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# THE SYNTHESIS OF ENANTIOMERICALLY PURE DIENE AND DIENYL COMPLEXES OF IRON

by

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This thesis is the author's own account of work carried out by the author under the supervision of Dr. J. A. S. Howell. No part of the work incorporated in this thesis has been incorporated in a thesis submitted for a Higher Degree at any University.

TO MY PARENTS

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## ABSTRACT

This thesis describes two general methods for the preparation of substituted (1,3-diene)$Fe(CO)_3$ and $[(\eta^5\text{-dienyl})Fe(CO)_3]^+$ complexes in an optically pure form. Nucleophilic attack by chiral alkoxides, phosphines and amines on $[(\eta^5\text{-cyclohexadienyl})Fe(CO)_3]^+$ salts has resulted in the formation of diastereoisomeric pairs. Resolution has been achieved by chromatography or by fractional crystallization, and the purity of the separated diastereoisomers monitored by $^{13}C$ or $^{31}P$ n.m.r. spectroscopy. Enantiomerically pure (+) and (-) $[(2\text{-MeO-}\eta^5\text{-}C_6H_6)Fe(CO)_3]^+$ salts have been prepared via the chromatographic separation of their menthoxy diastereoisomers, followed by protonation of the menthoxy residue. Further elaboration of (2S)-(+)-$[(2\text{-MeO-}\eta^5\text{-}C_6H_6)Fe(CO)_3][PF_6]$ has been carried out via the Wittig reaction on the readily prepared phosphonium adduct, followed by protonation to give (2S)-(5R)-(+)$[(2\text{-MeO-5Me-}\eta^5 C_6H_5)Fe(CO)_3][PF_6]$. Attempts are described to eliminate, by nucleophilic displacement, the resolving chiral residue from unsubstituted (1,3-diene)$Fe(CO)_3$ complexes, in order to retain the configuration at the chiral quaternary carbon. Phosphine reduction from the separated diastereoisomer $[(5\text{-exo-}PPh_2\text{menthyl-}C_6H_7)Fe(CO)_3]$-$[BF_4]$, has been achieved using $LiAlD_4$, to give chiral $(C_6H_7D)Fe(CO)_3$.

$[(\eta^5\text{-}C_6H_7)Fe(CO)_2L^*]^+$ (where L*=(+)$PPh_2$menthyl, (+)$PPh_2CH_2CH$-(Me)Et) have been prepared by the irradiation of $Fe(CO)_4L^*$ in the presence of cyclohexadiene, followed by hydride ion abstraction with $Ph_3CBF_4$ to generate the dienyl salts. Nucleophilic attack by $CN^-$ on $[(\eta^5\text{-}C_6H_7)Fe(CO)_2PPh_2\text{menthyl}]^+$ proceeds with asymmetric

induction, to give the 5-exo cyano complex, as a mixture of diastereoisomers in the ratio of 2:1.

The preparation of (trans-1-butadiene)$Fe(CO)_2PPh_2$menthyl has been achieved by two separate routes, either the irradiation of (trans-1-butadiene)$Fe(CO)_3$ with (+)$PPh_2$menthyl, or the irradiation of $Fe(CO)_4$(+)$PPh_2$menthyl in the presence of trans-1-phenylbutadiene. Both routes proceed with the same degree of asymmetric induction, to give two diastereoisomers in the ratio of 2:1.

## ABBREVIATIONS

| | |
|---|---|
| bda | benzylideneacetone |
| br | broad |
| chd | cyclohexadiene |
| chpt | cycloheptatriene |
| cot | cyclo-octatetraene |
| d | doublet |
| Fp | $(C_5H_5)Fe(CO)_2$ |
| i.r. | infra red |
| m | multiplet |
| Me | methyl |
| n.m.r. | nuclear magnetic resonance |
| Ph | phenyl |
| q | quartet |
| s | singlet |
| t | triplet |
| TCNE | tetracyanoethylene |
| THF | tetrahydrofuran |
| u.v. | ultra violet |

# CONTENTS

# CHAPTER I

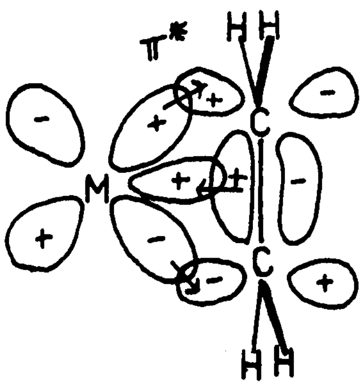
## TRANSITION METAL $\pi$ COMPLEXES IN ORGANIC SYNTHESIS

### 1.1 Introduction

Transition metal olefin complexes have been the subject of extensive investigations over the past twenty-five years. The properties of these compounds make them uniquely suitable to act as intermediates in organic synthesis. Co-ordination to a metal can activate, de-activate or protect double bonds from electrophilic or nucleophilic attack. By distinguishing between one side of the organic molecule and the other, the metal permits stereospecific reactions to occur. Highly reactive organic molecules of theoretical interest, or of importance as synthetic intermediates have been complexed. Metal complexation has allowed many unique transformations more easily than would be possible by conventional organic synthesis.

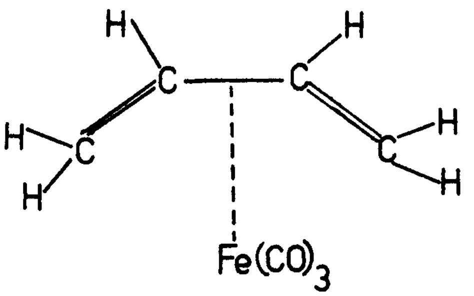
Much work has been carried out on tricarbonyl(1,3-diene)iron complexes because of the cheapness and ready availability of iron. This chapter is not intended as an exhaustive review of iron $\pi$ complexes but rather to illustrate the reactivity modifications which unsaturated molecules undergo when complexed to iron, and how these changes have been utilised in organic synthesis. Several reviews in this area have been recently published notably by Pearson and Birch.[1-8] Other approaches to organic synthesis via transition metal complexation such as work by Semmelhack on (arene)$Cr(CO)_3$ derivatives[9] or Trost on the steric consequences of Pd systems[10] cannot be dealt with here.

The unique reactivity of transition metal compounds is associated with the ability of the partially filled d orbitals to become involved in geometrically defined bonding with a variety of ligands, in order to obtain a share in more electrons, usually enough to complete their co-ordination spheres and attain the electronic configuration of the next higher inert gas. The Dewar-Chatt-Duncanson model (1) for describing bonding between transition metals and $\pi$ complexes is now well established.[11] This model involves overlap of the $\pi$ electron density of the olefin with a $\sigma$-type acceptor orbital on the metal atom, and synergistic back donation from filled metal orbitals of suitable symmetry into $\pi$ antibonding orbitals of the olefin.

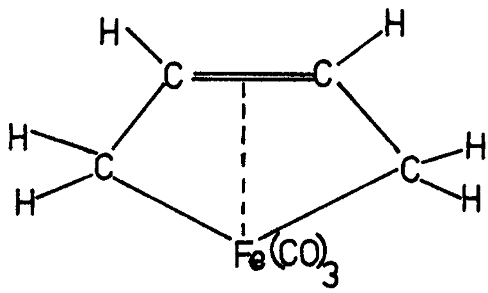



(1)

The two components are interdependent; as one component increases, it tends to promote an increase in the other, thus keeping the metal-olefin bond essentially electroneutral. It is an over-simplification to treat bonding in conjugated diene systems as two separate olefin metal bonds. Bonding in (butadiene)$Fe(CO)_3$ can be represented by two extremes.



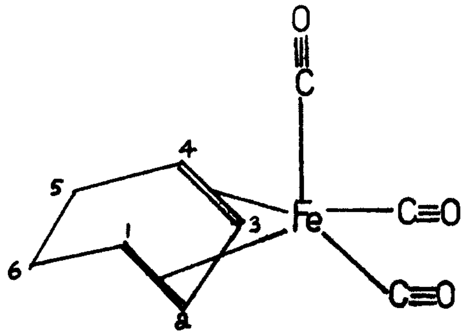
(2)



(3)

(2) implies there are two independent metal monolefin interactions, whereas (3) suggests σ bonds between the metal and terminal carbons, coupled with a metal monolefin interaction at C-2 and C-3. The $^{13}$C-H coupling constants of (butadiene)$Fe(CO)_3$ indicate that all the C-H bonds are essentially $sp^2$ hybrids thus favouring (2).[12] However the terminal $CH_2$ hydrogen and terminal substituent groups were found to be rotated out of planarity so that the bonding of Fe at C1,4 differs somewhat from that at C2,3 implying a degree of $sp^3$ character and favouring (3). Subsequent $^{13}$C n.m.r. data from substituted (1,3-diene) $Fe(CO)_3$ derivatives suggests that structure (3) makes an important contribution to bonding in these complexes.[13] Therefore an adequate representation of bonding in these complexes is somewhere between the two extremes.

There are a number of theoretical treatments of bonding in metal $\eta^4$-polyene complexes in the literature.[14] The structure of (1,3-diene)$Fe(CO)_3$ complexes has been investigated by X-ray crystallography.[15] The co-ordination geometry of (cyclohexadiene)$Fe(CO)_3$ (4) is square pyramidal with two carbonyl carbon atoms and the mid-points of the formal double bonds defining the basal plane.



(4)

Carbons 1-4 of the diene unit are planar, whilst carbons 5 and 6 are bent away from the iron atom. The bond lengths of the diene unit are approximately equal, longer than the double bonds C1-C2/C3-C4 in free cyclohexadiene but significantly shorter than the single bond C2-C3 in the free ligand.

In order to utilise these complexes in organic synthesis, it is necessary to be able to add or remove the complexing group efficiently, but at the same time it must be stable to a variety of reagents. (1,3-Diene)$Fe(CO)_3$ complexes are readily prepared by refluxing the diene with $Fe(CO)_5$ in dibutyl ether for 10-30 hours,[16] or the more reactive but less available $Fe_3(CO)_{12}$ in boiling benzene.[17] A milder procedure is refluxing the diene with $Fe_2(CO)_9$ in acetone or diethyl ether. Since these reagents can produce double bond isomerizations, a wide range of dienes can be employed. Heat sensitive dienes have been complexed with iron by the use of labile ($\alpha\beta$-unsaturated ketone)$Fe(CO)_3$ complexes which act as transfer agents for the $Fe(CO)_3$ moiety.[18] Removal of the $Fe(CO)_3$ group is normally achieved by treating the complex with an oxidizing agent such as ceric ammonium nitrate, ferric chloride or cupric chloride,[19] at between 0°C and room temperature in acetone or ethanol. Trimethylamine N-oxide has also been used.[20]

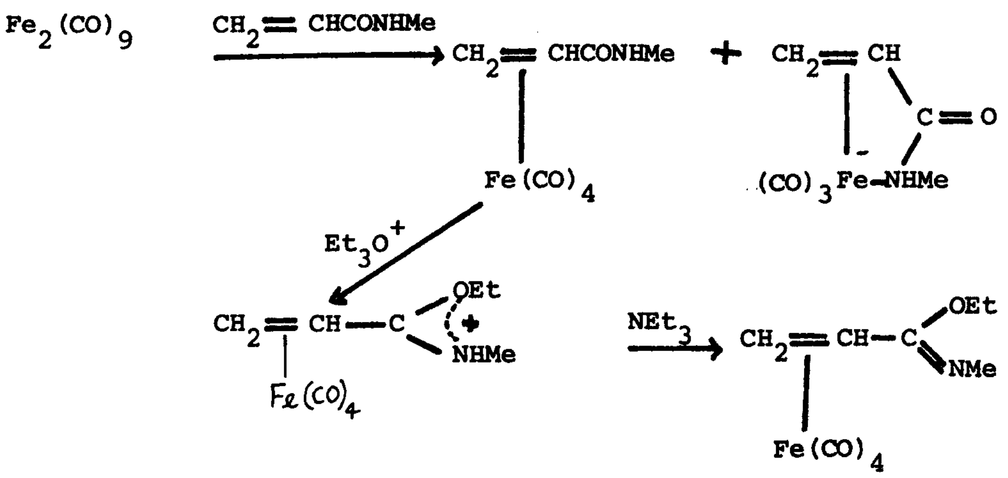
## 1.2 The Effects of Co-ordination to a Metal on the Reactivity of a $\pi$ Ligand

### 1.2.1 Metal Acts as a Protecting Group

Unprotected olefins are susceptible to oxidation and reduction, they undergo addition reactions with a variety of reagents, and a number of purely organic protecting methods have been described. Mono-olefins have been protected by halogenation. For example, 3-$\beta$-methoxyandrost-5-ene may be protected by dibromide during oxidation with chromium trioxide on another part of the molecule.[21] Epoxides and diols have also been used to protect olefins,[22] whereas conjugated dienes have been protected by reaction with a dienophile. Barton used the adduct of ergosterol with 4-phenyl-1,2,4-triazolin-3,5-dione to protect the diene during ozonolysis of the side chain. The diene system was regenerated by treatment with lithium aluminium hydride.[23] Complexation of a diene with $Fe(CO)_3$ profoundly modifies the properties of the diene in ways which can be utilised in organic synthesis. For instance, compounds of the general formula (diene)$Fe(CO)_3$ are inert to $Br_2$ and catalytic hydrogenation under conditions in which the free diene would react, nor do they undergo Diels-Alder reactions and are unaffected by concentrated sulphuric acid.[24] The metal therefore acts as a protecting group, since uncomplexed double bonds or other functional groups in the molecule display normal reactivity.

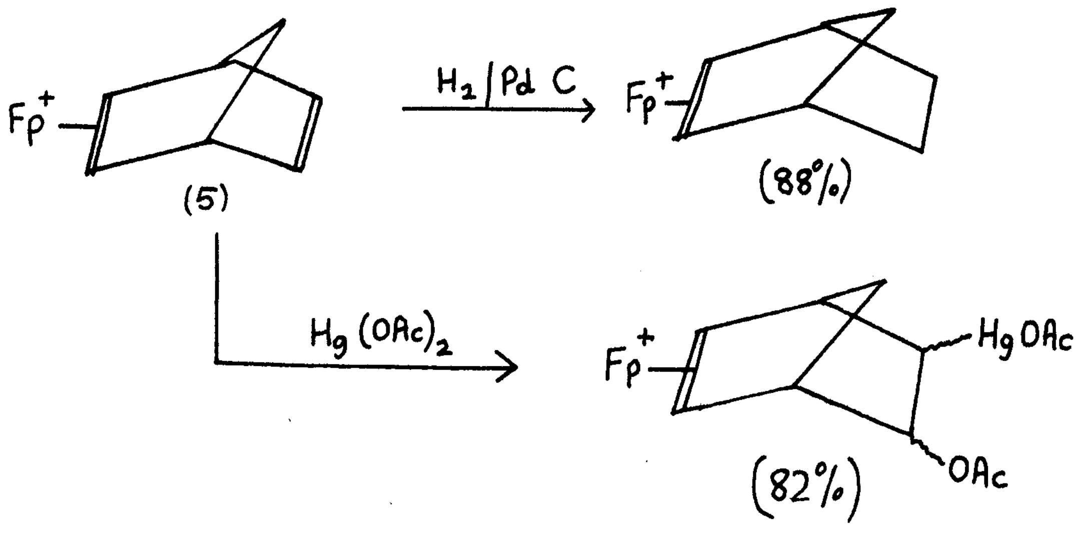
### 2.2.1 $\eta^2$-alkene Complexes

A range of chemistry may be carried out on functional groups whilst the $\eta^2$-alkene is protected by $Fe(CO)_4$. For instance Scheme I on the following page.[25]

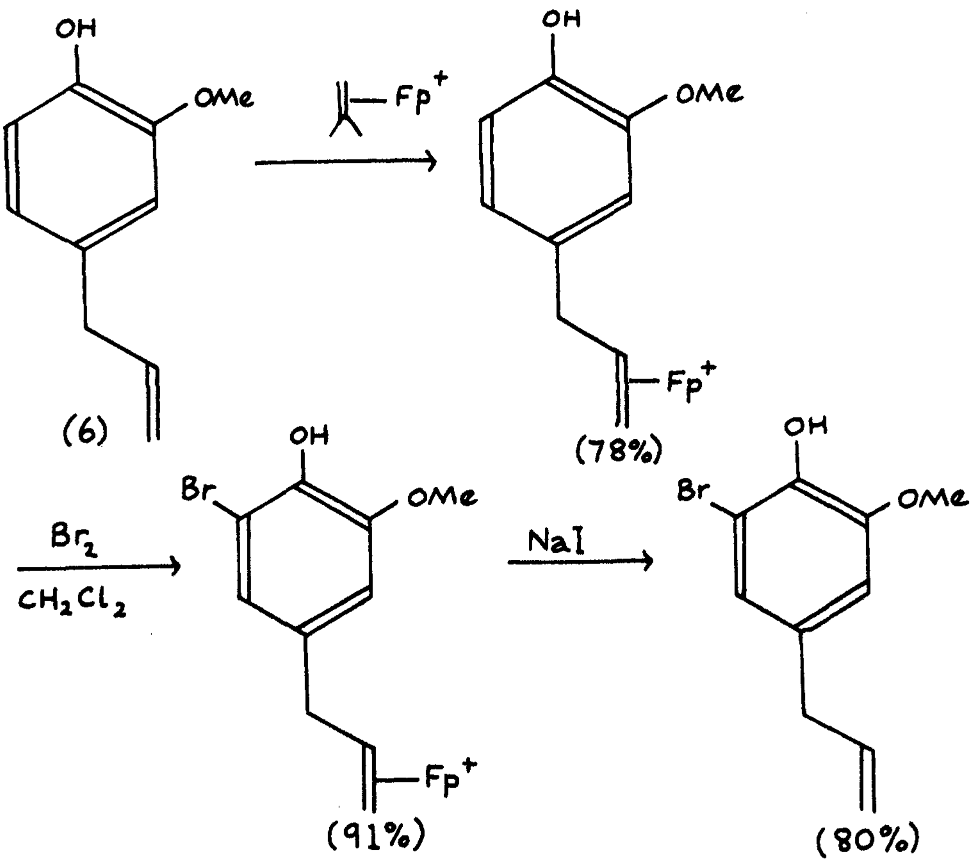


SCHEME I

Mono-olefinic bonds have also been selectively protected by the use of $(C_5H_5)FeCO_2$ (≡Fp) as a blocking group. The Fp(olefin)$^+BF_4^-$ complexes were prepared by thermal exchange reaction between readily available Fp(isobutylene)$^+BF_4^-$ and alkenes.[26] Monoprotected norbornadiene (5) readily underwent hydrogenation and acetoxy mercuration.

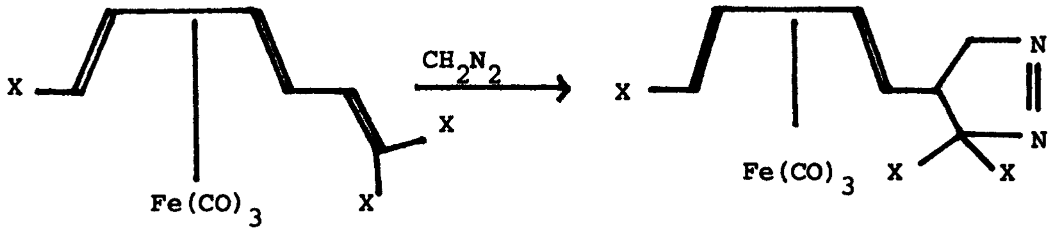


Selective aromatic substitution was carried out on eugenol (6) whilst the olefinic side chain was protected by co-ordination to the $Fp^+$ group. The free olefin was then conveniently regenerated upon treatment with NaI in acetone.



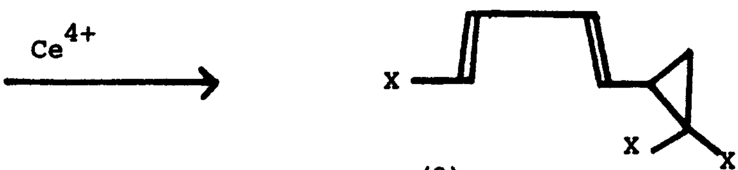

1.2.1.2 <u>Acyclic (diene)$Fe(CO)_3$ complexes</u>

$Fe(CO)_3$ has been complexed to two adjacent double bonds of a 1,3,5-triene, to act as a protecting group for the diene unit. Diazomethane adds specifically to the free double bond of triene (7) to give (8). Oxidation with $Ce^{4+}$ results in loss of nitrogen with concomitant decomplexation to yield (9).[27]



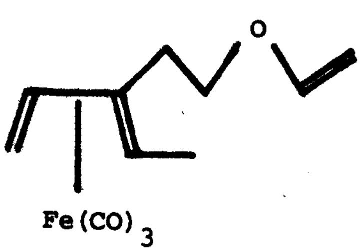

(7) (8)

$X = CO_2CH_3$

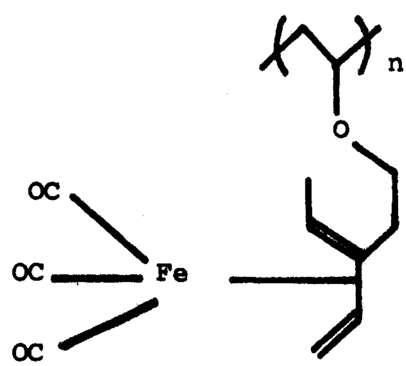



(9)

The ability of the $Fe(CO)_3$ moiety to act as a protecting group is illustrated by the synthesis of novel organometallic polymers containing ($\eta^4$-diene)iron as pendant groups. Tricarbonyl (3-vinyloxyethyl-1-4-$\eta^4$-1,3 pentadiene)iron (10) has been prepared as a monomer and polymerized by cationic initiators such as $BF_3.OEt_2$ at -20°C to give an air stable yellow elastomer (11) in 62% yield.[28]



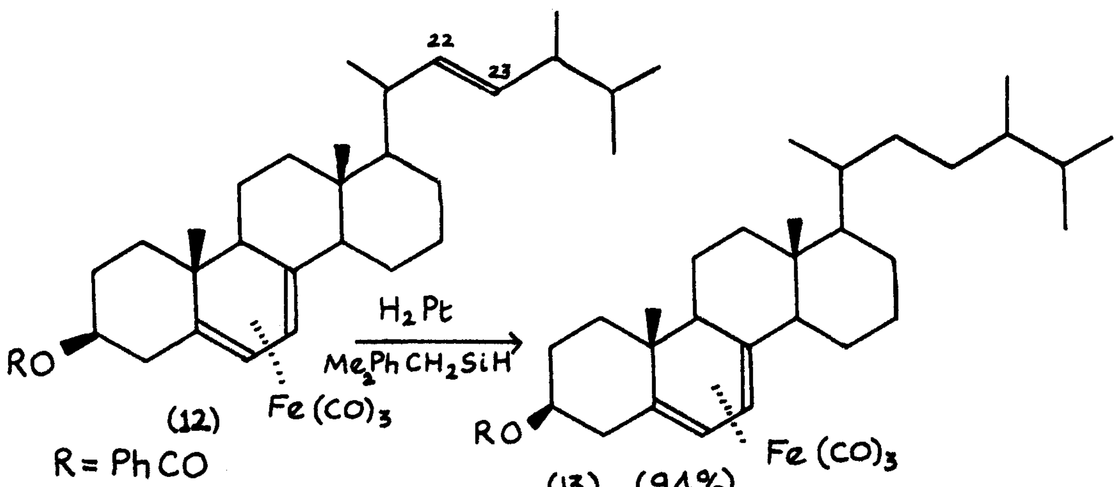

(10)




(11)

### 1.2.1.3 Cyclic(diene)$Fe(CO)_3$ complexes

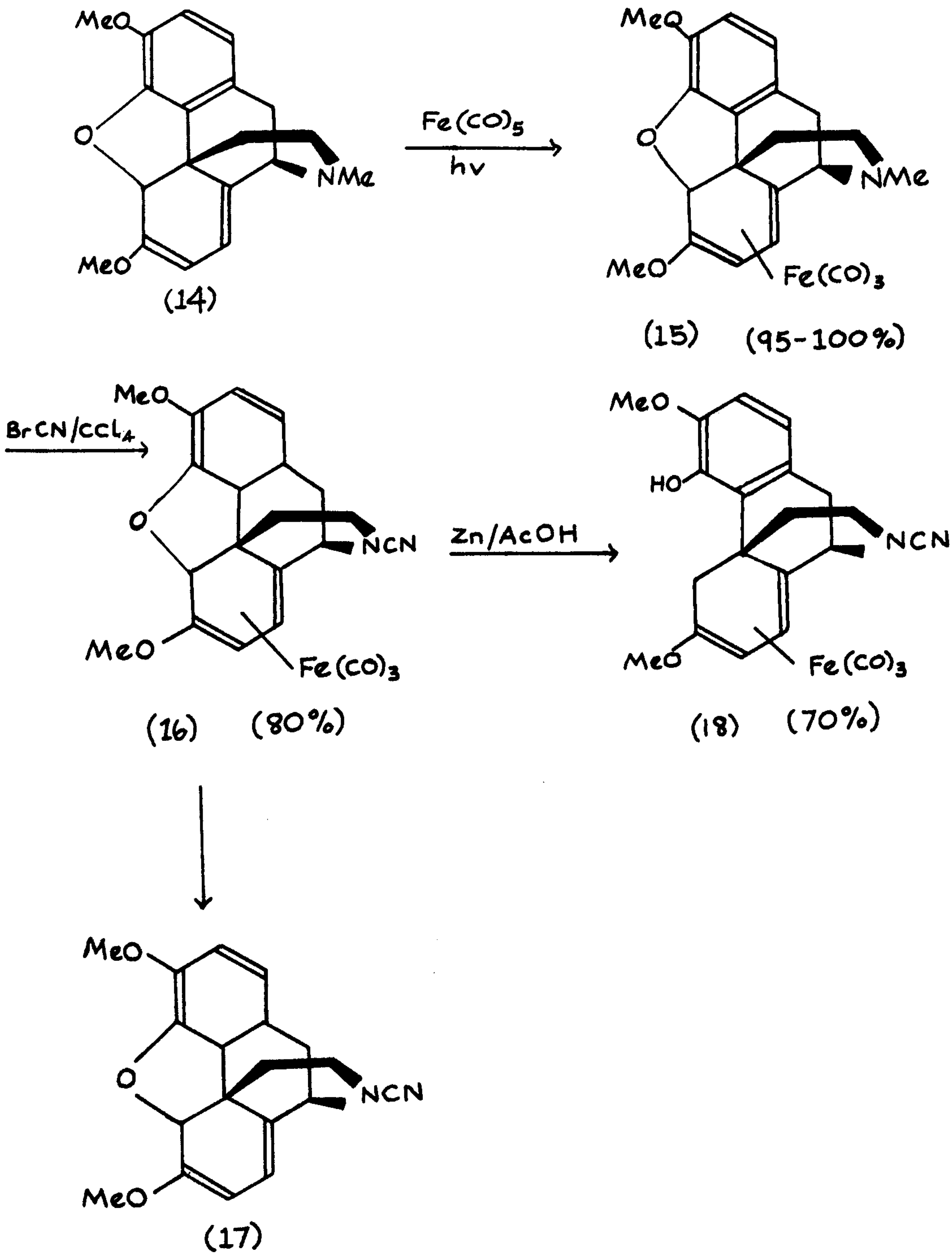
$Fe(CO)_3$ has been used to protect the B ring diene of ergosteryl benzoate, whilst the 22-23 double bond was selectively hydrogenated.[29] Complexation of ergosteryl benzoate to give the tricarbonyliron derivative (12) was readily achieved in 80% yield. Hydrogenation using Adams catalyst in the presence of benzyldimethylsilane gave (13). The free diene was then liberated by treatment with ethanolic ferric chloride.



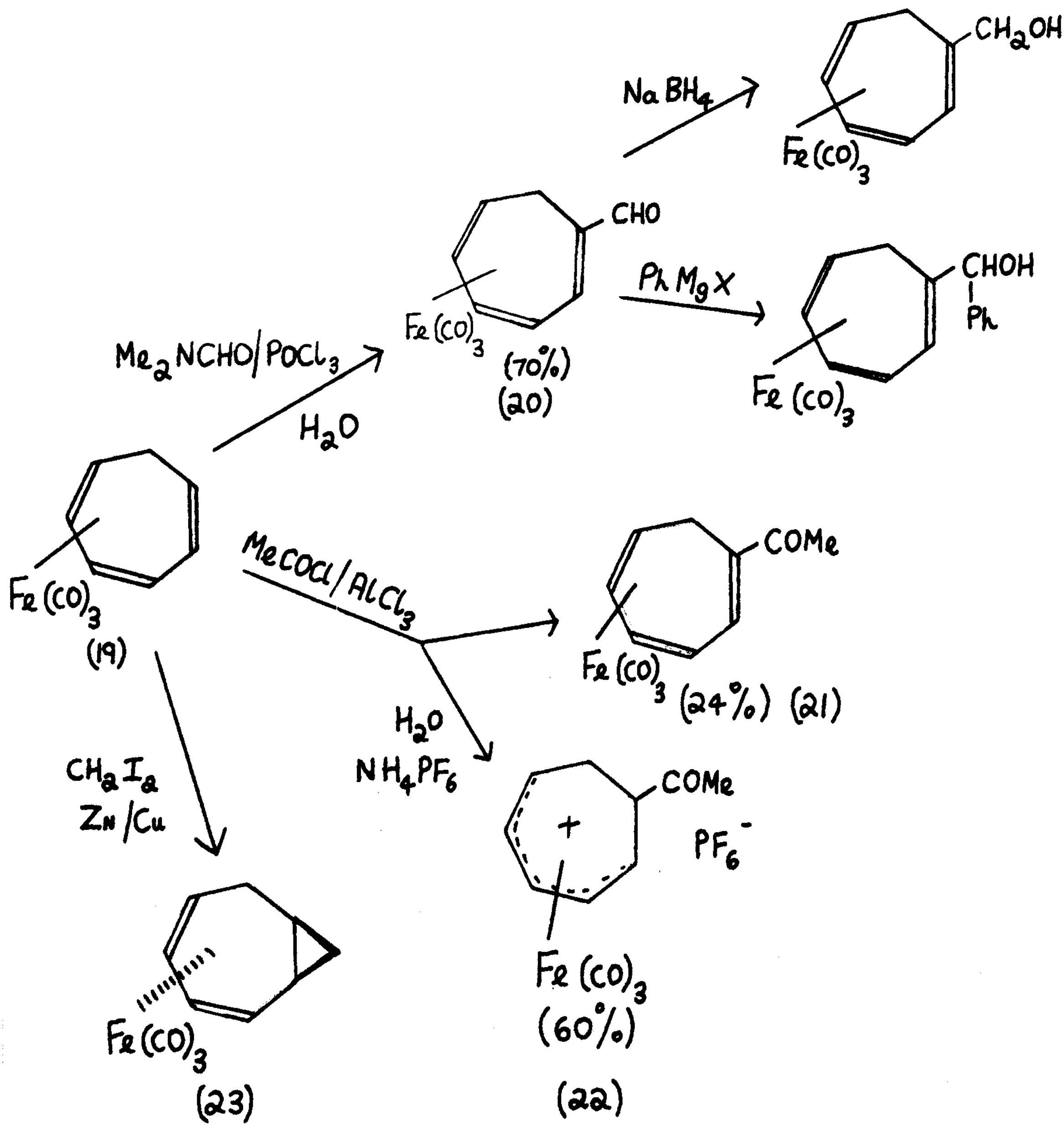

(12) R = PhCO

(13) (94%)

Complexation with $Fe(CO)_3$ has enabled the conversion of thebaine (14) to N-Cyanonorthebaine (17);[30] in the absence of $Fe(CO)_3$, extensive rearrangements of the skeleton result. Irradiation of (14) in the presence of $Fe(CO)_5$ gave (15) in excellent yield. The reaction with cyanogen bromide produced (16) followed by oxidation of the $Fe(CO)_3$ group to yield N-Cyanonorthebaine (17). Reduction with zinc and acetic acid resulted in the opening of the ether ring to generate (18).




The free double bond of (cycloheptatriene)$Fe(CO)_3$ (19) has been found to react with electrophilic reagents, whilst the complexed diene unit is unaffected. In contrast to the reactions of free cycloheptatriene, these reactions take place without concurrent polymerization or hydride abstraction to give the tropylium cation.[31]




(19) undergoes Vilsmeier formylation of the free double bond to produce (20). The reaction involves primary attack by a carbonium ion $[R_2N{=}C\lessgtr^{Cl}_{H}]^+$, followed by hydrolysis of the Vilsmeier type salt.[32] Reactions of the functional group CHO appear to be normal since reduction with $NaBH_4$ or a Grignard reagent gives the appropriate alcohol. Friedel-Crafts acylation of (19) occurs with

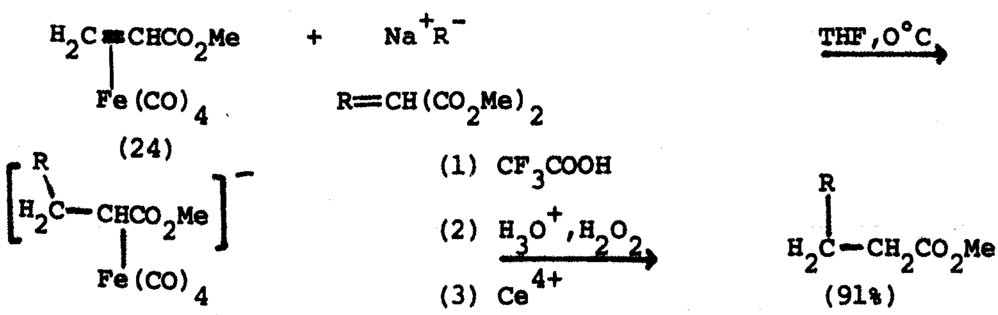
electrophilic substitution to give the neutral complex (21) and electrophilic addition to give the cationic complex (22). Similar products are obtained from the formylation and acylation of (cot)$Fe(CO)_3$. Carbene addition to (19) occurs only at the uncomplexed double bond which displays normal reactivity to yield (23). Methylene addition takes place stereospcifically on the face of the cycloheptatriene ring opposite to that occupied by the metal, to give a cyclopropane ring which is trans to the metal.[33]

### 1.2.2 The Metal Acts as an Activating and Directing Group

Co-ordination of an olefin to a metal can lead to significant changes in the reactivity and reaction patterns towards electrophilic and nucleophilic attack.

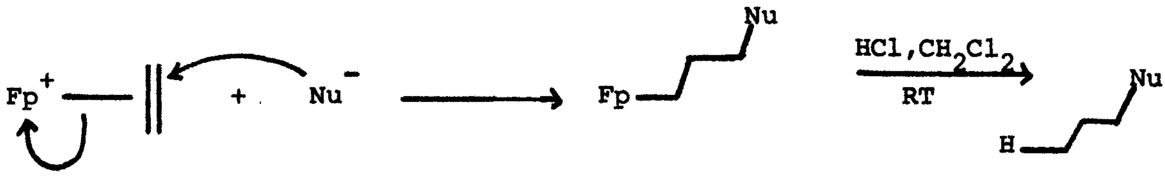
#### 1.2.2.1 $\eta^2$-Alkene Complexes

Simple olefins are very inert to nucleophilic attack. However olefins co-ordinated to $Fe(CO)_4$ or $Fp^+$ react with nucleophiles to give the $\sigma$-bonded iron complex. For example, (24) undergoes regiospecific nucleophilic addition with sodium dimethylmalonate via the anion (25) to give (26).[33a] $Fe(CO)_4$ serves as an efficient electron sink to stabilise the intermediate (25), and thereby provides the driving force for preferential nucleophilic attack on the co-ordinated olefin rather than at CO



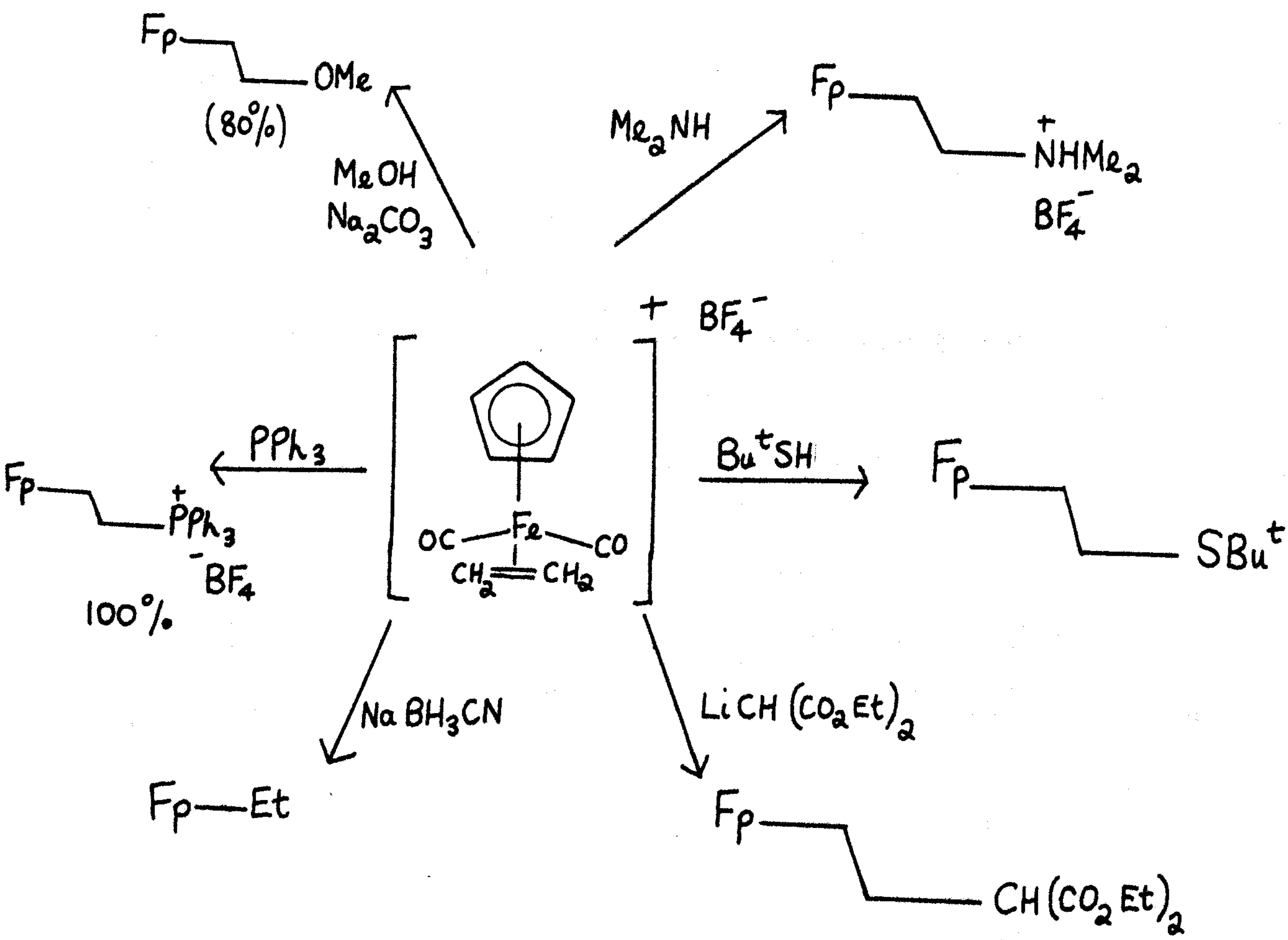

(25) (26)

$Fp(\eta^2\text{-alkene})^+$ complexes provide excellent substrates for the addition of nucleophiles to the co-ordinated alkenes to give the corresponding Fp(alkyl) complexes. The iron is readily removed by treatment with hydrochloric acid (Scheme II).



