

Synthesis and reactivity of arenes coordinated to cyclopentadienyliron cations

Alaa S. Abd-El-Aziz *, Shelly Bernardin

Department of Chemistry, The University of Winnipeg, Winnipeg, Manitoba, Canada R3B 2E9

Received 18 March 1999; accepted 10 June 1999

Contents

Abstract	220
1. Introduction	220
2. Monocyclopentadienyliron complexes of arenes	221
2.1 Synthesis via ligand exchange reactions	221
2.1.1 Conventional methods	221
2.1.2 Microwave method	222
2.2 Oxidation of ring substituents	224
2.2.1 Anilines	224
2.2.2 Toluenes	224
2.3 Arene complexes as electrophiles	225
2.3.1 Nucleophilic substitution	226
2.3.1.1 Reactions with carbon nucleophiles	226
2.3.1.2 Reactions with oxygen and sulfur nucleophiles	228
2.3.1.3 Reactions with nitrogen nucleophiles	230
2.3.2 Nucleophilic addition	232
2.3.2.1 Hydride	232
2.3.2.2 Carbanions	233
2.4 Deprotonation of arene substituents	235
2.5 Decomplexation reactions	239
3. Di- and polycyclopentadienyliron complexes of arenes	242
3.1 Synthesis	242
3.1.1 Ligand exchange reactions	242
3.1.2 Stepwise synthesis	243
3.1.3 Polymerization reactions	244
3.2 Functionalization reactions	247
3.3 Cleavage of etheric bonds in diiron species	247

* Corresponding author. Tel.: +1-204-7869335; fax: +1-204-7752114.

E-mail address: abdelaziz@uwinnipeg.ca (A.S. Abd-El-Aziz)

4. Characterization of arenes coordinated to cyclopentadienyliron moieties	247
5. Chemical and electrochemical reduction of arene complexes.	251
6. Applications of arene complexes in organic and polymer synthesis.	253
6.1 Heterocycles	254
6.2 Macrocycles	254
6.3 Polymer building blocks	255
7. Conclusion	260
References	260

Abstract

Over the past few decades, there has been tremendous interest in the chemistry of arenes coordinated to transition metal moieties due to their applications in the fields of organic and polymer synthesis. The electrophilicity of coordinated arenes allows for reactions with a number of carbon-, oxygen-, nitrogen- and sulfur-containing nucleophiles. This review describes the synthesis and reactivity of both mono- and polyiron arene complexes. Spectroscopic and electrochemical methods for the characterization of these coordination compounds are presented. The important synthetic applications of arene cyclopentadienyliron complexes are also described. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Cyclopentadienyliron; Arenes; Nucleophilic substitution; Nucleophilic addition

1. Introduction

Coordination of transition metal moieties to arenes has been extensively researched over the past three decades, due to their role as precursors in organic synthesis [1–11]. The complexation of arenes to tricarbonylchromium [12–33], tricarbonylmanganese [34–57], cyclopentadienylruthenium [5,10,58], pentamethylcyclopentadienylruthenium [5,10,59–64] and cyclopentadienyliron [7,65–67] moieties activates the aromatic ring towards nucleophiles due to the electron-withdrawing nature of the metallic moieties. Kinetic studies by Knipe et al. have demonstrated that the activation of metal-complexed halobenzenes towards nucleophilic reactions increases in the following order: $(\text{CO})_3\text{Cr} \ll \text{CpRu}^+ \text{ ca. } \text{CpFe}^+ < (\text{CO})_3\text{Mn}^+$ [68,69]. It was also found that the chlorine atom of the chlorobenzene cyclopentadienyliron complex has a mobility comparable to 2,4-dinitrochlorobenzene [70–73].

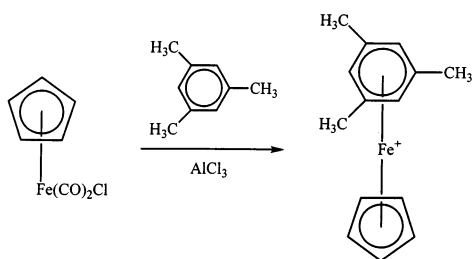
The aim of this review is to survey recent literature involving the synthesis and characterization of aromatic complexes of cyclopentadienyliron. This comprehensive overview will include the application of these coordination compounds in the preparation of organic and polymeric materials.

2. Monocyclopentadienyliron complexes of arenes

2.1. Synthesis via ligand exchange reactions

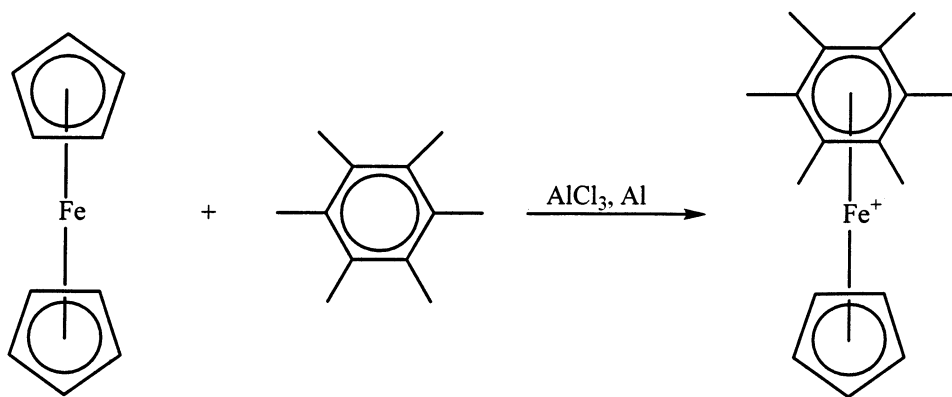
2.1.1. Conventional methods

The first synthesis of an arene coordinated to the cyclopentadienyliron moiety was reported in 1957 by Coffield et al., in which cyclopentadienyliron dicarbonyl chloride was reacted with mesitylene as shown in Scheme 1 [74,75]. Hydrolysis of the reaction mixture, followed by the addition of potassium iodide resulted in the formation of the η^6 -mesitylene- η^5 -cyclopentadienyliron(II) iodide salt. Although this reaction is still used for the preparation of pentamethylcyclopentadienyliron complexes [76,77], it does not allow for the complexation of a wide variety of arenes.



Scheme 1.

In 1963, Nesmeyanov reported the preparation of arene cyclopentadienyliron complexes from commercially available ferrocene in the presence of a Lewis acid (Scheme 2) [78,79]. This reaction was shown to be much more general, and has since allowed for the synthesis of several hundred different cyclopentadienyliron complexes [65,80]. The ligand exchange of ferrocene may be used to generate the complexes of benzene [78,81,82], alkylbenzenes [78,81–87], arylbenzenes [78,85,88–



Scheme 2.

93], halobenzenes [84,85,94,95], benzylethers [84,96,97], benzylamides [84,85], polycyclic compounds [85,88–90,98–112] and heterocycles [93,103,113].

The effects of changing the reactant ratios, catalysts, and reaction conditions have all been previously reviewed [65–67]. An excess of arene is typically used, particularly when the arene is polynuclear. As temperatures of 80–165°C are required, solid arenes may be melted [81], or an inert liquid such as decalin may be used as the solvent [114]. Higher yields may be obtained if low boiling point solvents such as cyclohexane, methylcyclohexane and heptane are used [87,89,90]. The yield of the ligand exchange reaction with ferrocene varies considerably with the nature of the arene. Electron-withdrawing substituents act to impede the reaction by coordinating to the Lewis acid, while benzenes containing electron-donating substituents form complexes in higher yields and under milder reaction conditions.

Current attention has focused on the modification of the reaction conditions for ligand exchange. Dyson and co-workers [115] have studied the effects of using an ionic liquid system consisting of 1-butyl-3-methylimidazolium chloride/aluminum chloride at lower temperatures than traditional methods. Results from this investigation revealed that higher yields were obtained under these milder conditions.

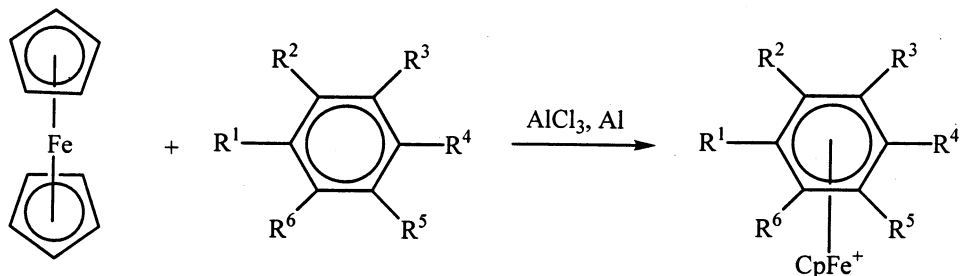
Ligand exchange reactions may also be performed with arene cyclopentadienyliron(II) complexes as starting materials. The starting arene (usually *p*-xylene) must be more acidic than the ligand which replaces it [100,116–119]. Ligand exchange is initiated by visible light, and must be carried out in a non-nucleophilic solvent. The excited complex liberates the original η^6 -arene ligand, which is then replaced by the more electron-rich ligand present in solution [117,120,121]. This method generally gives very high yields, although prior formation of a cyclopentadienyliron complexed arene by the ligand exchange of ferrocene is required.

Azogu reported a unique application of the ligand exchange of ferrocene with crude oil [122,123]. A complex mixture of aromatic hydrocarbons in petroleum was subjected to ligand exchange to form the cyclopentadienyliron derivatives. These complexes were then separated using thin-layer chromatography, and pyrolytic mass spectral analysis was used to determine the identities of the various aromatic substituents in the crude oil mixture.

2.1.2. Microwave method

Dabirmanesh et al. have illustrated that microwave dielectric heating may be used to induce the ligand exchange of ferrocene [124–126]. These reactions are complete within minutes, and in many cases result in substantially higher yields than traditional methods, although on a much smaller scale. In addition, this reaction allows for the preparation of complexes that have not been attainable via traditional methods (Scheme 3). Bromobenzene, for example, dehalogenates readily under the standard conditions required for the ligand exchange of ferrocene. However, when the same reagents are reacted in a conventional microwave oven, the complex is isolated in a 32% yield. The fluorobenzene complex has been

prepared without microwave dielectric heating in 10% yield [84], however, this may be increased to 47% using a microwave oven. Other new complexes which could not be synthesized using other methods include arenes with bulky alkyl substituents, phenols, benzyl alcohol and benzaldehyde.



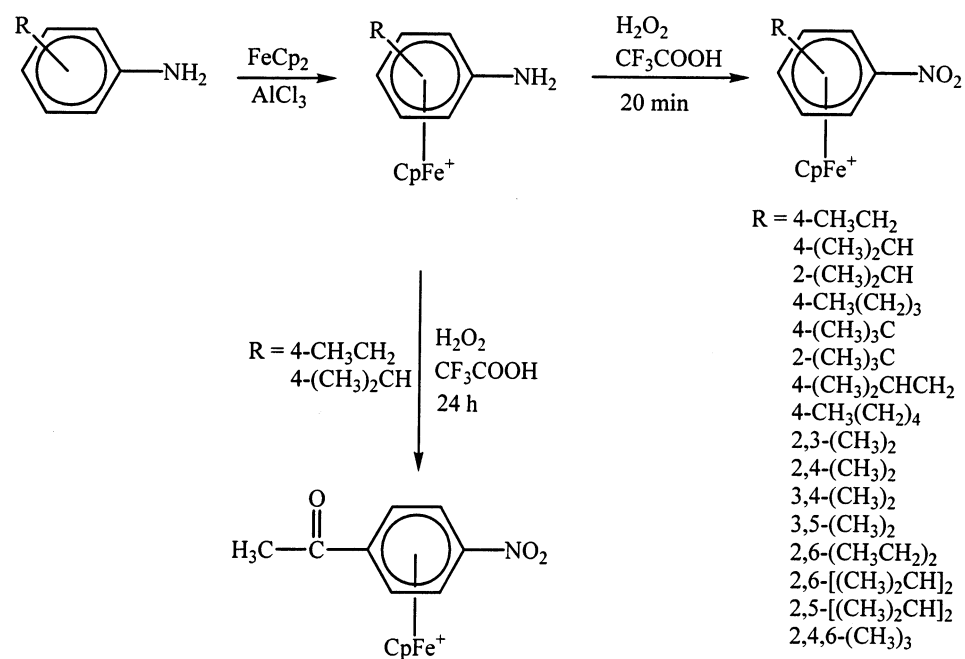
R ¹	R ²	R ³	R ⁴	R ⁵	R ⁶
Br	H	H	H	H	H
F	H	H	Cl	H	H
F	Cl	H	H	H	H
F	CH ₃	H	H	H	H
F	H	CH ₃	H	H	H
F	H	H	NH ₂	H	H
Cl	H	H	NH ₂	H	H
CH ₂ OH	H	H	H	H	H
CHO	H	H	H	H	H
Cl	H	H	CH ₂ OH	H	H
OH	H	H	H	H	H
C(CH ₃) ₃	H	H	CH ₃	H	H
C(CH ₃) ₃	H	C(CH ₃) ₃	H	H	H
C(CH ₃) ₃	H	H	C(CH ₃) ₃	H	H
C(CH ₃) ₃	H	C(CH ₃) ₃	H	C(CH ₃) ₃	H
OH	CH ₃	H	CH ₃	H	CH ₃

Scheme 3.

2.2. Oxidation of ring substituents

2.2.1. Anilines

The electrophilicity of arenes complexed to the cyclopentadienyliron moiety makes them susceptible to attack by nucleophiles. To exploit nucleophilic aromatic substitution as a synthetic reaction, these arenes must contain good leaving groups. Halobenzenes may be readily complexed to the cyclopentadienyliron moiety by the ligand exchange of ferrocene; however, the demand for better leaving groups has required the preparation of complexes containing substituents with stronger electron-withdrawing capacities. Coordinated nitroarenes may be prepared via the oxidation of their corresponding aniline analogues using hydrogen peroxide and trifluoroacetic acid [118,127–129]. This is the only available route to the synthesis of nitroarene complexes. Alkylaniline complexes may be selectively oxidized to alkylnitroarene or nitroacetophenone complexes. It has been found that oxidation of the amino group proceeds within 20 min, while oxidation of the alkyl substituent requires 24 h as shown in Scheme 4 [127].

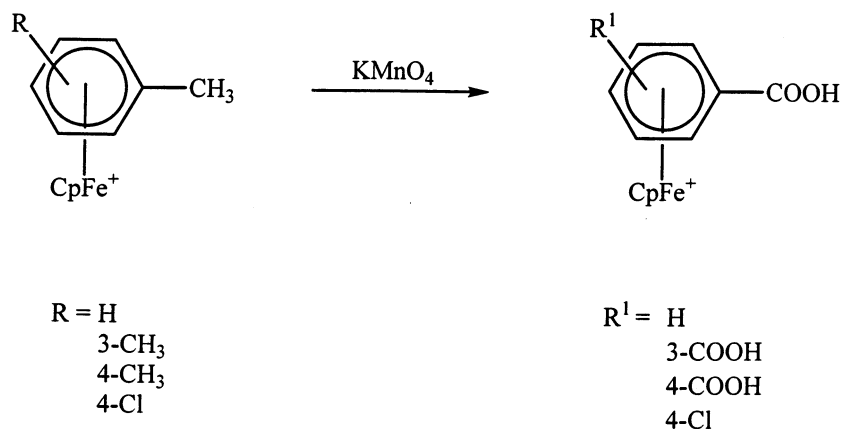


Scheme 4.

2.2.2. Toluenes

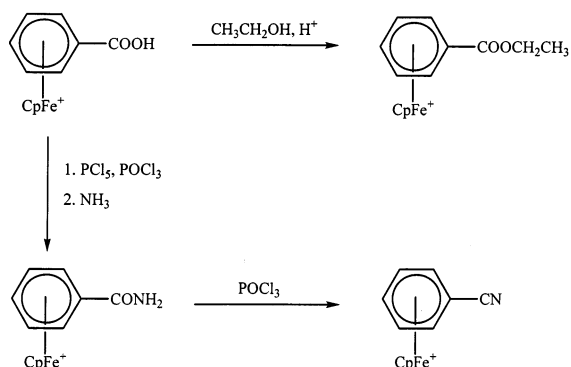
Nesmeyanov prepared benzoic acid complexes of cyclopentadienyliron by oxidizing the corresponding toluene, xylene and chlorotoluene complexes in aqueous solutions of potassium permanganate [95,130,131]. This method describes the first

synthesis of complexed acid-functionalized arenes as described in Scheme 5. These complexes are especially interesting as they cannot be prepared via ligand exchange of ferrocene due to the strong electron-withdrawing ability of the acid group.



Scheme 5.

The reactivity of complexed benzoic acid was explored through the preparation of the ester and amide derivatives, which were obtained via the intermediate acid chloride [95,130,131]. It was found that the amide could be subsequently converted to the nitrile by oxidation with POCl₃ as shown in Scheme 6.



Scheme 6.

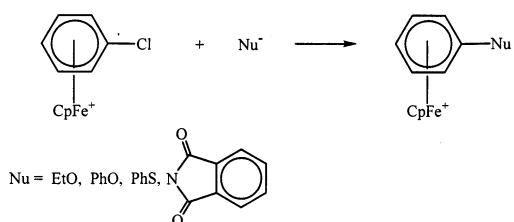
2.3. Arene complexes as electrophiles

Arenes that are complexed to transition metal moieties are susceptible to attack by nucleophiles due to their increased electrophilicity [132,133]. This inversion of polarity is due to electron-withdrawal initiated by the metallic moiety. The ability of the complexed arene to undergo nucleophilic substitution or addition reactions

under mild conditions allows for the preparation of a wide variety of aromatic molecules.

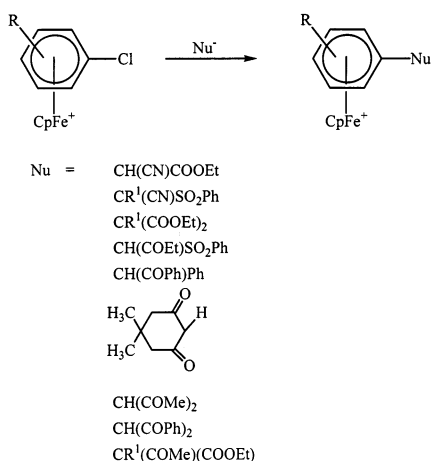
2.3.1. Nucleophilic substitution

Nesmeyanov and co-workers reported the first nucleophilic aromatic substitution reaction of a chlorobenzene cyclopentadienyliron complex in 1967 [97]. His original study included ethoxy, phenoxy, thiophenoxy and phthalimido nucleophiles as described in Scheme 7. This methodology has since been extended to include a number of different carbon-, oxygen-, sulfur- and nitrogen-containing nucleophiles.



Scheme 7.

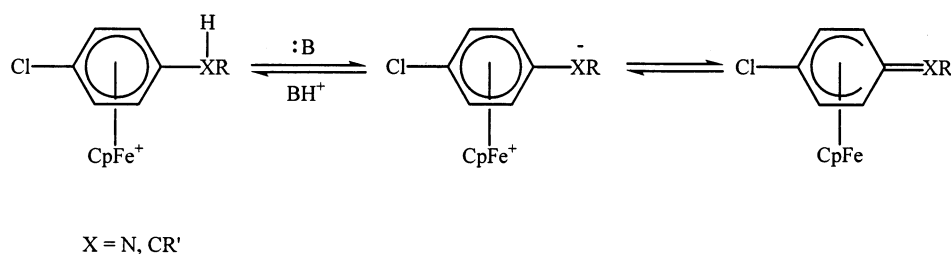
2.3.1.1. Reactions with carbon nucleophiles. The formation of carbon–carbon bonds is of paramount interest to synthetic chemists. This type of bond formation may be achieved by the reaction of complexed chloro- or nitrobenzenes with carbon nucleophiles, such as those derived from 1,3-diketones [134–137], malonates [129,135–141], alkyl acetoacetates [127,136,142], cyanoacetates [143,144] and arylphenylsulphonylacetonitriles [127,144,145] as shown in Scheme 8.



Scheme 8.

