STUDIES ON THE SUBSTITUTION CHEMISTRY OF TETRALIN-IRON CATIONS AND RELATED COMPLEXES

by

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ABSTRACT

The preparation and spectroscopic properties of substituted tetralin cyclopentadienyliron complexes are described. As a consequence of the activating influence of the cyclopentadienyliron ($CpFe^+$) group, the coordinated tetralin fragment in the arene complex $[CpFe^+(tetralin)]PF_6^-$ exhibits an enhanced susceptibility to attack by nucleophiles and an increased acidity of the benzylic hydrogens. These chemical properties have been utilized to carry out substitution reactions in the aromatic and saturated ring systems of the tetralin ligand. The resulting substitution patterns have been shown, by NMR spectroscopy, to affect the regio- and stereospecificity of electrophilic and nucleophilic additions to the complexed tetralin hydrocarbon.

Reactions of the cation $[CpFe^+(tetralin)]$ with hydride and carbon nucleophiles afford neutral cyclohexadienyl adducts. In each case, mixtures of two isomers are formed with low to moderate regioselectivity as shown by ^1H and ^{13}C NMR spectroscopy.

Treatment of the complex $[CpFe^+(tetralin)]PF_6^-$ with the base Bu^tOK results in the deprotonation of the benzylic hydrogens. Subsequent reactions of the deprotonated species with electrophiles (e.g. alkyl halides) afford mono-, tri-, and tetra-substituted tetralin derivatives which are formed with high stereoselectivity in most cases. A preference for exo-substitution by bulky electrophiles in the saturated ring is suggested by ^1H NMR spectroscopic data.

The addition of hydride and carbon nucleophiles to the coordinated aromatic ring of $[CpFe^+(\text{tetramethyltetralin})]PF_6^-$ proceeds stereo- and regiospecifically due to the steric influence of per-α-methylsubstitution in the saturated ring system. For example, phenyl-lithium addition to the tetramethyltetralin complex yields a single neutral phenyl-cyclohexadienyl adduct. Hydride abstraction of this adduct with Ph_3CBF_4 affords the cationic monophenyl-tetramethyltetralin derivative. Further treatment of the latter with phenyl-lithium followed by Ph_3CBF_4 produces the cationic diphenyl-tetramethyltetralin complex. Moderate selectivity is observed in the addition of hydride ion (from $LiBEt_3H$) to the complex $[CpFe^+(\text{tribenzyltetralin})]PF_6^-$; however, the analogous reaction involving nucleophilic attack by methyl carbanion (from CH_3Li) proceeds regiospecifically.

A preliminary study of the deprotonation chemistry of the heterocyclic arene complex $[CpFe^+(\text{tetrahydroquinoline})]PF_6^-$ is reported. Reactions with Bu^tOK and iodomethane afford N-methylated and per-α-methylated derivatives.

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LIST OF ABBREVIATIONS

Bu^t, t-butyl	tertiary butyl
Bu^n, n-butyl	primary butyl
Cp	cyclopentadienyl
d	doublet
DMF	dimethylformamide
DMSO	dimethylsulfoxide
Et	ethyl
h	hours
IR	infrared
m	multiplet
NMR	nuclear magnetic resonance
o-	ortho
p-	para
Ph	phenyl
ppm	parts per million
q	quartet
R	alkyl or aryl group
r.t.	room temperature
s	singlet
t	triplet
THF	tetrahydrofuran
X	halide

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PART 1

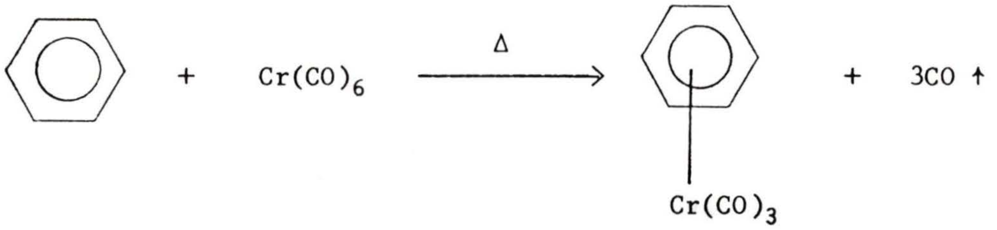
INTRODUCTION

Structure and Reactivity of Coordinated Arenes

A. General Review

The term 'arene' refers to unsaturated cyclic hydrocarbons containing one or more rings. In arene metal complexes, the six aromatic electrons of one ring are available for bonding to a transition metal centre.[1] The standard hapto notation[2] (e.g. η^6-arene) is often used to denote the number of carbon atoms of the arene ligand that are within bonding distance of the metal centre. The most familiar examples of arenes are benzene and substituted benzenes. Virtually all the transition metals form π-complexes with benzenoid aromatic molecules and extensive reviews of this subject have appeared in the literature.[3,4]

In 1919, Hein[5] isolated the first arene complexes of chromium; however, these compounds were not recognized as π-arene complexes until 1954. The by now well-known 'sandwich' complex bis(benzene)-chromium, $Cr(C_6H_6)_2$, was prepared by Fischer and coworker[6] in 1955 and later (1966) it was firmly established that the C–C distances are equal.[7] Mono-π-arene complexes, in which one arene group is present in the molecule together with other ligands are also known. For example, tricarbonylbenzenechromium was first prepared by Fischer and Ofele[8] in 1957 using chromium hexacarbonyl and dibenzenechromium in benzene; however, a simpler and more general method for synthesis of this type of type of complex was developed in 1959 by Nicholls and Whiting[9] who heated chromium hexacarbonyl under reflux in an excess of the aromatic compound, equation 1. Since these initial discoveries, hundreds of

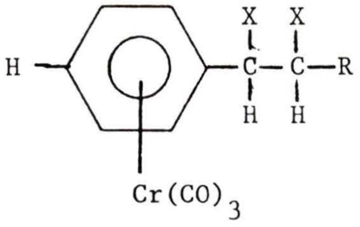


(1)

stable organometallic compounds containing arene ligands have been made, and their structures and chemical properties have been established.[4]

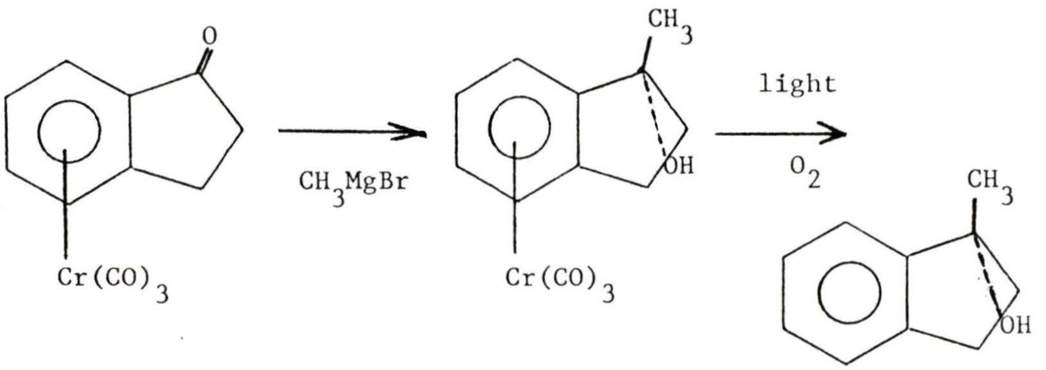
Application of arene complexes to organic synthesis has led to development of new areas of arene chemistry in recent years which have opened up a variety of uses of these materials as stoichiometric reagents and as catalysts. Comprehensive reviews and books on this subject have been published including those by Semmelhack,[10] Jaouen,[11,12] and Davies.[13] In particular, neutral arene-tricarbonylchromium complexes have attracted considerable attention as intermediates for organic synthesis due to several reasons: the preparation of the complexes is straightforward and result in excellent yields (80-90%), the complexes are air-stable solids, and only mild reaction conditions are required to remove the arene ligand from the metal.

The effects which result from changes in arene reactivity induced by metal complexation are central to the applications of arene-metal complexes to organic synthesis. Five general changes in arene reactivity have been observed[10] (see I-i): stabilization of side-chain cation sites, enhanced acidity of arene ring hydrogen substituents, stabilization of side-chain anion sites (activation of benzylic hydrogens), steric effects of the coordinated metal units, and nucleophilic aromatic addition and substitution reactions. The last three effects have especially specific applications to organic synthesis.



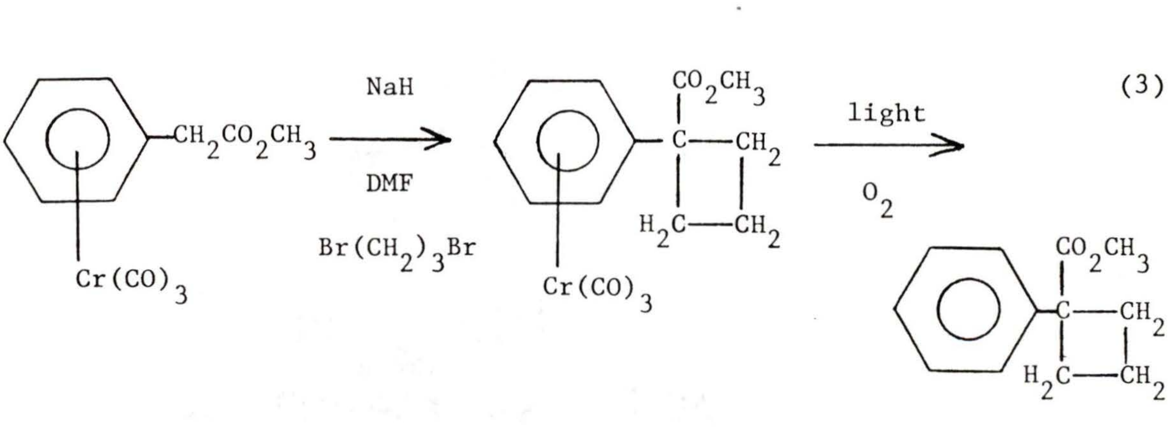
(I-i)

The tricarbonylchromium unit exerts a large steric blocking effect which is extremely useful in asymmetric organic synthesis. For example, when a functional group undergoing a reaction is part of an alicyclic ring which is fused ortho to the π-complexed arene, reactions occur exclusively from the side exo to the tricarbonylchromium moiety (i.e. from the uncoordinated face of the arene hydrocarbon). This effect is illustrated by the stereospecific synthesis of a tertiary alcohol[14] obtained, after decomplexation, by the addition of methylmagnesium bromide to the indanone complex, see equation 2.



(2)

The most dramatic effect of metal coordination of an arene is the significant reduction of electron density in the aromatic ring. This effect was first demonstrated by Nicholls and Whiting[15] who observed that (η^6-chlorobenzene)Cr(CO)$_3$ was converted to (η^6-anisole)Cr(CO)$_3$ with sodium methoxide in methanol, at a rate similar to p-nitrochlorobenzene;[15] thus, the Cr(CO)$_3$ group was shown to be comparable to the nitro group in electron withdrawing capabilities. As a consequence of this effect, there is a significant enhancement of the acidity of benzylic hydrogens (i.e. stabilization of benzylic carbanions) in η^6-alkylarene metal complexes. A direct application in synthesis was reported by Jaouen and coworkers[16] who carried out a double alkylation of the benzylic position of methyl phenylacetate at 25^{0}C, equation 3. By contrast, no alkylation occurred on the free aromatic ligand. The



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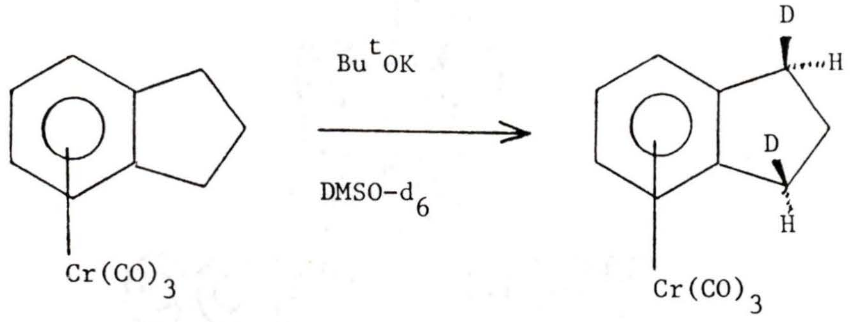
activation of benzylic hydrogens is further illustrated by the base-catalyzed stereoselective hydrogen-deuterium exchange of the benzylic hydrogens of (indan)$Cr(CO)_3$ (equation 4) reported by Trahanovsky and

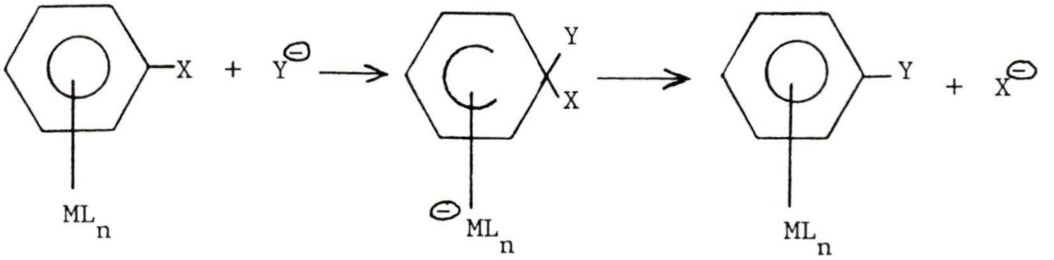


(4)

Card.[17] Exclusive exchange of the exo-hydrogens was attributed to a steric effect between the $Cr(CO)_3$ group and the base.

The withdrawal of electron density from the coordinated aromatic ring system also results in increased susceptibility of the latter to nucleophilic attack. The concept of polarity inversion has stimulated new chemistry in relation to nucleophilic aromatic substitution reactions. In organic chemistry, it is well known that nitro groups and other electron-withdrawing groups can reverse the reactivity of aromatic rings from electrophilic substitution to nucleophilic substitution reactions, resulting in the formation of cyclohexadienyl anions, which are also known as Meisenheimer complexes.[10] The main limitation in such reactions is the lack of mild techniques for removing activating groups such as nitro. By contrast, activating organometallic groups such as $Cr(CO)_3$ may be removed with relatively little difficulty affording free substituted arenes.

Nucleophilic addition reactions to π-complexed arenes represent the most developed area with respect to organic synthesis. Several hundred examples of such reactions are now known where the starting complex can have a formal charge of 0, +1 or +2, equation 5. The two-step sequence, addition of Y followed by elimination of X, parallels the established mechanism for nucleophilic aromatic substitution. In general, the addition proceeds in an exo-fashion, i.e. from the face of the π-arene ligand opposite from the metal. For example, Semmelhack and coworkers[18] demonstrated by x-ray crystallography that exo-addition of 2-lithio-1,3-dithiane occurs to the benzene-$Cr(CO)_3$ complex, equation 6. In the dithiane adduct, the five carbons of the dienyl unit are all coplanar and the remaining sixth carbon atom lies well above the pentadienyl plane; these structural observations also apply to



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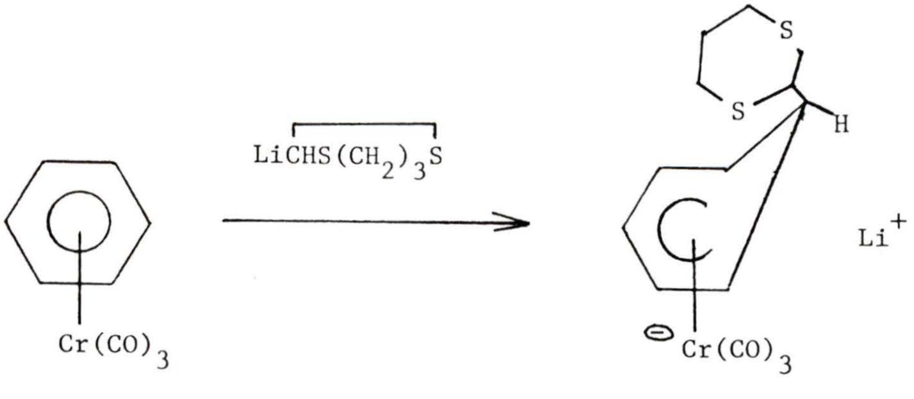
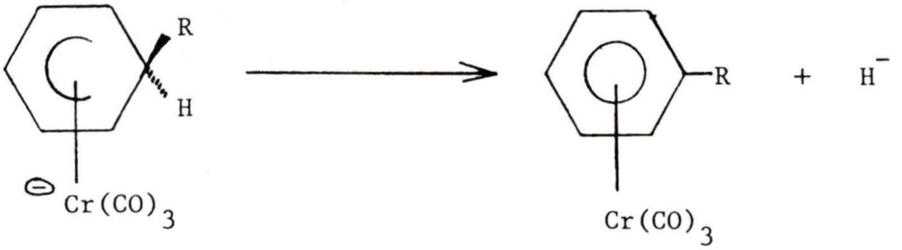


(6)

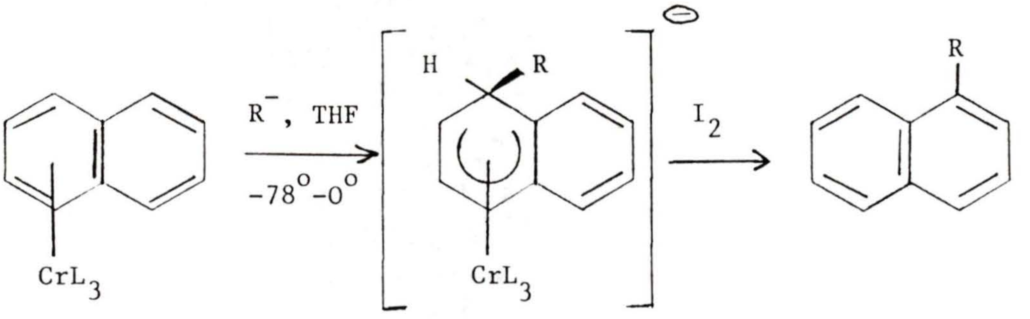
cyclohexadienyl adducts in general. The process of effecting nucleophilic substitution at a ring position without causing cleavage of the $Cr(CO)_3$ group has also been investigated. As represented in equation 7, successful substitution may be achieved via reaction of the



(7)

cyclohexadienyl complex with a suitable electrophilic reagent which is capable of endo-hydride abstraction. Although many oxidizing agents will induce loss of the endo-hydrogen and cause removal of the $Cr(CO)_3$ unit as well, no suitable reagent has yet been found to carry out the conversion shown in equation 7. The major advantage in maintaining the activating organometallic substituent is to allow further substitution reactions to take place at the arene ligand.

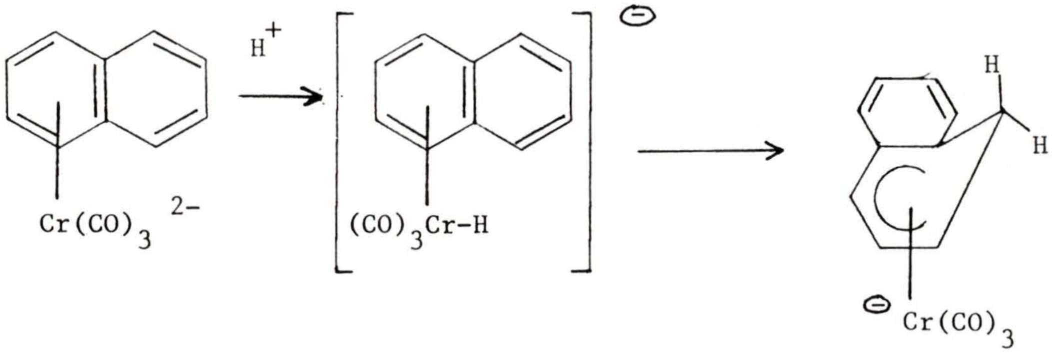
Reports of nucleophilic addition to complexed arenes, where the arene is not a benzene species, have appeared in the literature. For example, Kundig and Desobry[19] have investigated reactions of naphthalene chromium complexes with carbon nucleophiles which afford α-substituted arenes in high yield after oxidation of the anionic cyclohexadienyl complexes, equation 8. In these reactions, the intermediate



(8)

L = CO, phosphine or phosphite

cyclohexadienyl complexes were not isolated. By contrast, Rieke and Henry[20] have isolated the first cyclohexadienyl complex where the parent arene is a polynuclear aromatic, equation 9. As represented in equation



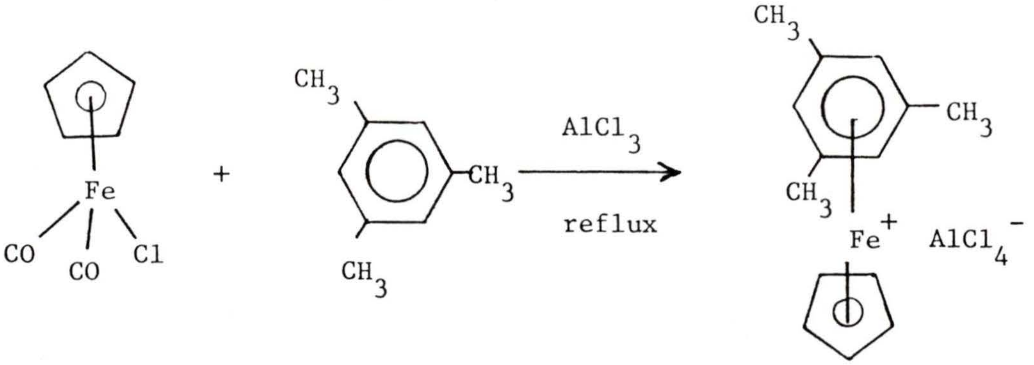
(9)

9, generation of the cyclohexadienyl occurred by α-protonation of the dianion of naphthalene-$Cr(CO)_3$. It was also established that the mode of electrophilic attack by H^+ was endo, presumably occurring after transfer of hydride from an intermediate chromium hydride species.

B. Cyclopentadienyliron arene complexes.

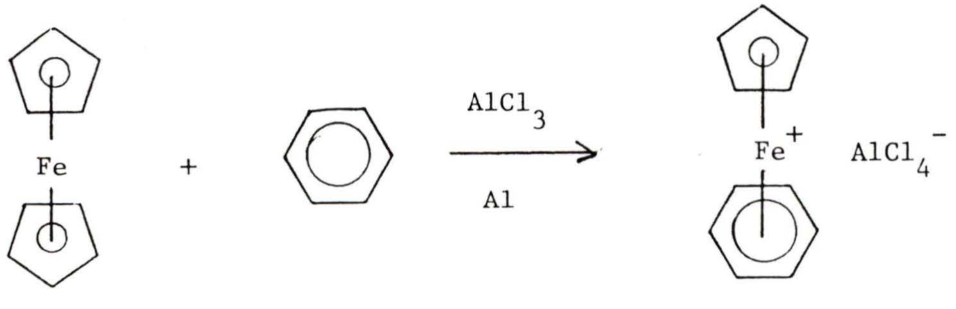
Activation of arene ligands <u>via</u> metal complexation to the $CpFe^+$ moiety has also been an area of great interest in recent years. The first example of an organometallic complex containing both a

η^5-cyclopentadienyl and a η^6-arene ring was reported by Coffield and coworkers[21] in 1957. Synthesis of this compound was carried out via treatment of η^5-cyclopentadienyliron(II)dicarbonyl chloride with aluminum chloride in refluxing mesitylene, equation 10. However, since the



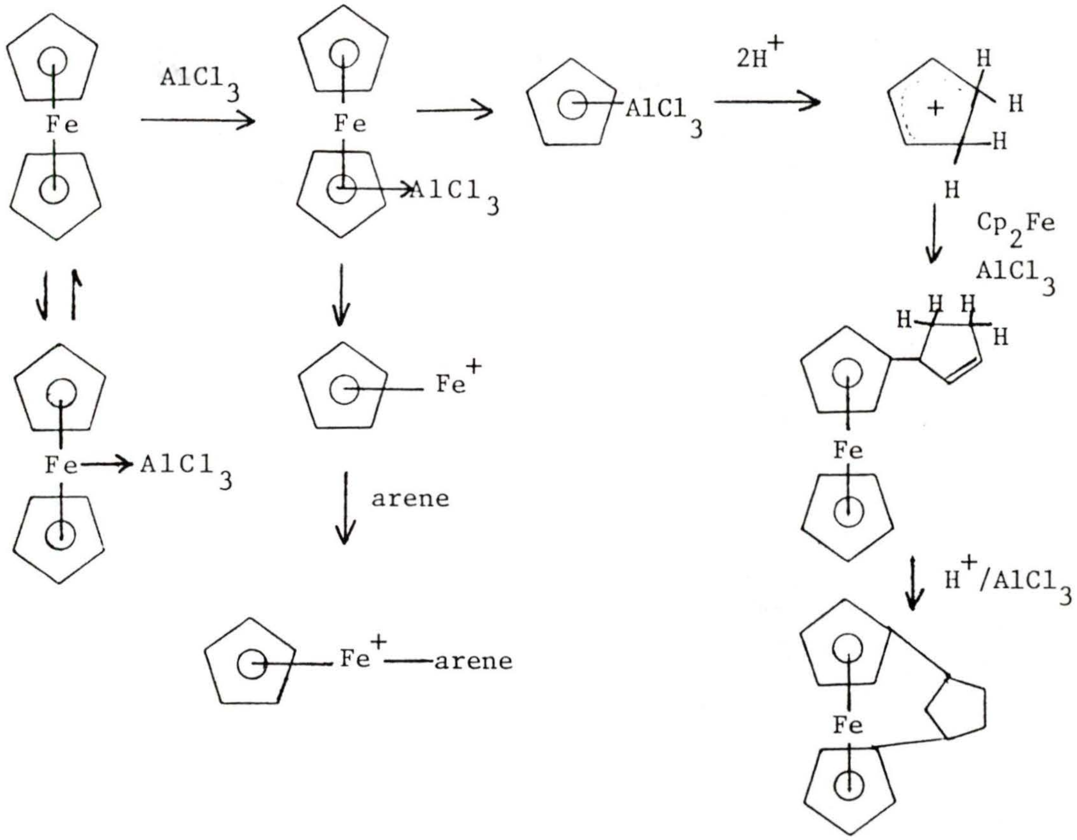
(10)

discovery of ferrocene in 1951, more convenient synthetic routes utilizing this inexpensive and accessible starting material have emerged. In 1963, Nesmeyanov and coworkers[22] invented a straightforward method of complexing arenes with the CpFe$^+$ unit via a ligand exchange reaction between one ring of ferrocene and the arene, equation 11. As shown in equation 11, $AlCl_3$ is the most common Lewis acid inducing the reaction



(11)

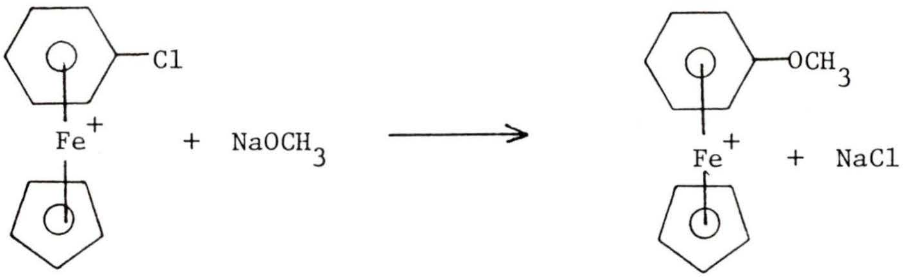
and aluminum powder is added to inhibit oxidation of ferrocene to ferricinium. The mechanism of ligand exchange has been investigated by Nesmeyanov and coworkers,[23,24] and Astruc and Dabard.[25] The basic mechanism (outlined in Scheme 1) shows that the aluminium chloride



Scheme 1. Proposed mechanism of $AlCl_3$-catalyzed ligand exchange reactions of ferrocene.

complexes with the electron rich Cp ring thus weakening the Cp-Fe bond which is cleaved subsequently and replaced by an arene-Fe bond. The resulting cyclopentadienyl anion would, after protonation, alkylate ferrocene to form cyclopentylferrocenes. A major feature of this reaction is that interaction of the metal centre with $AlCl_3$ can also occur, thus inhibiting the Cp-Fe cleavage; the resulting $AlCl_3$ adduct is destroyed upon hydrolysis which regenerated ferrocene and therefore significantly decreases the overall reaction yield. Despite this shortcoming, many $CpFe^+$ complexes have been synthesized using this method.[26]

An important feature of $[CpFe(arene)]^+$ complexes is the presence of a positive charge on these complexes which has important effects on their reactivity. The $CpFe^+$ unit provides an electron withdrawing effect which is exaggerated compared with the corresponding $Cr(CO)_3$ system due to the positive charge. This effect has been demonstrated by Nesmeyanov and coworkers[27] who observed that the reaction of a chlorobenzene derivative with sodium methoxide proceeded to give an efficient substitution for chlorine, equation 12. The reaction of sodium methoxide with p-chloronitrobenzene was also examined and showed a higher activation energy barrier (<u>ca.</u> 2 kcal/mol) than the analogous reaction shown in equation 12; thus the $CpFe^+$ moiety exhibits a significantly stronger activating effect than a p-nitro substituent.



(12)

Electron withdrawal from the arene ligand can be observed by examination of the ^1H and ^{13}C NMR spectra of the coordinated arene compounds. Coordination of aromatics causes significant changes in the chemical shifts of the ring protons relative to those of the free aromatic ligands. These changes were first investigated by Watts and coworkers[28] who obtained the ^1H NMR spectra of a series of methyl-substituted benzene iron cations (Table 1). In general, arene ring proton resonances are shifted upfield by <u>ca.</u> 0.7-1.0 ppm from the

Table 1. ^1H NMR spectroscopic data[28] for some CpFe(arene)$^+$ cations[a]

Compound	Arene protons (δ, ppm)	Cp protons (δ, ppm)	CH_3 (δ,ppm)
$[(\eta^6-C_6H_6)Fe(\eta^5-C_5H_5)]^+$	6.49	5.24	----
$[(\eta^6-CH_3-C_6H_5)Fe(\eta^5-C_5H_5)]^+$	6.40	5.18	2.55

Note: [a] d_6-acetone solutions.

free aromatic resonances. These upfield shifts have been attributed to a reduction in π-electron circulation within a ring due to the involvement of these electrons in bonding to the metal. In addition, Cp protons exhibit a downfield shift of <u>ca</u>. 0.8-1.1 ppm as compared with those of ferrocene. This is explained by the fact that the cation charge is partially delocalized to the Cp ring. ^{13}C NMR spectroscopic data for CpFe$^+$ complexes were reported initially by Hendrickson and coworkers[29] and Sutherland and coworkers.[30] Arene carbons are found generally at 78 ppm from tetramethylsilane; this represents an upfield shift of approximately 40 ppm from the uncomplexed aromatic. A comparison of the ^{13}C NMR spectral data for complexed[29] and uncomplexed benzene[31], and a theoretical value[31] for free Cp is shown in Table 2.

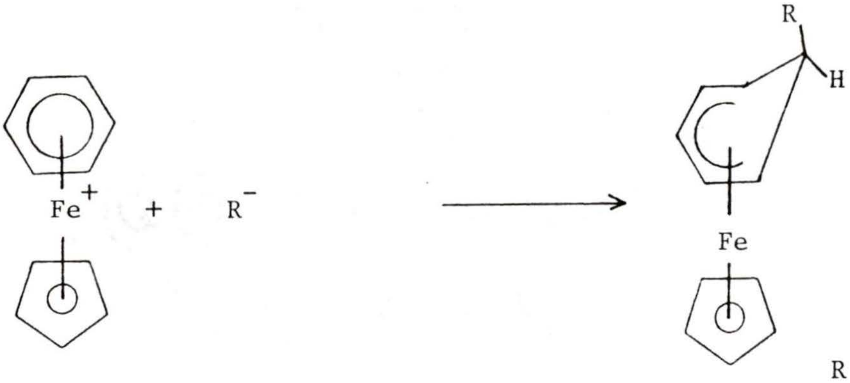
The large upfield shifts associated with the coordinated ring carbon resonances have been attributed to various factors including rehybridization of carbon atoms making them more saturated in character,[32] and changes in electron density in the sigma[33] and pi[34] system of the coordinated arene.

Table 2. ^{13}C NMR Spectroscopic Data[29] for Cp, benzene and CpFe(benzene)$^+$ compounds[a]

Compound	Arene carbons (ppm)	Cp carbons (ppm)
$[(\eta^6-C_6H_6)Fe(\eta^5-C_5H_5)]^+$	88.4	76.8
$(C_6H_6)^{31}$	128.5	
$(C_5H_5)^{31}$		103

Note:[a] CD_3CN solution.

Cyclopentadienyliron complexes of arenes have been used also as substrates for nucleophilic addition reactions. In 1962, Wilkinson and coworkers[35] first reported the preparations of some simple cyclohexadienyl complexes of iron. As shown in equation 13, nucleophilic addition of H^-, D^- and $C_6H_5^-$ to the benzene cation afforded the



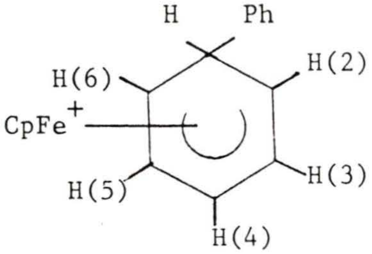
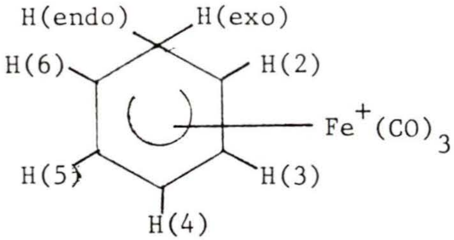
(13)

R = H, D, C_6H_5

corresponding neutral cyclohexadienyl complexes in which the nucleophiles were added exclusively to the six-membered ring. These results were in accordance with the theoretical arguments later proposed by Davies, Green and Mingos,[36] which state that nucleophilic attack occurs preferentially at even coordinated polyenes which have no unpaired electrons in their highest occupied molecular orbitals. Consequently, regioselective nucleophilic addition to CpFe(arene)$^+$ complexes is generally observed and proceeds via reaction at the arene ligand in preference to the Cp group.

Complete ^1H NMR spectroscopic data for the phenyl cyclohexadienyl adduct (equation 13) was reported by Wilkinson and coworkers[35] and are shown in Table 3. As is the case for all cyclohexadienyl-(cyclopentadienyl)iron complexes, the Cp resonance is shifted upfield by about 1 ppm relative to that of the cationic precursor; this may result from an increased electron density in the Cp ring. Unfortunately the ^1H NMR signals of the hydride and deuteride adducts (represented in equation 13) were not well resolved; however, those of a related complex $(\eta^5\text{-}C_6H_7)Fe(CO)_3BF_4$ were discernible and are shown in Table 3. As expected, H_{endo} showed coupling with H-2 and H-6 since H_{endo} makes a dihedral angle[37] of ca. 30^0 with them. The dihedral angle for H_{exo} with

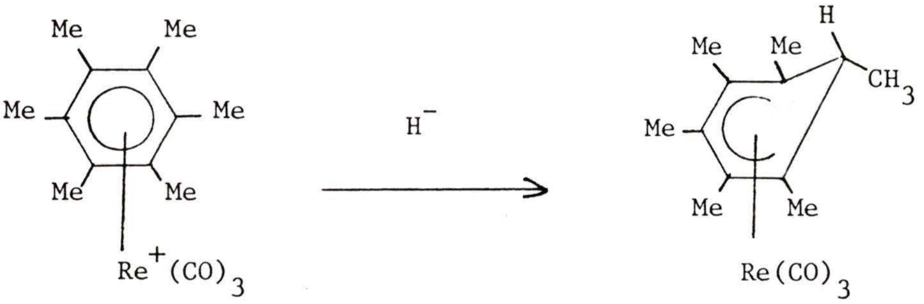
Table 3. ^{1}H NMR Spectroscopic Data[35] for Cyclohexadienyl Iron Complexes

COMPLEX[a]	PROTON	POSITION (ppm)	SIGNAL
	phenyl	6.9	m
		6.67	m
	4	5.8	t,1H,J(4-3) = 5.0 Hz
	C_5H_5	4.3	s,5H
	3, 5	c	c
	endo	3.49	t,1H,J(2-endo) = 6.5 Hz
	2, 6	2.73	t,2H,J(2-3) = 6.5 Hz
COMPLEX[b]			
	4	7.34	t,1H,J(4-3) = 5.5 Hz
	3, 5	5.92	dd,2H,J(3-2) = 6.0 Hz
	2, 6	4.34	dd,2H,J(2-endo) = 6.0 Hz
	endo	3.03	dt,1H,J(exo-endo) = 16.0 Hz J(endo-2) = 6.5 Hz
	exo	2.02	d,1H,J(exo-endo) = 15.0 Hz

Notes: [a] CCl_4 solution. [b] in liquid SO_2. [c] unresolved signals obscured by Cp resonance.

H-2 and H-6 is 90^0 and no coupling is observed.

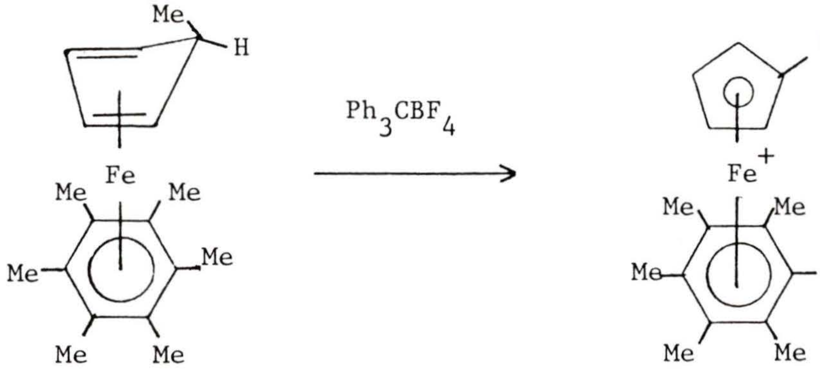
Following Wilkinson's report, Watts and coworkers[28,38] obtained a considerable amount of IR and NMR spectroscopic data for related cyclohexadienyl iron complexes. They established that nucleophiles always add stereospecifically to $CpFe(arene)^+$ cations from the exo-side of the arene fragment (i.e. the side of the ligand opposite the $CpFe^+$ moiety). In the IR spectra of the complexes bearing an exo-hydrogen, a strong band near or below 2800 cm^{-1} was assigned to the $C{-}H_{exo}$ stretching vibration. This assignment was based on results by Churchill and coworker[39] who observed an intense absorption at 2790 cm^{-1} in the IR spectrum of the cyclohexadienyl complex $(C_6Me_6H)Re(CO)_3$, obtained by hydride reduction of the hexamethylbenzene rheniumtricarbonyl cation, equation 14. An x-ray crystal structure determination of this hydride



(14)

adduct revealed the presence of an exo-hydrogen atom; thus the origin of the 2790 cm^{-1} band was confirmed. Hence all cyclohexadienyl adducts not containing an exo- hydrogen atom do not exhibit this absorption in their IR spectra.

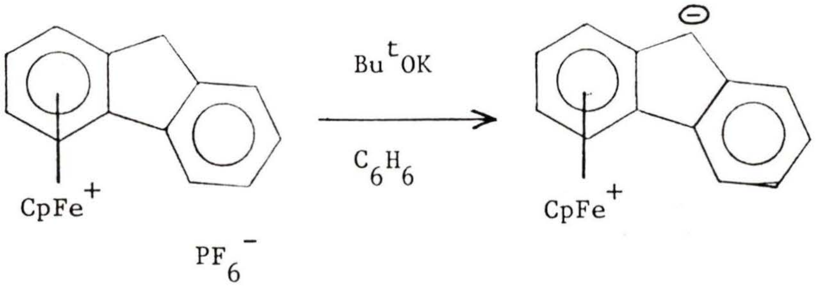
The reactions of cyclohexadienyl(cyclopentadienyl)iron complexes with hydride abstraction reagents have been reported by Watts and coworkers[38,40,41] and Nesmeyanov and coworkers.[43] Trityl tetrafluoroborate (Ph_3CBF_4) and N-bromosuccinimide (NBS) have been studied as reagents for transforming neutral cyclohexadienyl complexes to cationic arene complexes. The former reagent was shown to be stereospecific in the first example of endo-hydride abstraction from a cyclopentadiene complex,[38] equation 15.



(15)

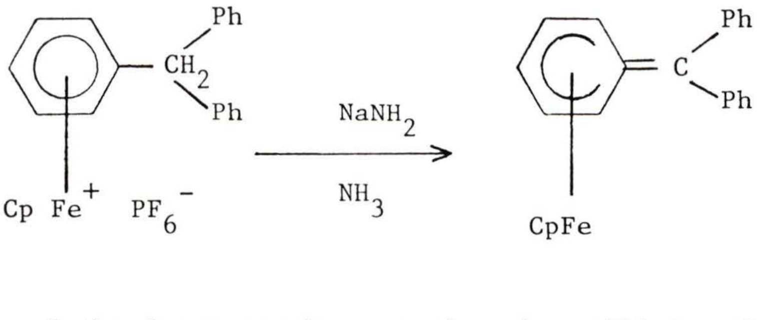
By contrast, NBS is generally less selective but will abstract exo-hydrogens preferentially if both exo- and endo-hydrogens are available. Nesmeyanov and coworkers[43] investigated reactions of Ph_3CBF_4 and NBS also with a series of exo-substituted cyclohexadienyl complexes. Their results showed that depending on the substituent R present in the complex, either hydride abstraction or R-abstraction or both processes could occur when reaction with NBS or Ph_3CBF_4 was carried out. In general, a large excess of the oxidant promoted R-abstraction and decomposition of the cyclohexadienyl complexes.

More recently the activation of benzylic hydrogens in arene ligands <u>via</u> complexation to the $CpFe^+$ unit has received much attention. Treichel and coworker[44] (1977) first described the deprotonation of the $CpFe(fluorene)^+$ cation with Bu^tOK in benzene which afforded a neutral zwitterionic species, equation 16. An x-ray crystallographic analysis of the product confirmed its zwitterionic formulation. By contrast,



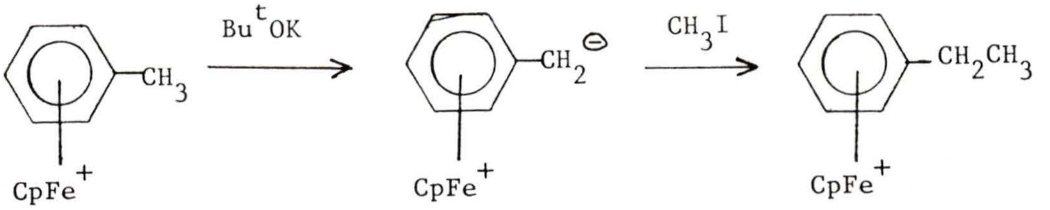
(16)

Helling and Hendrickson reported that deprotonation reactions of several coordinated aromatic ligands resulted in the formation of air- and water-sensitive products possessing more cyclohexadienyl than zwitterionic character.[45] For example, ^{1}H NMR spectroscopic data for the product resulting from the deprotonation of the triphenylmethane complex suggested a considerable cyclohexadienyl contribution to the structure of the product which bears an exocyclic double bond (see equation 17). In 1979 Sutherland and coworkers[46] explored synthetic



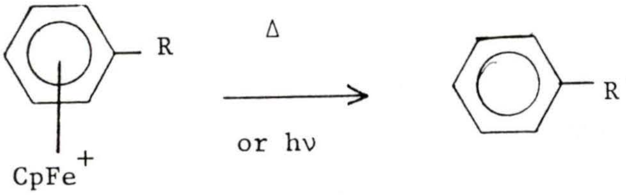
(17)

applications of the deprotonation reactions by utilizing the nucleophilic behaviour of numerous 'zwitterionic' species in reactions with various electrophilic substrates. For example, deprotonation of the toluene complex followed by the reaction with iodomethane afforded the ethylbenzene complex, equation 18. Thus nucleophilic reactions of 'zwitterionic' species provided a general method for the alkylation and



(18)

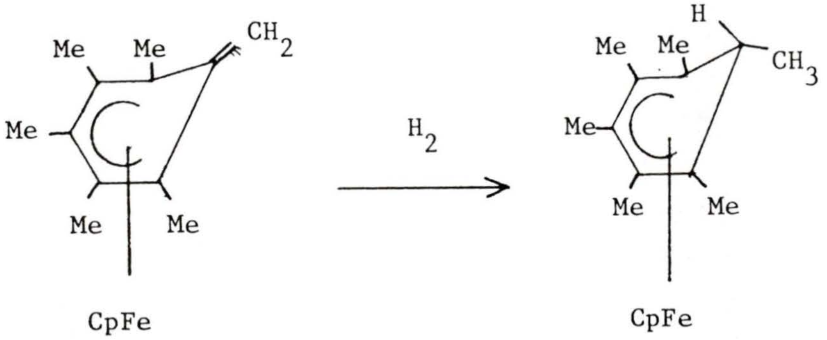
functionalization of CpFe(arene)$^+$ cations. Sutherland and coworkers had also shown that the aromatic ligand in CpFe$^+$ complexes could be regenerated as the substituted arene itself either photolytically[30] or in improved yields by pyrolytic sublimation[46] under reduced pressure, equation 19. Hence, these decomplexation reactions provided a way of



(19)

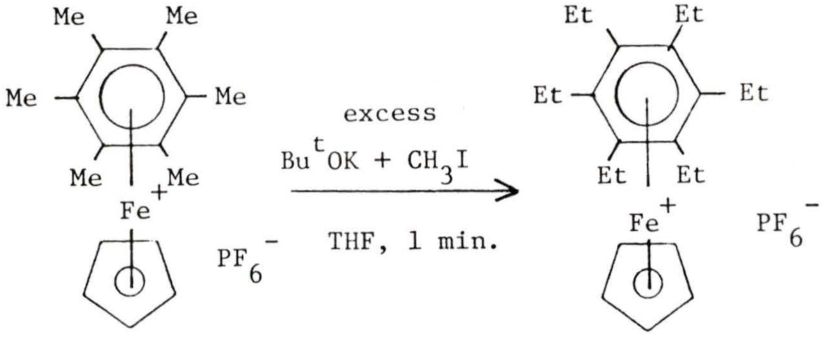
generating substituted arenes which may be more difficult to prepare <u>via</u> standard organic synthetic routes.

Although Sutherland and coworkers had used simple deprotonated arene complexes as intermediates in alkylation reactions, direct characterization of these unstable species was not carried out. In 1981, Astruc and coworkers[47] obtained the first x-ray crystal structure of a thermally stable deprotonated hexamethylbenzene complex which exhibited a cyclohexadienyl structure possessing an exocyclic double bond. This double bond character was also demonstrated by the hydrogenation of the deprotonated species to yield an endo-methyl cyclohexadienyl complex, equation 20. Thus, isolation and characterization of the exocyclic methylene complex illustrated that permethylation of the arene ligand provided stabilization of the deprotonated species. Confirmation of this conclusion was provided by the observation that the deprotonation of CpFe(pentamethylbenzene)$^+$ afforded a red product[48] which completely polymerized at room temperature. Therefore it was established that deprotonated CpFe(arene)$^+$ complexes are not stable when the arene ligand is not hexa-substituted.



(20)

In 1982 Astruc and coworkers reported several peralkylation reactions of iron complexes as a result of their studies of the electrochemistry of the CpFe$^+$(arene)/CpFe(arene) system.[49] The method used for a peralkylation reaction involved a one-step multiple formation of C–C bonds in the arene ligand <u>via</u> reaction of the corresponding CpFe$^+$ complex with excess Bu^{t}OK and organic halide. For example, permethylation of CpFe(hexamethylbenzene)$^+$ afforded the hexaethylbenzene derivative, equation 21. As shown by the formation of ethyl groups in

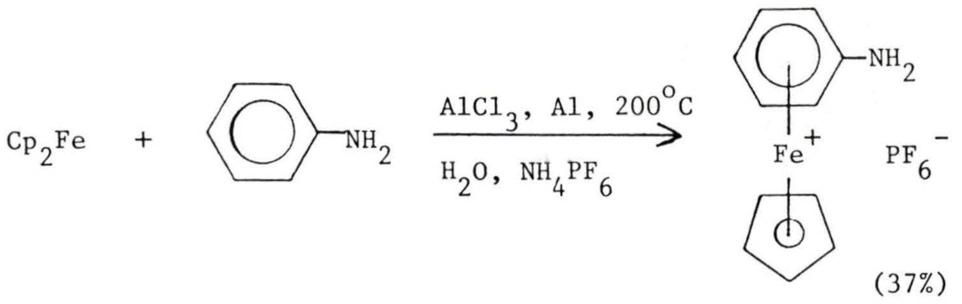


(21)

the product, steric constraints in the arene ligand limit the complete substitution of all the hydrogens in the methyl groups. In general the peralkylation reactions proceed cleanly and are of potential synthetic interest since the extension to polyfunctionalization of complexed arene ligands is an important consideration in gaining access to new substituted aromatic compounds.