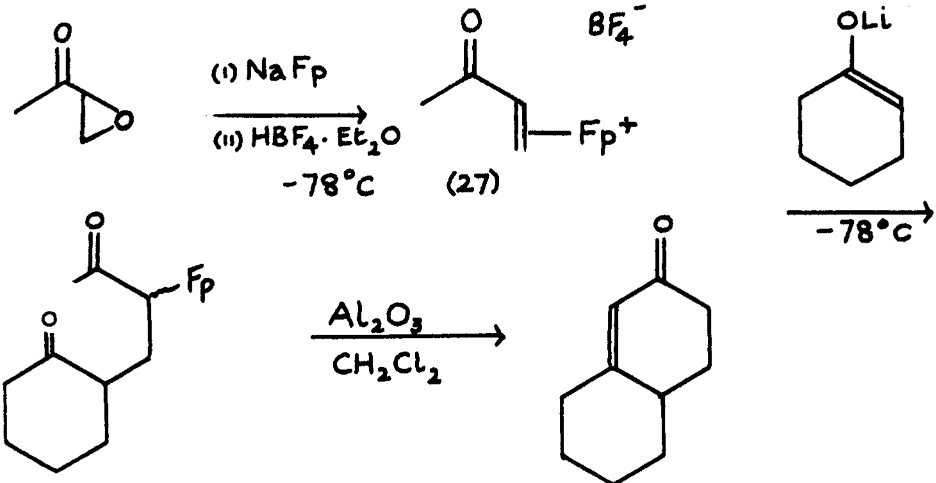

SCHEME II

A variety of addition reactions on $Fp(\text{alkene})^+$ complexes have been carried out using alkoxides, lithium enolates, amines, thiols and phosphines (Scheme III).[34]




SCHEME III Nucleophilic additions at $[Fe(C_5H_5)(CO)_2(C_2H_4)]^+$

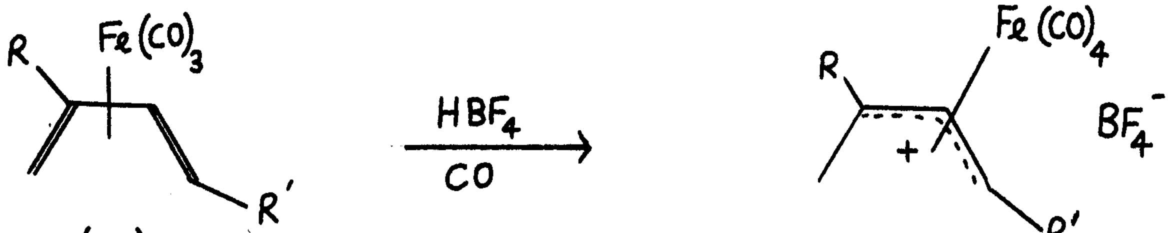
The $Fp^+$ complex of methyl vinyl ketone (27) readily undergoes metal assisted Michael addition with a variety of nucleophiles including lithium enolates.[35] Treatment of (28) with basic alumina in refluxing $CH_2Cl_2$ results in loss of Fp and cyclization to give (29).




(27) (28) 45% (29) 76%

### 1.2.2.2 $\eta^3$-Allyl Complexes

Simple $\eta^3$-allyl complexes of iron may be formed by the protonation of $\eta^4$-diene complexes. Stabilisation is due to electron donation by the metal. Treatment of tricarbonyl(butadiene)iron derivatives (30) with tetrafluoroboric acid in acetic anhydride under a CO atmosphere results in the formation of allyl-$Fe(CO)_4$ complexes (31).[36]



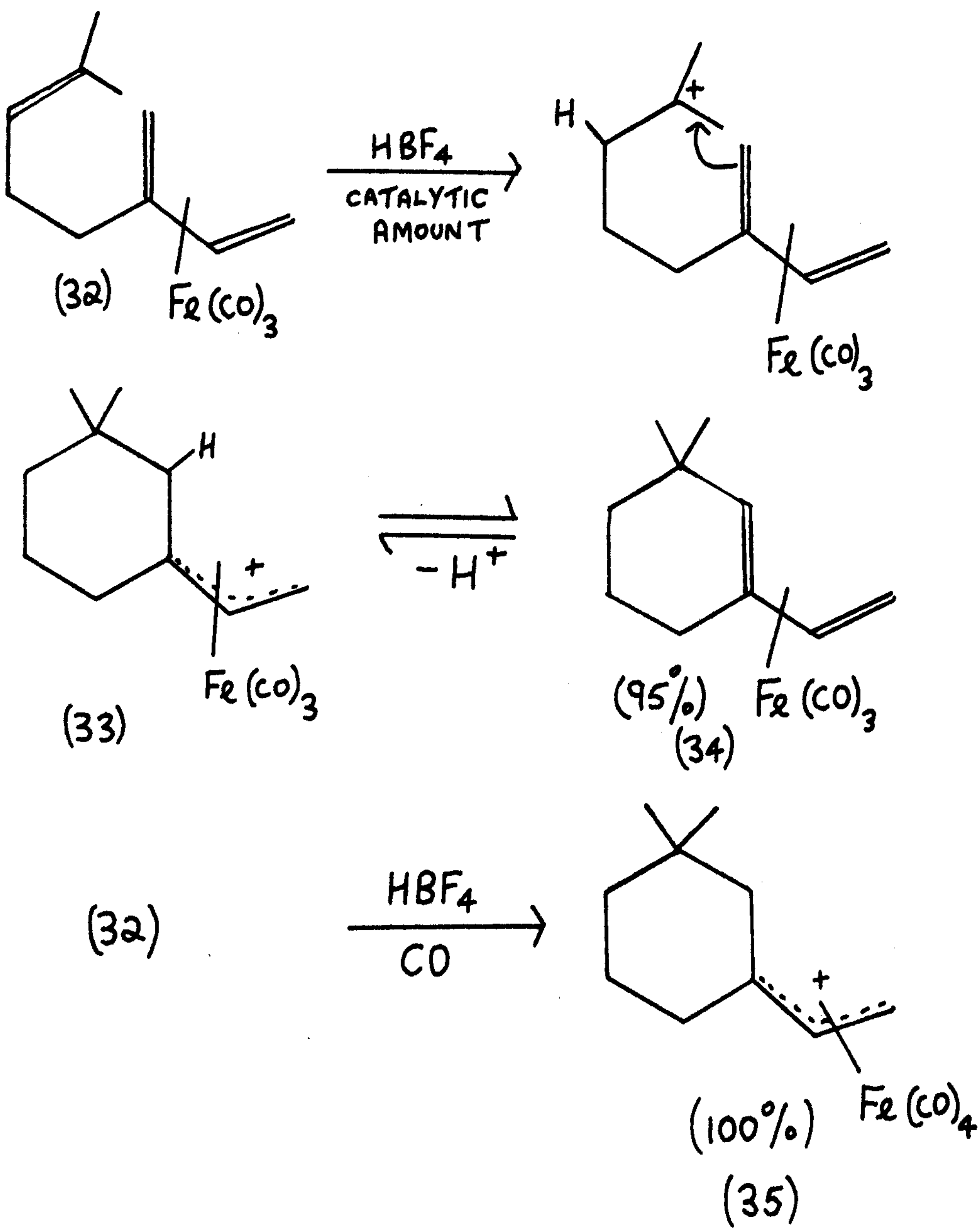

(30) (31)

R = R' = H

R = Me, R' = H

R = H, R' = Me

Tricarbonyl(myrcene)iron (32) is readily generated from the terpene myrecene; complexation allows skeletal rearrangements to take place.[37] Treatment of (32) with a catalytic amount of anhydrous tetrafluoroboric acid results in protonation of the uncomplexed double bond and cyclisation of the resulting carbocation to give the allyl complex (33), loss of a proton gives (34) in 95% yield. Treatment of (32) with one equivalent of anhydrous tetrafluoroboric acid under a CO atmosphere, results in a quantitative yield of the allyl $Fe(CO)_3$ complex (35).

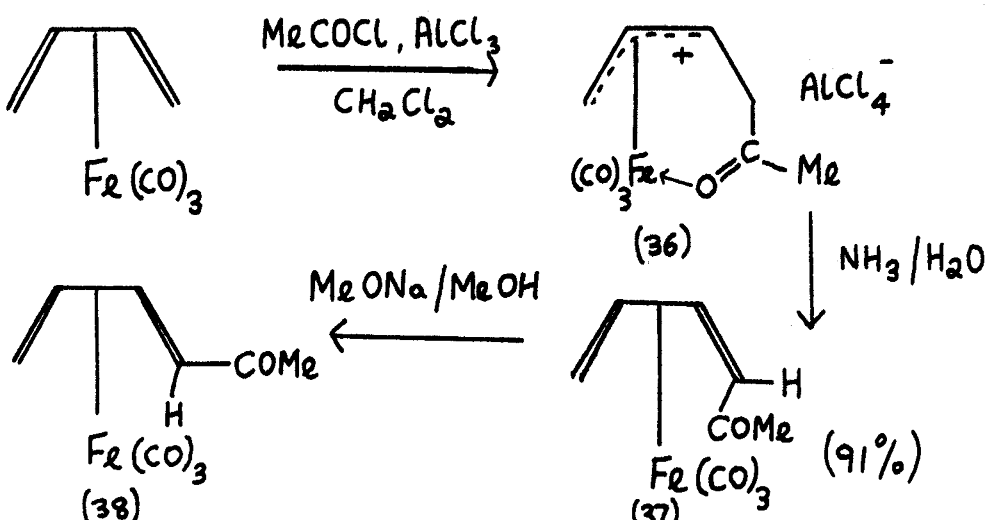


### 1.2.2.3 ($\eta^4$-diene)$Fe(CO)_3$ Complexes forming Chelating Allyl Compounds

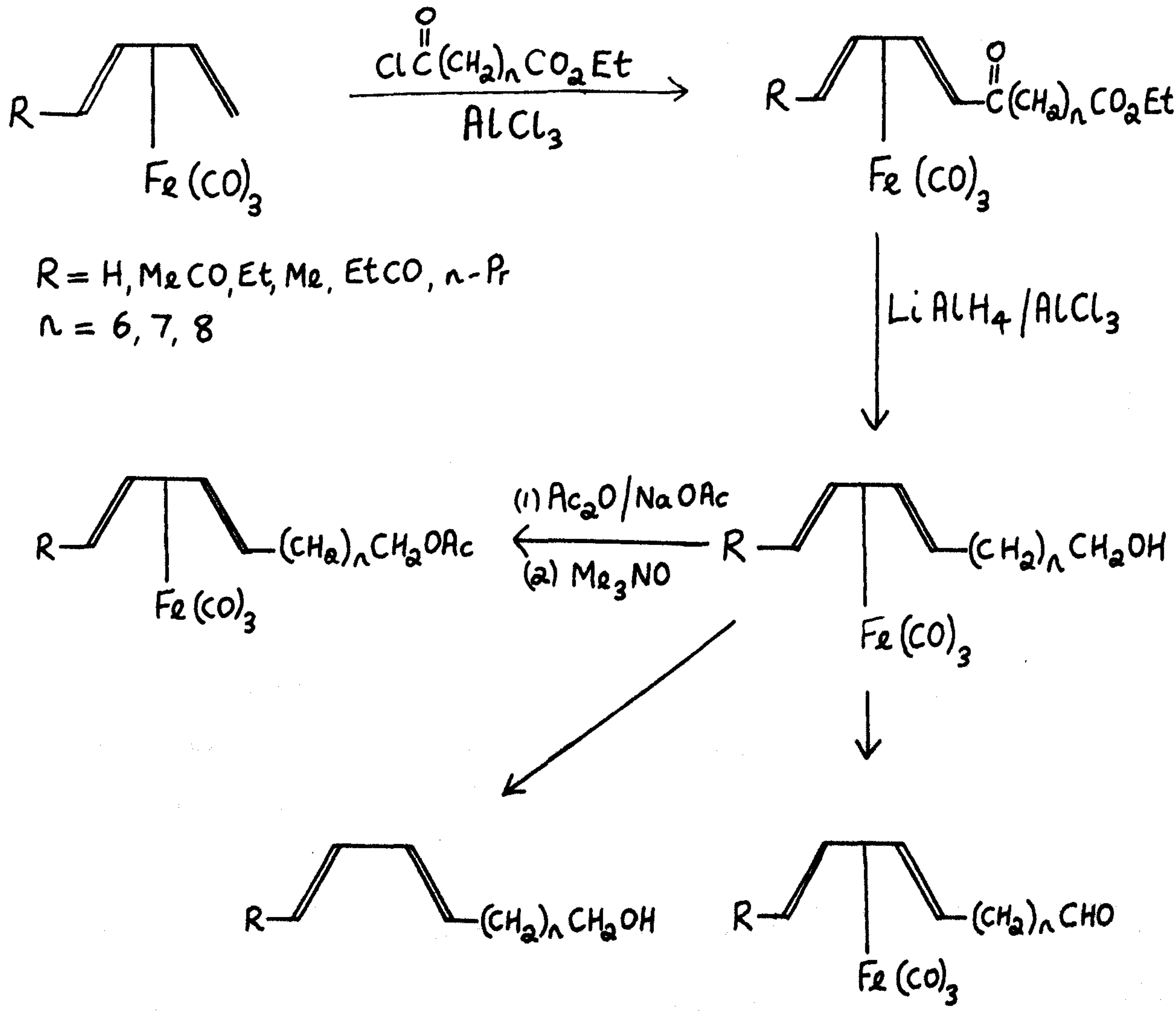
Systems containing $\eta^3$ as well as $\eta^1$ linkage to iron are very common. They are often derived from $\eta^4$-diene ligands by electrophilic additions, cycloadditions or the reactions of vinylcyclopropanes or monoepoxides with iron carbonyls.

(A) Electrophilic Additions to $\eta^4$-diene

Although attempted Friedel-Crafts acylation on an uncomplexed diene is uncontrollable, resulting in polymerisation, tricarbonyl(butadiene)iron is readily acylated in good yield (80-97%).[38] Electrophilic attack by the acyl cation occurs on the same side of the molecule as the iron atom, via an allyl intermediate (36). The stereochemistry of the product depends on the work up procedure; quenching the reaction mixture with cold aqueous ammonia gives the cis isomer (37) exclusively, whilst treatment of (37) with sodium methoxide in methanol gives only the trans isomer (38).

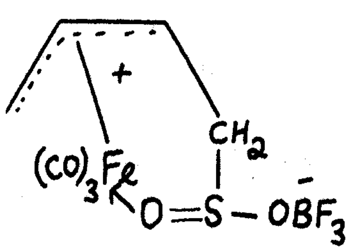



Knox has synthesized a variety of insect pheremones by the Friedel-Crafts acylation of tricarbonyl(butadiene)iron complexes (Scheme IV).[39]



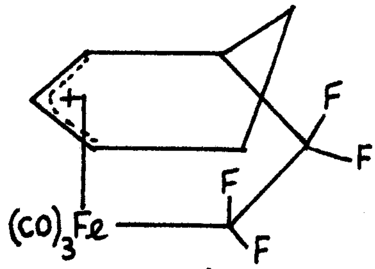

**SCHEME IV**

The electrophilic addition product (39) may be isolated when $BF_3$ gas is bubbled through a $SO_2$ solution of tricarbonyl(butadiene)-iron.[40]



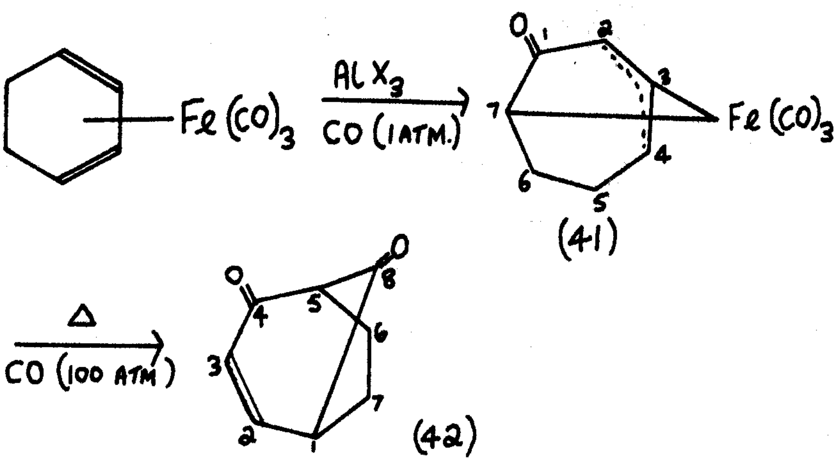
(39)

($\eta^4$-diene)$Fe(CO)_3$ complexes undergo addition with fluoroalkenes on the end face of the diene to give a novel $\sigma$ allyl complex, which links the diene with the metal.[41] For instance ultraviolet irradiation of tricarbonyl(cyclohexa-1,3-diene)iron with tetrafluoroethylene gives the novel cyclohexenyl derivative (40).




(40)

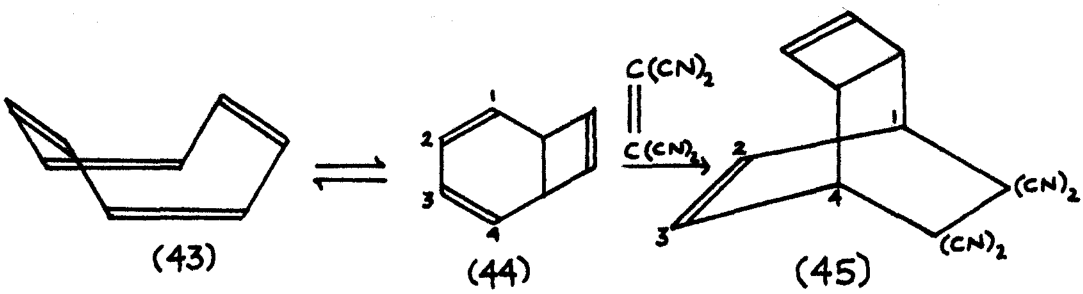
The reaction of tricarbonyl(cyclohexadiene)iron with $AlX_3$ in the presence of CO results in ring expansion to yield (41). The initial step is Lewis acid-base adduct formation at the iron atom. Liberation of the organic fragment (42) is accomplished by heating at 110°C in the presence of CO.[42]



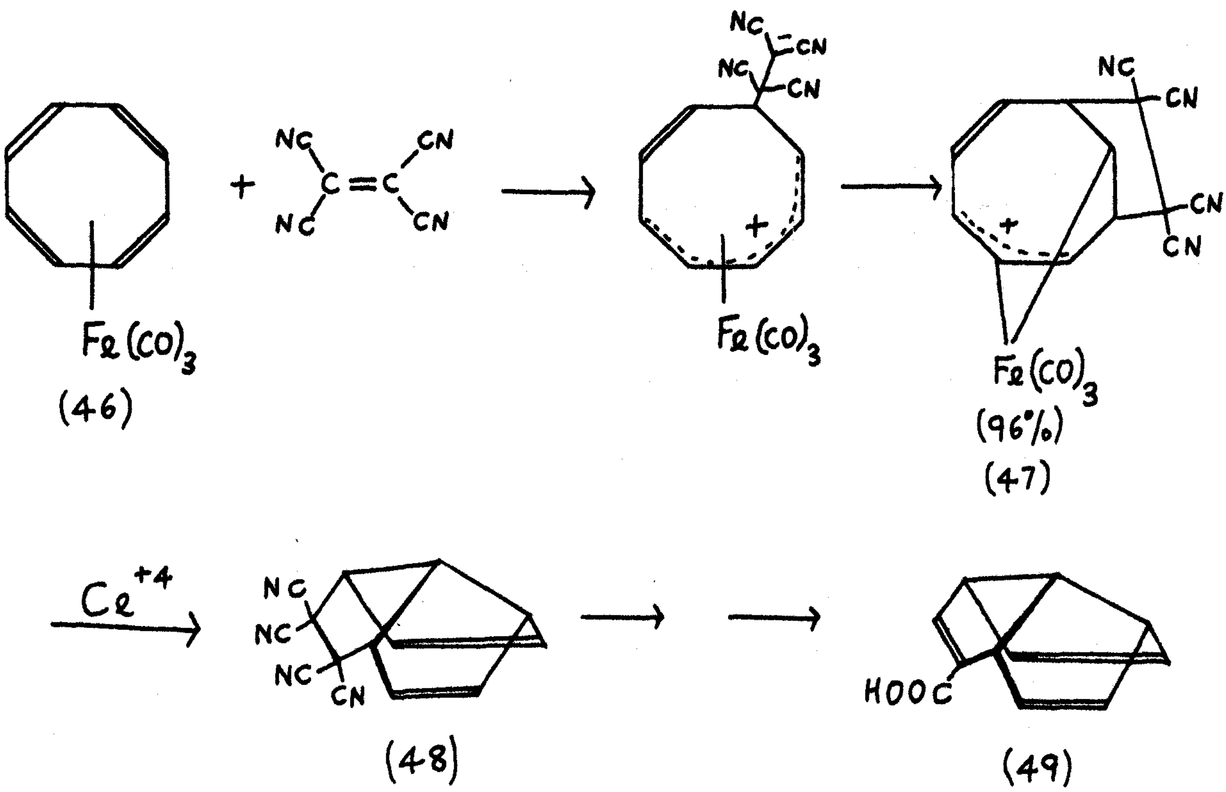

(41) (42)

(B) <u>Cyclo-addition to ($\eta^4$-diene) Complexes</u>

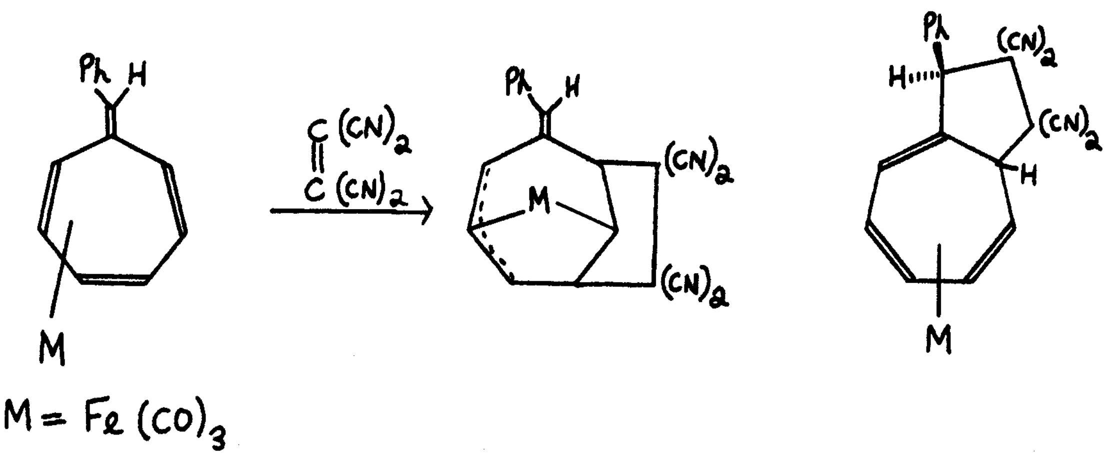
The cyclo-addition reaction of tetracyanoethylene (TCNE) with cyclo-octatetraene is an excellent example of a reactivity modification brought about through complexation of a metal to an olefin. Unco-ordinated cot (43) reacts with TCNE via its [4.2.0] bicyclic tautomeric form (44) (this is the preferred form since it gives a planar diene system which facilitates attack by the dienophile). 1,4-cyclo-addition occurs with TCNE in the classical Diels-Alder manner (45).[43]




However, addition of TCNE to (cot)Fe(CO)$_3$ (46) occurs via an unusual 1,3-cyclo-addition process to give the novel $\sigma$,allyl bonded iron complex (47).[44] Oxidation of the Fe(CO)$_3$ group with ceric ammonium nitrate gives (48), an important intermediate in the synthesis of 2-substituted triquinacene derivatives (49).

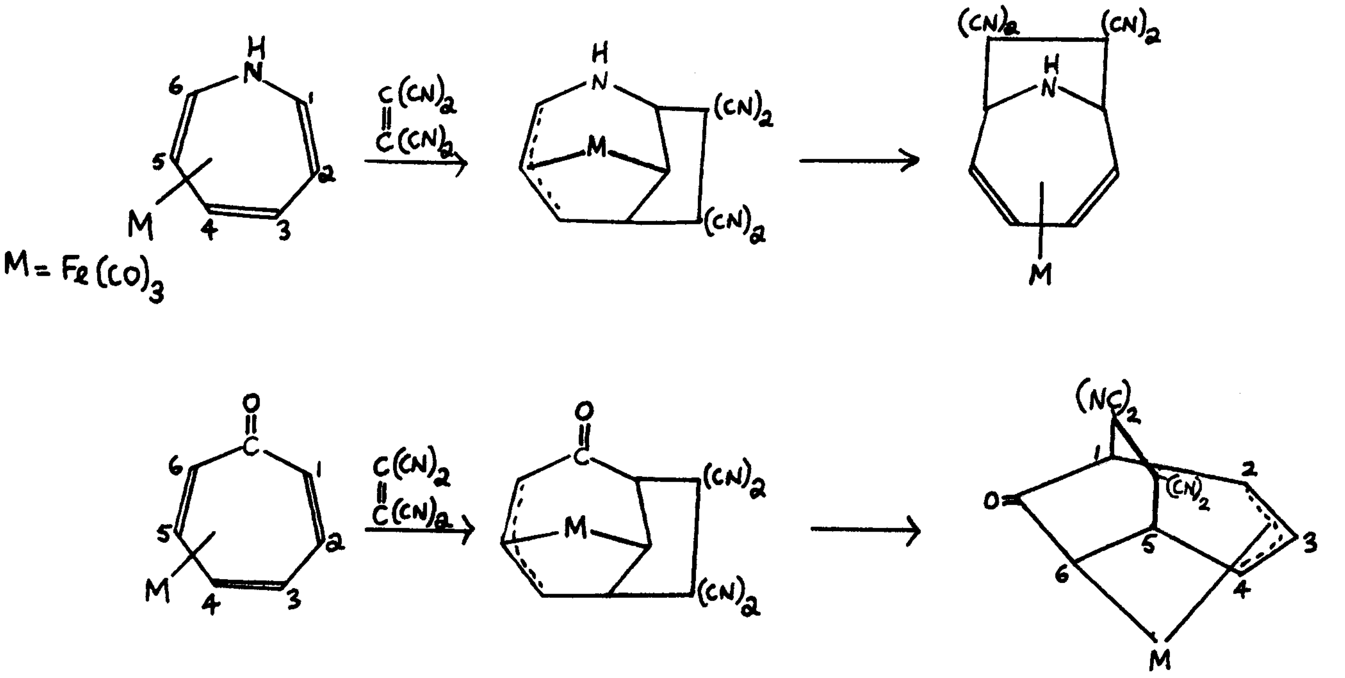


The addition of TCNE to (7-methylene cycloheptatriene)$Fe(CO)_3$ generates the 1,8-adduct and was initially thought[45] to provide a rare example of a cyclo-addition reaction in which a co-ordinated ligand appeared to undergo reaction by the same mechanism as the free ligand.[46] However, subsequent n.m.r studies showed that the reaction proceeded by initial 1,3-addition, followed by isomerization to the 1,8-adduct[47] (Scheme V). The unco-ordinated double bond is the first site of attack.



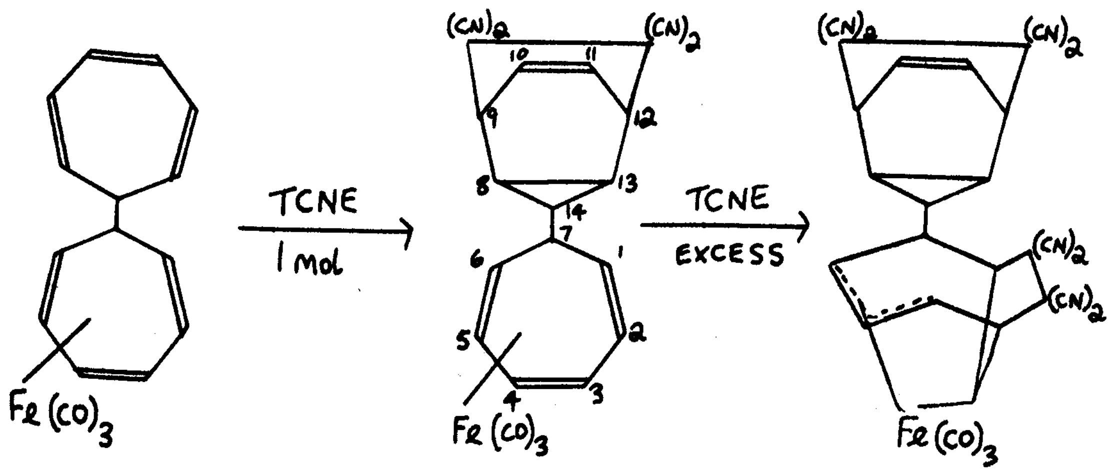

<u>SCHEME V</u>

Similarly the 1,6 addition product of TCNE to ($\eta^4$-azepine)$Fe(CO)_3$ was found to involve initial 1,3-addition,[48] and the 1,5-adduct of the ($\eta^4$-tropone)$Fe(CO)_3$ complex was shown to result from initial 1,3-attack[49] (Scheme VI - see following page).




SCHEME VI

A comparative study of the reactivity of TCNE with cycloheptatriene co-ordinated and non-co-ordinated to irontricarbonyl shows that the presence of $Fe(CO)_3$ deactivates the ring.[50] Initial attack by TCNE is on the non-co-ordinated cycloheptatriene unit in the expected 1,4-position,[51] whilst excess TCNE reacts with the co-ordinated ring to give the 1,3-adduct (Scheme VII).

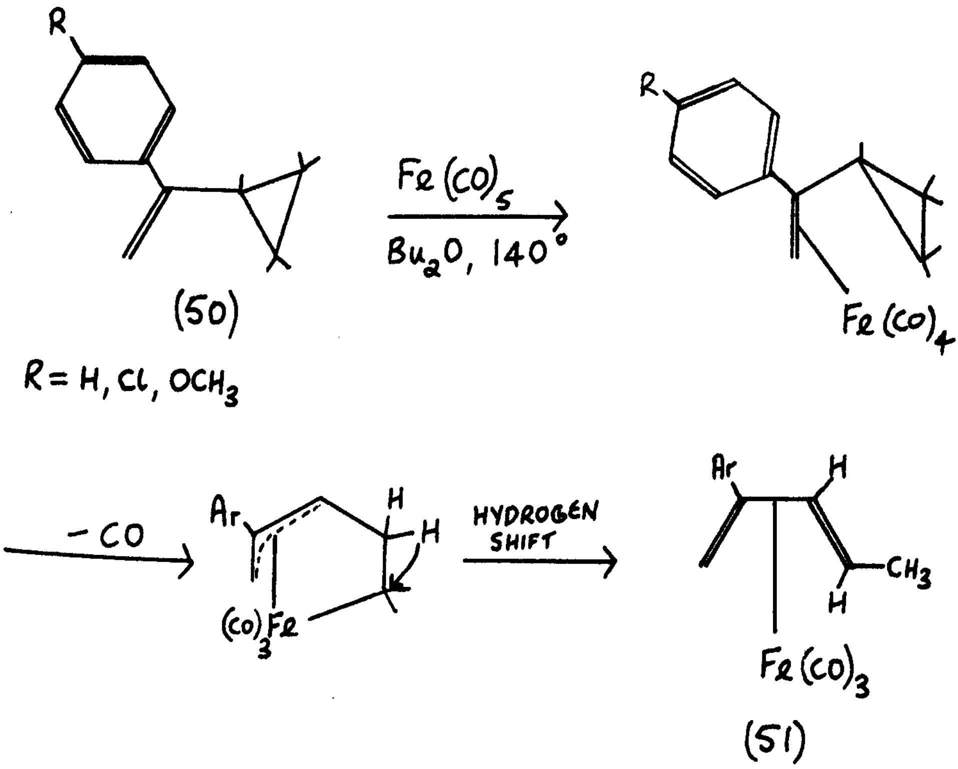



SCHEME VII

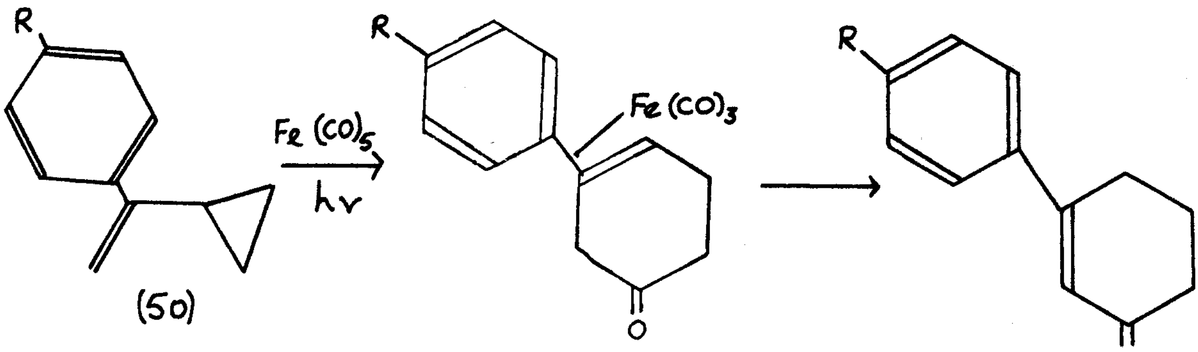
Other strong dienophiles used in cyclo-addition reactions include N-methyltriazolinedione,[52] diphenylketene,[53] hexafluoroacetone, 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene.[54]

(C) <u>Ring Opening of Vinylcyclopropanes</u>

Vinylcyclopropanes undergo ring opening when treated with $Fe(CO)_5$, the products are dependent on the reaction conditions. Treatment of 1-aryl-1 cyclopropylethylene (50) with $Fe(CO)_5$ under thermal conditions yields (51) via the following mechanism:-[55]



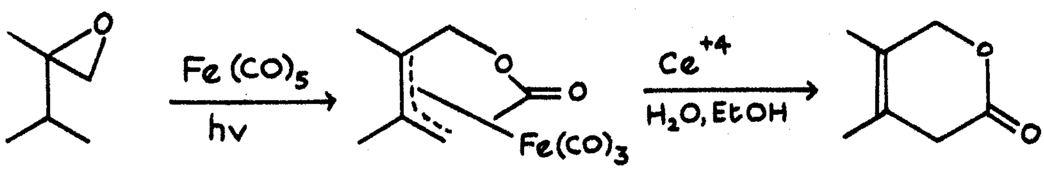

However, when (50) is irradiated carbonyl insertion becomes the major reaction pathway (52) to give the rearranged product (53).