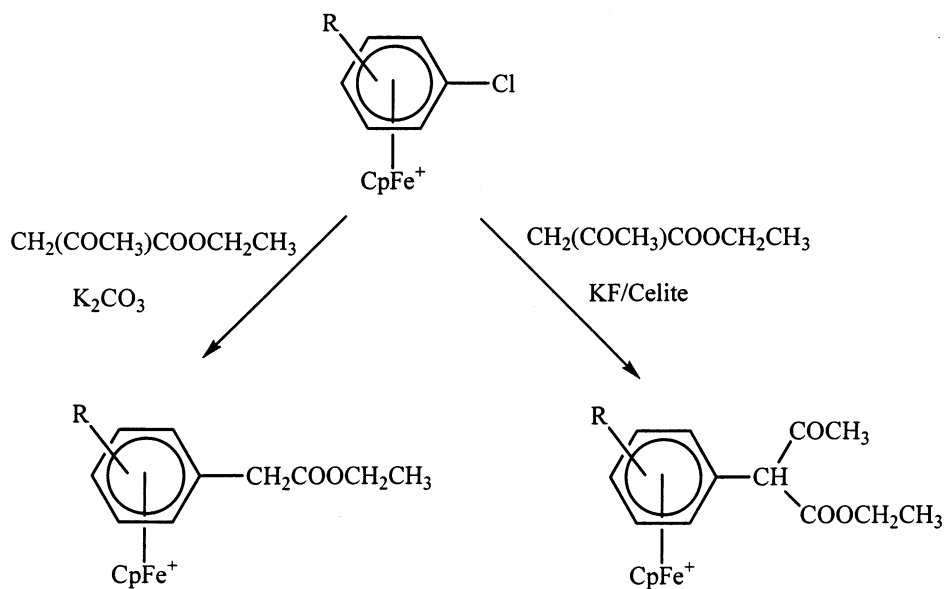
Reaction of primary or secondary carbanions with dichlorobenzene cyclopentadienyliron complexes gives substitution of only one chlorine atom, presumably due to

the formation of a zwitterion in basic solution (Scheme 9). The formation of this zwitterion increases the electron density on the aromatic ring, making the arene much less electrophilic. Reactions with tertiary carbanions readily yield disubstitution products, due to their inability to form the zwitterion [145].



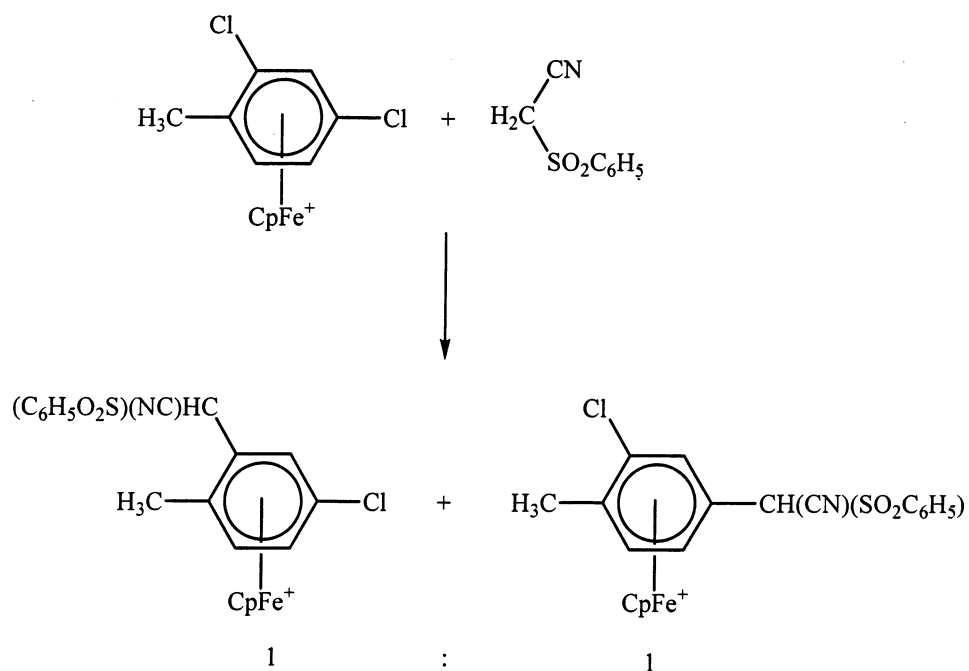
Scheme 9.

Interestingly, deacylation occurs when acetylacetone or alkylacetoacetates are used as nucleophiles [136,142,146]. This results in the formation of two products as shown in Scheme 10. Although deacylation is known to occur with purely organic substrates [147], it generally requires harsher reaction conditions than are used for iron-mediated substitution reactions. Therefore, it has generally been assumed that the metal plays a role in the deacylation reaction, although this role has not been elucidated as of yet [129,136]. Interestingly, when potassium fluoride-celite is used as a catalyst, no deacylation is observed for the reaction of alkylacetoacetates with the chloro- or nitrobenzene complexes, demonstrating that altering the reaction conditions may eliminate deacylation [135].



Scheme 10.

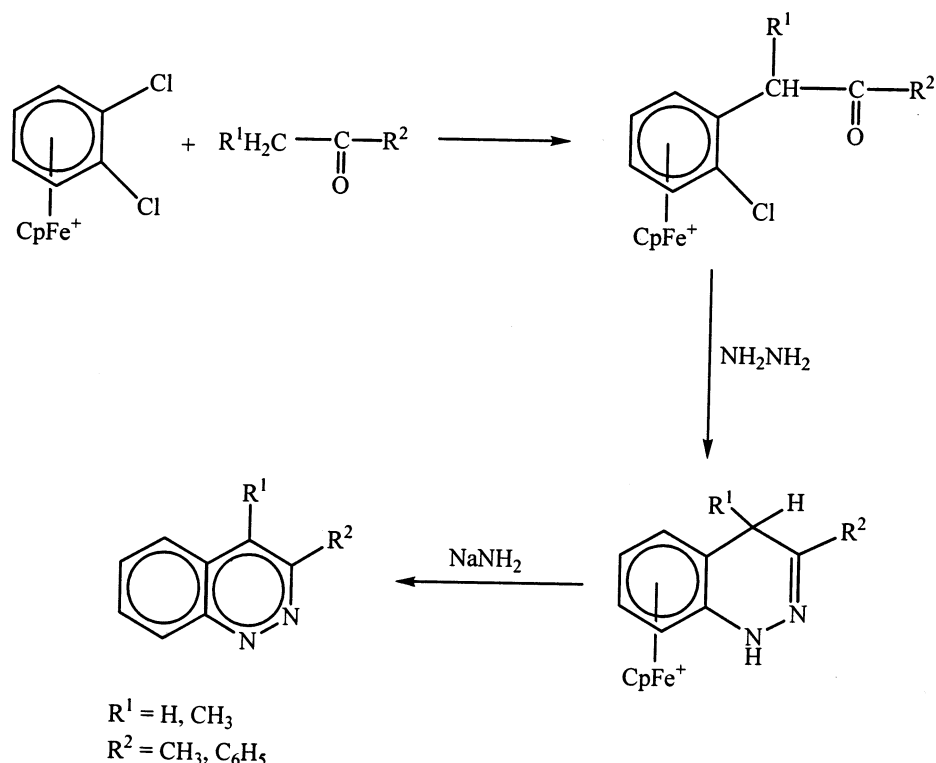
Studies on the steric effects of methyl substituents on the nucleophilic aromatic substitution of carbon nucleophiles have shown that these reactions are not hindered by crowding. The reaction of 2,5- or 2,6-dimethylchlorobenzene complex with phenylsulfonylacetonitriles resulted in the formation of the substitution products in very good yields. The 2,4-dichlorotoluene complex, in which one of the chlorine atoms is *ortho* to a methyl group, reacts with phenylsulfonylacetonitrile to give equimolar ratios of the two possible substitution products, which provides further evidence that steric effects of adjacent methyl groups are minor (Scheme 11) [144].



Scheme 11.

The cinnoline heterocyclic ring system, a component of many pharmaceuticals and herbicides, may be synthesized via metal-mediated nucleophilic aromatic substitution in three steps, beginning with the reaction of a 1,3-diketone with the *o*-dichlorobenzene complex (Scheme 12) [134]. Due to the formation of the zwitterion, only the monosubstituted product is obtained. Condensation of the resulting ketoarene complex with hydrazine yields the cyclic imine, where the remaining chlorine atom has been substituted by the nucleophilic amino group. Oxidation by sodium amide results in the aromatization of the heterocycle and liberation of cinnoline from the cyclopentadienyliron moiety.

2.3.1.2. Reactions with oxygen and sulfur nucleophiles. The formation of aryl ether and thioether bonds is of great interest, considering their prevalence in natural

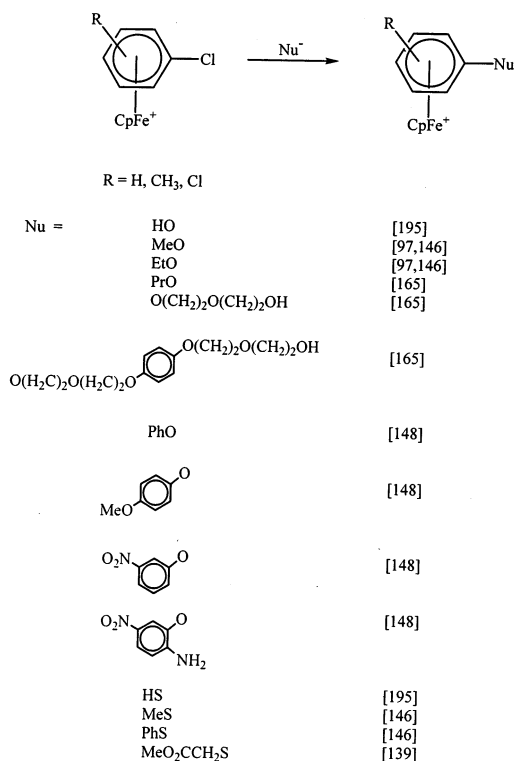


Scheme 12.

products. Due to the vast number of different alcohols, phenols, and mercaptans which may be used as nucleophiles, cyclopentadienyliron-assisted nucleophilic aromatic substitution offers an efficient synthetic route to this class of compounds (Scheme 13) [139,140,148].

Cyclopentadienyliron-mediated nucleophilic aromatic substitution represents an improved methodology in the formation of aryl ether bonds over more traditional methods such as the Ullmann ether synthesis [149]. Application of this chemistry for the synthesis of natural products has been explored by the reaction of complexed chloroarenes with phenoxy nucleophiles, resulting in the formation of the etheric backbone of vancomycin [148,150], as well as several dibenzodioxins [151]. Furthermore, estrane steroids containing terminal phenoxy groups can be coupled to cyclopentadienyliron arenes via this method, which may prove useful for metalloimmunoassay [152]. These biologically important molecules have been complexed to ruthenium [153–157], chromium [158–161] and manganese [162] using similar methods.

Although carbon nucleophiles disubstitute only when the carbanion is tertiary, alcohols and phenols readily disubstitute dichlorobenzene complexes [163]. Pearson has illustrated that the mobility of each chlorine atom is different, which allows for

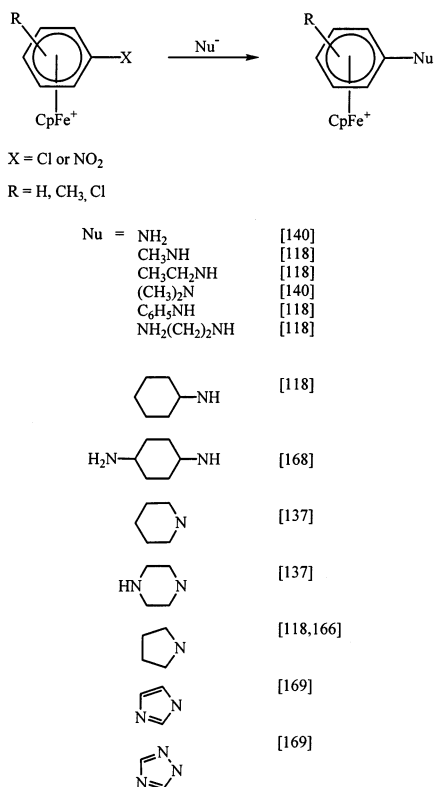


Scheme 13.

the formation of nonsymmetrical complexes [148,150,164,165]. By adjusting the reaction times and conditions, he was able to monosubstitute dichlorobenzene complexes with a variety of alkoxy nucleophiles. The remaining chlorine substituent may then be displaced by a different nucleophile. Reactions involving oxygen or sulfur nucleophiles can be carried out with 2,6-dimethylchlorobenzene or 2,6-dimethylnitrobenzene, demonstrating that these reactions are not sterically impeded [140].

2.3.1.3. Reactions with nitrogen nucleophiles. Amines and anilines are also sufficiently nucleophilic to react with complexed chloro- and nitroarenes, resulting in the formation of aryl amines (Scheme 14) [118,146,163,166–169]. Additional studies involving azides further demonstrate the ability of nitrogen-containing compounds to act as effective nucleophiles [170,171]. Roberts has recently used nucleophilic aromatic substitution to complex amino acids [172] and indoles [173] to the cyclopentadienyliron moiety.

Like primary and secondary carbanions, primary amines do not disubstitute dichloroarene complexes due to the formation of a zwitterion in basic solution [137,140,167]. However, the addition of a catalytic amount of glacial acetic acid



Scheme 14.

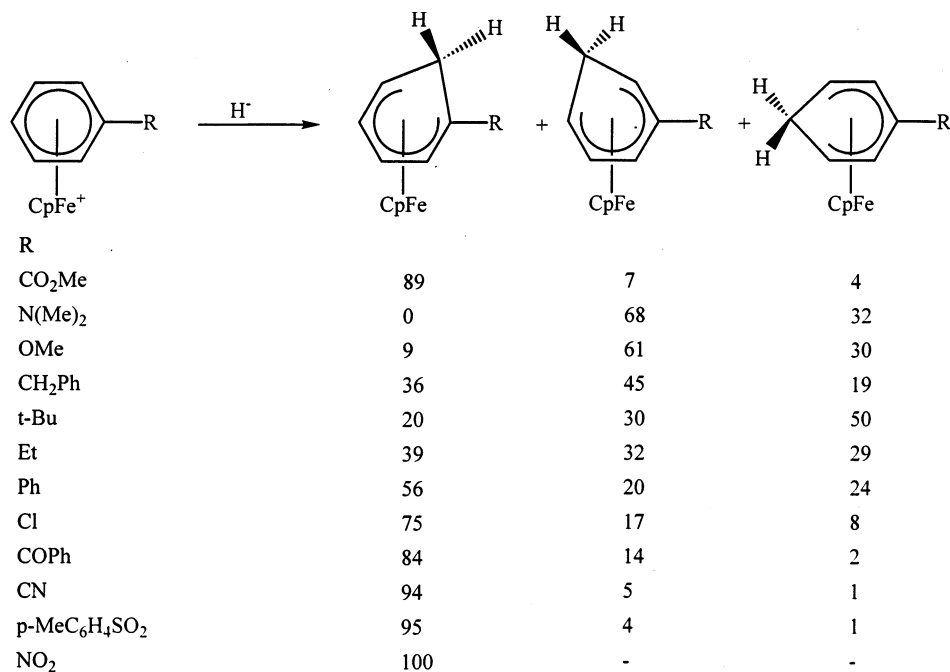
suppresses deprotonation to afford the disubstituted complex [134,167,174]. Thus the monosubstituted or disubstituted complex may be obtained by adjusting the reaction conditions.

The reactions of a series of amino nucleophiles with chloronitrobenzene complexes has allowed for the comparison of the mobility of the nitro and chloro leaving groups. It was found that the site of nucleophilic attack was highly dependent upon the nucleophilicity of the incoming nucleophile [175]. Weak bases, such as aniline ($\text{p}K_{\text{b}} = 9.4$), displace the nitro group, due to the stronger electron-withdrawing ability of this leaving group as compared to the chlorine substituent. Stronger bases, such as *n*-butylamine ($\text{p}K_{\text{b}} = 3.3$) and pyrrolidine ($\text{p}K_{\text{b}} = 2.7$), do not exhibit the same regioselectivity. In the reaction of *n*-butylamine or pyrrolidine with the *o*-chloronitrobenzene complex, substitution occurs exclusively at the chlorine substituent, due to the strong inductive effect of the adjacent nitro group. The *meta* and *para* isomers give mixtures of products.

2.3.2. Nucleophilic addition

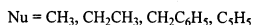
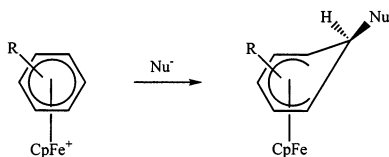
While ‘soft’ nucleophiles can effect nucleophilic aromatic substitution for a complexed arene containing a suitable leaving group, ‘hard’ nucleophiles add to the arene ring resulting in the formation of cyclohexadienyl adducts. Davies, Green and Mingos have reviewed the preference for addition to closed ligands with even-numbered hapticities over closed ligands with odd-numbered hapticities [176]. In agreement with these findings, addition has been found to occur exclusively to the complexed arene and not to the cyclopentadienyl ring. The presence of the bulky metal moiety causes addition of nucleophiles to occur exclusively *exo* to the arene ring. Confirmation of this *exo* addition has been accomplished by NMR and X-ray crystallographic studies [177]. Restoration of the aromaticity occurs via oxidation of the cyclohexadienyl adduct, which may be concurrent with demetallation of the arene [178,179].

2.3.2.1. Hydride. Studies on the addition of hydride to arene cyclopentadienyliron complexes have shown that the site of addition is dependent on the substituents located on the aromatic ring (Scheme 15) [81,96,180–182]. Sutherland and co-workers have examined hydride addition to $[(C_6H_5X)FeCp]^+$ and have found that when X is electron-donating, addition occurs in both the *meta* and *para* positions, whereas if X is electron-withdrawing, addition occurs predominantly *ortho*.



Scheme 15.

2.3.2.2. Carbanions. Carbanion nucleophiles which have been added to η^6 -arene- η^5 -cyclopentadienyliron complexes include CN^- [163,178–180,183,184], $\text{CH}_3\text{COCH}_2^-$ [178,180,185,186], CCl_3^- [187] and $(\text{CH}_3)_2(\text{CN})\text{C}^-$ [188]. Addition to η^6 -benzene- η^5 -cyclopentadienyliron complexes readily occurs when alkylolithium reagents are utilized as nucleophiles, yielding neutral cyclohexadienyl adducts as shown in Scheme 16 [189].

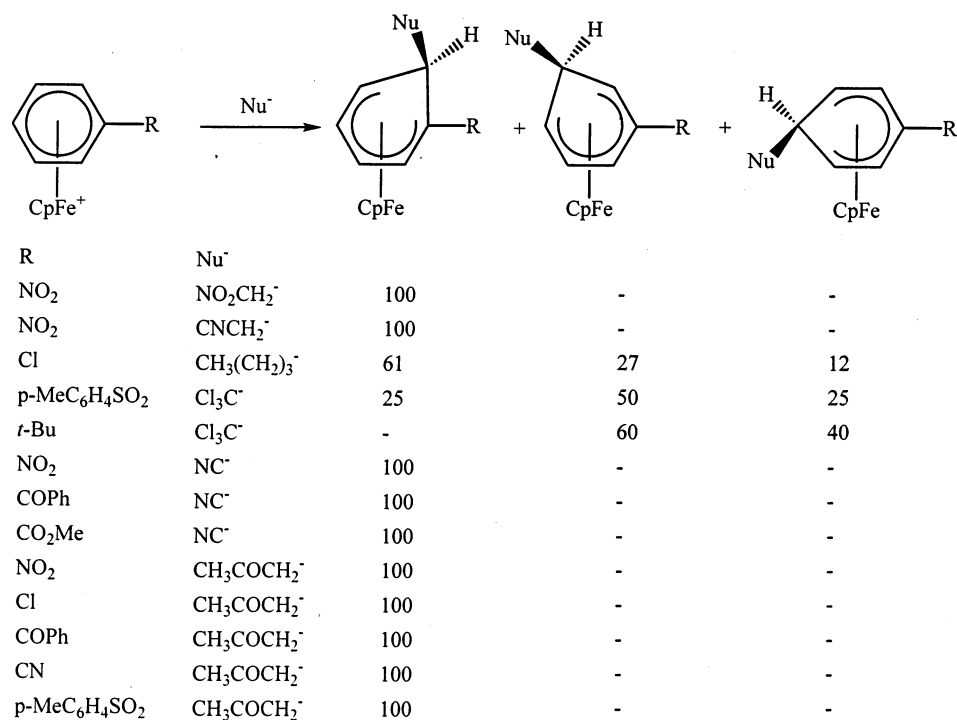


Scheme 16.

As previously mentioned, substituents on the arene ring have a profound influence on the site of nucleophilic attack. Alkyl substituents impose a steric effect, and it has been found that the addition of cyanide or acetyl to complexes containing a methyl group *ortho* to an electron-withdrawing group results in addition only to the free *ortho* site, with no *ipso* addition reported [180]. As a general rule for complexed arenes, electron-withdrawing substituents favor addition at the *ortho* and *para* positions, while electron-donating substituents favor addition at the *meta* position (Scheme 17).