An area of growing interest in recent years has been the synthesis and substitution chemistry of heteroarene CpFe$^+$ complexes. A recent review of heterocyclic π-complexes of the transition metals has appeared in the literature[50] which reflects the growing number of examples of π-bonded heteroaromatic complexes. Some of the major reasons for this recent interest include stabilization of reactive heterocyclic intermediates, formation of complexes of biologically significant compounds, and modification of heterocyclic chemistry upon complexation. In relation to the deprotonation chemistry of the CpFe$^+$ system, several reports of heteroarene complexes possessing α-hydrogens have appeared. In 1966 Nesmeyanov and coworkers[51] attempted the synthesis of the cation

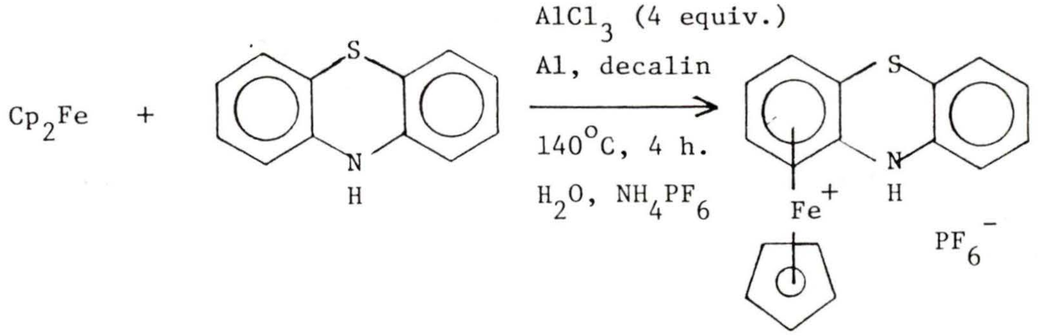
$[CpFe(aniline)]^+$ from the direct reaction with ferrocene but were unsuccessful. In 1977, Helling and Hendrickson[52] described the synthesis and deprotonation chemistry of $CpFe^+$ complexes containing diphenylamine, carbazole and benzimidazole as ligands. The reaction yields for these complexes were moderate except for the diphenylamine complex which was produced in only 6% yield. Subsequently the same workers[53] developed a procedure for successfully preparing the aniline complex. As shown in equation 22, this involved the use of excess $AlCl_3$ (mole ratio,



(22)

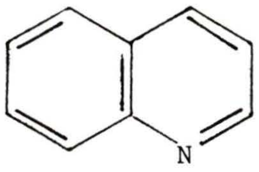
ferrocene/$AlCl_3$ ≃ 1/4) to compensate for the amount lost by coordination to the amine function of aniline, and the use of elevated temperatures (*ca.* $190-200^0$). Deprotonation and subsequent alkylation reactions of the aniline complex were also described, affording mono- and dimethylated derivatives.

In 1980 Sutherland and coworkers[54] investigated the exchange reactions of some polycyclic heteroaromatic systems with ferrocene. As an example, synthesis of the cationic phenothiazine complex using the improved method of Helling[53] proceeded in 22% yield (see equation 23).

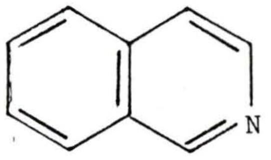


(23)

By contrast, attempts to synthesize complexes using pyridine, indole, quinoline (I-ii) or isoquinoline (I-iii) were unsuccessful.

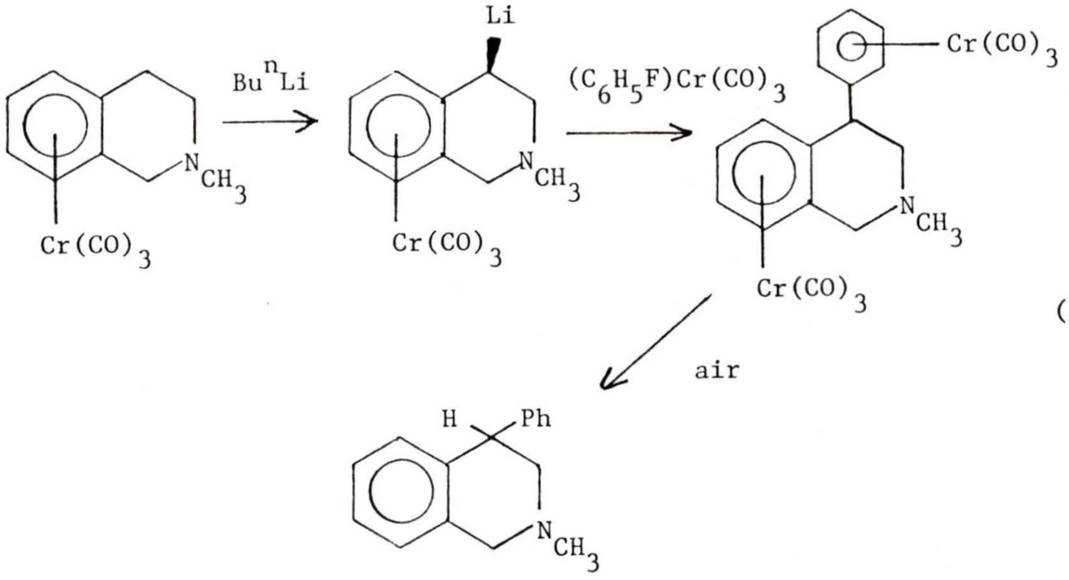


(I-ii)



(I-iii)

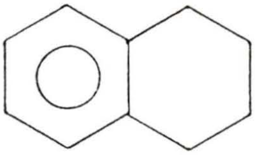
More recently in 1985, Davies and coworkers[55] described the stereoselective benzylic substitution reactions of an N-methyl-tetrahydroisoquinoline- Cr(CO)$_3$ complex. In all cases, exo-alkylated products resulted as a consequence of steric effects of the Cr(CO)$_3$ moiety. For example, deprotonation of the N-methyl-tetrahydroisoquinoline-Cr(CO)$_3$ complex with n-butyl-lithium followed by treatment with (C$_6$H$_5$F)Cr(CO)$_3$ afforded the exo-alkylated derivative (see equation 24). Subsequent decomplexation of the double complex yielded the free phenyl-substituted compound. The importance of



(24)

simple substituted tetrahydroisoquinolines is reflected in the pharmacological properties that they possess.[56]

Until now, little work has been accomplished in the area of activation of small polycyclic hydrocarbons by the $CpFe^+$ moiety. Apart from heteroarenes, most reports in the literature have focused on complexation reactions of benzene, substituted benzenes, polyaromatic hydrocarbons (e.g. pyrene[57]) and some cyclophanes.[58] The main objective of the research described in this thesis has been to examine the substitution chemistry of the hydrocarbon tetralin (I-iv) as a consequence of coordination to the $CpFe^+$ group. The $CpFe^+$(tetralin)



(I-iv)

complex, first reported by Nesmeyanov[22] in 1963, was chosen for study in view of its facile synthesis and accessibility. Since the $CpFe^+$ moiety is known to exhibit a significant activating effect in $CpFe^+$(arene) complexes primarily due to its positive charge, it may be expected that the tetralin fragment in the $CpFe^+$(tetralin) cation would undergo the reactivity changes which are normally observed for complexed arenes (e.g. increased acidity of benzylic hydrogens and increased susceptibility to nucleophilic attack).

The research reported in Part II of this thesis has been concerned with an assessment of the regio- and stereochemical changes involved in the benzylic carbanion substitution reactions and nucleophilic addition/substitution reactions of the cation $CpFe^+$(tetralin), and the effect of each of these operations one on the other. In related chemistry involving tetrahydroquinoline, this heterocyclic system has been shown to form a corresponding complex with the $CpFe^+$ unit and a preliminary investigation of the substitution chemistry of $CpFe^+$(tetrahydroquinoline) has been carried out.

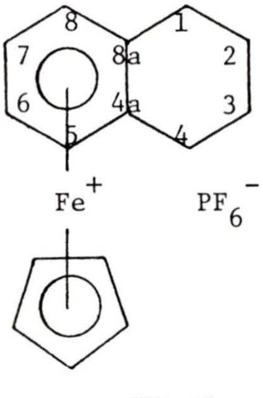
PART II

RESULTS AND DISCUSSION

A. Nucleophilic substitution in [CpFe$^+$(tetralin)]PF$_6^-$

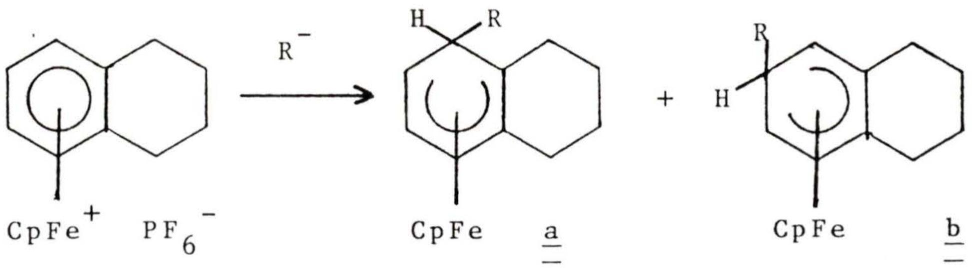
(i) Nucleophilic addition to [CpFe$^+$(tetralin)]PF$_6^-$

The addition of nucleophiles to the tetralin complex 1 (see II-i)



(II-i)

occurs exclusively at the unsubstituted positions of the aromatic ring-system of the $C_{10}H_{12}$ ligand, giving rise to the formation of neutral cyclohexadienyl complexes 2a,2b-6a,6b, equation 1. In all cases, a mixture of two isomers is formed since two distinguishable unsaturated



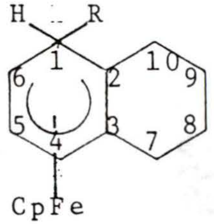
(1)

2a,2b R = H
3a,3b R = D
4a,4b R = n-butyl
5a,5b R = t-butyl
6a,6b R = C_6H_5

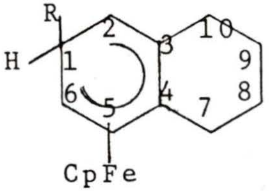
positions exist (7 and 8 or 5 and 6) in the aromatic ring of complex 1. The products 2a,2b - 6a,6b are red, air-sensitive, viscous oils which are soluble in polar and non-polar organic solvents and have been characterized by mass spectrometry, IR spectroscopy (see experimental section) and ^{1}H and ^{13}C NMR spectroscopy (see Tables 4-7). Owing to difficulties in physical manipulation of these complexes, satisfactory microanalytical data were not obtained, and attempts to separate the isomeric mixtures using alumina or silica gel chromatography were unsuccessful.

In accordance with results obtained for similar cyclohexadienyl complexes synthesized by Watts and coworkers[40], nucleophilic addition to complex 1 occurs stereospecifically from the exo-side of the arene ligand. This conclusion is supported by the IR spectra of compounds 3a,3b - 6a,6b since no absorption was detected in the range 2700 - 2800 cm^{-1} where bands characteristic of C-H$_{exo}$ stretching are expected[39]. The hydride adducts 2a and 2b, however, exhibit a strong band at 2760 cm^{-1} confirming the presence of C-H$_{exo}$ (see Figure 1).

Table 4. ^{1}H NMR Spectroscopic Data for Cyclohexadienyl Complexes 2a and 2b[a]



a



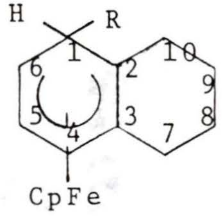
b

2a R = H
2b R = H

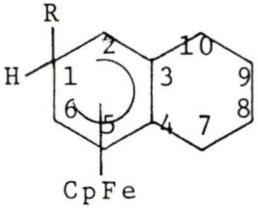
Complex	Cp (ppm)	H1-H6 (ppm)	H7-H10 (ppm)	R (ppm)	Ratio of isomers (2a/2b)
(2a)[b]	3.96(s,5H)	5.77(d,1H,H4) J(H4-H5)=4.9Hz 4.08(t,1H,H5) J(H5-H6,H4)=5.5Hz 2.38(dd,1H,$H1_{endo}$) J($H1_{endo}$-$H1_{exo}$)=12.3Hz J($H1_{endo}$-H6)=6.4Hz 2.13(t,1H,H6)	1.0-2.6[c]	1.96(d,1H,$H1_{exo}$) J($H1_{endo}$-$H1_{exo}$)=12.1Hz	58:42[d] 71:29[e]
(2b)	3.98(s,5H)	4.10(d,1H,H5)[f] H6[g] 2.50(m,1H,$H1_{endo}$) 2.05(d,1H,H2) J(H2-$H1_{endo}$)=6.4Hz	1.0-2.6[c]	1.77(d,1H,$H1_{exo}$) J($H1_{endo}$-$H1_{exo}$)=12.4Hz	

Notes: [a] C_6D_6 solution,all chemical shifts in δ(ppm). [b] major isomer. [c] series of broadened overlapping signals. [d] $NaBH_4$ reaction. [e] $LiBEt_3H$ reaction. [f] obscured by H-5 of isomer 2a. [g] not located.

Table 5. ^{13}C NMR Spectroscopic Data for Cyclohexadienyl Complexes 2a,2b,6a and 6b[a]



a



b

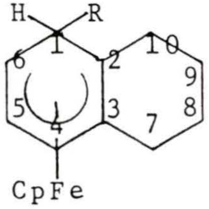
2a,2b R = H

6a,6b R = C_6H_5

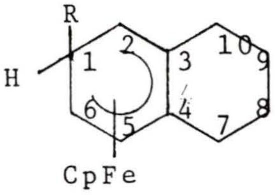
Complex	Cp (ppm)	$-CH_2-$ (ppm)	=CH- (ppm)	QUATERNARIES (ppm)	OTHERS (ppm)
(2a)[b]	74.1	22.9,23.4,29.2, 33.2,34.2 (C1,C7,C8,C9,C10)	24.4 (C6) 76.1 (C5) 77.3 (C4)	93.1,93.7,94.5 (C2,C3)[c]	
2b	74.4	23.6,27.4,29.5,30.5 (C1,C7,C8,C9,C10)	20.7,21.7(C2,C6) 72.7 (C5)	d	
6a	74.3	23.1,23.3,29.5,32.7 (C7,C8,C9,C10)	32.6(C6),75.7(C5) 76.0(C4)	92.7,93.0,93.4 (C2,C3)[e]	48.2(C1) 125.3-129.0($\underline{C}_6H_5$)[f] 146.7($\underline{C}_6H_5$ quat.)
6b	74.5	23.5,24.1,29.0,30.7 (C7,C8,C9,C10)	29.7,30.8(C2,C6) 75.9(C5)	d	41.8(C1) 125.3-129.0($\underline{C}_6H_5$)[f] 149.3($\underline{C}_6H_5$ quat.)

Notes: [a] C_6D_6 solution; chemical shifts measured in ppm. [b] major isomer. [c] also contains quaternary carbons of 2b. [d] same as for isomer a. [e] also contains quaternary carbons of 6b. [f] obscured by C_6D_6 signal.

Table 6. ^{1}H NMR Spectroscopic Data for Cyclohexadienyl Complexes **3a**,**3b**,**4a** and **4b**[a]



a



b

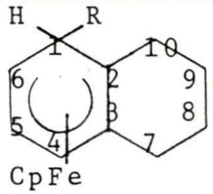
3a,**3b** R = D

4a,**4b** R = n-C_4H_9

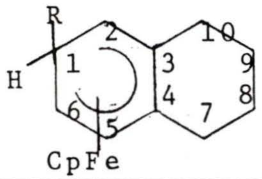
Complex	Cp (ppm)	H1-H6 (ppm)	H7-H10 (ppm)	R (ppm)	Ratio of isomers (a/b)
(**3a**)[b]	3.96(s,5H)	5.76(d,1H,H4) J(H5-H4)=4.8Hz 4.09(t,1H,H5) J(H5-H6,H4)=5.1Hz 2.20(m,1H,$H1_{endo}$) 2.11(t,1H,H6) J(H6-$H1_{endo}$,H5)=6.4Hz	1.0-2.5[c]		68:32
3b	3.98(s,5H)	4.1(d,1H,H5)[e] 2.50(m,1H,$H1_{endo}$) 2.03(dd,1H,H2) J(H2-$H1_{endo}$)=6.5Hz H6[d]	1.0-2.5[c]		
4a,**4b**	3.99(s) 3.96(s)	5.58(d,1H,H4) J(H4-H5)=4.9Hz	0.78-2.9[c]	0.78-2.9[c]	52:48

Notes: [a] C_6D_6 solution; all chemical shifts in δ(ppm). [b] major isomer. [c] series of broadened overlapping signals. [d] not located. [e] obscured by H-5 of isomer **3a**.

Table 7. ^{1}H NMR Spectroscopic Data for Cyclohexadienyl Complexes 5a,5b,6a and 6b[a]



a



b

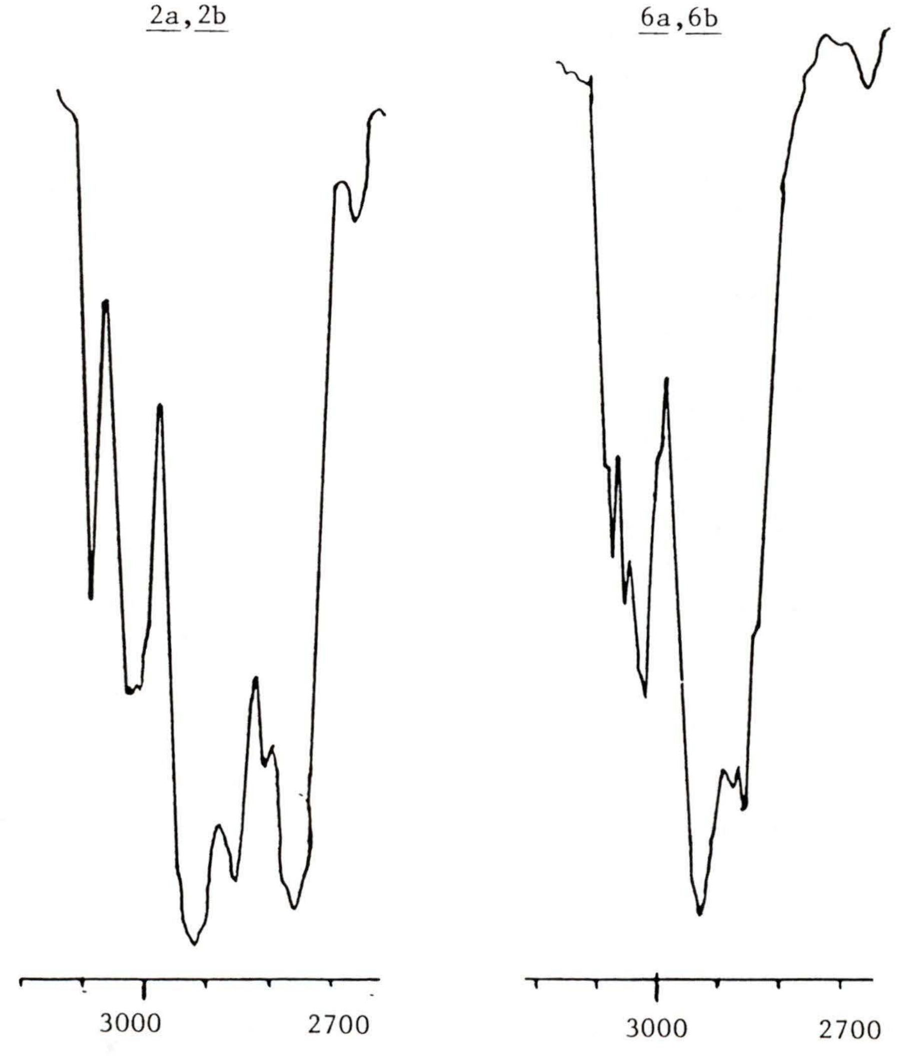
5a,5b R = t-butyl

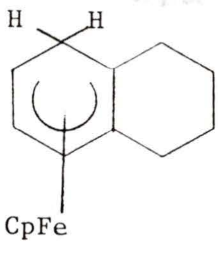
6a,6b R = C_6H_5

Complex	Cp (ppm)	H1-H6 (ppm)	H7-H10 (ppm)	R (ppm)	Ratio of isomers(a/b)
5a,5b	3.97(s,5H) 3.94(s,5H)	5.37(d,1H,H4)[e] J(H4-H5)=5.0Hz 4.06(d,1H,H5)[f] J(H5-H6)=5.9Hz 1.0-2.8[c]	1.0-2.8[c]	0.49(s,9H,C$\underline{H}_3$) 0.54(s,9H,C$\underline{H}_3$)	50:50
(6a)[b]	3.97(s,5H)	5.55(d,1H,H4) J(H4-H5)=4.9Hz 3.60(d,1H,H1$_{endo}$ J(H1$_{endo}$-H6)=6.5Hz H5[d] 2.63(t,1H,H6) J(H6-H1$_{endo}$,H5)=6.0Hz	1.0-1.9[c] 2.2-2.7[c]	6.90(m,$C_6\underline{H}_5$) 7.1(m,$C_6\underline{H}_5$)	64:36
6b	4.00(s,5H)	4.10(d,1H,H5) J(H5-H6)=6.1Hz 2.2-2.7[c]	1.0-1.9[c] 2.2-2.7[c]	6.90(m,$C_6\underline{H}_5$) 7.10(m,$C_6\underline{H}_5$)	

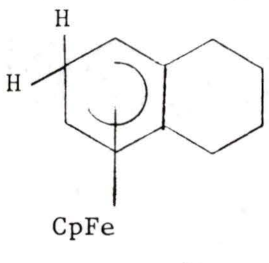
Notes: [a]C_6D_6 solution; all chemical shifts measured in δ(ppm). [b]major isomer. [c]series of overlapping signals. [d]obscured by Cp signals. [e]corresponding to 5a. [f]corresponding to 5b.

Figure 1. IR spectra of cyclohexadienyl complexes 2a,2b and 6a,6b in the 3000 cm^{-1} region

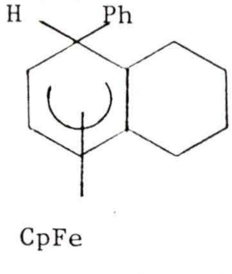




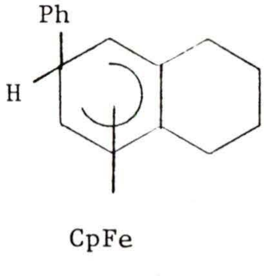
2a



2b

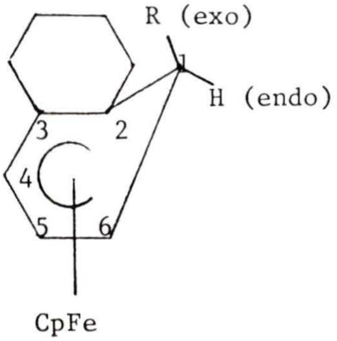


6a

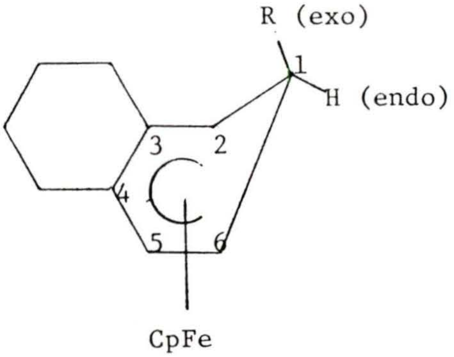


6b

The ^{1}H NMR spectra of compounds 2a,2b - 6a,6b, supports the existence of two isomers (II-ii and II-iii) giving rise to overlapping patterns.



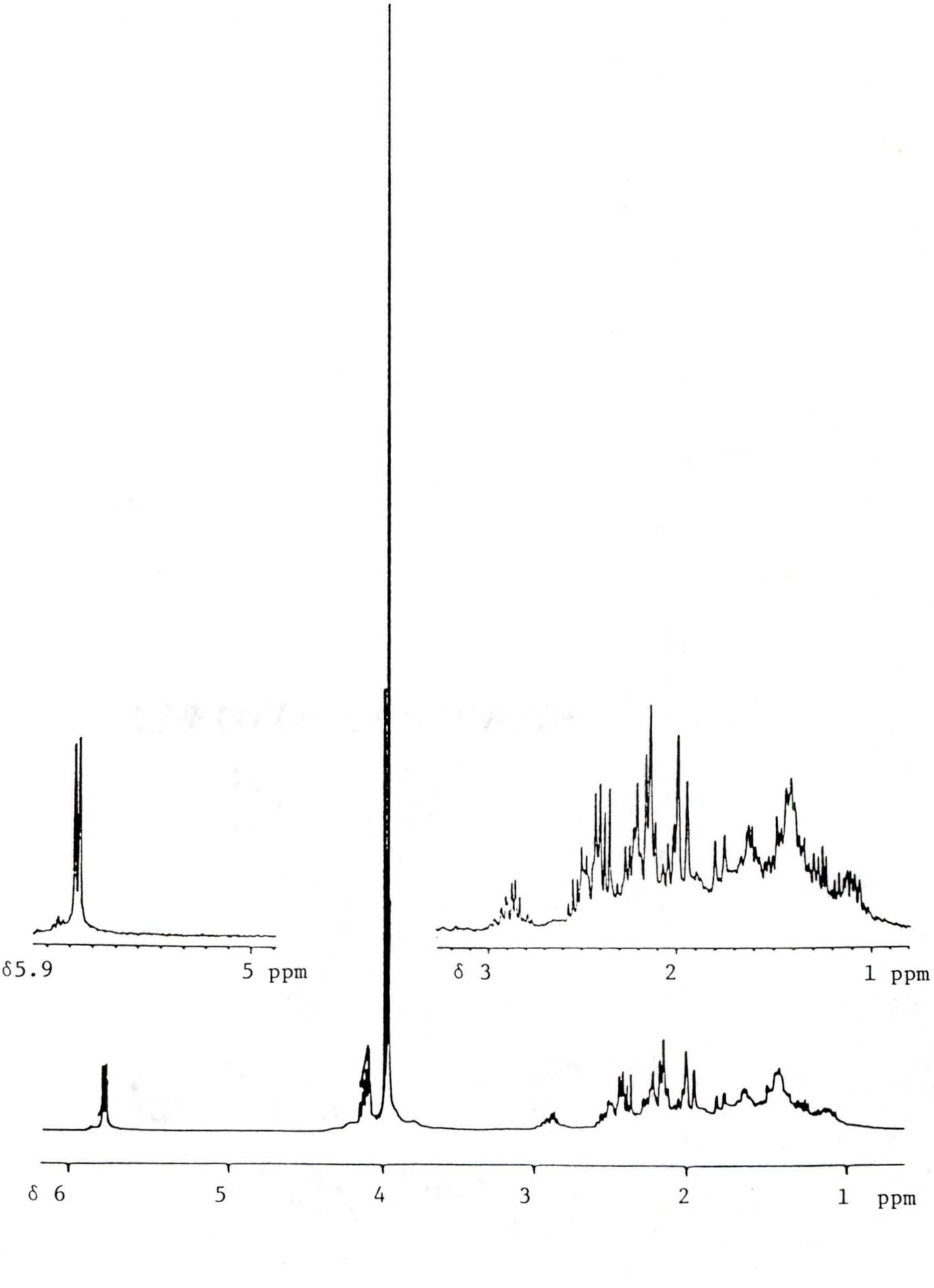
(II-ii) isomer a



(II-iii) isomer b

The reaction of complex 1 with $NaBH_4$ yields the isomeric mixture 2a,2b in *ca.* 58:42 ratio. Informative features in the ^{1}H NMR spectrum of this mixture (see Table 4) are the intense Cp resonances occurring at $\delta 3.95$ and 3.98 ppm; H-4 of 2a appearing as an isolated doublet at $\delta 5.77$ ppm ($J(H4\text{-}H5) = 4.9$Hz), and the exo-hydrogen atoms exhibiting two sets of doublets at $\delta 1.96$ and 1.77 ppm ($J(H_{exo}\text{-}H_{endo}) = 12.1$Hz). H_{exo} is coupled only to H_{endo}[35]; this result could be predicted by application of the Karplus equation and the fact that the dihedral angle between C-H_{exo} and C-(H-2) or C-(H-6) is *ca.* 90^0. The methylene resonances of the saturated ring-system and remaining cyclohexadienyl protons of both isomers are broad and overlap. The same compounds 2a,2b are formed with greater regioselectivity from the reaction of complex 1 with $LiBEt_3H$, *ca.* 71:29 ratio. Here it is possible to assign the cyclohexadienyl resonances

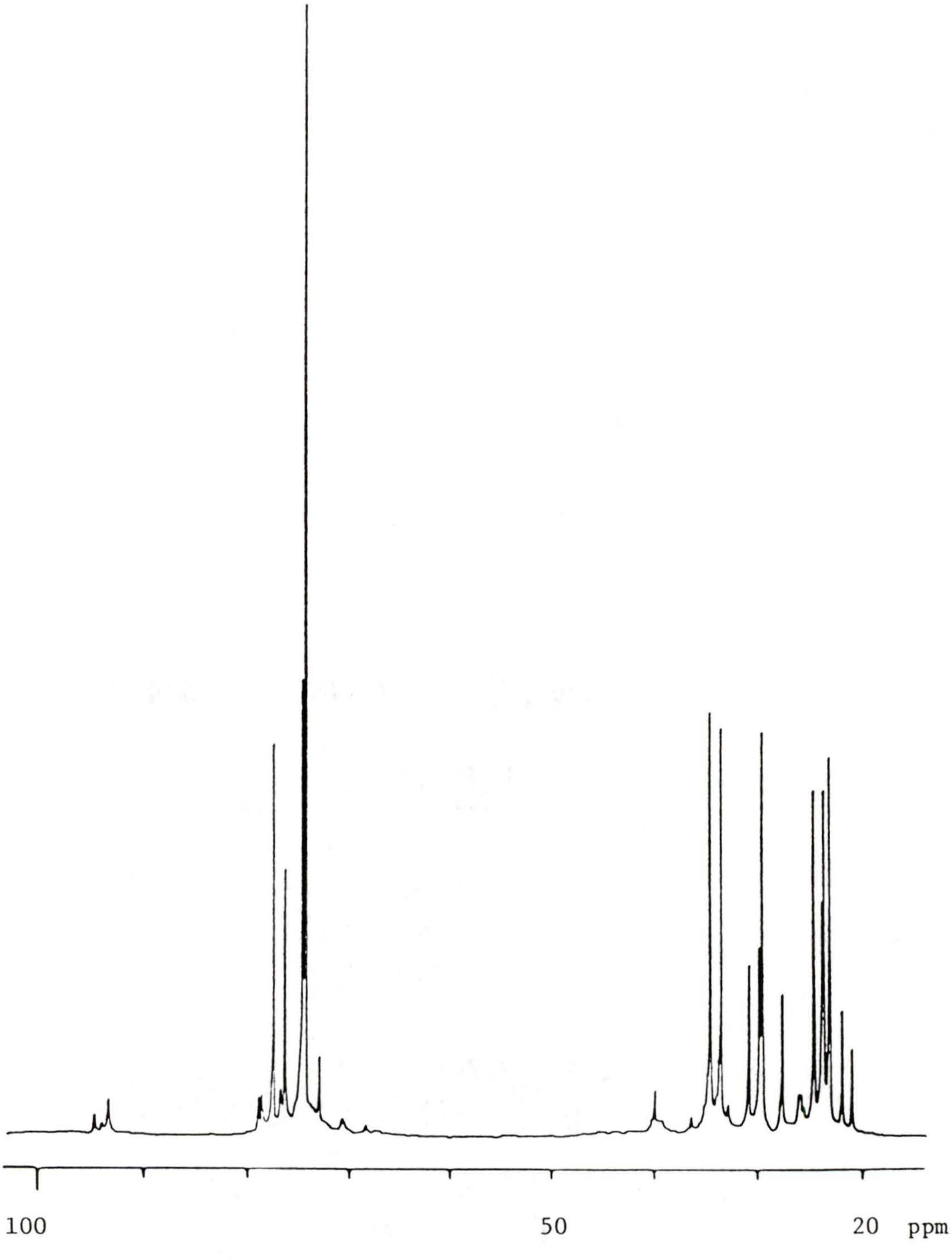
Figure 2. ^{1}H NMR spectrum of cyclohexadienyl adducts 2a,2b from reaction of $[CpFe(tetralin)]^{+}PF_6^{-}$ with $LiBEt_3H$



attributable to the major product which is compound 2a, shown by the relative integration of the low field doublet at δ5.77 ppm (H-4) with the more intense Cp signal (δ3.96 ppm) (see Figure 2). A triplet at δ4.08 ppm may be assigned to H-5 and is coupled to H-4 and H-6 (J(H-5 - H-6,4) = 5.5Hz). The endo proton is resolved as a doublet of doublets at δ2.38 ppm, showing coupling to both H_{exo} and H-6 ($J(H_{endo}$-H-6) = 6.4Hz). A triplet at δ2.13 ppm corresponds to H-6 which is coupled to H-5 and H_{endo}. The exo proton shows a doublet as expected at δ1.96 ppm due to geminal coupling with H_{endo}. The minor isomer 2b also shows a doublet (J = 12.4Hz) corresponding to H_{exo} at δ1.77 ppm and a smaller Cp signal at δ3.98 ppm. Other resonances due to 2b are obscured by those of the major product. These assignments for chemical shifts and coupling constants conform to expectations derived from data for known examples of cyclohexadienyl compounds arising from the exclusive addition of hydride ion to their corresponding six-membered aromatic ring-systems.[35,40,41,42]

The ^{13}C NMR data for mixtures of 2a,2b have also been examined (see Table 5 and Figure 3). Additional evidence for characterization of 2a as the major isomer is provided by C-4 and C-5 of the dienyl unit appearing at 77.3 and 76.1 ppm, respectively , since C-4 is a quaternary carbon in compound 2b. The remaining unsaturated resonance upfield at 24.4 ppm is assigned to C-6. The methylene carbons appear in the range 23-34 ppm

Figure 3. ^{13}C NMR spectrum of cyclohexadienyl adducts 2a,2b from reaction of $[CpFe(tetralin)]^{+}PF_6^{-}$ with $LiBEt_3H$



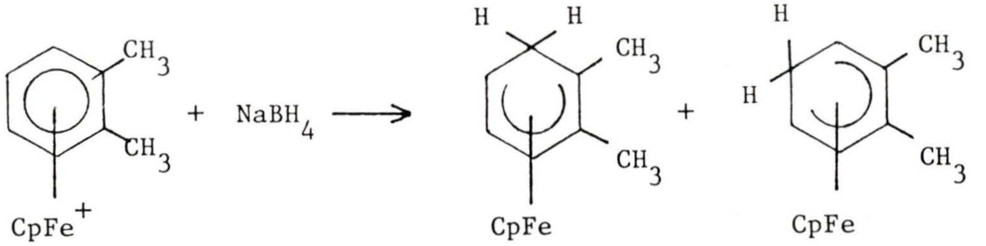
and the quaternary carbons resonate from 93 to 95 ppm. Resonances belonging to the minor product **2b** are similar to those of **2a** and are also shown in Table 5.

Formation of the deuterated analogues **3a**,**3b** from the reaction of complex **1** with $LiBEt_3D$, *ca.* 68:32 ratio, proceeds with almost the same degree of regioselectivity as observed in the $LiBEt_3H$ reaction. The ^1H NMR spectrum of **3a**,**3b** shows resonances (see Table 6) very similar to those for **2a**,**2b**; however, here a conspicuous feature is the absence of the upfield doublets corresponding to H_{exo}, confirming that the exo-position is occupied by deuterium. Based on this result indicating stereospecific addition of D^- to complex **1**, it is likely that H^- addition is occurring also in an exo-fashion. The IR spectrum of this mixture also contains a characteristic strong band at 2040 cm^{-1} due to C-D stretching. This shift in absorption frequency following deuteration is in agreement with that obtained from theoretical results. By the application of Hooke's law[63], the ratio of the C-H to C-D stretching frequencies, $\nu(C\text{-}H)/\nu(C\text{-}D)$, should equal 1.36 which is in accordance with the experimental result 1.35 obtained using the values 2760 and 2040 cm^{-1} for $\nu(C\text{-}H)$ and $\nu(C\text{-}D)$, respectively.

Reaction of complex **1** with phenyl-lithium produces the isomeric mixture **6a**,**6b**, *ca.* 64:36 ratio. This corresponds to regioselective addition of $C_6H_5^-$ which produces **6a** as the major product, established by the ^1H and ^{13}C NMR data for this mixture of compounds (Tables 5 and 7).

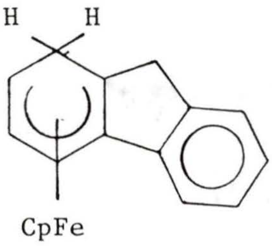
In the ^{1}H NMR spectrum of complex 6a (see Table 7), the expected cyclohexadienyl resonances are observed. The Cp resonance occurs at $\delta 3.97$ ppm and H-4 appears at $\delta 5.55$ ppm as a characteristic doublet. Of notable interest is the occurrence of a doublet due to H_{endo} at $\delta 3.60$ ppm, which is deshielded considerably relative to that for complex 2a as a consequence of its proximity to the phenyl group. The triplet corresponding to H-6 at $\delta 2.63$ ppm shows a similar deshielding effect; the signal due to H-5 is obscured by the Cp resonances although for the less abundant isomer 6b, H-5 is the only discernible resonance, appearing as a doublet at $\delta 4.10$ ppm. The ^{13}C NMR data for 6a,6b (see Table 5) show signals in the expected ranges for both isomers. One interesting feature is the position of the lines at 48.2 and 41.8 ppm corresponding to the C-1 atoms, which again show significant deshielding due to their close proximity to the phenyl group.

A purely steric view of these reactions involving $NaBH_4$, $LiBEt_3H$, $LiBEt_3D$ and phenyl-lithium as nucleophiles would suggest that in each case the predominant isomer should be b, (equation 1) which results from attack at the least hindered position 6 or 7 in complex 1; however, this is not observed, as is established from the foregoing spectral assignments. Other factors must therefore be involved in the predominant formation of compounds 2a, 3a and 6a. This selectivity is in contrast to results reported by Watts and coworkers[40] who observed no selectivity in hydride addition to the related o-xylene complex equation 2. The resulting isomeric products were formed *ca.* 1:1 ratio which indicated that all unsubstituted positions of the o-xylene complex were equally reactive. Similar reactions involving hydride addition to other methyl-substituted benzene complexes had shown that the ratio of the products in each case were formed with a statistical product distribution.

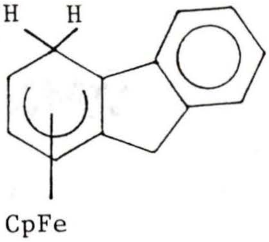


(2)

A cyclohexadienyl complex analogous to 2a has been reported by Treichel and Johnson,[49] who examined hydride addition to a fluorene complex $[CpFe(fluorene)]^+PF_6^-$ using $NaBH_4$. From this reaction, a mixture of at least two isomers was isolated which contained (II-iv) or (II-v) as the major product; however, no explanation regarding their formation was offered.

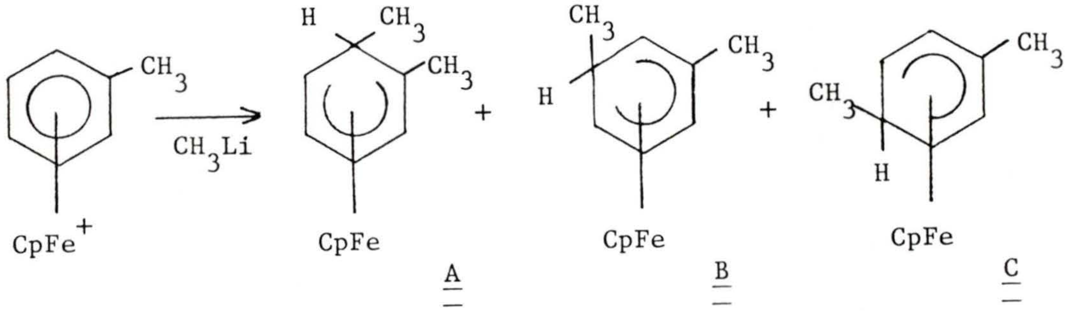


(II-iv)



(II-v)

The reaction of complex 1 with n-butyl- or t-butyl-lithium also resulted in nucleophilic addition to the tetralin ligand, yielding two isomers in each case, ratio *ca.* 50:50 for both **4a**,**4b** and **5a**,**5b**. The lack of selectivity observed here parallels results described by Watts and coworkers[40] who examined methyl-lithium as a nucleophilic reagent towards a toluene complex, equation 3. The resulting isomeric products A,B and C were formed with a statistical distribution (*ca.* 2:2:1 ratio, respectively).



(3)

Nesmeyanov and coworkers[79] have reported that the reaction of t-butyl-lithium with the [CpFe(benzene)]$^+$ cation leads to disproportionation of the arene complex, yielding some ferrocene but leaving much of the cation unchanged, equation 4. In contrast to this report, the formation of **5a**,**5b** proceeds in good yield without ferrocene

$$2[\mathrm{CpFe}(\eta^6\text{-}\mathrm{C_6H_6})]\mathrm{BF_4} \quad + \quad \text{t-butyl-Li} \quad = (\mathrm{Cp})_2\mathrm{Fe} \quad + \quad 2\ \mathrm{C_6H_6} \quad + \quad \mathrm{Fe}^{2+} \quad (4)$$

formation.

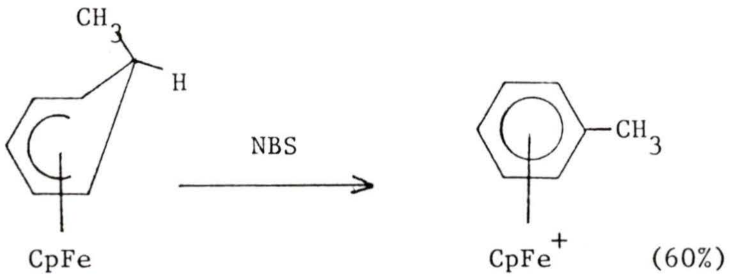
In the ^{1}H NMR spectra of the isomeric mixtures **4a**,**4b** and **5a**,**5b** (see Tables 6 and 7), assignment of the resonances is not straightforward due their overlapping patterns. However, prominent peaks in the ^{1}H NMR spectrum of **4a**,**4b** are the two Cp resonances at δ3.99 and 3.96 ppm, and

H-4 of 4a at δ5.58 ppm, and similarly for 5a,5b the Cp signals are obvious at δ3.97 and 3.94 ppm. In addition, H-4 of 5a appears at δ5.37 ppm, and two intense singlets upfield at δ0.49 and 0.54 ppm are assigned to the t-butyl groups. The lack of regioselectivity observed in these reactions precludes further assignment of the remaining cyclohexadienyl resonances to particular isomers. In comparison to the phenyl-lithium reaction, the n-butyl- and t-butyl-lithium reactions show an increased proportion of isomer b in their isomeric products: this may be a reflection of the increased steric bulk associated with the t-butyl and n-butyl groups.

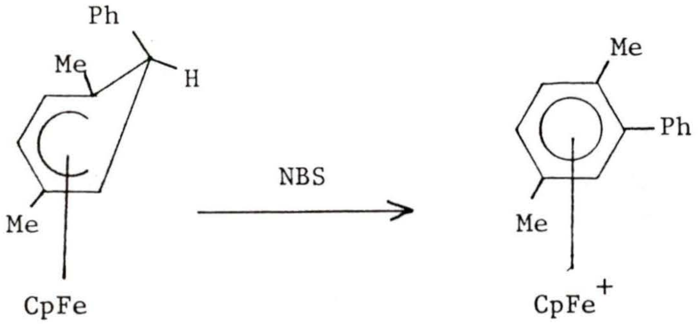
The mass spectra of the cyclohexadienyl complexes 2a,2b - 6a,6b (see experimental section) each show the expected parent peak as well as signals corresponding to Cp_2Fe^+ and $CpFe^+$. Such results are in agreement with those reported by Sutherland and coworkers[60] who have described the mass spectral fragmentation of some simple cyclohexadienyl complexes. The t-butyl adducts 5a and 5b revealed a prominent base peak at m/e 253 corresponding to loss of a t-butyl group. The phenyl adducts 6a and 6b showed a peak at m/e 253 arising from loss of a phenyl group.

(ii) Oxidation of cyclohexadienyl adducts

In order to complete a route for substitution into the coordinated aromatic ring of complex 1, oxidation of the cyclohexadienyl products was investigated (see Scheme 5). In 1969, Watts and coworkers[42] reported that conversion of the exo-substituted compounds exo-$(CH_3)C_6H_6FeCp$ and exo-$(C_6H_5)C_6(CH_3)_2H_4FeCp$ to their corresponding cations was possible only *via* treatment with N-bromosuccinimide(NBS) (equations 5 and 6); the same

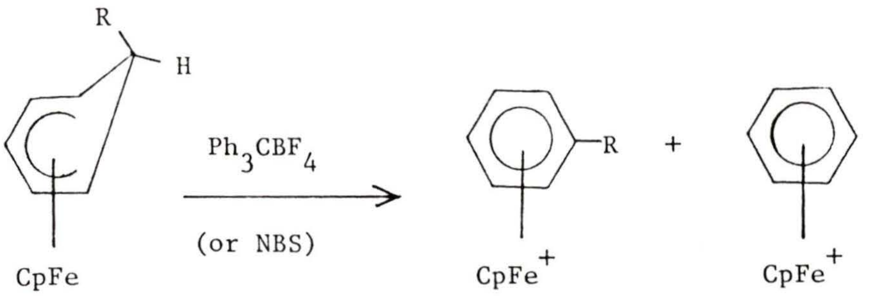


(5)



(6)

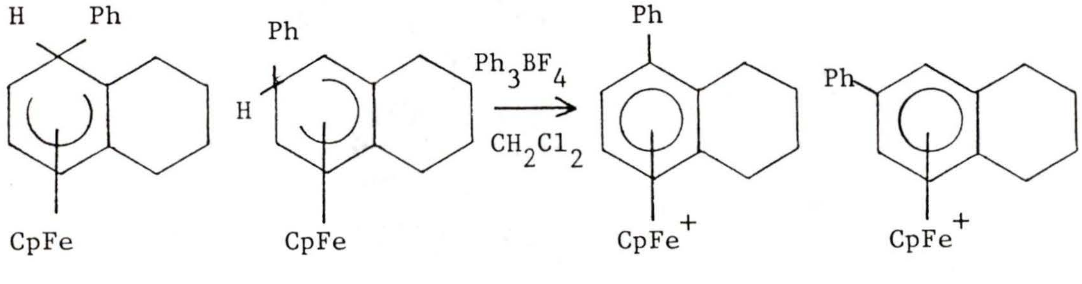
compounds failed to react with triphenylmethyl tetrafluoroborate $(Ph_3C)BF_4$. Contrary to these results, Nesmeyanov and coworkers[43] investigated similar reactions with NBS and $(Ph_3C)BF_4$ and discovered that endo-hydrogen abstraction or exo-R abstraction could occur, along with some decomposition, when either oxidant was reacted with certain cyclohexadienyl complexes, equation 7. A series reflecting the increasing tendency for exo-R abstraction was established: $R = CH_3 \ll C_5H_5 < C_2H_5 < C_6H_5CH_2$.



(7)

R = C_2H_5, $C_6H_5CH_2$, C_5H_5, CH_3

For example, upon examination of the complex containing R=CH_3, only endo-H abstraction occurred resulting in the exclusive formation of a toluene complex. This latter behaviour is paralleled in the reaction of the phenyl adducts 6a and 6b with triphenylmethyl tetrafluoroborate: the substituted cations 7a,7b are produced, *ca.* 62:38 ratio, equation 8.