(50) (52) (53)

(D) Ring Opening of Monoepoxides

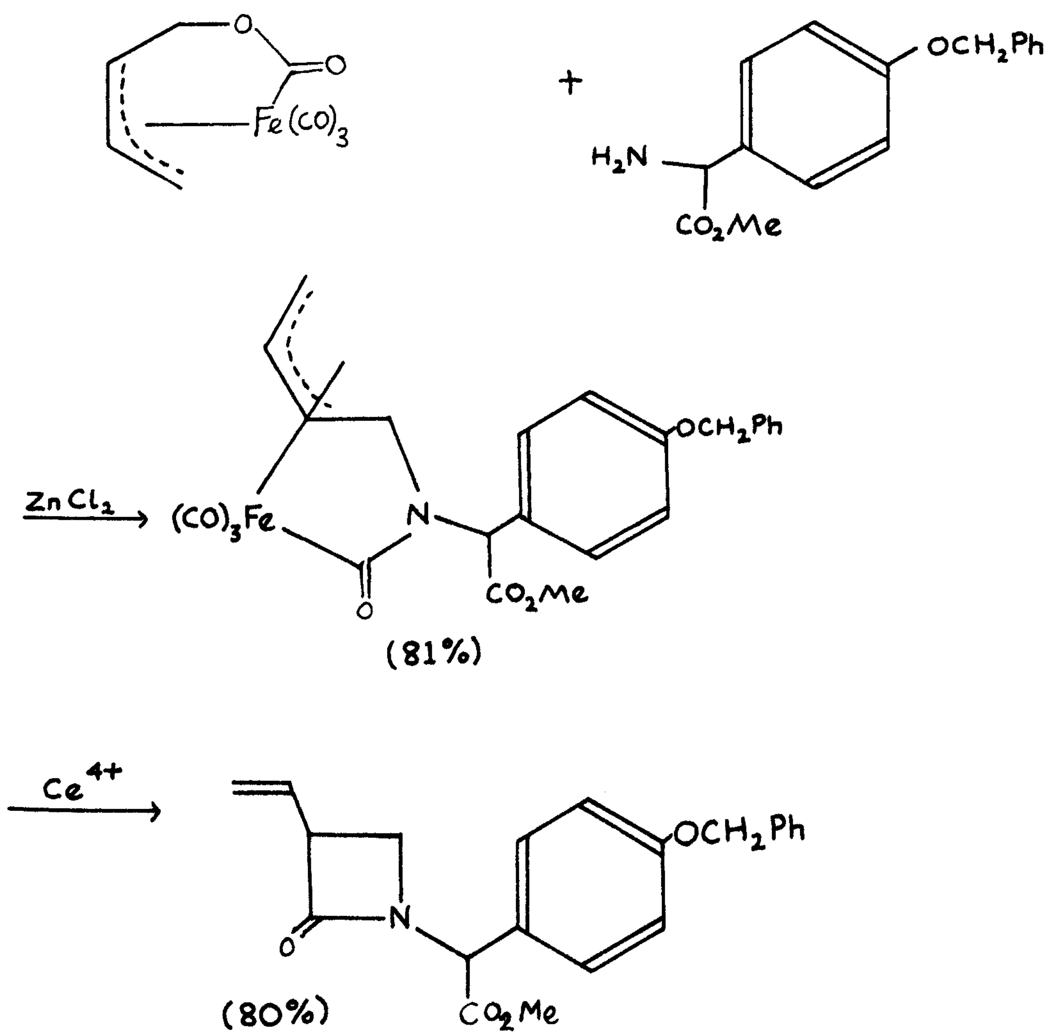
The reaction of monoepoxides with $Fe(CO)_5$ gives $\sigma$, allyl intermediate complexes which are subsequently oxidised to $\beta$-lactones (Scheme VIII).[56]




SCHEME VIII

The $\sigma$ allyl intermediate was found to react with amines in the presence of $ZnCl_2$ in an $S_N2$ type mechanism to give $\beta$-lactans. This has been used by Ley[57] in the synthesis of a novel class of $\beta$ lactan antibiotics, related to the nocardicins (Scheme IX).

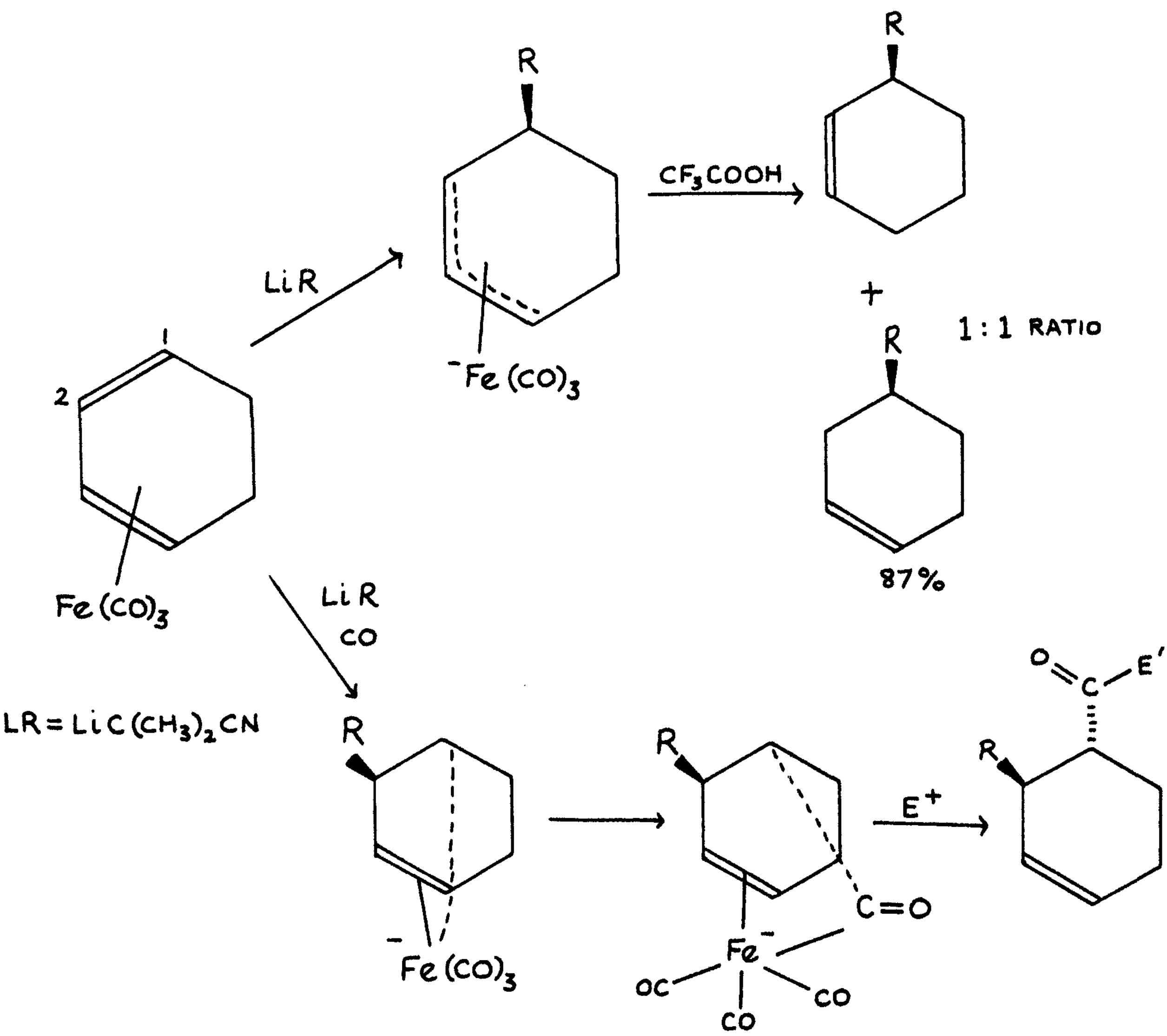
(See following page).




SCHEME IX

### 1.2.2.4 Nucleophilic attack on ($\eta^4$-diene)Fe(CO)$_3$ Complexes

Although free dienes are very inert to nucleophilic attack, complexation to a metal modifies the reactivity of the double bond. Semmelhack has recently reported that reactive carbanions will add to tricarbonyl(cyclohexa-1,3-diene)iron complexes to give a stable $\eta^3$ allyl intermediate which can be protonated with trifluoroacetic acid to produce substituted cyclohexenes in a 1:1 ratio.[58] A minor product arising from carbanion attack at C-2 of the diene ligand and subsequent CO insertion, becomes the major process if the addition of the carbanion to the diene complex is carried out under CO at 1.4-1.5 ATM[59] (Scheme X).

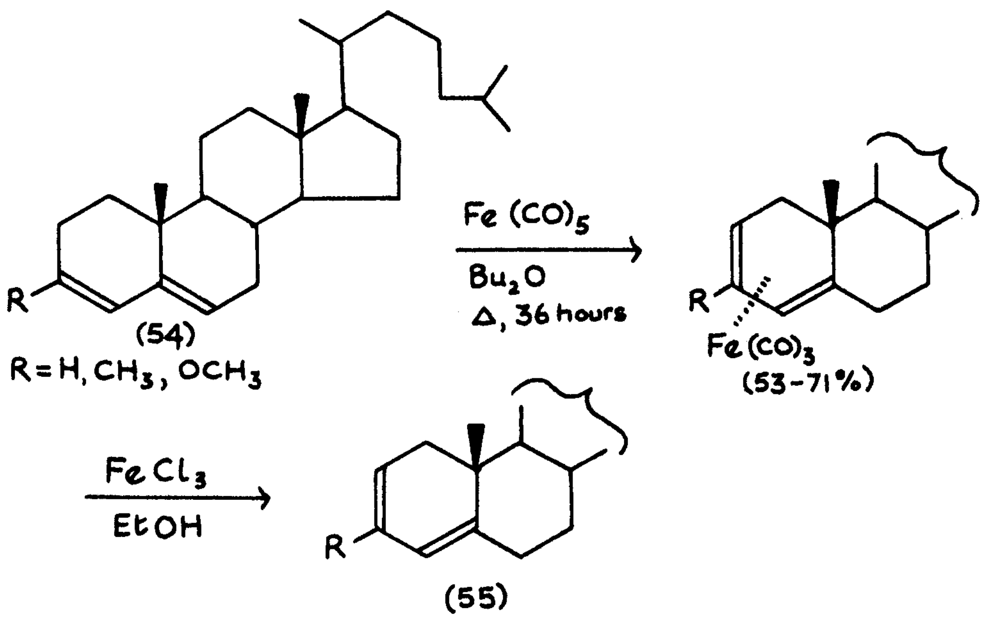



| $E^+$ | $E^-$ | YIELD |
|---|---|---|
| $CF_3COOH$ | H | 93 |
| $CH_3I$ | $CH_3$ | 87 |
| $O_2$ | OH | 97 |
| $CH_3OSO_2F$ | $OCH_3$ | 100 |

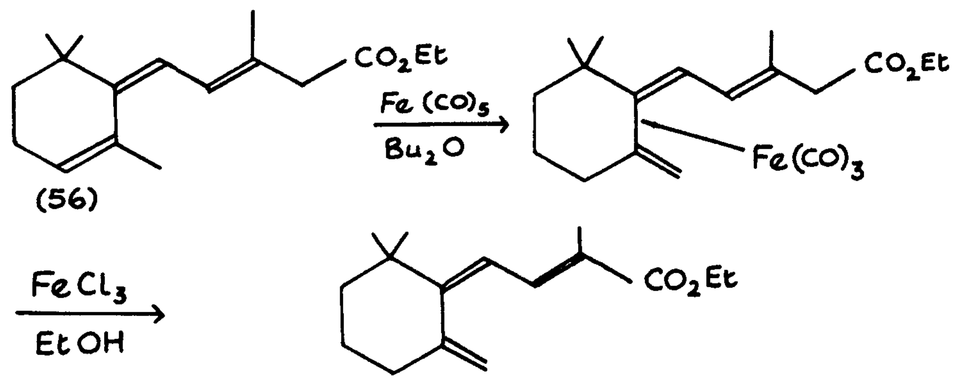
SCHEME X

### 1.2.3 Isomerization of Olefins

Many non-conjugated dienes including 1,4-cyclohexadienes rearrange to the corresponding conjugated dienes upon reaction with ironcarbonyl reagents. This leads to synthetic possibilities unobtainable with the non-co-ordinated diene. For example heteroannular steroidal dienes (54) have been converted into homoannular cis dienes by refluxing with pentacarbonyliron in dibutyl ether (55).[60]

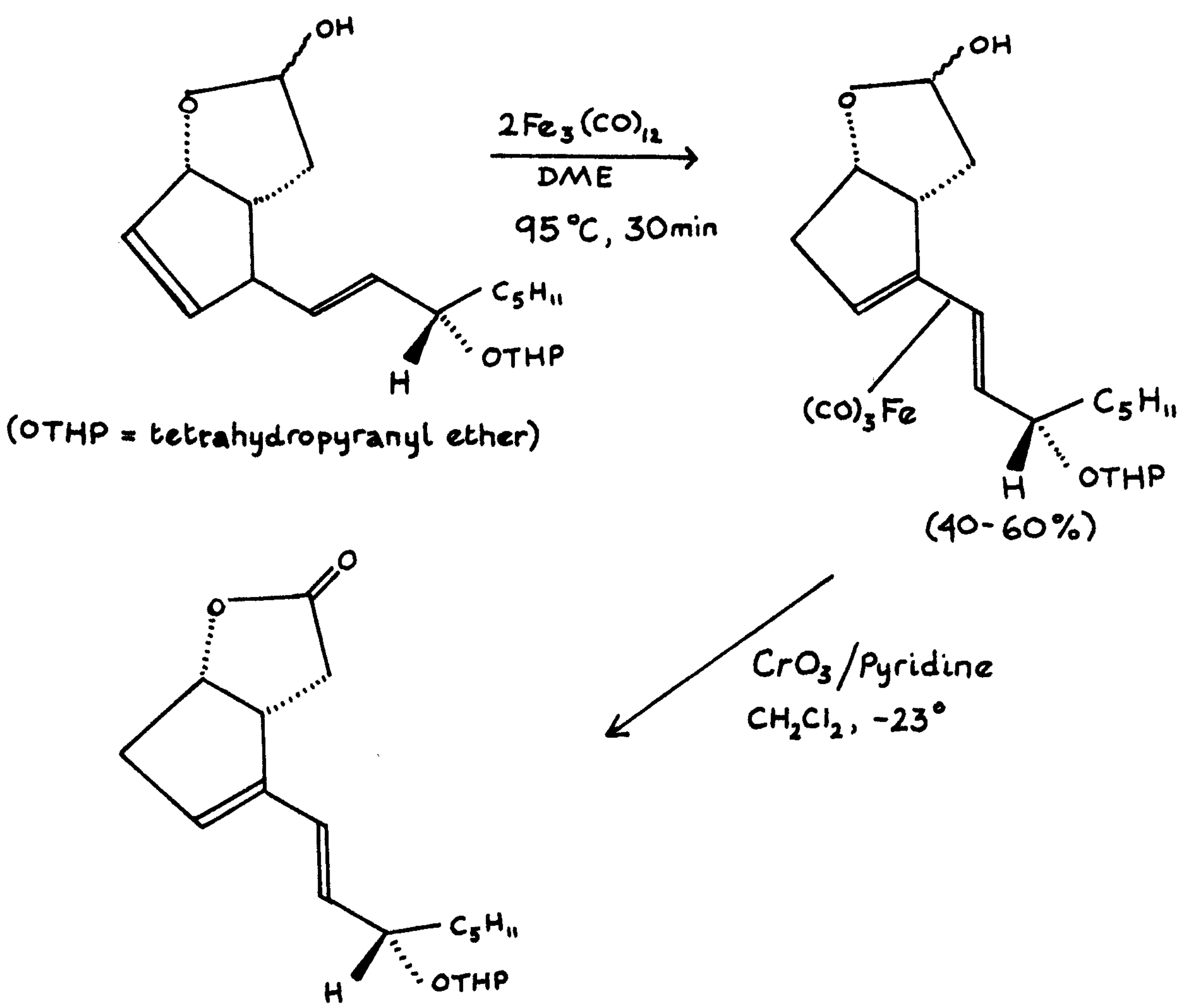



Cais and Maoz have reported the similar isomerization of (56) to (57) via the (diene)$Fe(CO)_3$ complex.[16]



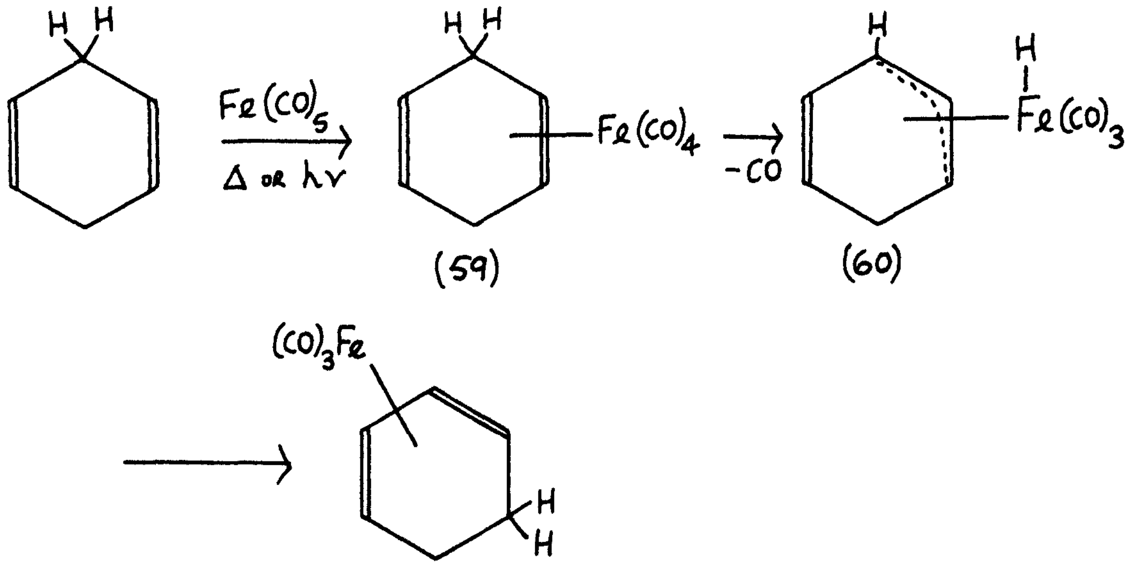

(56) (57)

Corey and Moinet have utilised the isomerization of unconjugated 1,4-dihydropyridines to 1,3-dihydropyridines in the synthesis of a prostaglandin C intermediate (58).[61]



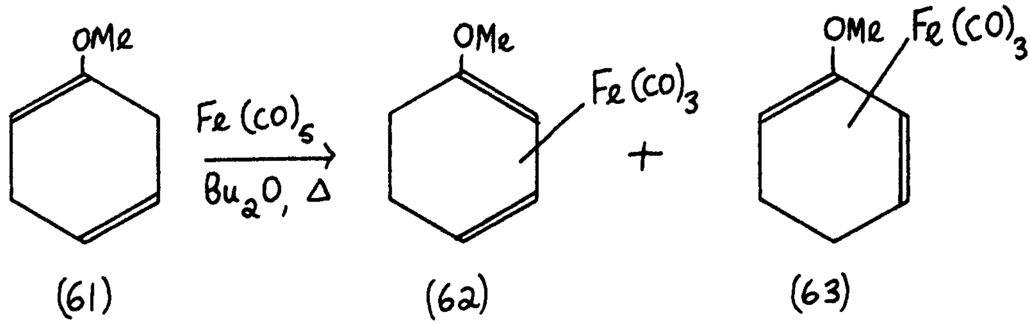

(58)

The isomerization of dienes during complexation is postulated to occur[6,62,63] by the initial complexation of $Fe(CO)_4$ to a double bond (59). Loss of CO follows, transfer of hydrogen to the iron results in the formation of a π allylic bond (60).



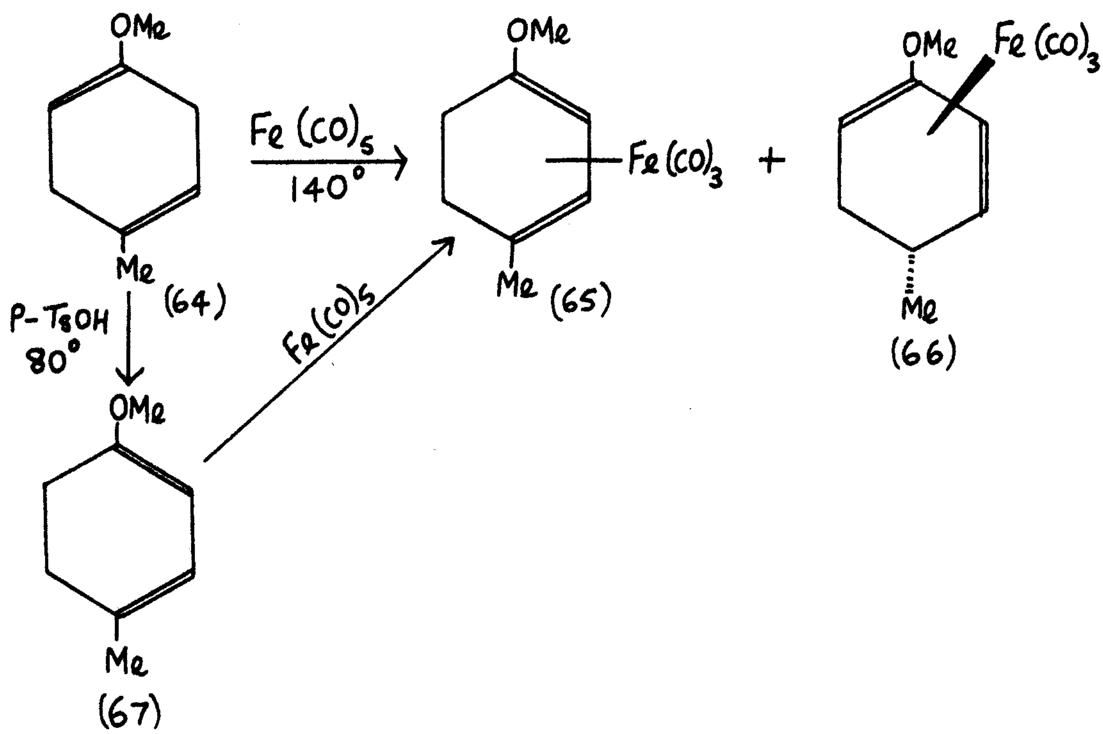

Transfer of hydrogen back to the carbon system gives the stable (1,3-diene)$Fe(CO)_3$ complex.

Birch and co-workers have prepared a variety of substituted tricarbonyl(cyclohexa-1,3-diene)iron complexes. These are readily accessible by the reduction of substituted aromatic compounds with sodium in liquid ammonia to give the corresponding cyclohexa-1,4-dienes. Treatment with pentacarbonyliron yields substituted (cyclohexa-1,3-diene)$Fe(CO)_3$ complexes. Benzenoid compounds used in this way include anisole,[64,65] 4-methyl anisole,[66] toluene, m- and p-xylene.[65] However, since substituted 1,4-dienes can be conjugated in two or more ways, isomeric mixtures of cyclohexa-1,3-diene $Fe(CO)_3$ complexes have been formed in these reactions. For example, treatment of 2,5-dihydro-anisole (61) with pentacarbonyl-iron gives (62) and (63) in a 50:50 ratio.

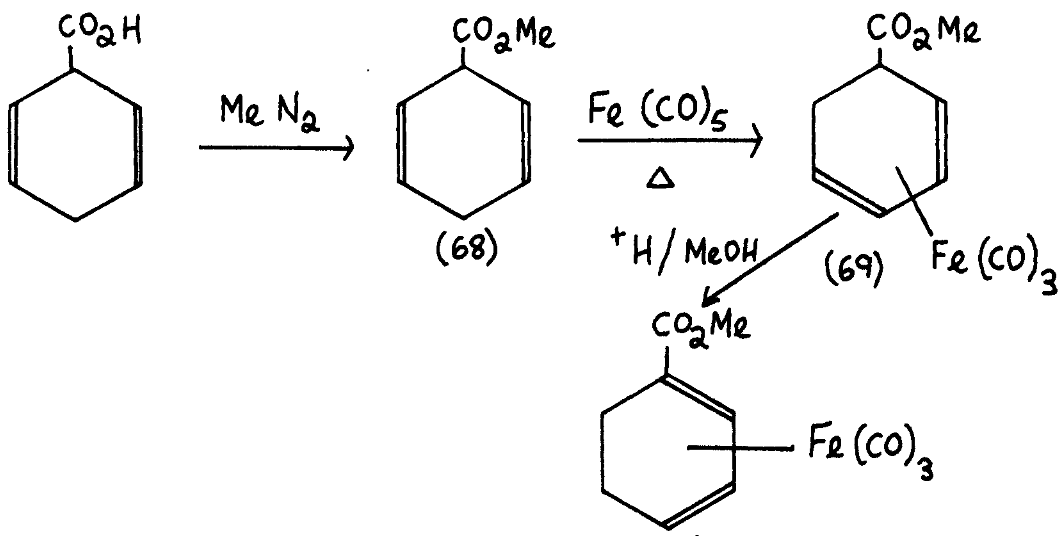



(62) and (63) can be separated by chromatography.[67] Separation on a larger scale is more conveniently achieved by the selective hydrolysis of the 1-MeO cyclohexadienyl salt, whilst the 2-MeO salt is unaffected.[68]

Isomers (65) and (66) are derived from 4-methyl,2,5-dihydro-anisole (64). However, Pearson[46] has developed an alternative route to the synthetically useful (65). Preconjugation of the 1,4-diene with a catalytic amount of p-toluene acid gives (67), subsequent treatment with $Fe(CO)_5$ results in the formation of only (65) in 80% yield.

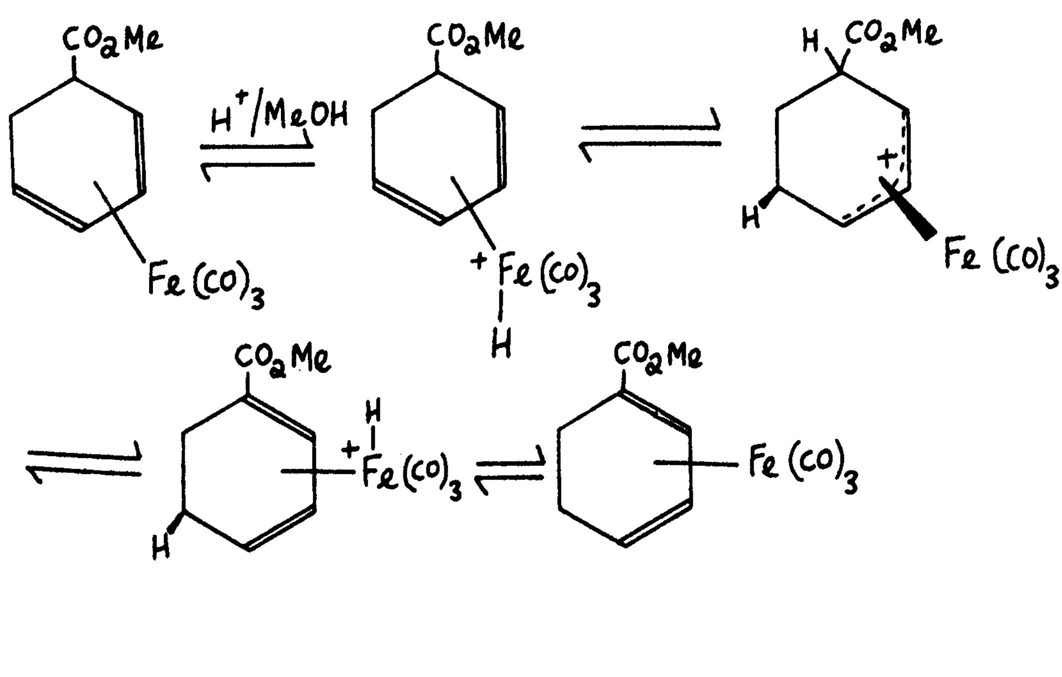


The reduction of benzoic acid followed by esterification with diazomethane, gives methyl-1,4-dihydrobenzoate (68). Treatment of (68) with pentacarbonyliron yields (69) as the major product in which the ester group remains on the $sp^3$ hybridized carbon atom.[69]



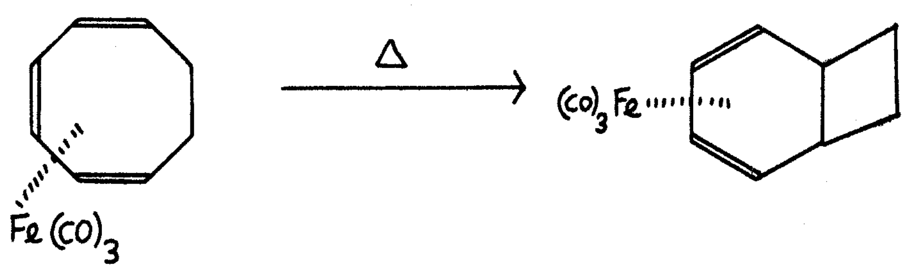

(68) (69) (70)

Acid catalysed isomerization of (69) to the stable isomer (70), occurs in the presence of methanolic acid. The postulated mechanism for the isomerization is given in Scheme XI.[70]



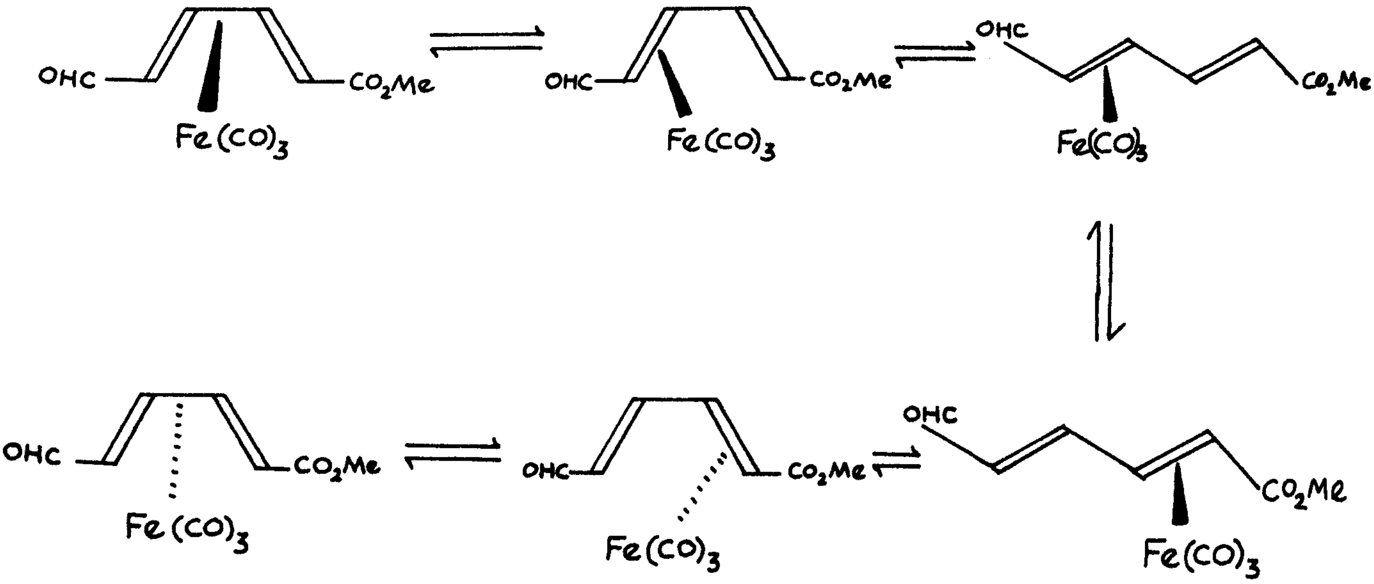

SCHEME XI

There are various types of isomerization observed in (polyene)-$Fe(CO)_3$ complexes. The $Fe(CO)_3$ group can migrate between double bonds in trienes and tetraenes, or from one face of the diene to the opposite one, leading to racemization. For example, the irontricarbonyl group migrates rapidly between the double bonds of cyclo-octatraene by 1,2-shifts. The equilibrium position of the mono- and bicyclic conformation adopted by cyclo-octatriene is shifted very much by co-ordination to iron.[71] At 102°C, the thermal isomerization of (71a) to (71b) is effectively complete, whilst for the free ligand 85% of the monocyclic form is present at 100°C. The shift in the equilibrium is due to the $Fe(CO)_3$ group forcing the complexed diene moiety into a nearly planar configuration, which is energetically unfavourable compared to the tub structure. Thus for the complexed molecule, (71b) is considerably less strained, and therefore energetically preferred.



(71a) (71b)

Whitlock has reported that the racemization of (+)-(methyl-5-formyl-2,4-pentadienoate)$Fe(CO)_3$ ($K_{rac}=1.42\times10^{-2}s^{-1}$ at 119°C) occurs by a first order process.[72] The proposed mechanism (Scheme XII) consists of three stages, the formation of the $\eta^2$-diene, rotation from s-cis to s-trans diene and a 1,3-shift of iron at the s-trans diene.



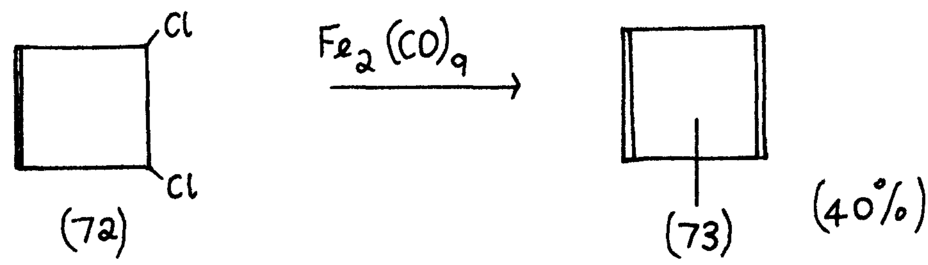

SCHEME XII

1.2.4 Stabilization of Highly Reactive Organic Molecules

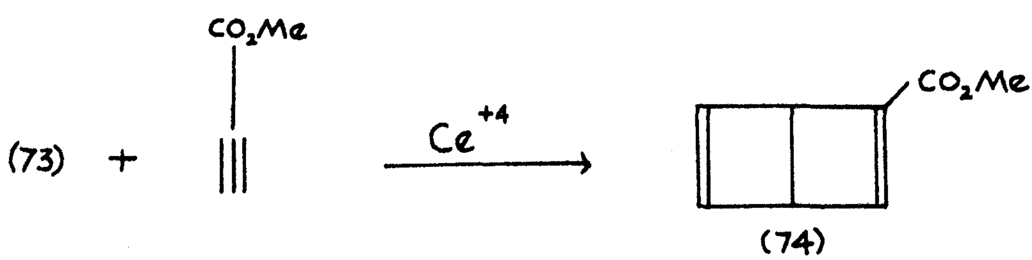
Several highly elusive and novel organic molecules have been isolated by complexation. Useful transformations have been carried out on these complexes, followed by the removal of the metal.