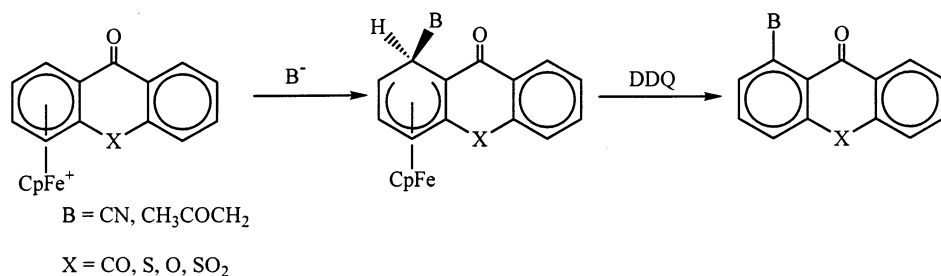
Nucleophilic addition results in the generation of a cyclohexadienyl adduct, which is no longer completely aromatic. This loss of aromaticity results in the formation of highly unstable cyclohexadienyl adducts which decompose rapidly at room temperature. The formation of the adduct may be confirmed by ^{13}C -NMR spectroscopy, where the resonance attributed to the *ipso* carbon is shifted over 50 ppm upfield from its position in the aromatic starting material [190]. To restore aromaticity, several workers have reacted these compounds with oxidizing agents such as ceric ammonium nitrate [185,186] and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) [178]. This results in cleavage of the metallic moiety, with isolation of the corresponding arene. Novikova et al. have recently reported the selective oxidation of the *endo* proton by trityl hexafluorophosphate to generate the rearomatized complex without demetallation [191]. However, this was followed by the subsequent addition of a trityl fragment to the cyclopentadienyl ring.

Nucleophilic addition is a particularly important route for the functionalization of arenes, and selective addition of anions may be achieved in many cases. The addition of acetyl or cyanide anion to a series of heterocyclic complexes results in selective addition to the complexed ring beta to the carbonyl (Scheme 18) [178]. Addition of cyanide to nitroarene complexes has been observed to occur exclusively *ortho* to the nitro group, which has allowed for an efficient synthesis of benzonitriles [184].

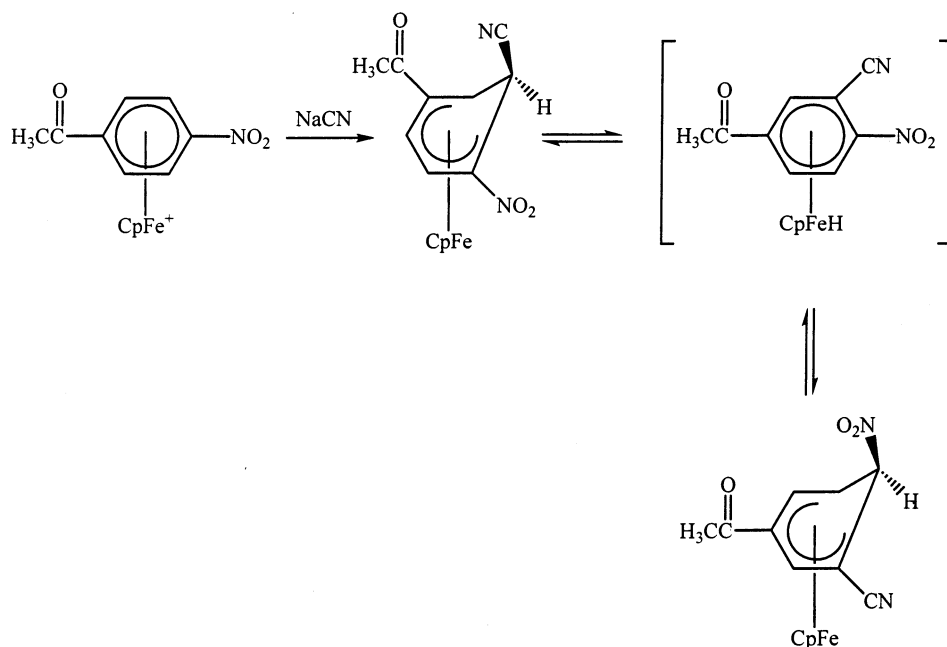


Scheme 17.

An interesting example of hydrogen migration following cyanide addition has recently been reported [184]. Addition of cyanide to the *p*-nitroacetophenone complex occurs selectively to the carbon atom *ortho* to the nitro group and *meta* to the acetyl group, due to the inductive and resonance effects of each functionality. The cyclohexadienyl adduct that results undergoes an isomerization reaction, resulting in migration of a hydrogen atom as shown in Scheme 19. Although this type of migration has been described previously for chromium and manganese complexes [192–194], this is the first reported example of such an isomerization in a cyclopentadienyliron complex.



Scheme 18.



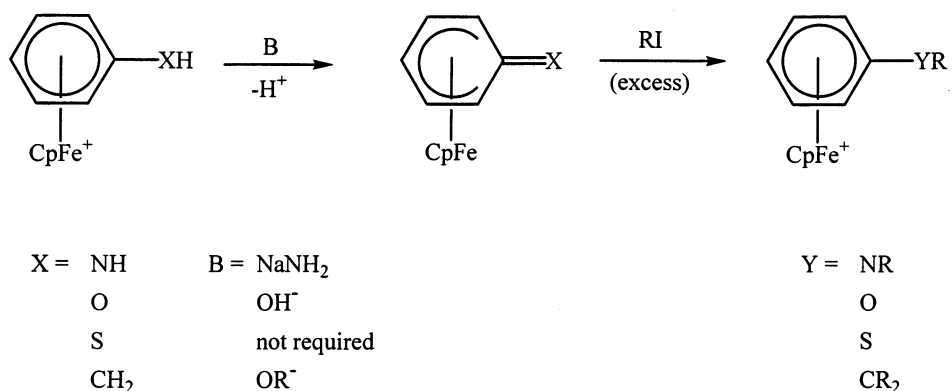
Scheme 19.

2.4. Deprotonation of arene substituents

The coordination of an aromatic ring to a transition metal moiety substantially increases the acidity of the aryl protons and the protons vicinal to the aromatic ring [2]. These vicinal protons may be abstracted to give a zwitterion, which may also exist, through resonance, as a cyclohexadienyliron complex with an exocyclic double bond. Heteroatoms may be deprotonated, and the complexes of aniline, phenol and thiophenol yield imines, ketones and thioketones, respectively [195]. Although strong bases are required to deprotonate the aniline and phenol complexes, deprotonation of the thiophenol complex occurs spontaneously as is described in Scheme 20. Reaction with an electrophile gives the corresponding arene complex, with no competitive addition to the complexed ring.

Carbon atoms adjacent to the complexed ring may also be deprotonated by hydroxide or *t*-butoxide anions, again resulting in the formation of an exocyclic double bond. This has been used to functionalize a variety of complexed polyaromatic hydrocarbons and heterocycles [196–198]. Interestingly, the deprotonated species may substitute a chlorine atom when reacted with a cyclopentadienyliron-complexed chloroarene, as shown in Scheme 21.

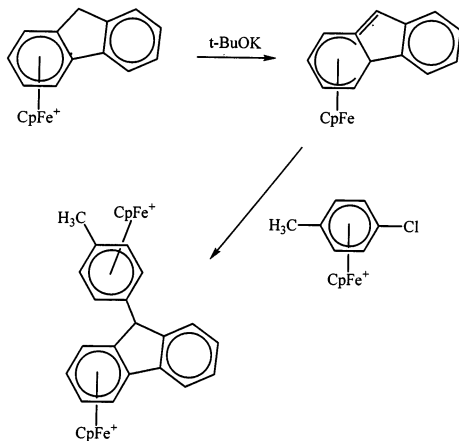
Deprotonation of methyl groups may be particularly useful when followed by alkylation [199] or arylation [200,201], resulting in an extension of the chain from the central complexed ring. This permits the preparation of dendrimeric materials which may be capable of molecular recognition or electrocatalysis. Growth of the



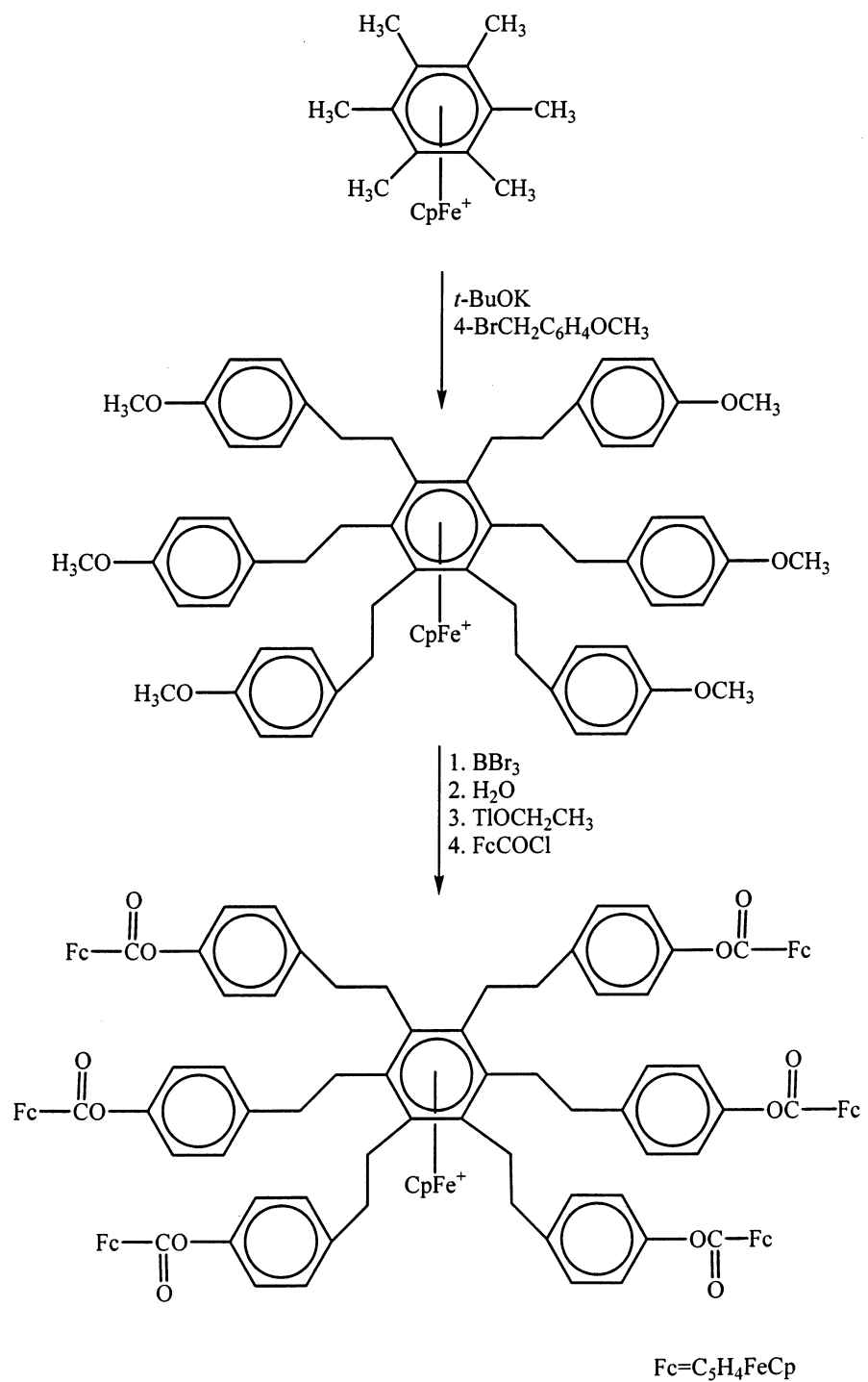
Scheme 20.

dendrimer may be effected in one of two ways. In the first, the core is the metallated hexamethylbenzene complex, with the first generation resulting from reaction with an electrophile following deprotonation [202–206]. An example of a dendrimer prepared by this method is shown in Scheme 22 [202]. Further generations may be added when the electrophile contains a reactive functional group. Alternatively, the dendrimer may be ‘capped’ with a variety of interesting end groups, including the ferrocenyl moiety [196,207].

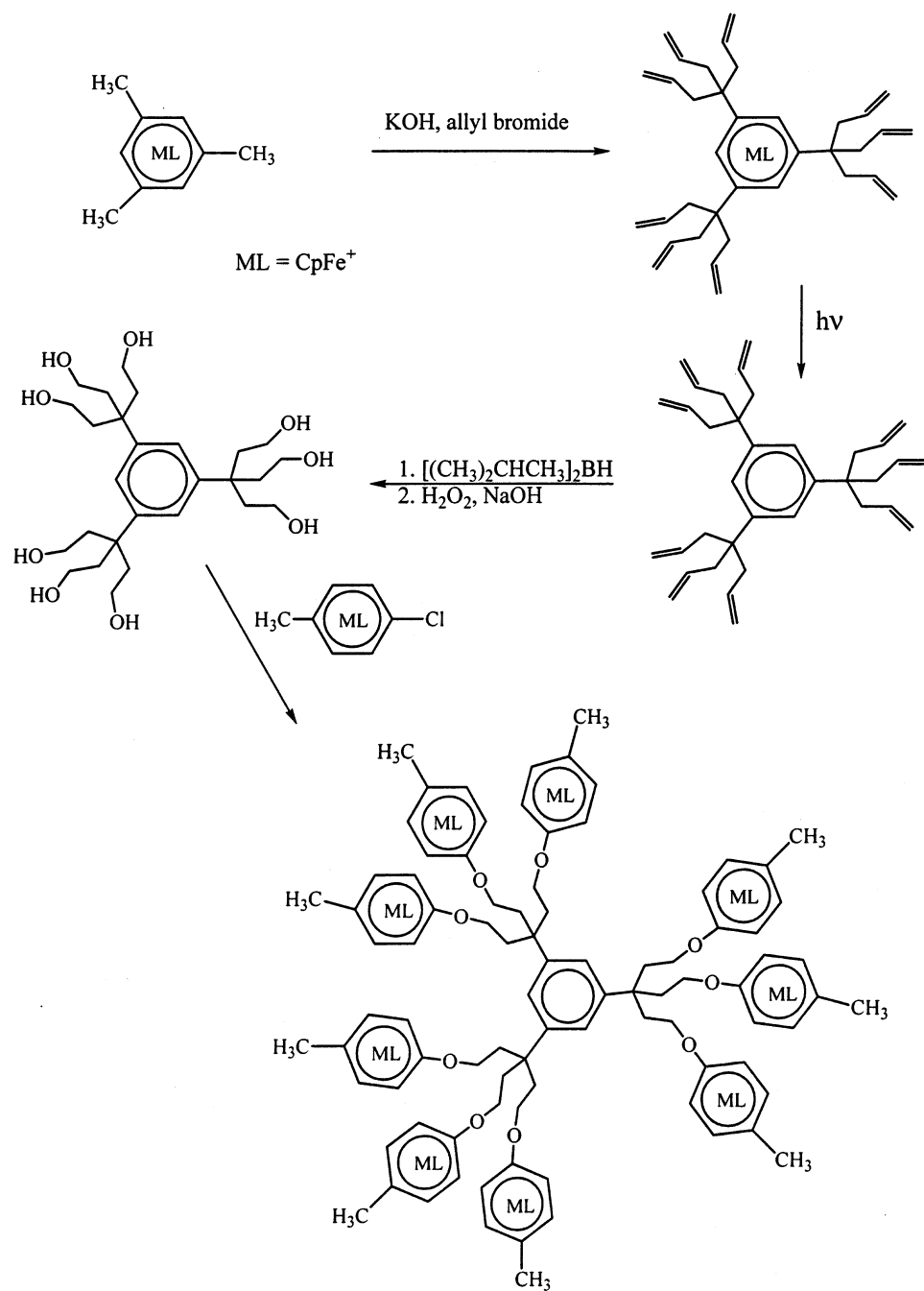
The second method for dendrimer synthesis also requires a cyclopentadienyliron-complexed polyalkylbenzene for the core [208,209]. The methyl groups are deprotonated, and reacted with an excess of allyl bromide. This product is then demetallated and hydrolyzed, resulting in a first generation capped with alcohol functionalities. These nucleophilic alcohols then displace a halide group from a complexed halobenzene, resulting in a metallated second generation. An example of a dendrimer prepared via this method is shown in Scheme 23 [208].



Scheme 21.

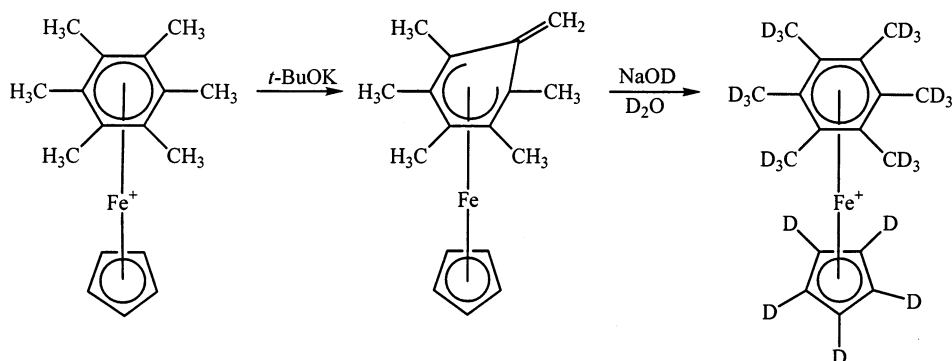


Scheme 22.



Scheme 23.

The increased acidity of vicinal protons results in a facile method for the perdeuteration of arenes complexed to the cyclopentadienyliron moiety (Scheme 24) [210]. The initial deprotonation of methyl groups with an alkoxide ion is required in order to improve the solubility of the complex in a heavy water mixture. This procedure allows for a 56% yield overall. For longer alkyl chains subjected to the same reaction conditions, only the methylene group adjacent to the complexed ring is deuterated, as would be expected, due to its increased acidity.



Scheme 24.

2.5. Decomplexation reactions

In previous sections, we have discussed the facile complexation of a wide variety of arenes to the cyclopentadienyliron moiety. This complexation results in a polarity inversion of the arene, making it susceptible to attack by nucleophiles. In order for this methodology to become a useful synthetic strategy, the arene must be liberated from the metallic moiety easily, and in high yield, yet the arene should not be so labile that the metallated intermediate itself cannot be isolated.

The cyclopentadienyliron moiety can be cleaved from the arene complex via three different methods. Pyrolysis requires an arene which is thermally stable, as reaction temperatures may exceed 200°C [137,170]. This can be done either in a solvent with a high-boiling point such as DMSO, or under vacuum in a pyrolytic sublimator. More recently, pyrolysis has been performed in a microwave oven. Graphite, a strong microwave absorber, is added to the complex, and this mixture is irradiated for approximately 2 min. This results in a nearly quantitative yield for the decomplexation of pentamethylbenzene and *N*-phenylcarbazole [125].

Darchen first reported the demetallation of cyclopentadienyliron-complexed arenes via electrolysis, which proceeds in the presence of an excess of phosphine ligand [211,212]. Since that report, electrolysis has been used successfully for the liberation of a variety of different arenes [213,214]. This method has the advantage of requiring much milder reaction conditions, while maintaining a yield comparable to, or better than pyrolysis [213]. Potentials required to electrolyze the complexes

are typically on the order of -1.50 to -2.00 V, and depend on the nature of the substituents on the aromatic ring [213].