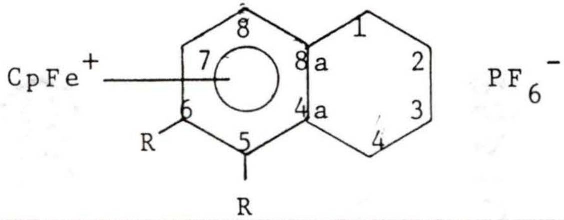


(8)

6a 6b 7a 7b

The absence of any tetralin complex 1, shown by the ^1H NMR data of cations 7a and 7b (see Table 8), confirms that the reaction proceeds exclusively by endo-H abstraction affording the phenyl-substituted complexes, in low yields (20%) which are comparable to those obtained by Nesmeyanov and coworkers.[43] Examination of the products using ^1H NMR

Table 8. ^{1}H and ^{13}C NMR Spectroscopic Data for Substituted Tetralin Complexes 7a and 7b[a]



7a $R_5 = C_6H_5$; $R_6 = H$

7b $R_5 = H$; $R_6 = C_6H_5$

Complex	H5-H8 (ppm)	Cp (ppm)	H1,H4 (ppm)	R_5,R_6 (ppm)	H2-H3 (ppm)
(7a,7b)[b]	6.34(m)[c]	5.23(s,5H)	2.6-3.22[e]	7.3(m)[c]	1.8-2.0[e]
	6.50(m)	5.03(s,5H)		7.54(m)	
	6.81(m)			7.74(m)	
				8.02(m)	

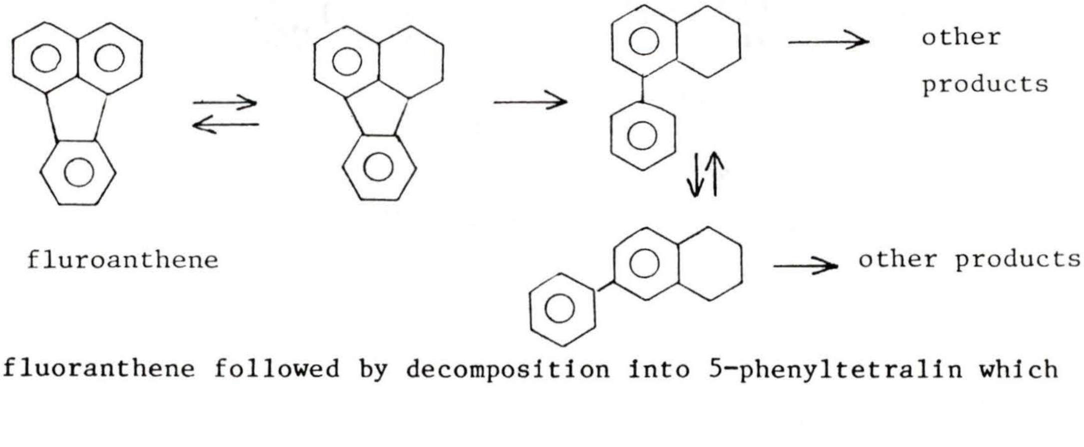
Complex	C1-C4 (ppm)	C5-C8 (ppm)	C4a,C8a (ppm)	Cp (ppm)	Others (ppm)
7a	22.3, 22.5	88.6, 87.8	102.6	78.6	131.0, 129.5 ($\underline{C}_6H_5$)
	22.9, 28.5	86.7 (C6,C7,C8)	103.7		136.2 ($\underline{C}_6H_5$ quat)
		C5[g]			
7b	f	85.0, 85.9, 87.8	104.5	79.2	130.0, 130.2 ($\underline{C}_6H_5$)
		(C5,C7,C8)	106.9		135.9 ($\underline{C}_6H_5$ quat)

Notes: [a] $(CD_3)_2CO$ solution; all chemical shifts in δ(ppm). [b] ratio of isomers is 62:38, 7a being the major isomer. [c] poorly resolved. [d] Cp signal corresponding to the major isomer 7a. [e] poorly resolved series of multiplets. [f] same as for 7a. [g] not located.

spectroscopy shows that two prominent Cp resonances occur at δ5.23 and 5.03 ppm, in approximately the same ratio as that observed for the starting materials 6a,6b, but the remainder of the spectrum is relatively uninformative; however, the ^{13}C NMR spectrum (see Table 8) is more useful. The Cp resonances occur at 78.6 and 79.2 ppm for 7a and 7b, respectively. Coordinated aromatic carbons extend from 85.0 to 88.6 ppm, and from 102.6 to 106.9 ppm for coordinated quaternary carbons. Uncoordinated aromatic carbons occur from 129.5 to 136.2 ppm as expected, and the methylene carbons appear in the range 22.3-28.5 ppm.

The major feature of the IR spectrum of the isomeric mixture 7a,7b is the characteristic strong band at 1050 cm^{-1} assigned to B-F stretching vibrations of the counterion. The mass spectrum of 7a,7b shows a base peak at m/e 209 corresponding to the free uncoordinated aromatic $C_{16}H_{16}$ ligand.

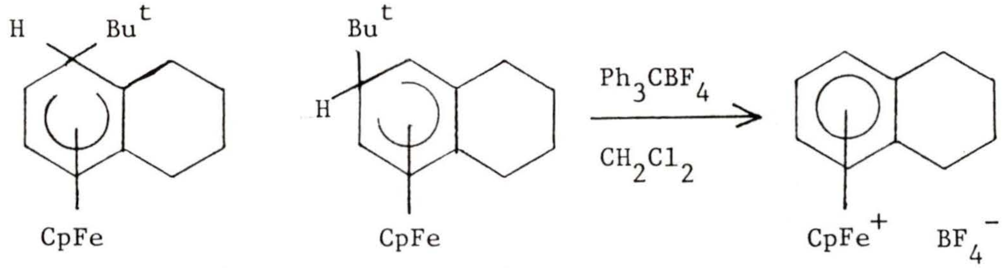
The formation of the isomeric free aromatic $C_{16}H_{16}$ ligands has been reported by Kikkawa and coworkers[76] who obtained these compounds *via* hydrocracking of fluoranthene over molten salt catalysts at 400°C, equation 9. The probable reaction route involves the hydrogenation of



(9)

fluoranthene followed by decomposition into 5-phenyltetralin which isomerises to form 6-phenyltetralin. Such reactions have been extensively used and applied in the industrial processing of petroleum feedstocks.[80]

Oxidation of the t-butyl adducts 5a,5b using Ph_3CBF_4 followed a different course, and resulted only in the formation of the starting tetralin complex 1 (7% yield) ,(equation 10) identified by its ^1H NMR spectrum. This result suggests that abstraction of the t-butyl groups is occurring, although the reaction is dominated by decomposition of the metal-arene constituents.



(10)

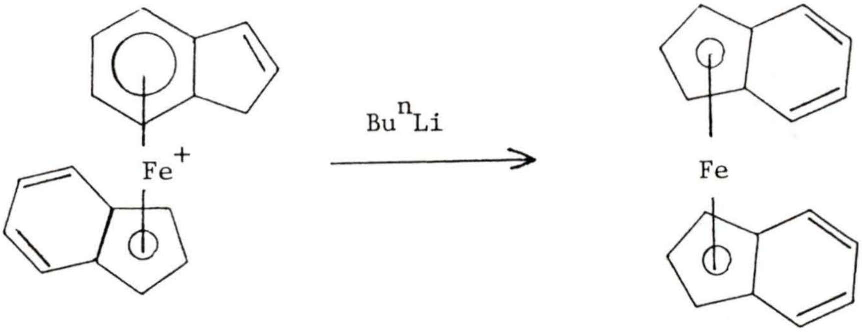
5a,5b

1

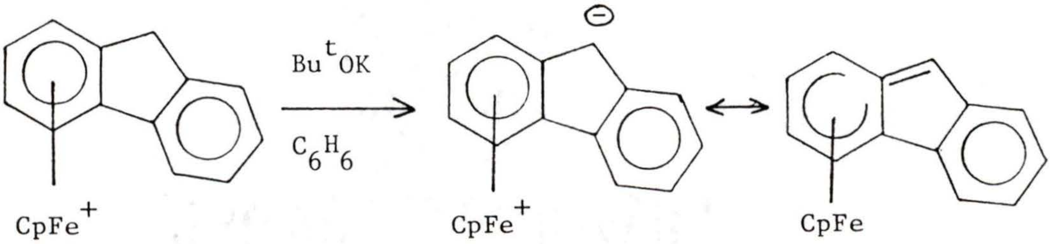
B. Benzylic substitution in $[CpFe^+(tetralin)]PF_6^-$

(i) Poly-α-substituted tetralin complexes

The reactions of complex 1 which have been discussed above illustrate the increased susceptibility of the tetralin ligand towards nucleophilic attack upon coordination to the $CpFe^+$ fragment. A further important consequence of metal complexation to a hydrocarbon ligand is the significant enhancement of the acidity of benzylic hydrogens (i.e. those α to the aromatic nucleus). In 1975 Treichel and Johnson reported the deprotonation reaction of $[(\eta^5\text{-indenyl})Fe(\eta^6\text{-indene})]^+$ with n-butyl-lithium, yielding bis(indenyl)iron[59] equation 11; however, no nucleophilic addition by n-butyl-lithium to the coordinated indene ring was observed. This report contrasts with the nucleophilic behaviour of n-butyl-lithium towards the tetralin complex 1, as represented by equation 1. In 1977, Treichel and Johnson also investigated the deprotonation of a fluorene complex with Bu^tOK as base; this yielded a thermally stable, air-sensitive, blue zwitterion[44], equation 12. An x-ray crystallographic structure determination of the deprotonated fluorene species indicated some degree of cyclohexadienyl character in terms of geometry, although its reactivity with electrophiles was more consistent with the zwitterionic representation. Sutherland and

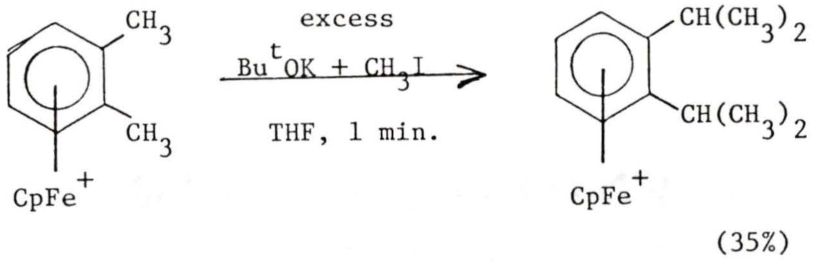


(11)



(12)

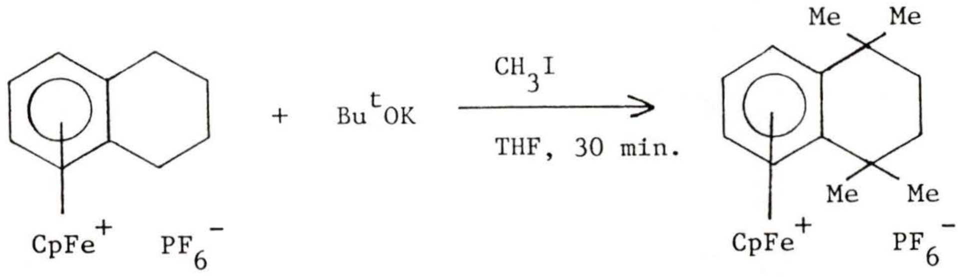
coworkers[61] have investigated numerous nucleophilic reactions of similar deprotonated complexes with different substrates, such as organic halides. The same type of reaction has also been used for a synthetic purpose by Astruc and coworkers[49] who demonstrated that peralkylation of $[CpFe(arene)]^+$ complexes takes place on reaction with an excess of base and an electrophilic alkylating reagent, (see equation 13).



(13)

As shown in equation 13, the reaction consists of a "one-step" multiple carbon-carbon bond formation. The absence of the formation of t-butyl groups indicated that the reaction was limited by the competing reaction of Bu^tOK with iodomethane[11] and by steric bulk in the coordinated hydrocarbon.

In order to diversify access to substituted tetralin complexes, reactions involving polysubstitution in the saturated ring of complex 1 were investigated. By comparison with the reactivity of the analogous o-xylene complex (i.e. equation 13), it is expected that complete alkylation of the benzylic hydrogens in complex 1 should occur (see Scheme 6). At room temperature, the reaction of complex 1 with a large excess of Bu^{t}OK and CH_3I (equation 14) affords an orange amorphous solid 8 which is soluble in polar organic solvents and has been fully



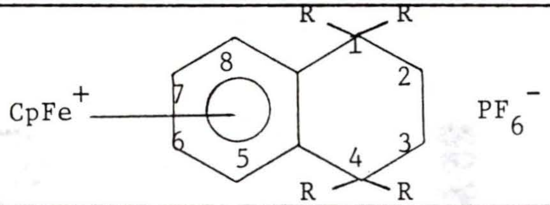
(14)

8

characterized by microanalytical data (see experimental section) and spectroscopic measurements (see Tables 9 and 10).

The ^1H NMR spectrum of complex 8 (see Table 9 and Figure 4) consists of two prominent singlets at δ1.28 and 1.69 ppm assigned to the exo- and endo-methyl groups, and an isolated singlet at δ5.21 ppm corresponding to the Cp group. Multiplets centred at δ1.76 and 1.95 ppm are due to methylene protons, and the four coordinated aromatic protons appear as a multiplet at δ6.52 ppm. Although an unambiguous assignment of the methyl resonances has not been made, the ^1H NMR data obtained for exo- and endo-methylated fluorene complexes (II-v and II-vi)[44] showed that the exo-methyl group resonated at a higher field (i.e. 1.59 ppm) relative to the endo-methyl group (1.96 ppm).

Table 9. ^{1}H NMR Spectroscopic Data for Substituted Tetralin Complexes 1,8,10 and 12[a]

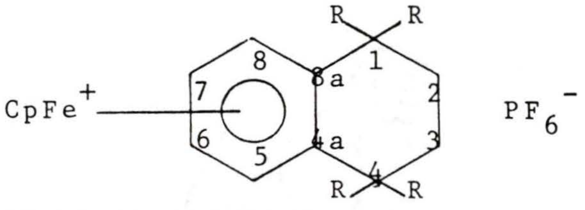


1 R=H
8 R=CH$_3$
10 R=C$_3$H$_5$
12 R$_{1\alpha}$=H; R$_{1\beta,4\alpha,4\beta}$=CH$_2$C$_6$H$_5$

Complex	H5-H8 (ppm)	Cp (ppm)	R$_{1\alpha}$R$_{4\alpha}$ (ppm)	R$_{1\beta}$R$_{4\beta}$ (ppm)	H2-H3 (ppm)
1	6.28(s,4H)	5.11(s,5H)	3.09(ddd,2H) J(H$_\alpha$-H$_\beta$) = 17Hz J(H4$_\alpha$-H3$_\alpha$) = 7.4Hz J(H4$_\alpha$-H3$_\beta$) = 5.1Hz	2.82(ddd,2H) J(H4$_\beta$-H3$_\beta$) = 7.2Hz J(H4$_\beta$-H3$_\alpha$) = 5.7Hz	2.00(m,2H,H2$_\alpha$,H3$_\alpha$) 1.86(m,2H,H2$_\beta$,H3$_\beta$)
8	6.52(m,4H)	5.21(s,5H)	1.69(s,6H)	1.28(s,6H)	1.95(m,2H,H2$_\alpha$,H3$_\alpha$) 1.76(m,2H,H2$_\beta$,H3$_\beta$)
10	6.51(m,4H)	5.25(s,5H)	6.09(m,2H,-C$\underline{H}$=) 4.9(=C$\underline{H}_2$)[b] 3.08(dd,2H,-C$\underline{H}$'H-) J(H'-H) = 13.3Hz J(H'-C$\underline{H}$=) = 7.5Hz 2.73(dd,2H,-CH'$\underline{H}$-) J(H-C$\underline{H}$=) = 7.4Hz	5.55(m,2H,-C$\underline{H}$=) 5.3(=C$\underline{H}_2$)[b] 2.45(dd,2H,-C$\underline{H}$'H-) J(H'-H) = 13.8Hz J(H'-C$\underline{H}$=) = 6.2Hz 2.26(dd,2H,-CH'$\underline{H}$) J(H-C$\underline{H}$=) = 8.2Hz	1.98(m,2H,H2 ,H3) 1.89(m,2H,H2 ,H3)

Notes: [a] d$_6$-acetone solutions; all chemical shifts measured in δ(ppm). [b] poorly resolved.

Table 9 continued

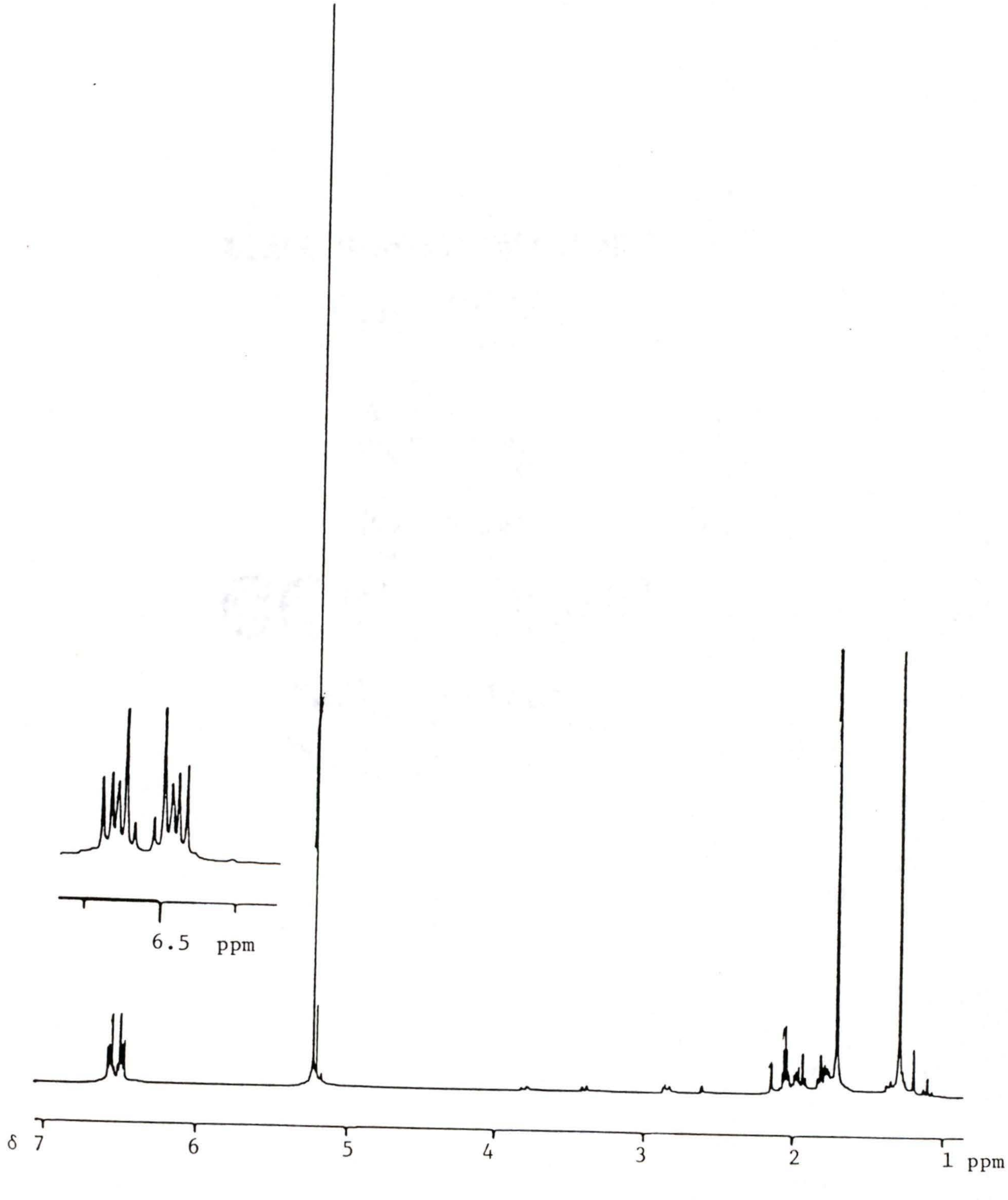


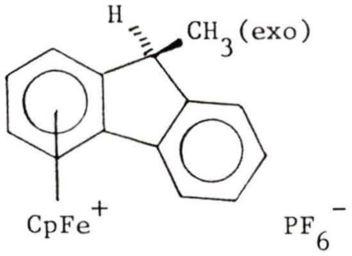
12 $R_{1\alpha}$ = H; $R_{1\beta,4\alpha,4\beta}$ = $CH_2C_6H_5$

Complex	H5-H8 (ppm)	Cp (ppm)	$R_{1\alpha}R_{4\alpha}$ (ppm)	$R_{1\beta}R_{4\beta}$ (ppm)	H2-H3 (ppm)
12	6.08(dd,1H,H8) J(H8-H7) = 6.7Hz J(H8-H6) = 0.98Hz 6.36(t,1H,H7) J(H7-H6) = 6.3Hz 6.63(m,2H,H5,H6)^b	5.29(s,5H)	3.72(d,1H,-CH'H-) 3.55(d,1H,-CH'H-) J(H'-H) = 13.0Hz 3.20(m,1H,H1$_\alpha$) 6.86-7.55(m,C_6H_5)^b	3.32(d,1H,-CH'H-) 2.53(d,1H,-CH'H-) J(H'-H) = 13.3Hz 2.18(dd,1H,-CH'H-) J(H'-H) = 13.8Hz J(H$_\alpha$-CH') = 7.1Hz 1.80(dd,1H,-CH'H-) J(H$_\alpha$-CH) = 9.6Hz 6.86-7.55(m, C_6H_5)^b	1.66-1.94 (m,4H)^b

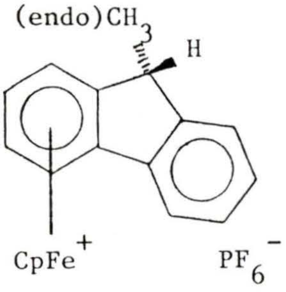
Notes: $^a d_6$-acetone solutions; all chemical shifts measured in δ(ppm). ^{b}poorly resolved.

Figure 4. ^{1}H NMR spectrum of $[CpFe(tetramethyltetralin)]^{+}PF_6^{-}$





(II-v)

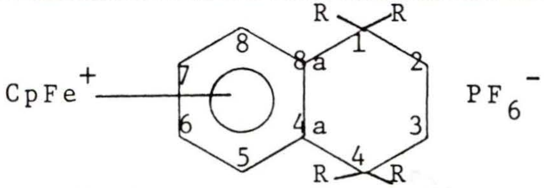


(II-vi)

The ^{13}C NMR spectrum of complex 8 (see Table 10 and Figure 5) includes a single resonance at 76.3 ppm due to the Cp ligand. Two lines at 31.3 and 32.5 ppm are assigned to the exo- and endo-methyl groups. Coordination of the aromatic ligand is again confirmed by the appearance of resonances at 83.8, 86.1 and 113.9 ppm attributed to the coordinated aromatic carbons. Of particular interest is the signal at 34.0 ppm assigned to the quaternary carbons in the saturated ring system, thus confirming tetra-substitution at the benzylic positions. The methylene carbons resonate slightly downfield at 34.1 ppm.

An important feature in the IR spectrum of complex 8 is the presence of a doublet with bands at 1380 and 1370 cm^{-1} of medium intensity, which may be assigned to the symmetrical CH_3 bending vibrations of the gem-dimethyl groups. As found in the IR spectra for all the hexafluorophosphate complexes reported in this work including complex 1, a very strong broad contour in the 830 cm^{-1} region is assigned to P-F stretching vibrations. Further support for the formulation of complex 8 is provided by its mass spectrum which shows a peak at m/e 188

Table 10. ^{13}C NMR Spectroscopic Data for Substituted Tetralin Complexes 1,8,10 and 12[a]

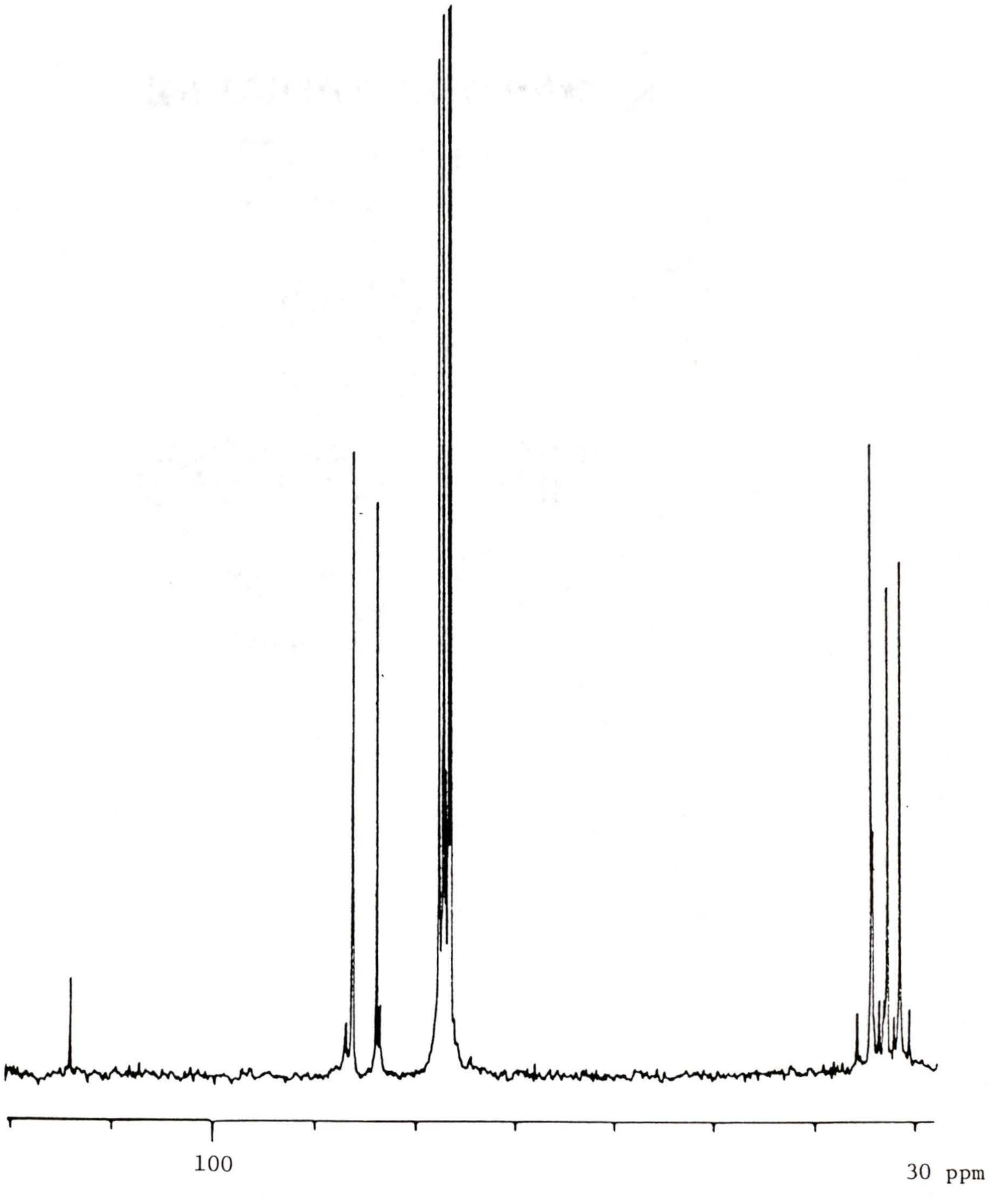


1 R = H
8 R = CH$_3$
10 R = C$_3$H$_5$
12 R$_{1\alpha}$ = H, R$_{1\beta,4\alpha,4\beta}$ = CH$_2$C$_6$H$_5$

Complex	C1-C4 (ppm)	C5-C8 (ppm)	C4a,C8a (ppm)	Cp (ppm)	Others (ppm)
1	28.9 (C1,C4) 22.6 (C2,C3)	87.3 (C5,C8) 87.9 (C6,C7)	104.8 (C4a,C8a)	78.1	
8[b]	34.0 (C1,C4) 34.1 (C2,C3)	83.8 (C5,C8) 86.1 (C6,C7)	113.9 (C4a,C8a)	76.3	31.3, 32.5 (-$\underline{C}H_3$)
10	40.1 (C1,C4) 27.4 (C2,C3)	85.4 (C5,C8) 86.6 (C6,C7)	113.9 (C4a,C8a)	77.4	45.0, 46.1(-$\underline{C}H_2$-) 134.4 (=$\underline{C}$H-) 119.9, 120.1 (=$\underline{C}H_2$)
12	41.0 (C1) 22.5,22.6(C2,C3) 44.4 (C4)	87.0, 87.5 87.3, 86.8	108.1 (C8a) 115.9 (C4a)	77.9	42.1,47.6,48.2(-$\underline{C}H_2$) 127.3,127.4,127.8, 128.7,129.0,129.3, 130.1,132.2,132.8, (-C$_6$H$_5$) 137.6,137.8,139.8 (-$\underline{C}_6$H$_5$ quat)

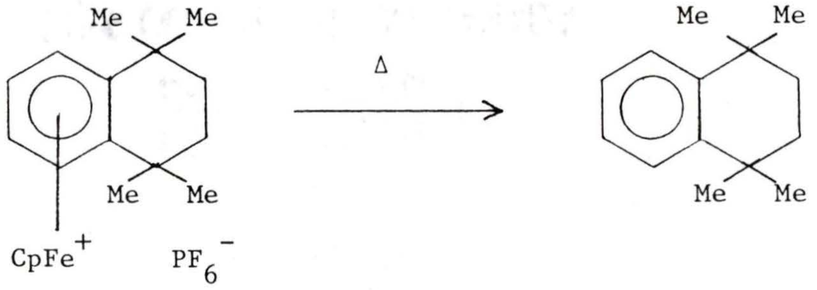
Notes: [a](CD$_3$)$_2$CO solution; all chemical shifts in ppm. [b]CDCl$_3$ solution.

Figure 5. ^{13}C NMR spectrum of $[CpFe(tetramethyltetralin)]^{+}PF_6^{-}$



corresponding to the free uncomplexed $C_{14}H_{20}$ ligand, with a base peak at m/e 173 arising from subsequent methyl loss.

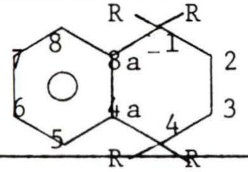
Pyrolytic sublimation of complex 8, following a method similar to that described by Sutherland and coworkers,[46] afforded the free aromatic hydrocarbon 9 (see equation 15) as a clear colourless oil, soluble in polar and non-polar organic solvents, and characterized by spectroscopic measurements (see Tables 11 and 12).



8 9 (15)

The ^1H NMR spectrum of the tetramethyltetralin compound 9 (see Table 11) which reflects its symmetrical substitution pattern, revealing a sharp singlet at δ1.28 ppm attributed to the four equivalent methyl groups. The methylene protons resonate as a singlet at δ1.69 ppm, and the uncomplexed aromatic protons appear as multiplets at δ7.31 and 7.12 ppm as expected. The ^{13}C NMR spectrum of 9 (see Table 12) exhibits one line at 31.9 ppm due to the methyl carbons. Saturated quaternary and methylene carbons appear at 34.2 and 35.2 ppm, respectively, and signals at 125.5 and 126.4 ppm are assigned to the unsaturated carbons. The most deshielded resonance occurs at 144.8 ppm corresponding to the unsaturated quaternary carbons.

Table 11. ^{1}H NMR Spectroscopic Data for Uncomplexed Substituted Tetralin Ligands 9, 11, and 13[a,c]

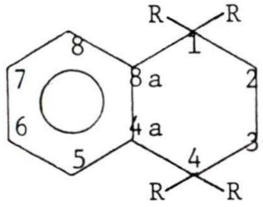


9 R = CH_3
11 R = C_3H_5
13 $R_{1\alpha}$ = H, $R_{1\beta,4\alpha,4\beta}$ = $CH_2C_6H_5$

Complex	H5-H8 (ppm)	$R_{1\alpha}R_{4\alpha}$ (ppm)	$R_{1\beta}R_{4\beta}$ (ppm)	H2-H3 (ppm)
9	7.31 (m,2H) 7.12 (m,2H)	1.28 (s,12H,-C$\underline{H_3}$)		1.69 (s,4H)
11	7.14 (m,2H) 7.25 (m,2H)	5.59 (m,4H,-C$\underline{H}$=) 5.02 (m,2H,=C$\underline{H_2}$)[b] 4.99(m,2H,=C$\underline{H_2}$)[b] 4.95(m,4H,=C$\underline{H_2}$)[b]	2,50 (dd,4H,-C$\underline{H}$'H-) J(H'-H) = 14.0Hz J(H'-C$\underline{H}$=) = 6.4Hz 2.21(dd,4H,-CH'$\underline{H}$-) J(H-C$\underline{H}$=) = 8.0Hz	1.69 (s,4H)
13	7.75 (d,1H) J(H-H')$_{ortho}$=7.6Hz 7.37 (t,1H) J(H-H')$_{meta}$=1.1Hz 7.02 (m,2H)	2.8 (m,1H,H_α) 3.49 (d,1H,-C$\underline{H}$'H-) 3.27 (d,1H,-CH'$\underline{H}$-) J(H'-H) = 13.3Hz 6.91 (m,-$C_6\underline{H_5}$) 7.22 (m,-$C_6\underline{H_5}$)	2.94 (d,1H,-C$\underline{H}$'H-) 2.81 (d,1H,-CH'$\underline{H}$-) J(H-H') = 13.3Hz 2.37 (dd,1H,CH_α(C$\underline{H}$'H-)-) J(H'-H) = 13.7Hz J(H_α-C$\underline{H}$') = 6.1Hz 1.88 (dd,1H,-CH_α(CH'$\underline{H}$)-) J(H_α-C$\underline{H}$) = 9.9Hz 6.91 (m,-$C_6\underline{H_5}$) 7.22 (m,-$C_6\underline{H_5}$)	1.97 (m,1H) 1.57 (dt,1H) J($H2_\alpha$-$H2_\beta$)=14.3Hz J(H2-H3)=3.8Hz 1.33 (m,2H)

Notes: [a]$CDCl_3$ solution. [b]poorly resolved. [c]chemical shifts measured in δ(ppm).

Table 12. ^{13}C NMR Spectroscopic Data for Uncomplexed Substituted Tetralin Ligands 9, 11, and 13[a]



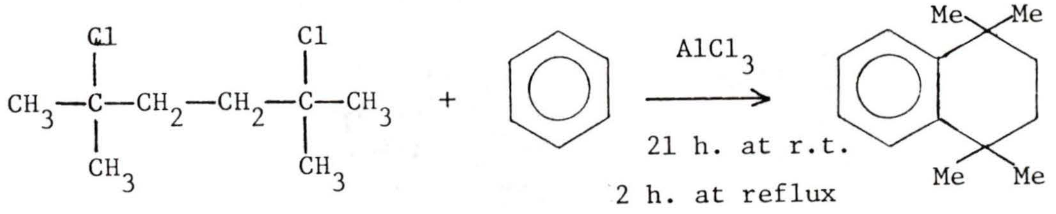
9 $R = CH_3$
11 $R = C_3H_5$
13 $R_{1\alpha} = H$, $R_{1\beta, 4\alpha, 4\beta} = CH_2C_6H_5$

Complex	C1-C4 (ppm)	C5-C8 (ppm)	C4a,C8a (ppm)	Others (ppm)
9	34.2 (C1,C4) 35.2 (C2,C3)	125.5 (C5,C8) 126.4 (C6,C7)	144.8	31.9 ($-\underline{C}H_3$)
11	40.0 (C1,C4) 26.8 (C2,C3)	125.5 (C5,C8) 127.2 (C6,C7)	142.7	46.3 ($-\underline{C}H_2-$) 117.2 ($=\underline{C}H_2$) 135.3 ($-\underline{C}H=$)
13	40.5 (C1) 22.3,25.0 (C2,C3) 42.9 (C4)	b	138.7 138.8	42.3,47.4,50.5 ($-\underline{C}H_2-$) 140.8,141.4,142.3, ($-\underline{C}_6H_5$ quat.) 125.5-131.0 ($-\underline{C}_6H_5$)

Notes: [a]$CDCl_3$ solution; all chemical shifts in ppm. [b]obscured by phenyl resonances.

In the IR spectrum of 9, characteristic bands associated with the gem-dimethyl groups are still present at 1385 and 1365 cm^{-1}. The mass spectrum of 9, which is similar to that observed for the iron complex 8, shows a molecular ion at m/e 188, and a peak corresponding to the loss of a methyl group occurs at m/e 173.

The preparation of compound 9 was reported by Bruson *et al.*[62] but no spectroscopic data have since been published. As shown in equation 16, the original preparation of this tetramethyltetralin was accomplished by condensation of 2,5-dichloro-2,5-dimethylhexane with benzene in the presence of excess aluminum chloride. This type of reaction, which fuses saturated ring systems to aromatic nuclei, is potentially significant for synthesis of polycyclic hydroaromatic skeletons on which various vitamin and hormone structures are based.



(16)

(61%)

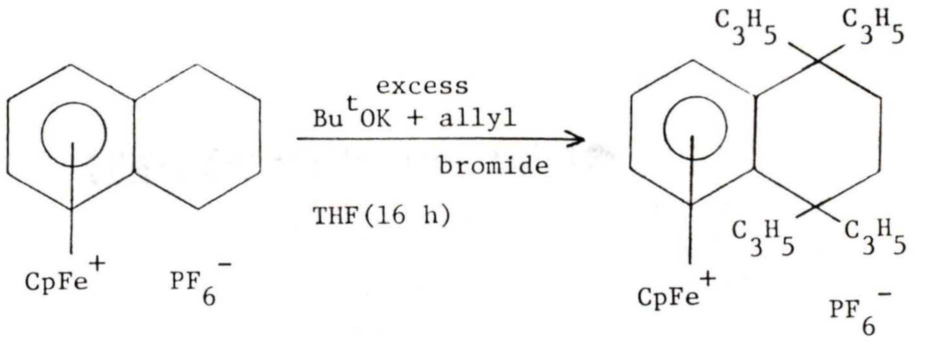
Consideration of the foregoing spectroscopic data confirms that complete substitution of the benzylic positions of complex 1 has occurred. The purity of the iron complex 8, however, appears to be dependent on the method of addition of the reagents. Formation of complex 8 occurs cleanly upon the addition of a THF solution of iodomethane to a dry mixture of Bu^tOK and complex 1, i.e. conditions similar to those employed by Astruc and coworkers.[49] However, when iodomethane is added to a THF solution of deprotonated 1, the expected colour changes occur but analysis of the final product (by ^1H NMR spectroscopy) reveals a complicated mixture of $CpFe^+$ compounds which may arise from varying degrees of substitution indicating that the competing reaction occurring between Bu^tOK and CH_3I may be a significant factor.

It is known[65] that iodomethane undergoes nucleophilic substitution by lithium ethoxide to form methylethylether and lithium iodide, equation

$$C_2H_5OLi \quad + \quad CH_3I \quad = \quad C_2H_5OCH_3 \quad + \quad LiI \qquad (17)$$

17. Attempts to synthesize a tetraethyl-substituted tetralin derivative from 1 using Bu^tOK and CH_3CH_2Br were unsuccessful since only complex 1 was recovered from the reaction, thus implying a considerable degree of reactivity between the base and alkyl halide.

In a similar reaction to that represented by equation 14, stirring a suspension in THF of complex 1 with Bu^tOK and allyl bromide produces cleanly the tetraallyltetralin complex 10 (see equation 18) as a light orange powder, regardless of the method of reagent addition. Tetra-substitution in the saturated ring system was confirmed again by



1 10

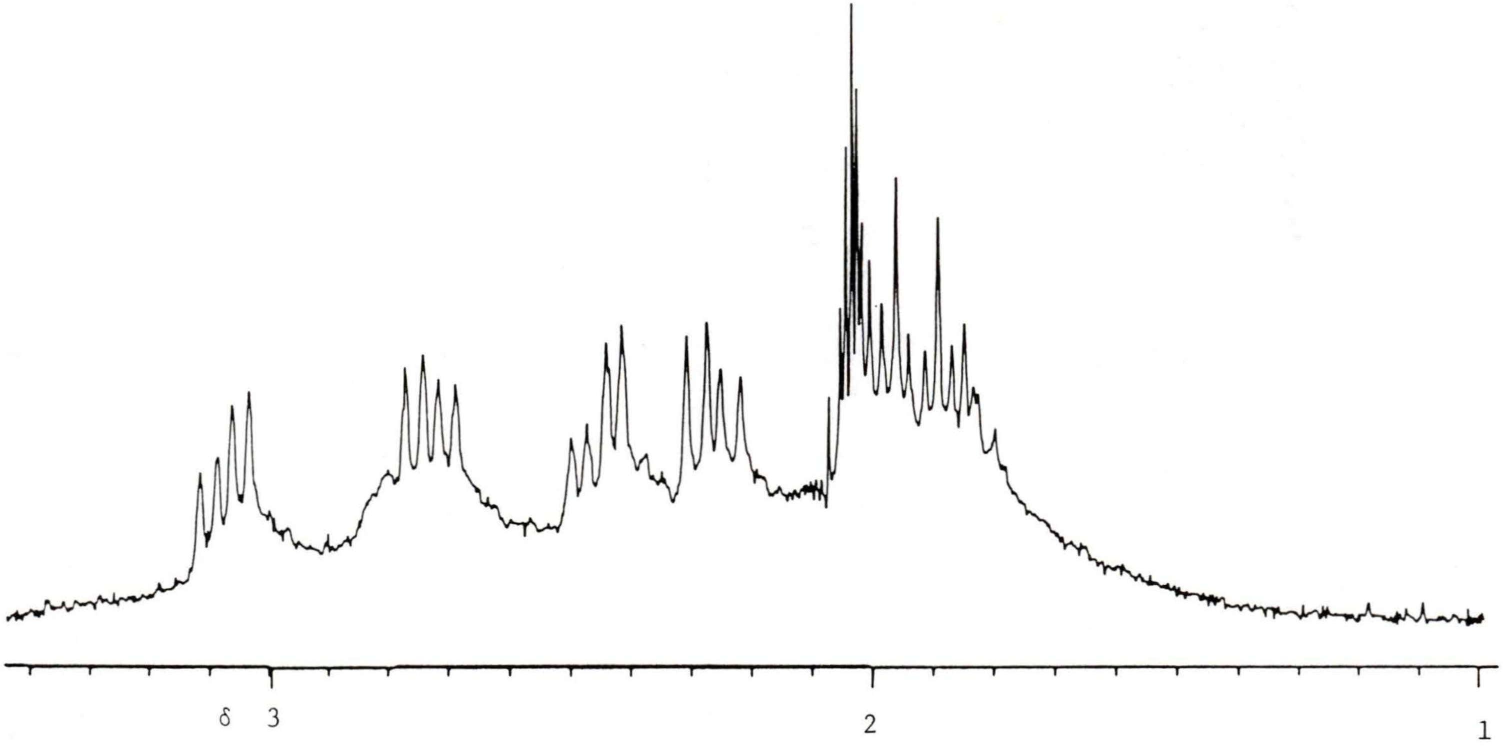
(18)

microanalytical (see experimental section) and spectroscopic data (see Tables 9 and 10). In contrast to the iodomethane reaction (equation 14), the allyl bromide reaction proceeds more slowly which may reflect the poorer ability of the bromide ion as a leaving group relative to the iodide ion.

The tetraallyltetralin complex 10 possesses spectroscopic characteristics which are very similar to those of the tetramethyl analogue 8. Of particular interest in the ^1H NMR spectrum of complex 10 (see Table 9 and Figure 6) are the allyl resonances: multiplets at δ6.09 and 5.55 ppm may be assigned to the $-C\underline{H}=$ (β) protons; unresolved multiplets at δ4.90 and 5.30 ppm are due to $=C\underline{H_2}$ (γ), and a series of doublets of doublets centred at δ3.08, 2.73, 2.45 and 2.26 ppm correspond to the saturated α-methylene protons.

In the ^{13}C NMR spectrum of complex 10 (see Table 10) allyl resonances exhibit lines at 45.0 and 46.1 ppm attributed to the α-methylene carbons, 119.9 and 120.1 ppm assigned to γ-methylene carbons, and 134.4 ppm corresponding to the unsaturated β-methine carbons. As shown by the α and γ signals, two sets of exo- and endo-allyl groups

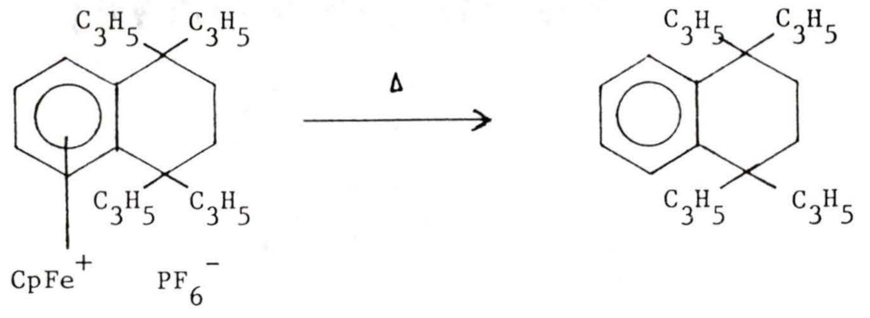
Figure 6. High field ^1H NMR spectrum of $[CpFe(tetraallyltetralin)]^+PF_6^-$



exist because of the $CpFe^+$ coordination. Also of interest are the saturated α-quaternary carbons which are more deshielded at 40.1 ppm relative to complex 8 due to the proximity of the allyl groups. The remaining Cp and coordinated aromatic resonances fall in the ranges previously found for complexes 1 and 8.

Bands representative of allyl groups feature prominently in the IR spectrum of complex 10: an absorption at 1640 cm^{-1} is assigned to the olefinic $\nu(C=C)$, a band at 1450 cm^{-1} is due to CH_2 in-plane bending (or scissoring), an absorption due to a scissoring vibration of the terminal methylene is seen at 1420 cm^{-1}, and the bands at 1000 and 920 cm^{-1} are assigned to the olefinic out-of-plane C-H bending vibrations. Some useful information is provided in the mass spectrum of the tetraallyltetralin derivative 10: a peak at m/e 347 corresponds to loss of a Cp group from the cationic complex, and a base peak at m/e 251 is attributed to the loss of an allyl group from the uncoordinated aromatic ligand.

Further confirmation of the formulation of complex 10 is provided by characterization of the uncoordinated tetralin derivative 11 obtained by the decomplexation reaction of complex 10, equation 19. No report of compound 11 has appeared in the literature.



10 11

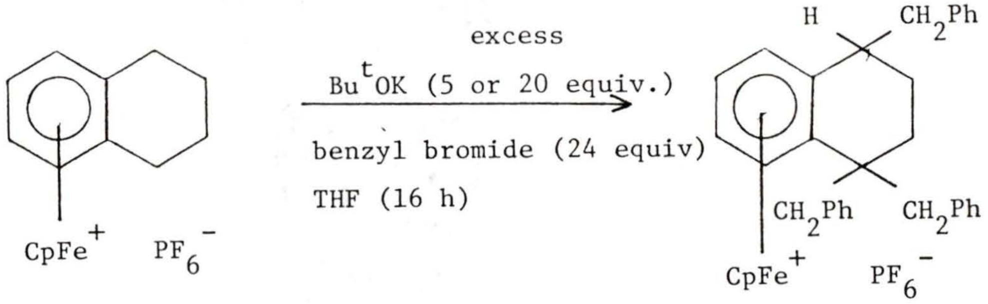
(19)

The main features of the ^{1}H NMR spectrum of compound 11 (see Table 11) are associated with the allyl groups. The allylic $-C\underline{H}=$ β-protons resonate as a multiplet at δ5.59 ppm and the remaining $=\underline{C}H_2$ γ-protons appear as poorly resolved multiplets at δ5.02, 4.99 and 4.95 ppm. The structure of the allylic α-methylene resonances shows two sets of doublets of doublets centred at δ2.50 and 2.21 ppm: with geminal coupling J(H'-H) = 14.0Hz and vicinal coupling J(H'-C$\underline{H}$=) = 6.4Hz and J(H-C$\underline{H}$=) = 8.0Hz, respectively.

In the ^{13}C NMR spectrum of compound 11 (see Table 12), allylic resonances show single lines at 46.3, 117.2 and 135.3 ppm assigned to $-\underline{C}H_2-(\alpha)$, $=\underline{C}H_2(\gamma)$, and $-\underline{C}H=(\beta)$, respectively thus confirming the presence of four equivalent allyl groups.

Absorptions in the IR spectrum of compound 11 (see experimental section) are similar to those observed for the corresponding cationic complex 10. Mass spectral data for the tetraallyltetralin compound 11 reveal an M+1 peak (CH_4 chemical ionization) at m/e 293 and a base peak at m/e 251 corresponding to the loss of one allyl group from the parent ion. In addition, peaks at m/e 211, and 169 are attributed to additional successive losses of two allyl groups.