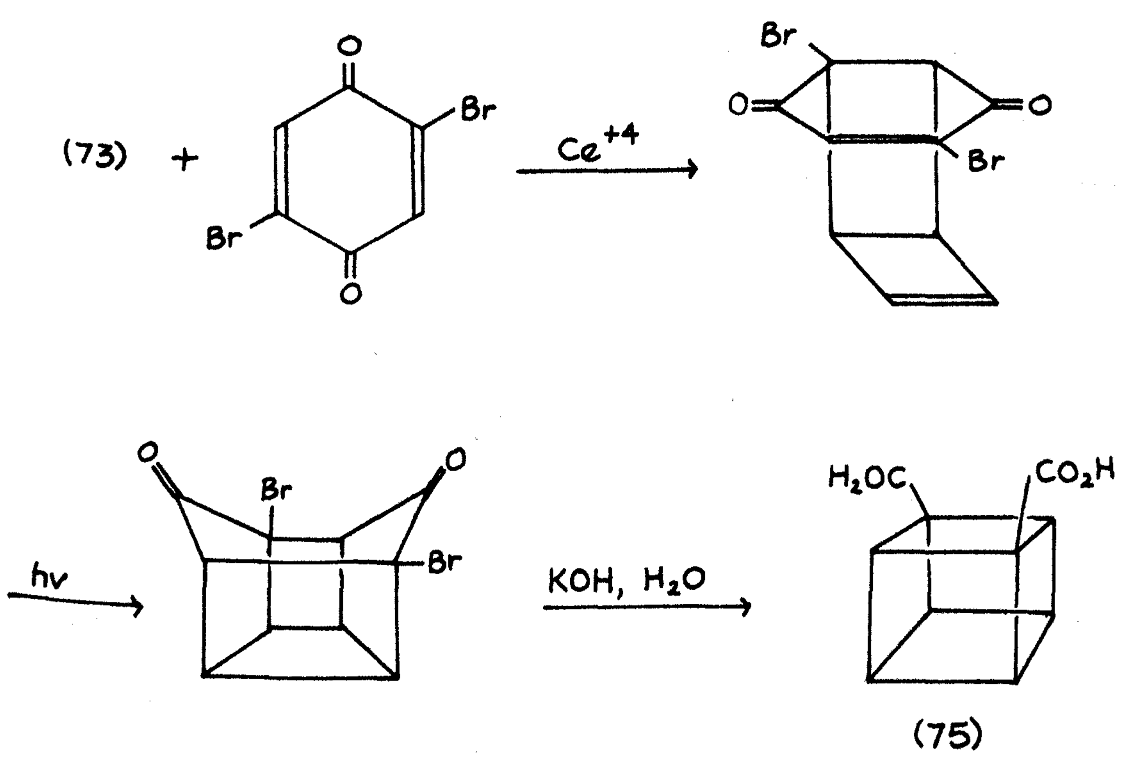
1.2.4.1 Cyclobutadiene

Although free cyclobutadiene is stable in a noble gas matrix at 8°K,[73] tricarbonyl(cyclobutadiene)iron (73) is a much more convenient form for use in organic synthesis. The synthesis and reactions of tricarbonyl(butadiene)iron complexes have been extensively reviewed.[74] Unsubstituted (73) was first isolated in 1965 by the treatment of cis-3,4-dichlorocyclobutene (72) with $Fe_2(CO)_9$.[75]




The synthetic potential of (73) lies in its use as a source of 'free' cyclobutadiene, which undergoes cyclo-addition reactions. A variety of novel compounds have been made, such as the 'Dewar benzene' derivative 2-methoxycarbonylbicyclo[2.2.0.]hexa-2-5-diene (74)[76] or the synthesis of the cubane ring system (75).[77]

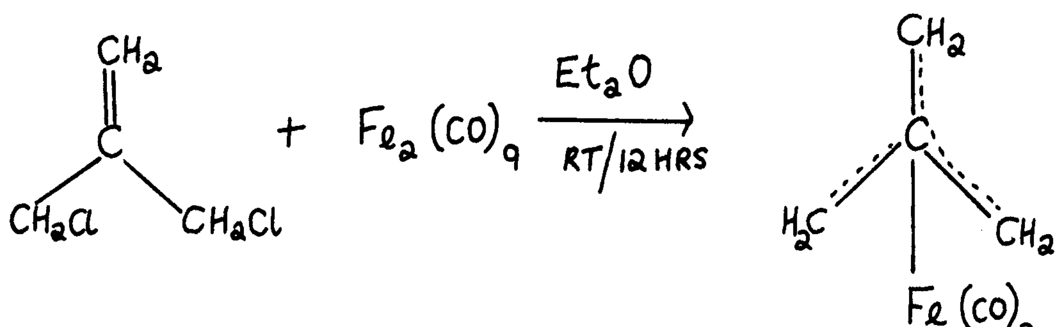


(73) undergoes electrophilic substitution to give $Fe(CO)_3(\eta^4\text{-}C_4H_3E)$. It behaves like an 'aromatic' compound; cyclobutadiene itself is antiaromatic. A range of electrophiles have been used (similar to those used for the substitution of ferrocene), such as MeCO (using $MeCOCl\text{-}AlCl_3$), CHO (using $PhMeNCHO\text{-}POCl_3$), and HgCl (using mercury II acetate, then NaCl).[74]

### 1.2.4.2 Trimethylene Methane

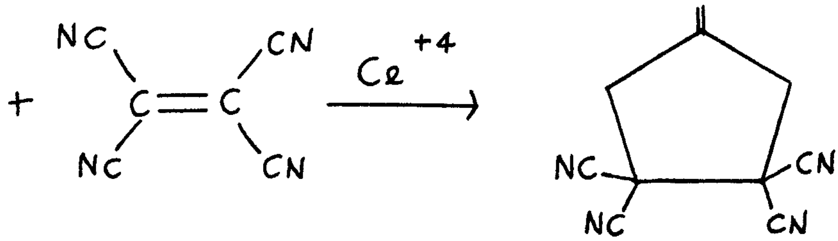
Trimethylene methane is a theoretically important intermediate, since the central carbon atom attains the maximum $\pi$ bond order possible for any carbon atom. This highly reactive intermediate with an observable electron spin resonance spectrum at -185°C,[78] is readily isolated as its tricarbonyl complex (76).[79]




(76) (30%)

The $^1H$ n.m.r. spectrum of (76) shows a sharp singlet at 2.0 p.p.m., indicating the equivalency of all hydrogens. No broadening of the proton signal was observed at -60°C, signifying a lack of valence tautomers. There has been little success in liberating the free ligand for synthetic application. Treatment of (76) with ceric ammonium nitrate in the presence of tetracyanoethylene gave the cyclo-addition product (77) in very low yield.[80]

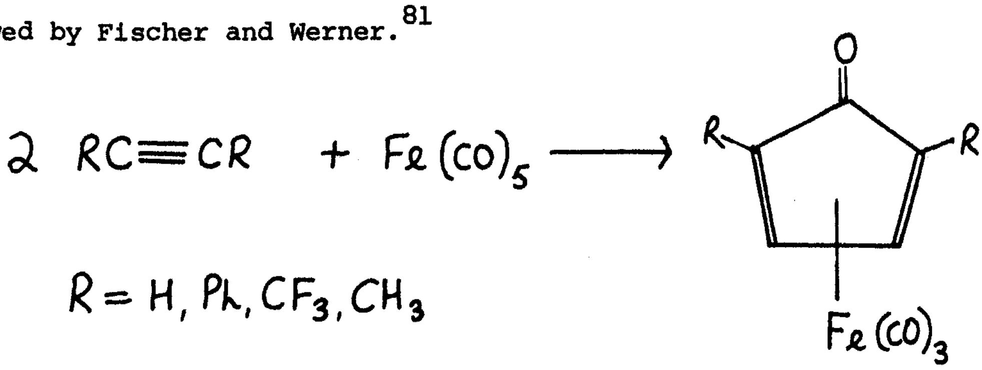
(76)



(4%)
(77)

1.2.4.3 Cyclopentadienone

Because of the polarity of the carbonyl group, cyclopentadienone is analogous to the cyclopentadienyl cation and exhibits anti-aromatic behaviour. A variety of tricarbonyl(cyclopentadienone)iron complexes (78) have been prepared by the reaction cf substituted acetylenes with $Fe(CO)_5$. Various synthetic approaches have been reviewed by Fischer and Werner.[81]



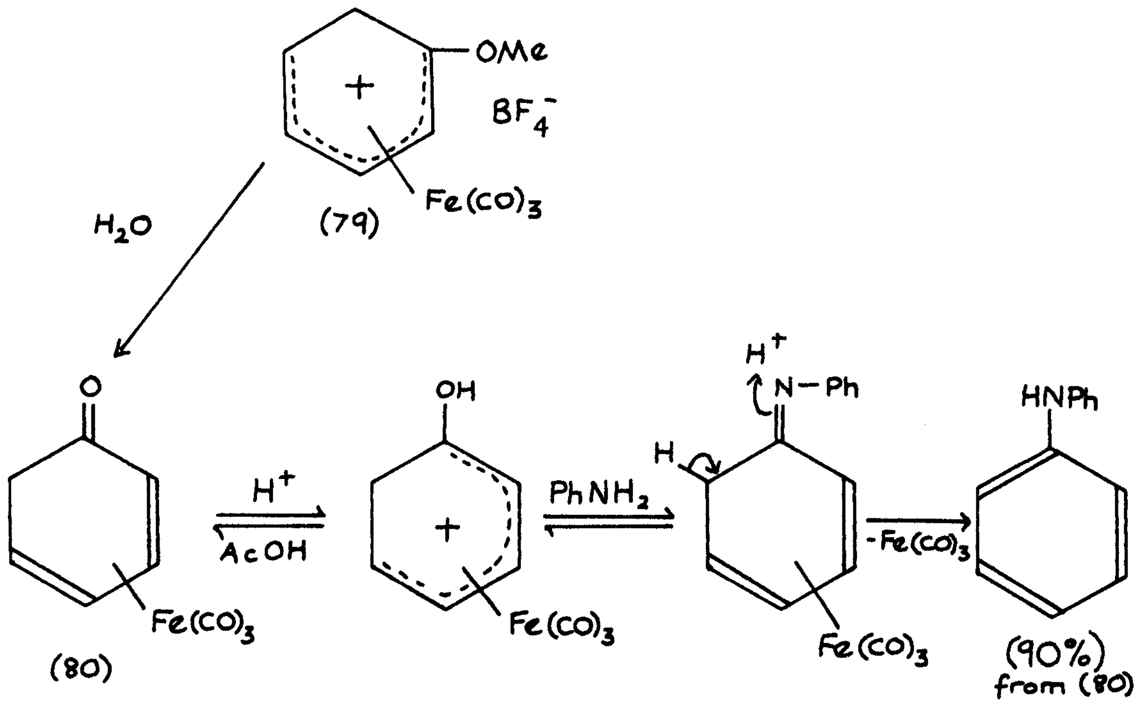
R = H, Ph, $CF_3$, $CH_3$

(78)

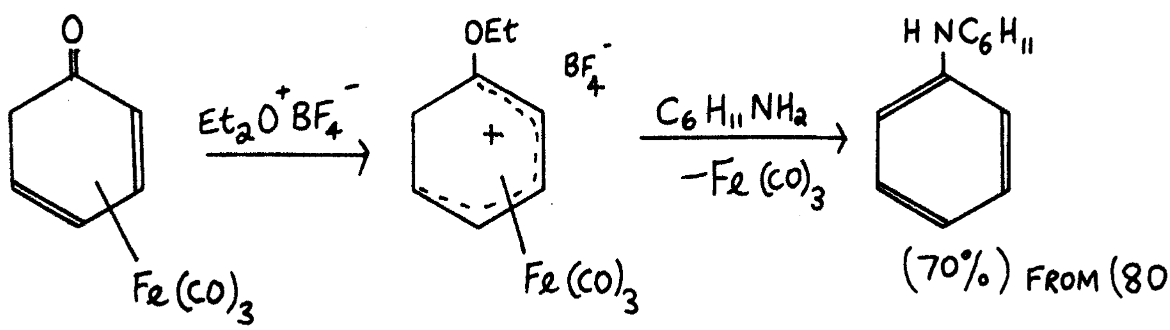
However, no attempt has been made to liberate the substituted cyclopentadienones for synthetic purposes.

1.2.4.4 Cyclohexadienone

Although cyclohexadienone is unstable with respect to its tautomer phenol, it can be stabilized as the tricarbonyliron complex (80) which is readily prepared by the hydrolysis of [(1-methoxy-cyclohexadienyl)$Fe(CO)_3$][$BF_4$][68] (79). (80) has been used as a means of N-phenylating amines as in schemes XIII and XIV.[82]

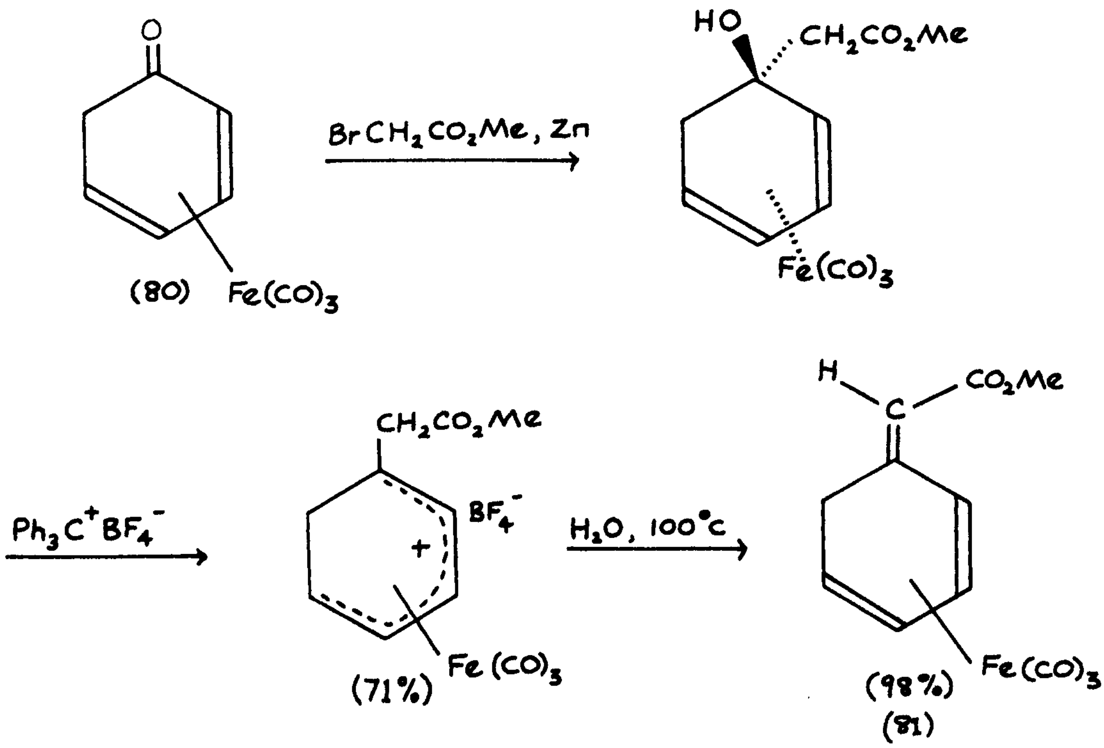



SCHEME XIII



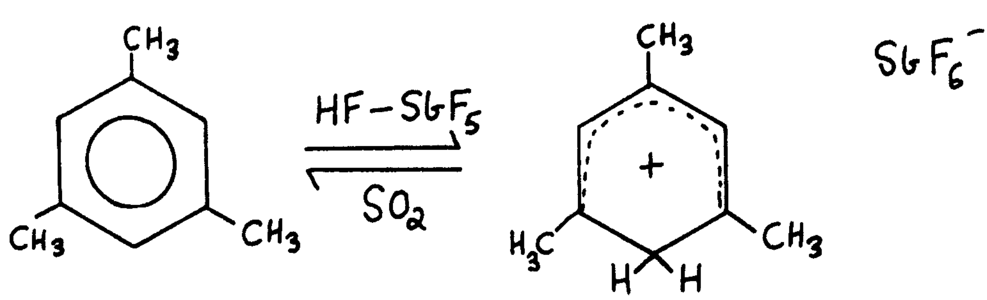

SCHEME XIV

(80) undergoes the Reformatsky reaction to give, eventually, the stabilized benzene tautomer (81).[83] (See following page).



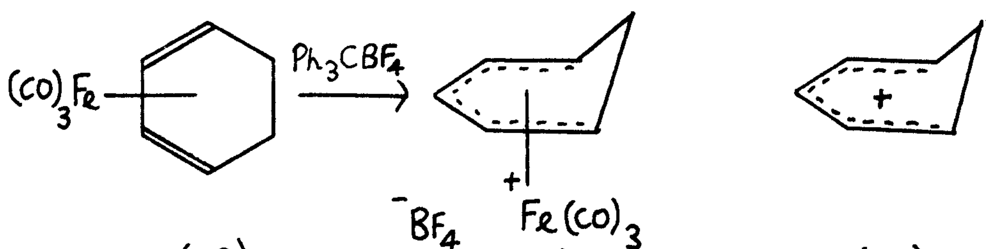

1.2.4.5 Cyclohexadienyl Cation

Only a few cyclohexadienyl derivatives (including the parent benzenium ion $C_6H_7^+$) have been prepared by the protonation of aromatic hydrocarbons by strong acids[84] and studied by $^1H$ and $^{13}C$ n.m.r. spectroscopy.[85]




By contrast, the cyclohexadienyl $Fe(CO)_3^+$ cation (83) is so stable that it can be purified by recrystallization from aqueous solutions.

(83) is readily prepared by hydride abstraction from tricarbonyl-(cyclohexadiene)iron (82) using $Ph_3C^+BF_4^-$, and is isolated as the yellow crystalline tetrafluoroborate salt.[86]

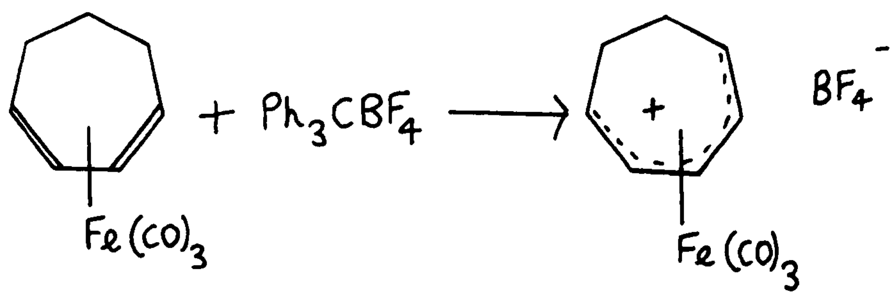


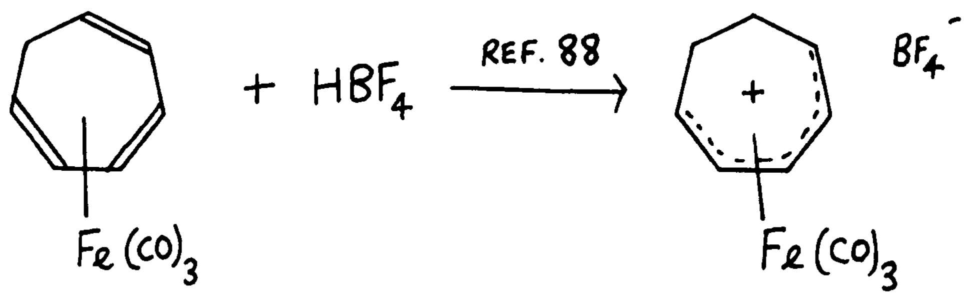
(82) (83) (84)

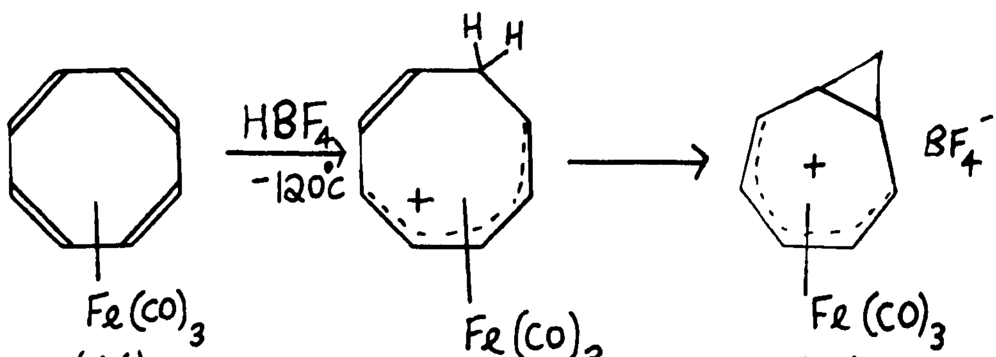
Stabilization of (83) is effected by electron donation from the 4 π electron system and also by back bonding from the filled metal orbitals to the empty non-bonding orbitals of the denyl system. A significant part of the charge is located on the iron.[87] Whilst the cyclohexadienyl cation (84) easily loses a proton to regenerate the benzene ring, loss of a proton from (83) does not occur. However (83) undergoes nucleophilic addition to give substituted (diene)$Fe(CO)_3$ complexes, which have great potential in organic synthesis (Section 1.2.5). Despite several attempts to prepare (benzene)$Fe(CO)_3$, none have been successful, possibly because considerable loss of electron delocalization of the aromatic sextet would be required in the benzene ligand for co-ordination to occur.

1.2.4.6 Cyclic Dienyl Cations

$[(Dienyl)Fe(CO)_3]^+$ complexes of larger rings are generated from the neutral parent diene complexes in two main ways; by hydride abstraction from an adjacent carbon of a diene system, or by the addition of a proton to a triene or polyene.





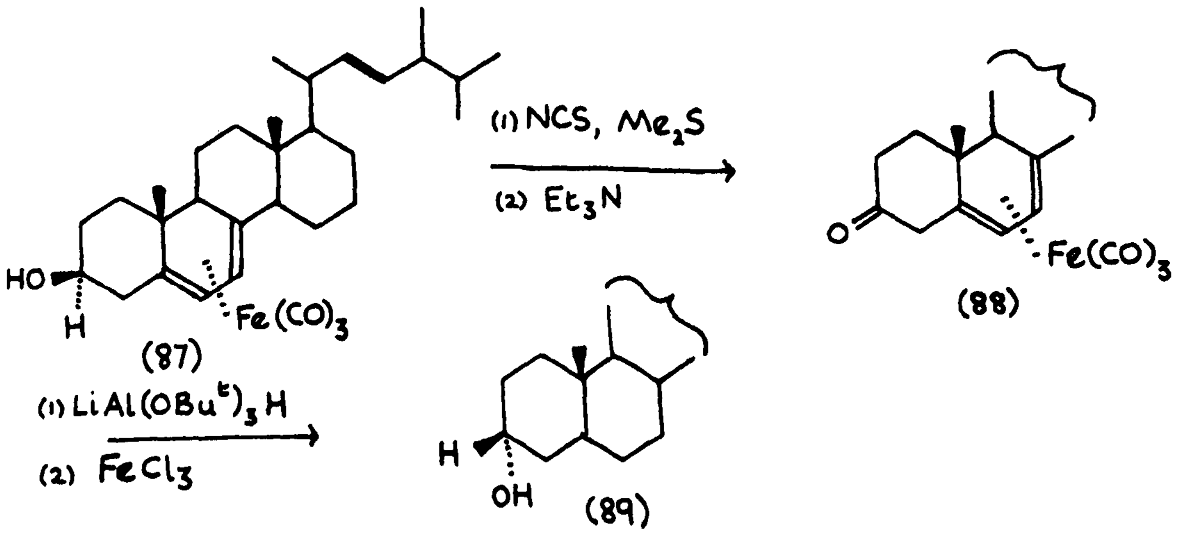


(46) (85) (86)

Seven membered ring dienyl complexes are stable at room temperature, but protonation of (cot)Fe$(CO)_3$ (46) gives the dienyl complex $[(\pi^5\text{-}C_8H_9)Fe(CO)_3]^+$ (85) which is stable in the eight membered ring form only at low temperature but rapidly isomerizes to the seven membered ring dienyl cation (86)[89] at room temperature.

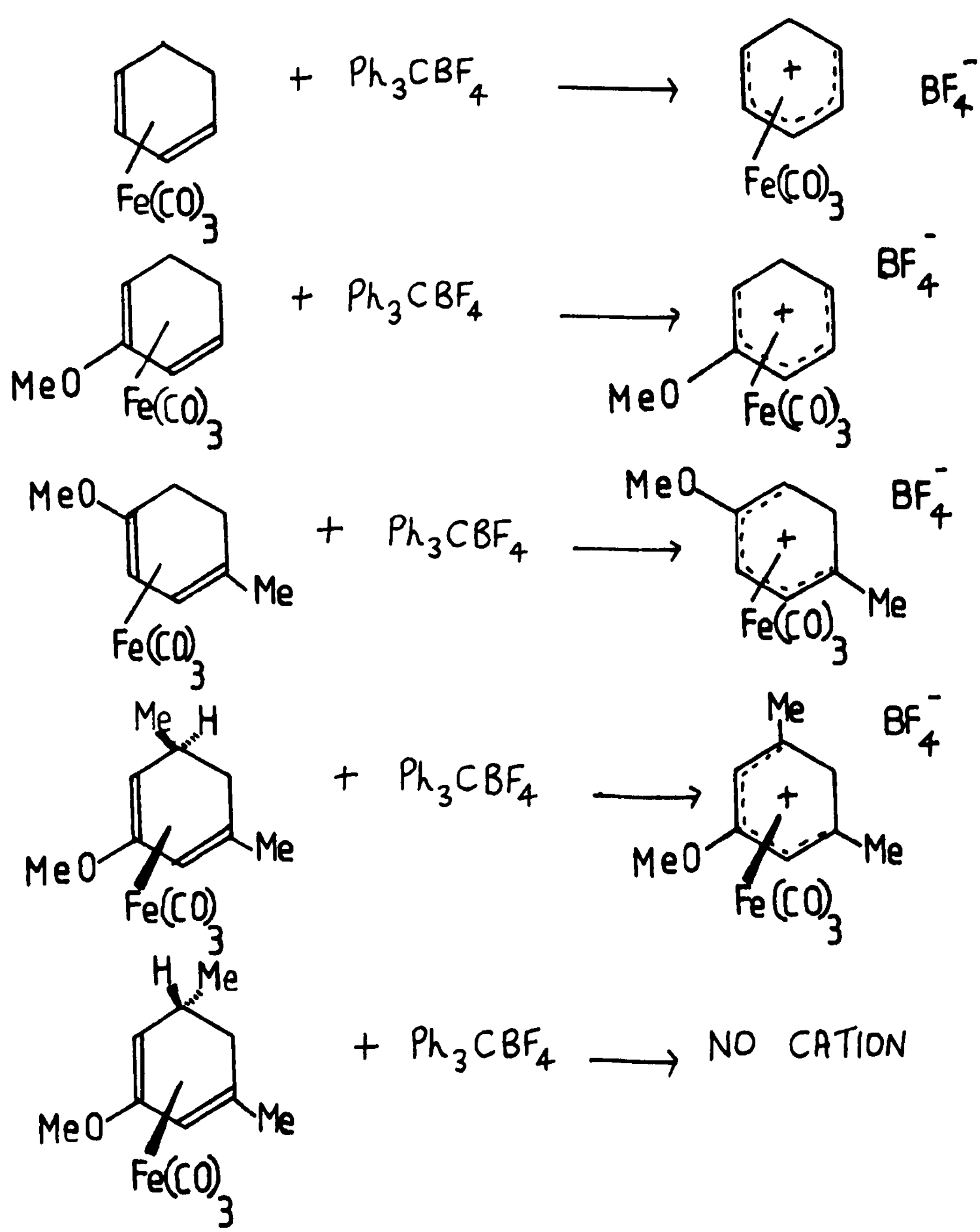
1.2.5 Stereo- and Regiochemical Control

Co-ordination to $Fe(CO)_3$ confers a third dimension on an organic molecule, which has several stereochemical consequences. It distinguishes between one side of the molecule and the other, often permitting totally stereospecific reactions because of the steric bulk of the metal. Complexation confers on an olefin the possibility of asymmetry; thus any unsymmetrically substituted 1,3-diene possessing a plane of symmetry passing through the double bonds, becomes asymmetric on co-ordination to the $Fe(CO)_3$ group, even though the free diene itself is not asymmetric. The presence of the metal not only has profound steric effects on the diene ring to which it is complexed, but can also effect the stereochemistry of reactions occurring elsewhere in the molecule. For example, complexation of ergosterol to $Fe(CO)_3$ converts the less hindered side of the ergosterol nucleus into the more hindered side, enabling hydride attack on a 3-carbonyl on the $\beta$ side of the molecule.[90] Oxidation of tricarbonyl(ergosterol)iron (87) through the dimethylsulphonium salt affords the ketone complex (88), in which the diene is prevented from becoming conjugated with the carbonyl group through co-ordination to the iron. Reduction of the ketone with lithium hydridotri-t-butoxyaluminate, followed by removal of $Fe(CO)_3$ gives exclusively the previously unknown epiergosterol (89).



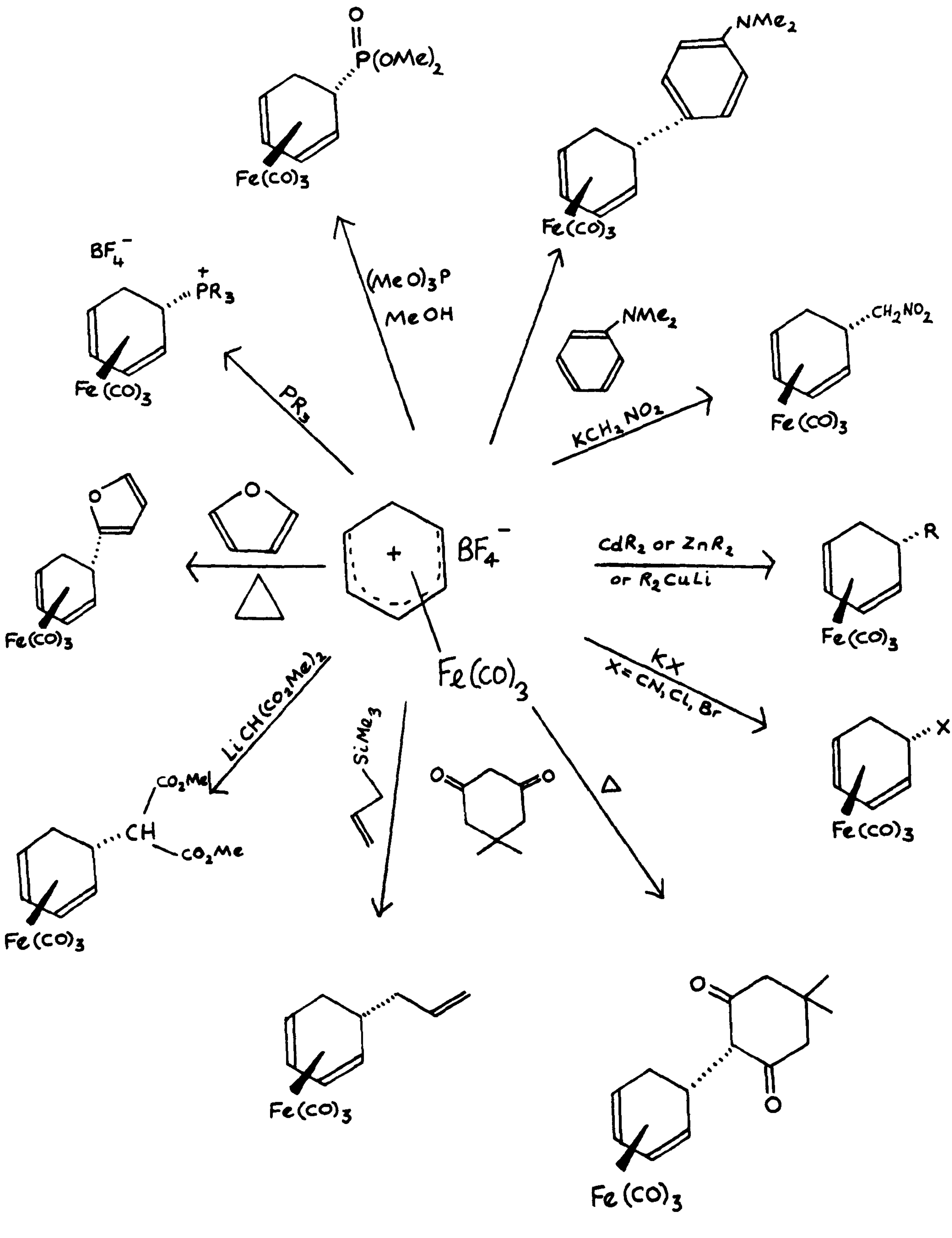
### 1.2.5.1 Tricarbonyl(Cyclohexadienyl)Iron Complexes

Tricarbonyl(cyclohexa-1,3-diene)iron complexes are stereospecifically attacked by trityl tetrafluoroborate[86] on the exo face of the diene (i.e. the face away from the metal) to yield the corresponding tricarbonyl(cyclohexadienyl)iron salts. The selectivity of hydride removal is partly sterically controlled and partly due to the electronic effects of substituents.[6] Where there is no hydrogen available on the exo face of the diene, hydride abstraction does not occur (Scheme XV).




SCHEME XV

Nucleophilic addition to tricarbonyl(cyclohexadienyl)iron salts takes place (with only few exceptions) on the exo face of the diene, and always at one of the terminal $sp^2$ carbons of the dienyl system. Because of the stereo and regiospecificity of this reaction, these complexes are very useful intermediates in organic synthesis. A wide range of nucleophilic reagents have been used to form new stereospecifically substituted C-X bonds (X=C,O,N,P,S). These include alkoxides,[64] enolate anions,[91] silyl enol ethers,[92] allyl silanes,[93] alkyl groups derived from boron,[94] zinc,[95] cadmium[96] and copper,[97] enamines,[61] nitromethane,[98] activated aromatics,[99] aromatic ethers,[100] phosphines,[101] phosphites and sulphites[102] (Scheme XVI - see following page).

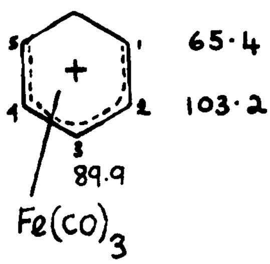


P(OMe)2
Fe(CO)3
NMe2
BF4−
PR3
(MeO)3P
MeOH
PR3
KCH2NO2
CH2NO2
BF4−
CdR2 or ZnR2
or R2CuLi
R
Fe(CO)3
KX
X=CN, Cl, Br
X
LiCH(CO2Me)2
CO2Me
CH
SiMe3


SCHEME XVI

1.2.5.2 Regiochemical Control

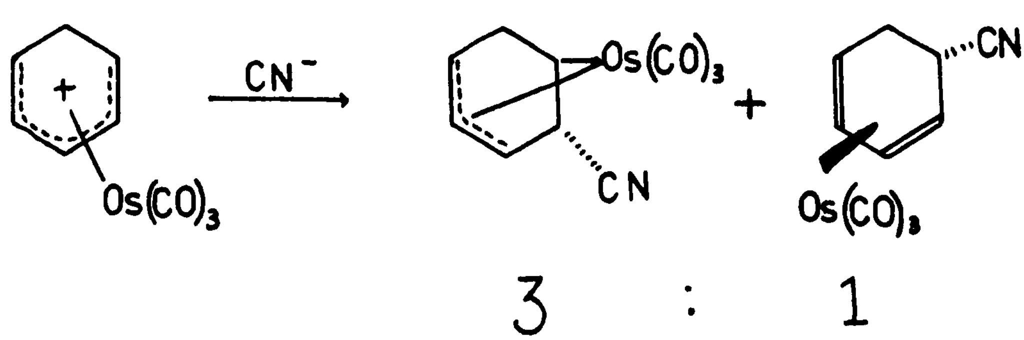
In contrast to some larger rings or derivatives of other metals, [tricarbonyl(cyclohexadienyl)iron][tetrafluoroborate] only undergoes nucleophilic attack at the terminal carbons of the dienyl system (C-1 & C-5). In this case, attack is not charge controlled, since the $^{13}C$ n.m.r. spectrum shows C-2 to be carrying the greatest positive charge.[103]




($\delta$ p.p.m.)

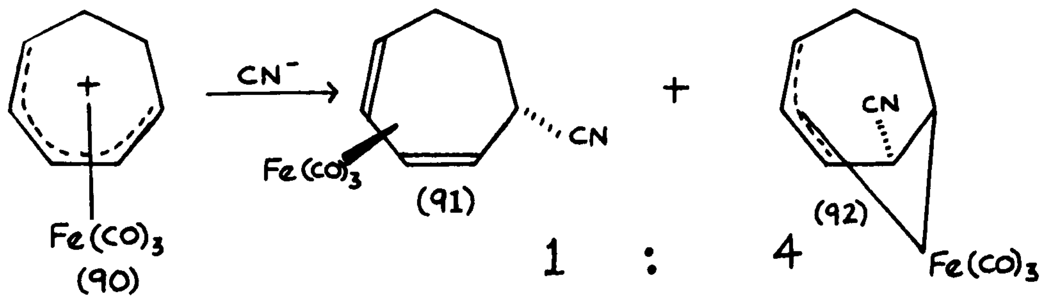
These shieldings reflect the population of the dienyl LUMO, by back donation of electrons from iron d-orbitals. It has been suggested that regiospecific attack at C-1 and C-5 is due to the higher free valence at these carbons.[104] This behaviour can also be attributed to the stability of the 1,3-diene complex and the strain of forming a $\eta^3, \eta^1$ linkage in a six membered ring.

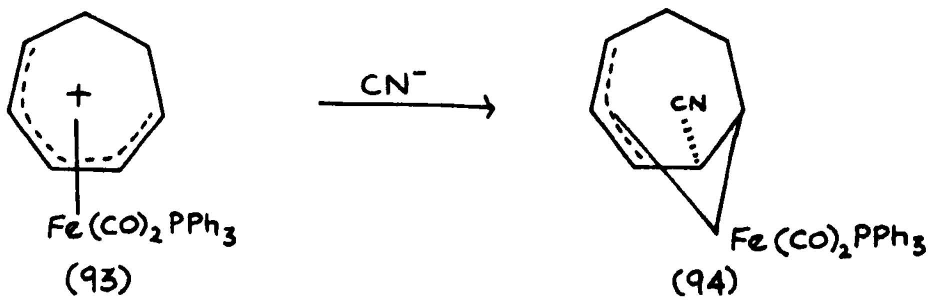
The site of attack on the dienyl system shows considerable variation with the metal, ring size, and the auxiliary ligands present. For example, the addition of hydride and cyanide to tricarbonyl(cyclohexadienyl)osmium occurs both at C-1 and C-2 to give the 1,3-diene and the $\sigma,\pi$allyl product[105] (Scheme XVII).



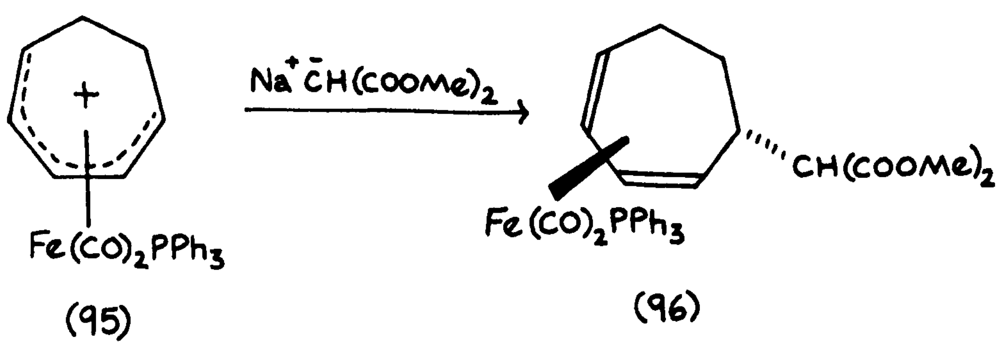

SCHEME XVII

In $[(\text{cycloheptadienyl})Fe(CO)_2L]^+$ attack occurs both at C-1 and C-2, the proportion depends upon the nucleophile, reaction conditions and the nature of the other ligands.[106] For instance, the reaction of (90) with cyanide gives a 1:4 mixture of (91) and (92) whilst the reaction of the triphenylphosphine derivative (93) yields only (94).

