amount of acetone and added dropwise to cold diethyl ether. The resulting yellow precipitate was collected in a crucible and dried.

3.4.6 Preparation of diesters 3.4 and 3.6

0.25 mmol of 1,1'-ferrocenedicarbonyl chloride and 0.50 mmol of the complexed alcohol, along with 0.5 mmol of pyridine were placed in a 25 mL round bottom flask. 5 mL of dichloromethane were added. The mixture was allowed to stir under nitrogen for four hours. At the end of this time, the mixture was poured into a 10% HCl solution. A concentrated solution of ammonium hexafluorophosphate was added. The organic layer was separated from the aqueous phase, which was extracted further with dichloromethane until the extracted layer was colourless. The combined organic phases were then washed once more with the dilute acid solution and then dried over anhydrous magnesium sulfate. Gravity filtration gave a clear orange solution, from which the solvent was removed under reduced pressure. When there was approximately 2 mL of solvent remaining, diethyl ether was added to the solution to cause the precipitation of an orange solid, which was collected on a crucible and dried.

3.4.7 Preparation of Macrocycle 3.7

0.04 mmol of diester **3.6** was placed in a 25 mL round bottom flask along with 0.04 mmol of 1,1'-ferrocenedicarbonyl chloride. These two components were dissolved in 5 mL of dichloromethane, and 0.01 mL of pyridine was added. The mixture was allowed to reflux for four hours. The flask was then cooled to room temperature, and the contents were poured into a 10% HCl solution. The flask was washed liberally with dichloromethane, which was then used to extract the aqueous layer. When the aqueous layer was only a pale yellow, the deep orange organic phase was washed once more with the dilute acid, and dried over magnesium sulfate. Gravity filtration, followed by vacuum distillation of the solvent left an orange oil, which was redissolved in acetone and added dropwise to cold ether. The resulting orange precipitate was collected in a fine crucible.

3.4.8 Esterification reaction using DCC

1 mmol of η^6-(benzoic acid)-η^5-cyclopentadienyliron(II) hexafluorophosphate was combined with 1.1 mmol of DCC in a 50 mL round bottom flask. 5 mL of DCM was added to the flask, which caused the formation of a yellow suspension. 1.2 mmol of benzyl alcohol was then added dropwise to the solution. After about 30 minutes, the reaction mixture appeared "gummy", and another 5 mL of dichloromethane was added.

After twenty four hours, the reaction mixture was filtered. The residue was rinsed well with dichloromethane until it was off-white in colour. The solvent of the filtrate was then removed under reduced pressure, leaving a yellow oil which was redissolved in a small amount of acetone. Addition of this dropwise to cold ether caused the formation of a brilliant yellow precipitate, which was collected on sintered glass.

4.0 References

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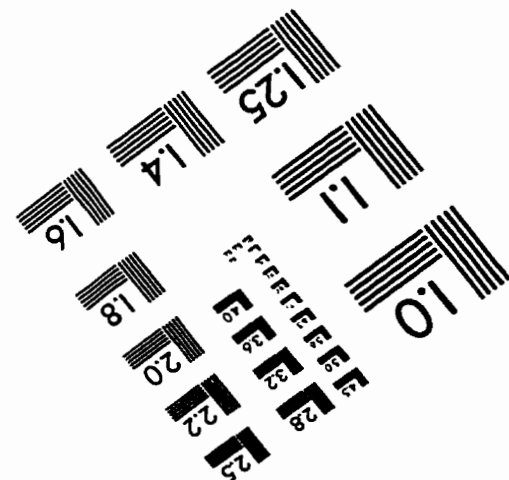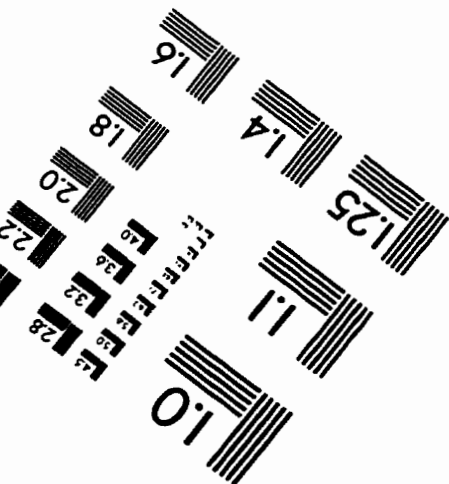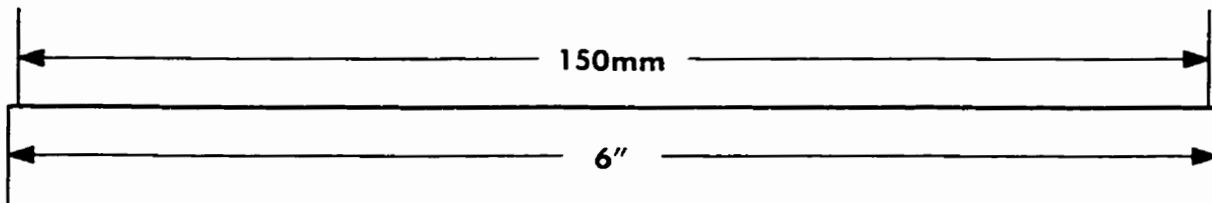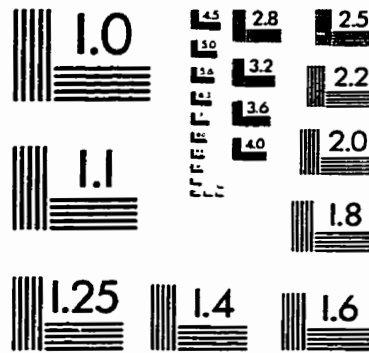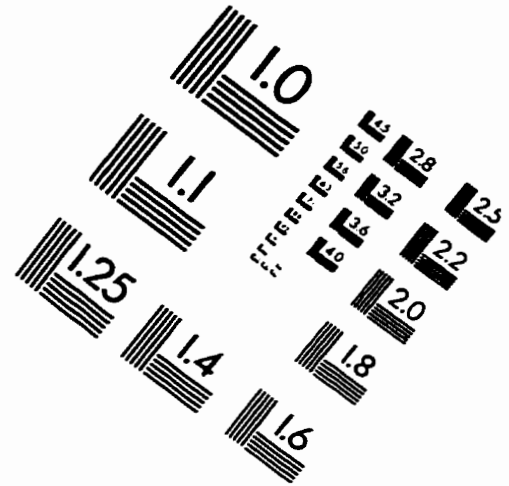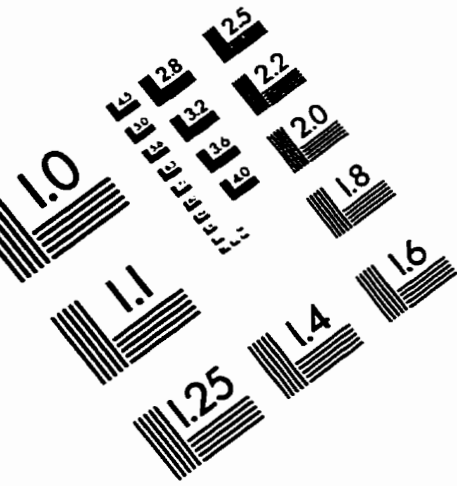
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