Per-α-substitution of complex 1 using Bu^tOK and benzyl bromide (see equation 20) was carried out also under conditions similar to those used

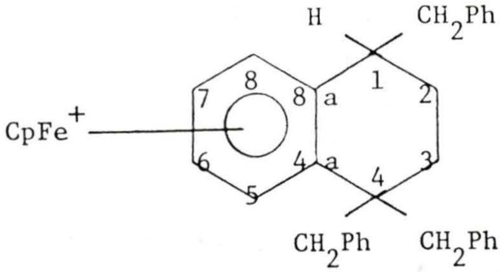


12

(20)

for the allyl bromide reaction; however, formation of the analogous tetrabenzyltetralin complex did not occur. Instead, incomplete substitution in the saturated ring is observed, yielding the pure tri-substituted complex 12 as a light beige solid. Again, full characterization of this product was possible on the basis of microanalytical data (see experimental section) and spectroscopic measurements (see Tables 9 and 10).

In the ^1H NMR spectrum of complex 12 (see Table 9), a single intense Cp signal is found at δ5.29 ppm confirming the formation of only one product: hence stereospecific substitution by the isolated benzyl group in the saturated ring is indicated. Of main interest are the signals arising from the benzyl groups. The most distinctive part of the spectrum is the aliphatic region, which consists of four doublets (J(H-H') = 13Hz) at δ3.72, 3.55, 3.32 and 2.53 ppm, and two doublets of doublets (J(H-C$\underline{H}$) = 7.1Hz) at δ2.18 and 1.80 ppm, all corresponding to the six methylene protons of the three benzyl groups. Of particular interest is the position of the multiplet at δ3.20 ppm assigned to the unsubstituted benzylic proton H-1 (II-vii). Such a deshielded signal



(II-vii)

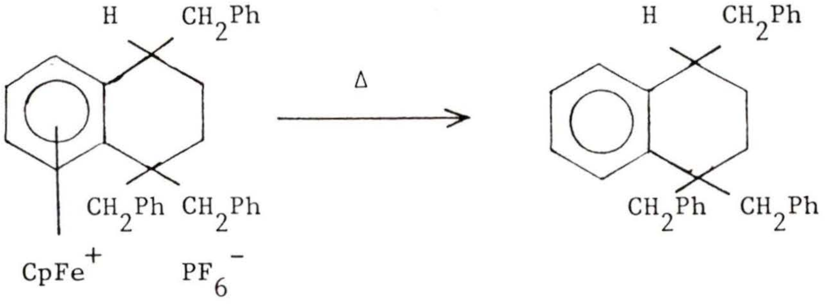
may imply occupation of the endo-position by this proton (by analogy with spectroscopic results established for methyl and methine groups in exo- and endo-positions reported by Treichel and Johnson[44]) and hence an exo-orientation for the adjacent benzyl group. A steric view of the reaction represented in equation 20 would suggest that occupation of the exo-position by a benzyl group is favoured, and unambiguous assignment of the stereochemistry of complex 12 cannot be made based on the NMR data alone.

Further support for the stereospecificity observed in the benzyl bromide reaction is provided by the ^{13}C NMR spectral data for complex 12 (see Table 10). The four lines at 22.5, 22.6, 41.0 and 44.4 ppm correspond to resonances from the saturated ring: the lines at 41.0 and 44.4 ppm are due to the methine and quaternary carbons, respectively, thus confirming tri-substitution in the saturated ring. Three methylene resonances arising from the benzyl groups occur at 42.1, 47.6 and 48.2

ppm. The lack of symmetry in the coordinated aromatic ring results in a complicated spectrum which includes four distinct lines in the range 86.8 to 87.5 ppm, and two inequivalent coordinated quaternary carbons show small signals at 108.1 and 115.9 ppm. In the uncoordinated aromatic region, twelve expected lines are observed in the range 127 to 140 ppm, showing conclusively the presence of three phenyl groups.

The IR spectrum for the tribenzyltetralin derivative 12 features prominent bands representative of the benzyl groups: strong absorptions at 695 and 750 cm^{-1} are assigned to the aromatic ring C-H out-of-plane bending vibrations of mono-substituted and ortho-disubstituted benzene rings. An intense band at 1450 cm^{-1} is associated with the methylene scissoring vibrations, and medium intensity absorptions occur at 1490 and 1600 cm^{-1} assigned to $\nu(C{=}C)$.

Supporting evidence for the substitution pattern introduced in complex 12 is again possible *via* spectral examination of the uncoordinated $C_{31}H_{30}$ ligand 13, obtained by the pyrolytic sublimation of the cation 12, equation 21.



12 13

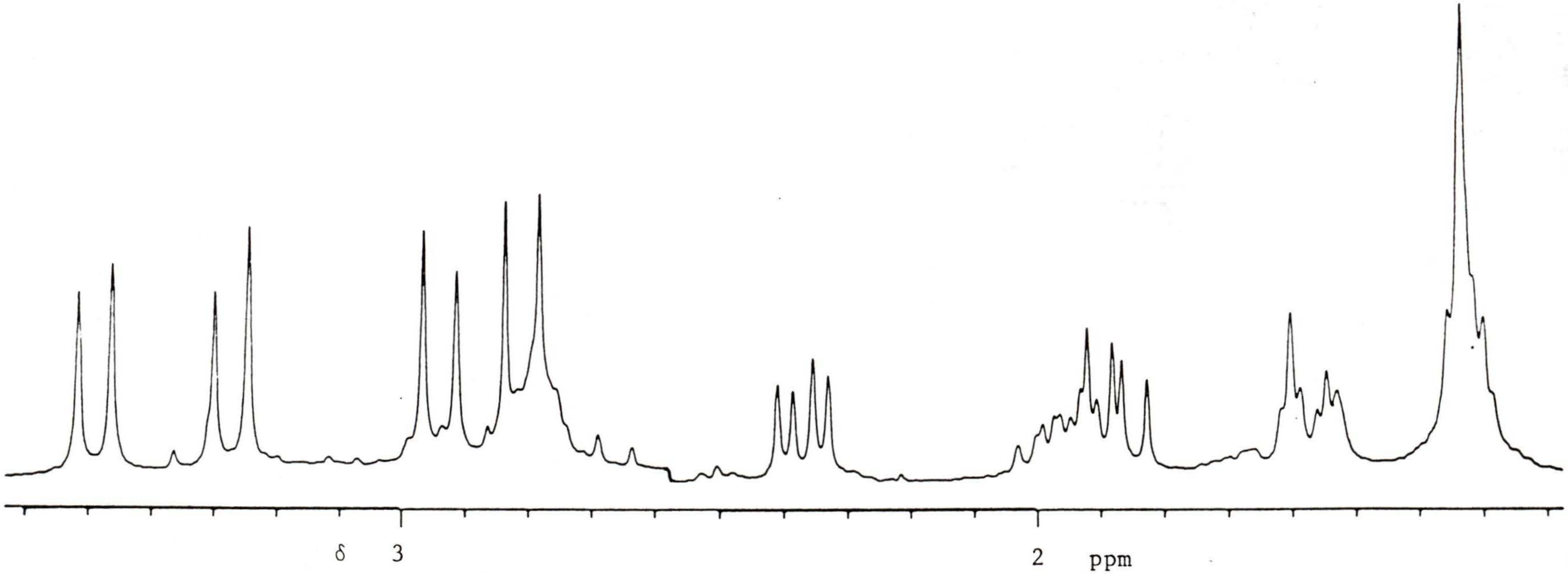
(21)

In the ^{1}H NMR spectrum of compound 13 (see Table 11 and Figure 7), signals corresponding to the six inequivalent methylene protons of the benzyl groups are similar to those observed for the iron complex 12: four doublets centred at δ3.49, 3.27, 2.94 and 2.81 ppm (J(H'-H) = 13.3Hz and two doublets of doublets centred at δ2.37 and 1.88 ppm (J(H-CH') = 6.1Hz, J(H-CH) = 9.9Hz) are in accordance with the asymmetry of the tri-substituted complex. The benzylic α-proton of the saturated ring appears as a multiplet at δ2.80 ppm, and three multiplets centred at δ1.97, 1.57 and 1.33 ppm are assigned to the methylene protons of the saturated ring.

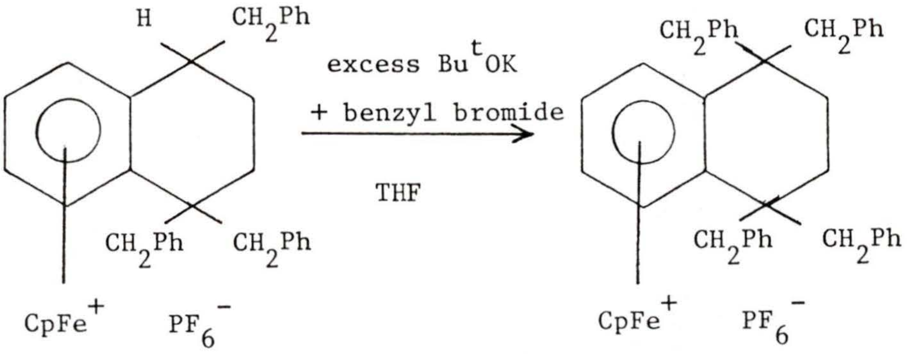
The ^{13}C NMR spectrum of compound 13 (see Table 12) shows signals at 42.3, 47.7 and 50.5 ppm corresponding to the three methylene carbons of the benzyl groups. Three quaternary carabons are associated with the phenyl groups occurring at 140.8, 141.4 and 142.3 ppm and the remaining aromatic carbons appear in the range 125.5-131.0 ppm. Two weak signals at 138.7 and 138.8 ppm are assigned to the inequivalent quaternary carbons of the ortho-disubstituted aromatic ring, again reflecting the unsymmetrical substitution in compound 13. The methine carbon resonates at 40.5 ppm, and the quaternary carbon in the saturated ring shows a low intensity line at 42.9 ppm. The most shielded lines occur at 22.3 and 25.0 ppm corresponding to the methylene carbons of the saturated ring.

The mass spectrum (CH_4 chemical ionization) of compound 13 reveals an M+1 peak at m/e 403. A base peak at m/e 325 corresponds to the loss of a phenyl group from the parent molecule, and a peak at m/e 311 arises from the loss of a benzyl group.

Figure 7. High field ^{1}H NMR spectrum of 1,2,3,4-tetrahydro-1,4,4-tribenzylnaphthalene



Consideration of the spectroscopic data for the tribenzyltetralin derivatives 12 and 13 indicates that complex 12 possesses three benzyl groups in the saturated ring, one arising from stereospecific electrophilic addition. To complete a synthetic route to the tetrabenzyl complex, treatment of complex 12 with a further excess of Bu^tOK and benzyl bromide affords the product 14 (equation 22) as a light orange powder, which is slightly soluble in acetone, but more soluble in acetonitrile. Characterization of complex 14 was carried out by microanalysis (see experimental section) and from the spectroscopic data of Tables 13 and 14.



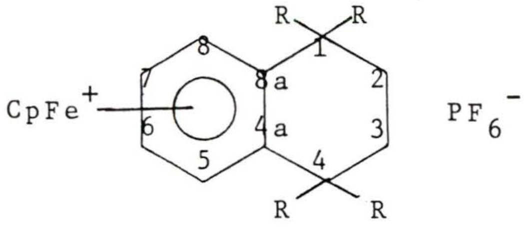
(22)

12

14

In the ^1H NMR spectrum of complex 14 (see Table 13), prominent signals include four well-separated doublets (integrating to two protons each) (δ3.50, 3.15, 2.92 and 2.15 ppm) corresponding to geminal coupling (J(H-H') = 13.4Hz) of the methylene protons in the four benzyl groups. These signals confirm the presence of two exo- and two endo-benzyl groups in the saturated ring. The existence of a single, pure product is again

Table 13. ^1H NMR Spectroscopic Data for Substituted Tetralin Complexes 14,16,17 and 19[a,j]



14 R = $CH_2C_6H_5$
16 $R_{1\alpha}$ = C_3H_5, $R_{1\beta,4\alpha,4\beta}$ = $CH_2C_6H_5$
17 $R_{1\alpha}$ = CH_3, $R_{1\beta,4\alpha,4\beta}$ = $CH_2C_6H_5$
$R_{1\beta}$ = CH_3, $R_{1\alpha,4\alpha,4\beta}$ = $CH_2C_6H_5$
19 $R_{1\alpha}$ = COC_6H_5, $R_{1\beta,4\alpha,4\beta}$ = $CH_2C_6H_5$
$R_{1\beta}$ = COC_6H_5, $R_{1\alpha,4\alpha,4\beta}$ = $CH_2C_6H_5$

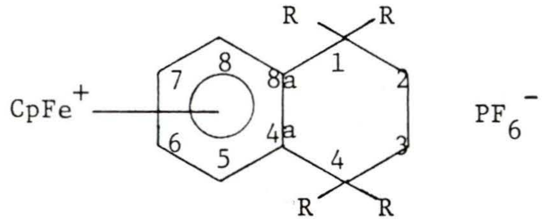
Complex	Cp(ppm)	H5-H8 (ppm)	$R_{1\alpha}R_{4\alpha}$(ppm)	$R_{1\beta}R_{4\beta}$(ppm)	H2-H3(ppm)
(14)[b]	5.02(s,5H)	5.94(m,4H)[c]	3.50(d,2H,-CH'H-) J(H'-H) = 13.1Hz 3.15(d,2H,-CH'H-) 6.3-7.6(m,$-C_6H_5$)[c]	2.92(d,2H,-CH'H-) J(H'-H) = 13.7Hz 2.15(d,2H,-CH'H-) 6.3-7.6(m,$-C_6H_5$)[c]	1.5-2.0(m,4H)[c]
(16)[d]	5.44(s,5H)	6.68(m,4H)	3.86(d,1H,-CH'H-) 3.71(d,1H,-CH'H-) J(H'-H) = 12.9Hz 3.39(dd,1H,-CH'H-) J(H'-H) = 13.9Hz J(H-CH=) = 7.0Hz 4.25(d,1H,=CH_2) $J(H-H')_{trans}$ = 16.5Hz 4.66(d,1H,=CH_2) $J(H-H')_{cis}$ =10.9Hz 5.15(m,1H,=CH-)[c] 7.0-7.7 (C_6H_5)[e]	3.55(d,1H,-CH'-H) 3.25(d,1H,-CH'H-) J(H'-H) = 12.9Hz 2.55(d,1H,-CH'H-) J(H'-H) = 13.6Hz 2.28(d,1H,-CH'H-) J(H'-H) = 14.2Hz 7.0-7.7 (C_6H_5)[e]	2.0(m,4H)[c]

Table 13 continued

Complex	Cp (ppm)	H5-H8 (ppm)	$R_{1\alpha}R_{4\alpha}$ (ppm)	$R_{1\beta}R_{4\beta}$(ppm)	H2-H3 (ppm)
(17)[h]	5.31(s,5H)[i]	6.59(m)[c] 6.39(m)[c]	1.53(s,3H,$-C\underline{H}_3$) 3.2-3.9(m,$-C\underline{H}_2-$)[f] 6.75-7.70($-C_6\underline{H}_5$)[e]	2.1-2.6(m,$-C\underline{H}_2-$)[f] 3.2-3.9 (m,$-C\underline{H}_2-$)[f] 6.75-7.70($-C_6\underline{H}_5$)[e]	1.83(m)[c]
	5.46(s,5H)			0.46(s,3H,$-CH_3$)	
(19)[g]	5.45(s,5H) 5.24(s,5H)	6.35(m) 6.56(m)	6.95-7.52($-C_6\underline{H}_5$)[e] 3.27-3.56($-C\underline{H}_2-$)[f] 2.35-2.70($-C\underline{H}_2-$)[f]	6.95-7.52($-C_6\underline{H}_5$)[e] 3.27-3.56($-C\underline{H}_2-$)[f] 2.35-2.70($-C\underline{H}_2-$)[f]	1.75-1.87(m)[c]

Notes: [a] $(CD_3)_2CO$ solution. [b] CD_3CN solution. [c] poorly resolved. [d] starting material 10 present (29%). [e] complex series of multiplets. [f] complex series of doublets. [g] mixture of two exo- and endo-benzoylated complexes *ca.* 55:45 ratio. [h] mixture of two exo- and endo-methylated complexes *ca.* 65:35 ratio. [i] major isomer. [j] all chemical shifts measured in δ(ppm).

Table 14. ^{13}C NMR Spectroscopic Data for Substituted Tetralin Complexes 14,16,17 and 19[a,h]



14 R = $CH_2C_6H_5$
16 $R_{1\alpha}$ = C_3H_5, $R_{1\beta,4\alpha,4\beta}$ = $CH_2C_6H_5$
17 $R_{1\alpha}$ = CH_3, $R_{1\beta,4\alpha,4\beta}$ = $CH_2C_6H_5$
$R_{1\beta}$ = CH_3, $R_{1\alpha,4\alpha,4\beta}$ = $CH_2C_6H_5$
19 $R_{1\alpha}$ = COC_6H_5, $R_{1\beta,4\alpha,4\beta}$ = $CH_2C_6H_5$
$R_{1\beta}$ = COC_6H_5, $R_{1\alpha,4\alpha,4\beta}$ = $CH_2C_6H_5$

Complex	C1-C4 (ppm)	C5-C8 (ppm)	C4a,C8a (ppm)	Cp (ppm)	Others (ppm)
(14)[b]	42.3(C1,C4) 26.8(C2,C3)	85.6(C5,C8) 86.1(C6,C7)	115.1	77.7	44.6, 47.8 $(-\underline{C}H_2-)$ 127.7,128.1,128.9,129.4, 132.9 $(-\underline{C}_6H_5)$ 137.4,138.1$(-\underline{C}_6H_5$ quat)
(16)[c]	40.9,42.2(C1,C4) 24.9,28.3(C2,C3)	85.4, 86.3 86.4, 86.9	114.1 115.6	77.7	43.5,46.6,46.8,49.4$(-\underline{C}H_2-)$ 119.9 $(=\underline{C}H_2)$ 134.0 $(=\underline{C}H-)$ 127.3,127.7,127.8,128.8, 129.0,132.1,132.2,132.8, $(-\underline{C}_6H_5)$ 137.7,138.0,138.1$(-\underline{C}_6H_5$ quat)
17	23.2,24.0(C2,C3) 37.8,38.8(C1,C4)	87.3 86.4	113.5 116.1	[d] 77.6	27.5 $(-\underline{C}H_3)$ 46.9,47.3,49.2 $(-\underline{C}H_2-)$ $(-\underline{C}_6H_5)$[f]
	e	e	e	77.7	39.9 $(-\underline{C}H_3)$ e

Table 14 (continued)

Complex	C1-C4 (ppm)	C5-C8 (ppm)	C4a,C8a (ppm)	Cp (ppm)	Others (ppm)
(19)[g]	22.3,22.4(C2,C3)	f	107.9	78.0	204.6, 210.0 ($\underline{C}O$)
	25.1,26.7(C2,C3)		109.1	77.8	136.5,137.0,137.5,137.9,
	57.3(C1)		115.6		138.0,139.3,139.7,139.8,
			117.1		($-\underline{C}_6H_5$ quat)
					127-133 ($-\underline{C}_6H_5$)

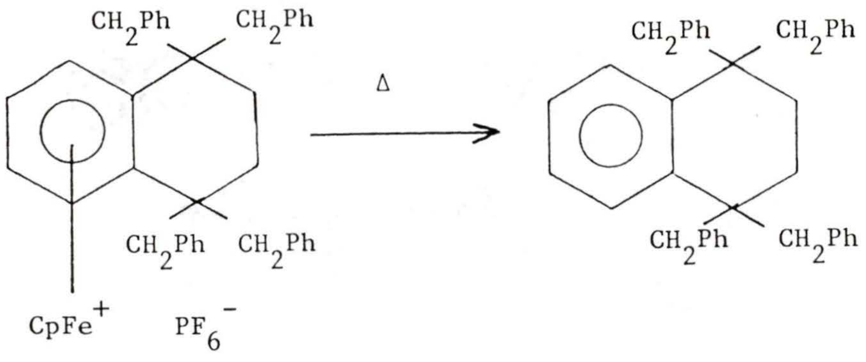
Notes: [a]$(CD_3)_2CO$ solution. [b]CD_3CN solution. [c]starting material 10 is present also. [d]major isomer. [e]signals of the minor isomer are obscured by those of the major isomer and starting material. [f]obscured by overlapping resonances. [g]mixture of exo- and endo-benzoylated complexes ca. 55:45 ratio. [h]all chemical shifts measured in δ(ppm).

supported by the single intense Cp resonance at δ5.02 ppm. The remainder of the spectrum consists of unresolved multiplets attributed to the coordinated and uncoordinated aromatic protons, and the β-methylene protons in the saturated ring.

In the ^{13}C NMR spectrum of complex 14 (see Table 14), two lines at 44.6 and 47.8 ppm assigned to benzylic methylene carbons confirm symmetrical substitution in the saturated ring by the four benzyl groups. Likewise one line at 42.3 ppm is attributed to the two equivalent quaternary α-carbons in the saturated ring, and another line appears at 26.8 ppm which is assigned to the equivalent methylene β-carbons. Existence of a symmetry plane bisecting the saturated carbocycle imposes a parallel effect on the coordinated aromatic ring, which exhibits two lines at 85.6 and 86.1 ppm, and a weak signal at 115.1 ppm assigned to the coordinated quaternary carbons.

The IR spectrum of the tetrabenzyltetralin complex 14 shows absorptions similar to those observed for the related tribenzyltetralin complex 12. The mass spectral data for complex 14 again reveals that decomposition of the cation occurs yielding the uncomplexed $C_{38}H_{36}$ ligand. A small peak at m/e 491 is attributed to the loss of two hydrogens from the ligand. Successive loss of three benzyl groups from the free ligand is observed at m/e 401, 310 and 220 (the base peak).

Decomplexation of the aromatic ring in complex 14 is again possible *via* pyrolytic sublimation of the cationic species (see equation 23)



(23)

14

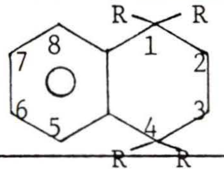
15

affording compound 15 which was characterized by spectroscopic measurements (see Tables 15 and 16).

In the ^{1}H NMR spectrum of the tetrabenzyltetralin compound 15 (see Table 15), the most characteristic signals are two doublets at δ2.90 and 2.59 ppm (J(H-H') = 13.5Hz) corresponding to methylene protons in the benzyl groups: thus four equivalent benzyl groups exist in the saturated ring. The ^{13}C NMR spectrum of compound 15 (see Table 16) also confirms symmetrical substitution by four benzyl groups. One line at 47.4 ppm is assigned to $\underline{C}H_2$ of the benzyl groups. Two equivalent α-quaternary and two equivalent β-methylene carbons exhibit single lines at 42.7 and 26.2 ppm, respectively. Resonances attributed to the ortho-disubstituted aromatic ring appear at 125.0, 128.8 and 142.4 ppm and phenyl resonances are observed at 125.9, 127.5 and 130.9 ppm, again indicative of the symmetrical substitution pattern.

IR spectroscopy for the tetrabenzyltetralin compound 15 shows strong bands similar to those observed for the corresponding iron complex 14.

Table 15. ^{1}H NMR Spectroscopic Data for Uncomplexed Substituted Tetralin Ligands 15,18 and 20[a,d]

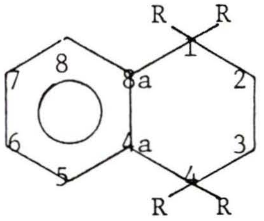


15 $R_{1\alpha,\beta,4\alpha,\beta} = CH_2C_6H_5$
18 $R_{1\alpha} = CH_3$, $R_{1\beta,4\alpha,4\beta} = CH_2C_6H_5$
20 $R_{1\alpha} = COC_6H_5$, $R_{1\beta,4\alpha,4\beta} = CH_2C_6H_5$

Complex	H5-H8 (ppm)	$R_{1\alpha}R_{4\alpha}$ (ppm)	$R_{1\beta}R_{4\beta}$ (ppm)	H2-H3 (ppm)
(15)[b]	7.20(m,2H) J(H-H')$_{ortho}$=6.0Hz J(H-H')$_{meta}$=3.4Hz 7.45(m,2H)	2.90(d,4H,-C$\underline{H}$'H-) 2.59(d,4H,-CH'$\underline{H}$-) J(H'-H) = 13.5Hz 6.83(m,-C$_6\underline{H}_5$) 7.12(m,-C$_6\underline{H}_5$)		1.53(s,4H)
18	6.75(m,1H) 6.85(m,1H) 6.92(m,1H) 7.26(t,1H)	0.95(s,3H,-C$\underline{H}_3$) 3.28(d,1H,-C$\underline{H}$'H-) 3.23(d,1H,-CH'$\underline{H}$-) J(H-H') = 13.7Hz 7.12(m,-C$_6\underline{H}_5$)	2.85(d,1H,-C$\underline{H}$'H-) 2.71(d,1H,-CH'$\underline{H}$-) 2.32(d,1H,-C$\underline{H}$'H-) 2.19(d,1H,-CH'$\underline{H}$-) J(H-H') = 13.3Hz 7.12(m,-C$_6\underline{H}_5$)	1.2(m,4H)
20	(6.6-8.1)[c]	3.46(d,1H,-C$\underline{H}$H'-) 3.25(d,1H,-CH$\underline{H}$'-) 3.22(d,1H,-C$\underline{H}$H'-) 3.19(d,1H,-CH$\underline{H}$'-) 2.91(d,1H,-C$\underline{H}$H'-) 2.78(d,1H,-CH$\underline{H}$'-) J(H-H') = 13.1Hz		(1.5-2.0)[c]

Notes: [a] $CDCl_3$ solution. [b] $(CD_3)_2CO$ solution. [c] complex series of multiplets. [d] all chemical shifts in δ(ppm)

Table 16. ^{13}C NMR Spectroscopic Data for Uncomplexed Substituted Tetralin Ligands 15,18 and 20[a]



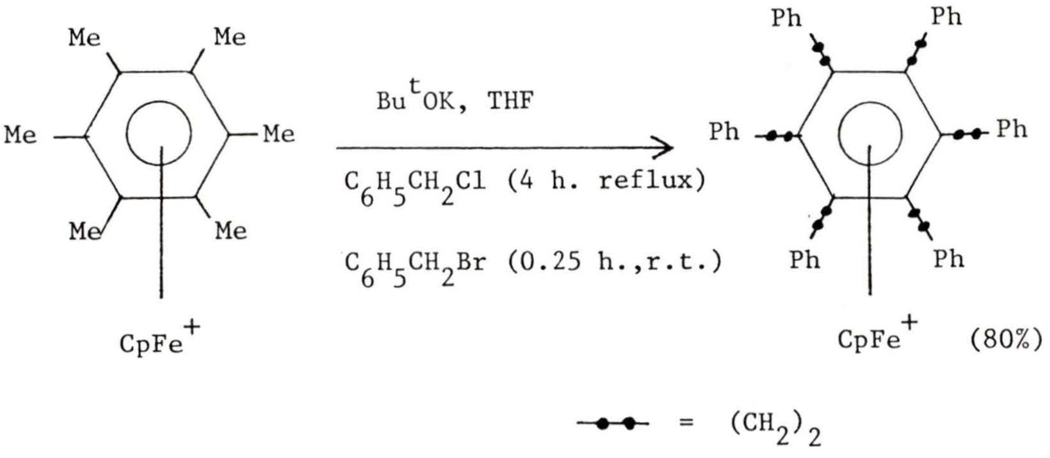
15 $R_1 = R_4 = CH_2C_6H_5$
18 $R_{1\alpha} = CH_3$, $R_{1\beta,4\alpha,4\beta} = CH_2C_6H_5$
20 $R_{1\alpha} = COC_6H_5$, $R_{1\beta,4\alpha,4\beta} = CH_2C_6H_5$

Complex	C1-C4 (ppm)	C5-C8 (ppm)	C4a,C8a (ppm)	Others (ppm)
15	42.7 (C1,C4) 26.2 (C2,C3)	125.0 (C5,C8) 128.8 (C6,C7)	142.4	47.4 $(-\underline{C}H_2-)$ 125.9, 127.5, 130.9 $(-\underline{C}_6H_5)$
18	43.1 (C1,C4) 28.6, 30.9 (C2,C3)	b	141.0 146.0	138.6, 138.7, 138.8, $(-\underline{C}_6H_5$ quat) 25.6 $(-\underline{C}H_3)$ 125.2-131.0 $(-\underline{C}_6H_5)$ 47.9, 48.0, 49.7 $(-\underline{C}H_2C_6H_5)$
20	57.3 (C1) (C4)[c] 24.9 (C2) (C3)[c]	(125.7-131.0)[d]	137.9-142.3	40.5,42.3,47.7,50.4$(-\underline{C}H_2-)$ 137.9,138.2,138.7,140.8, 141.3,142.3 (aromatic ring quaternaries) 205.2 $(\underline{C}O)$

Notes: [a] $CDCl_3$ solution. [b] obscured by phenyl resonances. [c] not located. [d] complex series of lines.

The mass spectrum of the ligand 15 shows a small molecular ion peak at m/e 493. Loss of one benzyl group is observed at m/e 401, followed by the loss of a phenyl group at m/e 324 which appears as the base peak. At m/e 310, subsequent loss of CH_2 from a second benzyl group is observed.

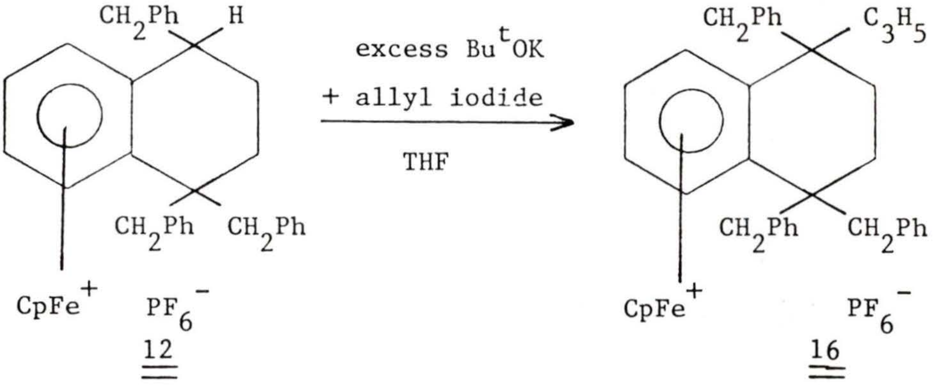
In a reaction analogous to that represented in equation 22, perbenzylation of a hexamethylbenzene complex using Bu^tOK and benzyl halide was investigated by Astruc and coworkers[49], equation 24. As shown in equation 24, only one hydrogen atom of each methyl group is



(24)

substituted with a benzyl group due to the steric bulk of the latter. A similar effect is observed in the synthesis of the tribenzyltetralin complex 12 in which the steric bulk of the benzyl group prevents the formation of a tetrabenzyltetralin derivative initially. Only after reacting complex 12 further with base and alkyl halide is the tetra-substituted complex produced.

Substitution of the remaining benzylic hydrogen in the tribenzyltetralin derivative 12 with other alkyl groups was also investigated. The reaction of complex 12 with excess Bu^{t}OK and allyl iodide produces complex 16 as a light beige powder (see equation 25), which was characterized by spectroscopic measurements (see Table 13, 14 and experimental section). Satisfactory microanalytical data could not be obtained for complex 16 due to the presence of a small amount of starting material (detected by ^{13}C NMR spectroscopy).

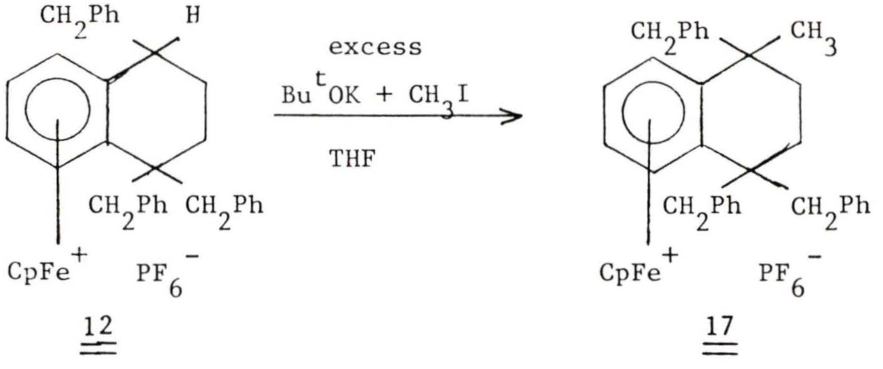


(25)

The ^{1}H NMR spectrum of complex 16 (see Table 13) shows one major Cp singlet at δ5.44 ppm corresponding to the target product, implying that addition of the allyl group to the saturated ring occurs stereospecifically; however, the stereochemistry of the complex again cannot be deduced solely from the NMR data. Resonances attributed to =C$\underline{H}_2$ γ-protons of the single allyl group appear as two doublets at δ4.25 ppm (J(H-H')$_{trans}$ = 16.5Hz and 4.66 ppm (J(H-H')$_{cis}$= 10.9Hz. The allyl =C$\underline{H}$- β-proton exhibits a multiplet at δ5.15 ppm, and one of the -C$\underline{H}_2$- α-protons is resolved as a doublet of doublets at δ3.39 ppm (J(H-H') = 13.9Hz, J(H-C$\underline{H}$=) = 7.0Hz. The six inequivalent methylene protons of the benzyl groups show six doublets in the range δ3.86-2.28 ppm. The remaining protons resonate in the expected ranges. Also present in the spectrum is a small Cp singlet at δ5.30 ppm attributed to unreacted tribenzyltetralin complex 12.

The ^{13}C NMR spectrum of complex 16 (see Table 14) is also consistent with the formation of one stereoisomer. An intense Cp line is observed at 77.7 ppm corresponding to one product. Asymmetry in the saturated ring is indicated by the presence of two quaternary signals at 40.9 and 42.2 ppm, and two methylene signals at 24.9 and 28.3 ppm. Of particular interest are four lines occurring in the range 43.5- 49.4 ppm which correspond to the methylene carbons of the allyl and benzyl groups. The allyl group also exhibits two lines at 119.9 and 134.0 ppm assigned to $=\underline{C}H_2(\gamma)$ and $=\underline{C}H-(\beta)$ protons, respectively. Associated with the three phenyl groups are eleven lines observed in the range 127.3-138.1 ppm as expected. In addition of these signals discussed above, smaller lines assigned to the starting material (i.e. complex 12) are also present.

In contrast to the stereospecific reaction represented in equation 25, the reaction of the tribenzyltetralin complex 12 with excess Bu^tOK and iodomethane results in the formation of complex 17 (see equation 26)



(26)

consisting of a mixture of two isomers which was confirmed by spectroscopic measurements (see Tables 13 and 14). Satisfactory microanalytical data could not be obtained due to contamination of this mixture by starting material 12.

The main feature of the ^{1}H NMR spectrum of complex 17 (see Table 13) is the presence of two singlets at δ0.46 and 1.53 ppm attributed to exo- and endo-methyl groups. Two Cp singlets are observed also at δ5.31 and 5.46 ppm in ca. 65:35 ratio, respectively, thus indicating that addition of the methyl group occurs stereoselectively. It is not known if the predominant isomer, showing a methyl singlet at δ1.53 ppm, contains an exo- or an endo-methyl group. However, by comparison with results reported by Treichel and Johnson[44] for exo- and endo-methylated fluorene compounds which showed that an exo-methyl group is shielded relative to an endo-methyl group, it may be that the major isomer of complex 17 contains an endo-methyl group adjacent to an exo-benzyl group. From a steric view, such an assignment appears reasonable since occupation of the exo-position by the bulkier benzyl group is preferred. The remainder of the spectrum is uninformative and consists of multiplets assigned to the methylene, phenyl and coordinated aromatic protons.

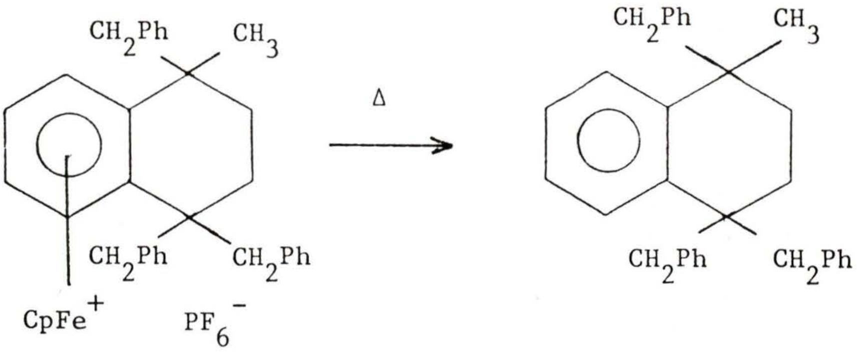
The ^{13}C NMR spectrum of complex 17 (see Table 14) shows two Cp signals at 77.6 and 77.7 ppm corresponding to the methylated products. Also present is a Cp line at 77.9 ppm attributed to starting material 12. Of particular interest are two methyl resonances at 27.5 and 39.9 ppm, thus confirming the presence of endo- and exo-methyl substituents. In addition, resonances attributable to the major isomer are assignable.

Methylene carbons of the benzylic groups show three lines at 46.9, 47.3, and 49.2 ppm. In association with the saturated ring, two quaternary α-carbons exhibit lines at 37.8 and 38.8 ppm and two methylene β-carbons appear at 23.3 and 24.0 ppm. Signals at 87.3 and 86.4 ppm, and two quaternary signals at 113.5 and 116.1 ppm are assigned to the coordinated aromatic ring. Assignment of resonances for the minor isomer is not practical due to their low intensity and masking by the major isomer and starting material.

In the IR spectrum of complex 17 (see experimental section), the most prominent feature is the strong absorption at 1385 cm^{-1}, absent in the IR spectrum of complex 12 and assigned to the symmetrical bending vibration of the methyl C-H bonds. The asymmetrical bending vibration of the CH_3 group overlaps the scissoring vibration of the methylene groups occurring at 1450 cm^{-1}.

The mass spectrum of complex 17 shows a small peak at m/e 457 attributed to loss of a methyl group from $[C_{32}H_{32}Fe]^+$. Decomplexation of the aromatic ring is observed at m/e 417 corresponding to the free aromatic molecule $C_{32}H_{32}$. Loss of a methyl group from this free ligand occurs at m/e 401. Additional losses of two benzyl groups are observed at m/e 311 and 221. Also present is a peak at m/e 186 corresponding to Cp_2Fe^+.

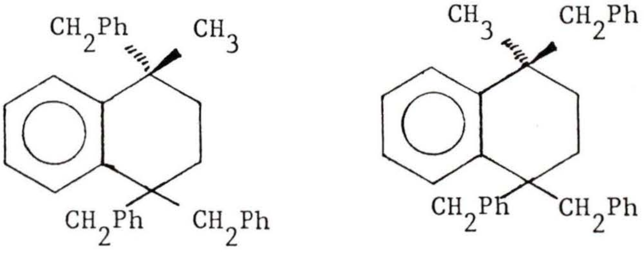
Pyrolytic sublimation of the iron complex 17 (see equation 27) affords the single compound 18 as a colourless oil, which was characterized by spectroscopic measurements (see Tables 15 and 16).



17 18

(27)

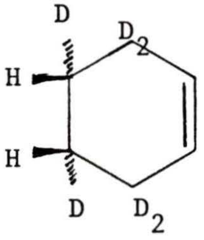
In the ^1H NMR spectrum of compound 18 (see Table 15), a singlet upfield at δ0.95 ppm may be assigned to the methyl group. This result is expected if there is rapid interconversion between conformational isomers of compound 18. Since compound 18 would be expected to possess two diastereomers (II-viii) containing axial and equatorial methyl groups,



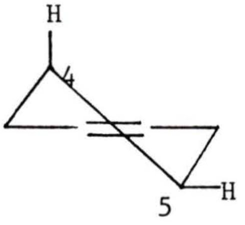
(II-viii)

the corresponding ^1H NMR spectrum should give rise to two methyl signals. However, if the axial and equatorial positions are made indistinguishable by a rapid interconversion process, then only one averaged methyl signal should be observed, as is the case. Hence, this result implies that the saturated ring is sufficiently flexible to allow rapid interconversion between conformers. Also of interest are the inequivalent methylene protons associated with the benzyl groups which are indicated by the presence of a series of six doublets occurring in the range δ3.28-2.19 ppm, J(H-H') = 13.3Hz.

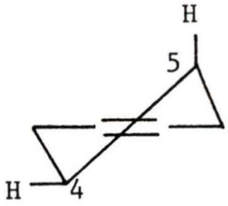
Conformational properties of the related cyclohexene system were studied by Anet and Haq[81]. ^{1}H NMR spectroscopic results for cyclohexene-cis-3,3,4,5,6,6-d_6 (II-ix) revealed a single band at δ1.58 (-50°C) which



(II-ix)



(II-x)



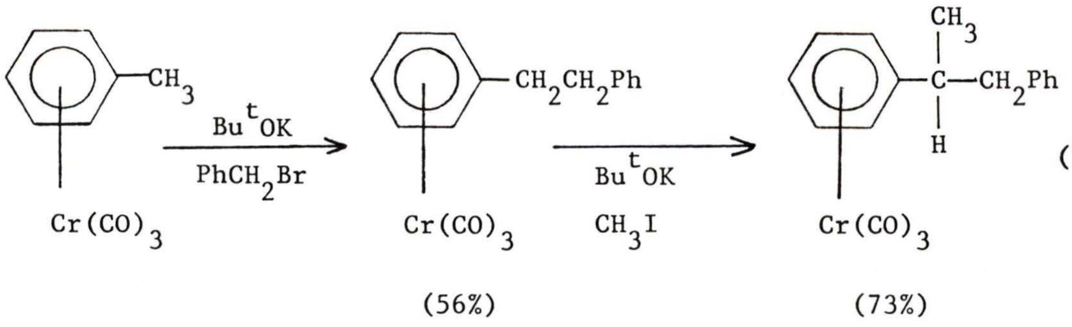
(II-xi)

at -164°C began to resolve into a doublet. The interpretation of these results involved the half-chair conformations (II-x) and (II-xi) which interconvert very rapidly at room temperature. In (II-x), H-4 is axial while H-5 is equatorial, and vice versa in (II-xi). The presence of two bands below -164°C in the spectrum of H-4 and H-5 indicates that the rate of ring inversion at these temperatures is sufficiently low that the spectrum is no longer the average of (II-x) and (II-xi).

The ^{13}C NMR spectrum of compound 18 (see Table 16) exhibits a single methyl resonance at 25.6 ppm, again indicative of indistinguishable axial and equatorial methyl groups as a consequence of conformational changes occurring in the saturated ring system. Other interesting features include three lines at 47.9, 48.0 and 49.7 ppm which are assigned to the methylene carbons of the benzylic groups, and three quaternary signals at 138.6, 138.7 and 138.8 ppm which are associated with the phenyl groups.

The IR spectrum of compound 18 is essentially similar to that observed for the iron complex 17. The mass spectrum of the compound 18 is less informative than that obtained for the corresponding iron complex; however, a small peak at m/e 326 arises from the loss of a benzyl group from $C_{32}H_{32}$, and a base peak occurs at m/e 91 attributed to a benzyl group $C_6H_5CH_2^+$.

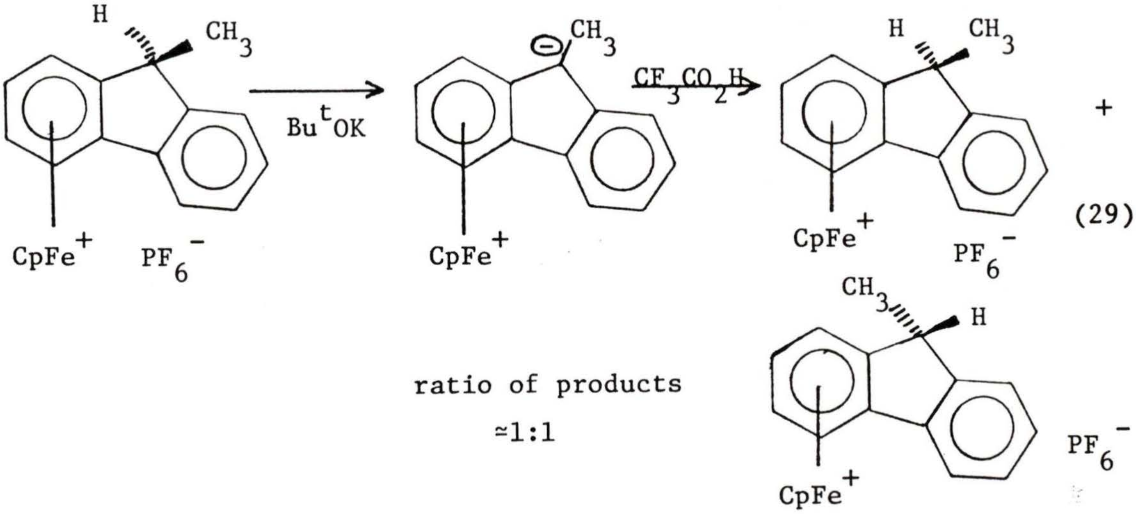
Under conditions similar to those used for the synthesis of complex 17, Jaouen and Simonneaux[78] prepared a $Cr(CO)_3$ complex containing both methyl and benzyl groups in the arene ligand, equation 28. These



(28)

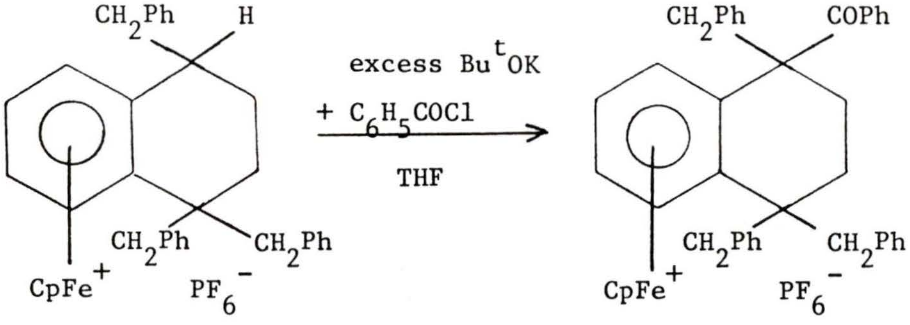
alkylation reactions showed regioselectivity in that only benzylic hydrogens α to the coordinated aromatic ring were substituted.

In 1973, Treichel and Johnson examined the deprotonation of an exo-methylated fluorene complex and subsequent reprotonation reaction which proceeded non-stereospecifically,[44] equation 29. As shown in



equation 29, reprotonation resulted in an almost equimolar mixture of exo- and endo-methylated complexes. These results indicated that the small electrophile H^+ showed no selectivity towards endo- or exo-protonation and that the methyl substituent possesses no steric demands. By contrast, reaction of the deprotonated tribenzyltetralin complex 12 with iodomethane proceeds stereoselectively. This result implies that the steric requirement of the benzyl group, relative to the smaller methyl group, may be a dominant factor in determining the ratio of diastereomers present in the final product.

As discussed above, stereoselective substitution of an α-hydrogen in complex 12 by a methyl group occurs yielding a mixture of two diastereomers. In a similar manner, the reaction of the tribenzyltetralin complex 12 with excess Bu^tOK and benzoyl chloride affords complex 19 as a light beige solid, equation 30.



(30)

12

19

As shown by spectroscopic measurements (see Tables 13, 14 and experimental section), the reaction represented in equation 30 produces a mixture of two isomers, in addition to some unreacted starting material; consequently, analytically pure product could not be obtained.

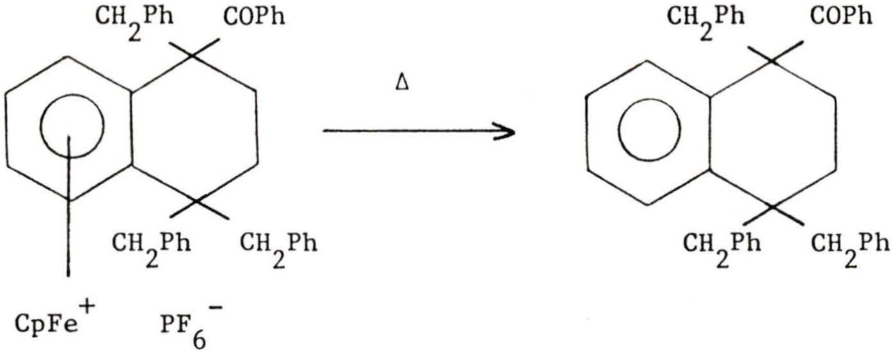
The ^1H NMR spectrum of complex 19 (see Table 13) contains two intense Cp singlets at $\delta 5.45$ and 5.24 ppm in ca. 55:45 ratio, suggesting the presence of exo- and endo-benzoylated complexes. As indicated by this ratio, benzoyl addition to the carbanionic site of complex 12 occurs with little stereoselectivity, so that most of the spectrum of complex 19 shows overlapping multiplet patterns and is not very useful. The observed lack of stereoselectivity may be a consequence of the similar steric requirements of the benzoyl and benzyl fragments.