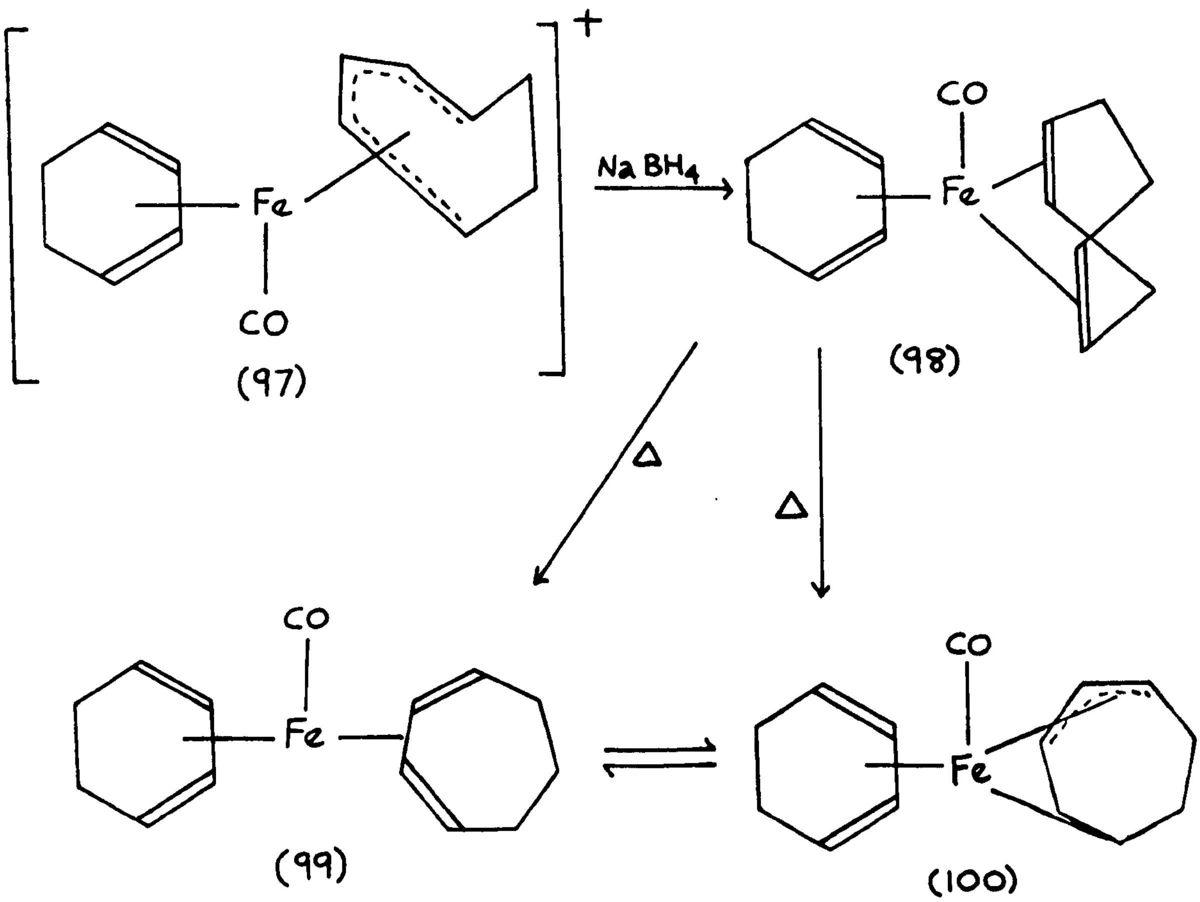


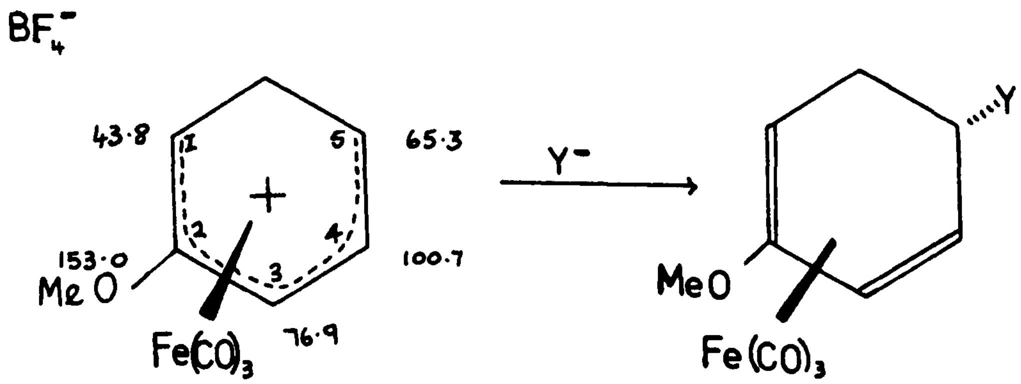

Altering the character of the nucleophile has a profound effect on the regioselectivity of a reaction. (95) reacts with dimethyl sodiomalonate to give exclusively (96) in 90-100% yield.[107]



Attack at C-3 occurs rarely; an example is the unstable 1,4-diene (98) obtained from the reduction of (97) with $NaBH_4$.[108] Thermal isomerization of (98) by warming in heptane gave an equilibrium mixture of the stable 1,3-diene and $\sigma,\pi$allyl complex (99 & 100).

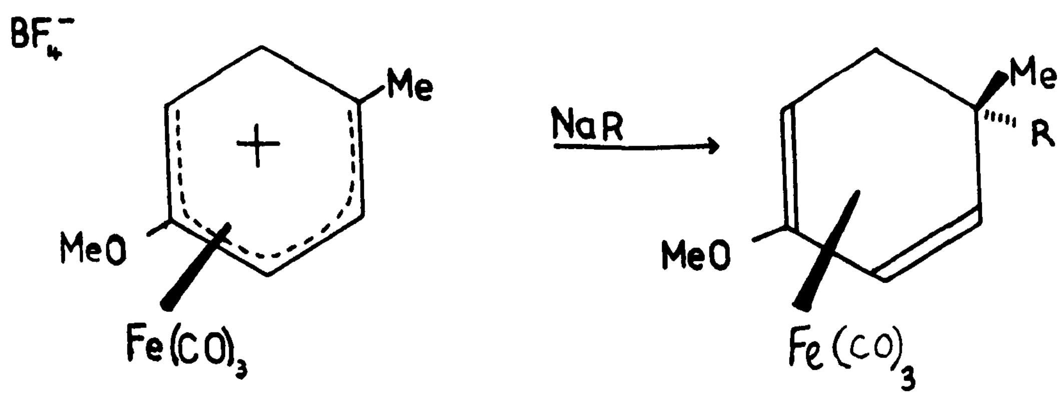



Substituents on the [(cyclohexadienyl) Fe(CO)$_3$]$^+$ ring have an effect on the site of nucleophilic addition. The 2-MeO-substituted salt (101) reacts with nucleophiles exclusively at the C-5 terminus. The $^{13}$C n.m.r. spectrum of (101) shows that electron donation from the MeO group results in C-1 being at much higher field (43.8 p.p.m.) than C-5 (65.3 p.p.m.) and therefore carrying less positive charge than C-5.[103]




(101)

The observed directing effect of (101) is probably charge controlled, and superimposed on the existing orbital control. Pearson and co-workers studied the reaction of (102) with carbanion nucleophiles (i.e. where the C-5 position was substituted) to investigate the strength of the para directing effect of the MeO group.[109] They found that addition took place exclusively at the methylated terminus in high yield, resulting in the creation of a quaternary centre.

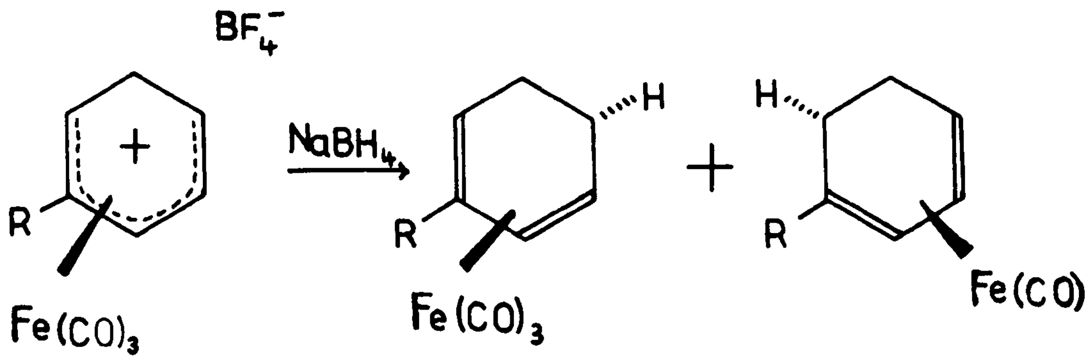



(102)

$R = CH(CO_2Et)_2$ (89%)

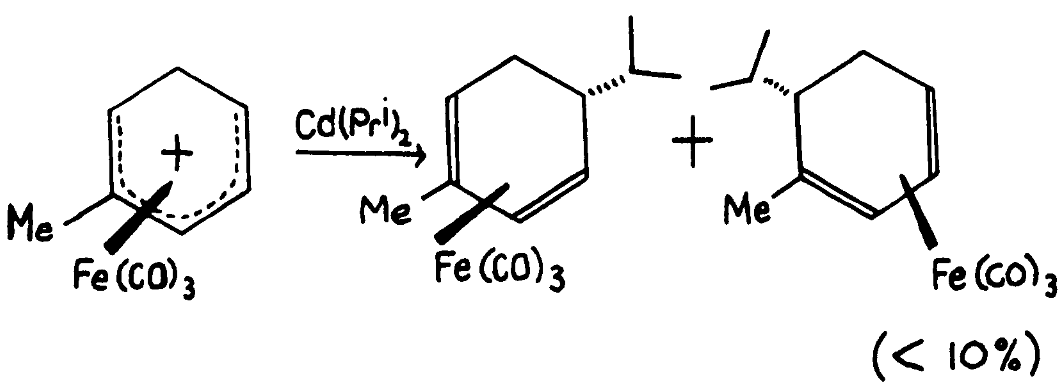
$R = CN$ (90-95%)

Regio control depends on the nature of the substituents, where these are weakly directing groups a mixture of product will occur. For instance, sodium borohydride reduction of (103) ($R=CH_3$ or $CO_2CH_3$) yielded a 1:1 mixture of (104) and (105). The chemical shifts for C-1 and C-5 from the $^{13}C$ n.m.r. spectra of both salts showed them to be very similar. Consequently, reduction was non-selective.[103] However, reduction of (103) when R= MeO gave (104) exclusively.




(103) (104) (105)

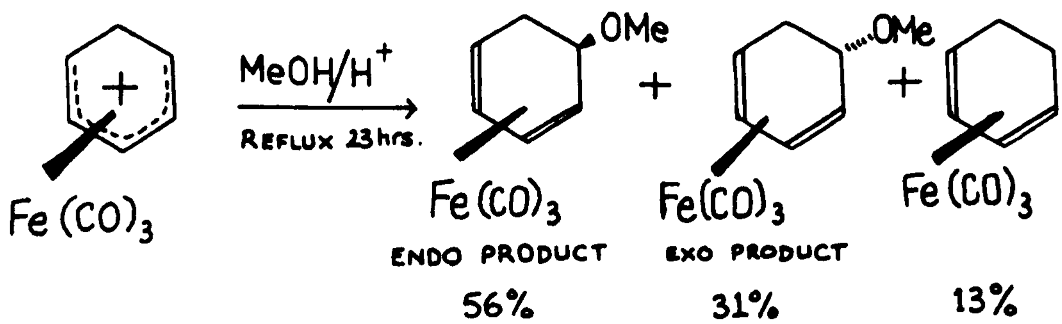
With a more bulky nucleophile, attack at C-1 is sterically hindered by the C-2 substituent and addition at C-5 predominates. For example, the regioselective alkylation of the 2-Me salt with Cd or Zn isopropyl[110] (Scheme XVIII).




SCHEME XVIII

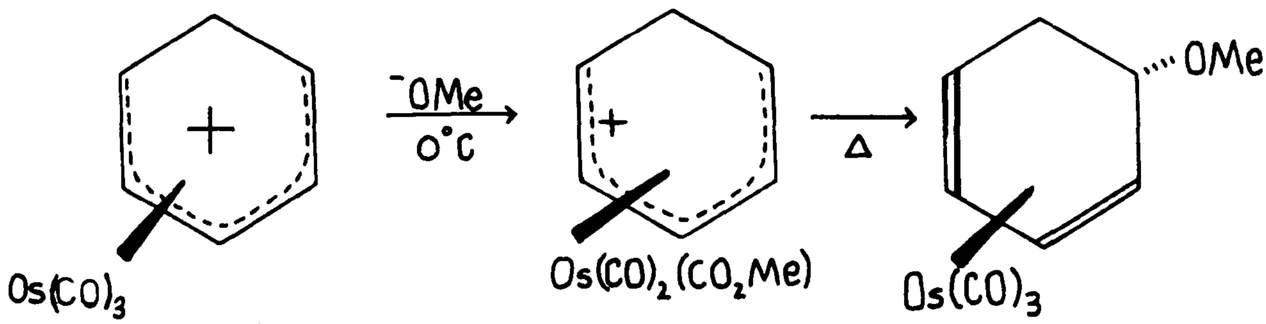
### 1.2.5.3 Stereochemical Control

Where the reaction is irreversible, nucleophilic addition to $Fe(CO)_3$ dienyl salts normally takes place on the side of the molecule opposite the tricarbonyliron group. This stereospecificity has been attributed to steric and electronic factors. Endo addition at [(cyclohexadienyl) $Fe(CO)_3$]$^+$ was first demonstrated by Lewis and co-workers, who found that nucleophilic addition of $MeO^-$ gave initially the exo isomer, but after refluxing in methanol with a catalytic amount of acid, the endo isomer was the major product (Scheme XIX).[111]



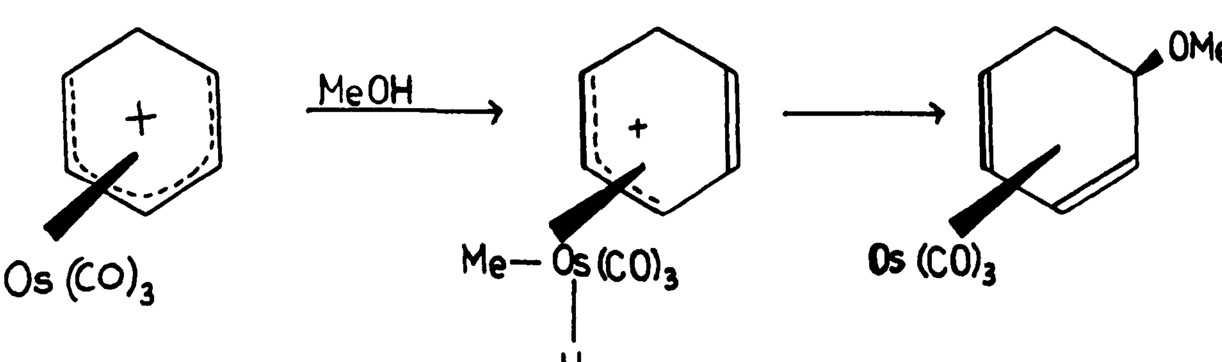

SCHEME XIX

It was found that for the endo addition of a nucleophile to the dienylium ring to occur, addition to the exo face must be reversible in the presence of acid and the endo form possess enough thermodynamic stability. A possible mechanism for the reversible formation of the endo complex, is nucleophilic attack on a co-ordinated CO ligand to give a co-ordinated methoxy carbonyl group, followed by migration of the $RO^-$ group onto the endo face of the ring. Alternatively, direct nucleophilic attack at the metal, followed by rearrangement might occur. However, the carbomethoxy complex $(C_6H_7)Os(CO)_2(CO_2Me)$ (107), the first product of methoxide attack on the (tricarbonyl)(cyclohexadienyl)osmium cation (106) at 0°C, was found on heating to undergo stereospecific rearrangement to give $(5\text{-exo-}C_6H_7OMe)Os(CO)_3$ (108).[112]



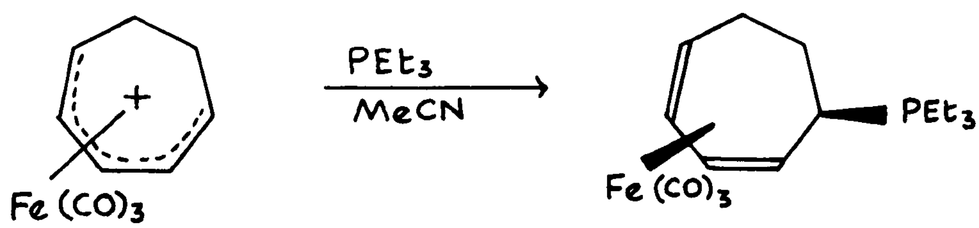

(106) (107) (108)

Since the reaction follows first order kinetics, its mechanism must be dissociative, involving reversal of the addition to generate the cation. Like its iron analogue (108) yields the endo-methoxy complex on refluxing in methanol. It has been suggested that the reaction proceeds via the oxidative addition of methanol to the metal according to Scheme XX.




SCHEME XX

Nucleophilic addition of alkylphosphines in acetonitrile to the (cycloheptadienylium)$Fe(CO)_3$ cation was found to give the 5-endo isomer.[113] Initially a red intermediate was formed and the reaction was suggested to occur via a metal assisted pathway (Scheme XXI).




SCHEME XXI

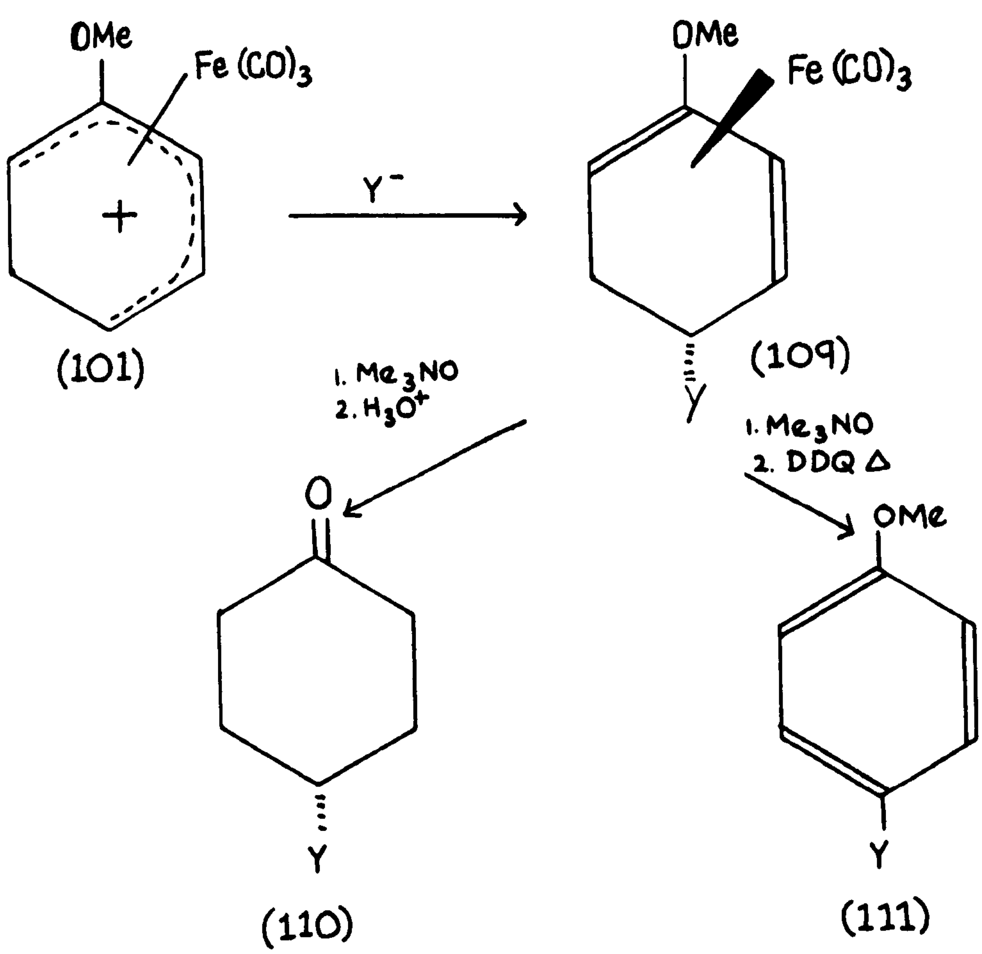
In contrast, phenyl substituted phosphines formed only the 5-exo isomer, presumably due to steric inhibition of the metal assisted pathway. Also nucleophilic attack of alkyl phosphines in $CH_2Cl_2$ proceeded by direct attack on the ring, with no red intermediate, giving the 5-exo product.

Although recent kinetic studies by Kane-Maguire and co-workers on $Fe(CO)_3$ dienyl systems have concluded that nucleophilic attack occurs directly on the organic moiety,[114] mechanisms involving metal or CO ligand participation cannot be excluded in all cases.

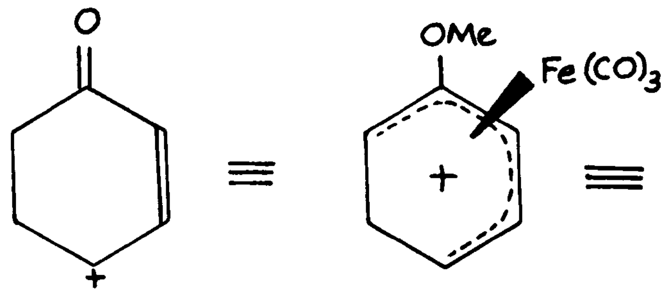
## 1.3 Tricarbonyl(diene)iron Complexes in Organic Synthesis

Although many accounts appear in the literature of the reactions of (cyclohexadiene)$Fe(CO)_3$ complexes, few attempts have been made to put them to any real synthetic application in organic chemistry. One notable exception is the work of Birch et al.,[5] which has demonstrated the usefulness of such complexes in organic synthesis. For example, the reactions of (cyclohexadienone)Fe(CO)$_3$ (Section 1.2.4.4). This section reviews the recent work by Pearson on the synthesis of some fairly complex natural products via (cyclohexadiene)Fe(CO)$_3$ derivatives.

As previously mentioned (Section 1.2.5.1), the dienyl salt (101) reacts with nucleophiles regiospecifically, due to the powerful directing effect of the methoxy group to give (109) exclusively.

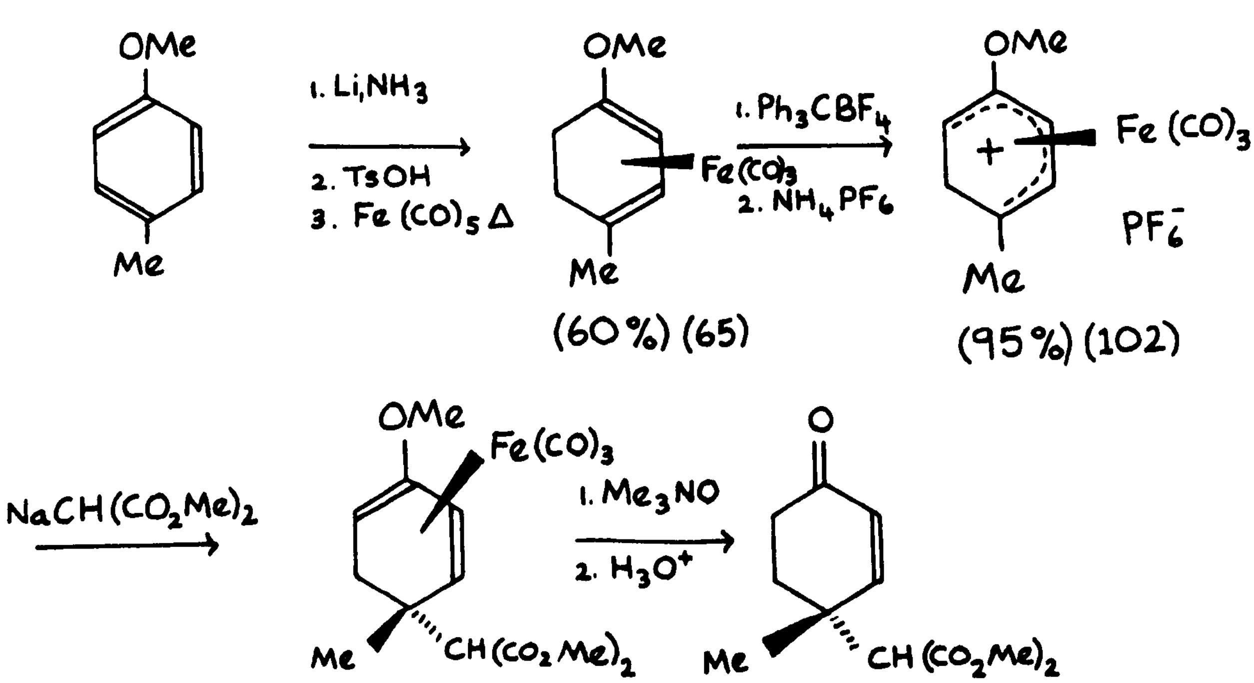



Removal of the Fe(CO)$_3$ group gives either 4-substituted cyclohexenones (110) or 4-substituted anisoles (111), depending on the reagents used. Therefore in the language of synthons (101) can be regarded as the synthetic equivalent of the cyclohexenone γ-cation (112), or the 4-anisyl cation equivalent (113).




(112) (101) (113)

Pearson and co-workers have recently made use of these properties in the synthesis of some fairly complex natural products via (cyclohexadienyl)Fe(CO)$_3$ cations.[1,4,115] They utilised the ready availability in high yield of 4,4 disubstituted cyclohexenones, e.g. (115). It was found that (65) readily prepared from p-methylanisole, underwent hydride abstraction to give (102). Nucleophilic addition with enolate nucleophiles occurred exclusively at the methylated terminus, giving (114) in quantitative yield.[116]




(60%) (65)

(95%) (102)

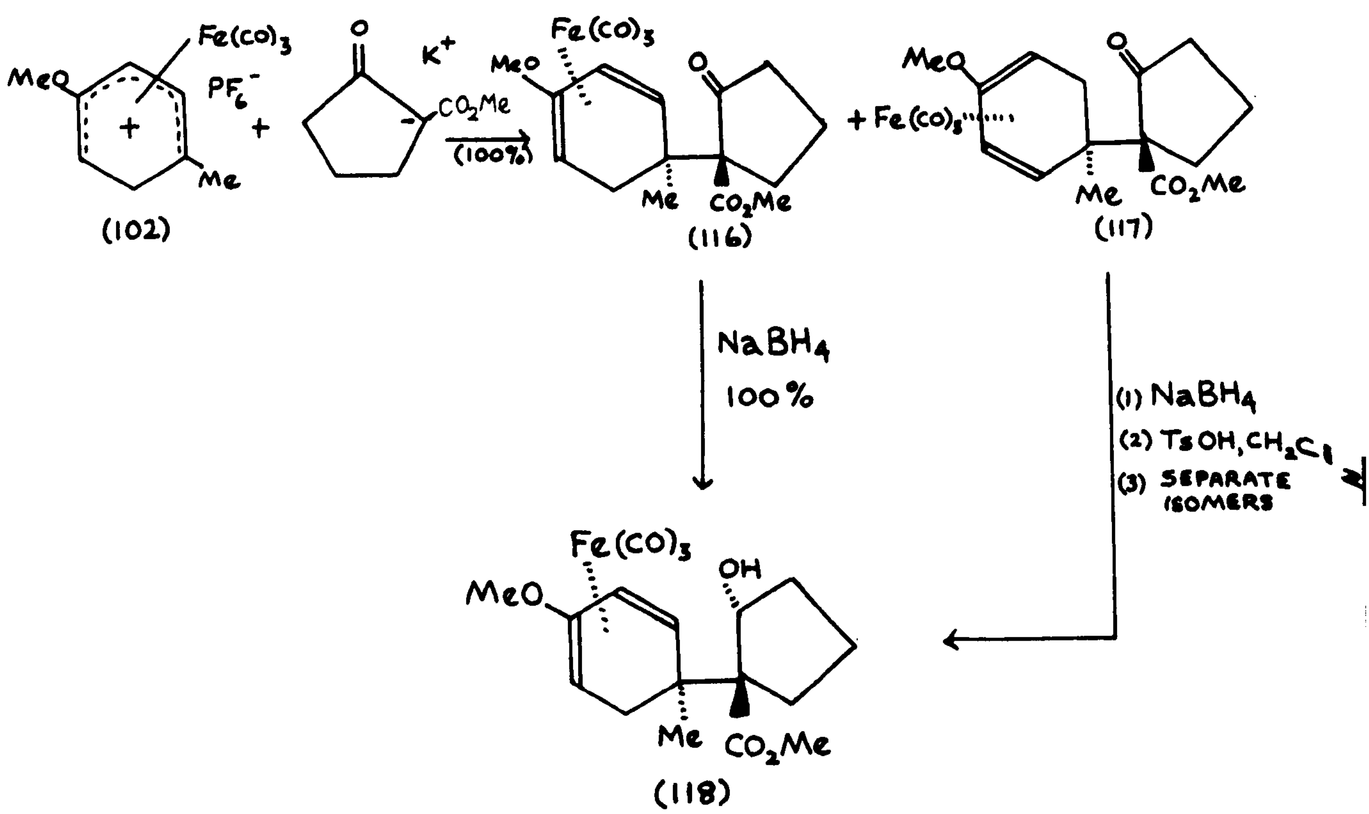
(100%) (114)

(80-90%) (115)

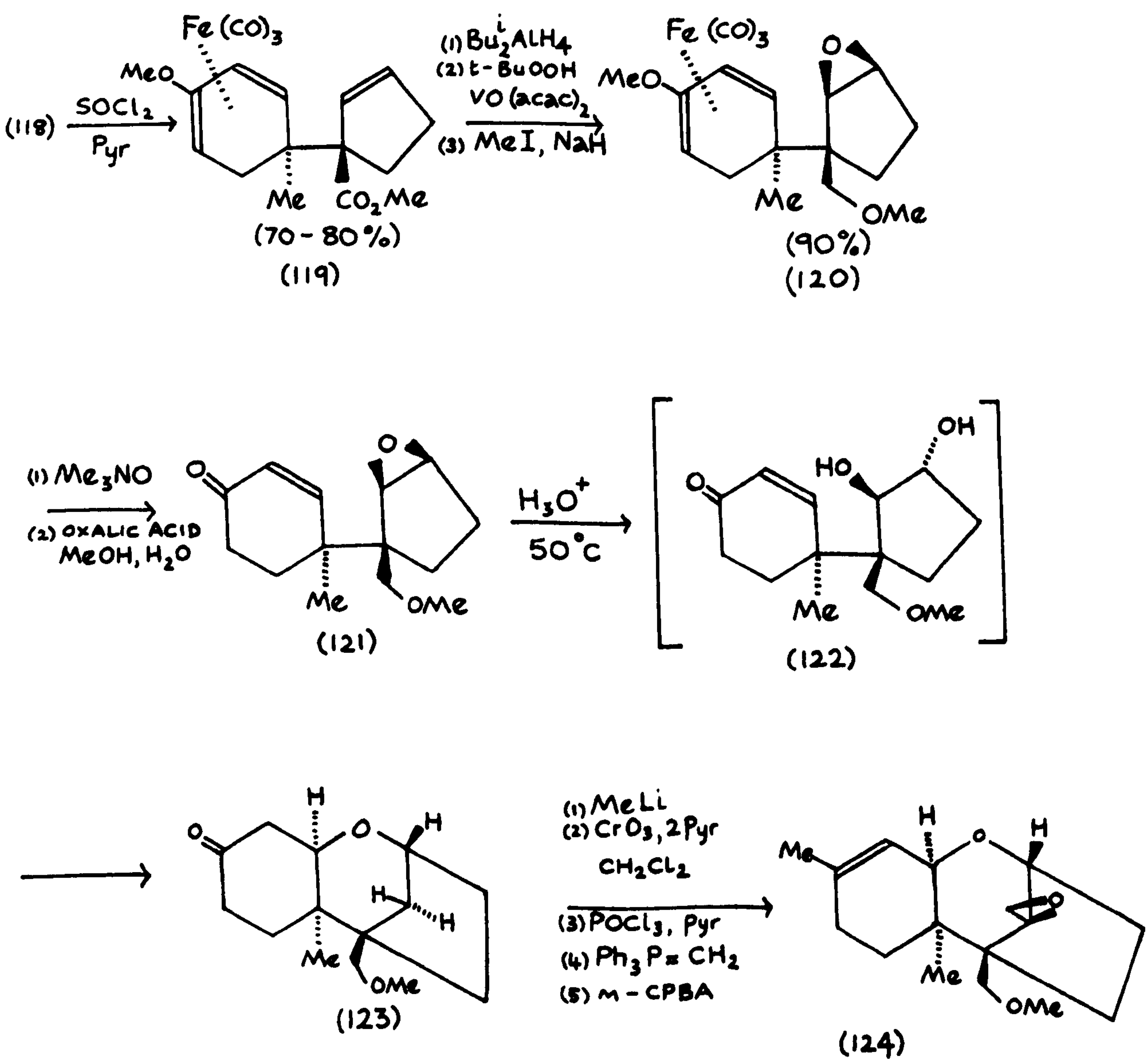
The synthetic potential of 4,4 disubstituted cyclohexenones was utilised by Pearson as a means of connecting 2 or more rings together, necessary in approaches to the synthesis of steroids,[117] alkaloids, trichothecenes and various spirocyclic compounds.

### 1.3.1 Trichothecene Synthesis

Trichothecenes are a group of tricyclic sesquiterpenes produced by microbes, which show a number of interesting pharmacological properties such as antifungal and cytostatic activity and are of considerable interest as anti-cancer agents.



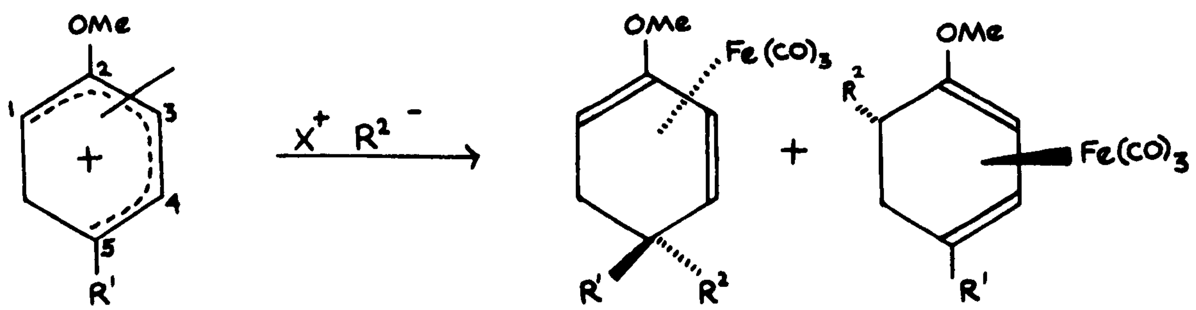
The initial step in the construction of the trichothecene ring system was the reaction of (102) with methyl 2-oxo-1-potassiocyclopentane carboxylate.[118] This produced a mixture of diasteroisomers (116) and (117) (due to two enantiomers from $Fe(CO)_3$ complexation onto an achiral diene, and nucleophilic addition $\alpha$ or $\beta$ to the carboxylate group). Only isomer (116) had the right stereochemsitry for the synthesis of trichothecene analogues, however, the formation of (117) was not a disadvantage, since the two isomers were separated by chromatography, and found to be interconvertible. Both (116) and (117) were converted into the hydroxy ester (118) of the appropriate stereochemistry, in yields of more than 80% from (102).[119]



(118) was readily dehydrated to give the unsaturated ester (119) which was then converted into the epoxide derivative (120), with reduction of the ester. The $Fe(CO)_3$ group was then removed with anhydrous trimethylamine-N-oxide and the resulting dienol ether hydrolysed with mild acid to yield (121). The epoxide group was cleaved with aqueous acid under more forcing conditions (122) and simultaneously underwent Michael cyclization to produce the tricyclic intermediate (123). The subsequent steps were analogous to those used by Still[120] in a recent synthesis of trichodermin, in which an intermediate similar to (123) was elaborated to the target molecule. Thus the synthesis of (124), 12,13-epoxy-14-methyltrichothecene, an interesting and unnatural trichothecene analogue was achieved.

### 1.3.2 Aspidosperma Alkaloids

(±)-Aspidospermine and (±)-limaspermine have been synthesized via 4,4-disubstituted cyclohexenones produced from (cyclohexadienyl) $Fe(CO)_3$ salts. It was found that whilst nucleophilic addition at (102) ($R^1 = Me$) occurred exclusively at C-5 to give only (127), more sterically demanding substituents (125) & (126) ($R^1 = Et, (CH_2)_2OMe$) produced mixtures of regioisomers (127) & (128).[121]

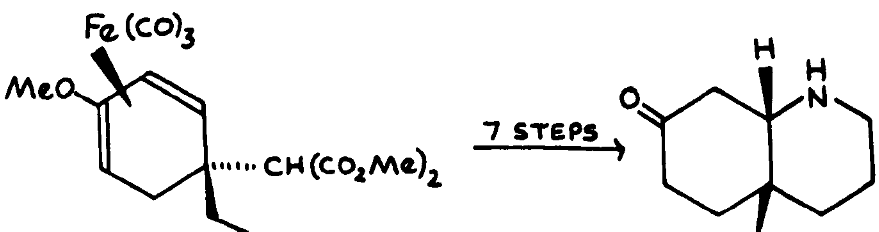



(102) $R' = Me$
(125) $R' = Et$
(126) $R' = (CH_2)_2OMe$

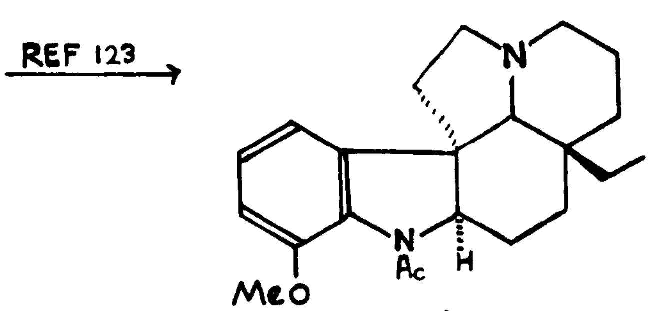
(127) (128)

$R^2 = CH(CO_2Me)$

Interestingly, the ratio of (127) to (128) produced, varied with the countercation $X^+$, and regioselectivity was found to depend on the degree of association between the enolate nucleophile and the counter cation. Thus, the reaction of dimethyl lithiomalonate with (125) gave a 75:25 mixture of (127) and (128), whilst dimethyl potassiomalonate gave an 85:15 mixture. Better selectivity for the C-5 substituted dienyl terminus was attained using a 2-iso-propoxy substituent rather than a 2-methoxy substituent. Complex (129) has been elaborated[122] into an advanced decahydroquinoline intermediate (130) which was previously used by Stork and Dolfin in the total synthesis of aspidospermine (131).[123]

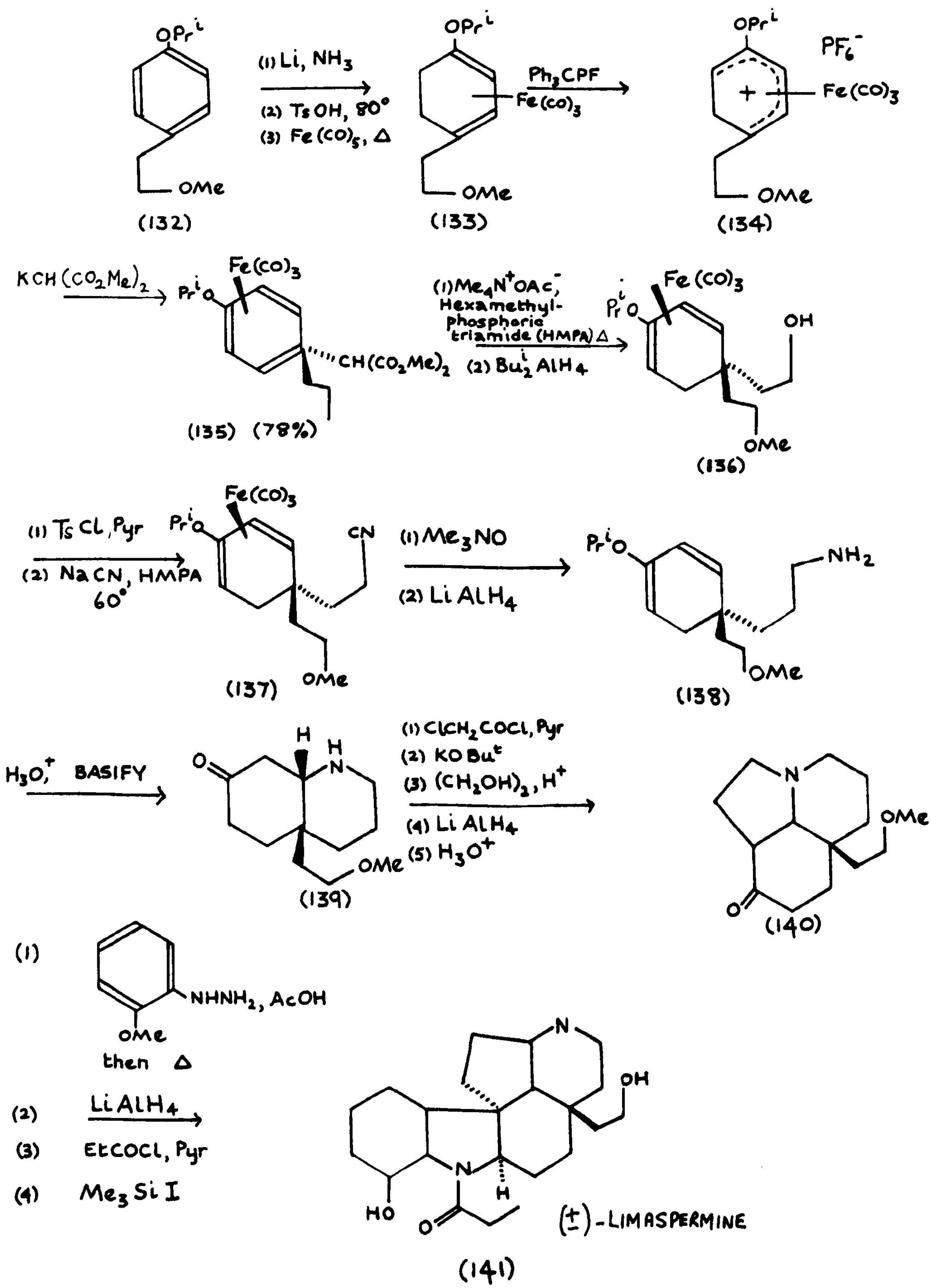



(129) (130)




(131)

Pearson and co-workers have achieved two total syntheses of the alkaloid (±)limaspermine,[124,125] one via (134) readily prepared from the appropriately substituted aromatic compound.