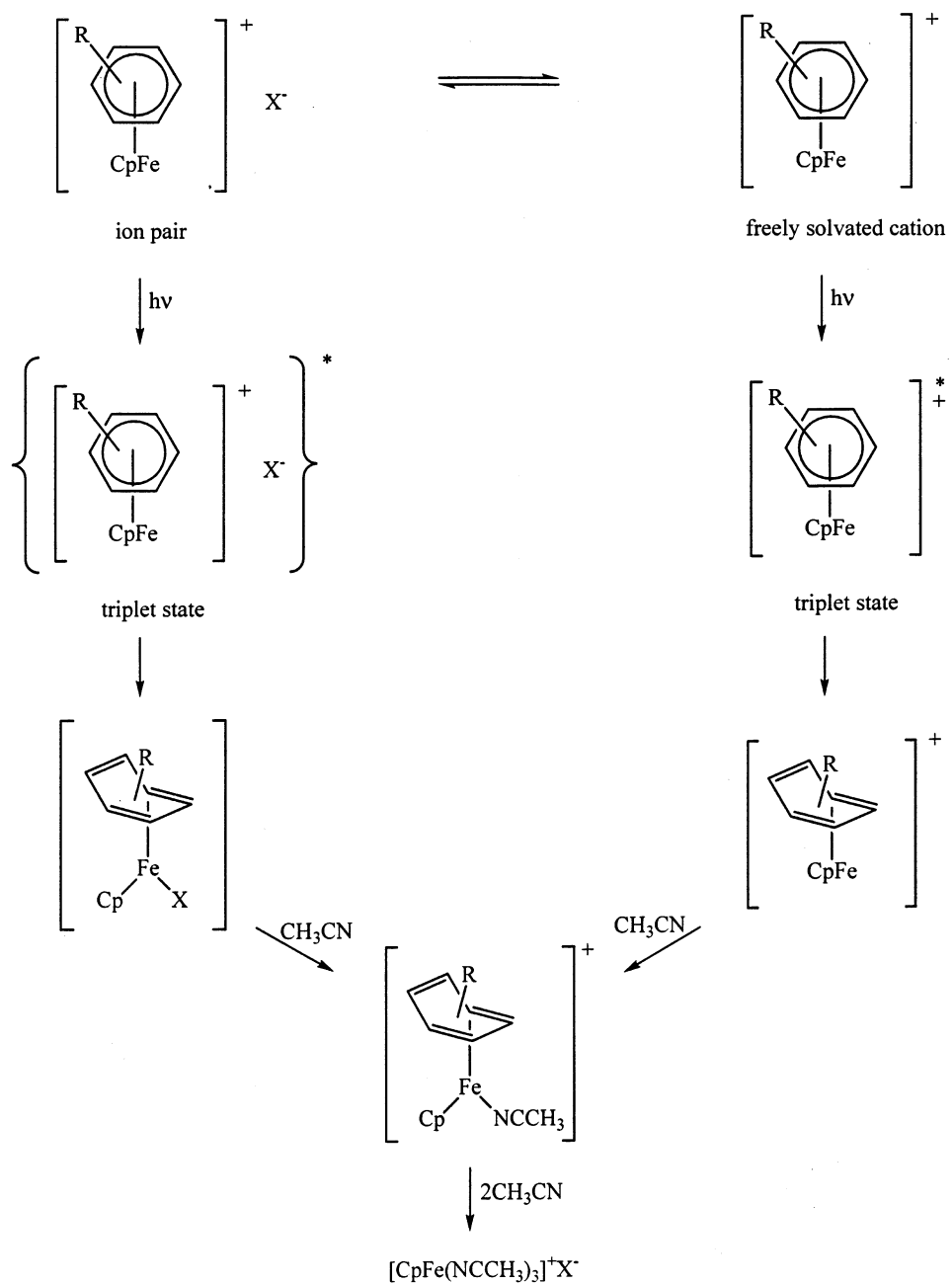
The first report of the demetallation of cyclopentadienyliron complexes by exposure to visible light appeared in the literature in 1970 [215]. Since that initial communication, photolysis has been used routinely to cleave the cyclopentadienyliron moiety from arene complexes. This method has the advantage that the arene to be liberated need not be heat-stable, and may contain functional groups sensitive to reduction. Photolytic demetallation usually results in high yields, and isolation of the arene from side products (ferrocene and iron salts) may be accomplished via column chromatography or extraction.

The mechanism of photolysis has been studied by several workers, and has been found to be dependent on the reaction solvent. Nucleophilic solvents increase the quantum yield of the reaction, suggesting that they may ligate to the metal to form intermediate complexes [216]. In the absence of a nucleophilic solvent, the counterion will affect the quantum yield, indicating that anions present in solution may also weakly coordinate to the metal atom. Thus the quantum yield increases in the order: $\text{CH}_2\text{Cl}_2 < \text{CH}_3\text{CN} < \text{CH}_3\text{OH} < \text{H}_2\text{O} < \text{propylene carbonate}$, for solvents, and in the order: $\text{SbF}_6^- \text{ ca. } \text{AsF}_6^- \text{ ca. } \text{PF}_6^- \ll \text{ClO}_4^- \text{ ca. } \text{Br}^- < \text{BF}_4^- < \text{CF}_3\text{SO}_3^-$ for counterions [217]. Because of solubility requirements, as well as the ease of isolation of the organic product, acetonitrile is commonly used as the photolytic solvent.

A mechanism for the photolytic liberation of an arene from the cyclopentadienyliron moiety has been suggested by Schuster (Scheme 25) [218]. In this mechanism, the complex is first excited to the triplet state, causing ring slippage of the arene from η^6 to η^4 . Coordination by the solvent results in the formation of $[\text{CpFe}(\text{NCCH}_3)_3]^+$, which has been inferred by ultraviolet absorption at 550 nm, although it has not been isolated [120,218]. This species then decomposes to form ferrocene and various iron salts.

Pearson has investigated the photolysis of a number of cyclopentadienyliron arene complexes in acetonitrile with a small amount of $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$ buffer solution. It was found that the precipitation of $\text{Fe}(\text{OH})_3$ and evolution of CO_2 drove the reaction toward complete conversion to products [219]. This simple change in reaction conditions afforded a 30–40% increase in yield as compared to photolysis in acetonitrile solution.

The interesting photolytic behavior of arene complexes of cyclopentadienyliron has led to the study of these compounds as potential photoinitiators. One tremendous advantage of these compounds is that they absorb in the visible region of the electromagnetic spectrum, allowing them to be used in conditions where high-energy radiation may cause damage [220]. Alteration of the arene ligand allows for the preparation of initiators having maximum absorption at a desired wavelength [221,222]. This class of photoinitiators has been successful in the polymerization of epoxides [222–224], methyl methacrylate [220], styrene [220] and pyrrole [225]. They have also been used as important constituents of holographic recording materials [226], and to synthesize phosphoferrocene derivatives via triple decker sandwich complexes [227].



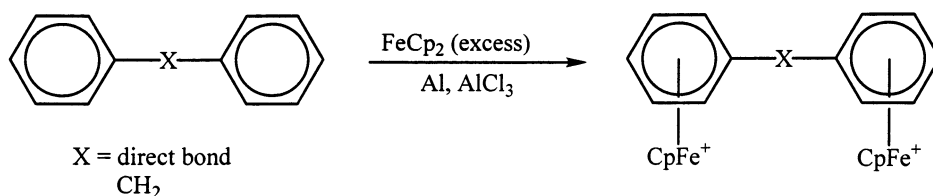
Scheme 25.

3. Di- and polycyclopentadienyliron complexes of arenes

3.1. Synthesis

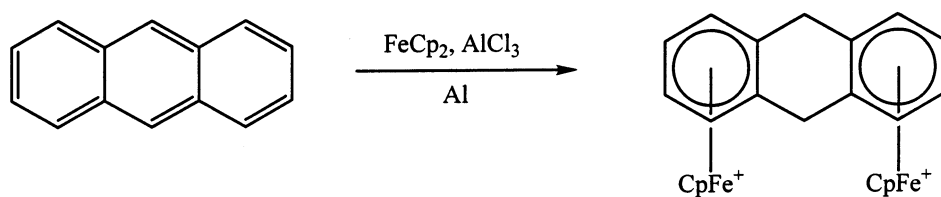
3.1.1. Ligand exchange reactions

Bimetallic systems have been prepared from polynuclear aromatics by the reaction of the arene with an excess of ferrocene in the presence of a Lewis acid (Scheme 26) [228]. Unfortunately, the yields for this type of reaction are generally poor, and isolation of the bimetallic complex may be complicated by the formation of the monometallic analogue.



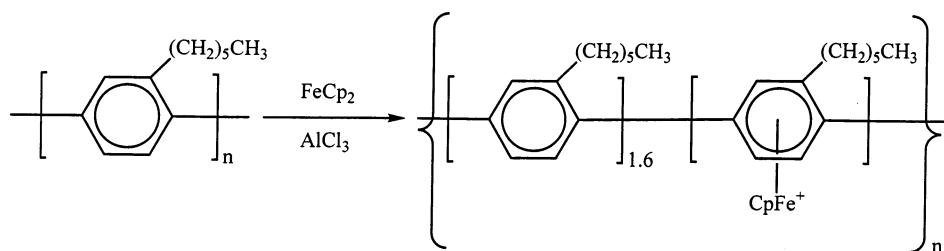
Scheme 26.

The preparation of bimetallics via ligand exchange is further complicated by side reactions, such as hydrogenation. Sutherland and co-workers were the first to systematically study this reaction, which occurs during the ligand exchange of polynuclear aromatic hydrocarbons [90,98,107–109] (Scheme 27). Anthracene, which has 14 electrons available in π -orbitals, should not form a bimetallic complex, even in the presence of a large excess of ferrocene. However, through the course of ligand exchange, a solvent-mediated hydrogenation reaction takes place, resulting in the formation of the 9,10-dihydroanthracene bimetallic complex. Phenanthrene, which also has 14 π -electrons, displays a similar behavior [104].



Scheme 27.

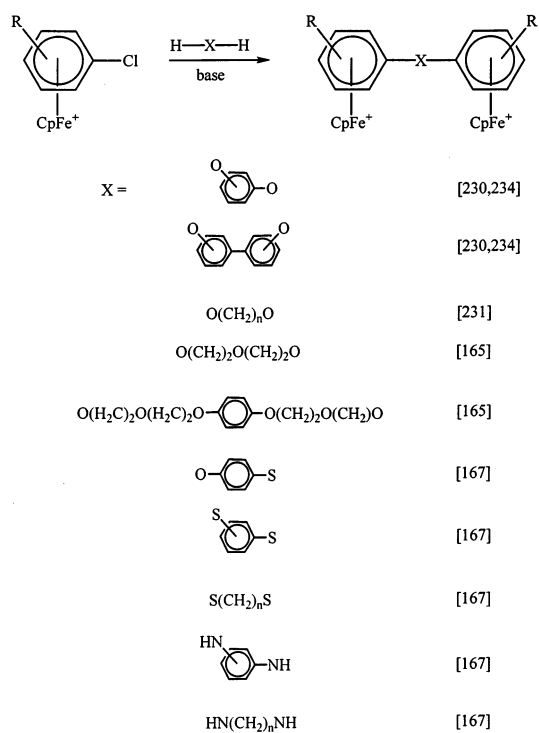
A single report has dealt with the preparation of polymetallated species via the ligand exchange of ferrocene (Scheme 28) [229]. Poly(*n*-hexylphenylene) was reacted with ferrocene and aluminum chloride in refluxing cyclohexane to give a metallated oligomer which was characterized by IR and UV–vis spectroscopy. The relative ratio of complexed to uncomplexed *n*-hexylphenylene rings was found by elemental analysis to be 1:1.6. However, due to the low molecular weight of the complexes used in this study, the average chain contained only four cyclopentadienyliron moieties.



Scheme 28.

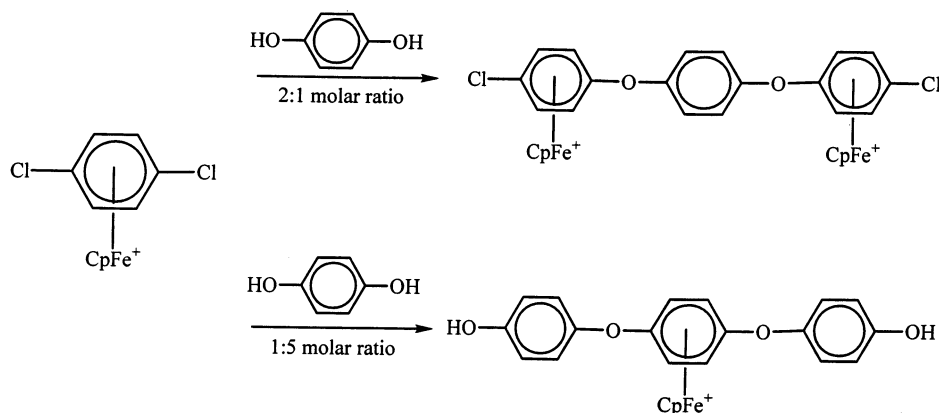
3.1.2. Stepwise synthesis

The most versatile method for the preparation of bi- and polymetallic species is via nucleophilic aromatic substitution [230]. Unlike ligand exchange, yields of $\text{S}_{\text{N}}\text{Ar}$ reactions are generally quite high, and proceed under mild reaction conditions. An additional advantage of this methodology is that it allows for the incorporation of etheric, thioetheric and amino bridges between the complexed arene rings (Scheme 29) [165,167,230–235].



Scheme 29.

Adjustment of the molar ratio of nucleophile to complex allows for greater flexibility of the resulting products. For example, using an excess of hydroquinone as a nucleophile generates the monometallic species, whereas a 2:1 molar ratio of the dichlorobenzene complex to the nucleophile leads to the formation of the bimetallic species (Scheme 30) [233,235]:



Scheme 30.

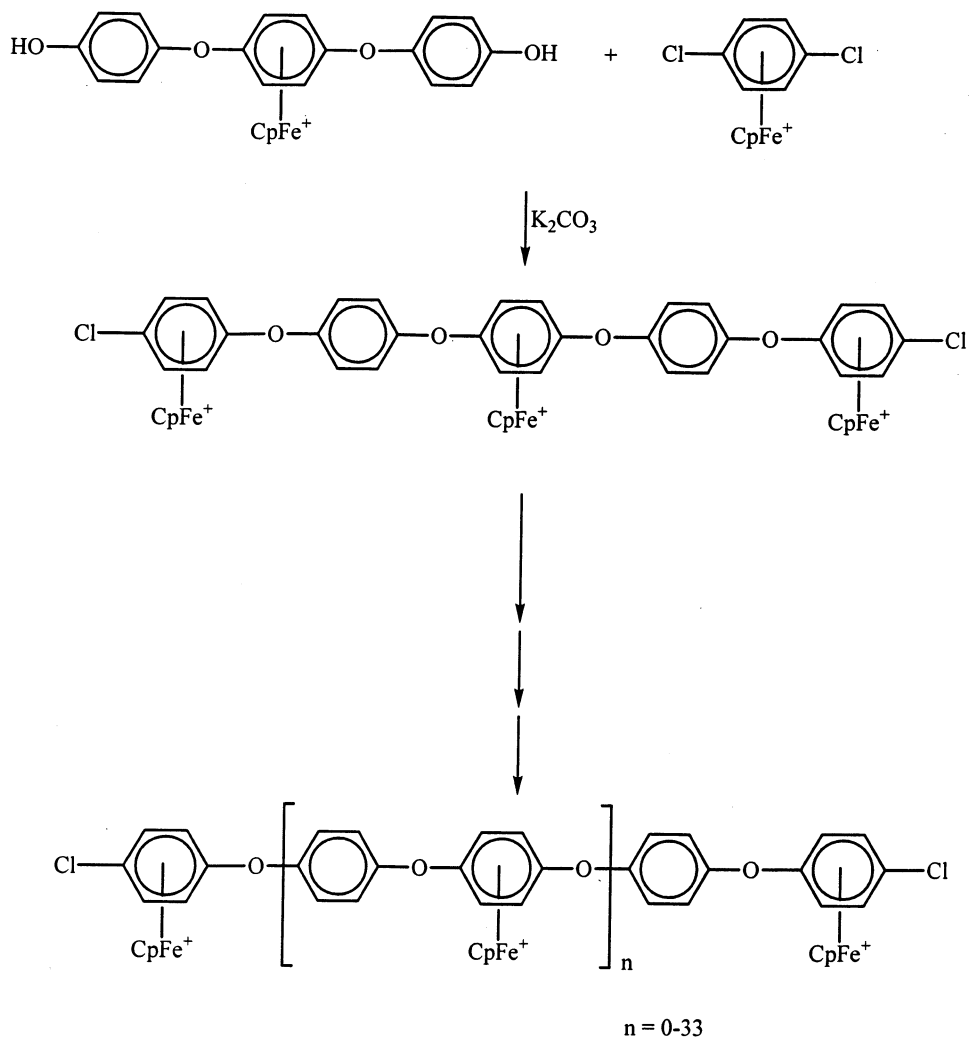
Thiols, due to their high nucleophilicity, give only sulfur-bridged bimetallics, regardless of the ratio of nucleophile to product. These sulfur-bridged complexes may be oxidized in the presence of *m*-chloroperbenzoic acid to give the corresponding sulfones [232,236]. Primary amines also form bimetallic species due to the formation of the zwitterion [167].

Metallated macromolecules may be prepared through stepwise nucleophilic aromatic substitution reactions (Scheme 31). This process has been used to synthesize oligomers containing up to 35 metals in the backbone of the chain, and is unique in that it allows for the synthesis of monodisperse oligomeric aromatic ethers in a controlled fashion [233,235]. Cleavage of the metal moiety results in the isolation of the purely aromatic ethers, which are engineering thermoplastics.

3.1.3. Polymerization reactions

While the stepwise synthesis of oligomeric ethers makes it possible to control the polydispersity, these materials may also be synthesized in a single step. An equimolar ratio of the dichlorobenzene complex and a dinucleophile in highly concentrated solution results in the formation of polydisperse polymeric chains [237,238]. Although the molecular weight of the metallated polymers cannot be measured directly [58–60], demetallation by photolysis or thermolysis affords the purely organic polymer in good yield (Scheme 32). The organic polymer may then be characterized by gel permeation chromatography.

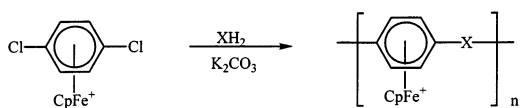
In addition to the synthesis of homopolymers, block co-polymers were synthesized by using a bimetallic starting complex containing terminal chlorine atoms.



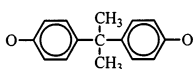
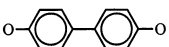
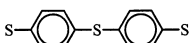
Scheme 31.

This allows for the introduction of many different functionalities into the backbone of the polymer in a controlled fashion (see Scheme 33).

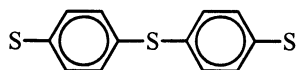
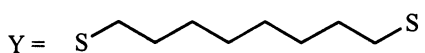
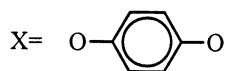
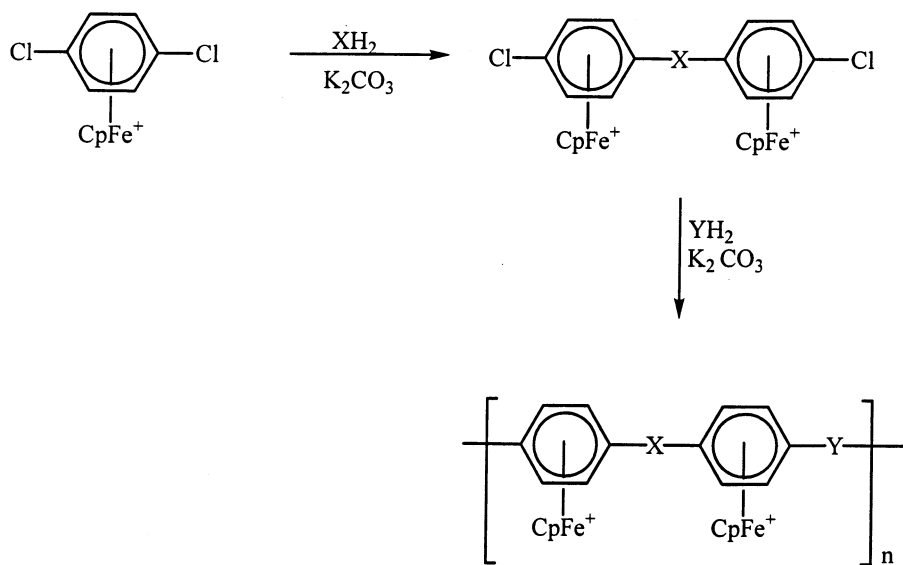
One of the aims of this research was the preparation of industrially important polymers and copolymers under mild conditions. Poly(phenylene sulfide) is a commonly used engineering thermoplastic which suffers from poor solubility in most solvents. However, when the corresponding organometallic polymer is formed, the material is soluble in common organic solvents such as acetone, acetonitrile and *N,N*-dimethylformamide, which may facilitate processing [238].



X =



Scheme 32.



Scheme 33.

3.2. Functionalization reactions

The functionalization of bi- and polymetallic complexes via nucleophilic addition has recently been described [190]. As in the monometallic case, the site of addition is influenced by the substituents located on the aromatic ring (Scheme 34). Hydride or cyanide ion were added to a series of aryl ethers which contained between two and eight metallic moieties. Although the hydride anion did not add selectively, cyanide added only in the positions *meta* to the etheric bridge of the polymetallic series. Rearomatization, coupled with demetallation, was performed by oxidation with DDQ.

The regiospecificity of the cyanide addition reaction is particularly important when the tremendous versatility of the cyano group is considered. Nitriles may be routinely and easily converted to acids, amines, amides and esters, which suggests that this reaction may have applications in organic synthesis.