Confirmation of the presence of two isomers in complex 19 is provided by the ^{13}C NMR spectroscopic data (see Table 14). Four lines associated with the β-methylene carbons in the saturated ring are observed at 22.3, 22.4 and 26.7 ppm. A conspicuous signal at 57.3 ppm is attributed to the quaternary α-carbon of the saturated ring, adjacent to the carbonyl group for both isomers. The coordinated aromatic quaternary carbons exhibit four lines at 107.9, 109.1, 115.6 and 117.1 ppm. Eight lines associated with the quaternary carbons of the phenyl groups are observed in the range 136.5-139.8 ppm, and two intense Cp signals occur at 78.0 and 77.8 ppm. Overlapping signals occur for the phenyl groups, coordinated aromatic rings and benzylic methylene groups; hence no useful information is obtainable from them. Of special interest, however, are two small intensity signals occurring downfield at 204.6 and 210.0 ppm. These are assigned to the two different carbonyl groups providing conclusive evidence for the existence of two benzoylated complexes.

The most characteristic absorption in the IR spectrum of complex 19 is due to $\nu(C{=}O)$ at 1680 cm^{-1}, which is typical of a carbonyl group in conjugation with a phenyl group.

The mass spectrum of complex 19 reveals a base peak at m/e 507 indicating that decomposition of the cation occurs affording the free aromatic $C_{38}H_{34}O$ compound. An additional peak at m/e 417 indicates the subsequent loss of a benzyl group.

Decomplexation of cation 19 produces the corresponding free aromatic 20 (see equation 31) which was characterized by spectroscopic data (see



19 20

(31)

Tables 15 and 16).

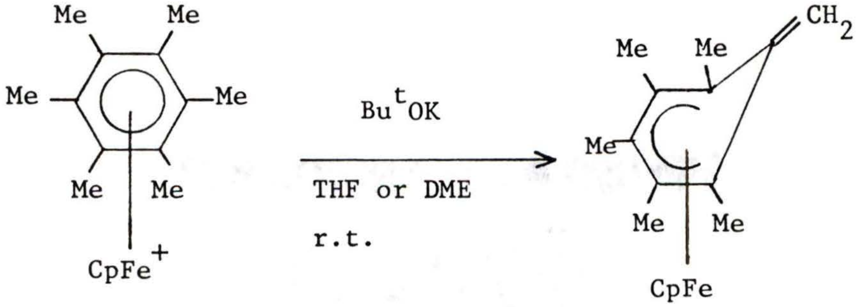
As shown by the ^{1}H NMR spectrum of compound 20 (see Table 15), only one set of signals is observed implying rapid interconversion between axial and and equatorial benzoyl groups. The most characteristic part of the spectrum shows a series of doublets observed in the range δ3.46-2.78 ppm (J(H-H') = 13.1Hz which correspond to the six inequivalent methylene protons of the benzyl groups.

In the ^{13}C NMR spectrum of compound 20 (see Table 16) five lines occurring in the range 24.9-50.4 ppm are assigned to the methylene carbons of the molecule. A conspicuous line at 57.3 ppm corresponds to the deshielded saturated quaternary carbon adjacent to the carbonyl group. Another small intensity line at 205.2 ppm is assigned to the carbonyl carbon. Associated with with the aromatic rings are six small signals appearing in the range 137.9-142.3 ppm due to the quaternary carbons.

Confirmation of the presence of a carbonyl group in compound 20 is provided again by the IR spectroscopic data which shows a prominent band at 1680 cm^{-1} due to ν(C=O).

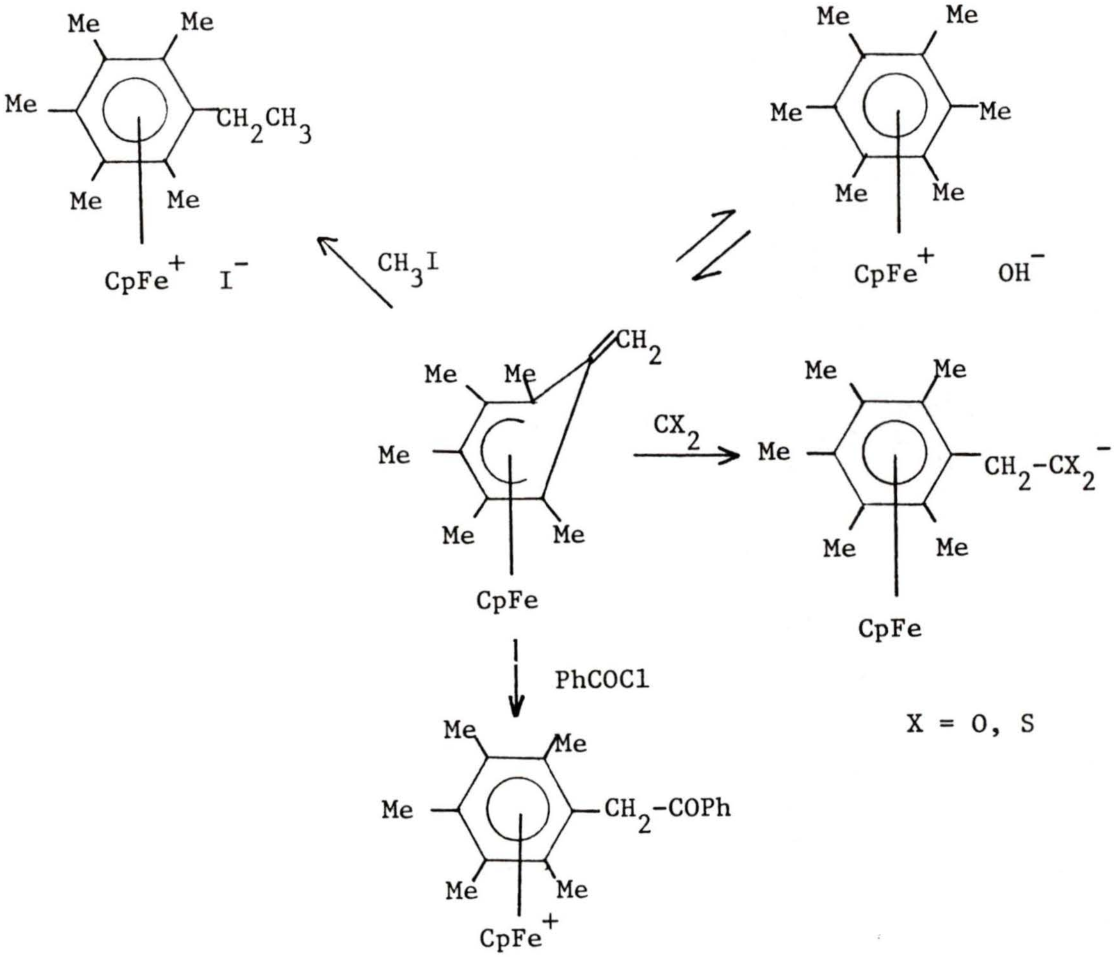
(ii) Mono-α-substituted tetralin complexes

Summarizing the implications of the preceding analysis of data for the polysubstituted complexes 8 - 20, it is evident that the reactivity of the deprotonated intermediates generated by the action of strong base follows a pattern consistent with carbanionic behaviour. In practice this provides a straightforward pathway for "one-step" polysubstitution reactions; although these have been conducted under inert atmosphere conditions the isolation of the very air-sensitive deprotonated intermediates is not necessary. In 1979, Astruc and coworkers obtained a crystalline organo-iron derivative *via* deprotonation of a hexamethylbenzene complex, equation 32; this unusual thermally stable product was characterized by x-ray crystallography.[64] The results of the x-ray structure determination are best interpreted in terms of a



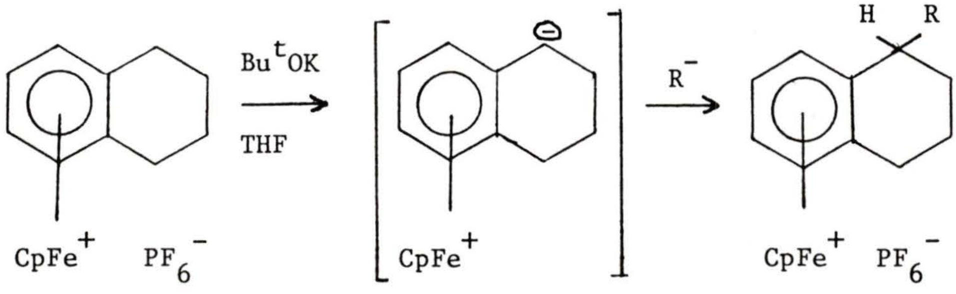
(32)

cyclohexadienyl representation for the deprotonated species rather than a zwitterionic formulation. As shown in Scheme 2, the deprotonated species is hygroscopic and the exocyclic carbon exhibits nucleophilic properties.[48,64]



Scheme 2. Nucleophilic Reactions of a deprotonated $[CpFe(C_6Me_6)]^+$ complex

To investigate further the scope of mono-substitution in the saturated ring-system of tetralin complexes, isolation of the product resulting from deprotonation of complex $\underline{\underline{1}}$ was attempted but only brown, insoluble materials could be recovered. These observations parallel results obtained by Astruc and coworkers[48] who concluded that deprotonated [CpFe(arene)]$^+$ complexes are kinetically unstable when the arene ligand is less than hexa-substituted. For example, the deprotonation of CpFe$^+$(pentamethylbenzene) affords a stable red powder at low temperature; however, complete polymerization occurs at room temperature. Subsequent reactions of the deprotonated complex 1 with electrophiles (see equation 33) afforded the products 21 - 23 in



(33)

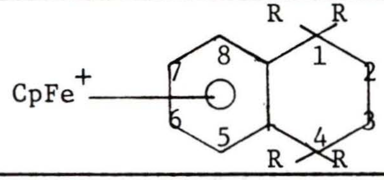
21 R = CH_3 23 R = $COCH_3$

22 R = COC_6H_5

relatively low yields (range 10-50%): these were characterized by spectroscopic measurements (see Tables 17 and 18) together with microanalytical data for complexes 21 and 22 (see experimental section).

The pale yellow mono-methylated complex 21 shows two Cp signals at δ5.12 and 5.17 ppm (ca. 72:28 ratio) in the ^{1}H NMR spectrum (see Table 17), suggesting the presence of exo- and endo-methylated complexes. The most characteristic signals are resolved as two doublets upfield at δ1.31 and 1.63 ppm ($J(H-C\underline{H}_3)$ = 7.0Hz) which may be assigned to exo- and endo-methyl resonances Sutherland and coworkers[71] also examined the synthesis of an α-methyltetralin complex using iodomethane as the

Table 17. ^{1}H NMR Spectroscopic Data for Mono-substituted Tetralin Complexes 21-23 [a]



PF$_6^-$

21 $R_{1\alpha} = CH_3$, $R_{1\beta,4\alpha,4\beta} = H$
$R_{1\beta} = CH_3$, $R_{1\alpha,4\alpha,4\beta} = H$
22 $R_{1\alpha} = COC_6H_5$, $R_{1\beta,4\alpha,4\beta} = H$
23 $R_{1\alpha} = COCH_3$, $R_{1\beta,4\alpha,4\beta} = H$

Complex	Cp (ppm)	H5-H8 (ppm)	$R_{1\alpha}R_{4\alpha}$(ppm)	$R_{1\beta}R_{4\beta}$(ppm)	H2-H3 (ppm)
(21)[b]	5.12(s,5H)[d]	6.30(m)	3.30(q,1H,H1$_\alpha$) J(H1$_\alpha$-C$\underline{H}_3$) = 6.7Hz 3.10(m,1H,H4$_\alpha$)[c]	1.31(d,3H,-C$\underline{H}_3$) J(H-C$\underline{H}_3$) = 7.1Hz 2.84(m,1H,H4$_\beta$)[c]	1.6-2.3(m)[c]
	5.17(s,5H)		1.63(d,3H,-C$\underline{H}_3$) J(H-C$\underline{H}_3$) = 6.9Hz 2.84(m,1H,H4$_\alpha$)[c]	3.10(m,1H,H4$_\beta$)[c] H1$_\beta$[e]	
22	5.25(s,5H)	6.34(m,2H) 6.44(m,2H)	8.16(dd,2H,-C$_6\underline{H}_5$) J(H-H')$_{ortho}$= 7.9Hz J(H-H'')$_{meta}$= 1.4Hz 7.71(t,1H,-C$_6\underline{H}_5$) J(H-H')$_{ortho}$ =7.3Hz 7.59(t,2H,-C$_6\underline{H}_5$) J(H-H')$_{ortho}$ =7.4Hz 3.15(m,1H,-C$\underline{H}_2$-)	5.48(t,1H,H1$_\beta$) J(H1$_\beta$-C$\underline{H}_2$-)=6.1Hz 2.88(m,1H,-C$\underline{H}_2$-)	1.84(m,1H) 2.62(m,1H) 2.88(m,1H) 3.15(m,1H)
23	5.13(s,5H)	6.34(m,4H)	2.31(s,3H,-C$\underline{H}_3$) 3.09(m,1H)	4.45(t,1H,H1$_\beta$) J(H1$_\beta$-C$\underline{H}_2$) =6.3Hz 2.80(m,1H)	1.79(m,1H) 2.5(m,1H) 2.80(m,1H) 3.09(m,1H)

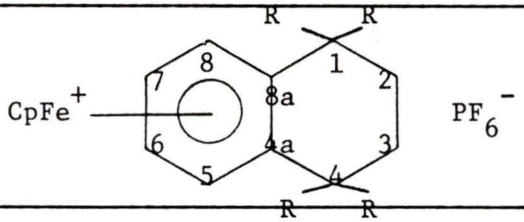
Notes: [a] $(CD_3)_2CO$ solution. [b] Mixture of two exo- and endo-methylated complexes ca.72:28 ratio from CH_3I reaction and ca.82:18 ratio from $(CH_3)_3OBF_4$ reaction. [c] poorly resolved. [d] major isomer.

electrophilic reagent. The reported ^{1}H NMR spectrum of this complex exhibited signals similar to those of complex 21, although the proportion of methylated isomers present was not given. Again, by comparison with spectroscopic data obtained by Treichel and Johnson[44] it seems likely that the major isomer (with Cp and CH_3 signals at δ5.12 and 1.31 ppm, respectively) corresponds to the exo-methylated product. From a purely steric view, this assumption appears reasonable since the uncoordinated face of the hydrocarbon will be sterically less hindered than that coordinated by the $CpFe^{+}$ unit. A distinctive quartet at δ3.30 ppm is assigned to the α-methine proton adjacent to the methyl group in the major isomer. The remaining protons associated with both isomers show only overlapping broadened signals.

The ^{13}C NMR spectrum of complex 21 (see Table 18) confirms its existence as a mixture of exo- and endo-isomers: two methyl signals are observed at 23.3 and 32.4 ppm. The major isomer exhibits a α-methine resonance at 33.3 ppm and three methylene signals at 31.6, 21.3 and 20.9 ppm. Two coordinated quaternary signals also appear at 105.0 and 109.8 ppm. Signals corresponding to the minor isomer which occur at 33.3, 30.8, 29.7 and 20.1 ppm are attributed to the saturated ring. The remainder of the resonances due to the coordinated aromatic ring systems of both isomers are obscured by overlapping patterns.

The IR spectrum of mono-methylated complex 21 features a prominent absorption at 1385 cm^{-1} assigned to the symmetrical bending vibration of the methyl C-H bonds, and is absent in the IR spectrum of the starting material 1.

Table 18. ^{13}C NMR Spectroscopic Data for Mono-substituted Tetralin Complexes 21-23[i]



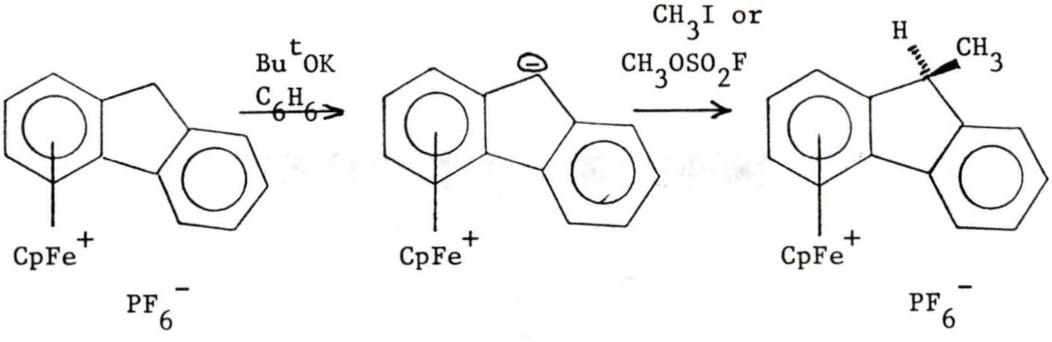
21 $R_{1\alpha} = CH_3$, $R_{1\beta,4\alpha,4\beta} = H$
$R_{1\beta} = CH_3$, $R_{1\alpha,4\alpha,4\beta} = H$
22 $R_{1\alpha} = COC_6H_5$, $R_{1\beta,4\alpha,4\beta} = H$
23 $R_{1\alpha} = COCH_3$, $R_{1\beta,4\alpha,4\beta} = H$

Complex	C1-C4 (ppm)	C5-C8 (ppm)	C4a,C8a (ppm)	Cp (ppm)	Others (ppm)
(21)[a,b]	33.3 (C1) 21.3, 20.9 (C2,C3) 31.6 (C4)	d	105.0, 109.8	77.3	32.4 ($-\underline{C}H_3$)
	33.3 (C1) 20.1, 29.7, 30.8, (C2,C3,C4)	d	e	78.1[c]	23.2 ($-\underline{C}H_3$)
(22)[f]	48.2 (C1) 28.1, 29.3 (C2,C4) 20.4 (C3)	87.8, 88.4 88.5, 89.1	103.6, 106.0	78.7	130.1,130.4,135.6, ($-\underline{C}_6H_5$) 136.8 ($-\underline{C}_6H_5$ quat) 202.3 ($\underline{C}O$)
(23)[g]	52.0 (C1) 28.7, 25.9 (C2,C4) 20.2 (C3)	87.3, 88.0 89.0	102.2, 104.8	78.3	208.1 ($\underline{C}O$) ($-\underline{C}H_3$)[h]

Notes: [a] CD_3CN solution. [b] mixture of exo- and endo-methylated isomers. [c] major isomer. [d] obscured by overlapping resonances. [e] same as for the major isomer. [f] CD_3NO_2 solution. [g] $(CD_3)_2CO$ solution. [h] obscured by d_6-acetone. [i] all chemical shifts measured in ppm.

An alternative route to complex 21 is provided by deprotonation of 1 with Bu^tOK followed by treatment with trimethyloxonium tetrafluoroborate $(CH_3)_3OBF_4$; this reaction proceeds with greater stereoselectivity. The ^1H NMR spectrum of the product (see Table 17) shows two doublets at $\delta 1.31$ and 1.63 ppm (ca. 82:18 ratio) thus indicating that the exo-methylated product may be dominant. This increase in stereoselectivity may be associated with increased steric bulk of the methylating reagent, $(CH_3)_3OBF_4$. Unfortunately, contamination of the product with a considerable amount of starting material 1 is evident from ^1H NMR data, and attempts to separate these components by chromatography have failed.

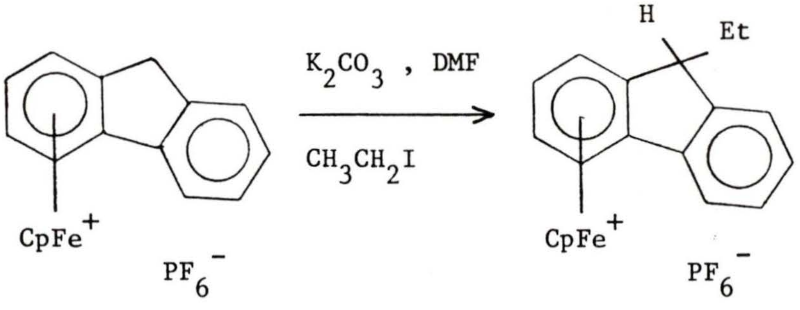
In contrast to the synthesis of complex 21, Treichel and Johnson reported the stereospecific mono-methylation of a deprotonated fluorene complex.[44] As shown in equation 34, using iodomethane or methylfluorosulfonate as the methylating reagent, a single



(34)

exo-methylated product was formed which was confirmed using x-ray crystallographic data. The lack of formation of a mixture of isomeric exo- and endo-methylated complexes implies that the conformation of the intermediate zwitterionic species may prevent access of the alkyl group to the endo-face of the deprotonated hydrocarbon. One obvious structural difference between the deprotonated fluorene complex and the deprotonated tetralin complex is the presence of a five-membered ring in the fluorene species which may be a contributing factor in determining the stereochemistry of electrophilic addition.

Attempts at preparing a mono-ethylated tetralin complex using ethyl bromide as alkylating reagent were unsuccessful; only unreacted starting material was recovered from the reaction. This result may be attributed to organic side reactions involving Bu^tOK and ethyl bromide as was discussed earlier for the synthesis of complex **8**. By contrast, Sutherland and coworkers have investigated the preparations of mono- and di-ethylated fluorene complexes with relative success.[71] As shown in equation 35, deprotonation of the fluorene complex with potassium



(60%)

(35)

carbonate followed by electrophilic substitution with iodoethane afforded the mono-ethylated product. The success of this reaction may be attributed to the use of the milder base K_2CO_3 ($pK_a = 10.33$)[68] which may have significantly greater reactivity with the fluorene complex than with the alkyl halide. Unfortunately, potassium carbonate and other bases weaker than Bu^tOK ($pK_a \simeq 17$)[68] are not strong enough to deprotonate the tetralin complex 1, whereas with the more acidic fluorene complex these weaker bases are suitable reagents.

The mono-benzoyl complex 22 and mono-acetyl complex 23 are produced from the reactions of deprotonated complex 1 with benzoyl chloride and acetyl chloride, respectively. In both cases, unreacted starting material 1 is again present in the products but successful purification has been accomplished using alumina chromatography (see experimental section). It is very likely that the polar nature of the acetyl and benzoyl groups facilitates these separations.

The ^1H NMR spectrum of the mono-benzoyl complex 22 (see Table 17) reveals a single intense Cp signal at δ5.25 ppm consistent with the existence of only one isomer. A major feature are the signals arising from the phenyl protons: a doublet of doublets centred at δ8.16 ppm (J_{ortho} = 7.9Hz , J_{meta} = 1.4Hz) is assigned to the two protons ortho to the carbonyl group; a triplet at δ7.71 ppm is assigned to the proton para to the carbonyl group; and another triplet at δ7.59 ppm is assigned to the two protons meta to the carbonyl group. A conspicuous triplet further upfield at δ5.48 ppm ($J(H-\underline{C}H_2)$ = 6.1Hz) arises from the α-methine proton which is significantly deshielded as a result of its proximity to the carbonyl group.

The ^{13}C NMR spectrum of the benzoyl derivative 22 (see Table 18) conclusively shows that stereospecific addition by a benzoyl group occurs. An intense Cp signal is observed at 78.7 ppm. Four lines appear in the range 130.1-136.8 ppm, indicative of one phenyl group. A weak, but distinct signal at 202.3 ppm is assigned to the carbonyl group.

Another distinctive line at 48.2 ppm is assigned to the methine carbon which experiences the deshielding effect of the adjacent CO group. The remaining signals confirm the asymmetrical substitution pattern introduced into the tetralin skeleton.

IR spectroscopy for the mono-benzoyl complex $\underline{\underline{22}}$ features bands representative of the benzoyl group: a strong absorption at 1675 cm^{-1} may be assigned to $\nu(C=O)$; weaker bands at 1595 and 1580 cm^{-1} arise from C=C stretching vibrations; and C-H out-of-plane bending vibrations are observed at 770 and 695 cm^{-1}, characteristic of a mono-substituted benzene ring.

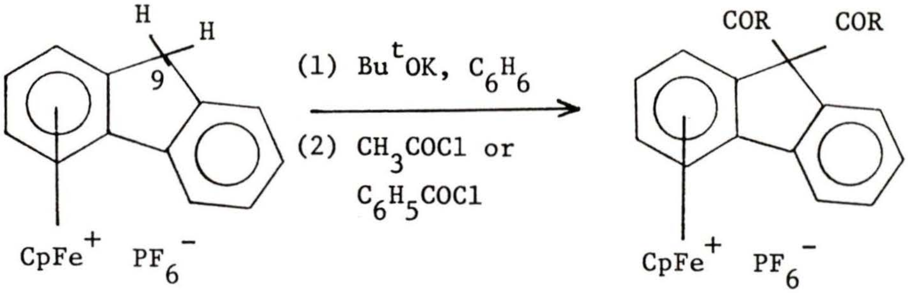
The ^1H NMR spectrum of the analogous acetyl derivative $\underline{\underline{23}}$ (see Table 17) is also consistent with stereospecific addition by an acetyl group. A single Cp resonance is observed at δ5.13 ppm. A prominent singlet upfield at δ2.31 ppm is attributed to the methyl group. The structure of the methine resonance again shows a triplet at δ4.45 ppm.

The ^{13}C NMR spectrum of the mono-acetyl complex $\underline{\underline{23}}$ (see Table 18) confirms the existence of only one product. As expected, one Cp resonance occurs at 78.3 ppm, and a weak signal at 208.1 ppm corresponds to one carbonyl group. In the saturated ring system, the deshielded α-methine carbon gives rise to a line at 52.0 ppm. The methyl signal was not located and is presumably overlapped by the d_6-acetone signal.

The IR spectrum of the mono-acetyl complex $\underline{\underline{23}}$ exhibits prominent absorptions associated with the acetyl group: a strong band at 1700 cm^{-1} is assigned to $\nu(C=O)$ and another strong absorption occurs at 1380 cm^{-1} due to the symmetrical bending vibration of the methyl C-H bonds.

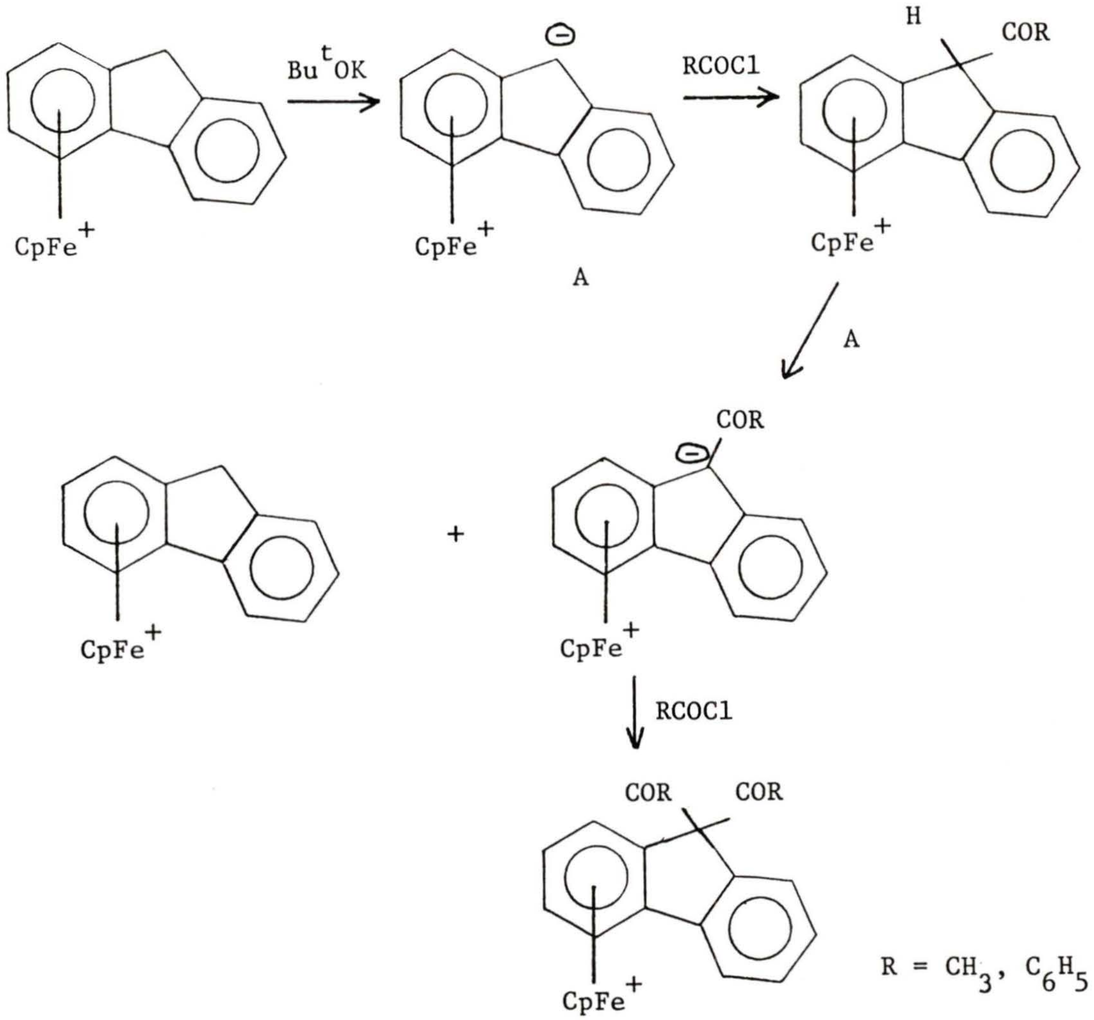
The mass spectrum of the acetyl derivative 23 shows complete decomplexation has occurred giving rise to the free aromatic molecule at m/e 175 (also the base peak). Subsequent loss of an acetyl group is observed at m/e 131.

In contrast to the mono-acylated tetralin complexes 22 and 23, Treichel and Johnson reported the synthesis of two di-acylated fluorene complexes.[44] In both cases only di-acylation was observed with benzoyl- and acetyl chloride, equation 36. The absence of the formation of mono-acylated products was attributed to the observation that the 9-endo hydrogen of intermediate exo-acylated complexes is very acidic and hence protonates the zwitterion. The resulting deprotonated mono-acylated complexes react further with the acyl halide affording the di-acylated products (see Scheme 3). Attempts to prepare mono-acylated fluorene products were unsuccessful; di-substitution was observed even by performing inverse addition experiments, i.e. the zwitterion (A) is added slowly to an excess of acyl halide thereby attempting to decrease the



(36)

$R = CH_3, C_6H_5$



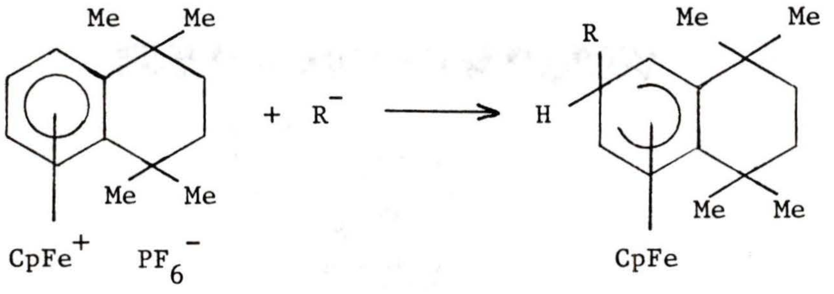
Scheme 3. Nucleophilic reactions of deprotonated fluorene complexes

concentration of (A) in the reaction mixture relative to the newly formed mono-acylated product. Examination of these reported results leads to the conclusion that the analogous mono-acylated tetralin complex is considerably less acidic relative to the mono-acylated fluorene complex; hence the formation of di-acylated products does not occur in the tetralin system.

C. Nucleophilic and benzylic substitution in [CpFe^{+}(tetralin)]PF$_6$$^{-}$

(i) Nucleophilic addition and substitution in [CpFe^{+}(tetramethyltetralin]PF$_6$$^{-}$

In order to determine if substitution in the saturated ring of the tetralin complex 1 had any influence on the pattern of nucleophilic addition to the coordinated aromatic ring system, the tetramethyltetralin complex 8 was reacted with various nucleophilic reagents, equation 37. The products 24 - 27, obtained as red oils, were characterized by mass spectrometry, IR spectroscopy (see experimental section) and ^{1}H and ^{13}C NMR spectroscopy (see Tables 19-21).



(37)

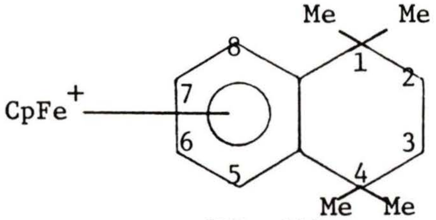
8

24 R = H 26 R = C_6H_6

25 R = D 27 R = n-butyl

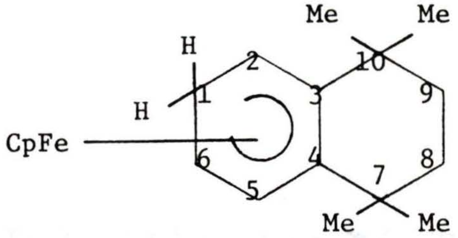
In contrast to the nucleophilic reactions of the tetralin complex 1 discussed previously, the reactions represented in equation 37 afford only one product in all cases.

The reaction of complex 8 with $LiBEt_3H$ or $NaBH_4$ affords the cyclohexadienyl product 24. The ^1H NMR spectrum of complex 24 (see Table 19) shows one intense Cp resonance at δ4.14 ppm which is indicative of regiospecific addition of hydride ion. The absence of a low field aromatic signal precludes the formation of the cyclohexadienyl isomer resulting from nucleophilic attack at the 5- or 8-position in complex 8 (see II-xii); thus, exclusive nucleophilic addition to the



(II-xii)

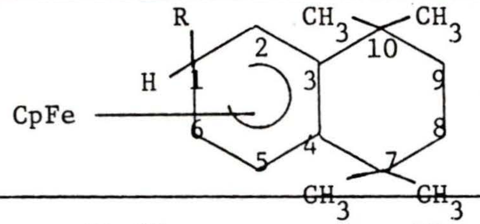
6- or 7-position is occurring which affords the isomer shown in (II-xiii). Signals are observed for the dienyl unit: a doublet



(II-xiii)

at δ4.06 ppm (J(H5-H6) = 6.6Hz) is assigned to H-5; H_{endo} is resolved as a doublet of triplets at δ2.56 ppm; a triplet at δ2.11 ppm is assigned to H-6; a doublet at δ2.20 ppm is due to H-2; and H_{exo} exhibits a doublet at δ1.61 ppm. The asymmetry present in complex 24 is reflected by the presence of four singlets in the range δ0.75-1.52 ppm which correspond to the four inequivalent methyl groups of the saturated ring.

Table 19. ^{1}H NMR Spectroscopic Data for Cyclohexadienyl Complexes 24 and 25[a,c]



24 R = H

25 R = D

Complex	Cp (ppm)	H1-H6 (ppm)	CH_3 (ppm)	H8-H9 (ppm)	R (ppm)
24	4.14(s,5H)	4.06(d,1H,H5) J(H5-H6) =6.6Hz 2.56(dt,1H,$H1_{endo}$) J($H1_{endo}$-$H1_{exo}$)=12.0Hz J($H1_{endo}$-H2,H6)=6.6Hz 2.11(t,1H,H6) J(H6-H5,$H1_{endo}$)=6.6Hz 2.02(d,1H,H2) J(H2-H1) =6.5Hz	1.52(s,3H,$-C\underline{H}_3$) 1.49(s,3H,$-C\underline{H}_3$) 1.15(s,3H,$-C\underline{H}_3$) 0.75(s,3H,$-C\underline{H}_3$)	1.3-1.9[b]	1.61(d,1H,$H1_{exo}$) J($H1_{exo}$-$H1_{endo}$)=12.1Hz
25	4.13(s,5H)	4.06(d,1H,H5) J(H5-H6) =6.6Hz 2.53(tt,1H,$H1_{endo}$) J($H1_{endo}$-H2,H6)=6.4Hz J($H1_{endo}$-D)= 2.0Hz 2.10(td,1H,H6) J(H6-H5,$H1_{endo}$)=6.6Hz J(H6-H2)=1.6Hz 2.00(dd,1H,H2) J(H2-H1)=6.6Hz J(H2-H6)=1.7Hz	1.51(s,3H,$-C\underline{H}_3$) 1.48(s,3H,$-C\underline{H}_3$) 1.14(s,3H,$-C\underline{H}_3$) 0.75(s,3H,$-C\underline{H}_3$)	1.3-1.9[b]	

Notes: [a] C_6D_6 solution. [b] series of overlapping multiplets. [c] all chemical shifts measured in δ(ppm).

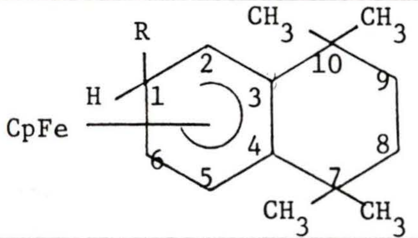
The ^{13}C NMR spectrum of complex 24 (see Table 21) confirms the regiospecificity of hydride addition. A single Cp signal is observed at 73.9 ppm, again indicative of one isomer. Signals attributed to the dienyl system are again distinctive: C-5 gives rise to a line at 73.7 ppm; two lines at 13.2 and 22.4 ppm are due to C-2 and C-6; C-1 appears at 27.5 ppm; and C-3, C-4 occur at 104.2 and 104.4 ppm. As expected, four methyl signals appear in the range 28.9-34.9 ppm, again indicative of the asymmetrical substitution pattern. Two weak signals at 32.9 and 33.9 ppm arise from the α-quaternary carbons C-7 and C-10, and two β-methylene resonances occur at 35.6 and 36.1 ppm due to C-8 and C-9.

In the IR spectrum of complex 24, prominent bands at 1380 and 1360 cm^{-1}, also observed for complexes 25-27, are attributed to the symmetrical CH_3 bending vibrations of the gem-dimethyl groups. A strong absorption at 2760 cm^{-1} confirms the presence of $C\text{-}H_{exo}$ in the cyclohexadienyl ring.

The mass spectrum of complex 24 shows the expected M+1 peak (CH_4 chemical ionization) at m/e 311. The base peak is observed at m/e 310, and an M-1 peak occurs at m/e 309. Of interest are the successive losses of four methyl groups observed at m/e 295, 281, 267 and 253.

The deuterated analogue 25 may be produced from the reaction of complex 8 with $LiBEt_3D$. The ^1H NMR spectrum of this product (see Table 19) shows signals similar to those of the non-deuterated complex 24, with an intense Cp singlet at δ4.13 ppm, confirming regiospecific deuteride addition; however the signal arising from H_{endo} which is coupled to the deuterium atom appears as a triplet of triplets,

Table 20. ^1H NMR Spectroscopic Data for Cyclohexadienyl Complexes 26 and 27[a,d]



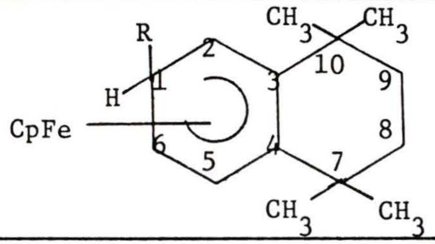
26 R = C_6H_5

27 R = n-C_4H_9

Complex	Cp (ppm)	H1-H6 (ppm)	CH_3 (ppm)	H8-H9 (ppm)	R (ppm)
26	4.16(s,5H)	H5[c] 3.61(t,1H,$H1_{endo}$) J($H1_{endo}$-H2,H6)=6.5Hz 2.65(dd,1H,H2) J(H2-$H1_{endo}$)=6.7Hz J(H2-H6)=1.6Hz 2.59(td,1H,H6) J(H6-$H1_{endo}$,H5)=6.5Hz J(H6-H2)=1.7Hz	1.44(s,3H,-$C\underline{H}_3$) 1.36(s,3H,-$C\underline{H}_3$) 0.88(s,3H,-$C\underline{H}_3$) 0.77(s,3H,-$C\underline{H}_3$)	1.2-1.7[b]	6.8-7.5(-$C_6\underline{H}_5$)[b]
27	4.14(s,5H)	3.95(d,1H,H5) J(H5-H6)=6.6Hz 2.47(td,1H,H6) J(H6-H5,$H1_{endo}$)=6.5Hz J(H6-H2)=1.6Hz 2.37(dd,1H,H2) J(H2-H1)=6.4Hz J(H6-H2)=1.6Hz 2.22(m,1H,$H1_{endo}$)	1.48(s,3H,-$C\underline{H}_3$) 1.41(s,3H,-$C\underline{H}_3$) 1.12(s,3H,-$C\underline{H}_3$) 0.81(s,3H,-$C\underline{H}_3$)	1.2-1.8[b]	0.83(t,3H,-$C\underline{H}_3$) J(H-$C\underline{H}_3$)=6.9Hz 1.2-1.8(-$C\underline{H}_2$-)[b]

Notes: [a] C_6D_6 solution. [b] series of overlapping multiplets. [c] obscured by Cp resonance. [d] all chemical shifts measured in δ(ppm).

Table 21. ^{13}C NMR Spectroscopic Data for Cyclohexadienyl Complexes 24,26 and 27[a,c]



24 R = H
26 R = C_6H_5
27 R = n-C_4H_9

Complex	Cp (ppm)	$-\underline{C}H_2-$ (ppm)	$=\underline{C}H-$ (ppm)	$-\underline{C}H_3$ (ppm)	Quaternaries (ppm)	Others (ppm)
24	73.9	36.1,35.6,27.5, 27.5(C1,C8,C9)	13.2,22.4 (C2,C6) 73.7(C5)	28.9 32.5 33.4 34.9	32.9,33.9 (C7,C10) 104.2,104.4 (C3,C4)	
26	73.9	35.5,35.8 (C8-C9)	24.3,30.4 (C2-C6) 72.5(C5) 41.8(C1)	29.1 32.3 32.8 34.3	32.0,33.4 (C7,C10) 101.6,104.0 (C3,C4) 148.4 ($-\underline{C}_6H_5$)	125.4-128.9 ($-\underline{C}_6H_5$)[b]
27	73.6	23.0,26.8,35.6, 36.0,41.0 (C8,C9,n-$\underline{C}_4H_9$)	22.0,31.2, 37.0 (C1,C2,C6) 71.2(C5)	14.3(Bu^n) 29.0 32.4 33.4 34.7	32.8,33.5 (C7,C10) 101.2,103.9 (C3,C4)	

Notes: [a]C_6D_6 solution. [b]obscured by d_6-benzene signal. [c]all chemical shifts measured in ppm.

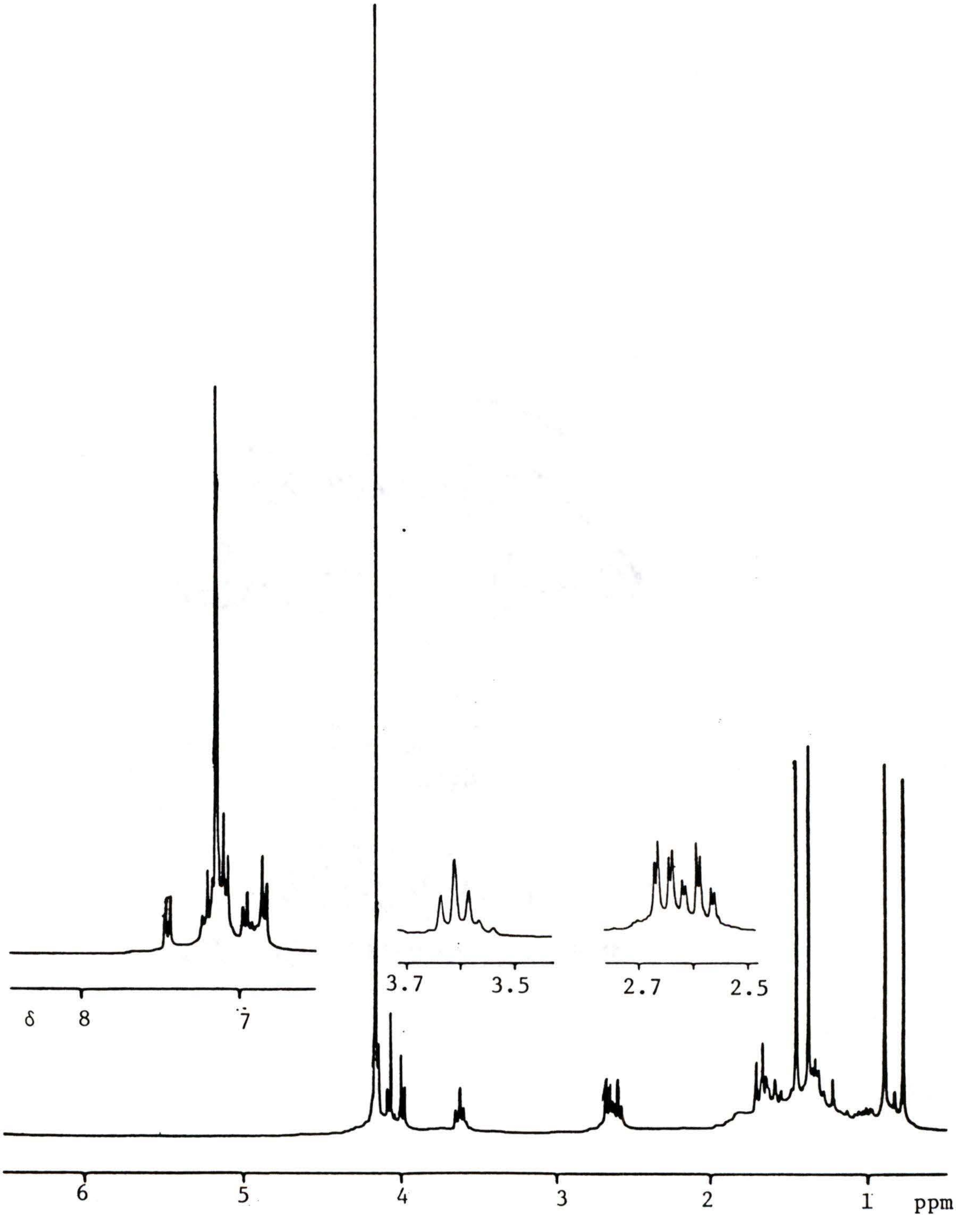
δ2.53 ppm ($J(H_{endo}-H6) = 6.4Hz$, $J(H_{endo}-D) = 2.0Hz$). The magnitude of $J(H_{endo}-D)$ is in agreement with the result obtained from theoretical considerations.[63] The ratio ν_H/ν_D (where ν refers to the magnetogyric ratio) is an approximate measure of J_{H-X}/J_{D-X} (where X refers to a particular nucleus). Using values of 26,753 and 4,107 radians $sec^{-1}gauss^{-1}$ for ν_H and ν_D, respectively, J_{H-X}/J_{D-X} is then approximately equal to 6.51. In comparison to the experimental ratio $J(H_{exo}-H_{endo})/J(D-H_{endo}) = 12.1/2.0 = 6.0$, there is fairly good agreement. Of particular importance is the absence of an upfield doublet due to H_{exo}: thus occupation of the exo-position by a deuterium atom is confirmed.

Further support for the existence of an exo-deuterium atom in complex **25** is provided in the IR spectrum. An intense absorption at 2030 cm^{-1} corresponds to the C-D stretching vibration, and no bands appear in the range 2700-2800 cm^{-1} expected for $C-H_{exo}$ stretching vibrations: thus, deuteride addition to complex **8** occurs stereospecifically as well.

In the mass spectrum of complex **25**, a molecular ion is observed at m/e 311 in accordance with the deuterated adduct. A weak signal at m/e 296 corresponds to a subsequent loss of CH_3, and a signal of medium intensity at m/e 121 arises from the $CpFe^+$ unit.