(1) Li, NH3
(2) TsOH, 80°
(3) Fe(CO)5, Δ
Ph3CPF
PF6-
Fe(CO)3
(132)
(133)
(134)
KCH(CO2Me)2
CH(CO2Me)2
(135) (78%)
(1) Me4N+OAc-, Hexamethylphosphoric triamide (HMPA) Δ
(2) Bui2AlH4
(136)
(1) TsCl, Pyr
(2) NaCN, HMPA 60°
(137)
(1) Me3NO
(2) LiAlH4
(138)
H3O+, BASIFY
(139)
(1) ClCH2COCl, Pyr
(2) KOBut
(3) (CH2OH)2, H+
(4) LiAlH4
(5) H3O+
(140)
(1) NHNH2, AcOH then Δ
(2) LiAlH4
(3) EtCOCl, Pyr
(4) Me3SiI
(±)-LIMASPERMINE
(141)

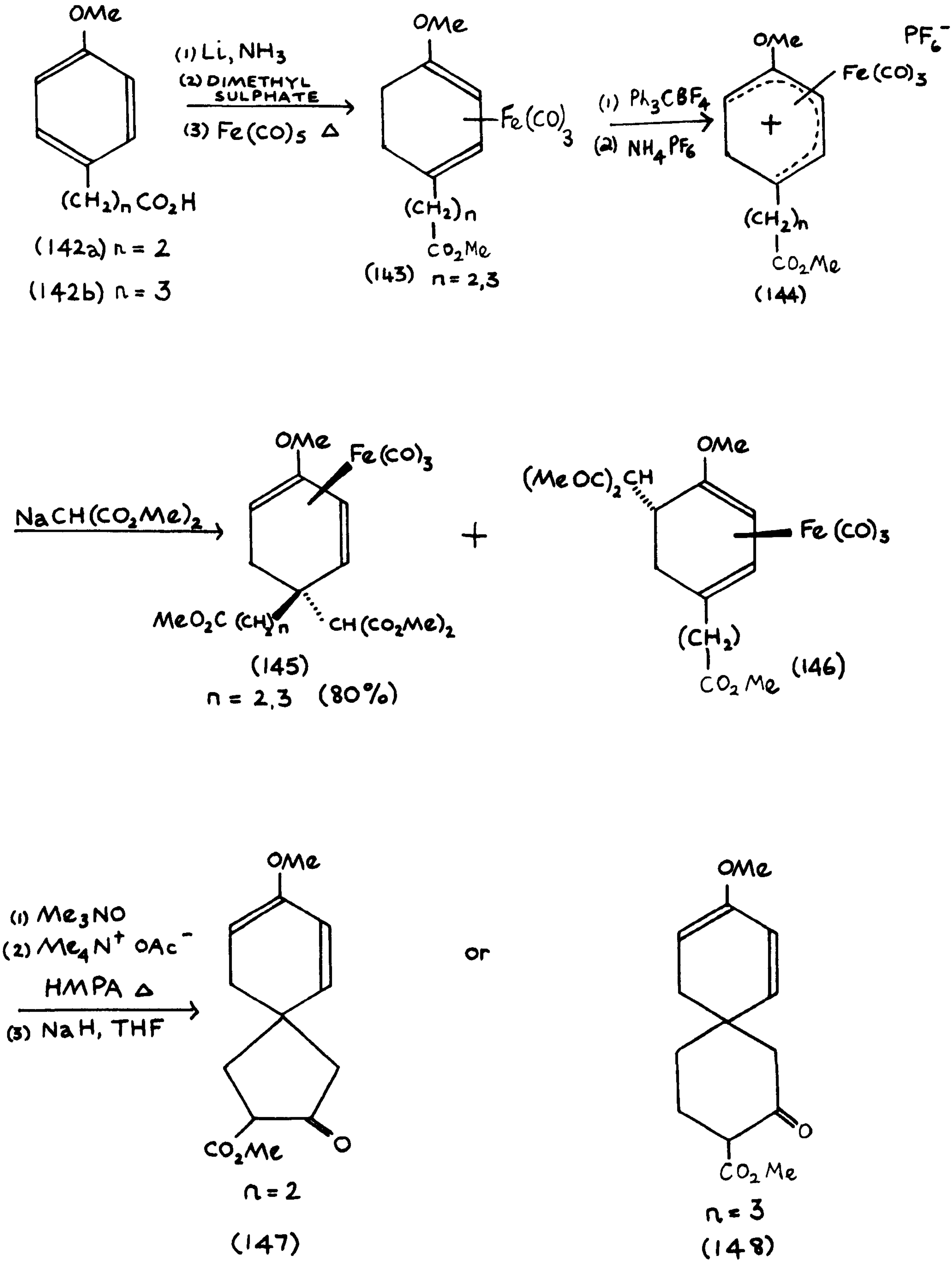
(134) underwent regioselective nucleophilic attack with dimethyl potassiomalonate to give (135) in 78% yield. Dimethoxycarbonylation gave the monoester, which was reduced to the alcohol (136). This was converted into the tosylate, which was readily displaced with a nitrile group (137). Removal of $Fe(CO)_3$ followed by $LiAlH_4$ reduction, afforded the primary amine (138). Hydrolysis with concomitant Michael cyclization gave the cis-decahydroquinoline derivative (139), which was converted into (±)limaspermine using methodology from related synthesis.[123,126]

### 1.3.3 Spirocyclic Compounds

Spiro[4.5]decane and spiro[5.5]undecane ring systems appear in a large variety of natural products. These sesquiterpenes have been synthesized by Pearson's group using both inter- and intramolecular nucleophilic attack on the (cyclohexadienyl)$Fe(CO)_3$ cation.

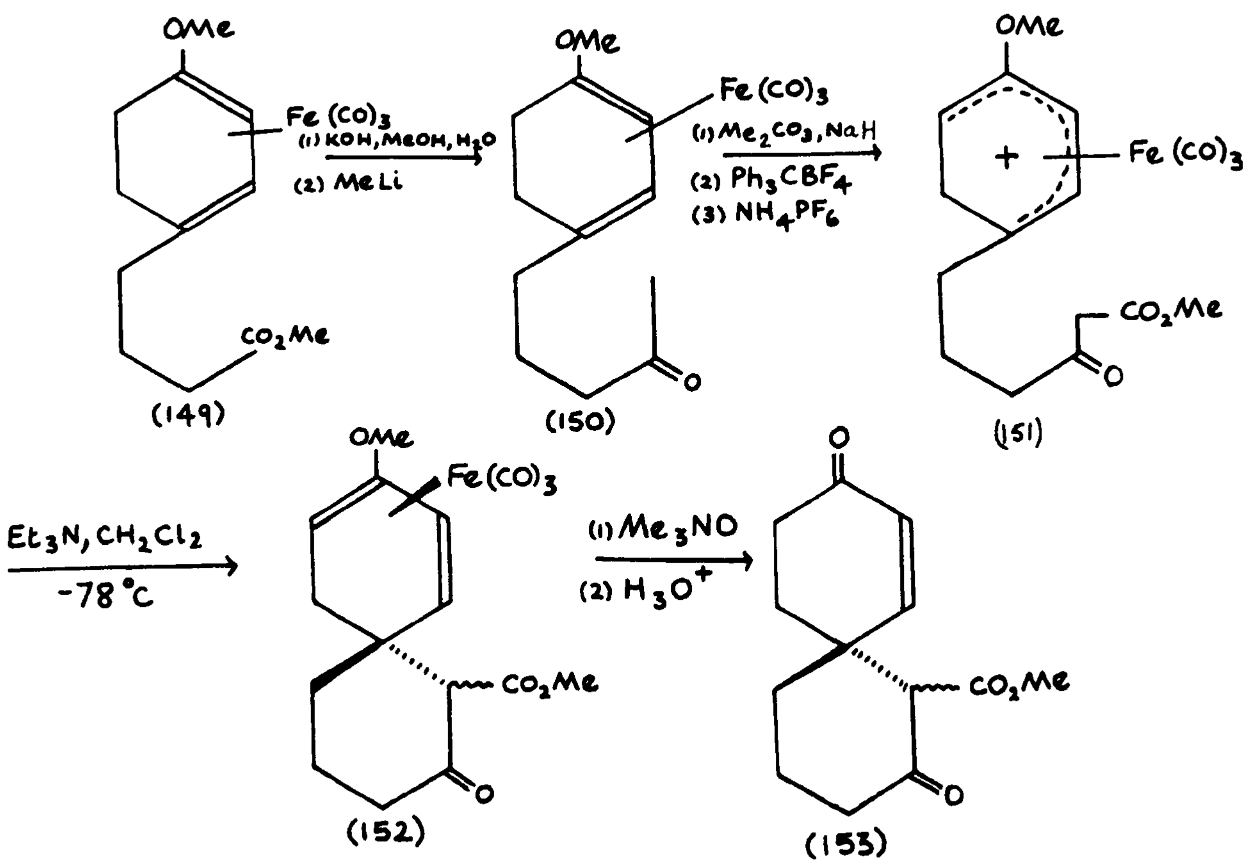
#### (A) Intermolecular Nucleophilic Addition

The spiro[4.5]decane (147) and the spiro[5.5]undecane (148) complexes were readily synthesized from p-methoxy cinnamic acid (142a) and 4(p-methoxyphenyl)butyric acid (142b).[116] The cyclohexadienyl salts (144) reacted with dimethyl sodiomalonate with 80% regioselectivity for the substituted terminus to give (145) and (146). They were converted into the desired spirocycles in three steps as shown on the following page.


OMe
(CH2)n CO2H
(142a) n = 2
(142b) n = 3
(1) Li, NH3
(2) DIMETHYL SULPHATE
(3) Fe(CO)5 Δ
OMe
Fe(CO)3
(CH2)n
CO2Me
(143) n = 2,3
(1) Ph3CBF4
(2) NH4PF6
OMe
PF6⁻
Fe(CO)3
+
(CH2)n
CO2Me
(144)
NaCH(CO2Me)2
OMe
Fe(CO)3
MeO2C (CH2)n
CH(CO2Me)2
(145)
n = 2,3 (80%)
+
OMe
(MeOC)2CH
Fe(CO)3
(CH2)
CO2Me
(146)
(1) Me3NO
(2) Me4N+ OAc⁻
HMPA Δ
(3) NaH, THF
OMe
CO2Me
O
n = 2
(147)
or
OMe
O
CO2Me
n = 3
(148)

(B) Intramolecular Nucleophilic Addition

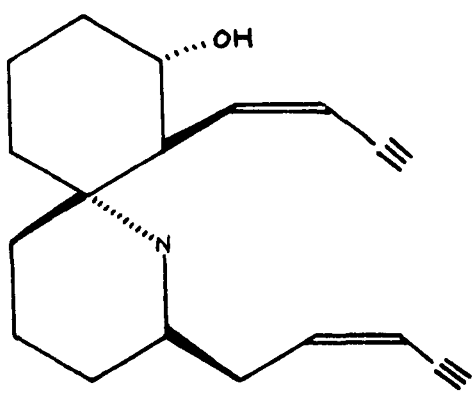
Spirocycles were also synthesized by intramolecular nucleophilic addition to the cyclohexadienyl complexes.[127] This required a lateral side chain which had an enolizable group.




The ester complex (149) was readily converted via the ketone (150) to the dienyl salt (151) containing a $\beta$ keto ester group in the lateral chain. Treatment of this compound with triethylamine at -78°C gave (152) in 90% yield, which was converted into the spiro[5.5]undecane compound (153).

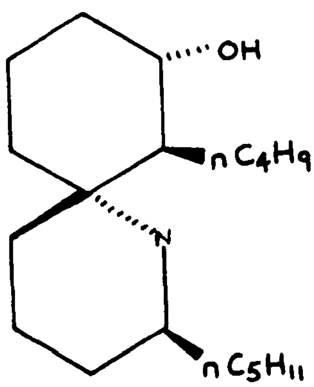
## 1.3.4 Azaspirocyclic Compounds

A large number of diverse alkaloids contain azaspirocyclic units. Histrionicotoxin (154), for example isolated from the skins of the Colombian from Dendrobates histrionicus, is of interest in neurophysiology as it reversibly blocks ion transport across the neuromuscular junction.



HISTRIONICOTOXIN

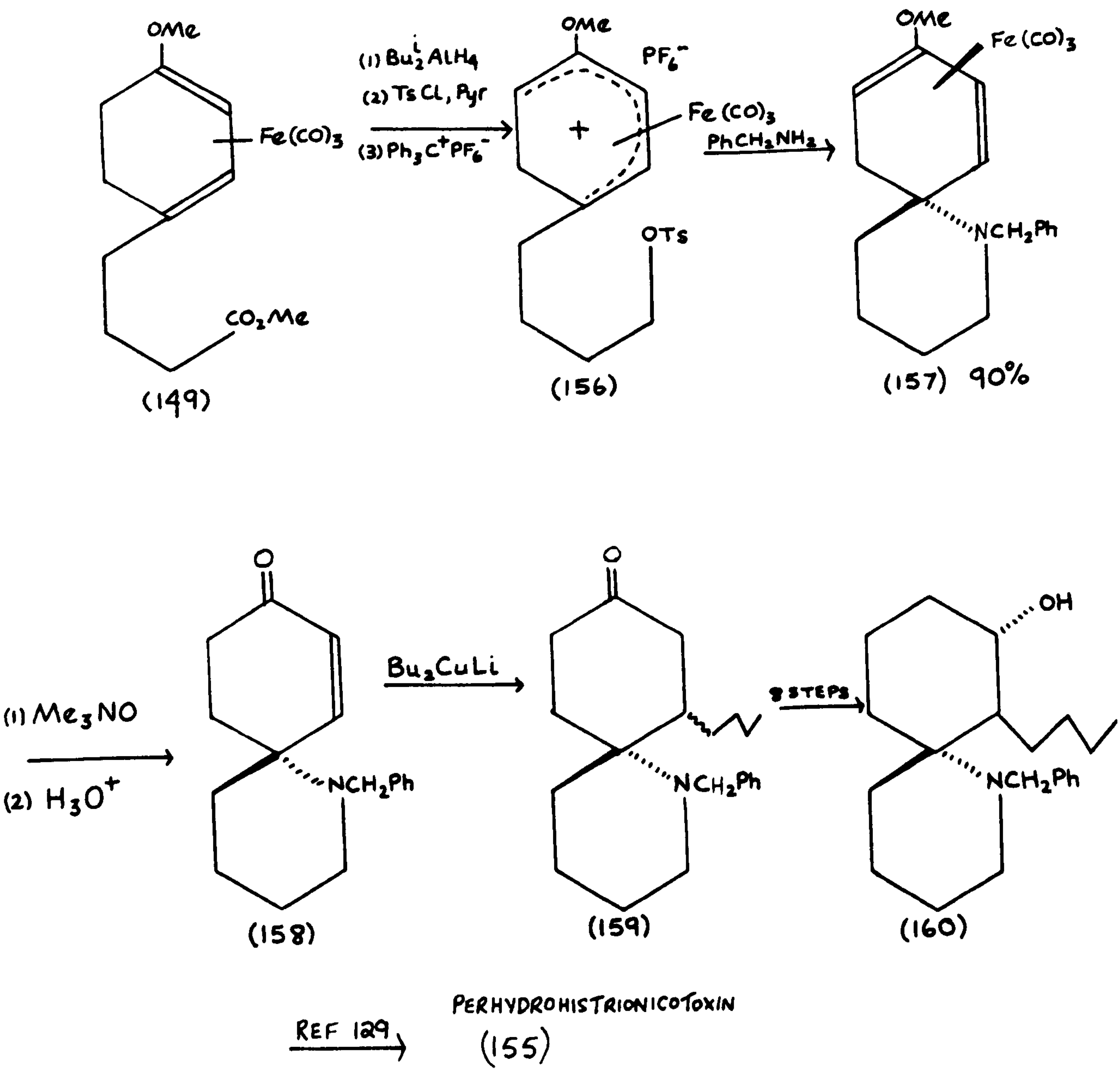
(154)



PERHYDROHISTRIONICOTOXIN

(155)

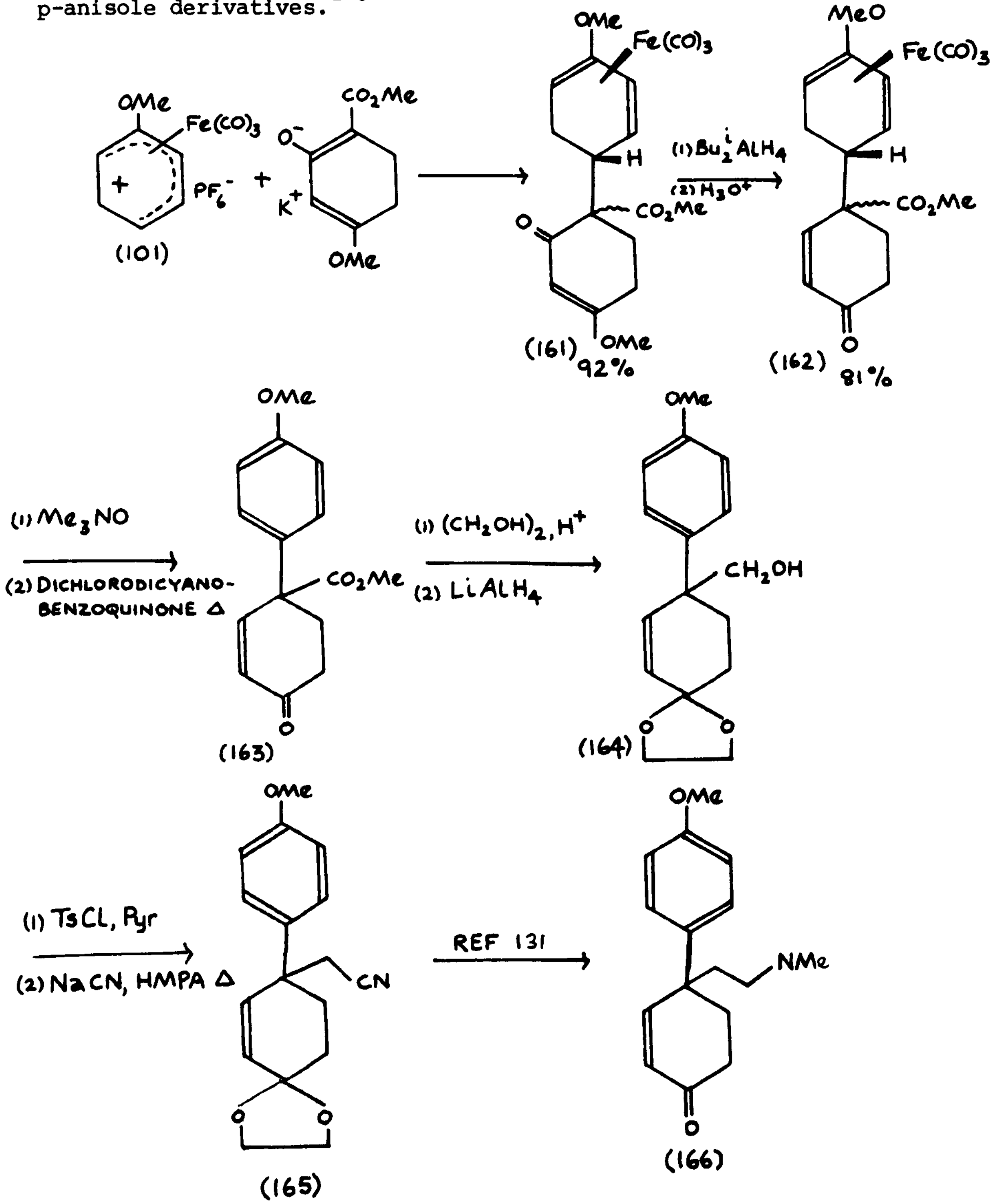
(154) itself is in short supply from natural sources, however perhydrohistrionicotoxin (155) also found to be biologically active has been synthesized by Pearson[128] using intramolecular nucleophilic attack on the (cyclohexadienyl) $Fe(CO)_3$ complex (149) (see following page).




The tosylate salt (156) reacted rapidly with benzylamine to give the azaspirocyclic complex (157) in 90% yield. Treatment with trimethylamide-N-oxide, followed by acid hydrolysis afforded the azaspirocyclic enone (158), a useful intermediate for the synthesis of a wide range of histrionicotoxin related compounds. Addition of lithium di-n-butylcuprate gave (159). This was elaborated in eight steps to (±)depentylperhydrohistrionicotoxin (160), which could be converted into perhydrohistrionicotoxin (155) by existing methodology.[129]

1.3.5 Sceletium Alkaloids

O-methyljoubertiamine (166), a sceletium alkaloid known to exhibit biological activity, has been synthesized by utilising the ability to convert 2-methoxycyclohexadienyl salts into p-anisole derivatives.[130]



(101) reacted with the potassium enolate to afford a high yield of complex (161), which was readily converted to the p-anisyl cyclohexenone (163). This was transformed into the nitrile via the primary alcohol and tosylate to give (165), an intermediate very closely related to a complex previously converted to O-methyljoubertiamine (166) by Sanchez and Tallabs.[131]

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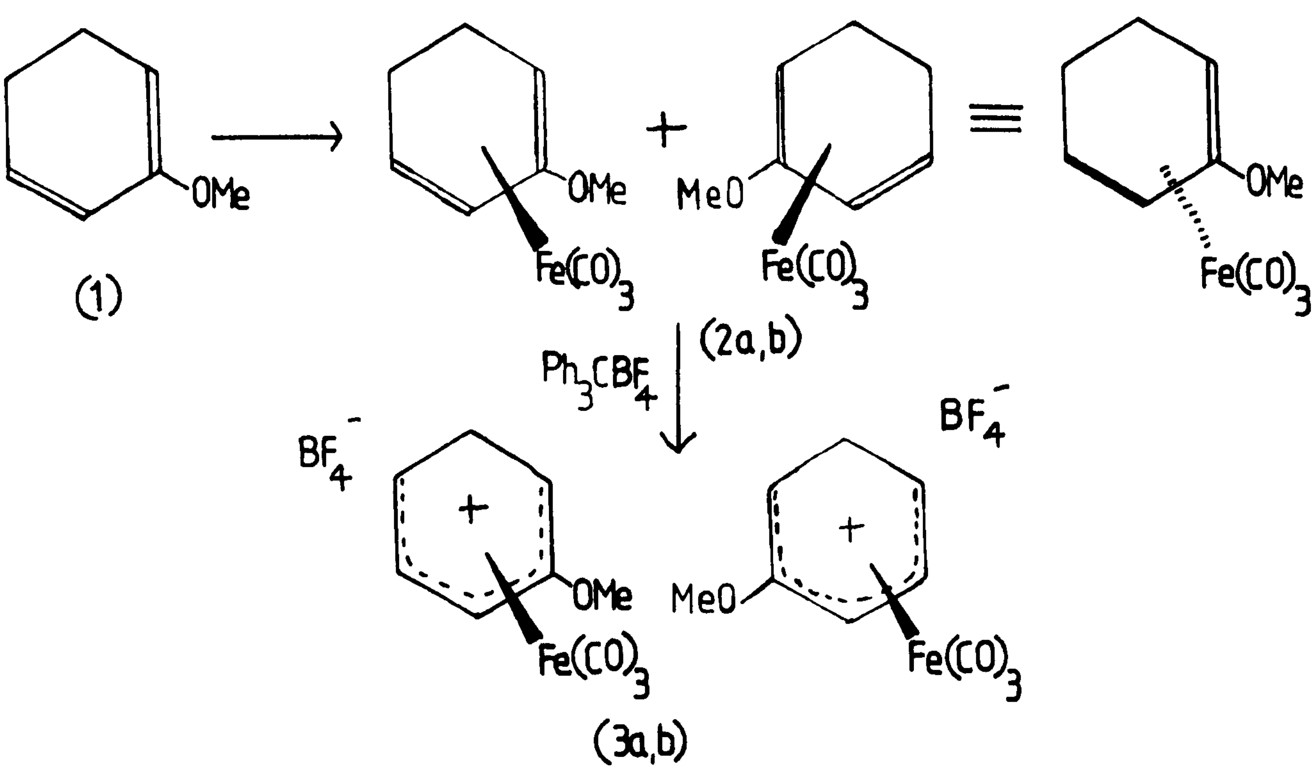
# CHAPTER 2

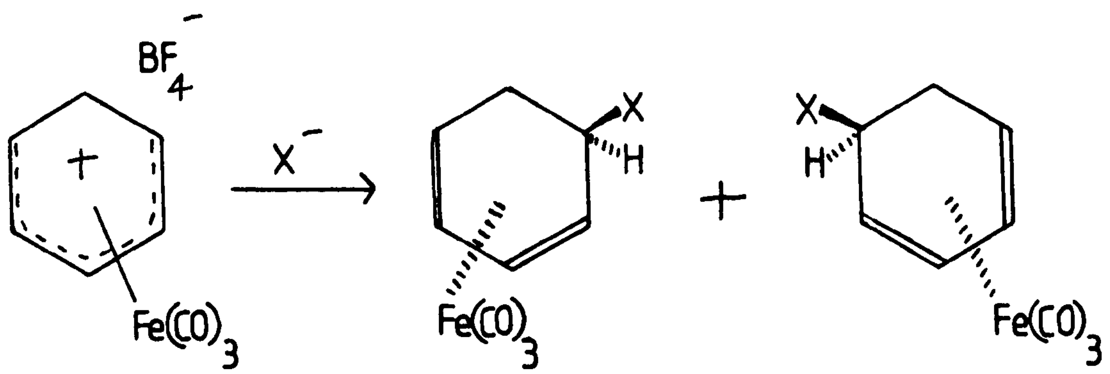
## RESOLUTION OF TRICARBONYL DIENE AND DIENYL IRON COMPLEXES BY MEANS OF CHIRAL NUCLEOPHILES

### 2.1 Introduction

The complexation of an $Fe(CO)_3$ group onto an unsymmetrically substituted 1,3-diene (for example, 1) confers the possibility of molecular asymmetry, since the metal distinguishes between the two faces of the diene. Thus, complexation of (1) yields a pair of enantiomeric complexes (2a,b), and regiospecific hydride abstraction in turn gives rise to two enantiomeric cations (3a,b).




If resolution of (3a) and (3b) is achieved, the regio and stereospecificity of nucleophilic attack results in the formation of a fully resolved asymmetric carbon centre. Removal of the metal then destroys the chirality associated with metal co-ordination. The unsubstituted [(cyclohexadienyl)Fe(CO)$_3$][BF$_4$] (4) salt is itself an achiral molecule; however nucleophilic addition creates an asymmetric carbon centre giving rise to the existence of two enantiomers (5) and (6).

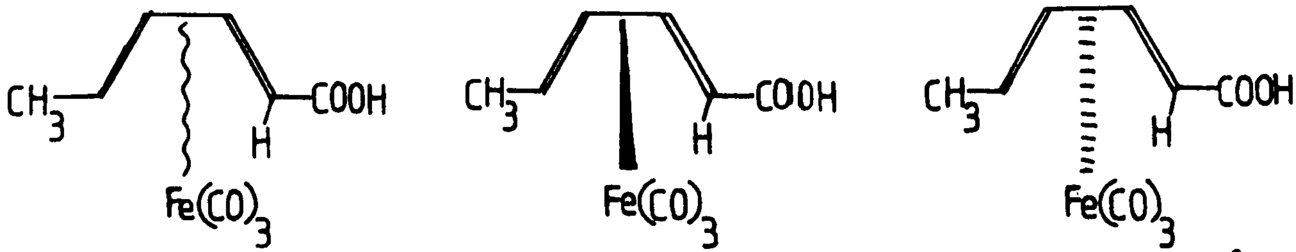



(4) (5) (6)

The resolution of such enantiomers would be very valuable in the application of such molecules in organic synthesis. Virtually all the work carried out on (1,3-diene)Fe(CO)$_3$ complexes has been with racemic mixtures, and only a few complexes have been obtained enantiomerically pure or enriched. These have been prepared by means of classical resolution, asymmetric complexation or kinetic/thermodynamic discrimination with varying degrees of success. Enantiomeric diene complexes do not interconvert. Although dynamic behaviour has been observed in n.m.r. spectra, this does not involve the iron atom transferring between the faces of the diene, but rather the non-rigidity of the tricarbonyl unit with respect to the diene.[1]

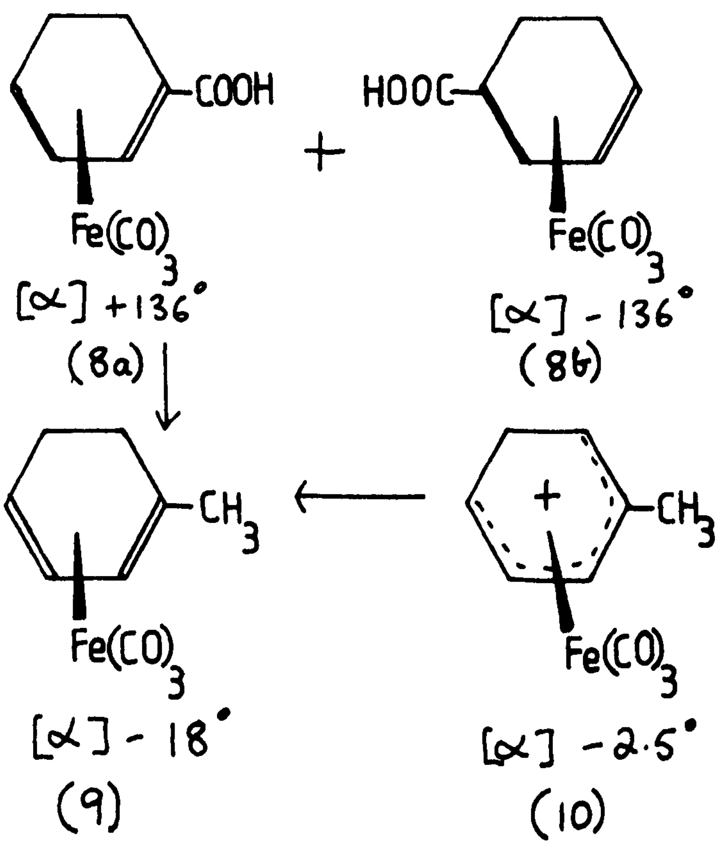
## 2.1.1 Classical Resolution

Resolution of these complexes has been carried out by classical means using functional groups attached to the 1,3-diene. The enantiomers of (7) have been fully resolved by fractional crystallization of the salts formed with (S)-1-phenylethylamine.[2] The absolute configurations of (trans, trans-2,4-hexadienoic acid)$Fe(CO)_3$ complexes were correlated to the measured specific rotation by the circular dichroism spectra.

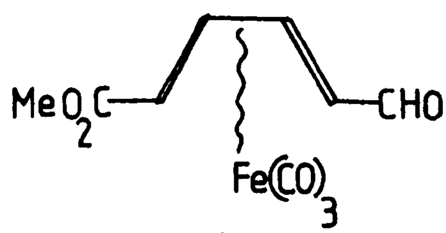


(7) $[\alpha] + 213°$ $[\alpha] - 204°$

Similarly the enantiomers of tricarbonyl(1-carboxycyclohexa-1,3-diene)iron (8a,b) were resolved by fractional crystallization of the salts of (S)-1-phenylethylamine.[3]



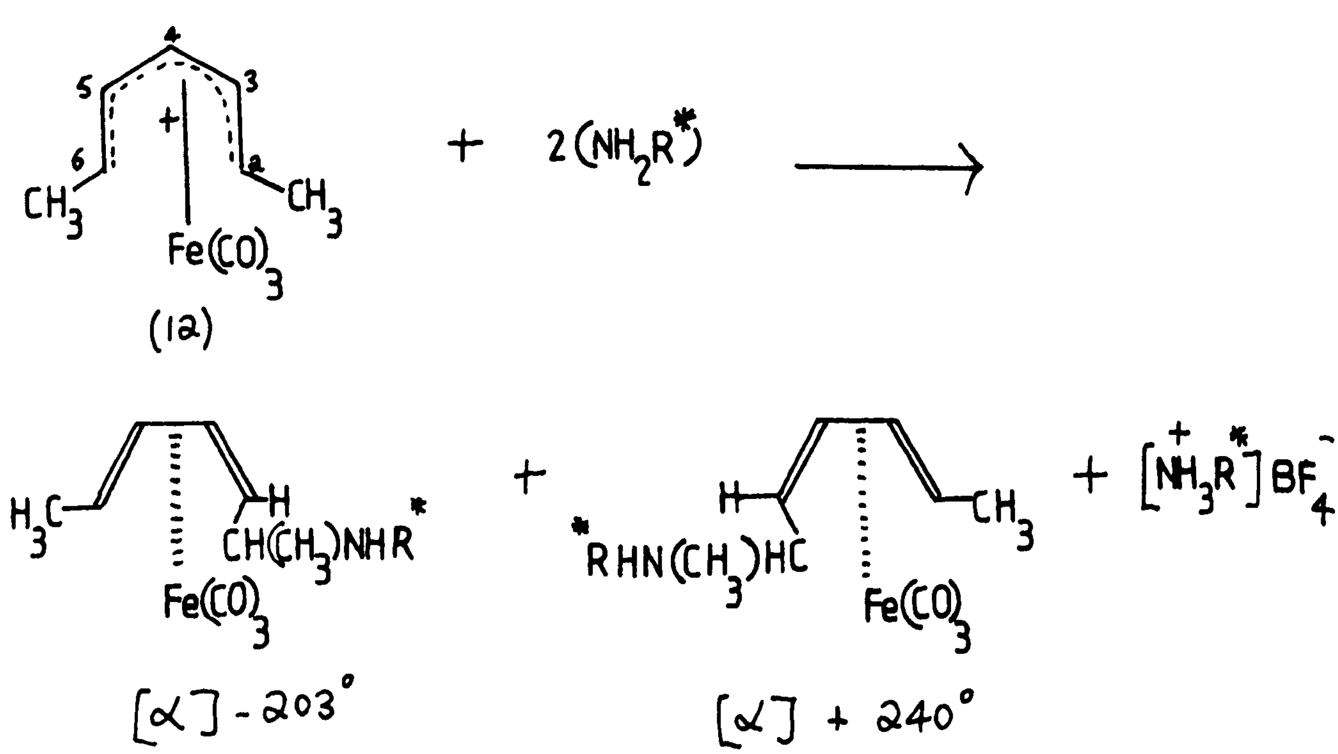
The absolute configuration of (8a) and (8b) was determined by reducing isomer (8a) to the 1-Me complex (9). This complex had previously been produced by borohydride reduction of the dienyl salt (10) of known absolute configuration.[4] Treatment of the enantiomers of (11) with (-)-ephedrine gave a pair of diastereoisomers, which were separated by fractional crystallization.[5]




(11)

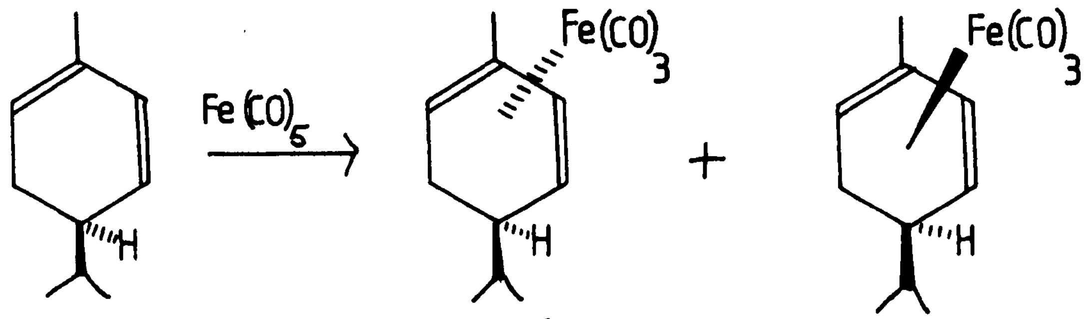
Exo-attack by nucleophiles on the carbon atoms 2 and 6 of the dienyl tricarbonyl cation (12) leads to the formation of an enantiomeric pair of complexes. However, the reaction of (12) with the chiral nucleophile (S)-1-phenylethylamine resulted in the formation of two diastereoisomers, which were separated by column chromatography.[6]

$R^* = CH(Me)Ph$



## 2.1.2 Asymmetric Complexation

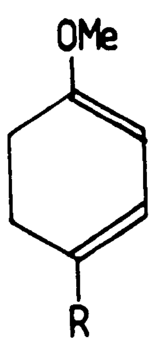
Optically active diene complexes have been produced by asymmetric complexation with natural dienes such as (-)-phellandrene (13) or (-)-carvone.[7] Complexation of (-)-phellandrene with $Fe(CO)_3$ yielded complexes (14) and (15) (4:1), showing the steric hindrance effect of the isopropyl group.