3.3. Cleavage of etheric bonds in diiron species

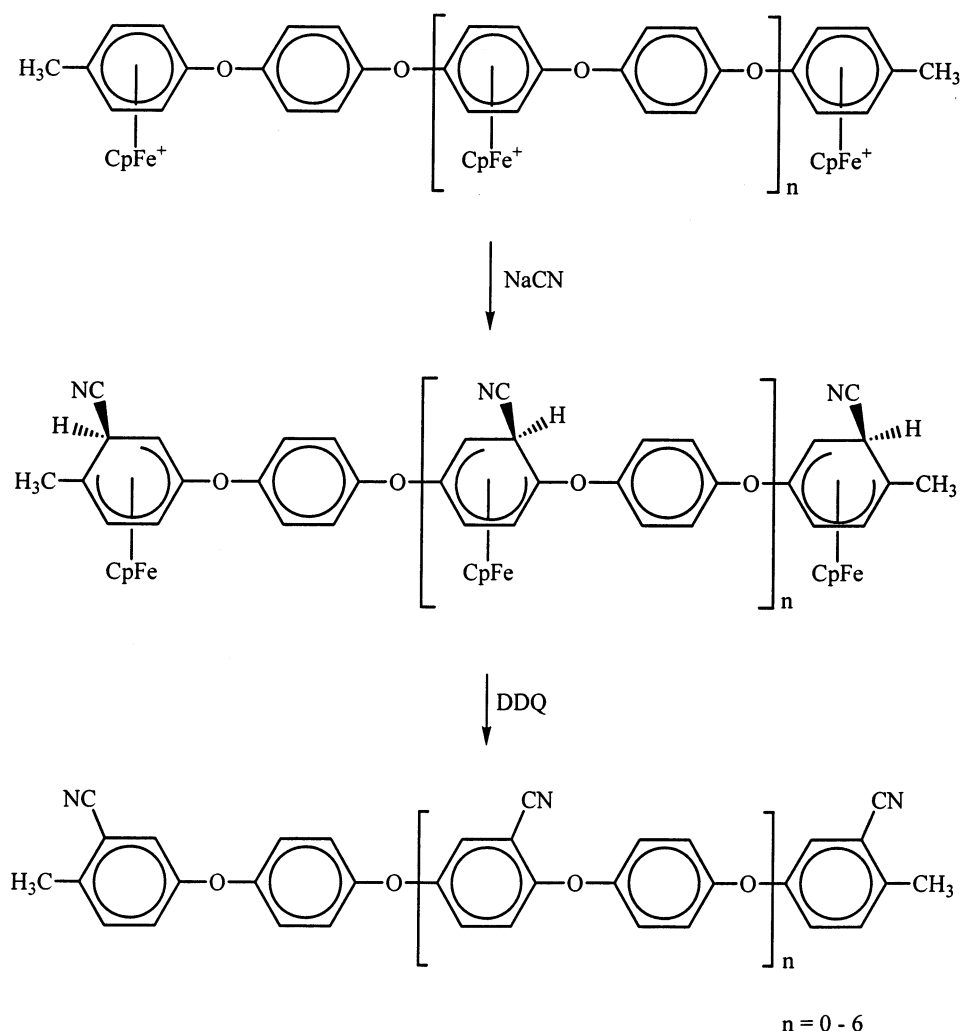
Bimetallic iron complexes may also serve as precursors for the synthesis of monometallic arenes. The preparation of phenolphthalein-bridged bimetallic species is readily accomplished by the reaction of phenolphthalein and a chlorobenzene complex, with potassium carbonate as the base (Scheme 35) [239]:

Reaction of these compounds with a primary amine results in a cleavage of the etheric bond to generate the complexed aniline species. This is thought to occur via a tertiary carbocation, which is formed when the lactone ring of phenolphthalein opens in basic media (Scheme 36):

Although some reports concerning the cleavage of etheric bonds for cyclopentadienyliron complexes have appeared in the literature [110,240], only one report mentions a possible mechanism. Interesting in its own right, this reaction also leads to the synthesis of a number of substituted aniline complexes which may not be synthesized by a simple nucleophilic aromatic substitution, such as the complexes of *N*-4-aminobutylaniline and *N*-6-aminohexylaniline.

4. Characterization of arenes coordinated to cyclopentadienyliron moieties

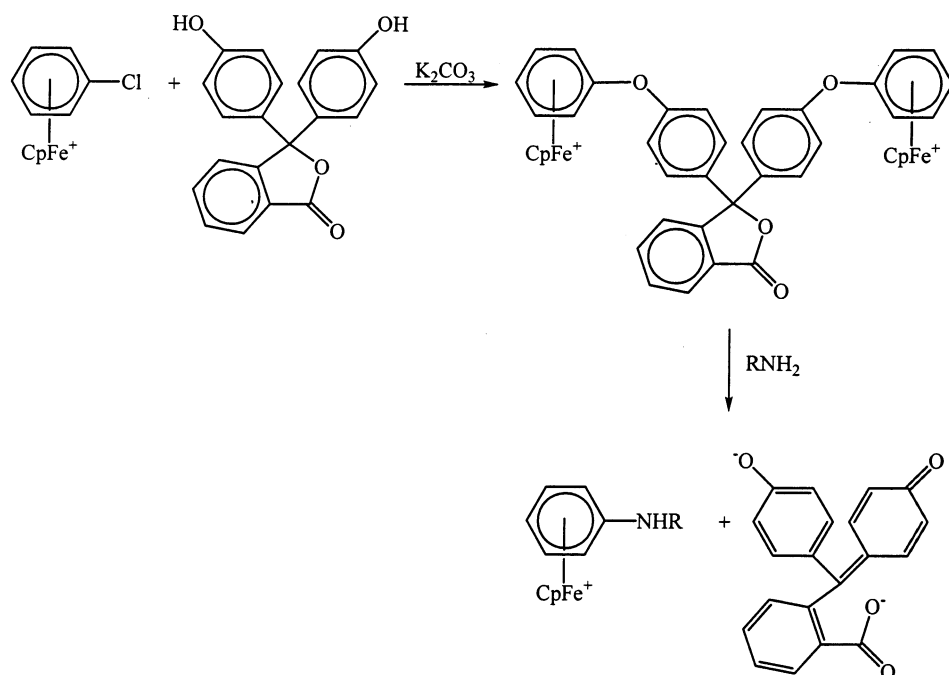
A variety of different methods have been used to characterize cyclopentadienyliron compounds. Extensive studies of the IR absorption of these complexes were completed several decades ago [241]. Mass spectrometric studies have been somewhat limited due to the low volatility of these metallated species, with only a few studies of fragmentation patterns reported [242,243]. Characterization using UV–vis spectrophotometry has also been examined [244,245]. Definitive information regarding the structural conformations of these complexes has been obtained by X-ray crystallography [66,80,167,233]. However, one of the most utilized techniques for the characterization of organoiron species is nuclear magnetic resonance spectroscopy.



Scheme 34.

The ^1H and ^{13}C -NMR spectra of η^6 -benzene- η^5 -cyclopentadienyliron has several interesting characteristics when compared with the free arene. Most noticeable is a shift of the aromatic resonances upfield compared to uncomplexed benzene. This has been attributed to many factors, including metal-to-ligand π^* backbonding, ligand σ -to-metal donation and ligand π -to metal donation [246]. It is most likely that the approximately 1 ppm shift upfield is a result of all of these factors.

Also noticeable is a shift of the cyclopentadienyl resonances downfield from their position in ferrocene. Again, this shift is significant and is on the order of 1 ppm. Nesmeyanov has suggested that this is due to the presence of a positive charge on the iron atom, which is delocalized throughout the cyclopentadienyl ring [247].

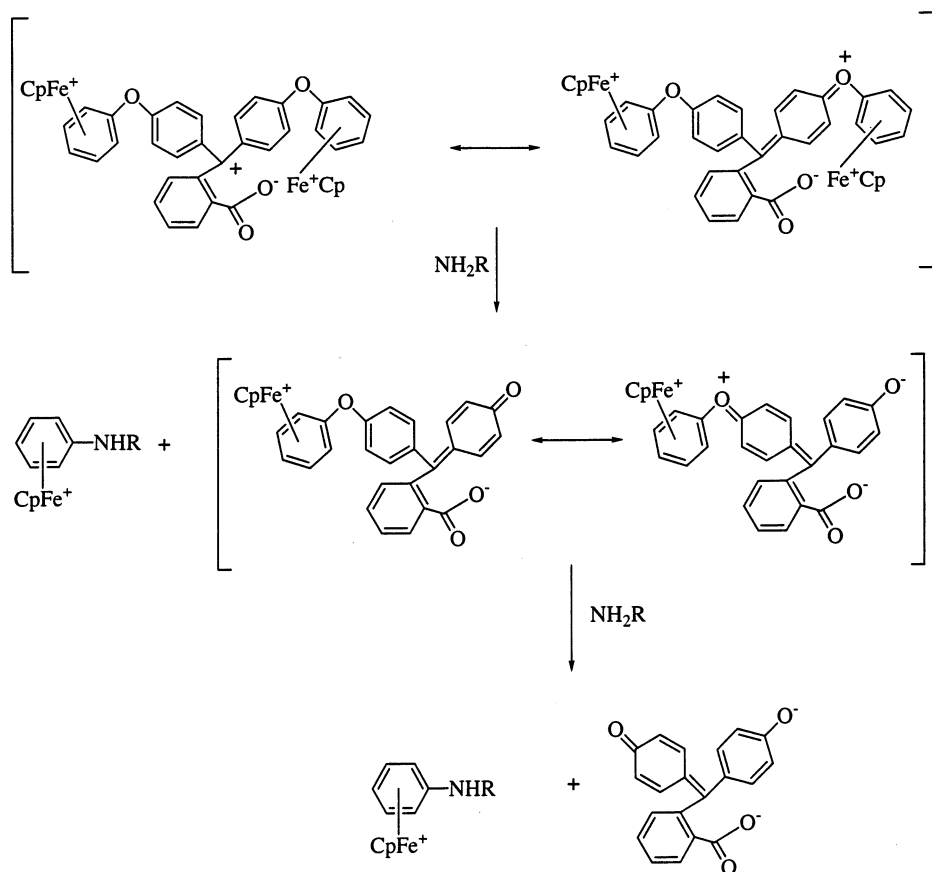


Scheme 35.

Noteworthy also is the large chemical shift of the quaternary carbons of cyclopentadienyliron complexed arenes. These carbons may be shifted as far as 80 ppm downfield from the methine carbons on the complexed ring. Steele explained that this was due to resonance between the aromatic ring and contributing zwitterions [246].

Two dimensional techniques have been used to characterize cyclopentadienyliron complexes as well [248]. Long range coupling constants for the chiral η^6 -(2,6-dimethylphenylphenylsulfonylacetonitrile)- η^5 -(cyclopentadienyliron) salt have been determined through the use of HH- and DQ-COSY [249]. Restricted rotation about the arene-methine bond, which has been well-documented for the free arene, was confirmed by difference nOe spectroscopy, and was found to be significant. Restricted rotation about the nitrogen arene bond for complexed amino acids has also been evidenced by 1H - and ^{13}C -NMR studies undertaken by Roberts and Johnsen [172].

Cyclohexadienyliron adducts have also been studied extensively by NMR techniques [190]. Addition of hydride to a series of polymetallic complexes resulted in the formation of complex mixtures of isomers, which were resolved through the use of two dimensional techniques. HH-COSY allowed for the identification of individual isomers through connectivity. Once this was established, CH-COSY was used to determine the ^{13}C -NMR chemical shifts of the resonances for the individual isomers. Relative ratios were established by evaluating the peak areas of each isomer in the 1H -NMR spectrum [190].



Scheme 36.

Fernando and Roberts have used ^{13}C -NMR spectroscopy to estimate the dihedral angle of the complexed phenyl ring and the heterocycle for a series of complexed indoles prepared by nucleophilic aromatic substitution. This was done using the difference in the chemical shift between the *ortho* and *meta* carbon atoms on the complexed rings, from the derived relationship:

$$\cos^2 \theta = \frac{\Delta}{-7.6}$$

These calculations give values which are somewhat smaller than those found for the uncomplexed derivatives via molecular modeling experiments. This has been attributed to a larger barrier of rotation imposed by the presence of the metal moiety [173].

5. Chemical and electrochemical reduction of arene complexes

Transition metal complexes have displayed some promise in the area of electron transfer chain catalysis, due to the ability to oxidize or reduce the metal center [250–274]. Although the iron atom is in the (II) oxidation state in cyclopentadienyliron complexes, attempts to oxidize the metal center to the (III) state have thus far failed. However, these complexes may be chemically or electrochemically reduced, which results in the formation of an electron-rich species. η^6 -Arene- η^5 -cyclopentadienyliron complexes have been examined using polarographic and cyclic voltammetric methods, and have shown their potential as electron reservoirs [211,212,270].

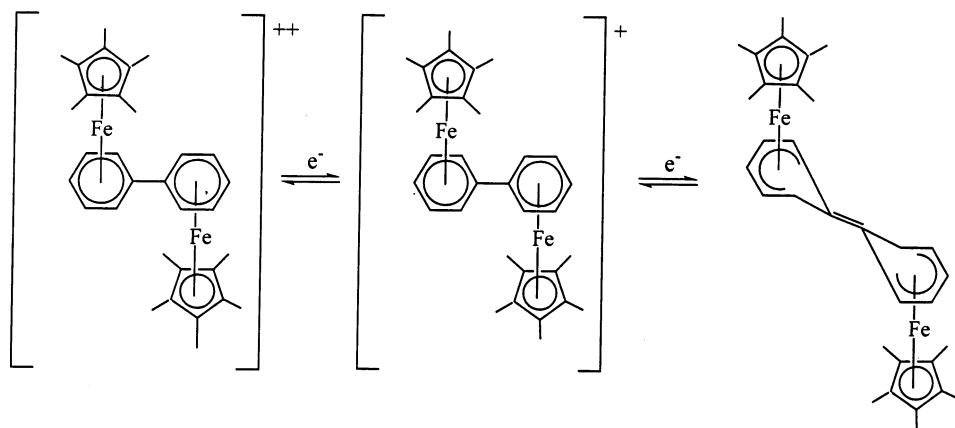
Early polarographic studies of arene complexes indicated the presence of two monoelectronic reduction waves; the first forming a 19-electron complex, and the second forming a very unstable 20-electron complex. [275–277]. Cyclic voltammetry has shown that the formation of the 19-electron complex is often reversible on the cyclic voltammetric time-scale, although attempts to isolate them have, in general, been unsuccessful, due to the radical nature of the complex. Until now, the only 19-electron complexes which have been effectively isolated are polyalkylbenzenes [250]. These are true metal radicals, which localize the unpaired electron primarily in the metal orbitals, as confirmed by Mössbauer and EPR studies. The cyclopentadienyl ring has very little contribution to the HOMO e_1^* , and the arene contributes even less.

A great deal of work by Astruc has shown that these polyalkylated compounds are, in fact, excellent reducing agents [278–280]. The 19-electron hexamethylbenzene complex may be generated chemically, by reduction with a sodium/mercury amalgam, and then itself reduce other chemical species cleanly, such as nitrate ion [281] and C_{60} [282]. This complex has also been shown to be an excellent electron transfer reagent for organometallic species, delivering a single electron to 17- or 18-electron complexes [283,284]. This complex may be used in redox titrations, due to the green-colored solution which is observed when it is in excess.

The reduction behavior of arene cyclopentadienyliron complexes is strongly influenced by the chemical and physical environment. The presence of substituents on the ring alters the potential at which the complex may be reduced. Arene complexes with electron-withdrawing substituents are reduced at lower negative potentials than those with electron-donating substituents [257]. Studies of the reduction of these complexes in different media demonstrate that the solvent system influences the kinetics of decomposition of the 19- and 20-electron species [258]. Cyclic voltammetric studies of arene complexes in DMF have shown that an increase in the concentration of acetonitrile decreases the chemical reversibility of the reduction process. This is presumed to be due to a solvent interaction with the reduced species, which catalyzes its decomposition. Consistent with this, a positive correlation was found between the nucleophilicity of the solvent and the rate at which decomposition occurred [285].

Astruc and co-workers have also studied the reduction behavior of bimetallic complexes using cyclic voltammetry [265,268]. The complexed biphenyl system was

reduced in two successive one-electron steps at $E^\circ = -1.27$ and -1.40 V, respectively (versus SCE in DMF) (Scheme 37) [250]. These results indicate rapid electrochemical communication, which is due to the direct linkage between the complexed phenyl rings. A more negative potential is thus required for the reduction of the second metallic moiety. This work was extended to include bridging heteroatoms when Bard found a similar communication in the reduction of the bimetallic complex of thianthrene [256].



Scheme 37.

The nature of the bridge between complexed arene rings influences the interactions between the two metal moieties. For the hydroquinone-bridged bimetallic, two reversible reductions were observed; one for the transition from the 36-electron complex to the 38-electron complex ($E_{1/2} = -1.75$ V vs. Fc/Fc^+) and the other for the transition from the 38-electron complex to the 40-electron complex ($E_{1/2} = -1.75$ V vs. Fc/Fc^+). Although the bimetallic cyclic voltammograms closely resemble those of the monometallics, the proposed two successive 2-electron reductions were confirmed using controlled potential coulometry, as shown in Fig. 1 [285].

It has been shown that for sulfur-bridged bimetallics, the increased electron density on the first iron center is dispersed across the bridge to the second metallic moiety, making it slightly more difficult to be reduced. These complexes show two distinct steps for the reduction of the 36-electron complex to the 37-electron complex, and the subsequent addition of another electron to form the 38-electron complex. Thus, in sulfur-bridged bimetallics, the reduction of one metal moiety influences the reduction potential of the other metal moiety on a CV time-scale. This electrochemical communication is in direct contrast with the analogous ether-bridged systems [285].

Studies of the polyether complexes were extended to include oligomers containing up to 5 metallic moieties. It was determined that these complexes dis-

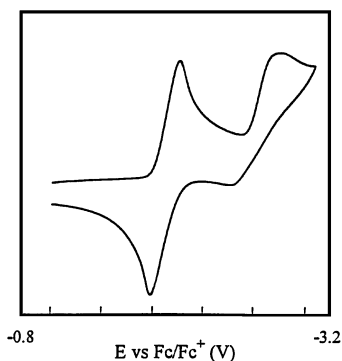


Fig. 1. Cyclic voltammogram at glassy carbon of 2.0 mM hydroquinone-bridged diiron complex in DMF, containing 0.1 M TBAP at 233 K, $\nu = 0.2 \text{ V s}^{-1}$.

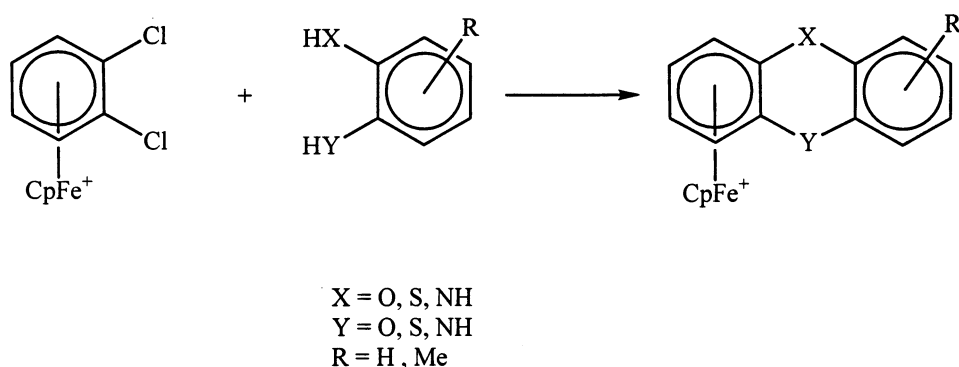
played similar electrochemical behavior to the mono- and diaryl ether complexes. Two reduction processes were observed, the first at -1.8 V , and the second at -2.8 V (vs. Fc/Fc^+). The stability of the pentairon complex following the first reduction was much lower than the mono- and diiron analogues. This instability made the complex difficult to analyze; however, related systems may be potentially useful as electron reservoirs [285].

6. Applications of arene complexes in organic and polymer synthesis

Traditionally, nucleophilic aromatic substitution has seen limited application in organic synthesis, due to the required presence of strong activating groups on the aromatic ring. These activating groups must often be removed, which increases the number of synthetic steps, and may require harsh reaction conditions, decreasing the overall yield. However, since the discovery of the electrophilicity of tricarbonylchromium complexes by Nichols and Whiting in 1959 [286], metal-assisted nucleophilic aromatic substitution has become an efficient route to the synthesis of a variety of new materials [9,18,25,34,44,57,60]. Although much of the literature has focused on the use of the tricarbonylchromium moiety in the activation of arenes, researchers such as Nesmeyanov [287], Astruc [66,80], Sutherland [65,67] and Pearson [288] have shown that the cyclopentadienyliron moiety is a viable alternative to tricarbonylchromium. Advantages of the cyclopentadienyliron moiety include the ease of complexation using inexpensive, commercially available starting materials. Kinetic studies have also shown that the cyclopentadienyliron moiety is a much stronger activating group than tricarbonylchromium. As a result, the cyclopentadienyliron moiety has found use in a variety of synthetic applications, including the novel synthesis of heterocycles, macrocycles and unique monomers for polymerization.

6.1. Heterocycles

The synthesis of dibenzodioxins and their derivatives has been of significant interest due to their potential use as anti-cancer agents [151]. While the condensation of 2-halogenophenols is one possible route to this class of compounds, metal-assisted nucleophilic aromatic substitution provides a much more efficient methodology [151,289]. Sutherland has shown that the reaction of suitable nitrogen-, oxygen- or sulfur-containing nucleophiles with the *o*-dichlorobenzene cyclopentadienyliron complex results in the formation of monometallic heterocycles in good yield, as shown in Scheme 38 [289]. Removal of the metal moiety by thermolysis allows for the isolation of the organic heterocycle.