The phenyl adduct **26** is formed from the reaction of complex **8** with phenyl-lithium. Again, the ^1H NMR spectrum of complex **26** (see Table 20 and Figure 8) confirms regiospecific addition of the phenyl group, as shown by the presence of one Cp resonance at δ4.16 ppm. The protons of

Figure 8. ^{1}H NMR spectrum of CpFe[η^5-phenyl-3,4(7,7,10,10-tetramethylbutano)-cyclohexadienyl]



the dienyl unit are considerably deshielded, relative to complexes 24 and 25, due to their proximity to the phenyl group: H_{endo} exhibits a triplet at δ3.61 ppm; H-2 gives rise to a doublet of doublets at δ2.65 ppm; H-6 occurs as a triplet of doublets at δ2.59 ppm; and the signal corresponding to H-5 is obscured by the Cp singlet.

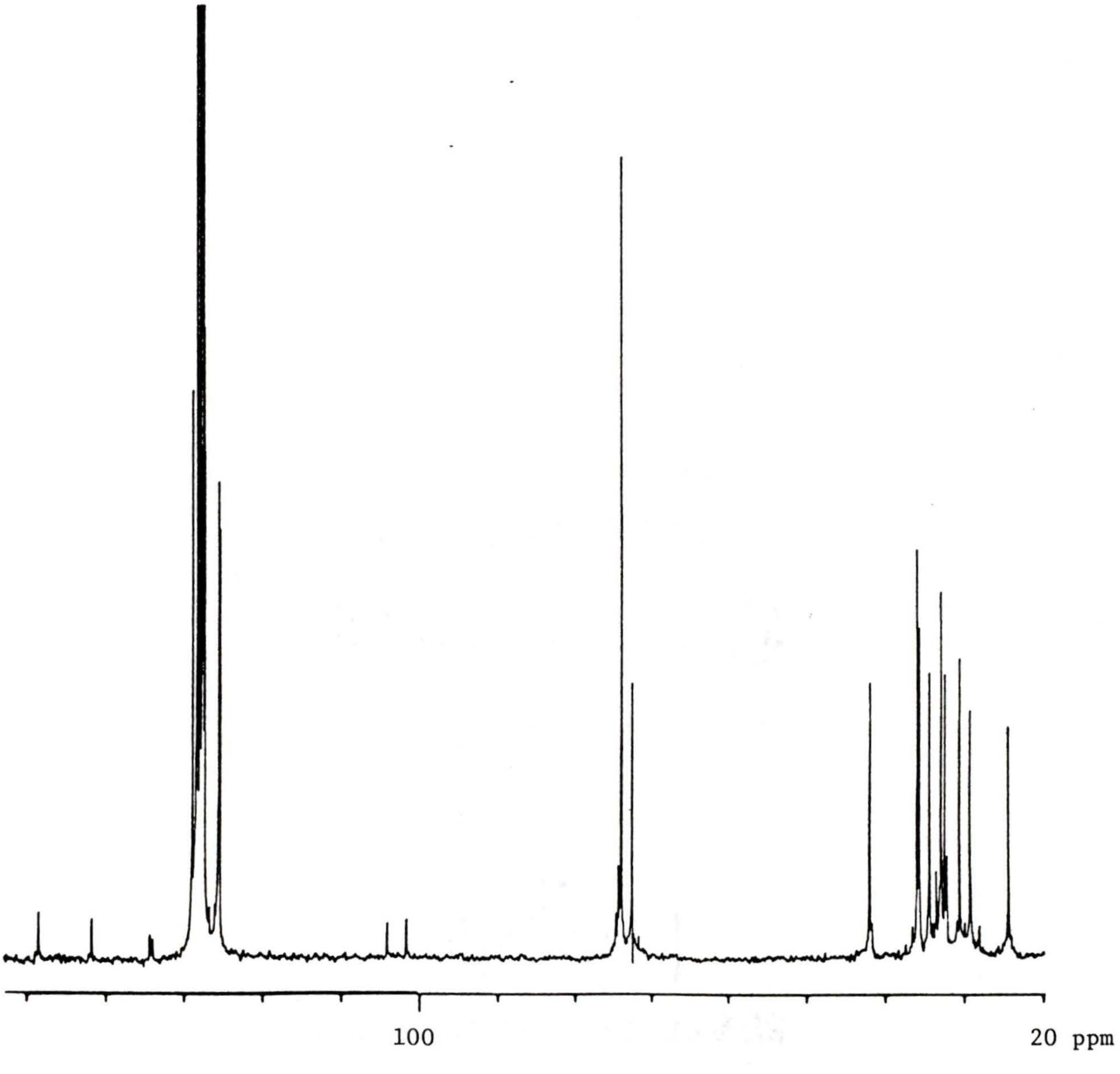
The ^{13}C NMR spectrum of complex 26 (see Table 21 and Figure 9) conclusively shows the existence of one isomer. Noteworthy features include the Cp signal at 73.9 ppm, lines at 24.3 and 30.4 ppm corresponding to C-2 and C-6, a signal 72.5 ppm which is assigned to C-5, and a line at 41.8 ppm which may be assigned to C-1 reflecting the deshielding influence of the phenyl group. A weak but distinctive signal at 148.4 ppm arises from the quaternary carbon of the phenyl group.

In the IR spectrum of complex 26, the presence of an exo-phenyl group is indicated by the absence of a band near 2800 cm^{-1} expected for the $C\text{-}H_{exo}$ stretching vibration.

The mass spectrum (CH_4 chemical ionization) of the phenyl adduct 26 shows the expected M+1 and M-1 peaks at m/e 387 and 385, respectively. Successive losses of two methyl groups are seen at m/e 372 and 358, and a small peak at m/e 309 arises from the loss of a phenyl group from the parent ion.

In a similar manner the n-butyl adduct 27 is formed from the reaction of complex 8 with n-butyl-lithium. The ^{1}H NMR spectrum of complex 27 (see Table 20) shows one Cp signal at δ4.14 ppm, again indicative of only one isomer. The structure of the resonances associated with the dienyl unit again conform to expectations. A triplet

Figure 9. ^{13}C NMR spectrum of CpFe[η^5-phenyl-3,4(7,7,10,10-tetramethylbutano)-cyclohexadienyl]



at δ0.83 ppm corresponds to the methyl protons of the n-butyl group ($J(\mathrm{H}\text{-}\underline{\mathrm{CH}_3}) = 6.9\mathrm{Hz}$). A series of complex overlapping multiplets occurring in the range δ1.2-1.8 ppm may be assigned to the methylene protons in the n-butyl group and in the saturated ring.

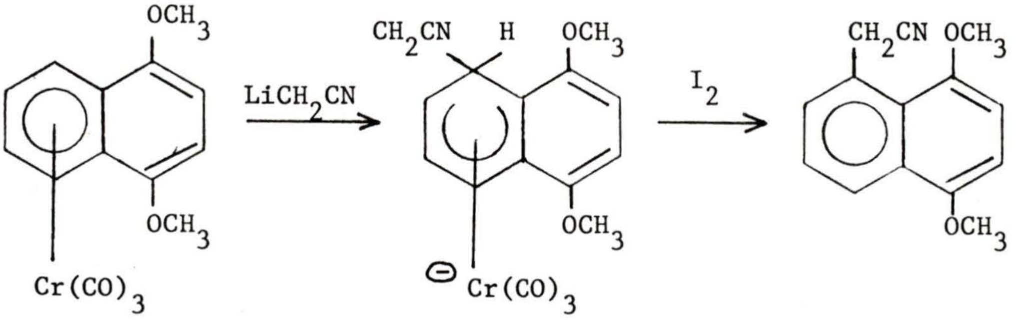
The ^{13}C NMR spectrum of complex 27 (see Table 21) confirms the existence of one n-butyl group in the dienyl system. A shielded methyl signal occurring at 14.3 ppm is assigned to the n-butyl group. In addition, five methylene signals are observed in the range 23.0-41.0 ppm attributed to the n-butyl group and the saturated ring.

Absorptions characteristic of the n-butyl group are observed in the IR spectrum of complex 27: a strong band at 1455 cm^{-1} is assigned to the methylene in-plane bending vibrations; and medium intensity bands at 1380 and 1450 cm^{-1} arise from symmetrical and asymmetrical bending vibrations of the methyl group. Again no bands are observed in the range 2700-2800 cm^{-1} indicating that the n-butyl group assumes an exo-orientation.

In the mass spectrum (CH_4 chemical ionization) of the n-butyl adduct 27, the expected M+1 peak occurs at m/e 367 with subsequent losses of three methyl groups occurring at m/e 351, 337 and 323. Also featured prominently is the base peak at m/e 309 corresponding to the loss of one n-butyl group from the parent ion.

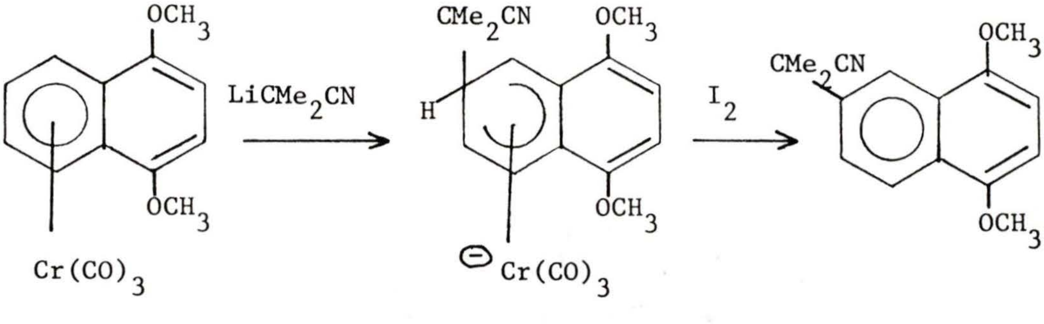
The identical regiospecificity observed in the nucleophilic addition reactions of H^-, D^-, $C_6H_5^-$ and n-$C_4H_9^-$ with the tetramethyltetralin complex 8 is consistent with a sterically controlled reaction in each case as a consequence of benzylic α-substitution in the saturated ring system. These results appear reasonable since positions 6 and 7 of complex $\underline{\underline{8}}$ (II-xii) represent the least hindered sites with respect to incoming nucleophiles.

Kundig and coworkers[77] have investigated the reaction of carbon nucleophiles with (1,4-dimethoxynaphthalene)tricarbonylchromium in order to study the factors involved in the regioselectivity of these reactions. Under conditions favoring kinetic control of the addition (i.e. low temperatures and short reaction times), the nucleophile 2-lithioacetonitrile afforded predominantly the α-substitution product, equation 38.



(38)

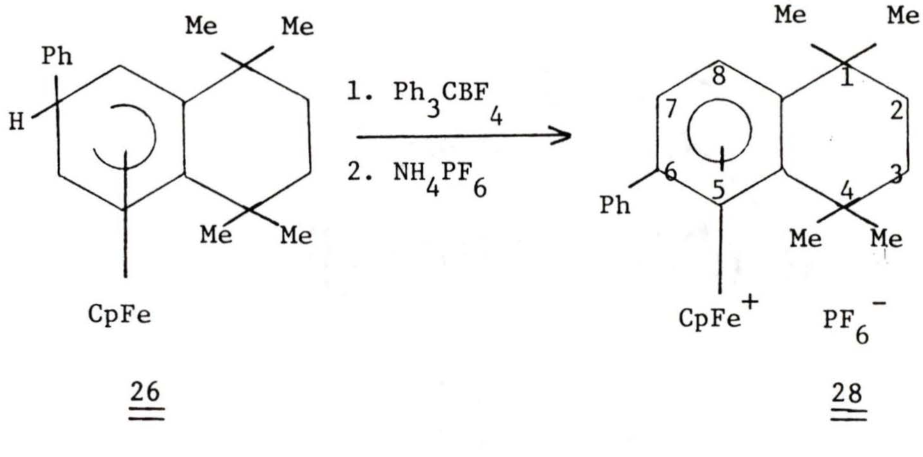
With the sterically more demanding 2-lithio-2-methylpropionitrile under similar conditions, the reaction of the chromium complex yielded predominantly β-addition, equation 39. Thus it was concluded that



(39)

steric effects dominated these reactions under kinetic control. Upon increasing the reaction times and temperatures, the additions yielded mainly the thermodynamically favored α-addition intermediates. However, reaction of the chromium complex with 2-lithio-2-methyl-1,3-dithiane resulted only in the regiospecific β-attack by the methyldithiane anion. This result was interpreted in terms of steric and electron-pair repulsion between the incoming anion and the methoxy group. In view of these observations, it is likely that for the cyclohexadienyl adducts 24 - 27, steric repulsions between the incoming nucleophiles and methyl groups are occurring.

To complete a route to substitution in the coordinated aromatic ring system of the tetramethyltetralin complex 8, the cyclohexadienyl complex 26 was treated with triphenylmethyl tetrafluoroborate affording the hydride abstraction product 28 as a light yellow powder, equation 40.



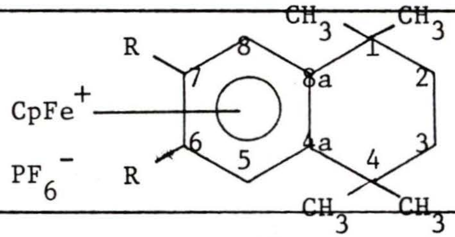
(40)

Full characterization of complex 28 has been carried out using microanalytical data (see experimental section) and spectroscopic measurements (see Table 22).

In the ^{1}H NMR spectrum of the mono-phenyl substituted complex 28 (see Table 22), one intense Cp singlet occurs at δ5.11 ppm, suggesting the presence on one $CpFe^{+}$ compound. Supporting evidence for the asymmetrical substitution pattern introduced in the coordinated aromatic ring is provided by the corresponding proton signals: a doublet at δ6.70 ppm is assigned to H-8, J(H8-H7) = 7.2Hz; a doublet of doublets centred at δ6.91 ppm is due to H-7 (J(H7-H5) = 1.7Hz); and a doublet also centred at δ6.91 ppm is assigned to H-5. The presence of an uncomplexed phenyl group is indicated by two multiplets centred at δ8.06 and 7.59 ppm. The asymmetrical substitution pattern introduced in the tetralin skeleton is again reflected by four distinct methyl singlets occurring in the range δ1.35-1.83 ppm.

Mono-substitution in the coordinated aromatic ring of complex 28 is confirmed in the ^{13}C NMR spectrum. Three lines at 82.5, 84.8 and 84.4 ppm are assigned to the three unsubstituted positions in the coordinated aromatic ring, and the remaining three coordinated quaternary carbons appear at 102.6, 114.7 and 115.2 ppm. Signals associated with the uncoordinated phenyl group appear at 128.9, 130.4 and 131.1 ppm, and the quaternary carbon occurs at 135.9 ppm. The IR spectrum of the cationic complex 28 exhibits very strong bands at 760 and 680 cm^{-1} attributed to out-of-plane bending vibrations of the aromatic C-H bonds. As expected, the conspicuous pair of peaks at 1380 and 1360 cm^{-1} arise from the symmetrical CH_3 bending vibrations, and a strong absorption at 1460 cm^{-1} is due to the CH_2 scissoring vibrations.

Table 22. ^{1}H and ^{13}C NMR Spectroscopic Data for Substituted Tetralin Complexes 28 and 31[a]



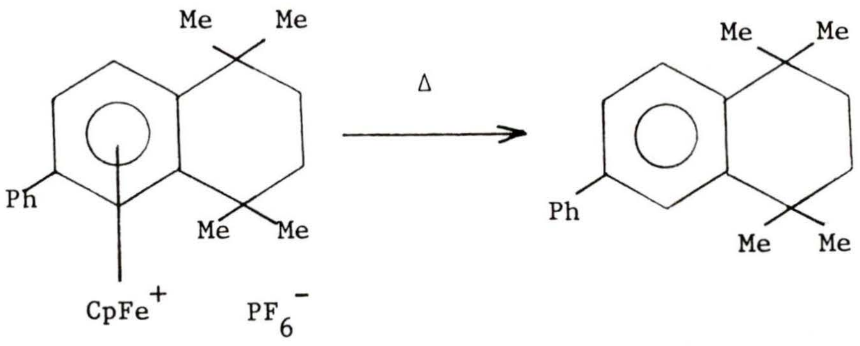
28 $R_6 = C_6H_5$, R = H
31 R_6 = R = C_6H_5

Complex	Cp (ppm)	H5–H8 (ppm)	CH_3 (ppm)	R_6,R_7 (ppm)	H2–H3 (ppm)
28	5.11(s,5H)	6.70(d,1H,H8) J(H8–H7)=7.2Hz 6.91(dd,1H,H7) J(H7–H5)=1.7Hz 6.91(d,1H,H5)	1.83(s,3H) 1.77(s,3H) 1.47(s,3H) 1.35(s,3H)	8.06(m,2H,$-C_6H_5$) 7.59(m,3H,$-C_6H_5$)	2.0(m,2H,H2$_\alpha$,H3$_\alpha$) 1.82(m,2H,H2$_\beta$,H3$_\beta$)
31	5.26(s,5H)	6.75(s,2H,H5,H8)	1.83(s,6H) 1.43(s,6H)	7.43(m,10H,$-C_6H_5$)	2.04(m,2H,H2$_\alpha$,H3$_\alpha$) 1.89(m,2H,H2$_\beta$,H3$_\beta$)

Complex	C1–C4 (ppm)	C5–C8 (ppm)	C4a,C8a (ppm)	Cp (ppm)	Others (ppm)
28	35.1 (C1,C4) 34.7,35.0(C2–C3)	82.5,84.4,84.8, (C5,C7,C8) 102.6 (C6)	114.7, 115.2	78.5	31.5,32.76,32.81($-CH_3$) 128.9,130.4,131.1($-C_6H_5$) 135.9 ($-C_6H_5$ quat.)
31	35.0 (C1,C4) 34.9 (C2,C3)	85.7 (C5,C8) 103.5 (C6,C7)	114.8	79.5	129.5,130.2,131.8($-C_6H_5$) 136.2 ($-C_6H_5$ quat) 31.4, 32.9 ($-CH_3$)

Note:[a] $(CD_3)_2CO$ solution; all chemical shifts measured in δ(ppm).

Decomplexation of the cation 28 affords the free aromatic compound 29 (equation 41) characterized by spectroscopic measurements (Table 23).



(41)

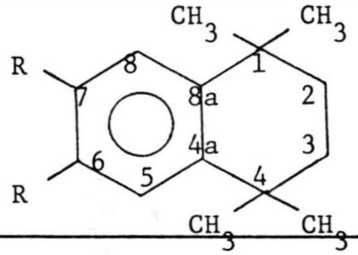
28 29

The ^{1}H NMR spectrum of the uncomplexed aromatic 29 shows two large singlets at δ1.31 and 1.33 ppm corresponding to the two pairs of gem-dimethyl groups. The β-methylene protons exhibit a singlet at δ1.71 ppm and the remaining aromatic protons give rise to overlapping multiplet patterns in the range δ7.24-7.58 ppm.

In the ^{13}C NMR spectrum of compound 29, important features include two lines at 31.85 and 31.9 ppm attributed to the gem-dimethyl groups, and six lines appearing in the range 124.4-128.6 ppm which are assigned to the aromatic rings. Also of particular interest are four weak signals at 138.4, 141.6, 144.0 and 145.2 ppm which are due to the quaternary aromatic carbons.

The mass spectrum of compound 29 shows a prominent M+1 peak (CH_4 chemical ionization) at m/e 265 (also the base peak). Also observed is a peak at m/e 249 corresponding to loss of one methyl group.

Table 23. ^{1}H and ^{13}C NMR Spectroscopic Data for Uncomplexed Substituted Tetralin Ligands 29 and 32[a,c]



29 $R_6 = C_6H_5$, R = H

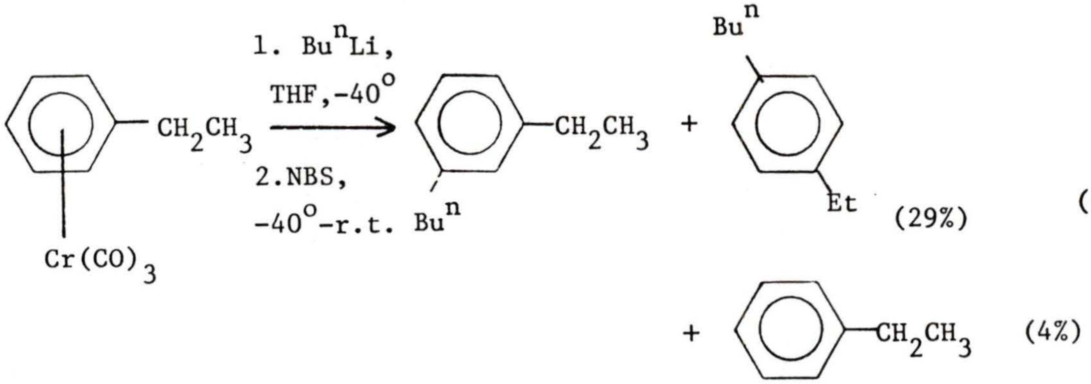
32 $R_6 = R = C_6H_5$

Complex	H5-H8 (ppm)	CH_3 (ppm)	H2-H3 (ppm)	R_6,R_7 (ppm)
29	7.24-7.58(m)[b]	1.31(s,6H) 1.33(s,6H)	1.71(s,4H)	7.24-7.58(m)
32	7.33(s,2H)	1.34(s,12H)	1.73(s,4H)	7.15(m)

Complex	C1-C4	C5-C8	C4a,C8a	Others
29	34.1,34.4 (C1,C4) 35.1,35.2 (C2,C3)	124.4, 125.3 126.8, 126.9 (C5,C7,C8,$\underline{C}_6H_5$)	138.4,141.6,144.0, 145.2(C4a,C6,C8a,$\underline{C}_6H_5$)	127.1,128.6(-$\underline{C}_6H_5$) 31.85,31.9 (-$\underline{C}H_3$)
32	34.2 (C1,C4) 35.3 (C2,C3)	126.2, 128.8 (C5,C8,-$\underline{C}_6H_5$)	137.6,141.9,144.2 (C4a,C8a,C6,C7,$\underline{C}_6H_5$)	127.8,130.0 (-$\underline{C}_6H_5$) 31.9 (-$\underline{C}H_3$)

Notes: [a] $CDCl_3$ solution. [b] obscured by phenyl resonances. [c] all chemical shifts measured in δ(ppm).

The regiospecific substitution by the phenyl group observed in compound 29 is most likely controlled by a steric effect introduced in the molecule by the four methyl substituents. In a similar type of reaction, regioselective substitution was observed in the n-butylation of (ethylbenzene)$Cr(CO)_3$ (see equation 42) which was reported by Trahanovsky and Card.[75] As shown in equation 42, meta-substitution is predominant

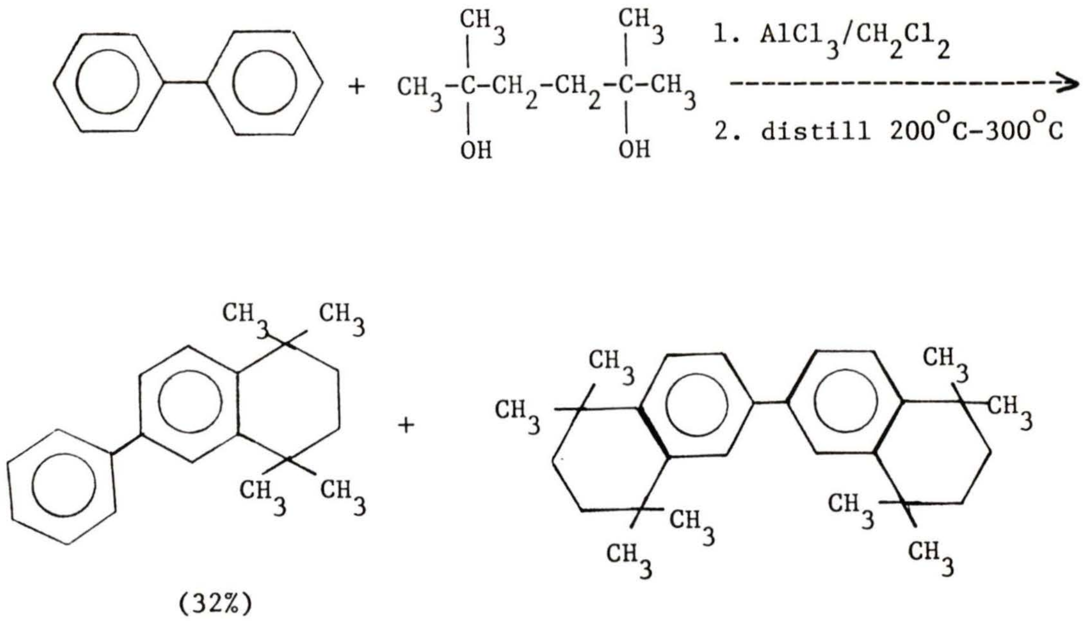


(42)

which is indicative that the positions ortho to the ethyl substituent are sterically inaccessible with respect to substitution reactions. Likewise in the tetramethyltetralin system, the aromatic positions ortho to the saturated ring system are sterically protected as exemplified in the synthesis of compound 29.

The ^1H and ^{13}C NMR spectroscopic data for compound 29 are identical with those reported in the literature.[73] Pétraud and coworkers investigated the organic synthesis of this aromatic compound from the reaction of biphenyl and 2,5-dimethyl-2.5-hexanediol in the presence of aluminum chloride, equation 43.

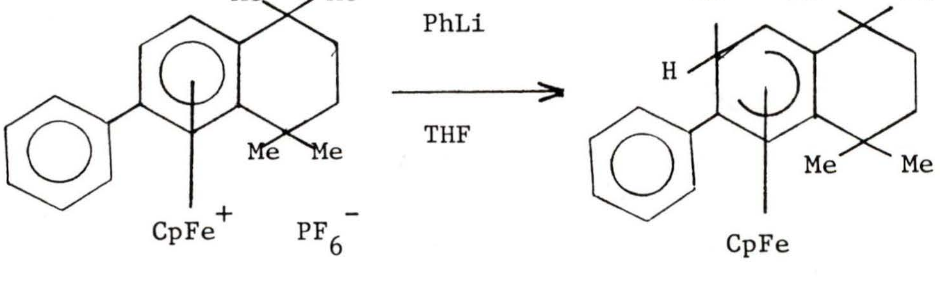
In addition to the monocycloalkylated product, the bicycloalkylated hydrocarbon was also formed which was separated using chromatography.



(43)

Such reactions have been utilized for the functionalization of polycyclic aromatic hydrocarbons.

In order to observe the pattern of nucleophilic addition to the mono-substituted coordinated aromatic ring of complex 28, the latter was treated with phenyl-lithium yielding the expected neutral cyclohexadienyl complex 30 (see equation 44) which was characterized by spectroscopic

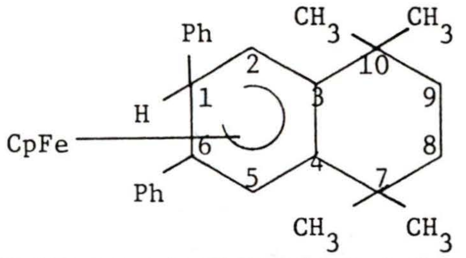


28 30

(44)

measurements (see Table 24).

Table 24. ^{1}H and ^{13}C NMR Spectroscopic Data for Cyclohexadienyl Complex $\underline{\underline{30}}^{a,e}$



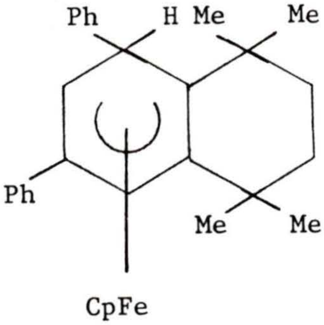
$\underline{\underline{30}}$

Complex	Cp (ppm)	H1-H6 (ppm)	$-C\underline{H}_3$ (ppm)	H8-H9 (ppm)	$-C_6\underline{H}_5$ (ppm)
$\underline{\underline{30}}$	4.16(s,5H)	6.88-7.67($-C_6\underline{H}_5$)[b] 6.70(dd,1H,H1$_{endo}$) J(H1$_{endo}$-H2)=7.2Hz J(H1$_{endo}$-H5)=1.5Hz 5.28(d,1H,H5) J(H5-H1$_{endo}$)=1.2Hz 3.20(d,1H,H2) J(H2-H1$_{endo}$)=7.0Hz	1.79(s,3H) 1.50(s,3H) 0.90(s,3H) 0.77(s,3H)	2.00(m) 1.74(m)	6.88-7.67 ($-C_6H_5$)[b]

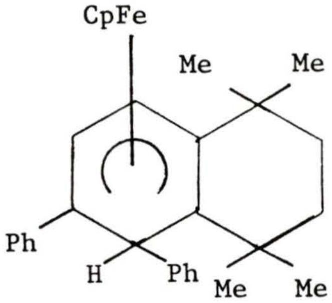
Complex	Cp	$-\underline{C}H_2-$	$=\underline{C}H-$	$-\underline{C}H_3$	Quaternaries	Others
$\underline{\underline{30}}$	75.9	35.4,35.9 (C8,C9)	74.1(C5) 25.3(C2) 43.6(C1)	28.9,32.5 32.8,34.1	101.5,103.1(C3,C4) (C6,C7,C10)[d] 146.5,146.8 ($-\underline{C}_6H_5$)	124.3-128.9 ($-\underline{C}_6H_5$)[c]

Notes: [a] C_6D_6 solution. [b] complex series of multiplets. [c] obscured by C_6D_6 signal. [d] not located. [e] all chemical shifts measured in δ(ppm).

The ^1H NMR spectrum of complex 30 (see Figure 10) exhibits one Cp signal at δ4.16 ppm, indicating the formation of only one isomer. In this spectrum, the lowest field dienyl signal appears as a doublet of doublets at δ6.70 ppm which does not correspond to the most aromatic proton of the dienyl unit as would be expected. In addition, examination of the structural formulae for the other two possible isomers (shown in II-xiv, and II-xv) precludes the assignment of the signal at δ6.70 ppm to the most aromatic dienyl proton: hence , these isomers do not arise from



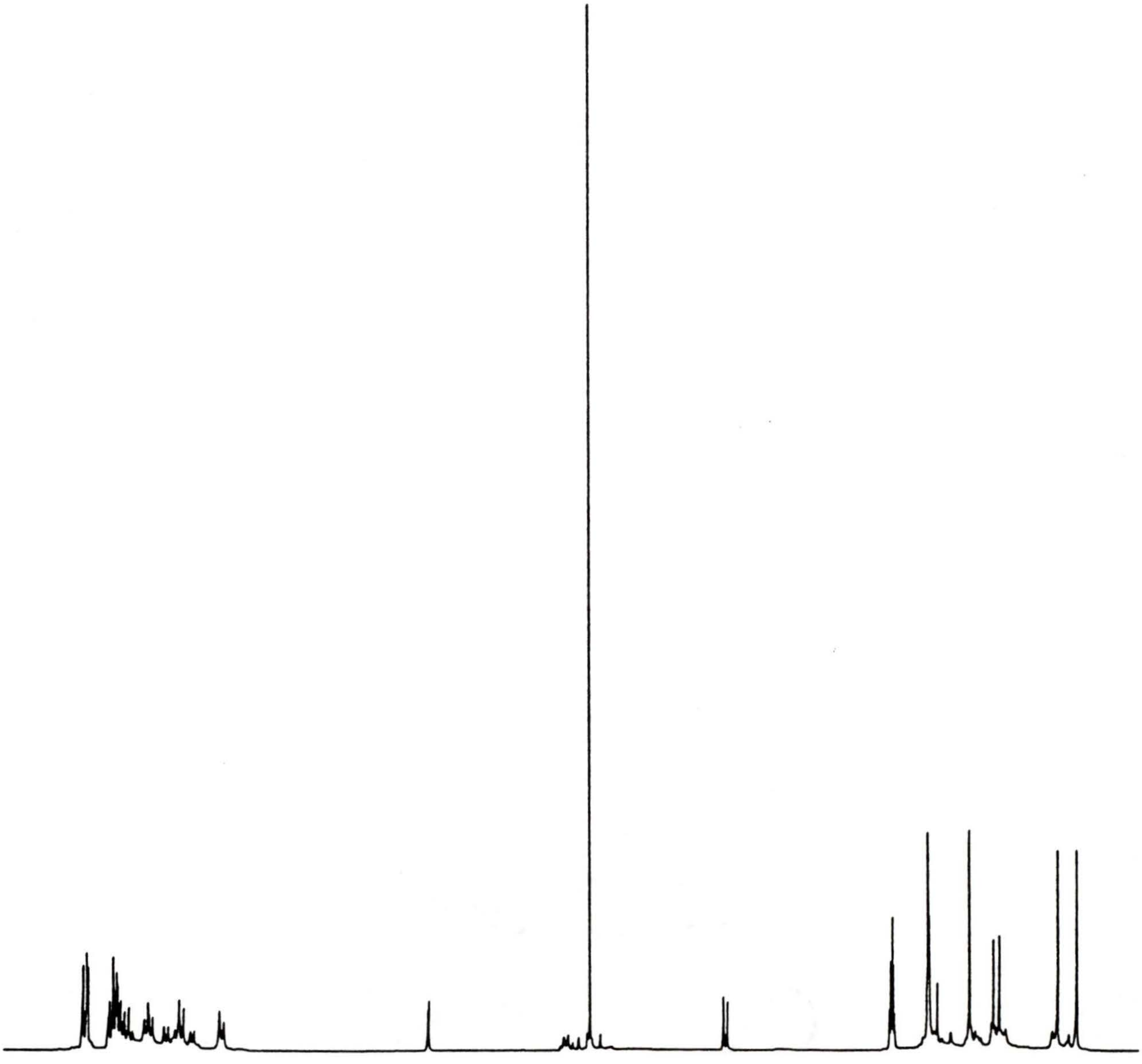
(II-xiv)



(II-xv)

the reaction represented in equation 32. Consequently, it is reasonable to attribute the doublet of doublets to H-1 or H_{endo} ($J(H_{endo}-H2)$ = 7.2Hz, $J(H_{endo}-H5)$ = 1.5Hz) in complex 30 since this proton is deshielded considerably due to the influence of the neighbouring phenyl groups. The remaining protons of the dienyl unit, H-5 and H-2, both show doublet structures at δ5.28 and 3.20 ppm, respectively. An asymmetrical substitution pattern is again reflected by the presence of four methyl

Figure 10. ^{1}H NMR spectrum of CpFe[η^5-phenyl-3,4(7,7,10,10-tetramethylbutano)-6-phenylcyclohexadienyl]



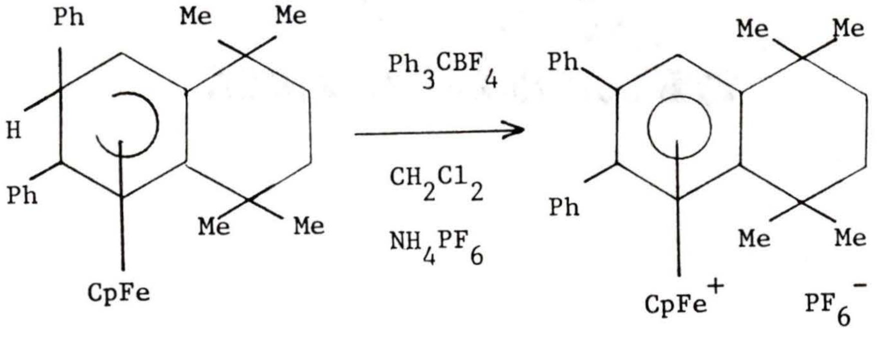
singlets occurring in the range 0.77-1.79 ppm.

The ^{13}C NMR spectrum of complex 30 shows one Cp signal at 75.9 ppm, again indicative of only one isomer. For the cyclohexadienyl ring system, the expected resonances are observed: lines at 74.1, 43.6 and 25.3 ppm are assigned to C-5, C-1 and C-2, respectively; C-6 was not located; and the coordinated quaternary carbons C-3 and C-4 exhibit lines at 101.5 and 103.1 ppm, respectively. Also of interest are the two uncoordinated quaternary carbons occurring at 146.5 and 146.8 ppm.

The IR spectrum of complex 30 again confirms exo-attack by $C_6H_5^-$ into the coordinated aromatic ring of cation 28 as shown by the absence of absorptions in the region 2700-2800 cm^{-1}.

The mass spectrum (CH_4 chemical ionization) of cyclohexadienyl complex 30 exhibits an M+1 peak at m/e 464, followed by the loss 1f one methyl group at m/e 449. Also observed is a peak at m/e 265 corresponding to the loss of a phenyl and CpFe group from the parent ion.

Confirmation of the formulation of complex 30 is provided by oxidation of this cyclohexadienyl species with trityl tetrafluoroborate yielding the expected hydride ion abstraction product 31, equation 45. Full characterization of the product was accomplished using microanalytical data (see experimental section) and spectroscopic measurements (see Table 22).



(45)

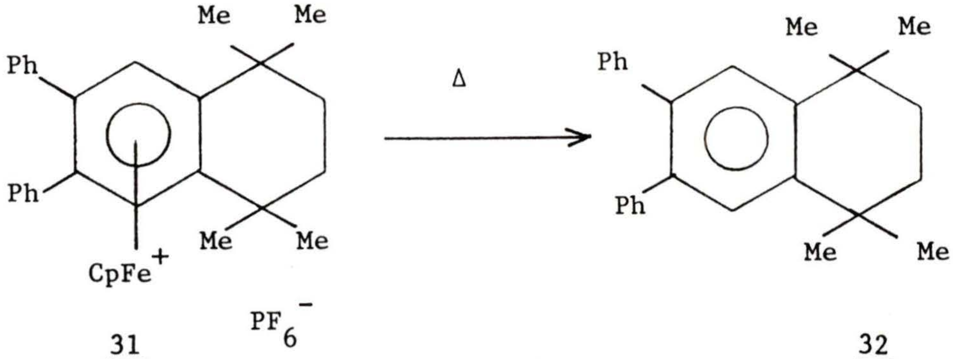
30

31

The ^{1}H NMR spectrum of the diphenyl-substituted complex 31 confirms the symmetrical substitution pattern present in the coordinated aromatic ligand. Two prominent singlets at δ1.43 and 1.83 ppm are assigned to the exo- and endo-methyl groups. Of particular interest is the small intensity singlet occurring at δ6.75 ppm due to the two protons of the coordinated aromatic ring system, again indicative of a plane of symmetry bisecting the hydrocarbon fragment.

The ^{13}C NMR spectrum of complex 31 provides additional evidence for di-substitution in the coordinated aromatic ring system: one line at 85.7 ppm corresponds to the two equivalent unsubstituted sp^2 carbons in the complexed aromatic ring; the two complexed quaternary carbons adjacent to the two phenyl groups exhibit a weak signal at 103.5 ppm; and the two complexed quaternary carbons adjacent to the saturated ring system show one line at 114.8 ppm. Associated with the phenyl groups are three lines occurring at 129.5, 130.2 and 131.8 ppm, and one quaternary signal at 136.2 ppm, conclusively showing the existence of two equivalent phenyl substituents.

Further support for the formulation of complex 31 is provided by characterization of the free aromatic ligand 32 obtained by pyrolytic sublimation of the cation 31, equation 46. The compound 32 was



31 32 (46)

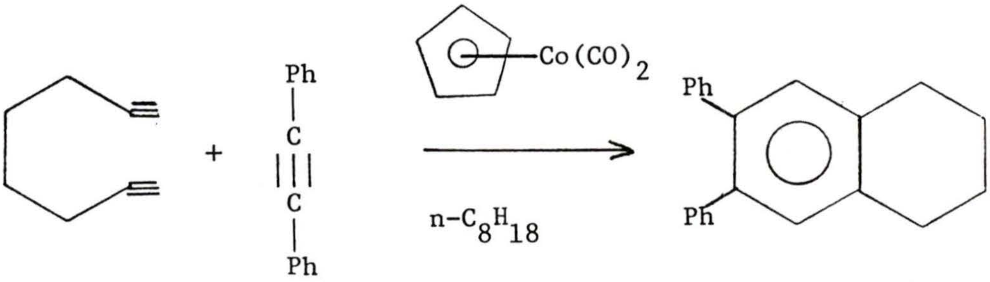
characterized by spectroscopic measurements (see Table 23 and experimental section).

The free aromatic compound 32 exhibits a relatively simple ^{1}H NMR spectrum confirming the symmetry present in the molecule. Three singlets at δ1.34, 1.73 and 7.33 ppm correspond to the four equivalent methyl groups, the four β-methylene protons and two equivalent protons of the ortho-disubstituted aromatic ring, respectively.

The ^{13}C NMR spectrum of compound 32 also confirms the symmetrical substitution pattern introduced into this tetralin derivative. One intense signal at 31.9 ppm corresponds to the methyl groups. The two equivalent unsubstituted carbons in the ortho-disubstituted ring and two carbons of the phenyl groups show two small lines at 126.2 and 128.8 ppm. Two intense lines at 127.8 and 130.0 ppm are attributed also to the phenyl carbons. As expected, three unsaturated quaternary signals are observed at 137.6, 141.9 and 144.2 ppm.

The mass spectrum for compound 32 shows a base peak at m/e 341 (CH_4 chemical ionization) which corresponds to the M+1 ion. Also observed is a medium intensity peak at m/e 326 arising from the subsequent loss of a methyl group.

Although the free tetralin derivative 32 had not been previously reported a related compound, 1,2,3,4-tetrahydro-6,7-diphenylnaphthalene, has been prepared by Hillard and Vollhardt[74] utilizing the cooligomerization of 1,7-octadiyne with diphenylacetylene catalyzed by dicarbonylcyclopentadienyl-cobalt, equation 47. As shown in equation 47



(47)

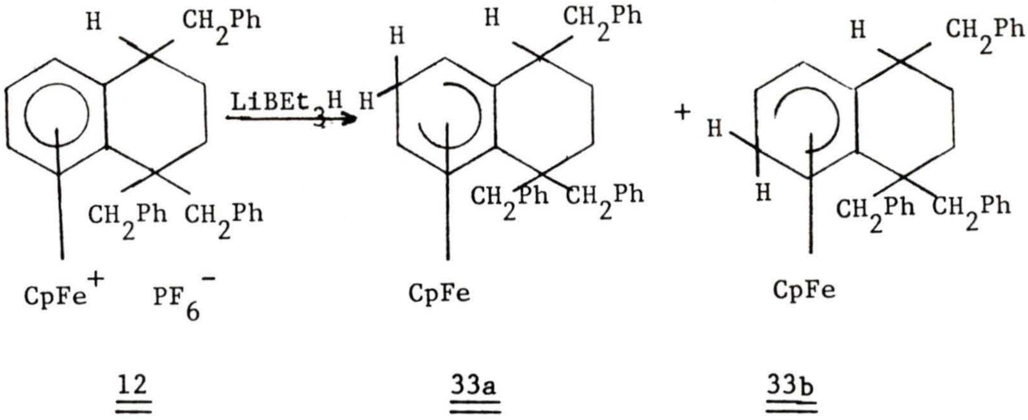
(21%)

this reaction has been used to approach the problem of preparing polycycles containing functionalized benzene rings with control of substitution, a process which is achieved usually by relatively tedious aromatic substitution sequences. The new route (see equation 47) represents an alternative method involving the cyclization of suitable precursors to a molecule containing a newly formed benzene ring, thus allowing for extensive control of substitution in the aromatic ring. In contrast to the iron-assisted substitution reactions represented in equations 44 and 45, the cyclization reaction of equation 47 achieves the desired substitution pattern in the product in the absence of benzylic substitution in the saturated ring.

Examination of the preceding spectroscopic data for complexes 28-32 unambiguously establishes that *via* nucleophilic addition and hydride ion abstraction reactions, mono- and di-substitution in the coordinated aromatic ring system of the tetramethyltetralin complex 8 can occur regiospecifically under the influence of substitution in the saturated ring. To determine if the tribenzyltetralin complex 12 showed similar behaviour towards nucleophilic attack, reactions of complex 12 with nucleophiles were also carried out.

(ii) Nucleophilic addition to $[CpFe^+(tribenzyltetralin)]PF_6^-$

The reaction of complex 12 with $LiBEt_3H$ affords a mixture of isomeric cyclohexadienyl complexes 33a,33b as an orange solid (see equation 48) which was characterized by spectroscopic measurements (see Tables 25, 26 and experimental section).

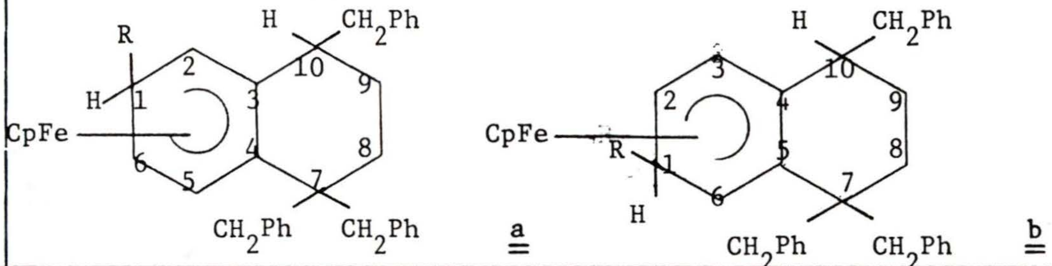


(48)

The ^1H NMR spectrum of the neutral products 33a and 33b (see Table 25) shows two Cp singlets at δ4.09 and 4.05 ppm (*ca.* 67:33 ratio), suggesting the presence of two isomers. Due to the asymmetrical substitution pattern in the cationic complex 12, positions 5 to 8 on the coordinated aromatic are all distinguishable, hence a total of four isomers are possible from the reaction. However, the absence of low field aromatic signals in the range δ6–7 ppm indicates that products resulting from nucleophilic attack at positions 5 and 8 in complex 12 are not present: thus, isomers resulting from hydride addition to positions 6 and 7 are produced, as represented in equation 48. As a consequence of the regioselectivity observed here, it is possible to assign signals corresponding to the major product; however, it is not possible to deduce the structural formulation of either the major or minor product solely on the basis of ^1H and ^{13}C NMR data.

For the major isomer, the ^1H NMR spectrum shows an intense Cp singlet at δ4.05 ppm. Signals associated with the cyclohexadienyl ring are distinct: the most aromatic proton of the dienyl unit exhibits a

Table 25. ^1H NMR Spectroscopic Data for Cyclohexadienyl Complexes 33a, 33b and 34[a,i]



33a R = H
33b R = H
(34)[g] R = CH_3

Complex	Cp (ppm)	H1-H6 (ppm)	H8-H10 (ppm)	Benzyl (ppm)	R (ppm)
(33a,33b)[c]	4.09(s,5H)[e]				
	4.05(s,5H)[f]	4.22(d,1H,H3 or H5) J(H3-H2) = 6.2Hz $H1_{endo}$[b] 2.12(td,1H,H2(33b) or H6(33a)) J(H2-$\underline{H1}_{endo}$)=5.8Hz J(H2-H6) = 1.6Hz 2.07(d,1H,H6(33b) or H2(33a)) J(H6-$\underline{H1}_{endo}$)=7.1Hz	3.53(m,1H,H10) 1.4-2.0 ($H8_{\alpha,\beta}$,$H9_{\alpha,\beta}$)[d]	3.79(d,1H,$-C\underline{H}H'-$) 3.40(d,1H,$-CH'\underline{H}-$) J(H'-H) = 13.4Hz 3.08(d,1H,$-C\underline{H}'H-$) 2.76(d,1H,$-CH'\underline{H}-$) J(H'-H) = 12.7Hz 2.49(dd,1H,$-C\underline{H}'H-$) J(H'-H) = 12.3Hz J(H'-H10) = 6.3Hz 1.90(dd,1H,$-CH'\underline{H}-$) J(H-H10) = 9.1Hz 7.0-7.4 ($-C_6\underline{H}_5$)[h]	1.64(d,1H,$H1_{exo}$ J($H1_{exo}$-$H1_{endo}$) = 12.8Hz

Table 25 (continued)

Complex	Cp (ppm)	H1-H6 (ppm)	H8-H10 (ppm)	Benzyl (ppm)	R (ppm)
(34)[g]	4.06(s,5H)	4.17(d,1H,H3 or H5) J(H-H')$_{ortho}$=6.3Hz 2.52(t,1H,H2 of b or H6 of a) 2.44(d,1H,H6 of b or H2 of a) H1$_{endo}$[b]	H10[b] 1.2-2.0[d] (H8$_{\alpha,\beta}$,H9$_{\alpha,\beta}$)	3.90(d,1H,-C$\underline{H}$'H-) 3.34(d,1H,-CH'$\underline{H}$-) 3.04(d,1H,-C$\underline{H}$'H-) 2.80(d,1H,-CH'$\underline{H}$-) J(H-H') = 13.2 Hz 2.33(dd,1H,-C$\underline{H}$'H-) J(H'-H10) = 5.4 Hz 1.92(dd,1H,-CH'$\underline{H}$-) J(H-H10) = 10.9 Hz 6.9-7.3 (-C$_6\underline{H}_5$)[h]	0.09(d,3H,-C$\underline{H}_3$) J(H1$_{endo}$-C$\underline{H}_3$)= 6.4Hz

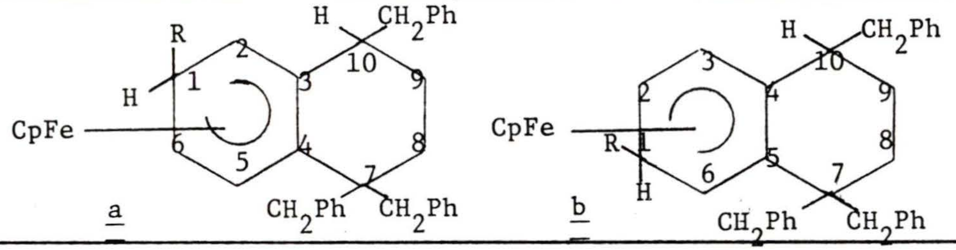
Notes:[a] C_6D_6 solution.[b] not located.[c] isomers 33a,33b obtained in ca. 67:33 ratio.[d] series of complex overlapping multiplets.[e] resonances of the minor isomer were obscured by the major isomer.[f] major isomer.[g] the structural formula of complex 34 is not possible to deduce from NMR data alone.[h] obscured by C_6D_6 signal.[i] all chemical shifts measured in δ(ppm).

doublet at δ4.22 ppm (J_{ortho} = 6.2Hz); the proton adjacent to the most aromatic proton gives rise to a triplet of doublets at δ2.12 ppm (J_{meta} = 1.6Hz); one of the dienyl protons adjacent to the methylene group shows a doublet at δ2.07 ppm (J(H-H_{endo}) = 7.1Hz; H_{exo} appears as a doublet at δ1.64 ppm; and H_{endo} was not located. The benzyl groups also show conspicuous signals corresponding to the inequivalent methylene protons: four doublets appear at δ3.79, 3.40, 3.08 and 2.76 ppm; and two doublets of doublets occur at δ2.49 and 1.90 ppm (J(H-H10) = 6.3Hz, J(H'-H10) = 9.1Hz). Resonances attributable to the minor isomer were obscured by those of the major isomer.