(R-) [α] -265°   [α] +12°   [α] -16°

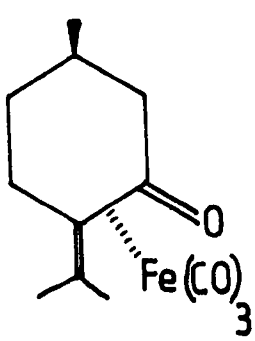
(13)   (14)   (15)

Partially resolved tricarbonyl(diene)iron complexes have been prepared by the transfer of the $Fe(CO)_3$ moiety from an optically active donor, to an unsymmetrically substituted 1,3-diene (16) and (17).[8] Naturally occurring chiral α, β-unsaturated ketones such as (+)-pulegone and (-)-3-βacetyloxypregna-5-16-diene-20-one form tricarbonyl($\eta^4$-enone)iron complexes (18) and (19) which act as a convenient optically active source of $Fe(CO)_3$ moiety transfer.[9]

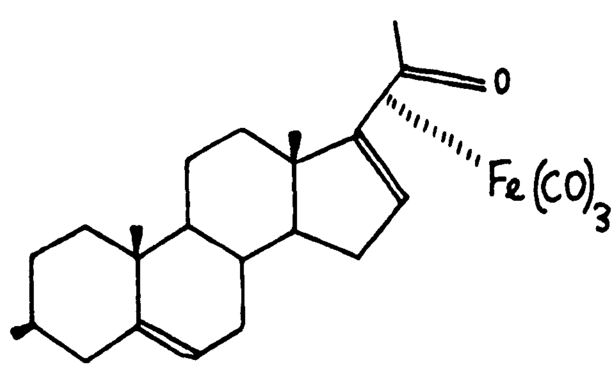



(16) R=H

(17) R=Me

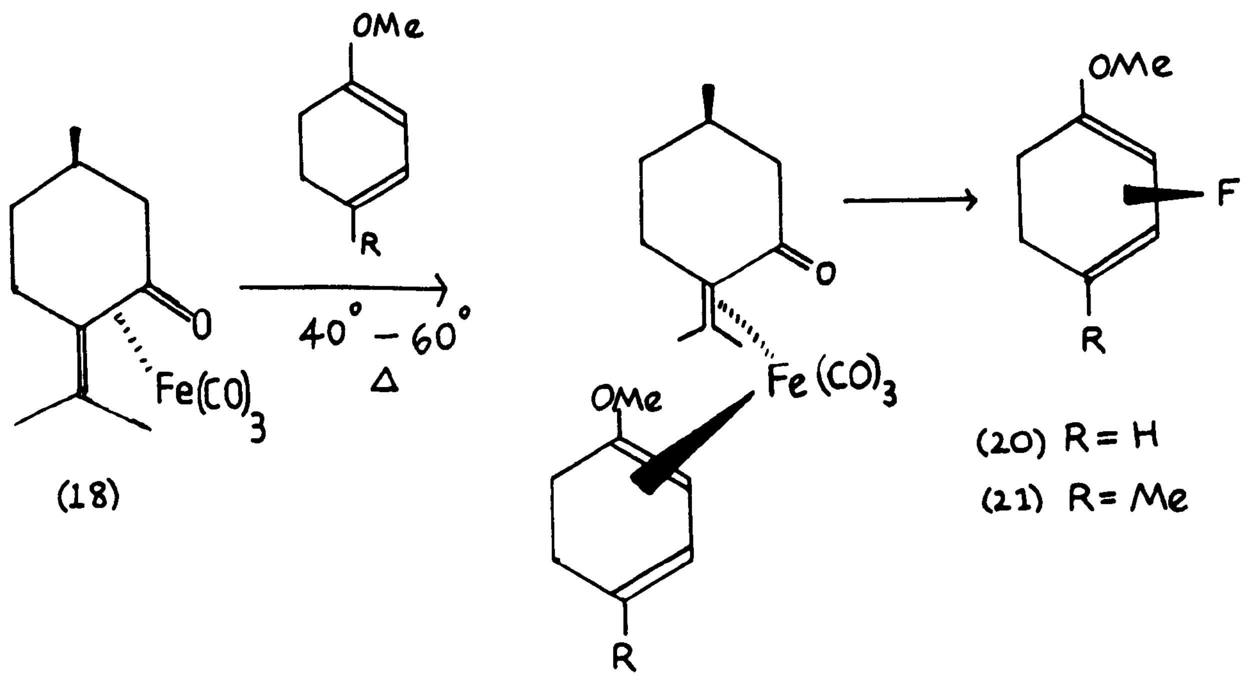



(18)




(19)

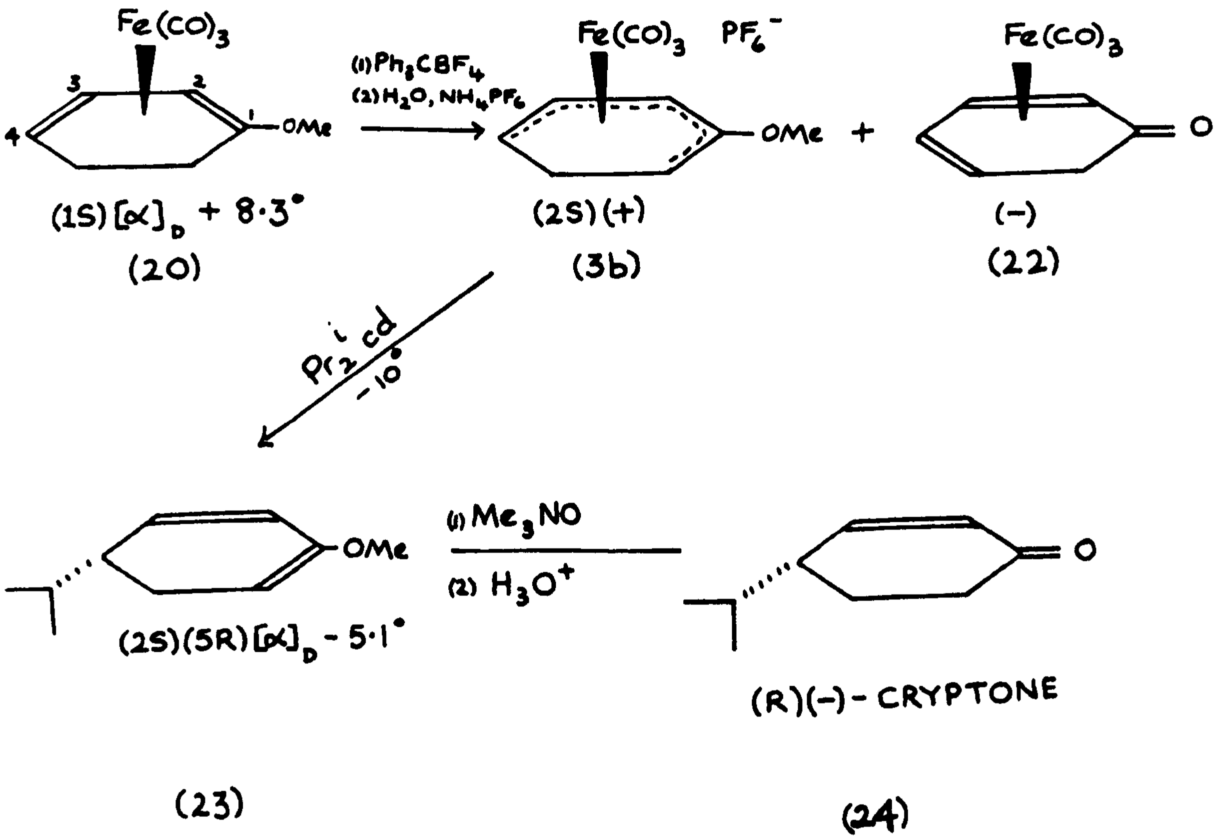
When complex (18) was reacted with (16) or (17), the enantiomeric excess of the (1,3-diene)$Fe(CO)_3$ complex formed was only 10%. The reaction of (19) with (16) or (17) gave a higher enantiomeric excess (up to 40%). Since one face of (19) is far more sterically hindered than the other, complexation is expected to occur almost exclusively on the less hindered side. The stereochemical outcome of the $Fe(CO)_3$ transfer reaction is thought to be determined by the first approach of the 1,3-diene to the donor complex. Cleavage of the metal-ketone bond occurs to produce an intermediate which then decomposes to give the product. Thus the iron remains bonded to the same face of the diene without scrambling (Scheme I).




SCHEME I

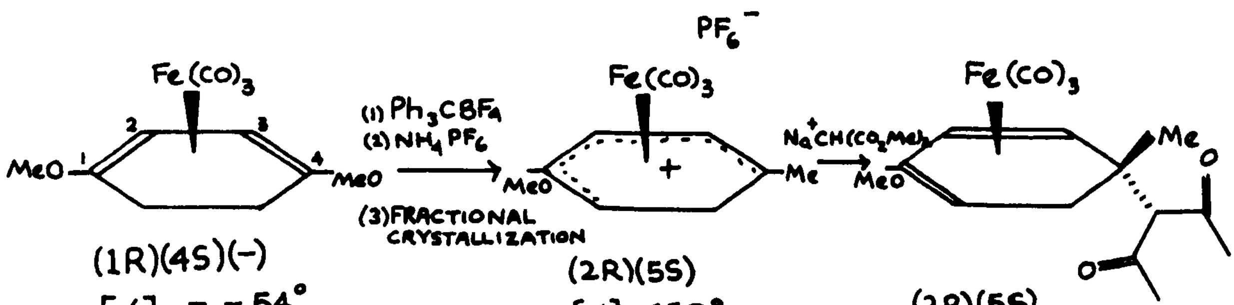
The low enantiomeric excess of the 1,3-diene complexes formed is probably due to lack of specificity in the initial complexation of the enone. Also the temperature necessary for the transfer reaction to proceed results in some thermal liberation of iron carbonyl, which is then able to complex with the free diene.

The absolute configurations of (20) and (21) were established by conversion of the enantiomerically enriched samples into natural products of known configuration.[4,10] (Scheme II) (20), with an enantiomeric excess of ca. 4% obtained by asymmetric complexation with [(+)-(pulgone)]Fe$(CO)_3$ (18),




SCHEME II

was converted to the (+)2-MeO dienyl salt (3b) although the dienone (22) was the major product. Alkylation with di-isopropylcadmium gave (23) in 55% yield. Removal of Fe$(CO)_3$ and hydrolysis produced (-)-cryptone (24). Comparison of the ORD spectrum of (24) with an authentic specimen of (R)-(-)-cryptone indicated absolute configurations as drawn in Scheme II. Since alkylation of $[(\text{dienyl})Fe(CO)_3]^+$ complexes is stereospecific, the absolute configuration of the cation is also known. An enantiomerically pure sample of (2R,5S)-(-)-[(2-methoxy-5-methylcyclohexadienyl) Fe $(CO)_3]PF_6$ (25) has been prepared by fractional crystallization of an enantiomerically enriched sample obtained by asymmetric complexation with (19).[11]




(1R)(4S)(-) $[\alpha]_D = -54°$ (21)

(2R)(5S) $[\alpha]$-138° (25)

(2R)(5S) (26)

The neutral diene (21) underwent unambiguous hydride abstraction to give salt (25) ($[\alpha]$= -73°MeCN). Enantiomerically pure (25) $[\alpha]$-138° was obtained after three fractional crystallizations. The optical purity of (25) was confirmed by n.m.r. spectroscopy. (25) was converted to the dimethylmalonate derivative (26). The $^1$H n.m.r. spectrum recorded in the presence of the optically active shift reagent tris(3-trifluoroacetyl D-camphorato)europium III, showed that only one isomer was present. The method provides a general means for determining the enantiomeric purity of dienyl salts.[12]

## 2.1.3 Kinetic and/or Thermodynamic Discrimination

Chiral nucleophiles (Table 1) were found to react with the enantiomers of [(2MeO-cyclohexadienyl)Fe$(CO)_3$][$PF_6$] (3a and 3b) at different rates. When a deficiency of chiral nucleophile was added to the dienyl salt, the recovered unreacted salt was enantiomerically enriched.

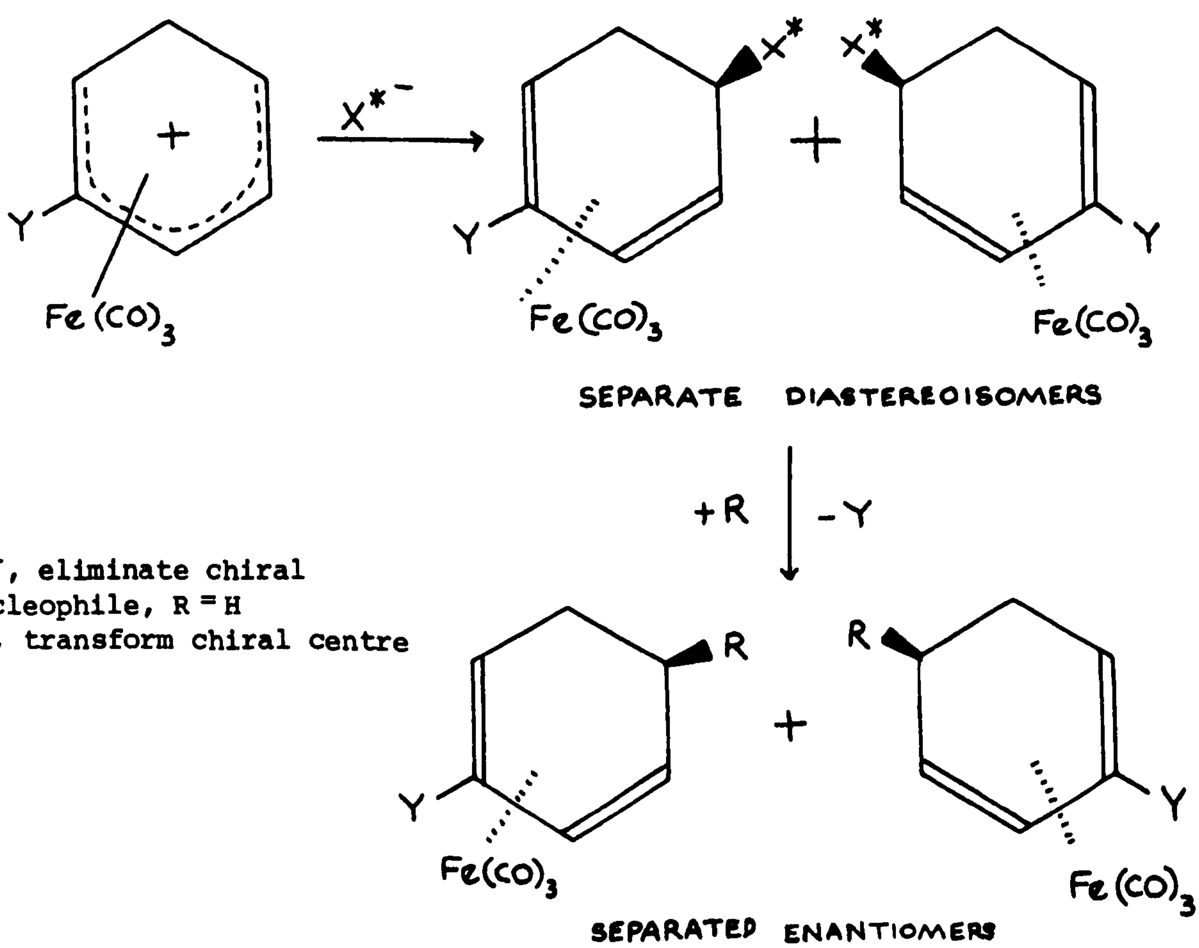
TABLE 1

| CHIRAL NUCLEOPHILE | % ENANTIOMIC EXCESS OF (4)-(R)-(-) OR (5)-(S)-(+) RECOVERED | REFERENCE |
|---|---|---|
| ENOL TRIMETHYL ETHER OF (+)-CAMPHOR | ca 15% (R)-(-) | 13 |
| (R)-(+)-1-PHENYLETHYLAMINE | could not be measured (S)-(+) | 14 |
| (S,S)-(-)-O-PHENYLBIS-(1,2-METHYLPHENYLPHOSPHINE) | 6-11% (S)-(+) | 15 |
| (-)-MENTHYLDIPHENYLPHOSPHINE | 11% (S)-(+) | 16 |
| (S)-(S)-(-)-CHIRAPHOS | 1.5% (R)-(-) | 16 |

The degrees of enantiomeric enrichment obtained by asymmetric complexation (up to 40%) or kinetic/thermodynamic discrimination (up to 11%) are too low to form the basis for satisfactory enantioselective synthesis. The remainder of this thesis gives an account of two general methods for preparing these complexes in an optically pure form. Chapter 2 describes work on the resolution of [(dienyl-Fe$(CO)_3$]$^+$ salts involving the separation of diastereoisomeric pairs obtained by nucleophilic attack using chiral alkoxides, phosphines and amines. Chapter 3 investigates some reactions of enantiomerically pure diene and dienyl iron complexes. Chapter 4 describes the degree of asymmetric induction achieved by achiral nucleophilic attack on [(dienyl)Fe$(CO)_2$L*]$^+$ complexes where L* is a chiral ligand.

### 2.1.4 Reactions Using Chiral Nucleophiles

Nucleophilic attack on $[(\eta^5\text{-cyclohexadienyl})Fe(CO)_3]^+$ (4) by a chiral nucleophile, results in the formation of a diastereoisomeric pair. Separation by chromatography or fractional crystallization followed by the elimination of the nucleophile, provides a route to enantiomerically pure dienyl complexes. Alternatively, an optically pure substituted diene may be obtained if the chiral nucleophile is transformed by substitution or other means into an achiral substituent - Scheme III (provided the reaction does not proceed via an intermediate containing a plane of symmetry.)




$Y = R^1$, eliminate chiral nucleophile, $R = H$

$Y = H$, transform chiral centre

SCHEME III

Chiral nucleophiles which appear promising are alkoxides, phosphines and amines. Accounts of their reactivity with $[(\eta^5$-dienyl)$Fe(CO)_3]^+$ complexes have appeared in the literature, and they are available commercially in an optically active form, or can be readily synthesized. Chiral alkoxides are easily prepared by proton abstraction from chiral alcohols, a variety of which are available. The reaction of complex (4) with simple alkoxides is known to proceed via exo attack at carbon-5 to give a neutral substituted diene compound. However, an exo-endo equilibrium was found to occur when (5-exo-$MeOC_6H_7$)$Fe(CO)_3$ was refluxed in MeOH in the presence of acid for several hours (Chapter 1.2.5.3). The relative amount of endo isomer formed when R= Et or $Pr^i$ decreases substantially as the alcohol becomes more sterically demanding.[17]

Phosphine addition to $[(\eta^5$-dienyl)$Fe(CO)_3]^+$ complexes is also a well established reaction which has been studied mechanistically in some detail.[18] The simple second order rate law Rate = $k$ [irondienyl complex]$[PR_3]$ observed for the addition of a range of phosphines and phosphites to $[(C_6H_7)Fe(CO)_3][BF_4]$ (4) supports the mechanism of direct addition at the dienyl ring to give the phosphonium salt. Addition of phosphines to $[(2\text{-}MeOC_6H_6)Fe(CO)_3][BF_4]$ (3) is generally 5-10 times slower than for (4), since electron donation from the 2-MeO group tends to reduce the reactivity of the dienyl salt to nucleophilic attack. Two types of chiral phosphine reagents are available; chiral tertiary phosphines, where the phosphorus atom is the centre of chirality, and alkyl centred chiral phosphines, where optical activity resides at an alkyl carbon atom attached to the phosphorus.

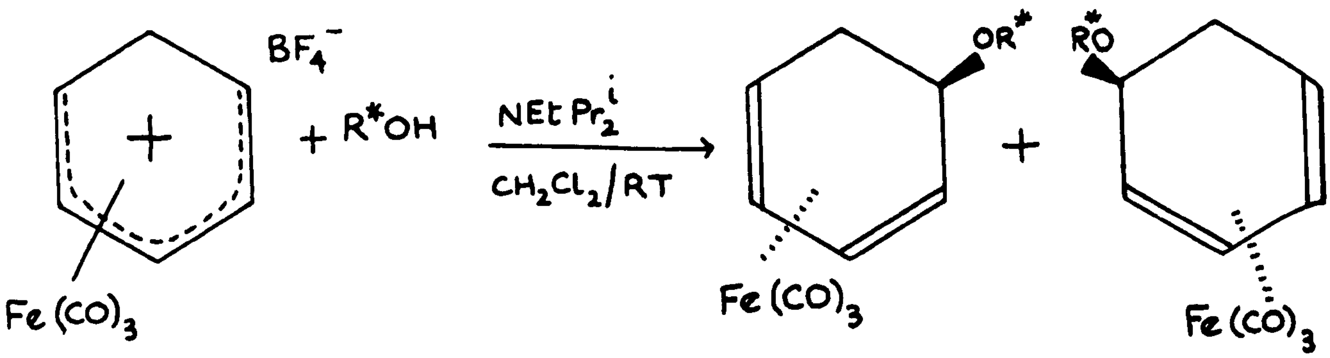
The latter are more readily prepared, since chiral alkyl derivatives are commercially available in a fully resolved form. However, the use of a chiral tertiary phosphine is probably more likely to lead to asymmetric induction, since the chiral centre is closer to the reaction site.

The reaction of cyclic and acyclic dienyl iron cations with amines has been studied mechanistically. It proceeds by exo addition at the terminal dienyl carbons to give an ammonium salt, which is deprotonated by the addition of a second mole of amine.[6,14]

## 2.2 Results and Discussion

### 2.2.1 Chiral Alkoxides

We have investigated the treatment of complex (4) with (S)(-)-$HOCH_2CH(Me)Et$ or (-)-menthol in the presence of the hindered base $NEtPr^i_2$ as a deprotonating agent. Good yields of the diastereoisomers (27a,b) and (28a,b) are obtained.

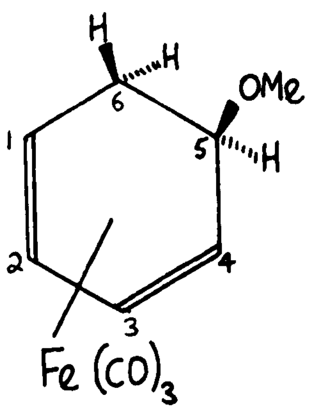



(4)

| | OR* | YIELD |
|---|---|---|
| (27a,b) | (S)(-)-$OCH_2CH(Me)Et$ | 98% |
| (28a,b) | (-)-$OC_{10}H_{19}$ (menthoxy) | 95% |

The $^{13}C$ and $^{1}H$ n.m.r. spectra (Table 2) of the diastereoisomeric pairs (27a,b) and (28a,b) are assigned on the basis of off-resonance and spin-decoupling experiments, and by comparison with the model 5exo-methoxy complex (29).[19]

TABLE 2 $^{13}C$ n.m.r. Data for Complex (29)

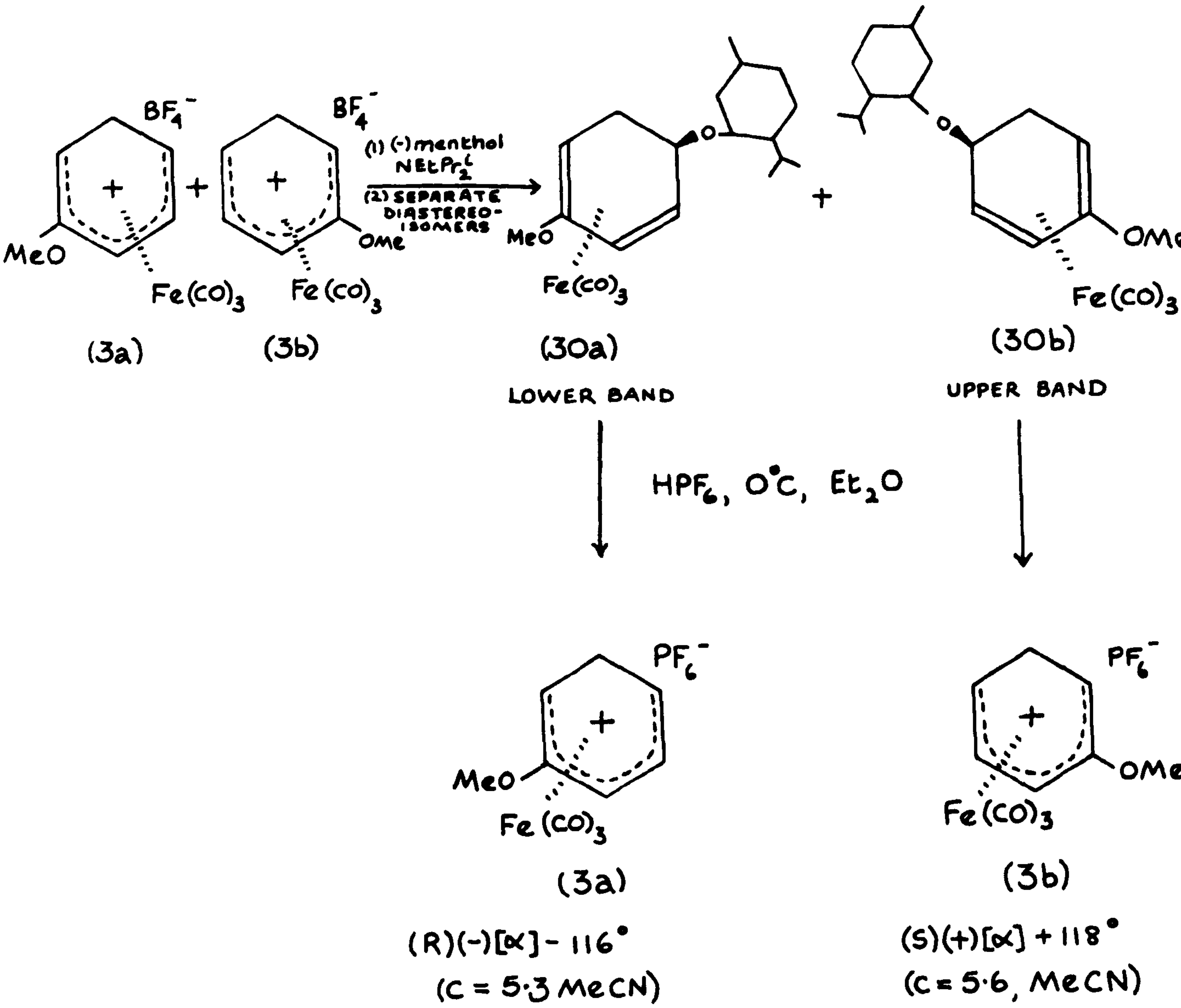



| $^{13}C$ ASSIGNMENT (p.p.m. from $SiMe_4$ in $CDCl_3$ solution) | | MULTIPLICITIES (off-resonance decoupled spectra) |
|---|---|---|
| C2,3 | 87.3 | d |
| | 84.9 | d |
| C1,4 | 56.3 | d |
| | 55.7 | d |
| C5 | 75.9 | d |
| C6 | 30.4 | t |
| OMe | 59.3 | q |

The inner diene carbon resonances of complex (29) are assigned on the basis of their characteristic low field position. Assignments of the outer diene and methoxy resonances are made with the aid of the off-resonance decoupled spectrum, the methoxy group being furthest downfield at 59.3 ppm and appearing as a quartet. A doublet is found for C-5 at 75.9 ppm. The methylene carbon (C-6) is observed as a triplet at 30.4 ppm. Thus the assignment of the $^{13}C$ spectrum of (28a,b) is achieved by comparison with complex (29) and the spectrum of free menthol. A doubling of many $^{13}C$ resonances is observed for (28a,b) (figure I), indicating that an equimolar mixture of diastereoisomers is present. The mixture (28a,b) may be separated in a total yield of 43% by preparative thin-layer chromatography on silica gel using light petroleum/ethyl acetate 95/5 as eluant.

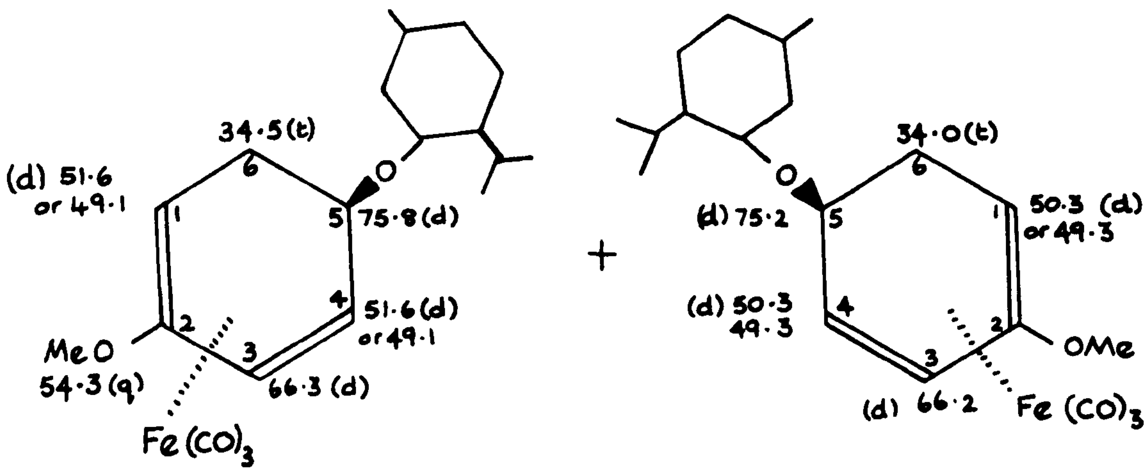
The $^{13}C$ spectra for the separated diastereoisomers are given in figures II and III. The $^{1}H$ spectra of the separated diastereo-isomers are, however, essentially coincident and the resonances listed in Table 2 refer to the diastereoisomeric mixture. Treatment of (28a) or (28b) with $HPF_6$ generate, of course, achiral (4). Chapter 3, however, describes attempts at elimination of the menthoxy residue which maintain the chirality at the quaternary carbon. Separation of the diastereoisomeric pair (27a,b) has not been attempted; individual $^{13}C$ resonances for the two diastereoisomers are not observed, and consequently it would be difficult to monitor by n.m.r. the degree of separation achieved.

Treatment of the 2-methoxy cation (3a,b) with (-)-menthol gives (30a,b) in 93% yield. Due to the strong para directing effect of the 2-MeO substituent (Chapter 1.2.5.2), nucleophilic attack occurs exclusively at carbon 5. (See following page).




The $^{13}$C spectra again show an equimolar mixture of the diastereoisomers (30a,b) (figure IV) indicating no asymmetric induction. The diastereoisomers may be readily separated by preparative thin-layer chromatography on silica gel using light petroleum/diethyl ether 90/10 as eluant, in a total yield of 75%. The $^{13}$C resonances of the separated diastereoisomers (complete spectra given in figures V and VI) are again assigned with the aid of off-resonance decoupled spectra and by comparison with the model complex (29) and the spectrum of free menthol.

$^{13}$C n.m.r. Data




(30a) LOWER BAND

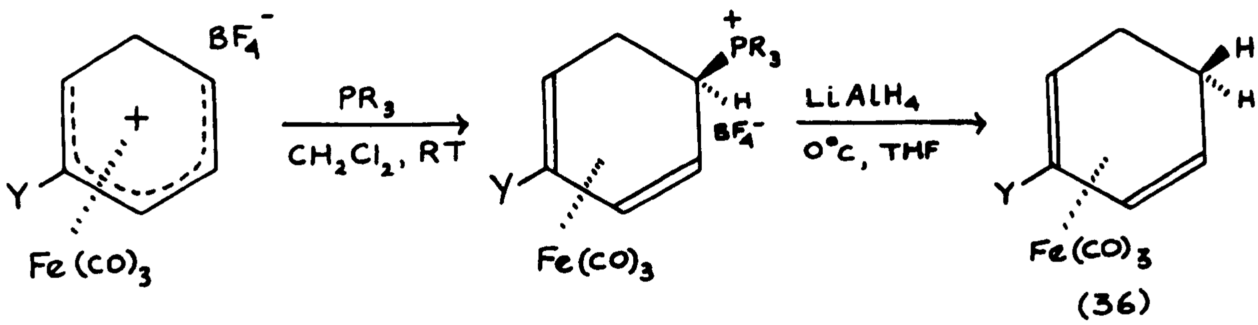
(30b) UPPER BAND

The inner diene resonances (C-2) show a large up-field shift compared with the unsubstituted diene (complex 28a,b), due to electron donation from the methoxy substituent. No resonance is observed for the quaternary carbon C-3. The outer diene carbon resonances (C-1 and C-4) also show an up-field shift due to an increase in electron density, both appearing as a doublet in the off-resonance spectra. A quartet is found for the methoxy substituent at 54.3. Other resonances are similar to those found for complexes (28a,b).

Elimination of the menthoxy group by protonation with $HPF_6$ is accomplished in about 80% yield to give enantiomerically pure samples of the 2-methoxy salt (3a,b). The absolute configurations of (3a,b) and (30a,b) can be drawn with confidence, since enantiomerically enriched samples of (3a,b) obtained by asymmetric complexation, have been converted into natural products of known configuration (Chapter 2.1.2).[10] After the completion of our work, Birch and co-workers reported the resolution of the 2-methoxy salt (3a,b) via the separation of (30a,b).[20] The optical rotation obtained for the enantiomerically pure salts were in agreement with the values given here, whilst the optical rotations of the $BF_4^-$ salts were found to be notably different [(R)-(-) [$\alpha$]-139.4° (C=0.6,MeCN), (S)-(+)-[$\alpha$]+136° (C=0.6,MeCN)].The influence of the anion must therefore be taken into account when assessing the extent of resolution of a complex.

## 2.2.2 Chiral Phosphines

We have investigated the reaction of complex (4) with the chiral phosphine (S)-(+)-PMePrPh.[21] Good yields of the stable phosphonium salt (31a,b) are isolated as an off-white precipitate. (See following page).




(4) Y = H
(3) Y = OMe

| | $PR_3$ | Y | % YIELD |
|---|---|---|---|
| (31a,b) | (S)-(+)-PMePrPh | H | 63% |
| (32a,b) | (+)-$PPh_2(C_{10}H_{19})$= menthyl | H | 97% |
| (33a,b) | (S)-(+)-$PPh_2[CH_2CH(Me)Et]$ | H | 86% |
| (35a,b) | (+)-$PPh_2(C_{10}H_{19})$= menthyl | OMe | 98% |

(For simplicity the above scheme shows the arbitrary configuration of only one of the diastereoisomers).

It was thought that the use of a chiral phosphine, where the phosphorus was at the centre of chirality might result in asymmetric induction. The $^{31}P$ n.m.r. spectrum (figure VII) clearly shows that the diastereoisomers exist in an equimolar ratio.