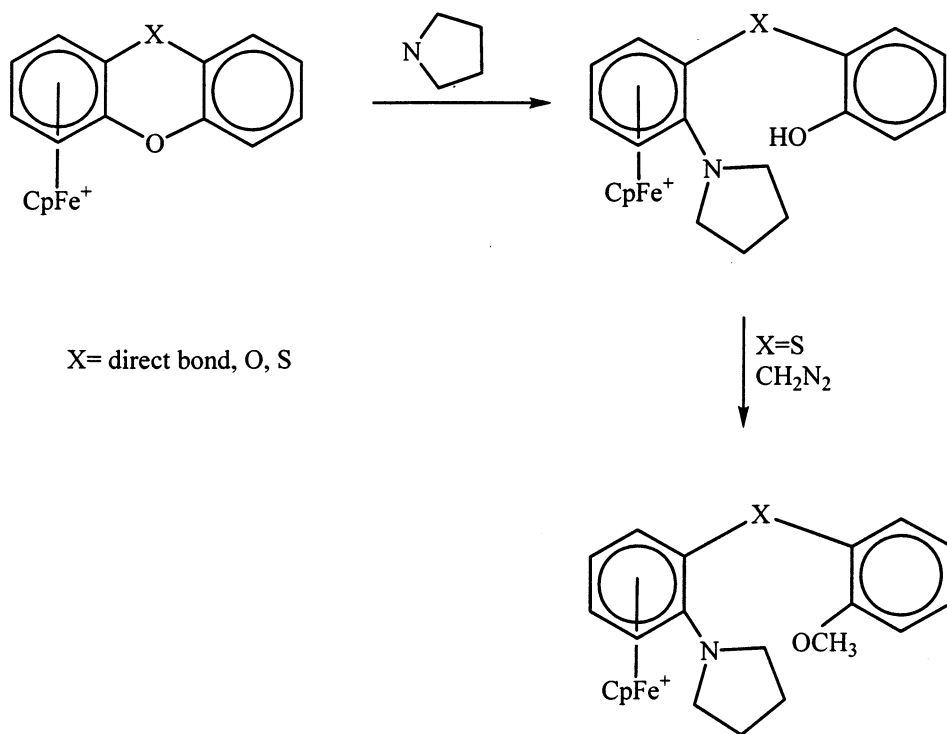


Scheme 38.

It has been demonstrated that the complexed heterocycles may be opened by nucleophiles, again due to the strong electron-withdrawing ability of the cyclopentadienyliron moiety. Reaction of pyrrolidine with a variety of heterocycles resulted in ring opening exclusively at the oxygen atom, even in the presence of nitrogen or sulfur heteroatoms (Scheme 39) [290]. This study was extended to include other nitrogen and carbon nucleophiles in the ring opening of the xanthone complex [291]. Degradation of this type of heterocyclic ring system may be of ecological interest, as dioxins are a class of persistent environmental toxins.

6.2. Macrocycles

Interest in the synthesis of macrocyclic compounds stems from their possible applications in catalysis, selective complexation and polymer chemistry [292–294]. The incorporation of aromatic subunits into the backbone of the macrocycle increases its rigidity and stability in harsh environments. However, the preparation of these compounds via traditional organic methods requires harsh reaction conditions and suffers from low yields [295,296]. These difficulties may be overcome through the use of metal-mediated nucleophilic aromatic substitution [297,298].



Scheme 39.

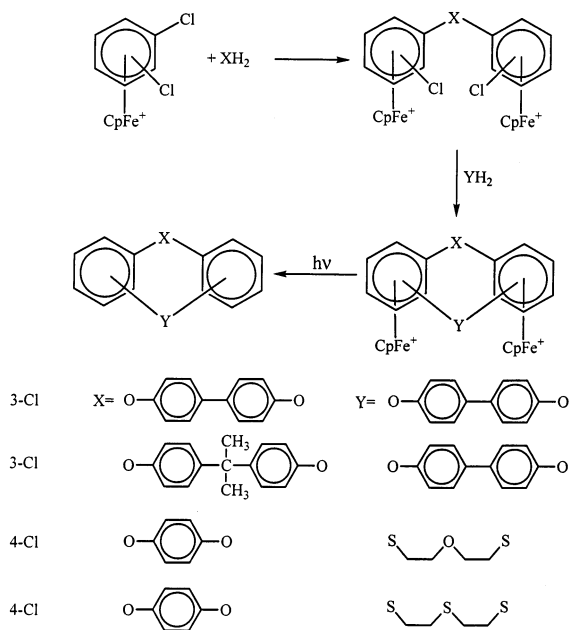
The cyclopentadienyliron moiety has been used in the synthesis of a variety of cyclic aryl ethers. The first step involves the reaction of two equivalents of *m*- or *o*-dichlorobenzene complex with one equivalent of the bridging nucleophile. Subsequent reaction of the bimetallic species with a second bridging nucleophile generates the metallated macrocycle, which may be demetallated by photolysis (Scheme 40) [299]. This stepwise methodology allows for the synthesis of symmetrical and nonsymmetrical macrocycles in good yields.

6.3. Polymer building blocks

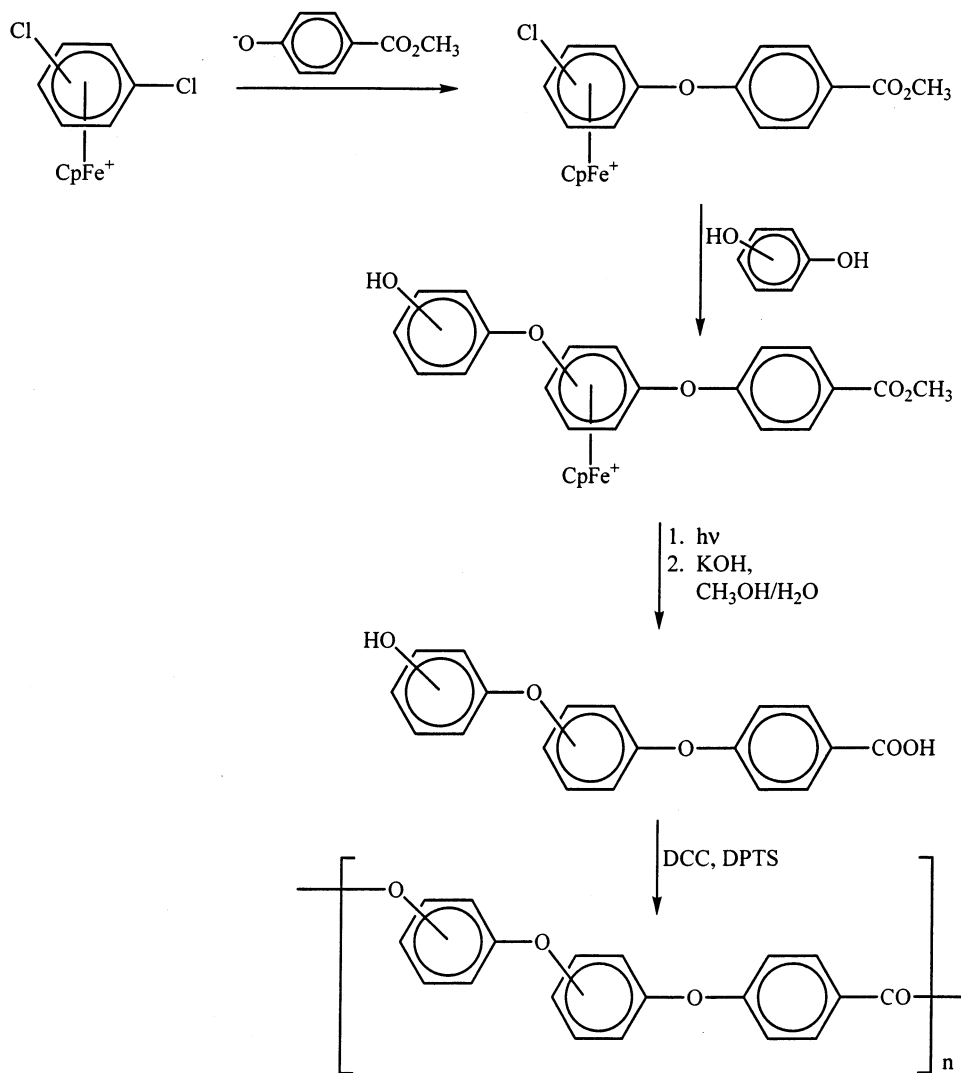
Poly(aryl ethers) are of great importance industrially as engineering thermoplastics, due to their thermal and mechanical properties. However, methods of generating aryl ethers are limited to the Ullmann ether synthesis [149], coupling reactions catalyzed by metal salts [300,301] and nucleophilic aromatic substitution [302,303]. While the Ullmann ether synthesis and coupling reactions are currently used to prepare these compounds, harsh reaction conditions and poor yields accompany these methods. In contrast, metal-assisted nucleophilic aromatic substitution allows for a much more efficient method for the preparation of aryl ethers, permitting the synthesis of novel monomers for polymerization.

Pearson and co-workers have used the cyclopentadienyliron moiety to synthesize unique monomers designed to retain their structural sequences upon heating [164]. This was accomplished in four steps, beginning with selective substitution of a single chlorine atom of a dichlorobenzene complex by methyl-4-hydroxybenzoate (Scheme 41). Substitution of the remaining chlorine substituent with hydroquinone or resorcinol resulted in the formation of the complexed diaryl ether. The metal moiety was removed photolytically and subsequent hydrolysis gave the nonsymmetrical diaryl ether terminating in a phenoxy and carboxylic acid substituent. Polymerization resulted in the formation of a high molecular weight polyester, which showed remarkable thermal stability. This was due in part to the incorporation of aryl ether bonds, which are known to be thermally stable. More significant, however, was the absence of rearrangement due to transesterification reactions, which occur at high temperature. Rearrangement was precluded because of the design of the polymer, which consists of the same sequence regardless of the extent of transesterification.

The ring-opening metathesis polymerization (ROMP) of norbornene, in the presence of transition metal-based catalysts has been industrially important since 1976 [304]. However, the low glass transition point of polynorbornene has limited its use in high-temperature applications. In order to extend the use of polynorbornene to higher temperatures, workers have shown that functionalization of the polynorbornene backbone improves its thermal stability [305,306].



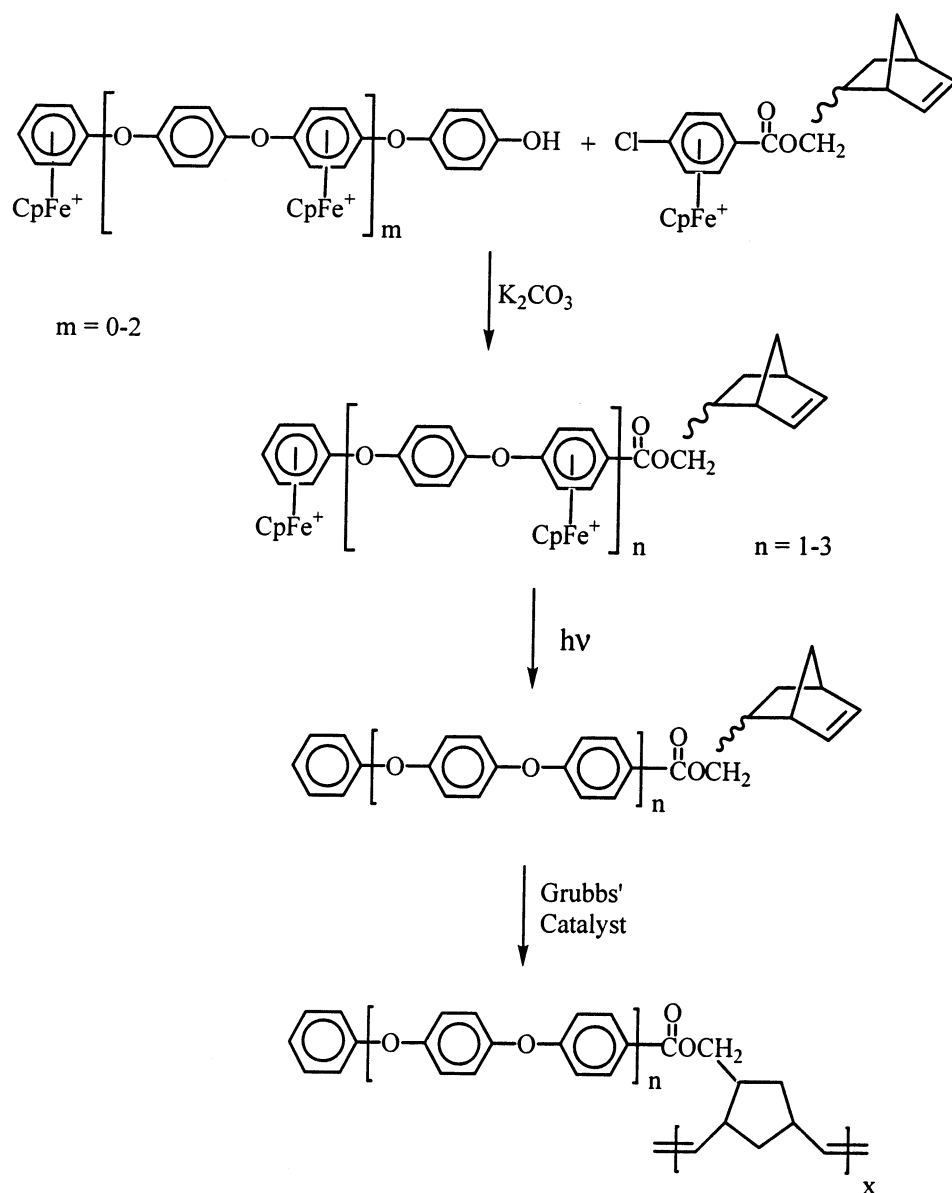
Scheme 40.



Scheme 41.

It has recently been demonstrated that functionalization of polynorbornene with pendent aryl ether and ester chains results in an increase in the glass transition temperature. Preparation of the norbornene monomer was accomplished by the condensation of *exo,endo*-5-norbornene-2-methanol with chlorobenzoic acid complex. Growth of the pendent aryl ether chain proceeded using metal-mediated nucleophilic aromatic substitution. Photolytic demetallation yielded the organic monomer, which was then subjected to ROMP, giving high molecular weight polymers with narrow polydispersities. Thermal analysis of the resulting polymeric

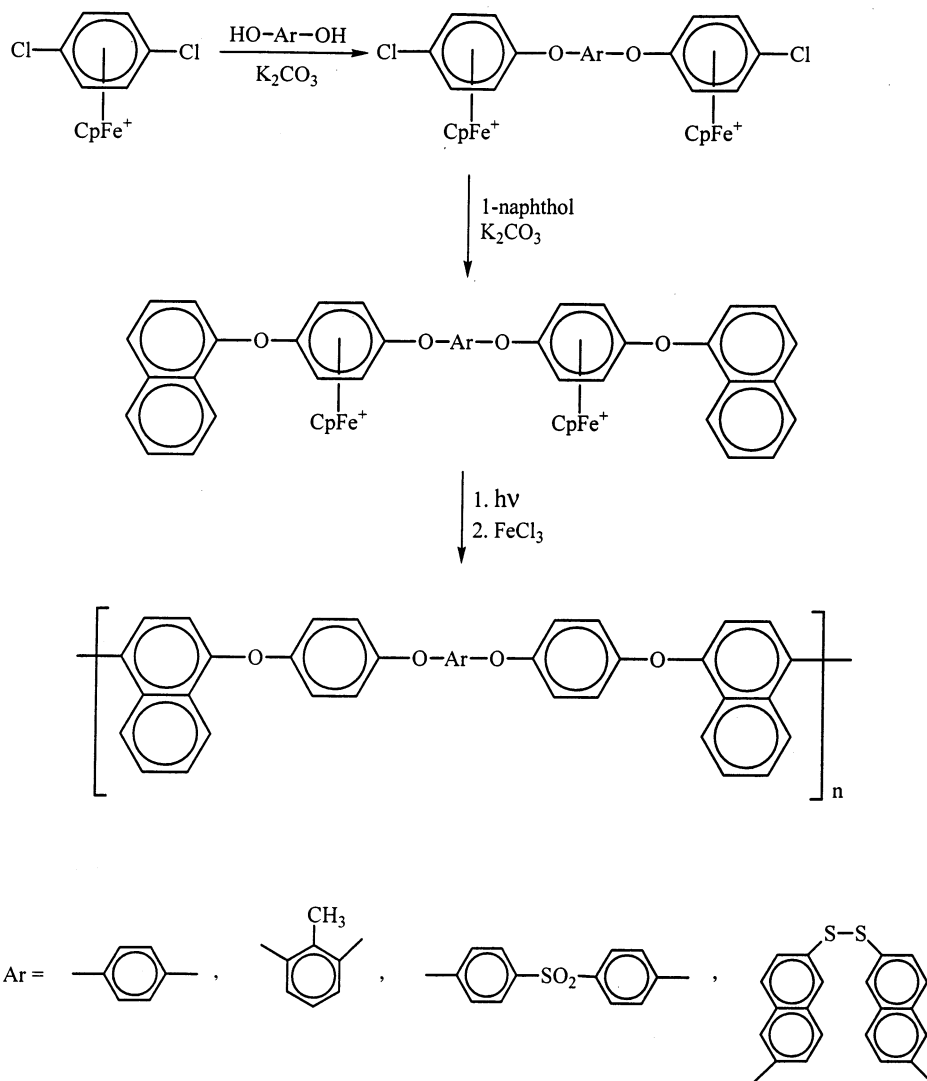
materials showed significant increases in the glass transition temperatures and decomposition points in comparison to unsubstituted polynorbornene [307] (Scheme 42).



Scheme 42.

Scholl polymerization creates aryl carbon–carbon bonds between naphthyl sub-units of monomers in the presence of ferric chloride [308–313]. Metal-assisted

nucleophilic aromatic substitution may be used to create novel monomers. Dichlorobenzene complexes were reacted with several different nucleophiles to generate the corresponding bimetallic species. These were then ‘capped’ with 1-naphthol, to create the metallated monomers. Demetallation by photolysis, followed by polymerization resulted in the preparation of thermally stable, high molecular weight polymers (Scheme 43) [314].



Scheme 43.

7. Conclusion

Arenes coordinated to cyclopentadienyliron have been used extensively in recent years due to the increased electrophilicity of the arene. These complexes have been used as intermediates in organic synthesis, and have displayed their ability to act as electron transfer catalysts. Use of these complexes in polymer synthesis has allowed for the preparation of both organic and organometallic polymers. The organoiron system has advantages over other transition metal moieties due to the ease of complexation, the commercial availability of the starting materials, the mild experimental conditions as well as the higher activation towards nucleophilic addition and substitution reactions.

References

- [1] S.G. Davies, *Organotransition Metal Chemistry: Applications to Organic Synthesis*, Pergamon Press, Toronto, 1982.
- [2] M.F. Semmelhack, *J. Organomet. Chem. Lib.* 1 (1976) 361.
- [3] R.B. King, in: E.A. Koerner von Gustorf, F.W. Grevels, I. Fischler (Eds.), *The Organic Chemistry of Iron*, vol. 2, Academic Press, New York, 1981, pp. 155.
- [4] L.A.P. Kane-Maguire, E.D. Hondig, D.A. Sweigart, *Chem. Rev.* 84 (1984) 525.
- [5] R.M. Moriarty, U.S. Gill, Y.Y. Ku, *J. Organomet. Chem.* 350 (1988) 157.
- [6] E.P. Kündig, *Pure Appl. Chem.* 57 (1985) 1855.
- [7] L. Balas, D. Jhurry, L. Lataxague, S. Grelier, Y. Morel, M. Hamdani, N. Ardoin, D. Astruc, *Bull. Soc. Chim. Fr.* 127 (1990) 401.
- [8] M.F. Semmelhack, in: B.M. Trost, I. Fleming (Eds.), *Comprehensive Organic Synthesis*, vol. 4, Pergamon Press, New York, 1991.
- [9] M.F. Semmelhack, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), *Comprehensive Organometallic Chemistry II*, vol. 12, Pergamon Press, New York, 1995.
- [10] M.A. Bennett, *Coord. Chem. Rev.* 166 (1997) 225.
- [11] Y.K. Kang, H.-K. Lee, S.S. Lee, Y.K. Chung, G. Carpenter, *Inorg. Chim. Acta* 261 (1997) 37.
- [12] M.F. Semmelhack, H.T. Hall, *J. Am. Chem. Soc.* 96 (1974) 7091.
- [13] M.F. Semmelhack, H.T. Hall, *J. Am. Chem. Soc.* 96 (1974) 7092.
- [14] C.A.L. Mahaffy, P.L. Pauson, *Inorg. Synth.* 19 (1979) 154.
- [15] R.D. Rogers, J.L. Atwood, T.A. Albright, W.A. Lee, M.D. Rausch, *Organometallics* 3 (1984) 263.
- [16] E.P. Kündig, C. Perret, S. Spichiger, *J. Organomet. Chem.* 286 (1985) 183.
- [17] I.I. Oleinic, P.P. Kun, V.V. Litvak, V.D. Shteingarts, *Zh. Org. Khim.* 24 (1988) 929.
- [18] G.B. Richter-Addo, A.D. Hunter, N. Wichrowska, *Can. J. Chem.* 68 (1990) 41.
- [19] M.E. Wright, *Organometallics* 8 (1989) 407.
- [20] M.E. Wright, *Macromolecules* 22 (1989) 3256.
- [21] G.B. Richter-Addo, A.D. Hunter, *Inorg. Chem.* 28 (1989) 4063.
- [22] A. Goti, M.F. Semmelhack, *J. Organomet. Chem.* 470 (1994) C4.
- [23] H.R. Allcock, A.A. Dembek, E.H. Klingenberg, *Macromolecules* 24 (1991) 5208.
- [24] S. Maiorana, C. Baldoli, P. Del Buttero, M. Di Ciolo, A. Papagni, *Synthesis (Stuttgart)* 5 (1998) 735.
- [25] F. Rose-Munch, C. Le Corre-Susanne, F. Balssa, E. Rose, J. Vaisserman, E. Licandro, A. Papagni, S. Maiorana, W.-D. Meng, G.R. Stephenson, *J. Organomet. Chem.* 545–546 (1997) 9.
- [26] L.C.F. Chao, A. Deckens, J.F. Britten, M.J. McGlinchey, *Can. J. Chem.* 73 (1995) 1196.
- [27] M.J. McGlinchey, *Organometallics* 14 (1995) 5273.
- [28] M. Uemura, R. Miyake, M. Shiro, Y. Hayashi, *Tetrahedron Lett.* 32 (1991) 4569.
- [29] T.J. Müller, *Tetrahedron Lett.* 38 (1997) 1025.