The ^{13}C NMR spectrum of complexes 33a and 33b (see Table 26) gives rise to two unique sets of signals attributable to the two isomers. For the major isomer the Cp resonance occurs at 74.5 ppm. Associated with the cyclohexadienyl ring are distinct signals: lines occurring at 20.5 and 21.5 ppm are assigned to C-2 and C-6 of 33a or 33b; C-3 of 33b or C-5 of 33a shows a line at 74.3 ppm; C-1 exhibits a line at 27.0 ppm; and the quaternary carbons C-4 and C-5 of 33b or C-3 and C-4 of 33a show lines at 103.3 and 97.8 ppm. As expected, three benzyl methylene resonances exhibit signals at 43.4, 48.6 and 48.9 ppm, and three uncoordinated quaternary signals appear at 139.0, 139.5 and 141.7 ppm. Signals associated with the minor isomer are similar to those described above for the major product.

In the mass spectrum (CH_4 chemical ionization) of 33a and 33b, the expected M+1 ion appears at m/e 525 followed by successive losses of two benzyl groups at m/e 433 and 342. A peak at m/e 311 corresponds to a

Table 26. ^{13}C NMR Spectroscopic Data for Cyclohexadienyl Complexes 33a,33b and 34[a,g]



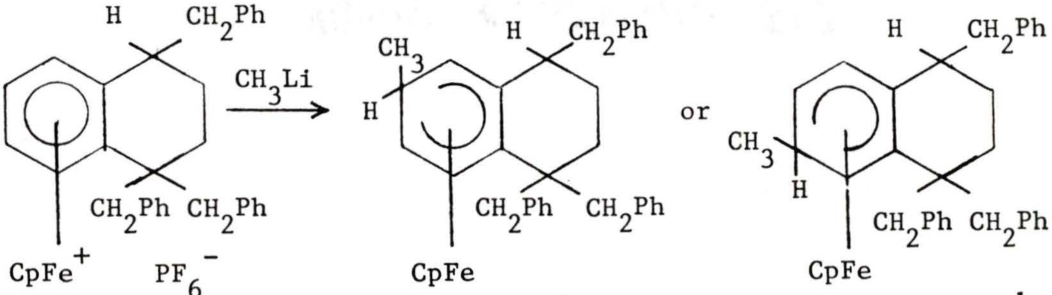
33a R = H
33b R = H
(34)[f] R = CH_3

Complex	Cp (ppm)	$-\underline{C}H_2-$ (ppm)	$=\underline{C}H-$ (ppm)	Quaternaries (ppm)	Other (ppm)
33a,33b	74.5[d]	22.9,23.0(C8,C9) 27.0 (C1) 43.3,48.6,48.9 $(-\underline{C}H_2C_6H_5)$	20.5,21.5(C2,C6) 43.0 (C10) 74.3(C3 or C5)	41.5 (C7) 103.3 (C4) 97.8(C5 or C3) 139.0,139.5,141.7, $(-\underline{C}_6H_5)$	126.0-132.6$(-\underline{C}_6H_5)$[b]
	74.6	24.6,25.8,28.4 43.9,46.4, (C1,C8,C9,$-\underline{C}H_2C_6H_5$)	16.5,24.8(C2,C6) 42.3 (C10) 76.9 (C5)	99.1(C3 or C5) 105.1 (C4) (C7)[c] $(-\underline{C}_6H_5)$[d]	126.0-132.6$(-\underline{C}_6H_5)$[b]
(34)[f]	74.3	22.4,23.3(C8,C9) 50.3,48.2,44.0 $(-\underline{C}H_2C_6H_5)$	32.4,32.5,33.1 (C1,C2,C6) 42.4 (C10) 74.5(C3 of b or C5 of a)	41.1 (C7) 102.4, 97.1, (C4,C5 of b or C3,C4 of a) 138.9,139.6,141.5, $(-\underline{C}_6H_5)$	126.0-132.6$(-\underline{C}_6H_5)$[b] 26.8 $(-\underline{C}H_3)$

Notes: [a] C_6D_6 solution. [b] obscured by d_6-benzene. [c] not located. [d] obscured by major isomer peaks. [e] major isomer [f] the structural formula of complex 34 is not possible to deduce from NMR data alone. [g] all chemical shifts measured in ppm.

loss of CpFe from the ion at m/e 433. Further loss of a phenyl and methylene group, from the m/e 311 signal, is indicated by peaks at m/e 235 and 221, respectively. A base peak occurs at m/e 91, attributable to a benzyl group.

The reaction of the tribenzyltetralin derivative 12 with methyl-lithium was carried out also yielding only one isomer. This methyl adduct 34 was isolated as an orange solid (see equation 49).



(49)

a

b

12

34

which was characterized by spectroscopic measurements (see Tables 25, 26 and experimental section). Again the exact formulation of the product 34 (i.e. isomer a or b) cannot be determined from the spectral data alone.

The ^1H NMR spectrum of the cyclohexadienyl complex 34 (see Table 25) shows one Cp signal at δ4.06 ppm indicative of only one isomer. The regiospecificity observed here is indicative that an electronic and/or steric influence may be involved in the reaction. Again, the absence of low field signals in the range δ6-7 ppm suggests that the methyl carbanion addition has occurred at the 6 or 7 position of complex 12.

The dienyl unit exhibits signals similar to those found for related complexes 33a and 33b. The signal arising from the methyl group gives rise to a distinct doublet at δ0.09 ppm ($J(H_{endo}-C\underline{H}_3)$ = 6.4Hz).

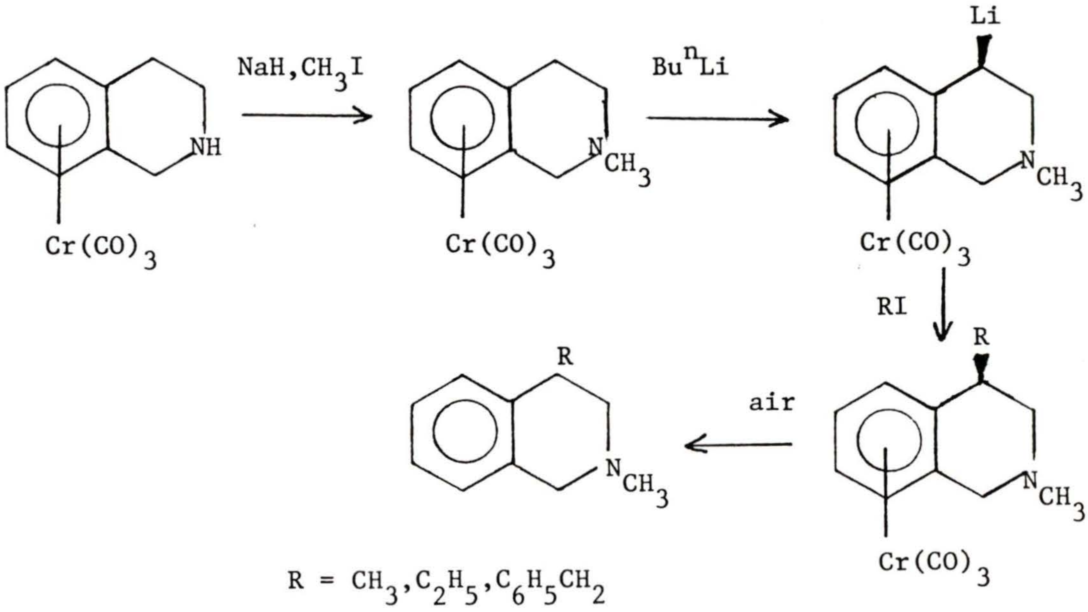
The ^{13}C NMR spectrum of the methyl adduct 34 (see Table 26) confirms regiospecific addition by the methyl carbanion. Two important features are the presence of one methyl signal at 26.8 ppm and one Cp signal at 74.3 ppm. The cyclohexadienyl carbons give rise to distinct signals: lines at 32.4, 32.5 and 33.1 ppm are assigned to C-1, C-2 and C-6 of either isomer a or b; a line at 74.5 ppm is due to C-3 of isomer b or C-5 of isomer a; and the two quaternary carbons exhibit weak signals at 102.4 and 97.1 ppm. As usual, the benzyl groups exhibit three methylene resonances at 44.0, 48.2 and 50.3 ppm and three quaternary signals at 138.9, 139.6 and 141.5 ppm.

In the IR spectrum of complex 34, the absence of an absorption in the range 2700-2800 cm^{-1} confirms the presence of an exo-methyl group: thus methyl carbanion addition occurs stereospecifically also.

The mass spectrum of the complex 34 exhibits several useful signals. Of main interest is an M+1 peak at m/e 539 as expected. An M^+ peak at m/e 538 is observed to undergo the successive loss of a methyl and phenyl group at m/e 523 and 447, respectively. Another series of signals originates from the M^+ peak: loss of CpFe is observed at m/e 417, followed by the loss of a methyl group at m/e 403; and further loss of three benzyl groups is observed at m/e 311, 221 and 131.

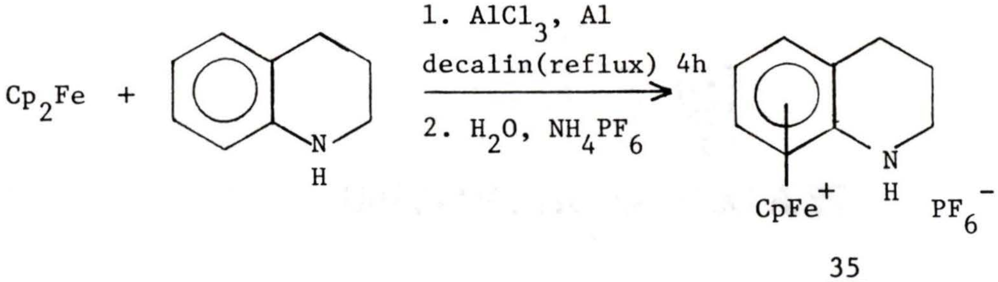
D. Benzylic substitution in $[CpFe^+(tetrahydroquinoline)]PF_6^-$

Extension of the substitution chemistry discussed earlier in this work into heterocyclic arene chemistry has also been examined briefly. Heteroarene-cyclopentadienyl iron complexes have been studied by Sutherland and coworkers[66] as part of their interest in the application of these systems in organic synthesis. More recently, Davies and coworkers[55] have investigated the substitution chemistry of some tetrahydroisoquinoline-$Cr(CO)_3$ complexes since many of these simple substituted heterocycles exhibit significant pharmacological activities (see Scheme 4). For example, the synthesis of 4-hydroxy-1,2,3,4-tetrahydroisoquinoline derivatives are of interest since these compounds are involved in alcohol addiction.[67]



Scheme 4. Nucleophilic reactions of deprotonated tetrahydroisoquinoline-$Cr(CO)_3$ complexes.

To provide an entry into the substitution chemistry of the corresponding iron system, the CpFe$^+$ complex of tetrahydroquinoline was synthesized using a procedure similiar to that reported by Helling and Hendrickson.[53] As shown in equation 50, the direct ligand exchange

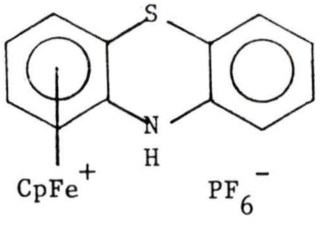


35

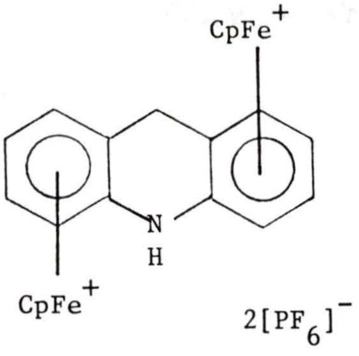
(50)

between 1,2,3,4-tetrahydroquinoline and ferrocene, effected in the presence of aluminum chloride and aluminum powder, affords the expected heterocyclic complex 35 as a bright orange powder (30%) which was fully characterized by microanalysis (see experimental section) and spectroscopic measurements (see Tables 27 and 29).

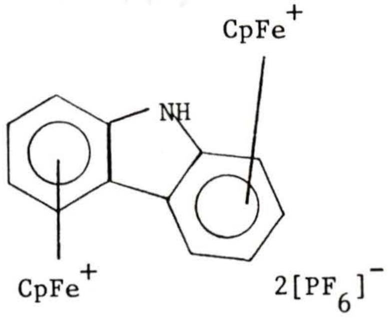
Heterocyclic iron complexes related to product 35 have been synthesized by Sutherland and coworkers[54] and are shown below (II-xvi, II-xvii, and II-xviii).



(II-xvi)



(II-xvii)



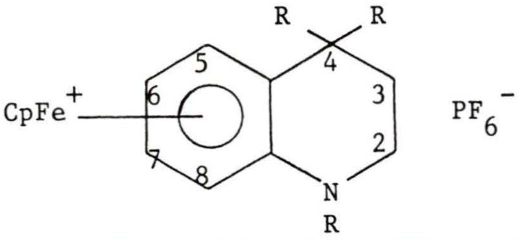
(II-xviii)

In accordance with the preparation of these known complexes, the synthesis of the new cationic species 35 also proceeds with reasonable success only if a large excess of $AlCl_3$ and elevated temperatures (190-200^{0}C) are used.

The ^{1}H NMR spectrum of complex 35 (see Table 27) shows one intense Cp signal at δ4.91 ppm, indicating a pure CpFe$^+$ complex. Metal complexation of the aromatic ring system is confirmed by the presence of two doublets and two triplets in the range δ5.68-6.05 ppm (J_{ortho} = 6.1Hz) which are assigned to the four coordinated aromatic ring protons. The β-methylene protons of the saturated ring exhibit a series of four multiplets in the range δ3.45-2.05 ppm, and the two α-methylene protons give rise to a doublet of triplets at δ2.92 ppm ($J(H_{4\alpha}-H_{4\beta})$ = 16.7Hz, $J(H_{4\alpha}-H_{3\alpha,\beta})$ = 5.3Hz) and a multiplet centred at 2.69 ppm.

In the ^{13}C NMR spectrum of complex 35 (see Table 29), one Cp signal at 76.6 ppm is indicative of only one product. Again, coordination of the aromatic ring is confirmed by four lines occurring in the range

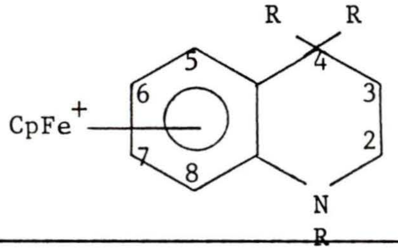
Table 27. ^{1}H NMR Spectroscopic Data for Substituted Tetrahydroquinoline Complexes 35, 38 and 39[a]



35 R_1 = H, $R_{4\alpha}$ = $R_{4\beta}$ = H
38 R_1 = CH_3, $R_{4\alpha}$ = $R_{4\beta}$ = H
39 R_1 = $R_{4\alpha}$ = $R_{4\beta}$ = CH_3

Complex	Cp (ppm)	H5–H8 (ppm)	H2–H3 (ppm)	R_1 (ppm)	$R_{4\alpha}R_{4\beta}$ (ppm)
35	4.91(s,5H)	5.68(d,1H) $J(H-H')_{ortho}$=6.4Hz 5.88(t,1H) $J(H-H')_{ortho}$=5.7Hz 5.96(t,1H) 6.05(d,1H)	3.45(m,1H,$H2_\alpha$) 3.24(m,1H,$H2_\beta$) 2.20(m,1H,$H3_\alpha$) 2.05(m,1H,$H3_\beta$)	not located	2.92(dt,1H,$H4_\alpha$) $J(H4_\alpha-H4_\beta)$ = 16.7Hz $J)H4_\alpha-H3_{\alpha,\beta})$ = 5.3Hz 2.69(m,1H,$H4_\beta$)
38	4.97(s,5H)	5.74(dd,1H) $J(H-H')_{ortho}$=6.6Hz 5.95(td,1H) $J(H-H')_{ortho}$=5.8Hz 5.98(dd,1H) 6.04(td,1H) $J(H-H')_{ortho}$=6.0Hz $J(H-H')_{meta}$=1.4Hz	3.44(m,2H,$H2_\alpha$,$H2_\beta$) 2.24(m,1H,$H3_\alpha$) 2.05(m,1H,$H3_\beta$)	3.10(s,3H,-$C\underline{H}_3$)	2.95(m,1H,$H4_\alpha$) 2.71(m,1H,$H4_\beta$)

Table 27 (continued)

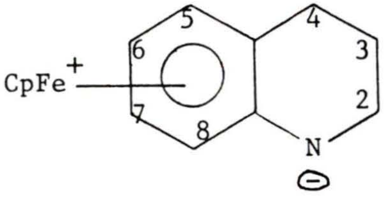


$\underline{\underline{39}}$ $R_1 = R_{4\alpha} = R_{4\beta} = CH_3$

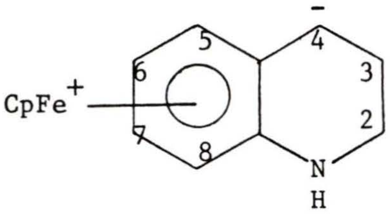
Complex	Cp (ppm)	H5-H8 (ppm)	H2-H3 (ppm)	R_1 (ppm)	$R_{4\alpha}R_{4\beta}$ (ppm)
$\underline{\underline{39}}$	4.96(s,5H)	6.17(d,1H) J_{ortho}=6.1Hz 6.10(t,1H) 5.96(t,1H) 5.82(d,1H)	3.48(m,2H,$H_{2\alpha,2\beta}$) 2.33(m,1H,$H3_\alpha$) 1.89(dt,1H,$H3_\beta$) J($H3_\alpha$-$H3_\beta$) = 13.6Hz	3.08(s,3H,-C$\underline{H}_3$)	1.21(s,3H,-C$\underline{H}_3$) 1.60(s,3H,-C$\underline{H}_3$)

Note: $^a(CD_3)_2CO$ solution; all chemical shifts measured in δ(ppm).

Table 28. ^{1}H NMR Spectroscopic Data for Deprotonated Tetrahydroquinoline Complexes 36 and 37[a,b,e]



36

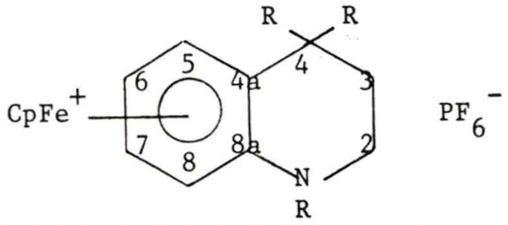


37

Complex	Cp (ppm)	H5-H8 (ppm)	H1-H4 (ppm)
36	4.00(s,5H)	6.29(d,1H) $J(\text{H-H}')_{ortho}$ = 8.1Hz 6.69(t.1H) $J(\text{H-H}')_{ortho}$ = 7.1Hz 6.92(d,1H) 7.02(t,1H) $J(\text{H-H}')_{ortho}$ = 7.5Hz	2.78(m,2H,$\text{H2}_{\alpha,\beta}$) 2.51(t,2H,$\text{H4}_{\alpha,\beta}$) J(H4-H3) = 6.3Hz 1.57(m,2H,$\text{H3}_{\alpha,\beta}$)
37	3.83(s,5H)	4.84(t,1H) $J(\text{H-H}')_{ortho}$ = 5.6Hz 4.51(d,1H) $J(\text{H-H}')_{ortho}$ = 7.7Hz 4.31(m,2H)	3.17(m,2H,$\text{H2}_{\alpha,\beta}$) 1.7-1.9[c] (2H,$\text{H3}_{\alpha,\beta}$) (H1,H4)[d]

Notes: [a] C_6D_6 solution. [b] Ratio of products ca. 81:19, respectively. [c] complex series of multiplets. [d] not located. [e] all chemical shifts measured in δ(ppm).

Table 29. ^{13}C NMR Spectroscopic Data for Substituted Tetrahydroquinoline Complexes 35, 38 and 39[a]



35 $R_1 = H$, $R_{4\alpha} = R_{4\beta} = H$
38 $R_1 = CH_3$, $R_{4\alpha} = R_{4\beta} = H$
39 $R_1 = R_{4\alpha} = R_{4\beta} = CH_3$

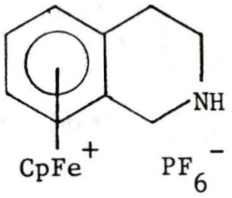
Complex	R_1 (ppm)	C2–C4 (ppm)	C5–C8 (ppm)	C4a,C8a (ppm)	Cp (ppm)	$R_{4\alpha}R_{4\beta}$ (ppm)
35		41.0 (C2) 26.8 (C4) 21.2 (C3)	68.2, 79.9 85.3, 86.8	125.1 (8a) (4a)[b]	76.6	
38	39.0 ($-\underline{C}H_3$)	50.8 (C2) 27.4 (C4) 21.3 (C3)	65.5, 80.2 85.1, 86.9	b	76.1	
39	39.0 ($-\underline{C}H_3$)	47.3 (C2) 35.8 (C3) (C4)[a]	66.4, 79.2 83.0, 85.3	93.5 (4a) 125.4 (8a)	75.7	28.3 ($-\underline{C}H_3$) 30.0 ($-\underline{C}H_3$)

Notes: [a] $(CD_3)_2CO$ solution; all chemical shifts measured in ppm. [b] not found.

68.2-86.8 ppm. As expected, C-2 of the saturated ring is deshielded at 41.0 ppm relative to C-3 and C-4 which give rise to lines at 21.2 and 26.8 ppm, respectively.

IR spectroscopy for complex 35 shows an intense absorption at 3440 cm^{-1} attributed to N-H stretching vibrations. The mass spectrum for complex 35 gives rise to a peak at m/e 254 which corresponds to the cation $CpFe^+(C_9H_{11}N)$. A prominent signal at m/e 186 arises from Cp_2Fe^+, and the base peak occurs at m/e 133 due to the free aromatic ligand.

Attempts at synthesizing the isomeric complex [tetrahydroisoquinoline-FeCp]$^+PF_6^-$ (II-xix) have been unsuccessful.



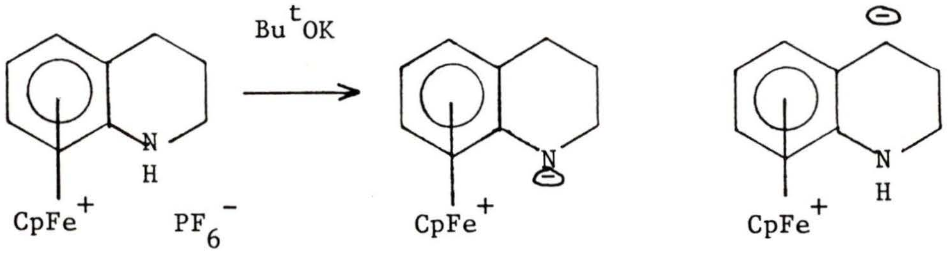
(II-xix)

Although the efficient synthesis of the analogous $Cr(CO)_3$ complex, obtained via thermolysis of hexacarbonylchromium with the heteroarene, has been reported in good yield (90%) by Davies and coworkers,[55] problems associated with the formation of the analogous iron complex may be due to decomposition of the heterocyclic ligand which could be facilitated by the presence of $AlCl_3$. Cleavage of amines, initiated by their nucleophilic attack at cyanogen bromide, is well known as the von Braun reaction,[68] equation 51.

$$R_3N + BrCN = R_2NCN + RBr \qquad (51)$$

In particular, the ease of cleavage of R groups follows the order: allyl, benzyl > methyl > ethyl.[69] In relation to the tetrahydroisoquinoline system, a possible reaction is that cleavage at the benzylic position adjacent to the nitrogen 2-position is initiated by nucleophilic attack at aluminum chloride. Although this has not been confirmed, it may be one of the dominant side reactions involved in the preparation of the tetrahydroisoquinoline iron complex.

Electrophilic substitution chemistry of the tetrahydroquinoline complex 35 has been investigated (see Scheme 7). Prior to carrying out substitution reactions, the deprotonation of complex 35 with Bu^tOK (equation 52) was examined by ^1H NMR spectroscopy.



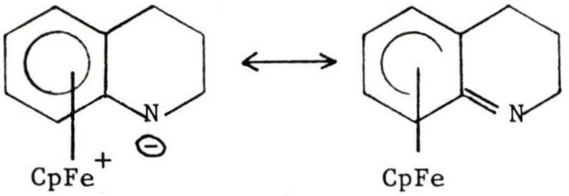
(52)

35 36 37

Ratio of products 81:19

As shown by the ^1H NMR spectrum of the neutral products 36 and 37 (see Table 28), two Cp singlets appear at δ4.00 and 3.83 ppm (ca. 81:19 ratio, respectively) indicative of the presence of two different deprotonated species. As expected, the higher intensity signals of the major product 36 correspond to the species resulting from deprotonation at the nitrogen. This result is in accordance with the fact that N-H hydrogens are usually more acidic than C-H hydrogens since nitrogen is more electronegative than carbon.[68] In addition, deprotonated species 36 and 37 are sufficiently air-stable to allow characterization by ^{1}H NMR spectroscopy, an observation which contrasts with the extreme air- and moisture-sensitivity of deprotonated tetralin complex 1. For complex 36, the most characteristic signals are associated with the coordinated ring: two doublets occur at δ6.29 and 6.92 ppm and two triplets appear at δ6.69 and 7.02 ppm (J_{ortho} = 7.6Hz). For the saturated ring region, the most deshielded multiplet occurring at δ2.78 ppm may be assigned to the methylene protons H-2$_{\alpha,\beta}$ adjacent to the deprotonated nitrogen atom. A triplet at δ2.51 ppm (J(H4-H3) = 6.3Hz) may arise from the benzylic α-protons H-4$_{\alpha,\beta}$, and a multiplet centred at δ1.57 ppm may be assigned to the β-methylene protons H-3$_{\alpha,\beta}$.

The positions of these absorption patterns may provide support for the formulation of complex 36 as one of the following: a zwitterionic species, a cyclohexadienyl complex, or an intermediate between these two structures, 36a and 36b. The four signals appearing in the range δ6.29-

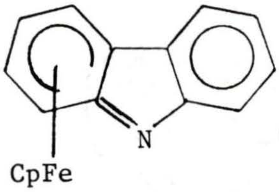


36a

36b

7.02 ppm are all significantly deshielded relative to the resonance patterns characteristic of cyclohexadienyl complexes which have been described by Watts and coworkers.[40] These results imply that canonical form 36a makes a significant contribution to the structure of complex 36 since signals appearing in the range δ6-7 ppm are most characteristic of π-complexed arene protons.

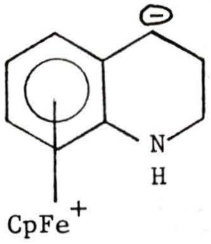
One example of a related deprotonated complex, which has been described by Helling and Hendrickson,[52] is shown in (II-xx). For the



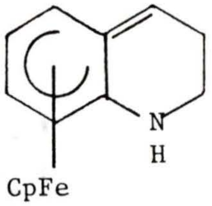
(II-xx)

coordinated ring protons of this complex, the corresponding signals appeared in the range δ5.5-7.2 ppm indicating a structure intermediate between the zwitterionic and cyclohexadienyl formulations.

For the minor product 37, which is present in a relatively negligible amount, the signals associated with the coordinated ring are significantly shielded relative to those of complex 36: a triplet occurs at δ4.84 ppm, J_{ortho} = 5.6Hz), a doublet appears at δ4.51 ppm (J_{ortho} = 7.7Hz), and a multiplet is observed at δ4.31 ppm (integrating to two protons). These spectroscopic data imply that for the structure of complex 37, the canonical form 37b makes a greater contribution than



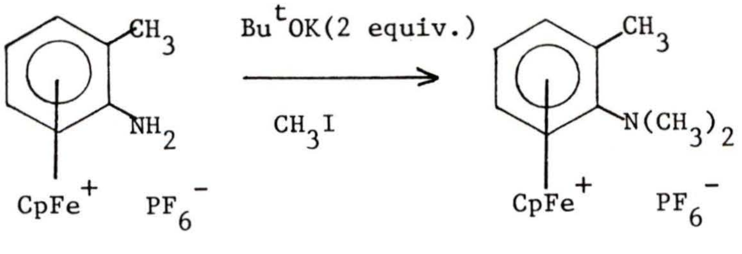
37a



37b

37a since cyclohexadienyl proton absorptions usually occur at higher field than those of η^6-coordinated aromatic rings.

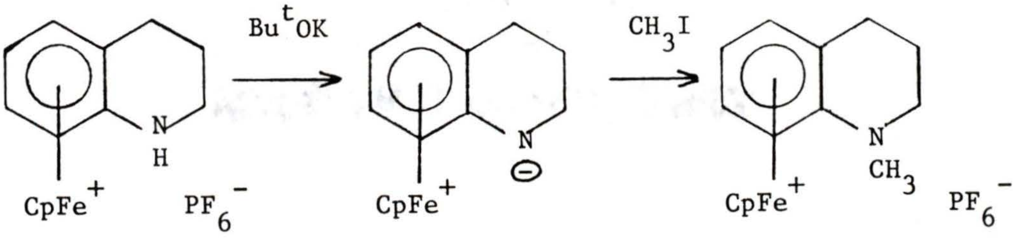
The results discussed above parallel those reported by Sutherland and coworkers[70] who carried out deprotonation studies on iron complexes from o-, m- and p-toluidines. The results from this investigation showed that if an α-amino hydrogen and at least one benzylic hydrogen are both present in the arene moiety, deprotonation with base takes place exclusively at the nitrogen. As shown in equation 53, the deprotonation



(53)

of the o-toluidine complex with Bu^tOK and subsequent treatment with excess CH_3I affords only the N,N-dimethylated complex.

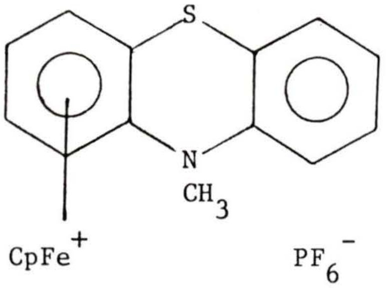
In view of the results discussed above, it was apparent that the reaction of deprotonated 35, consisting mainly of complex 36, with iodomethane would result in the formation of the N-methylated complex 38, equation 54. Complex 38, a bright orange powder, was fully characterized by microanalysis (see experimental section) and spectroscopic measurements (see Tables 27 and 29).



(54)

35 38

In the ^{1}H NMR spectrum of complex 38 (see Table 27), one Cp signal is observed at δ4.97 ppm, indicative of only one product. The most characteristic signal is a deshielded singlet at δ3.10 ppm which may be assigned to the N-methyl group; hence, preferential electrophilic substitution at the nitrogen site is indicated. The position of this methyl signal is similar to that of a related complex, [CpFe(methylphenothiazine)]$^+$PF$_6^-$ (II-xxi), synthesized by Sutherland and coworkers.[71] The methyl group for this complex exhibits a singlet at



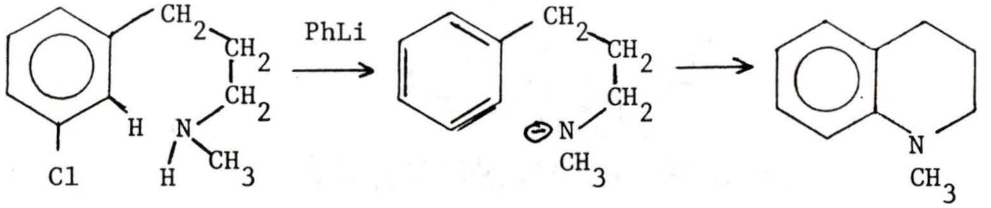
(II-xxi)

δ3.5 ppm, thus indicating that N-methylation occurs in complex 38. Other interesting features include two doublets of doublets at δ5.74 and 5.98 ppm, and two triplets of doublets at δ5.95 and 6.04 ppm (J_{ortho} = 6.1Hz, J_{meta} = 1.4Hz) arising from the complexed aromatic protons.

The ^{13}C NMR spectrum of complex 38 (see Table 29) confirms that methylation occurs only at the nitrogen atom: a distinct line at 39.0 ppm is assigned to the methyl group which is considerably deshielded due to its proximity to the nitrogen atom. Another interesting feature is a signal at 50.8 ppm which may be assigned to C-2, the methylene carbon directly adjacent to the N-methyl moiety.

In the IR spectrum of the N-methylated complex 38 the absence of an absorption near 3400 cm^{-1} confirms that N-H is no longer present. The mass spectrum of complex 38 shows a small intensity signal at m/e 253 corresponding to loss of a methyl group from $[CpFe(C_{10}H_{13}N)]^{+}$. The free uncoordinated methylated ligand $C_{10}H_{13}N$ gives rise to a signal at m/e 147 which is followed by the loss of CH_3 at m/e 132.

The organic synthesis of the known heterocyclic compound N-methyl-tetrahydroquinoline has been reported by Konig and Huisgen,[72] equation 55.

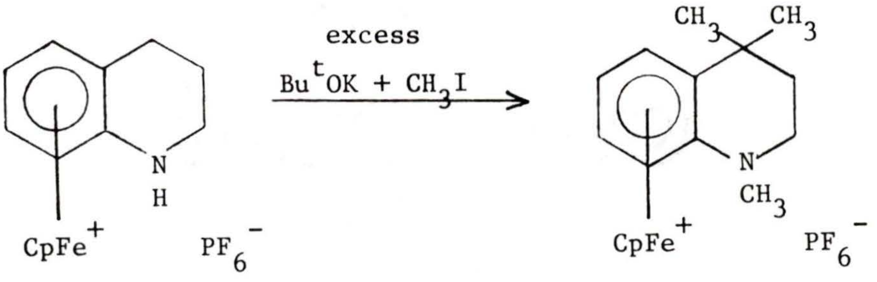


(55)

As shown in equation 55, the ring closure principle involves the formation of a benzyne intermediate having a side chain bearing a strong nucleophile which can add intramolecularly to the six-membered ring. The metal-assisted route represented in equation 41 may therefore provide an alternate pathway to the synthesis of this compound.

Per-α-substitution in the tetrahydroquinoline complex 35 was also accomplished *via* reaction with excess Bu^tOK and iodomethane, which afforded complex 39 as a bright orange powder, equation 56. Full characterization of complex 39 was possible again using microanalysis (see experimental section) and spectroscopic measurements (see Tables 27 and 29).

In the ^1H NMR spectrum of the per-α-methylated complex 39 (see Table 27), one Cp singlet at δ4.96 ppm is again indicative of a pure complex. Featured prominently in the spectrum are three singlets at δ1.21, 1.60 and 3.08 ppm confirming the presence of three inequivalent methyl groups.



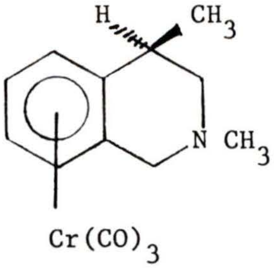
(56)

35 39

confirming the presence of three inequivalent methyl groups.

In the ^{13}C NMR spectrum of complex 39 (see Table 29) the presence of three methyl signals conclusively proves the formulation of this cation: two lines at 28.3 and 30.0 ppm are due to the exo- and endo-methyl groups, and the N-methyl group shows a deshielded signal at 39.0 ppm, as expected.

One example of a heterocyclic arene complex in which substitution has occurred at both the benzylic and amino sites has been reported by Davies and coworkers[55] and is shown in (II-xxii). Only a single

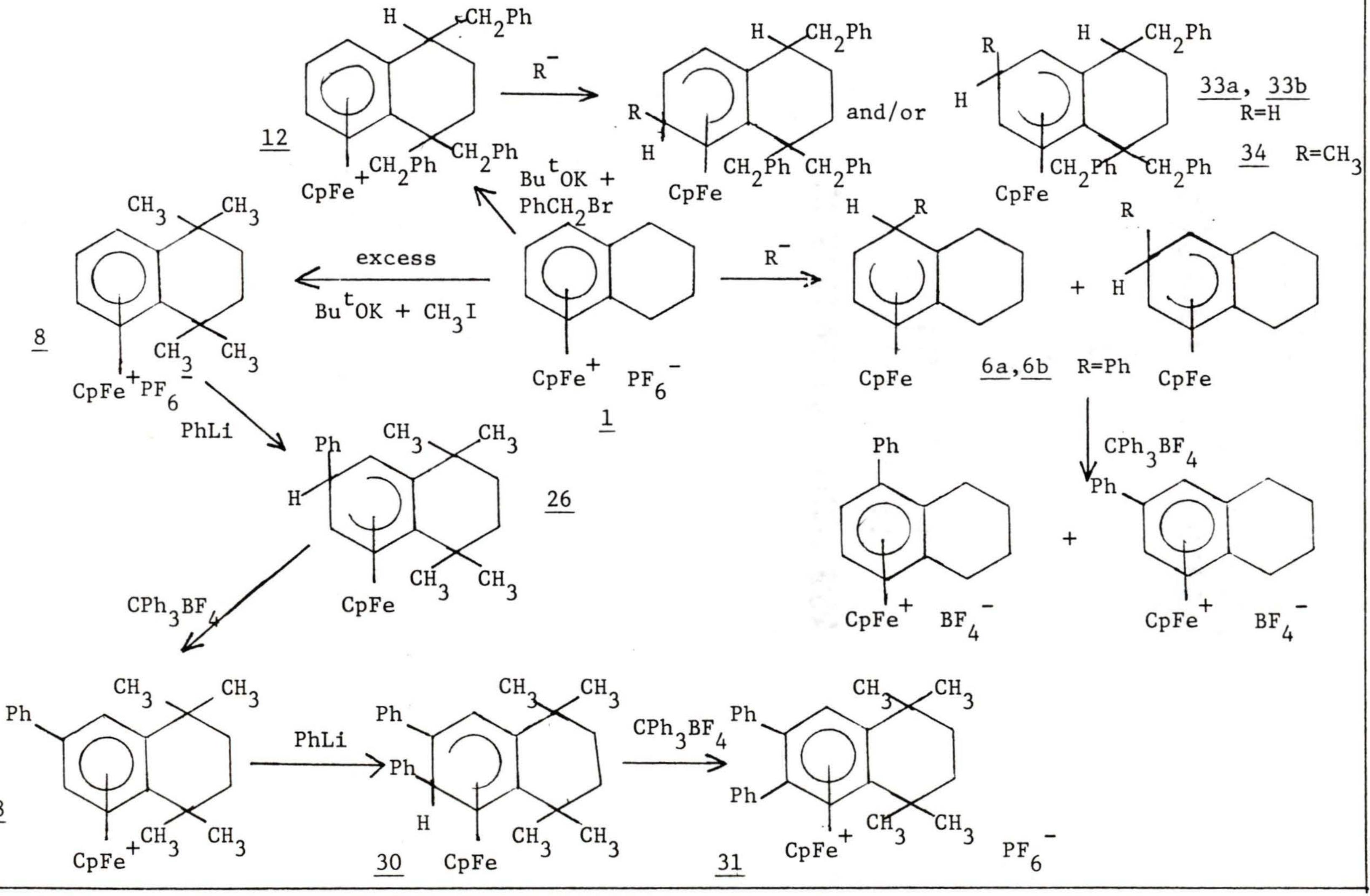


(II-xxii)

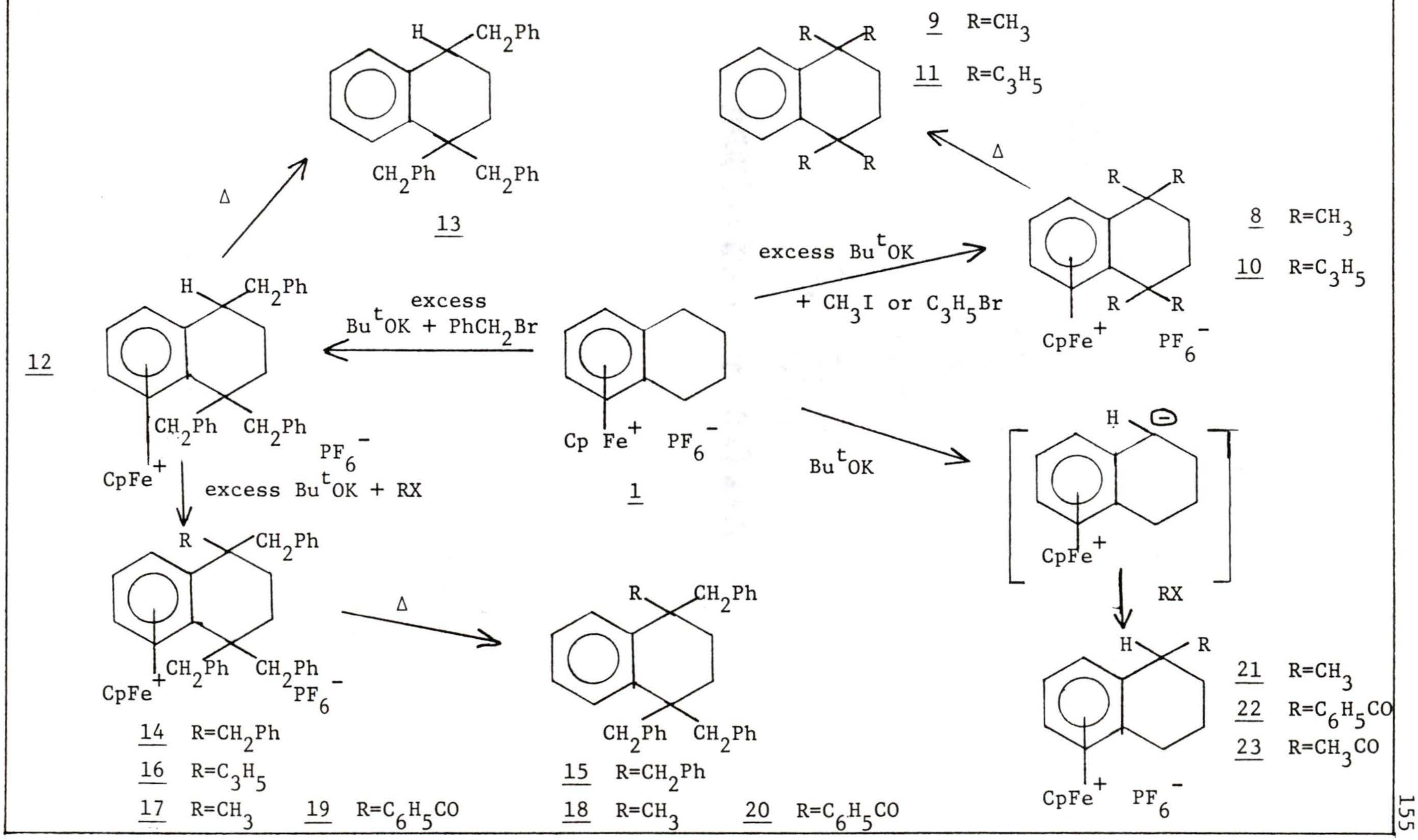
diastereomer of the $Cr(CO)_3$ complex, containing an exo-substituted methyl group, was observed indicating stereospecific electrophilic addition had occurred. This behaviour sharply contrasts with the iron system in which the formation of the mono-methylated tetralin derivative 21 discussed earlier proceeds with 72% stereoselectivity for the exo-methylated diastereomer. These observations indicate that the bulk of the $Cr(CO)_3$ moiety is greater than that of the $CpFe^+$ fragment in protecting the endo-face of an arene molecule. Although mono-methylation at the benzylic site of complex 39 has not been carried out, by analogy with complex 21 it is likely that results similar to those observed for the latter will be obtained.

In conclusion, it is evident from the results discussed above that substitution chemistry in the tetralin fragment of complex 1 may be accomplished *via* nucleophilic addition/hydride abstraction reactions (see Scheme 5) or benzylic carbanion substitution reactions (see Scheme 6). Nucleophilic addition to the coordinated aromatic ring of cationic complex 1 produces mixtures of isomeric neutral cyclohexadienyl compounds. In certain cases, considerable α-regioselectivity is observed although no rationale for these results has been found. For example generation of the phenyl adducts 6a and 6b, occurring with moderately high α-regioselectivity (64%) for compound 6a, is possible from the reaction of complex 1 with phenyl-lithium. Subsequent oxidation of 6a and 6b with Ph_3CBF_4 regenerates cationic complexes 7a and 7b, each containing known monophenyl-substituted tetralin ligands. By contrast, oxidation of t-butyl adducts 5a and 5b with Ph_3CBF_4 produces only complex

Scheme 5. Substitution chemistry of [CpFe(tetralin)]$^+PF_6^-$ *via* nucleophilic addition/hydride abstraction



Scheme 6. Summary of benzylic carbanion substitution reactions of $[CpFe(tetralin)]^+PF_6^-$



1 in low yield which implies that alkyl group abstraction is a dominant process here.

Benzylic carbanion substitution reactions in the saturated ring system of complex 1 afford tetra-, tri- and mono-substituted complexes. For example, per-α-methylation of complex 1, proceeding *via* deprotonation with excess Bu^{t}OK and reaction with excess iodomethane, results in the formation of the tetramethyltetralin complex 8. In a similar reaction using benzyl bromide as the alkylating reagent, the target complex (i.e. per-α-benzylated complex) is not obtained initially; instead, the tribenzyltetralin complex 12 is formed stereospecifically. This tri-substituted pattern may reflect the steric requirements of the benzyl group. Further reaction of complex 12 with excess base and benzyl bromide affords the expected tetrabenzyltetralin complex 14; however, other tetra-substituted derivatives may be obtained also using similar electrophilic reagents, e.g. allyl iodide, methyl iodide and benzoyl chloride. In these chiral tetralin derivatives 16-19, diastereomeric mixtures are present in all cases, except for the allyl adduct 16 which is formed stereospecifically. Spectroscopic data for the methyl and benzoyl adducts 17 and 19, respectively, show a high degree of stereoselectivity for complex 17 relative to complex 19: these results imply that the steric demand of the benzyl group is greater than that of the methyl group, but comparable to that of the benzoyl group. Mono-substituted complexes may be formed also *via* deprotonation of complex 1, isolation of the resulting "zwitterionic" species, and subsequent electrophilic attack. Examination of the spectroscopic data for complexes 21-23 suggest that stereospecific exo-addition by the electrophile is preferred for groups larger than methyl (e.g. benzoyl, acetyl).