- [30] M.F. Semmelhack, H.-G. Schmalz, *Tetrahedron Lett.* 37 (1996) 3089.
- [31] N. Taniguchi, M. Uemura, *Tetrahedron Lett.* 38 (1997) 7199.
- [32] C. Baldoli, P. Del Buttero, S. Maiorana, *Tetrahedron Lett.* 33 (1992) 4049.
- [33] A.J. Pearson, A.V. Gontcharov, P.D. Woodgate, *Tetrahedron Lett.* 37 (1996) 3087.
- [34] W.H. Miles, P.M. Smiley, H.R. Brinkman, *J. Chem. Soc. Chem. Commun.* (1989) 1897.
- [35] W.H. Miles, H.R. Brinkman, *Tetrahedron Lett.* 33 (1992) 589.
- [36] Y.K. Yun, K.K. McDaniel, *Tetrahedron Lett.* 36 (1995) 4931.
- [37] W.J. Ryan, P.E. Peterson, Y. Cao, P.G. Willard, D.A. Sweigart, C.D. Baer, C.F. Thompson, Y.K. Chung, T.-M. Chung, *Inorg. Chim. Acta* 211 (1993) 1.
- [38] A.J. Pearson, P.R. Bruhn, S.-Y. Hsu, *J. Org. Chem.* 51 (1986) 2137.
- [39] D.M. LaBrush, D.P. Eyman, N.C. Baenziger, L.M. Mallis, *Organometallics* 10 (1991) 1026.
- [40] P.L. Pauson, J.A. Segal, *J. Chem. Soc. Dalton Trans.* (1975) 1677.
- [41] A.J. Pearson, P.R. Bruhn, *J. Org. Chem.* 56 (1991) 7092.
- [42] P.J.C. Walker, R.J. Mawby, *Inorg. Chim. Acta* 7 (1973) 621.
- [43] J.L. Moler, D.P. Eyman, J.M. Nielson, A.M. Morken, S.J. Schauer, D.B. Snyder, *Organometallics* 12 (1993) 3304.
- [44] S. Sun, G.B. Carpenter, D.A. Sweigart, *J. Organomet. Chem.* 512 (1996) 257.
- [45] M.V. Gaudet, A.W. Hanson, P.S. White, M.J. Zaworotko, *Organometallics* 8 (1989) 826.
- [46] Y.K. Chung, P.J. Willard, D.A. Sweigart, *Organometallics* 1 (1982) 1053.
- [47] C. Renard, R. Valentic, F. Rose-Munch, E. Rose, J. Vaisserman, *Organometallics* 17 (1998) 1587.
- [48] L.A.P. Kane-Maguire, D.A. Sweigart, *Inorg. Chem.* 18 (1979) 700.
- [49] A.J. Pearson, P.Y. Zhu, W.J. Youngs, J.D. Bradshaw, D.B. McConville, *J. Am. Chem. Soc.* 115 (1993) 10376.
- [50] S. Sun, C.A. Dullaghan, G.B. Carpenter, D.A. Sweigart, S.S. Lee, Y.K. Chung, *Inorg. Chim. Acta* 262 (1997) 213.
- [51] C.A. Dullaghan, G.B. Carpenter, D.A. Sweigart, *Chem. Eur. J.* 3 (1997) 75.
- [52] R.D. Pike, G.B. Carpenter, *Organometallics* 12 (1993) 1416.
- [53] B.C. Roell Jr., K.F. McDaniel, W.S. Vaughan, T.S. Macy, *Organometallics* 12 (1993) 224.
- [54] T.-Y. Lee, Y.K. Kang, Y.K. Chung, R.D. Pike, D.A. Sweigart, *Inorg. Chim. Acta* 214 (1993) 125.
- [55] R.D. Pike, D.A. Sweigart, *Synlett* (1990) 565.
- [56] K. Woo, P.J. Willard, D.A. Sweigart, N.W. Duffy, B.H. Robinson, J. Simpson, *J. Organomet. Chem.* 487 (1995) 111.
- [57] G.R. Krow, W.H. Miles, P.M. Smiley, W.S. Lester, Y.J. Kim, *J. Org. Chem.* 57 (1992) 4040.
- [58] J.A. Segal, *J. Chem. Soc. Chem. Commun.* (1985) 1338.
- [59] A.A. Dembek, P.J. Fagan, M. Marsi, *Macromolecules* 26 (1993) 2992.
- [60] A.A. Dembek, P.J. Fagan, M. Marsi, *Polym. Mater. Sci. Eng.* 71 (1994) 158.
- [61] P.J. Fagan, M.D. Ward, J.V. Caspar, J.C. Calabrese, P.J. Krusic, *J. Am. Chem. Soc.* 110 (1988) 2981.
- [62] P.J. Fagan, M.D. Ward, J.C. Calabrese, *J. Am. Chem. Soc.* 111 (1989) 1698.
- [63] T.P. Gill, K.R. Mann, *Organometallics* 1 (1982) 485.
- [64] D.T. Glatzhofer, Y. Liang, M.A. Khan, P.J. Fagan, *Organometallics* 10 (1991) 833.
- [65] R.G. Sutherland, *J. Organomet. Chem. Lib.* 3 (1977) 311.
- [66] D. Astruc, *Tetrahedron* 39 (1983) 4027.
- [67] R.G. Sutherland, M. Iqbal, A. Piórko, *J. Organomet. Chem.* 302 (1986) 307.
- [68] A.C. Knipe, S.J. McGuinness, W.E. Watts, *J. Chem. Soc. Perkin Trans. II* (1981) 193.
- [69] A.C. Knipe, S.J. McGuinness, W.E. Watts, *J. Chem. Soc. Chem. Commun.* (1979) 842.
- [70] A.N. Nesmeyanov, N.A. Vol'kenau, L.S. Isaeva, I.N. Bolesova, *Dokl. Akad. Nauk SSSR* 183 (1968) 834.
- [71] V.V. Litvak, L.S. Filatova, N.Y. Khalikova, V.D. Shteingarts, *Zh. Org. Khim* 16 (1980) 336.
- [72] V.V. Litvak, L.S. Filatova, G.A. Selivanova, V.D. Shteingarts, *Zh. Org. Khim* 16 (1980) 342.
- [73] P.C.B. Gomes, E.J.S. Vichi, P.J.S. Moran, A.F. Neto, M.L. Maroso, J. Miller, *Organometallics* 15 (1996) 3198.
- [74] T.H. Coffield, V. Sandel, R.D. Closson, *J. Am. Chem. Soc.* 79 (1957) 5826.
- [75] T.H. Coffield, R.D. Closson, U.S. Patent 3,130,214.

- [76] J-R Hamon, D. Astruc, *Organometallics* 8 (1989) 2243.
- [77] H. Rabaâ, M. Lacoste, M.-H. Delville-Desbois, J. Ruiz, B. Gloaguen, N. Ardoin, D. Astruc, A. Le Beuze, J.-Y. Saillard, J. Linares, F. Varret, J.-M. Dance, E. Marquestaut, *Organometallics* 14 (1995) 5078.
- [78] A.N. Nesmeyanov, N.A. Vol'kenau, I.N. Bolesova, *Dokl. Akad. Nauk SSSR* 149 (1963) 615.
- [79] A.N. Nesmeyanov, N.A. Vol'kenau, I.N. Bolesova, *Tetrahedon Lett.* 25 (1963) 1725.
- [80] D. Astruc, *Top. Curr. Chem.* 160 (1991) 47.
- [81] I.U. Khand, P.L. Pauson, W.E. Watts, *J. Chem. Soc. C* (1968) 2257.
- [82] R.B. King, *Organomet. Synth.* 1 (1963) 138.
- [83] D. Astruc, R. Dabard, *C.R. Acad. Sci. Paris Ser. C* 269 (1970) 689.
- [84] E.I. Sirotkina, A.N. Nesmeyanov, N.A. Vol'kenau, *Izv. Akad. Nauk SSSR Ser. Khim.* (1969) 1524.
- [85] A.N. Nesmeyanov, N.A. Vol'kenau, I.N. Bolesova, *Dokl. Akad. Nauk SSSR* 166 (1966) 607.
- [86] D. Astruc, R. Dabard, *Tetrahedron* 32 (1976) 245.
- [87] D. Astruc, R. Dabard, *J. Organomet. Chem.* 96 (1975) 283.
- [88] W.H. Morrison, E.Y. Ho, D.N. Hendrickson, *J. Am. Chem. Soc.* 96 (1974) 3603.
- [89] C.C. Lee, R.G. Sutherland, B.J. Thomson, *J. Chem. Soc. Chem. Commun.* (1972) 902.
- [90] R.G. Sutherland, S.C. Chen, J. Pannekoek, C.C. Lee, *J. Organomet. Chem.* 101 (1975) 221.
- [91] D.A. Owen, A. Siegel, R. Lin, D.W. Slocum, B. Conway, M. Moronski, S. Duraj, *Ann. N.Y. Acad. Sci.* 333 (1980) 90.
- [92] C.C. Lee, R.G. Sutherland, B.J. Thomson, *J. Chem. Soc. Chem. Commun.* (1971) 1071.
- [93] J.F. Helling, W.A. Hendrickson, *J. Organomet. Chem.* 141 (1977) 99.
- [94] I.U. Khand, P.L. Pauson, W.E. Watts, *J. Chem. Soc. C* (1968) 2261.
- [95] A.N. Nesmeyanov, N.A. Vol'kenau, E.I. Sirotkina, V.V. Deryabin, *Dokl. Akad. Nauk SSSR* 177 (1967) 1110.
- [96] I.U. Khand, P.L. Pauson, W.E. Watts, *J. Chem. Soc. C* (1969) 116.
- [97] A.N. Nesmeyanov, N.A. Vol'kenau, I.N. Bolesova, *Dokl. Akad. Nauk SSSR* 175 (1967) 606.
- [98] R.G. Sutherland, W.J. Pannekoek, C.C. Lee, *Can. J. Chem.* 56 (1978) 1782.
- [99] G. Schmitt, W. Keim, J. Fleischhauer, U. Walbergs, *J. Organomet. Chem.* 152 (1978) 315.
- [100] E.D. Laganis, R.G. Finke, V. Boekelheide, *Proc. Natl. Acad. Sci. USA* 78 (1981) 2657.
- [101] A.R. Koray, *J. Organomet. Chem.* 212 (1981) 233.
- [102] A.R. Koray, *J. Organomet. Chem.* 232 (1982) 345.
- [103] C.C. Lee, A. Piorko, R.G. Sutherland, *J. Organomet. Chem.* 248 (1983) 357.
- [104] C.C. Lee, K.J. Demchuk, W.J. Pannekoek, R.G. Sutherland, *J. Organomet. Chem.* 162 (1978) 253.
- [105] A.W. Hanson, *Cryst. Struct. Commun.* 11 (1982) 901.
- [106] A.W. Hanson, *Cryst. Struct. Commun.* 11 (1982) 1395.
- [107] R.G. Sutherland, S.C. Chen, W.J. Pannekoek, C.C. Lee, *J. Organomet. Chem.* 117 (1976) 61.
- [108] R.G. Sutherland, W.J. Pannekoek, C.C. Lee, *J. Organomet. Chem.* 129 (1977) C1.
- [109] R.G. Sutherland, W.J. Pannekoek, C.C. Lee, *Ann. N.Y. Acad. Sci.* 295 (1980) 192.
- [110] R.M.G. Roberts, J. Silver, A.S. Wells, S.P. Wilkinson, *J. Organomet. Chem.* 327 (1987) 247.
- [111] M.R. Benites, F.R. Fronczek, A.W. Maverick, *J. Organomet. Chem.* 516 (1996) 17.
- [112] J.W. Johnson, P.M. Treichel, *J. Chem. Soc. Chem. Commun.* (1976) 688.
- [113] C.C. Lee, B.R. Steele, R.G. Sutherland, *J. Organomet. Chem.* 141 (1980) 265.
- [114] A.N. Nesmeyanov, N.A. Vol'kenau, L.S. Shilovtseva, *Dokl. Akad. Nauk. SSSR* 160 (1965) 1327.
- [115] P.J. Dyson, M.C. Gossel, N. Srinivasan, T. Vine, T. Welton, D.J. Williams, A.J.P. White, T. Zigras, *J. Chem. Soc. Dalton Trans.* (1997) 3465.
- [116] B.E. Eaton, E.D. Laganis, V. Boekelheide, *Proc. Natl. Acad. Sci. USA* 78 (1981) 6564.
- [117] T.P. Gill, K.R. Mann, *J. Organomet. Chem.* 216 (1981) 65.
- [118] C.C. Lee, U.S. Gill, M. Iqbal, C.I. Azogu, R.G. Sutherland, *J. Organomet. Chem.* 231 (1982) 151.
- [119] R.T. Swann, V. Boekelheide, *J. Organomet. Chem.* 231 (1982) 143.
- [120] T.P. Gill, K.R. Mann, *Inorg. Chem.* 22 (1983) 1986.
- [121] T.P. Gill, K.R. Mann, *Inorg. Chem.* 19 (1980) 3007.
- [122] C.I. Azogu, *Anal. Chim. Acta* 125 (1981) 171.
- [123] C.I. Azogu, *J. Chromatogr.* 219 (1981) 349.

- [124] Q. Dabirmanesh, R.M.G. Roberts, J. Organomet. Chem. 542 (1997) 99.
- [125] Q. Dabirmanesh, S.I.S. Fernando, R.M.G. Roberts, J. Chem. Soc. Perkin Trans. 1 (1995) 743.
- [126] Q. Dabirmanesh, R.M.G. Roberts, J. Organomet. Chem. 460 (1993) C28.
- [127] A.S. Abd-El-Aziz, W. Boraie, N. Al-Salem, S.A. Sadek, K.M. Epp, J. Chem. Soc. Perkin Trans. 1 (1997) 1469.
- [128] A.S. Abd-El-Aziz, K.M. Epp, Polyhedron 14 (1995) 957.
- [129] C.C. Lee, A.S. Abd-El-Aziz, R.L. Chowdhury, A. Piórko, R.G. Sutherland, Synth. React. Inorg. Met. Org. Chem. 16 (1986) 541.
- [130] E.I. Sirotkina, A.N. Nesmeyanov, N.A. Vol'kenau, Izv. Akad. Nauk SSSR Ser. Khim. (1969) 1524.
- [131] A.N. Nesmeyanov, N.A. Vol'kenau, E.I. Sirotkina, Izv. Akad. Nauk SSSR Ser. Khim. (1967) 1170.
- [132] B. Nichols, M.C. Whiting, J. Chem. Soc. (1976) 551.
- [133] M.F. Semmelhack, Ann. N.Y. Acad. Sci. 295 (1977) 36.
- [134] R.G. Sutherland, A.S. Abd-El-Aziz, A. Piórko, U.S. Gill, C.C. Lee, J. Heterocycl. Chem. 25 (1988) 1107.
- [135] R.G. Sutherland, A.S. Abd-El-Aziz, A. Piórko, C.C. Lee, Synth. Commun. 17 (1987) 393.
- [136] R.M. Moriarty, U.S. Gill, Organometallics 5 (1986) 253.
- [137] A.S. Abd-El-Aziz, C.C. Lee, A. Piórko, R.G. Sutherland, Synth. Commun. 18 (1988) 291.
- [138] A. Piórko, A.S. Abd-El-Aziz, C.C. Lee, R.G. Sutherland, J. Chem. Soc. Perkin Trans. 1 (1989) 469.
- [139] R.M. Moriarty, U.S. Gill, Y.Y. Ku, Polyhedron 7 (1988) 2685.
- [140] A.S. Abd-El-Aziz, C.C. Lee, A. Piórko, R.G. Sutherland, J. Organomet. Chem. 348 (1988) 95.
- [141] A.S. Abd-El-Aziz, C.C. Lee, A. Piórko, R.G. Sutherland, in: R.B. King, J.J. Eisch (Eds.), Organometallic Syntheses, vol. 4, Elsevier, Lausanne, 1988, p. 188.
- [142] A.S. Abd-El-Aziz, S. Tesfalidet, C.R. de Denus, K. Lezynska, Synth. Commun. 23 (1993) 1415.
- [143] A.S. Abd-El-Aziz, C.R. de Denus, Synth. Commun. 22 (1992) 581.
- [144] A.S. Abd-El-Aziz, C.R. de Denus, J. Chem. Soc. Perkin Trans. 1 (1993) 293.
- [145] A.S. Abd-El-Aziz, C.R. de Denus, H.M. Hutton, Can. J. Chem. 73 (1995) 289.
- [146] C.C. Lee, A.S. Abd-El-Aziz, R.L. Chowdhury, U.S. Gill, A. Piórko, R.G. Sutherland, J. Organomet. Chem. 315 (1986) 79.
- [147] A.P. Krapcho, Synthesis (1982) 805.
- [148] A.J. Pearson, J.G. Park, P.Y. Zhu, J. Org. Chem. 57 (1992) 3582.
- [149] A.A. Moroz, M.S. Shvartsberg, Russ. Chem. Rev. 43 (1974) 679.
- [150] A.J. Pearson, J.G. Park, S.H. Yang, Y.-H. Chuang, J. Chem. Soc. Chem. Commun. (1989) 1363.
- [151] R.C. Cambie, S.J. Janssen, P.S. Rutledge, P.D. Woodgate, J. Organomet. Chem. 420 (1991) 387.
- [152] A. Piórko, R.G. Sutherland, A. Vessières-Jaouen, G. Jaouen, J. Organomet. Chem. 512 (1996) 79.
- [153] R.M. Moriarty, Y.Y. Ku, U.S. Gill, J. Chem. Soc. Chem. Commun. (1987) 1493.
- [154] R.M. Moriarty, Y.Y. Ku, U.S. Gill, Organometallics 7 (1988) 661.
- [155] R.M. Moriarty, Y.Y. Ku, U.S. Gill, R. Gilardi, R.E. Perrier, M.J. McGlinchey, Organometallics 8 (1989) 960.
- [156] D. Vichard, M. Gruselle, H. El Amouri, G. Jaouen, J. Chem. Soc. Chem. Commun. (1990) 1765.
- [157] F. Urbanos, M.A. Halcrow, J. Fernandez-Baeza, F. Dahan, D. Labroue, B. Chaudret, J. Am. Chem. Soc. 115 (1993) 3484.
- [158] G. Jaouen, Pure Appl. Chem. 58 (1986) 596.
- [159] J.C. Gill, B.A. Marples, J.R. Traynor, Tetrahedron Lett. 28 (1987) 2643.
- [160] H. Künzer, M. Thiel, Tetrahedron Lett. 29 (1988) 1135.
- [161] H. Künzer, M. Thiel, Tetrahedron Lett. 29 (1988) 3223.
- [162] K. Woo, G.B. Carpenter, D.A. Sweigart, Inorg. Chim. Acta 220 (1994) 297.
- [163] C.C. Lee, C.H. Zhang, A.S. Abd-El-Aziz, A. Piórko, R.G. Sutherland, J. Organomet. Chem. 364 (1989) 217.
- [164] A.J. Pearson, A.M. Gelormini, Macromolecules 27 (1994) 3675.
- [165] A.J. Pearson, A.M. Gelormini, J. Org. Chem. 60 (1995) 281.

- [166] R.L. Chowdhury, C.C. Lee, A. Piórko, R.G. Sutherland, *Synth. React. Inorg. Met. Org. Chem.* 15 (1985) 1237.
- [167] A.S. Abd-El-Aziz, K.M. Epp, C.R. de Denus, G. Fisher-Smith, *Organometallics* 13 (1994) 2299.
- [168] A.J. Pearson, A.M. Gelormini, M.A. Fox, D. Watkins, *J. Org. Chem.* 61 (1996) 1297.
- [169] R.M.G. Roberts, *J. Organomet. Chem.* 430 (1992) 327.
- [170] C.C. Lee, C.I. Azogu, P.C. Chang, R.G. Sutherland, *J. Organomet. Chem.* 220 (1981) 181.
- [171] R.G. Sutherland, P.C. Chang, C.C. Lee, *J. Organomet. Chem.* 234 (1982) 197.
- [172] R.M.G. Roberts, E. Johnsen, *J. Organomet. Chem.* 544 (1997) 197.
- [173] S.I.S. Fernando, R.M.G. Roberts, *J. Organomet. Chem.* 474 (1994) 133.
- [174] T.H. Lowry, K.S. Richardson, *Mechanism and Theory in Organic Chemistry*, Harper and Row, New York, 1987, pp. 702–709.
- [175] A.S. Abd-El-Aziz, A. Piórko, C.C. Lee, R.G. Sutherland, *Can. J. Chem.* 67 (1989) 1618.
- [176] S.G. Davies, M.L.H. Green, D.M.P. Mingos, *Tetrahedron* 24 (1978) 3047.
- [177] P.L. Pauson, *J. Organomet. Chem.* 200 (1980) 207.
- [178] R.G. Sutherland, R.L. Chowdhury, A. Piórko, C.C. Lee, *J. Org. Chem.* 52 (1987) 4618.
- [179] R.G. Sutherland, C.H. Zhang, A. Piórko, C.C. Lee, *Can. J. Chem.* 67 (1989) 137.
- [180] C.H. Zhang, R.L. Chowdhury, A. Piórko, C.C. Lee, R.G. Sutherland, *J. Organomet. Chem.* 346 (1988) 67.
- [181] R.G. Sutherland, C.H. Zhang, R.L. Chowdhury, A. Piórko, C.C. Lee, *J. Organomet. Chem.* 333 (1987) 367.
- [182] J.F. McGreer, W.E. Watts, *J. Organomet. Chem.* 110 (1976) 103.
- [183] R.G. Sutherland, R.L. Chowdhury, A. Piórko, C.C. Lee, *J. Organomet. Chem.* 319 (1987) 379.
- [184] A.S. Abd-El-Aziz, W. Boraie, N.T. Gavel, *Organometallics* 18 (1999) 1562.
- [185] R.G. Sutherland, R.L. Chowdhury, A. Piórko, C.C. Lee, *Can. J. Chem.* 64 (1986) 2031.
- [186] R.G. Sutherland, R.L. Chowdhury, A. Piórko, C.C. Lee, *J. Chem. Soc. Chem. Commun.* (1985) 1296.
- [187] R.G. Sutherland, C. Zhang, A. Piórko, *J. Organomet. Chem.* 419 (1991) 357.
- [188] A. Zimniak, *Bull. Acad. Pol. Sci. Ser. Sci. Chim.* 27 (1979) 743.
- [189] A.N. Nesmeyanov, N.A. Vol'kenau, *Izv. Akad. Nauk SSSR Ser. Khim.* (1975) 1151.
- [190] A.S. Abd-El-Aziz, D.A. Armstrong, S. Bernardin, H.M. Hutton, *Can. J. Chem.* 74 (1996) 2073.
- [191] L.N. Novikova, I.V. Shchirina-Eingorn, N.A. Ustynyuk, P.V. Petrovskii, L.I. Denisovich, *Russ. Chem. Bull.* 46 (1997) 1007.
- [192] W. Lamanna, M. Brookhart, *J. Am. Chem. Soc.* 102 (1980) 3490.
- [193] G.A.M. Munro, P.L. Pauson, *J. Chem. Soc. Chem. Commun.* (1976) 134.
- [194] G. Jaouen, R. Dabard, *J. Organomet. Chem.* 21 (1970) P43.
- [195] J.F. Helling, W.A. Hendrickson, *J. Organomet. Chem.* 168 (1979) 87.
- [196] C.C. Lee, U.S. Gill, R.G. Sutherland, *J. Organomet. Chem.* 206 (1981) 89.
- [197] R.G. Sutherland, B.R. Steele, K.J. Demchuk, C.C. Lee, *J. Organomet. Chem.* 181 (1979) 411.
- [198] C.C. Lee, B.R. Steele, K.J. Demchuk, R.G. Sutherland, *Can. J. Chem.* 57 (1979) 946.
- [199] F. Moulines, D. Astruc, *J. Chem. Soc. Chem. Commun.* (1989) 614.
- [200] C. Valério, B. Gloaguen, J-L Fillaut, D. Astruc, *Bull. Soc. Chim. Fr.* 133 (1996) 101.
- [201] J-R Hamon, J.Y. Saillard, A. Le Beuze, M.J. McGlinchey, D. Astruc, *J. Am. Chem. Soc.* 104 (1982) 7549.
- [202] J.-L. Fillaut, D. Astruc, *J. Chem. Soc. Chem. Commun.* (1993) 1320.
- [203] J-L Fillaut, J. Linares, D. Astruc, *Angew. Chim. Int. Ed. Engl.* 33 (1994) 2460.
- [204] J-L Fillaut, R. Boese, D. Astruc, *Synlett* (1992) 55.
- [205] F. Moulines, D. Astruc, *Angew. Chim. Int. Ed. Engl.* 27 (1988) 1347.
- [206] C. Moinet, E. Raoult, *J. Organomet. Chem.* 229 (1982) C13.
- [207] J-L Fillaut, D. Astruc, *New J. Chem.* 20 (1996) 945.
- [208] F. Moulines, L. Djakovitch, R. Boese, B. Gloaguen, W. Thiel, J-L Fillaut, M-H Delville, D. Astruc, *Angew. Chim. Int. Ed. Engl.* 32 (1993) 1075.
- [209] F. Moulines, L. Djakovitch, J-L Fillaut, D. Astruc, *Synlett* (1992) 57.
- [210] J-R Hamon, P. Hamon, S. Sinbandhit, P. Guenot, D. Astruc, *J. Organomet. Chem.* 413 (1991) 243.

- [211] A. Darchen, J. Organomet. Chem. 302 (1986) 389.
- [212] A. Darchen, J. Chem. Soc. Chem. Commun. (1983) 768.
- [213] R.G. Sutherland, A.S. Abd-El-Aziz, A. Piórko, A.S. Baranski, C.C. Lee, Synth. Commun. 19 (1989) 189.
- [214] A.S. Abd-El-Aziz, A. Piórko, A.S. Baranski, R.G. Sutherland, Synth. Commun. 19 (1989) 1865.
- [215] A.N. Nesmeyanov, N.A. Vol'kenau, L.S. Shilovtesa, Dokl. Akad. Nauk SSSR 190 (1970) 857.
- [216] J.L. Schrenk, M.C. Palazzotto, K.R. Mann, Inorg. Chem. 22 (1983) 4047.
- [217] A.M. McNair, J.L. Schrenk, K.R. Mann, Inorg. Chem. 23 (1984) 2633.
- [218] D.R. Chrisope, K.M. Park, G.B. Schuster, J. Am. Chem. Soc. 111 (1989) 6195.
- [219] A.J. Pearson, L. Sun, J. Polym. Sci. A Polym. Chem. 35 (1997) 447.
- [220] P. Wang, Y. Shen, S. Wu, E. Adamczak, L.-Å. Lindén, J.F. Rabek, J. Macromol. Sci. Pure Appl. Chem. A 32 (1995) 1973.
- [221] A. Roloff, K. Meier, M. Riediker, Pure Appl. Chem. 58 (1986) 1267.
- [222] K. Meier, H. Zweifel, J. Imaging Sci. 30 (1986) 174.
- [223] W.J. Gwathney, L. Lin, C. Kutal, I.J. Amster, Org. Mass Spectrom. 27 (1992) 840.
- [224] T. Karatsu, Y. Shibuki, N. Miyagawa, S. Takahara, A. Kitamura, T. Yamaoka, J. Photochem. Photobiol. A Chem. 107 (1997) 83.
- [225] J.F. Rabek, J. Lucki, M. Zuber, B.J. Qu, W.F. Shi, J. Macromol. Sci. Pure Appl. Chem. A 29 (1992) 297.
- [226] T. Ishikawa, Y. Kuwabara, K. Koseki, T. Yamaoka, SPIE 1461 (1991) 73.
- [227] D. Böhm, F. Heinemann, D. Hu, S. Kummer, U. Zenneck, Collect. Czech. Commun. 62 (1997) 309.
- [228] C.C. Lee, K.J. Demchuk, R.G. Sutherland, Synth. React. Inorg. Met. Org. Chem. 8 (1978) 361.
- [229] H. Funaki, H. Aramaki, H. Nishihara, Synth. Metals 74 (1995) 59.
- [230] A.S. Abd-El-Aziz, D.C. Schriemer, Inorg. Chim. Acta 202 (1992) 123.
- [231] A.S. Abd-El-Aziz, Y. Lei, C.R. de Denus, Polyhedron 14 (1995) 1585.
- [232] A.S. Abd-El-Aziz, C.R. de Denus, K.M. Epp, Proc. Indian Acad. Sci. Chem. Sci. 107 (1995) 877.
- [233] A.S. Abd-El-Aziz, C.R. de Denus, M.J. Zaworotko, L.R. MacGillivray, J. Chem. Soc. Dalton Trans. (1995) 3375.
- [234] A.S. Abd-El-Aziz, D.C. Schriemer, C.R. de Denus, Organometallics 13 (1994) 374.
- [235] A.S. Abd-El-Aziz, C.R. de Denus, J. Chem. Soc. Chem. Commun. (1994) 663.
- [236] A.S. Abd-El-Aziz, K.M. Epp, Y. Lei, S. Kotowich, J. Chem. Res. S (1995) 182.
- [237] A.S. Abd-El-Aziz, E.K. Todd, K.M. Epp, Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem. 39 (1998) 300.
- [238] A.S. Abd-El-Aziz, E.K. Todd, K.M. Epp, J. Inorg. Organomet. Polym. 8 (1998) 127.
- [239] A.S. Abd-El-Aziz, S.A. Bernardin, K. Tran, Tetrahedron Lett. 40 (1999) 1835.
- [240] F. Moulines, L. Djakovitch, M.-H. Delville-Desbois, F. Robert, P. Gouzerh, D. Astruc, J. Chem. Soc. Chem Commun. (1995) 463.
- [241] I. Pavlik, P. Kriz, Coll. Czech. Chem. Commun. 31 (1961) 4412.
- [242] D.E. Games, A.H. Jackson, L.A.P. Kane-Maguire, K. Taylor, J. Organomet. Chem. 88 (1975) 345.
- [243] C.C. Lee, R.G. Sutherland, B.J. Thomson, Tetrahedron Lett. 26 (1976) 2625.
- [244] R.A. Stukon, N.A. Vol'kenau, A.N. Nesmeyanov, V. Goldanskii, Izv. Akad. Nauk SSSR Ser. Khim. 8 (1966) 1472.
- [245] S.P. Solodovnik, A.N. Nesmeyanov, N.A. Vol'kenau, O.G. Garkusha, V.A. Petrakova, L.S. Kotova, Dokl. Akad. Nauk SSSR 258 (1981) 415.
- [246] B.R. Steele, R.G. Sutherland, C.C. Lee, J. Chem. Soc. Dalton Trans. (1981) 529.
- [247] A.N. Nesmeyanov, I.F. Leshchova, Y.A. Ustynyuk, Y.I. Sirotkina, I.N. Bolesova, L.S. Isayeva, N.A. Vol'kenau, J. Organomet. Chem. 22 (1970) 689.
- [248] A.S. Abd-El-Aziz, J. Mol. Struct. 405 (1997) 93.
- [249] A.S. Abd-El-Aziz, P. Hazendonk, C.R. de Denus, H.M. Hutton, Inorg. Chim. Acta 219 (1994) 221.
- [250] D. Astruc, Electron Transfer and Radical Processes in Transition Metal Chemistry, VCH, NewYork, 1995.

- [251] D.H. Evans, Chem. Rev. 90 (1990) 739.
- [252] W.E. Geiger, Prog. Inorg. Chem. 33 (1985) 275.
- [253] W.E. Geiger, N.G. Connelly, Adv. Organomet. Chem. 24 (1985) 87.
- [254] N.G. Connelly, W.E. Geiger, Adv. Organomet. Chem. 23 (1984) 1.
- [255] R.E. Dessy, L.A. Bares, Acc. Chem. Res. 5 (1972) 415.
- [256] R.Q. Bligh, R. Moulton, A.G. Bard, A. Piorko, R.G. Sutherland, Inorg. Chem. 28 (1989) 2652.
- [257] A.S. Abd-El-Aziz, A.S. Baranski, A. Piorko, R.G. Sutherland, Inorg. Chim. Acta 147 (1988) 77.
- [258] A.S. Abd-El-Aziz, K. Winkler, A.S. Baranski, Inorg. Chim. Acta 194 (1992) 207.
- [259] D.T. Pierce, W.E. Geiger, J. Am. Chem. Soc. 114 (1992) 6063.
- [260] L.I. Denisovich, S.P. Gubin, Russ. Chem. Rev. 46 (1977) 27.
- [261] R.M. Neilson, M.J. Weaver, Organometallics 8 (1989) 1636.
- [262] W.J. Bowyer, W.E. Geiger, J. Am. Chem. Soc. 107 (1985) 5657.
- [263] J.D.L. Holloway, W.E. Geiger, J. Am. Chem. Soc. 101 (1979) 2038.
- [264] D. Obendorf, H. Schottenberger, C. Reiker, Organometallics 10 (1991) 1293.
- [265] M. Lacoste, H. Rabaa, D. Astruc, N. Ardoin, F. Varret, J.-Y. Saillard, A. Le Beuze, J. Am. Chem. Soc. 112 (1990) 9548.
- [266] M.-H. Desbois, D. Astruc, Organometallics 8 (1989) 1841.
- [267] V. Guerchais, D. Astruc, J. Organomet. Chem. 316 (1986) 335.
- [268] M. Lacoste, F. Varret, L. Toupet, D. Astruc, J. Am. Chem. Soc. 109 (1987) 6504.
- [269] M.-H. Desbois, D. Astruc, New J. Chem. 13 (1989) 595.
- [270] C. Moinet, E. Roman, D. Astruc, J. Electroanal. Chem. 121 (1981) 241.
- [271] D. Astruc, Angew. Chem. Int. Ed. Engl. 27 (1988) 643.
- [272] M. Channon, M.L. Tobe, Angew. Chem. Int. Ed. Engl. 21 (1982) 1.
- [273] J.N. Verpeaux, M.-H. Desbois, A. Madonik, C. Amatore, D. Astruc, Organometallics 9 (1990) 630.
- [274] D. Astruc, Acc. Chem. Res. 19 (1986) 377.
- [275] A.N. Nesmeyanov, L.I. Denisovich, S.P. Gubin, N.A. Vol'kenau, E.I. Sirotkina, I.N. Bolesova, J. Organomet. Chem. 20 (1969) 169.
- [276] R.E. Dessy, F.E. Stary, R.B. King, M. Waldrop, J. Am. Chem. Soc. 88 (1966) 471.
- [277] D. Astruc, R. Dabard, E. Laviron, C.R. Acad. Sci. Paris Ser. C 269 (1969) 608.
- [278] J.C. Green, M.R. Kelly, E.A. Seddon, D. Astruc, J.-R. Hamon, P. Michaud, Organometallics 2 (1983) 211.
- [279] D. Astruc, Chem. Rev. 88 (1988) 1189.
- [280] D. Astruc, New. J. Chem. 16 (1992) 305.
- [281] A. Buet, A. Darchen, C. Moinet, J. Chem. Soc. Chem. Commun. (1979) 447.
- [282] C. Bossard, S. Rigaut, D. Astruc, M-H Delville, G. Félix, A. Février-Bouvier, J. Amiel, S. Flandrois, P. Delhaës, J. Chem. Soc. Chem. Commun. (1993) 333.
- [283] J.R. Morrow, D. Astruc, Bull. Soc. Chem. Fr. 129 (1992) 319.
- [284] D. Astruc, in: F.R. Hartley (Ed.), The Chemistry of the Metal–Carbon Bond, vol. 4, Wiley, New York, 1987, p. 625.
- [285] A.S. Abd-El-Aziz, C.R. de Denu, K.M. Epp, S. Smith, R.J. Jaeger, D.T. Pierce, Can. J. Chem. 74 (1996) 650.
- [286] B. Nicholls, M.C. Whitting, J. Chem. Soc. Lon. 75 (1959) 551.
- [287] A.N. Nesmeyanov, Adv. Organomet. Chem. 10 (1972) 79.
- [288] A.J. Pearson, Iron Compounds in Organic Synthesis, Academic Press, New York, 1994.
- [289] R.G. Sutherland, A. Piorko, U.S. Gill, C.C. Lee, J. Heterocycl. Chem. 19 (1982) 801.
- [290] C.C. Lee, A. Piorko, B.R. Steele, U.S. Gill, R.G. Sutherland, J. Organomet. Chem. 256 (1983) 303.
- [291] C.C. Lee, U.S. Gill, R.G. Sutherland, J. Organomet. Chem. 267 (1984) 157.
- [292] M.J. Mullins, E.P. Woo, D.J. Murray, M.T. Bishop, Chemtech, August (1993) 25.
- [293] D.E. Kime, J.K. Norymberski, J. Chem. Soc. Perkin Trans. 1 (1977) 1048.
- [294] M.J. Mullins, E.P. Woo, C.C. Chen, D.J. Murray, M.T. Bishop, K.E. Balon, Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem. 32 (1991) 174.
- [295] D.B. Amabilino, J.A. Preece, J.F. Stoddart, in: D. Parker (Ed.), Macrocyclic Synthesis: A Practical Approach, Oxford University Press, Oxford, 1996, p. 71.

- [296] G.W. Gokel, S.H. Korzeniowski, *Macrocyclic Polyether Synthesis*, Springer–Verlag, New York, 1982.
- [297] C. Baldoli, P. Del Buttero, S. Maiorana, A. Papagni, *J. Chem. Soc. Chem. Commun.* (1985) 1181.
- [298] J.W. Janetka, D.H. Rich, *J. Am. Chem. Soc.* 117 (1995) 10585.
- [299] A.S. Abd-El-Aziz, C.R. de Denus, M.J. Zaworotko, C.V.K. Sharma, *J. Chem. Soc. Chem. Commun.* (1998) 265.
- [300] R.G.R. Bacon, O.J. Stewart, *J. Chem. Soc.* (1965) 4953.
- [301] P. Kovacic, M.B. Jones, *Chem. Rev.* 87 (1987) 357.
- [302] V. Percec, R.S. Clough, P.L. Rinaldi, V.E. Litman, *Macromolecules* 27 (1994) 1535.
- [303] M. Ueda, H. Toyota, T. Ouchi, J.-I. Sugiyama, K. Yonetake, T. Masuko, T. Teramoto, *J. Polym. Sci. A Polym. Chem.* 31 (1993) 853.
- [304] H.R. Allcock, F.W. Lampe, *Contemporary Polymer Chemistry*, second ed., Prentice–Hall, New Jersey, 1990.
- [305] R.P. Chartoff, in: E.A. Turi (Ed.), *Thermal Characterization of Polymeric Materials*, vol. 1, second ed., Academic Press, New York, 1997, p. 484.
- [306] K.J. Ivin, J.C. Mol, *Olefin Metathesis and Metathesis Polymerization*, Academic Press, San Diego, 1997.
- [307] A.S. Abd-El-Aziz, A.L. Edel, K.M. Epp, H.M. Hutton, *New J. Chem.* 23 (1999) 569.
- [308] V. Percec, H. Nava, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* 28 (1987) 254.
- [309] V. Percec, J.H. Wang, Y.J. Oishi, *J. Polym. Sci. Part A. Polym. Chem.* 29 (1991) 949.
- [310] V. Percec, J.H. Wang, Y.J. Oishi, A.E. Feiring, *J. Polym. Sci. Part A. Polym. Chem.* 29 (1991) 265.
- [311] V. Percec, S. Okita, J.H. Wang, *Macromolecules* 25 (1992) 64.
- [312] V. Percec, J.H. Wang, Y.J. Oishi, *J. Polym. Sci. Part A. Polym. Chem.* 30 (1992) 439.
- [313] V. Percec, J.H. Wang, L. Yu, *Polym. Bull.* 27 (1992) 503.
- [314] A.S. Abd-El-Aziz, K.M. Epp, C.R. de Denus, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* 39 (1998) 408.