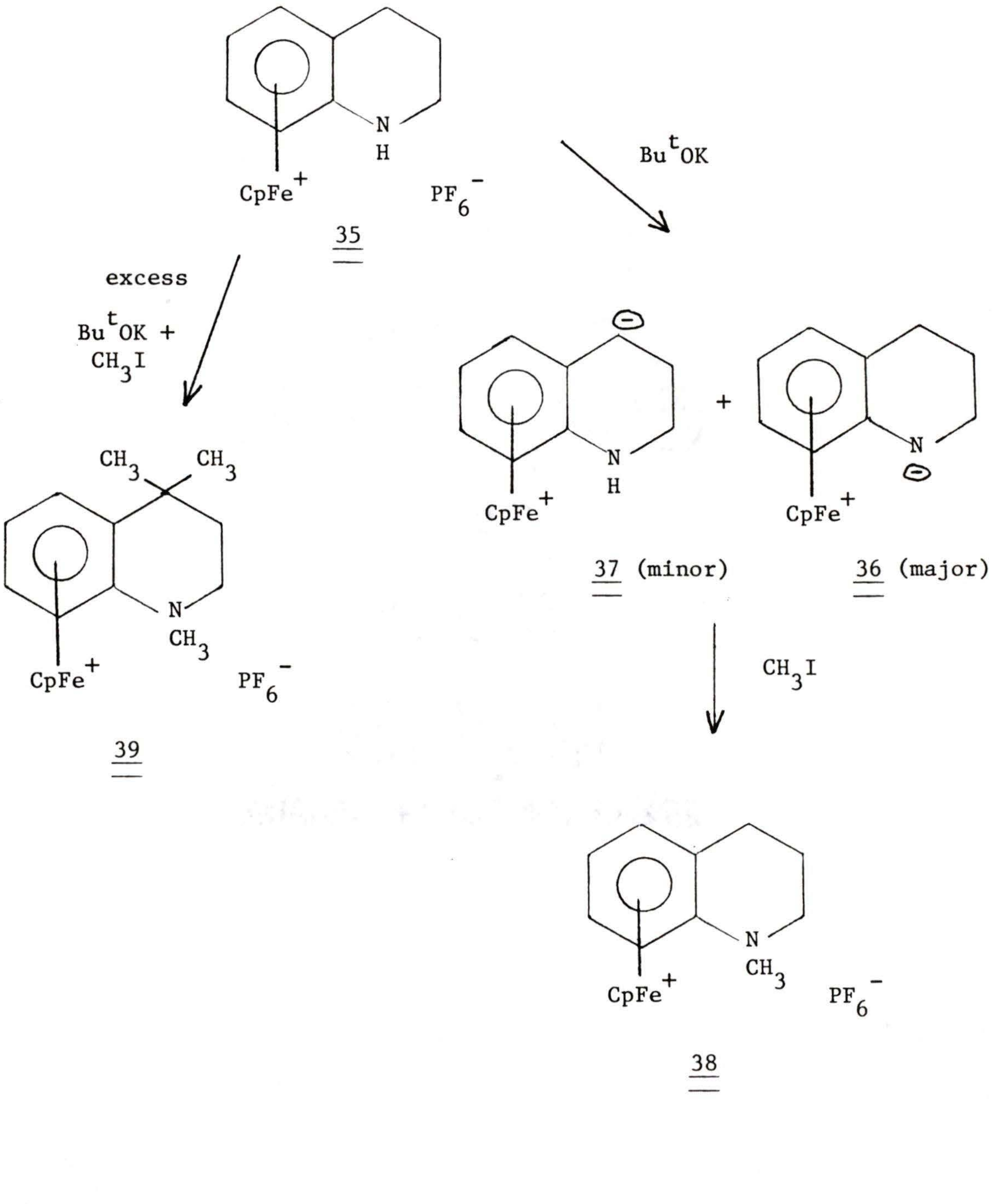
Pyrolytic sublimation of the tetra- and tri-substituted complexes produce the corresponding free aromatic compounds. For iron complexes 8 and 10, signals in the NMR spectra arising from exo- and endo-R groups become indistinguishable in the NMR spectra of the corresponding uncomplexed ligands due to the absence of the $CpFe^+$ moiety in the latter. Similar decomposition reactions for iron complexes containing a chiral centre which exists due to the presence of more than one type of R group in the saturated ring (e.g. 17 and 19), produce two diastereomeric organic ligands in each case which give rise to only one set of signals in the NMR spectra. For example, the decomplexation reaction of complex 17, which exhibits two methyl signals in the ^1H and ^{13}C NMR spectra, produces the free ligand 18 which shows only one set of signals in the ^1H and ^{13}C NMR spectra. This observation may be attributed to a rapid interconversion between diastereomers of compound 18 thus generating indistinguishable axial and equatorial methyl groups.

Substitution chemistry of complex 1 may be accomplished also utilizing both routes discussed above i.e. benzylic and nucleophilic substitution reactions. For example, nucleophilic attack by $C_6H_5^-$ into the coordinated aromatic ring system of the tetramethyltetralin complex 8 proceeds regio- and stereospecifically as shown by the formation of only a single isomer 26. In relation to per-α-substitution in the saturated ring of complex 8, this result implies that a steric factor is most likely involved in directing the orientation of nucleophilic addition into the complexed aromatic ring. Subsequent reaction of complex **26** with Ph_3CBF_4 produces the expected monophenyl-tetramethyltetralin derivative **28**. Further reaction of complex **28** with phenyl-lithium and Ph_3CBF_4 affords the diphenyl-tetramethyltetralin derivative **31**. These reactions demonstrate the steric control of substitution in the coordinated aromatic ring system of the tetralin fragment as a consequence of benzylic substitution in the saturated ring.

A brief examination of the substitution chemistry of the tetrahydroquinoline system (see Scheme 7) shows that initial deprotonation of complex **35** with Bu^tOK results in the preferential formation of an anion at the amino site, complex **36**. ^1H NMR spectroscopic data for complex **36** suggest a zwitterionic formulation which is also consistent with its reactivity towards iodomethane resulting in the formation of the N-methylated derivative **38**. Per-α-methylation of complex **35** is also possible *via* reaction with excess base and iodomethane which affords the trimethylated derivative **39**.

Further work in this area would involve observing the substitution pattern in the coordinated aromatic ring systems of these heterocycles and to investigate a more efficient synthetic route to the formation of $CpFe^+$(heteroarene) complexes.

Scheme 7. Deprotonation and electrophilic substitution reactions of $[CpFe(tetrahydroquinoline)]^+PF_6^-$



PART III

EXPERIMENTAL

A. General

All experimental manipulations were performed under an atmosphere of argon or dinitrogen using standard Schlenk techniques. Solvents were dried over a suitable reagent and freshly distilled under dinitrogen prior to use. Tetrahydrofuran, anhydrous diethyl ether and benzene were distilled from sodium/benzophenone, hexanes from $LiAlH_4$, and dichloromethane from calcium hydride. All other solvents were dried over molecular sieves before use. Other commercial chemicals were used as received.

Elemental analyses were performed by the Canadian Microanalytical Services Ltd., Vancouver. ^{1}H and ^{13}C NMR spectra were recorded by Mrs. C. Greenwood using a Bruker WM250 (250 MHz) spectrometer at 250 MHz for ^{1}H and 62.9 MHz for ^{13}C NMR experiments. All ^{1}H NMR chemical shifts were recorded in δ(ppm). Infrared spectra were obtained using a Perkin Elmer 283 Infrared Spectrophotometer. Mass spectra were recorded by Dr. D.L. McGillivray using a Finnigan 3300 Gas Chromatograph Mass Spectrometer.

B. Synthesis of Complexes

η^6-1,2,3,4-Tetrahydronaphthalene-η^5-cyclopentadienyliron hexafluorophosphate, 1.[30]

Ferrocene (11.2 g, 60 mmol), $AlCl_3$ (16 g, 120 mmol) and Al powder (1.6 g, 60 mmol) were refluxed in tetralin (100 ml) for 17 hours under N_2. After cooling the mixture, ice was added until the excess $AlCl_3$ was destroyed. Following filtration of the mixture, the greenish-brown aqueous layer was separated and washed with petroleum ether (b.p.30-60^0, 4x50 ml). Excess NH_4PF_6 (10 g) was added producing a bright yellow precipitate. The solid was filtered, dissolved in dichloromethane (60 ml), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The product was purified by passage through a neutral alumina column (20x3 cm^2). Elution with acetone was followed by evacuation of the eluate. Addition of diethyl ether and petroleum ether to a methanol solution of the eluate precipitated the product as a light yellow powder (15 g, 61%) with properties identical with those reported in the literature.[30] Anal. Calcd. for $C_{15}H_1F_6FeP$: C, 45.25; H, 4.30. Found: C, 46.87; H, 4.69.

m.p. 190-194^{0}C (lit. 202-204^{0}C)

IR (KBr): 3120 m, 2940 m, 2870 m, 1460 m, 1430 m, 1420 m, 830 s br, 555 s, 495 m, 470 m, 440 m, cm^{-1}.

Mass Spectrum, 300^{0}C probe temperature, CH_4 chemical ionization. (m/e, rel.int.): 254(2); 186(47); 133(91); 132(76); 131(57); 107(100); 104(58); 91(91).

η^5-2,3-butanocyclohexadienyl-η^5-cyclopentadienyliron, 2a; and η^5-3,4-butanocyclohexadienyl-η^5-cyclopentadienyliron, 2b.

Method A. A stirred suspension of 1 (0.50 g, 1.3 mmol) in THF (10 ml) was treated with NaBH$_4$ (0.15 g, 3.9 mmol). Addition of methanol (3 ml) resulted in vigorous bubbling and warming of the reaction mixture producing a clear bright red solution. After 5 minutes, the solution was evacuated to dryness. Extraction of the orange residue with petroleum ether (b.p.30-60^0C, 15 ml) was followed by the addition of distilled water (10 ml). The orange organic layer was separated and chromatographed on a neutral alumina column (8x3 cm^2). Elution with diethyl ether followed by evacuation of the eluate afforded an isomeric mixture of 2a and 2b (determined by ^{1}H NMR spectroscopy) as a red viscous oil (0.23 g, 70%).

Mass Spectrum, ambient probe temperature, electron impact.(m/e,rel.int.) 254(50); 253(86); 225(43); 188(28); 184(100); 121(53); 56(86).

IR (NaCl): 3090 m, 3020 m, 2920 s, 2860 s, 2760 s, 1490 w, 1440 s, 1430 s, 1105 s, 1000 s, 800 s cm^{-1}.

Method B. Using a procedure similar to Method A except that LiBEt$_3$H was used instead of NaBH$_4$ and no methanol was added, hydride reduction of 1 was carried out. The final product was obtained as a red oil (0.32 g, 97%) similar to that obtained using Method A.

η^5-Deuterio- 2,3-butanocyclohexadienyl-η^5-cyclopentadienyliron, 3a ; and η^5-Deuterio-3,4-butanocyclohexadienyl-η^5-cyclopentadienyliron, 3b .

To a stirred suspension of 1 (0.30 g, 0.75 mmol) in THF (10 ml) was added $LiBEt_3D$ (0.11 g, 1 mmol, 1 ml) resulting in a clear red solution immediately. Volatiles were removed *in vacuo* and the reaction mixture was worked up as in the preparation of 2a and 2b. The final product was obtained as a red oil (0.18g, 95%) consisting of an isomeric mixture of 3a and 3b.

Mass Spectrum, ambient probe temperature, electron impact.(m/e,rel.int.) 255(41); 254(26); 253(13); 226(21); 189(12); 186(10); 185(39); 121(82); 92(100).

IR (NaCl): 3090 s, 3010 s, 2920 s, 2850 s, 2800 s, 2040 s, 1450 s, 1440 s, 1430 s, 1345 m, 1270 m, 1240 m, 1100 s, 1050 m, 1000 s, 990 s, 800 s cm^{-1}.

η^5-n-butyl-2,3-butanocyclohexadienyl-η^5-cyclopentadienyliron, 4a ; and η^5-n-butyl-3,4-butanocyclohexadienyl-η^5-cyclopentadienyliron, 4b .

n-Butyllithium (8 mmol, 5 ml) in hexanes was added to a stirred suspension of 1 (0.20 g, 0.50 mmol) in THF (15 ml) at -78°C (acetone-dry ice slush). An immediate colour change from yellow to clear brown-orange occurred. After warming to room temperature the solution was evacuated to dryness. Extraction of the dark mixture with diethyl ether (15 ml) was followed by the addition of distilled water (10 ml). The orange organic layer was separated, and chromatographed on a neutral alumina column (8x3 cm^2). Elution with diethyl ether followed by evacuation of the eluate afforded an isomeric mixture of 4a and 4b as a red viscous oil (*ca.* 60% yield).

IR (NaCl): 3100 m, 3030 m, 2940 s, 2860 s, 1460 s,br, 1380 s, 1350 m, 1340 m, 1250 m, 1110 s, 1060 s,br, 810 s cm^{-1}.

η^5-t-butyl-2,3-butanocyclohexadienyl-η^5-cyclopentadienyliron, **5a** ; *and η^5-t-butyl-3,4-butanocyclohexadienyl- η^5-cyclopentadienyliron,* **5b** . Following a procedure similar to that described for the preparation of **4a** and **4b**, the reaction of complex **1** (1.0 g, 2.5 mmol) with t-butyllithium (7 mmol, 3 ml) in pentane gave an isomeric mixture of **5a** and **5b** as a red oil in 80% yield.

Mass Spectrum, ambient probe temperature, electron impact.(m/e,rel.int.)
310(1); 253(100); 185(12); 184(9); 121(42)

IR (NaCl): 3050 m, 3030 m, 2940 s, 2860 s, 1470 s, 1455 s, 1445 s, 1435 s, 1385 s, 1360 s, 800 s cm^{-1}.

η^5-Phenyl-2,3-butanocyclohexadienyl-η^5-cyclopentadienyliron, **6a** ;and *η^5-Phenyl-3,4-butanocyclohexadienyl-η^5-cyclopentadienyliron,* **6b** . Using a procedure similar to the preparation of **4a** and **4b**, the reaction of complex **1** (1.0 g, 2.5 mmol) with phenyllithium (4.6 mmol, 3.0 ml) in cyclohexane/diethyl ether yielded an isomeric mixture of **6a** and **6b** (96%).

Mass Spectrum, ambient probe temperature, electron impact.(m/e,rel.int.)
330(4); 329(4); 253(3); 208(5); 154(100).

IR (NaCl): 3080 m, 3060 m, 3020 m, 2920 s, 2880 s, 2860 s, 1600 m, 1490 s, 1480 s, 1445 s, 1435 s, 1105 s, 1070 m, 1025 m, 1000 m, 800 s, 730 s, 695 s cm^{-1}.

η^6-1,2,3,4-Tetrahydro-5-phenylnaphthalene-η^5-cyclopentadienyliron tetrafluoroborate, 7a ; and η^6-1,2,3,4-Tetrahydro-6-phenylnaphthalene-η^5-cyclopentadienyliron tetrafluoroborate, 7b .

To a stirred solution of 6a and 6b (0.80 g, 2.4 mmol) in dichloromethane (25 ml) was added triphenylmethyltetrafluoroborate (0.66 g, 2.0 mmol). An immediate colour change from clear red to opaque brownish-yellow occurred. After 30 minutes, the solvent was removed *in vacuo* and the oily brown material was washed in diethyl ether. Following the addition of dichloromethane (15 ml) and distilled water (20 ml), the red organic layer was separated, dried over $MgSO_4$, and purified by passage through an alumina column (15x3 cm^2). Elution with acetone gave an orange solution. After concentration and addition of diethyl ether, the product was obtained as a light orange solid (0.20 g, 20%) consisting of an isomeric mixture 6a and 6b.

m.p. 85-90^{0}C.

IR (KBr): 3100 m, 2930 m, 2860 m, 1625 w,br, 1380 s, 1050 s,br, 850 m, 760 m, 700 m cm^{-1}.

Mass Spectrum, 350^{0}C probe temperature, CH_4 chemical ionization. (m/e,rel.int.) 339(2); 209(100); 207(18); 187(6); 186(4).

Reaction of 5a and 5b with triphenylmethyltetrafluoroborate.

To a stirred solution of 5a and 5b (0.63 g, 2 mmol) in dichloromethane (10 ml) was added triphenylmethyltetrafluoroborate (0.66 g, 2 mmol). An immediate colour change from clear red to cloudy orange occurred. After

30 minutes, removal of the solvent and workup as for 7a and 7b were carried out. The final product, 1, was isolated as a yellow powder (0.05 g).

η^6-1,2,3,4-Tetrahydro-1,1,4,4-tetramethylnaphthalene-η^5-cyclopentadienyliron hexafluorophosphate, 8 .

To a mixture of complex 1 (3.0 g, 7.5 mmol) and Bu^{t}OK (12.6 g, 113 mmol) was added a solution of iodomethane (16 g, 113 mmol) in THF (100 ml). A vigorous reflux occurred and the solution colour changed from dark red to orange with the formation of a beige precipitate. Following 16 hours of stirring, the volatiles were removed in vacuo. The creamy solid was washed in diethyl ether, and then in distilled water (100 ml). The solid was filtered, dried over $MgSO_4$ in dichloromethane, concentrated in vacuo and was chromatographed on a neutral alumina column (15x3 cm^2). Elution with acetone followed by concentration to 10 ml and the addition of excess ether afforded the product as an orange powder (2.2 g, 64%).

Anal. Calcd. for $C_{19}H_{25}F_6FeP$: C, 50.24 ; H, 5.55.

Found: C, 51.60 ; H, 5.80.

m.p. 192^{0}C (decomposition)

IR (KBr): 3120 w, 2970 m, 2940 m, 2870 m, 1610 w, 1460 m, 1450 m, 1420 m, 1380 m, 1370 m, 870 s, 830 s, 830 s,br, 555 s, 495 m, 470 m cm^{-1}.

Mass Spectrum, 180^{0}C probe temperature, electron impact.(m/e, rel.int.): 188(24); 186(42); 173(100); 121(15)

1,2,3,4-Tetrahydro-1,1,4,4-tetramethylnaphthalene, 9 .

A sample of complex 8 (0.24 g, 0.53 mmol) was pyrolyzed by heating under vaccuum and the volatiles collected on a cold finger at -78^{0}C. The resulting yellowish sublimate was dissolved in diethyl ether and purified by passage down a short alumina column (5x3 cm^2) affording the product as a clear colourless oil,(*ca.* 45% yield) after evaporation of the solvent.
Mass Spectrum, ambient probe temperature, electron impact.(m/e,rel.int.) 188(15); 173(71); 131(100).
IR (NaCl): 3100 w, 3070 w, 3030 w, 2970 s, 2940 s, 2860 s, 1605 w, 1490 s, 1445 s, 1390 s, 1365 s, 1075 s, 1045 s, 810 w, 755 s, 540 m cm^{-1}.

η^6-1,2,3,4-Tetrahydro-1,1,4,4-tetraallylnaphthalene-η^5-cyclopentadienyliron hexafluorophosphate, 10 .

A stirred suspension of complex 1 (0.41 g, 1.0 mmol) in THF (40 ml) was treated with Bu^{t}OK (2.2 g, 20 mmol) resulting in a dark red solution. After five minutes, allyl bromide (6.1 g, 50 mmol) was added. During 16 hours of stirring the colour gradually faded to light orange-brown with the formation of a beige precipitate. Volatiles were removed *in vacuo*, and the light beige solid was worked up in distilled water and purified by alumina chromatography as for the synthesis of complex 8.
Precipitation of the product from methanol/diethyl ether afforded a light orange powder (0.28 g, 49%). Anal. Calcd. for $C_2H_{33}F_6FeP$: C, 58.08 ; H, 5.96. Found : C, 57.39 ; H, 5.65.

m.p. 204^{0}C

IR (KBr): 3120 w, 3080 w, 2980 w, 2950 w, 2860 w, 1640 m, 1450 m, 1420 m, 1000 m, 920 br, 870 m, 830 s,br, 560 s, 470 m cm^{-1}.

Mass Spectrum, 250^{0}C probe temperature, CH_4 chemical ionization. (m/e,rel.int.): 347(1); 251(100); 211(7); 210(5); 209(16); 187(25); 186(21); 169(14).

1,2,3,4-Tetrahydro-1,1,4,4-tetraallylnaphthalene, 11 .

Following a method similar to the preparation of 9, pyrolytic sublimation of complex 10 afforded the product 11 as a colourless oil (52%).

Mass Spectrum, ambient probe temperature, CH_4 chemical ionization (m/e,rel.int.): 333(0.4); 321(0.6); 293(8); 291(4); 279(7); 252(20); 251(100); 211(11); 210(3); 209(14); 169(14).

IR (NaCl): 3070 s, 3020 w, 3010 w, 2980 s, 2920 s, 1640 s, 1600 w, 1485 s, 1440 s, 1415 m, 990 s, 910 s, 810 w, 750 s, 700 w cm^{-1}.

η^6-1,2,3,4-Tetrahydro-1,4,4-tribenzylnaphthalene-η^5-cyclopentadienyl iron hexafluorophosphate, 12 .

Following the procedure outlined in the preparation of complex 10, the reaction of complex 1 (0.82 g, 2.1 mmol) with Bu^{t}OK (1.1 g, 10 mmol) and benzyl bromide (3.4 g, 20 mmol) afforded the product 12 as a light beige powder,(0.92 g,67%).

Anal. Calcd. for $C_{36}H_{35}F_6FeP$: C, 64.68 ; H, 5.28. Found : C, 64.84 ; H, 5.80.

m.p. 190-194^{0}C

IR (KBr): 3080 br, 3020 m, 2940 br, 2860 m, 1600 m, 1490 m, 1450 s, 1420 m, 1260 w, 1075 w, 1030 w, 830 s,br, 750 s, 700 s, 555 s, 470 m cm^{-1}.

Mass Spectrum, 300^{0}C probe temperature, electron impact. (m/e,rel.int.): 402(0.2); 311(9); 186(74); 121(39); 107(100); 91(89).

1,2,3,4-Tetrahydro-1,4,4-tribenzylnaphthalene, 13 .

Following a procedure similar to that described for the preparation of compound 9, pyrolytic sublimation of complex 12 afforded a 40% yield of 13 as a colourless oil.

Mass Spectrum, 100^{0}C probe temperature, CH_4 chemical ionization. (m/e,rel.int.): 443(7); 431(6); 403(40); 325(100); 311(39); 222(18).

IR (NaCl): 3090 m, 3060 m, 3030 m, 2930 m, 2860 m, 1600 m, 1495 m, 1450 m, 760 m, 750 m, 730 m, 695 s cm^{-1}.

η^6-1,2,3,4-Tetrahydro-1,1,4,4-tetrabenzylnaphthalene-η^5-cyclopentadienyliron hexafluorophosphate, 14 .

To a stirred suspension of complex 12 (1.0 g,1.5 mmol) in THF (40 ml) was added Bu^{t}OK (1.8 g, 15.6 mmol) resulting in a dark red solution. Benzyl bromide (6.7 g, 39 mmol) was added and the mixture was stirred for 22 hours resulting in a gradual colour change to creamy orange. Volatiles were removed *in vacuo* and the excess benzyl bromide was extracted into diethyl ether. Following filtration, the orange solid was washed with water, dissolved in acetone/acetonitrile (1:1) and dried over $MgSO_4$, evaporated to dryness, and chromatographed on a neutral alumina column

(15x3 cm^2). Elution with acetonitrile, followed by evaporation of the solvent and precipitation from methanol/diethyl ether afforded a light orange powder (0.81 g, 71%).

Anal.Calcd. for $C_{43}H_{41}F_6FeP$: C, 68.08 ; H, 5.45 . Found: C, 67.39 ; H, 5.75

m.p. 190^0C (decomposition)

IR (KBr): 3030 m, 2940 m, 2870 w, 1710 m, 1600 m, 1495 s, 1450 s, 1420 m, 1385 s, 830 s,br, 750 s, 700 s, 560 s, 475 m cm^{-1}.

Mass Spectrum, 200^0C probe temperature, CH_4 chemical ionization. (m/e,rel.int.): 491(0.7); 415(7); 401(14); 324(4); 310(9); 220(100); 206(18).

1,2,3,4-Tetrahydro-1,1,4,4-tetrabenzylnaphthalene, 15 .

Using a procedure similar to the preparation of compound 9, pyrolytic sublimation of complex 14 afforded compound 15 as a colourless oil (40%).

Mass Spectrum, 200^0C probe temperature, electron impact. (m/e,rel.int.): 493(0.4); 491(0.6); 403(16); 401(25); 391(23); 324(100); 310(54); 220(43).

IR (NaCl): 3090 m, 3060 s, 3030 s, 2930 s, 2860 s, 1600 s, 1580 w, 1495 s, 1450 s, 1285 m, 1075 m, 1030 m, 910 m, 800 w, 760 s, 695 s, 640 m, 545 m cm^{-1}.

η^6-1,2,3,4-Tetrahydro-1-allyl-1,4,4-tribenzylnaphthalene-η^5-cyclopentadienyliron hexafluorophosphate, 16 .

Using the method outlined in the preparation of complex 10, the reaction of complex 12 (0.40 g, 0.60 mmol) with Bu^{t}OK (0.34 g, 3.0 mmol) and allyl iodide (2.2 g, 13 mmol) afforded the product 16 (0.10 g, 25%) as a beige solid.

Anal. Calcd. for $C_{39}H_{39}F_6FeP$: C, 66.11 ; H, 5.55 . Found: C, 64.19 ; H, 5.58.

m.p. 157^{0}C

IR (KBr): 3080 w, 3060 w, 3030 w, 2930 m, 1630 m, 1600 m, 1500 m, 1450 m, 1380 s, 840 s,br, 750 m, 700 s, 560 s cm^{-1}.

η^6-1,2,3,4-Tetrahydro-1,4,4-tribenzyl-1-methylnapthalene-η^5-cyclopentadienyliron hexafluorophosphate, 17 .

A stirred suspension of complex 12 (0.4 g, 0.6 mmol) in THF (40 ml) was treated with Bu^{t}OK (0.3 g, 2.7 mmol) resulting is a dark red solution. After 5 minutes, iodomethane (6.8 g, 48 mmol, 3 ml) was added to give a creamy white precipitate and an orange solution. After stirring for 20 hours, the volatiles were removed in vacuo. The remaining beige solid was dissolved in dichloromethane (20 ml) and washed with distilled water (50 ml). After separation of the orange organic layer, it was dried over $MgSO_4$, concentrated and purified by passage through a neutral alumina column (20x3 cm^2). Elution with acetone followed by concentration of the eluate and addition of excess diethyl ether afforded the product as a light orange solid (0.16 g, 39%), consisting of a mixture of two isomers.

Anal. Calcd. for $C_{37}H_{37}F_6FeP$: C, 65.11 ; H, 5.46. Found: C, 63.40 ; H, 5.69.

m.p. 144-149^{0}C

IR (KBr): 3090 w, 3060 w, 3030 w, 2940 m, 2860 w, 1600 m, 1495 m, 1450 m, 1385 s, 830 s,br, 750 m, 700 s, 555 s, 470 m,br, cm^{-1}.

Mass Spectrum, 300^{0}C probe temperature, CH$_4$ chemical ionization. (m/e,rel.int.): 457(1); 417(5); 415(7); 401(5); 339(40) 325(70); 311(13); 249(33); 235(23); 221(86); 187(41); 186(26); 145(100).

1,2,3,4-tetrahydro-1,4,4-tribenzyl-1-methylnaphthalene, 18 .

Following the procedure outlined in the preparation of 9, pyrolytic sublimation of complex 17 afforded a 40% yield of compound 18 as a colourless oil.

IR (NaCl): 3080 m, 3060 m, 3020 s, 2920 s, 2850 s, 1600 s, 1490 s, 1450 s, 1380 m, 1260 m, 1080 m, 1030 m, 800 m, 760 s, 700 s cm^{-1}.

Mass Spectrum,ambient probe temperature, electron impact.(m/e,rel.int.): 326(3); 91(100).

η^6-Tetrahydro-1-benzoyl-1,4,4-tribenzylnaphthalene-η^5-cyclopentadienyliron hexafluorophosphate, 19 .

To a stirred suspension of complex 12 (0.30 g, 0.45 mmol) was added Bu^{t}OK (0.15 g, 1.4 mmol) resulting in a dark red solution. After 5 minutes benzoyl chloride (2.4 g, 17 mmol, 2 ml) was added resulting in a light clear orange solution which was stirred for one hour. Volatiles were removed *in vacuo* and the remaining oily material was washed in diethyl ether which precipitated a solid. The reaction was worked up as in the preparation of complex 17. Precipitation of the final product from methanol/diethyl ether afforded a light beige solid (0.10 g, 29%). m.p. 155-160^{0}C

IR (KBr): 3100 w,br, 3060 w, 3030 w, 2940 w, 1730 w, 1680 m, 1600 m, 1495 m, 1450 m, 1420 m, 1380 s, 830 s,br, 750 m, 700 s, 560 s cm^{-1}.

Mass Spectrum, 380^{0}C probe temperature, CH_4 chemical ionization. (m/e,rel.int.): 547(10); 535(29); 507(100); 417(38)

1,2,3,4-Tetrahydro-1-benzoyl-1,4,4-tribenzylnaphthalene, 20 .

Following the method outlined in the preparation of compound 9, pyrolytic sublimation of complex 19 afforded the product 20 as a an oil (40%).

IR (NaCl): 3100 m, 3070 s, 3040 s, 2940 s, 2860 m, 1680 s, 1600 s, 1500 s, 1455 s, 765 s, 755 s, 700 s cm^{-1}.

η^6-1,2,3,4-Tetrahydro-1-methylnaphthalene-η^5-cyclopentadienyliron hexafluorophosphate, 21 .

Method A. To a stirred mixture of complex 1 (1.0 g, 2.5 mmol) and Bu^{t}OK (0.84 g, 7.5 mmol) was added THF (20 ml) resulting in a dark red solution. After 5 minutes, solvents were removed in vacuo and hexanes (60 ml) added. Following filtration over celite (trademark for diatomaceous earth and related products used for filtering), the red solution was concentrated to 15 ml and cooled to 0^{0}C. Upon addition of iodomethane (5.3 g, 38 mmol, 2 ml) a light orange precipitate was formed. After stirring for one hour, the supernatant was removed and the yellow solid washed in diethyl ether. Following the addition of aqueous NH_4PF_6, the yellow hexafluorophosphate salt was isolated, dried over $MgSO_4$ in dichloromethane and concentrated to 5 ml. Addition of excess diethyl ether precipitated the product as a yellow powder (0.10 g, 10%) consisting of a mixture of exo- and endo-methylated isomers in ca. 2.5:1 ratio. Anal. Calcd. for $C_{16}H_{19}F_6FeP$: C, 46.63 ; H, 4.65 . Found : C, 46.70 ; H, 4.61.

m.p. 164-171°C

IR (KBr): 3120 m, 2940 m, 2880 w, 1460 m, 1420 m, 1385 m, 865 s, 830 s, 560 s, 470 m cm^{-1}.

Method B. To a stirred mixture of complex 1 (0.5 g, 1.3 mmol) and Bu^tOK (1.4 g, 13 mmol) was added THF (80 ml) resulting in a dark red solution. After ten minutes, solvents were removed in vacuo and hexanes (60 ml) were added. After filtration and concentration to 10 ml, $(CH_3)_3OBF_4$ (0.6 g, 3.8 mmol) in dichloromethane (10 ml) was added. After fifteen minutes, a bright yellow precipitate formed and stirring continued until the supernatant was near colourless. Following isolation of the precipitate and workup with NH_4PF_6, 20 mg of product (4% yield) was obtained consisting of the exo-methylated isomer and starting material.

η^6-1,2,3,4-Tetrahydro-1-benzoylnaphthalene-η^5-cyclopentadienyliron hexafluorophosphate, 22 .

A stirred suspension of complex 1 (0.30 g, 0.75 mmol) in THF (8 ml) was treated with Bu^tOK (o.84 g, 7.5 mmol) resulting in a dark red solution.

Following the addition of hexanes (100 ml) and filtration of the mixture, benzoyl chloride (3.6 g, 26 mmol) was added resulting in a light orange precipitate. Workup of the reaction mixture was carried out as for 18 . Precipitation of the product from methanol/diethyl ether afforded a yellow powder (0.18 g, 47%).

Anal. Calcd. for $C_{22}H_{21}F_6FeOP$: C, 52.61 ; H, 4.21 . Found : C, 52.86 ; H, 4.40.

m.p. 182^{0}C

IR (KBr): 3100 m, 2950 m, 1680 s, 1450 m, 1420 m, 1380 s, 1220 s, 980 m, 830 s,br, 770 m, 690 m, 560 m cm^{-1}.

η^6-1,2,3,4-Tetrahydro-1-acetylnaphthalene-η^5-cyclopentadienyliron hexafluorophosphate, 23 .

Following a procedure similar to the preparation of compound 22, The acetyl derivative was made using acetyl chloride. The crude product was purified by column chromatography (20x3 cm^2) using neutral alumina. Using a 1:9 mixture of acetone/dichloromethane a yellow band was eluted from the column and identified as starting material (^{1}H NMR spectroscopy). Elution of the remaining orange band with pure acetone afforded an orange solution. After evaporation of the eluate, addition of methanol and excess diethyl ether precipitated the product as a light yellow powder (0.25 g, 32%).

m.p. 115-120^{0}C

IR (KBr): 3120 m, 2960 m, 2880 w, 1700 s, 1460 m, 1420 m, 1380 s, 1170 m, 830 s,br, 560 s, 505 m, 475 m cm^{-1}.

Mass Spectrum, 250^0C probe temperature, CH_4 chemical ionization. (m/e,rel.int.): 187(30); 186(23); 175(100); 131(25); 107(73).

η^5-3,4-(7,7,10,10-tetramethylbutano)-cyclohexadienyl-η^5-cyclopentadienyliron, 24 .

Following method A outlined for the synthesis of complexes 2a and 2b, the reaction of complex 8 (0.11 g, 0.24) with $NaBH_4$ (0.038 g, 1.0 mmol) gave a 50% yield of complex 24 as an orange oil. Using method B described previously for 2a and 2b, the reaction of complex 8 (0.17 g, 0.37 mmol) with $LiBEt_3H$ (0.11 g, 1 mmol) resulted in a 95% yield of 24.

IR (NaCl): 3100 w, 3010 w, 2960 s, 2920 s, 2860 m, 2760 s, 1630 w, 1455 m, 1380 m, 1360 m, 1290 m, 1110 m, 800 s cm^{-1}.

Mass Spectrum, 70^0C probe temperature, CH_4 chemical ionization. (m/e,rel.int.): 311(86); 310(100); 309(50); 297(32); 296(36); 295(28); 283(32); 282(36); 281(22); 269(18); 268(20); 267(15); 255(12); 254(15); 253(13); 245(9); 241(7); 240(8); 239(13).

η^5-Deuterio-3,4-(7,7,10,10-tetramethylbutano)cyclohexadienyl-η^5-cyclopentadienyliron, 25 .

Using a procedure similar to the preparation of 3a and 3b, the reaction of complex 8 (0.17 g, 0.37 mmol) with $LiBEt_3D$ (0.11 g, 1,mmol) afforded the deuterated complex 25 as a red oil (92%).

IR (NaCl): 3100 m, 3020 s, 2960 s,br, 2920 s,br, 2860 s, 2030 s, 1470 m, 1460 s, 1380 s, 1355 s, 1280 m, 1110 s, 1070 m, 1000 s, 940 m, 805 s cm^{-1}.

Mass Spectrum,ambient probe temperature, electron impact.(m/e,rel.int.): 311(23); 296(5); 254(54); 240(85); 213(100); 199(45); 157(47); 121(54).

η^5-Phenyl-3,4-(7,7,10,10-tetramethylbutano)cyclohexadienyl-η^5-cyclopentadienyliron, 26 .

Following the procedure outlined in the preparation of 4a and 4b, the reaction of complex 8 (0.10 g, 0.22 mmol) with phenyllithium (0.14 ml, 0.22 mmol) gave a 59% yield of 26 as an orange viscous oil.

IR (NaCl): 3100 w, 3060 w, 3030 m, 2960 s, 2930 s, 2870 s, 1600 m, 1490 m, 1460 m, 1380 m, 1360 m, 1110 m, 805 s, 760 s, 690 s cm^{-1}.

Mass Spectrum, ambient probe temperature, CH_4 chemical ionization. (m/e, rel.int.): 387(12); 386(8); 385(2); 373(3); 372(2.5); 371(1.3); 359(2.5); 358(1.4); 345(1.6); 344(0.9); 309(2.5); 155(100).

η^5-n-Butyl-3,4-(7,7,10,10-tetramethylbutano)cyclohexadienyl-η^5-cyclopentadienyliron, 27 .

Using the procedure described for the preparation of 4a and 4b, from the reaction of complex 8 (0.10 g, 0.22 mmol) and n-butyllithium (0.21 ml, 0.22 mmol) a 58% yield of 27 was obtained as an orange oil.

IR (NaCl): 3100 w, 3060 w, 3020 w, 2960 s, 2920 s, 2860 s, 1620 w, 1485 w, 1455 w, 1380 m, 1360 m, 1110 m, 1000 m, 800 s cm^{-1}.

Mass Spectrum, ambient probe temperature, CH_4 chemical ionization. (m/e,rel.int.): 367(23); 366(19); 365(23); 353(9); 352(10); 351(14); 339(12); 338(11); 337(12); 325(6); 324(5); 323(12); 309(100).

η^6-1,2,3,4-Tetrahydro-1,1,4,4-tetramethyl-6-phenylnaphthalene-η^5-cyclopentadienyliron hexafluorophosphate, 28 .

To a stirred solution of complex 26 (0.34 g, 0.88 mmol) in dichloromethane (15 ml) was added triphenylmethyltetrafluoroborate (0.33 g, 1 mmol). An immediate colour change from clear bright red to opaque red occurred. After ten minutes, workup of the reaction mixture was carried out as for 7a and 7b. The final product was isolated as the light yellow hexafluorophosphate salt (0.089 g, 19%). Anal. Calcd. for $C_{25}H_{29}F_6FeP$: C, 56.62 ; H, 5.51 . Found : C, 57.04 ; H, 5.63 .

m.p. 208^{0}C

IR (KBr): 3090 w, 2960 s, 2920 s, 2860 m, 1590 br, 1480 m, 1460 s, 1410 m, 1380 m, 1360 m, 820 s,br, 760 m, 680 m, 550 s cm^{-1}.

1,2,3,4-Tetrahydro-1,1,4,4-tetramethyl-6-phenylnaphthalene, 29 .

Using a method similar to the preparation of 9, pyrolytic sublimation of complex 28 afforded a 44% yield of 29 as a colourless oil.

Mass Spectrum, ambient probe temperature, CH_4 chemical ionization. (m/e,rel.int.): 305(3); 293(13); 265(100); 264(41); 249(36).

IR (NaCl): 3070 m, 3040 m, 2970 s, 2930 s, 2860 s, 1600 m, 1485 s, 1460 s, 1400 m, 1390 m, 1365 s, 1260 m, 1070 m, 1045 m, 895 m, 830 s, 765 s, 750 s, 695 s, 540 m cm^{-1}.

η^5-Phenyl-3,4-(7,7,10,10-tetramethylbutano)-6-phenylcyclohexadienyl-η^5-cyclopentadienyliron, 30 .

Using the method outlined in the synthesis of 4a and 4b, the reaction of complex 29 (0.10 g, 0.19 mmol) and phenyl-lithium (0.38 ml, 0.57 mmol) afforded the product 30 as a red oil (90%).

IR (NaCl): 3070 m, 3040 m, 2970 m, 2940 m, 2870 m, 1600 m, 1485 m, 1460 m, 1430 m, 1385 m, 1360 m, 810 m, 760 m, 735 s, 695 s cm^{-1}.

Mass Spectrum, ambient probe temperature, CH_4 chemical ionization.

(m/e,rel.int.): 464(3); 463(12); 462(7); 449(1); 448(1); 265(42).

η^6-1,2,3,4-Tetrahydro-1,1,4,4-tetramethyl-6,7-diphenylnaphthalene-η^5 cyclopentadienyliron hexafluorophosphate, 31 .

A stirred solution of complex 30 (0.73 g, 1.6 mmol) in dichloromethane (30 ml) was treated with triphenylmethyltetrafluoroborate (2.1 g, 6.4 mmol). Workup of the reaction mixture as in 7a and 7b afforded the product as the yellow hexafluorophosphate salt (0.080 g, 8%). Anal. Calcd. for $C_{31}H_{33}F_6FeP$: C, 61.40 ; H, 5.48 . Found : C, 62.62 ; H, 5.69 .

m.p. 157^{0}C

IR (KBr): 3130 w, 2970 m, 2880 w, 1650 br, 1460 m, 1425 m, 1385 s, 830 s,br, 765 m, 700 m, 560 m cm^{-1}.

1,2,3,4-Tetrahydro-1,1,4,4-tetramethyl-6,7-diphenylnaphthalene, 32.

Following the method described in the preparation of 9, pyrolytic sublimation of complex 31 afforded a 40% yield of 32 as a white oily solid.

Mass Spectrum,100^{0}C probe temperature, CH_4 chemical ionization.
(m/e,rel.int.): 369(18); 341(100); 326(50).
IR (KBr): 3060 w, 3020 w, 2950 s, 2920 s, 2860 m, 1600 w, 1475 m, 1455 m, 1440 m, 1380 s, 1360 m, 1260 m, 1070 m, 900 m, 765 s, 690 s cm^{-1}.

η^5-3,4(7,7,10-tribenzylbutano)cyclohexadienyl-η^5-cyclopentadienyliron, 33a and η^5-4,5(7,7,10-tribenzylbutano)cyclohexadienyl-η^5-cyclopentadienyliron, 33b

Using method A outlined in the preparation of 2a and 2b, the reaction of complex 12 (0.10 g, 0.15 mmol) with $NaBH_4$ (0.04 g, 1.1 mmol) resulted in 90% yield of 33a and 33b as an orange solid. Following method B described for 2a and 2b, the reaction of complex 12 (0.12 g, 0.18 mmol) with $LiBEt_3H$ (0.11 g, 1 mmol) afforded a mixture of 33a and 33b as an orange solid (95%).
m.p. 67-70^0
IR (KBr): 3080 w, 3060 w, 3020 m, 2920 m, 2860 m, 2780 m, 1600 w, 1490 m, 1450 m, 810 m, 750 m, 740 m, 690 s cm^{-1}.
Mass Spectrum, 300^{0}C probe temperature, CH_4 chemical ionization.
(m/e,rel.int.): 525(25); 524(2); 458(0.9); 433(1.0); 403(0.8); 402(0.8); 401(1.7); 342(1.2); 325(8); 311(6); 235(5); 221(15); 187(41); 186(33); 145(17); 131(19); 95(62); 93(91); 91(100).

Reaction of η^6-1,2,3,4-Tetrahydro-1,4,4-tribenzylnaphthalene-η^5-cyclopentadienyliron hexafluorophosphate 12 with methyllithium, 34 .

Following a procedure similar to the preparation of 4a and 4b, the reaction of complex 12 (0.11 g, 0.17 mmol) and methyllithium (0.12 ml, 0.17 mmol) afforded an 80% yield of the product 34 as an orange solid. m.p. 60-61^{0}C

IR (KBr): 3080 w, 3060 w, 3020 m, 2930 m, 2860 m, 1600 m, 1490 m, 1450 m, 810 m, 750 m, 700 s cm^{-1}.

Mass Spectrum, 300^{0}C probe temperature, CH_4 chemical ionization. (m/e,rel.int.): 539(8); 538(3); 523(1); 447(4); 417(3); 415(2); 403(2); 401(3); 325(23); 311(7); 221(29); 187(18); 186(11); 131(13); 91(100).

η^6-1,2,3,4-Tetrahydroquinoline-η^5-cyclopentadienyliron hexafluorophosphate, 35 . Ferrocene (5.5 g, 30 mmol), $AlCl_3$ (40 g, 300 mmol), Al powder(0.81 g, 30 mmol) and tetrahydroquinoline (10.6 g, 80 mmol, 10 ml) were refluxed in decalin (80 ml) for four hours under nitrogen. After cooling the dark mixture in an ice bath, ice was added slowly until all remaining excess $AlCl_3$ was destroyed. After filtration of the mixture, the bright orange aqueous layer was separated and washed in petroleum ether (b.p.30-60^{0}C). The addition of excess NH_4PF_6 precipitated an orange solid which was filtered, dissolved in dichloromethane, dried over $MgSO_4$, concentrated in vacuo and chromatographed on a neutral alumina column (20x3 cm^2). After elution with acetone the eluate was evacuated to dryness, and redissolved in methanol. The addition of excess diethyl ether and petroleum ether precipitated a bright orange powder (3.6 g, 30%). Anal. Calcd. for $C_{14}H_{16}F_6FeNP$: C, 42.13; H, 4.04; N, 3.51. Found: C, 43.99; H, 4.35; N, 3.13.

m.p. 162-163^{0}C

IR (KBr): 3440 s, 3120 m, 2950 m, 2880 m, 1570 s, 1525 m, 1500 m, 1470 m, 1435 m, 1420 m, 1385 m, 1355 m, 1330 m, 1295 m, 830 s,br, 560 s, 450 m cm^{-1}.

Mass Spectrum, 300^{0}C probe temperature, CH_4 chemical ionization. (m/e,rel.int.): 398(0.4); 379(0.5); 310(0.6); 254(2.5); 253(1.2); 240(0.9); 239(1); 187(12); 186(24); 134(90); 133(100).

Reaction of η^6-1,2,3,4-Tetrahydroquinoline-η^5-cyclopentadienyliron hexafluorophosphate 35 with Bu^{t}OK.

To a mixture of complex 35 (0.10 g, 0.25 mmol) and Bu^{t}OK (0.10 g, 0.89 mmol) was added THF (5 ml) resulting in the formation of a bright red solution. Volatiles were removed in vacuo and the product was extracted with hexanes (20 ml). After filtration of the mixture, the filtrate was evacuated to dryness resulting in a reddish oil consisting of a mixture of two compounds 36 and 37.

η^6-N-methyl-1,2,3,4-tetrahydroquinoline-η^5-cyclopentadienyliron hexafluorophosphate, 38 .

A stirred suspension of complex 35 (0.15 g, 0.38 mmol) in THF (15 ml) was treated with Bu^{t}OK (0.13 g, 1.1 mmol) resulting in a bright red solution. after five minutes volatiles were removed in vacuo and the neutral product was extracted with hexanes (40 ml). After filtration of the mixture, iodomethane (4.6 g, 32 mmol, 2ml) was added to the clear orange filtrate resulting in the formation of a yellow precipitate. Following removal of the supernatant, the solid was dissolved in distilled water and precipitated as an orange solid using excess NH_4PF_6. The solid was filtered, dried over $MgSO_4$ in dichloromethane and concentrated in vacuo. The sample was purified by passage through a neutral alumina column (15x3 cm^2). Elution with acetone followed by concentration of the eluate and addition of excess diethyl ether precipitated the product as an orange powder (80 mg, 50%). Anal. Calcd. for $C_{15}H_{18}F_6FeNP$: C, 43.61; H, 4.39; N, 3.39. Found: C, 42.72; H, 4.37; N, 3.25.

m.p. 207-209^{0}C (decomposition)

IR (KBr): 3120 m, 2960 m, 1560 s, 1510 m, 1495 m, 1420 m, 1385 m, 1330 s, 1210 m, 830 s,br, 660 m, 560 s, 460 m cm^{-1}.

Mass Spectrum, 300^{0}C probe temperature, electron impact.(m/e,rel.int.): 398(0.8); 253(0.8); 239(3); 186(43); 147(83); 146(100); 132(14); 131(18); 130(21); 121(19); 107(59).

η^6-N-methyl-4,4-dimethyl-1,2,3,4-tetrahydroquinoline-η^5-cyclopentadienyliron hexafluorophosphate, 39 .

Using the method outlined in the synthesis of complex 8, the reaction of complex 35 (0.4 g, 1.0 mmol) with Bu^tOK (1.4 g, 12 mmol) and iodomethane (3.7 g, 26 mmol) afforded the product 39 as a bright orange powder (0.22 g, 50%).

Anal. Calcd. for $C_{17}H_{22}F_6FeNP$: C, 46.28; H, 5.03; N, 3.17. Found: C, 46.68; H, 5.12; N, 2.91. m.p. 143-145^{0}C

IR (KBr): 3120 w, 2960 m,br, 1560 s, 1420 m, 1380 w, 1330 s, 1205 m, 1100 m, 830 s,br, 560 s, 440 m cm^{-1}.

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