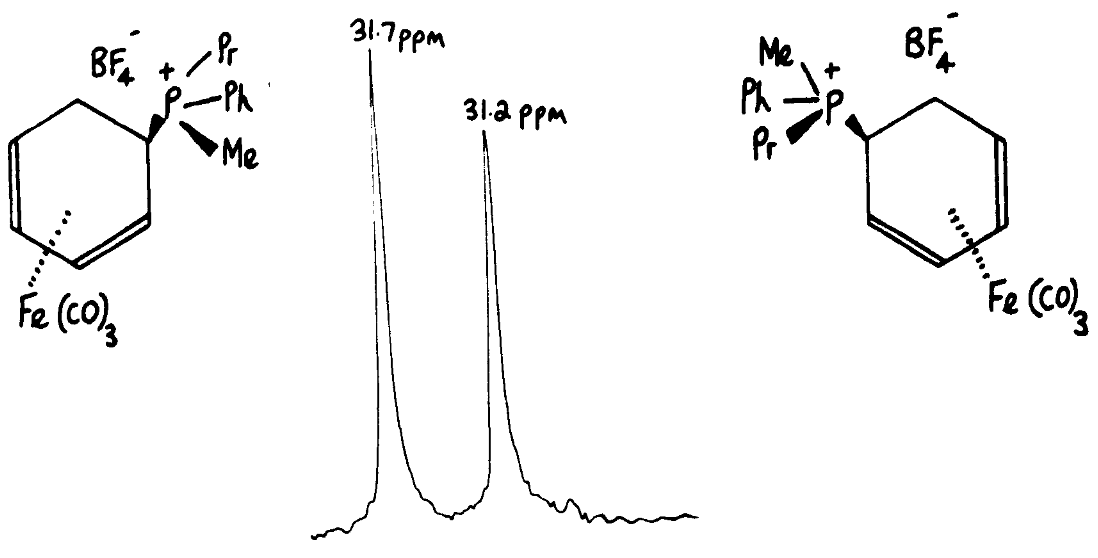



FIG. VII $^{31}P$ n.m.r. spectrum of diastereoisomers (31a,b)

(the configurations are arbitrarily drawn)

This promoted the use of alkyl centred chiral phosphines; since the optically active alkyl groups used were commercially available in a fully resolved form, the lengthy resolution step associated with the synthesis of a tertiary phosphine was avoided. (The synthesis of (S)-(+)PMePhPr itself involves the introduction of a resolved chiral centre, to convert an enantiomeric mixture into diastereoisomers which could then be separated by fractional crystallization.[21]) (+)-Neomenthyldiphenylphosphine, however, is easily prepared by the displacement of the hydroxy group of (-)-menthol with chloride to give (-)-menthyl chloride. Nucleophilic attack on the menthyl chloride by sodium diphenylphosphide proceeds by $S_N2$ reaction to give the desired product.[22]

(+)-Neomenthyldiphenylphosphine and (S)-(+)$PPh_2[CH_2CH(Me)Et]$ (prepared by a similar procedure from the alcohol $HOCH_2CH(Me)Et$[22,23]), react with (4) to give good yields of the phosphonium salts (32a,b) and (33a,b). The $^{31}P$ n.m.r. spectra again show that the complexes exist as equimolar diastereoisomeric mixtures, exhibiting two resonances of equal intensity (figure VIII)(see following page).

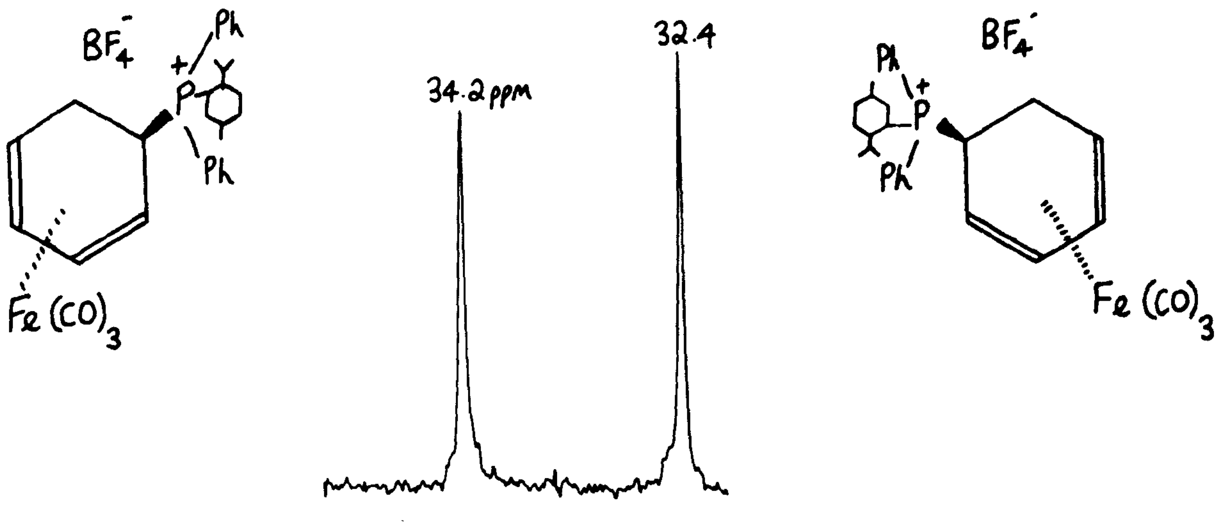



FIG. VIII $^{13}$P n.m.r. Spectrum of (32a,b)
(the configurations are arbitrarily drawn)

The diastereoisomeric pair (32a,b) may be readily separated by fractional crystallization. Good yields of pure (32a) (70% of the theoretical maximum, of greater than 98% purity by $^{31}$P n.m.r. - figure IX) are obtained from early fractions, while later fractions provide smaller yields (41%) which is substantially enriched in isomer (32b) (ca. 90% by $^{31}$P n.m.r. - figure X).

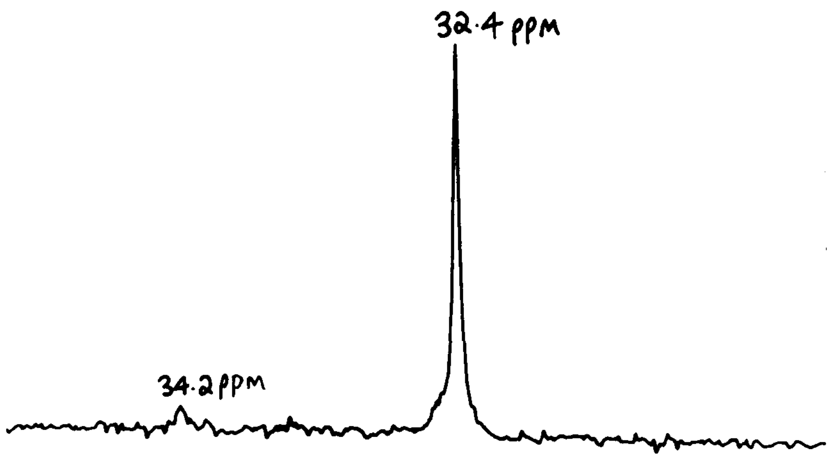



FIG. IX $^{31}$P n.m.r. Spectrum of (32a)

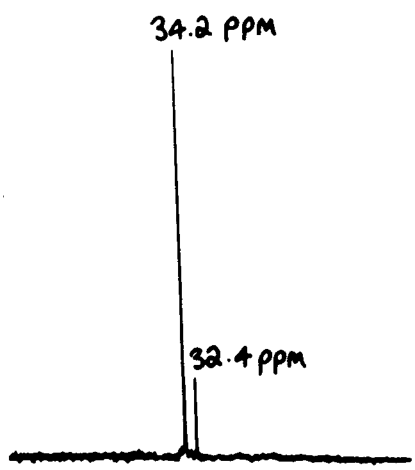
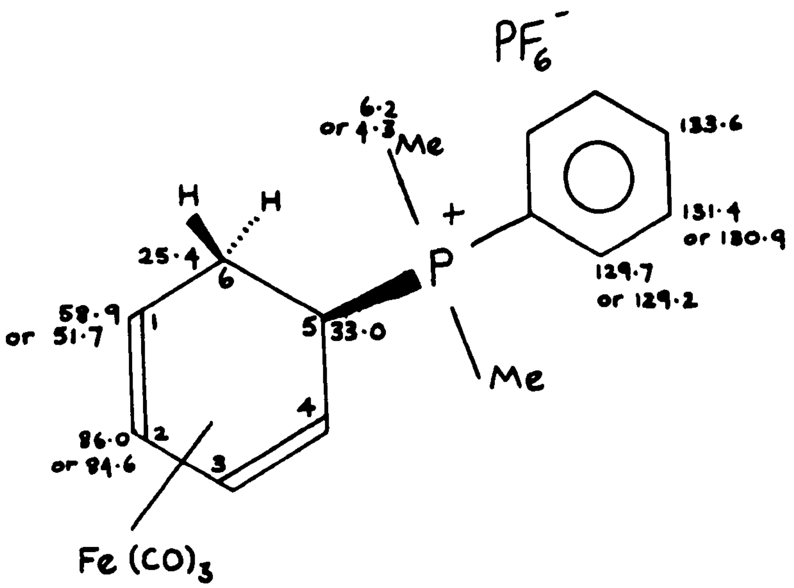



FIG. X $^{31}$P n.m.r. Spectrum of (32b)

There is no evidence of phosphine dissociation, which would allow diastereoisomeric interconversion to occur. No line broadening of the $^{31}P$ n.m.r. resonances of compound (31a,b) at up to 55°C in $CDCl_3$ is observed, while samples of (32a) kept in $CDCl_3$ solution for hours show no detectably conversion into (32b). This is in contrast to the related benzene complex $[(C_6H_6)_2Fe]^{2+}$, which was found to undergo reversible phosphine addition.[24]

The $^{13}C$ n.m.r. spectra of the phosphonium salts (Table 4) were assigned on the basis of off-resonance experiments, and by comparison with the model 5-exoPMePh complex (34).[25]




$^{13}C$ n.m.r. Data Complex (34)

The inner and outer diene carbon resonances of (34) are assigned on the basis of their characteristic low field position. The assignment of C-5 at 33.0 ppm is made due to the large phosphorus-carbon coupling of 40.3Hz. The $^{13}C$ spectrum of racemic (32a,b) showed a doubling of many resonances, consistent with the presence of two diastereoisomers (Table 4). The resolving centre may be eliminated from (32a) by reduction with $LiAlH_4$ to give achiral (36); this reaction is discussed in more detail in Chapter 3.

The 2-methoxy cation (3) reacts with (+)-neomenthyldiphenylphosphine exclusively at the C-5 terminus to yield (35a,b). The $^{31}P$ n.m.r. spectrum again shows an equimolar diastereoisomeric mixture.

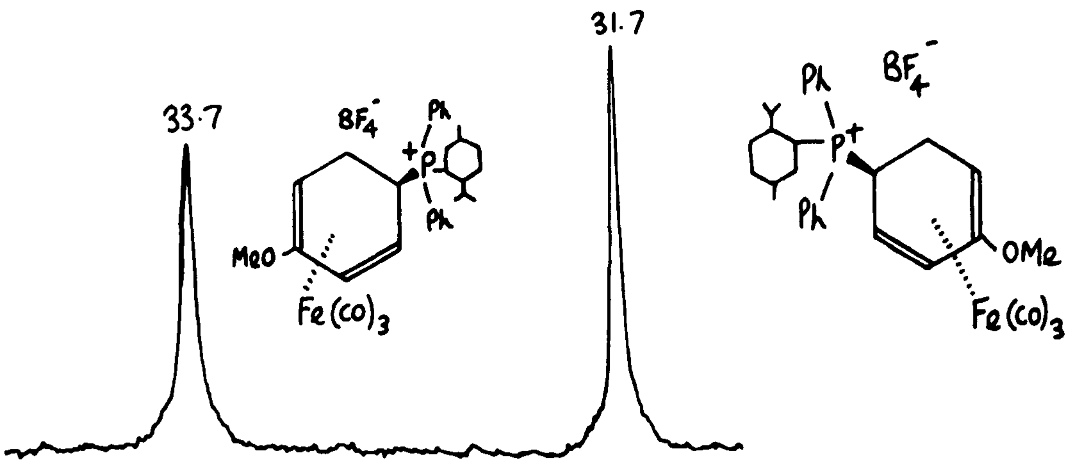
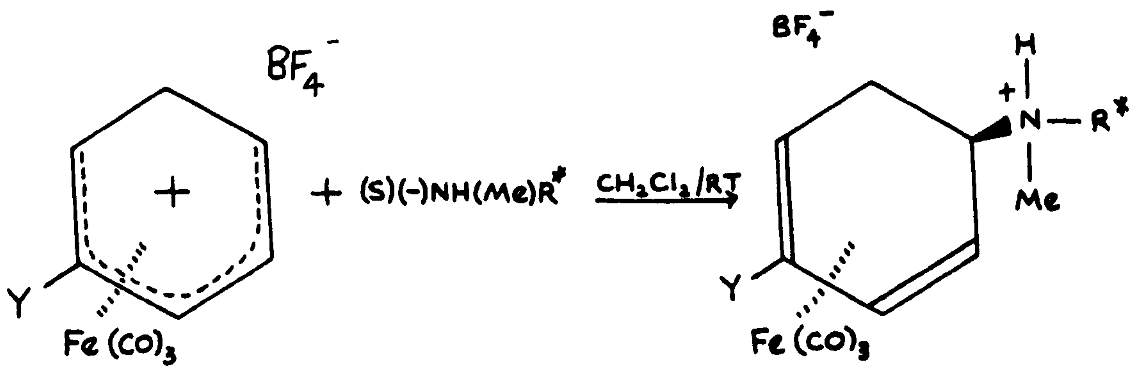



FIG. XI $^{31}P$ n.m.r. Spectrum of (35a,b)
(configurations are arbitrarily drawn)

Elimination of the chiral phosphine with $LiAlH_4$ from separated (35a) or (35b), would give enantiomerically pure (2-MeO-cyclohexadiene)$Fe(CO)_3$ (2a) or (2b). Several attempts have been made to separate the diastereoisomeric mixture (35a,b) by fractional crystallization using a variety of solvent mixtures; $CH_2Cl_2$ at -40°C, $CH_2Cl_2/Et_2O$ in various ratios and temperatures between -30°-0°C, $CHCl_3/Et_2O$ at -30°C. Unfortunately, none of these attempts have been successful.

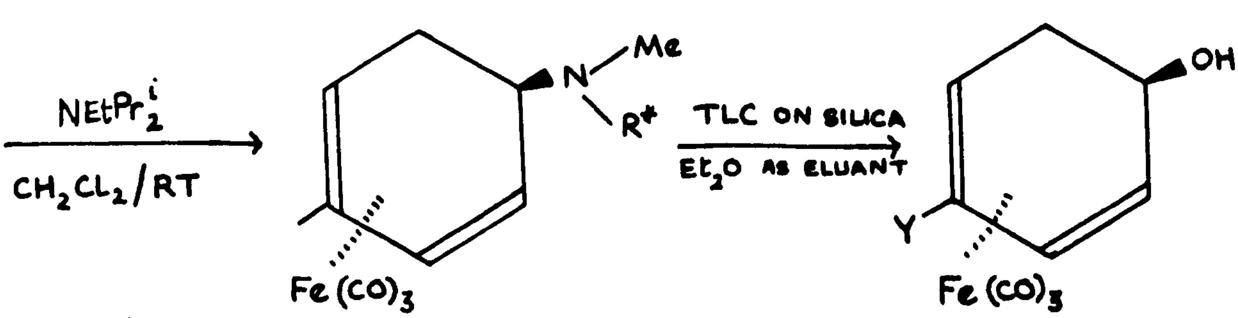
2.2.3 Chiral Amines

We have found that treatment of complex (4) with an equimolar amount of (S)-(-)NH(Me)[CH(Me)Ph] in $CH_2Cl_2$ gives (37a,b). The tetrafluoroborate salt could be precipitated by the addition of diethyl ether to give a yellow solid in 75% yield. Although analytically pure samples have not been obtained, the ammonium salt exhibited ν (CO) bands at a somewhat higher frequency (2053 and 1994 br $cm^{-1}$ in $CH_2Cl_2$) than for neutral tricarbonyl(diene)-iron complexes. Deprotonation of (37a,b) is carried out in situ by the addition of a small excess of the hindered base $NEtPr^i_2$ to give the neutral amine (39a,b) in 98% yield.




(4) Y = H
(3) Y = OMe

| R* | Y |
|---|---|
| (37a,b) - CH(Me)Ph | H |
| (38a,b) - CH(Me)Ph | OMe |

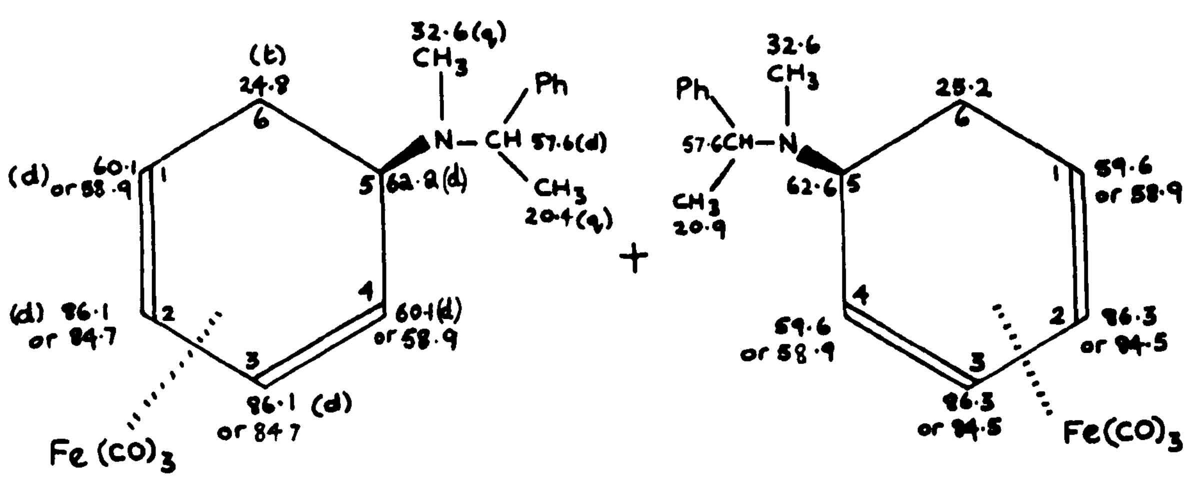



| R* | Y |
|---|---|
| (39a,b) - CH(Me)Ph | H |
| (40a,b) - CH(Me)Ph | OMe |

(41) Y = H

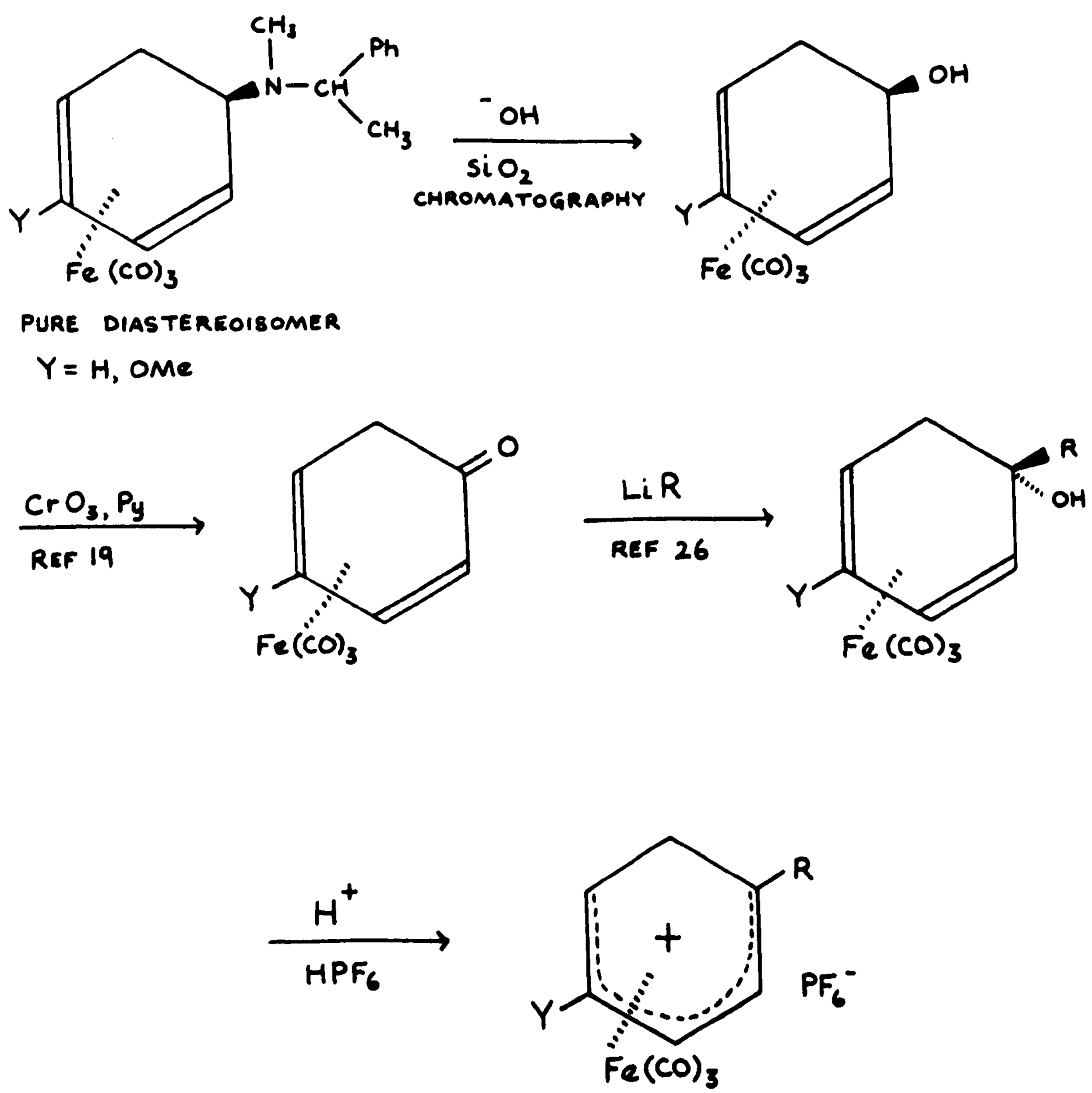
The above scheme shows the arbitrary configuration of only one of the diastereoisomeric pairs. From the $^{13}C$ spectrum of (39a,b), a doubling of many resonances indicates that an equimolar mixture of diastereoisomers is present (Table 5 and figure XII). The diastereoisomeric pair (39a,b) may be readily separated by fractional crystallization from light petroleum, and their purity monitored by $^{13}C$ n.m.r. The less soluble isomer (39a) may be isolated in a pure state in 64% yield (figure XIII), whilst later fractions give a substantial enrichment of isomer (39b) (ca. 80% pure by $^{13}C$ n.m.r. - figure XIV) in 94% of the theoretical maximum yield.

<u>$^{13}C$ n.m.r. Data</u>
(configurations are arbitrary)



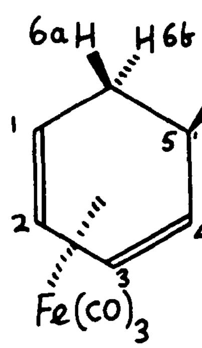
(39a) (39b)

The $^{13}C$ resonances of the separated diastereoisomers are assigned with the aid of off-resonance decoupled spectra, and by comparison with the spectrum of free N,$\alpha$-dimethylbenzylamine. Attempts to separate (39a,b) by preparative thin-layer chromatography result in hydrolysis to the exo-alcohol (41), identified by comparison with an authentic sample prepared by the hydrolysis of (4).[19] The synthetic utility of enantiomerically pure (41) lies in its ready transformation into optically active (cyclohexadienone)-$Fe(CO)_3$, and hence by alkylation and the elimination of the hydroxyl group, to a chiral substituted dienyl salt (Scheme IV).

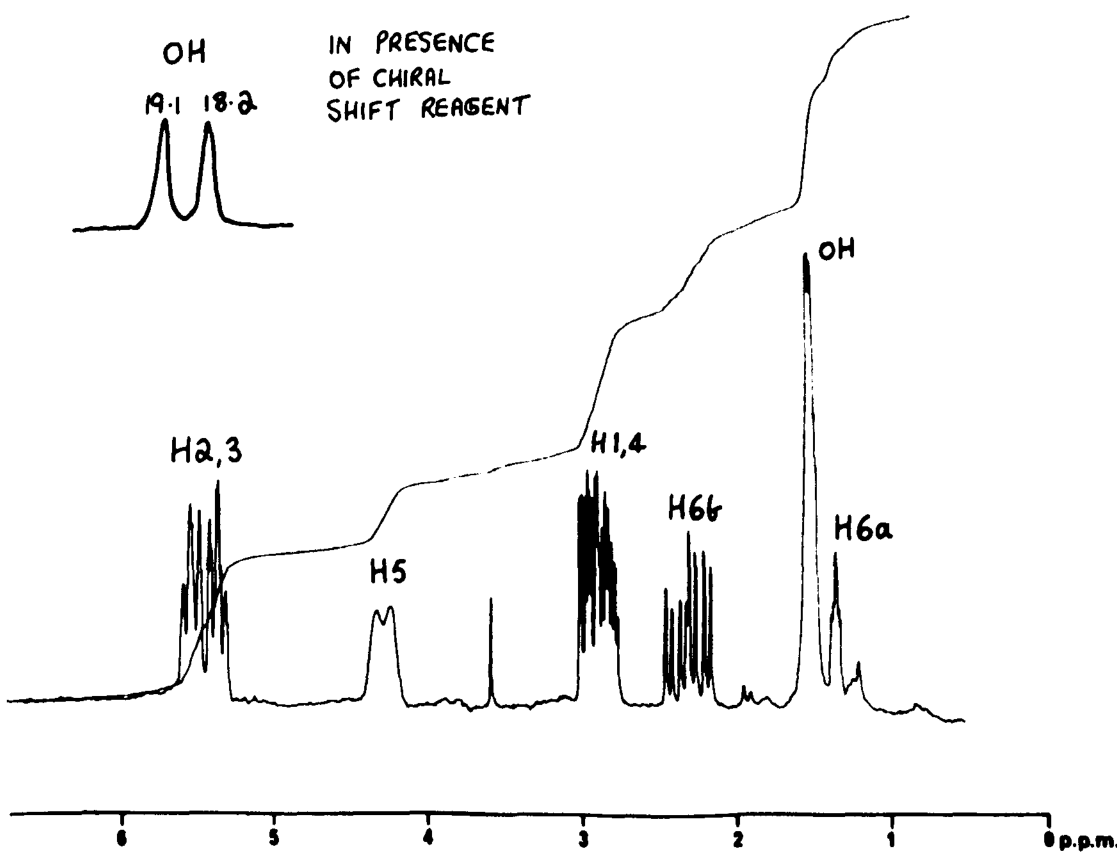



SCHEME IV

In order to determine whether the configuration at the resolved carbon centre was retained in the alcohol (41), the $^{1}H$ n.m.r. spectrum of (41) formed by the hydrolysis of pure diastereoisomer (39a), was examined using the chiral shift reagent tris[3-(heptafluoropropylhydroxymethylene)-D-camphorato]europium (III) (figure XV).

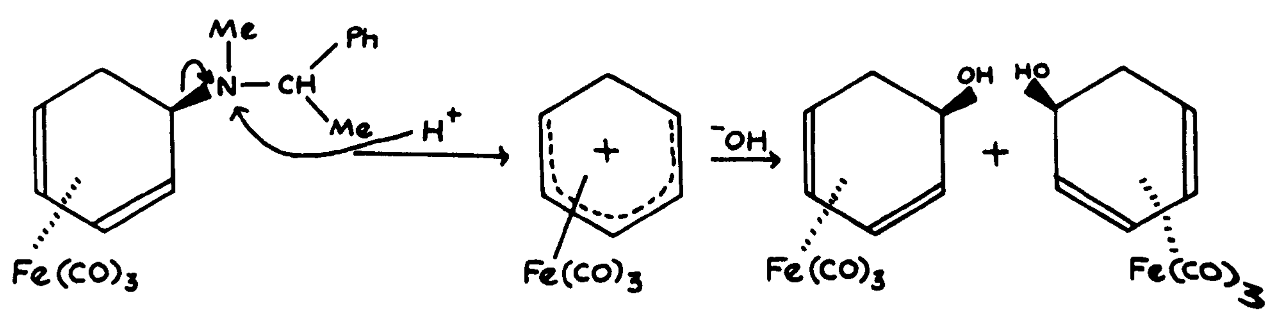



(41)




<u>FIG. XV</u> <u>$^{1}H$ n.m.r. spectrum of (41) formed by the hydrolysis of (39a)</u>
In the presence of chiral shift reagent, the OH resonance appears as two broad peaks, indicating that racemization has occurred to

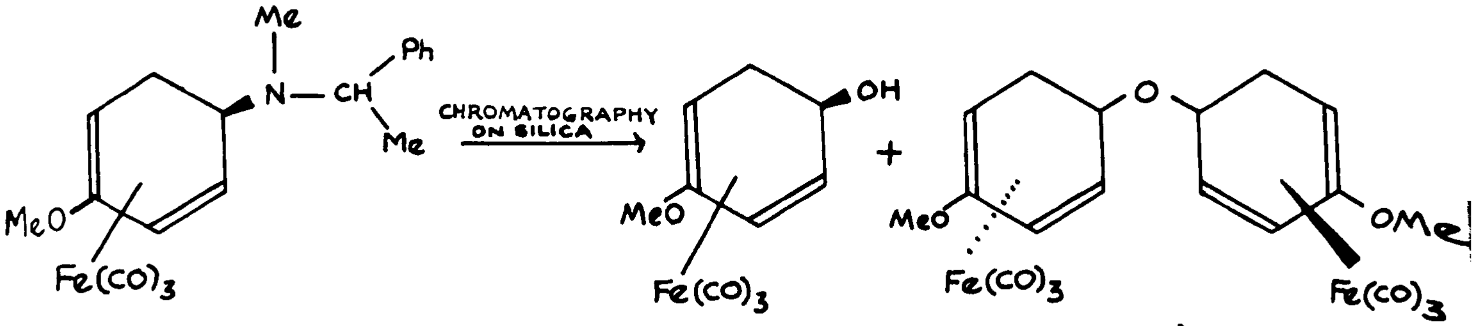
give an equimolar mixture of enantiomers. Hydrolysis must therefore proceed via an intermediate containing a plane of symmetry; initial loss of the amine residue must be proton induced to generate achiral (4), and addition of hydroxide can then occur to give an equimolar racemic mixture of (41).



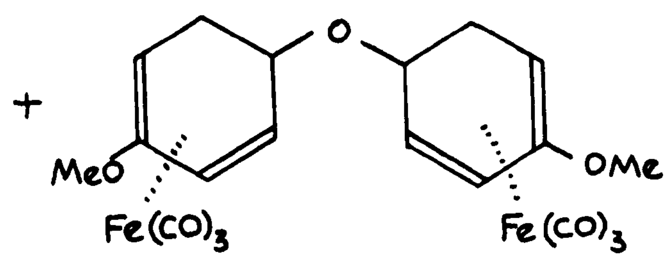

PURE (39a) (4) RACEMIC MIXTURE OF (41)

Attempts at elimination of the amine residue which maintain the chirality of the resolved carbon centre, are described in Chapter 3.

The reaction of the 2-methoxy cation (3) with (S)-(-)-NH(Me)-[CH(Me)Ph] occurs exclusively at carbon-5 via the intermediate ammonium salt (38a,b) to produce (40a,b) in 98% yield. The $^{13}C$ n.m.r. spectrum again shows an equimolar mixture of diastereoisomers (Table 5). Diastereoisomers (40a,b) are isolated as a yellow oil, attempted fractional crystallization with light petroleum at 0° or 30° was unsuccessful. Chromatography of (40a,b) on silica or Florisil results in the partial or complete hydrolysis to the alcohol (42), together with a small amount of the dimer (43a,b).




(40a,b) (42) (43a)




(43b)

An authentic sample of (42) prepared by the base hydrolysis of (3),[19] was also found to be contaminated by (43a,b) in the ratio of 3:1, alcohol to dimer. The dimeric complex is probably formed by proton abstraction from (42) under basic conditions, giving an alkoxide ion which could attack unreacted (3). Attempted chromatography of the alcohol (42) resulted in its partial conversion to (43a,b). The dimer exists as two diastereoisomers; where the metal is on opposite sides of the rings (43a), and where the metal is on the same side of both rings, a doubling of resonances is observed in the ratio of 2:1 in the $^{13}C$ n.m.r. spectrum (figure XVI). (43a) is thought to be the major isomer, since nucleophilic attack on unreacted (3) by the alkoxide ion will be sterically favoured when the metal is complexed to opposite faces of the diene rings. The $^{13}C$ spectra of (43a,b) was similar to that of (42) (Table 5), except the C-5 resonances which were shifted to a lower field due to the deshielding effect of the ether.

## 2.3 Experimental

All reactions were performed under nitrogen using purified degassed solvents. The compounds $[(\eta^5-C_6H_7)Fe(CO)_3][BF_4]$,[27] $[(\eta^5-2MeOC_6H_6)Fe(CO)_3][BF_4]$,[28] $Ph_3CBF_4$, (S)-(+)-PMePrPh (+16.8°),[21] (+)-$PPh_2(C_{10}H_{19})$ (+94°),[22] (S)-(+)-$PPh_2(C_5H_{11})$ (+42°),[22,23] and (S)-(-)-NH(Me)[CH(Me)Ph] (-74°)[30] were prepared by literature methods. (-)-Menthol (-50°) and (S)-(-)-$HOCH_2CH(Me)Et$ (-6.3°) were purchased commercially. Light petroleum ether refers to that fraction boiling between 40° and 60°C. Chromatographic alumina refers to neutral type 507C supplied by Fluka. The silica gel used for thin-layer chromatography was type $PF_{254}$ obtained from Merck, whilst for column chromatography 60-120 mesh silica gel was used, supplied by B. D. H. Chemical Ltd. N.m.r. spectra were recorded on a JEOL FX-100 spectrometer. Chemical shifts were measured in parts per million from tetramethylsilane. Proton decoupled $^{13}C$ spectra were run in $CDCl_3$. I.r. spectra were run on a Pye Unicam SP2000 spectrometer. CHN analyses were performed by a Perkin-Elmer 240 Elemental Analyzer. Optical rotations were measured on a Bellingham and Stanley polarimeter at a wavelength of 589 nm in all cases. Optical rotations are given in parentheses and agree with published values.

(a) Preparation of tricarbonyl(5-exo-menthoxycyclohexa-1,3-diene)iron (28a,b)

To a stirred suspension of complex (4) (1.9 g, 6.2 mmol) and (-)-menthol (2.0 g, 12.8 mmol) in $CH_2Cl_2$ (40 $cm^3$) was added $NEtPr^i2$ (0.96 g, 7.4 mmol). A clear yellow solution was formed after stirring for 5 min at room temperature, this was stirred for an additional 30 min. The solvent was removed under reduced pressure and the residue extracted with light petroleum. The yellow oil was chromatographed on a Grade II alumina column using light petroleum/diethyl ether as eluant to give the product (28a,b) (2.2 g) as a yellow oil. An analytical sample was purified by distillation (102°C, ca. 0.01 mm Hg). Yield: 95%. Calc. for $C_{19}H_{26}FeO_4$: C, 60.95; H, 7.00. Found: C, 61.6; H, 7.10%. I.r. (hexane): 2044 and 1985 br $cm^{-1}$. Complexes (27a,b) and (30a,b) were prepared in an identical manner. Yield of (27a,b):98%. Calc. for $C_{14}H_{18}FeO_4$: C, 54.9; H, 5.95. Found: C, 55.3; H, 5.95%. I.r. (hexane): 2044 and 1988 br $cm^{-1}$. Yield of (30a,b): 93%. Calc. for $C_{20}H_{28}FeO_5$: C, 59.4; H, 7.00. Found: C, 59.35; H, 6.90%. I.r. (hexane): 2042 and 1983 br $cm^{-1}$.

(b) Separation of complexes (28a,b) and (30a,b)

The diastereoisomeric pair (28a,b) was separated by repeated chromatography (3 times) on silica gel preparative plates using light petroleum/ethyl acetate (95:5) as eluant. A complete separation (as judged by $^{13}C$ n.m.r. spectroscopy) in a total yield of 43% was achieved. Complexes listed in Table 2 as (28a) and (28b) were recovered from the lower and upper bands respectively. The diastereoisomers (30a,b) were separated more readily than (28a,b) by chromatography on silica gel preparative plates in a total yield of 75% using light petroleum/diethyl ether (90:10) as eluant. The compounds listed as (30a) and (30b) in Table 1 were recovered from the lower and upper bands respectively.

(c) Regeneration of [tricarbonyl($\eta^5$-2methoxycyclohexadienyl)-iron][hexafluorophosphate] (3a,b) from separated diastereoisomers (30a,b)

Enantiomerically pure dienyl salt (3a,b) was regenerated by dissolving the separated diastereoisomers (30a,b)(ca. 600 mg of each) in diethyl ether (25 $cm^3$) at 0°C, followed by the addition to a small excess of $HPF_6$ (75% aqueous). The dienyl salt precipitated immediately and was collected by filtration, washed with diethyl ether, and reprecipitated from acetone-diethyl ether. Yield: 80%. The separated enantiomeric pair (3a,b) exhibited equal but opposite rotations: (R)-(-)-isomer (generated from 30a) $[\alpha]_D^{20°}$ -116° (c=5.3, MeCN); (S)-(+)-isomer (generated from 30b) $[\alpha]_D^{20°}$ +118 (C=5.6;MeCN).

(d) Preparation of [tricarbonyl(5-exo-Neomenthyldiphenylphosphinecyclohexa-1,3-diene)iron][tetrafluoroborate] (32a,b)

To a stirred suspension of [tricarbonyl($\eta^5$-cyclohexadienyl)iron]-[tetrafluoroborate] (4) (2.5 g, 8.2 mmol) in $CH_2Cl_2$ (30 $cm^3$) was added (+)-$PPh_2(C_{10}H_{19})$ (2.9 g, 9.0 mmol). Immediate dissolution occurred to give a yellow solution which was stirred for 30 mins. The yellow gum, obtained on the removal of the solvent under reduced pressure, solidified on standing in diethyl ether (100 $cm^3$) for 1 hr at 0°C. The pale yellow solid (5.0 g) was filtered off, washed repeatedly with diethyl ether, and dried under vacuum. Yield: 97%. Anal. Calc. for $C_{31}H_{36}BF_4FeO_3P$: C, 59.05; H, 5.75. Found: C, 59.0; H, 6.05%. I.r. ($CH_2Cl_2$): 2053 and 1993br $cm^{-1}$.

Diastereoisomers (31a,b), (33a,b) and (35a,b) were prepared in an identical manner. Yield of (31a,b): 63%. Calc. for $C_{19}H_{22}BF_4FeO_3P$: C, 48.35; H, 4.70. Found: C, 48.05; H, 4.70%. I.r. ($CH_2Cl_2$): 2054 and 1992br $cm^{-1}$. Yield of (33a,b): 86%. Calc. for $C_{26}H_{28}BF_4FeO_3P$: C, 55.55; H, 5.05. Found: C, 55.65; H, 4.85%. I.r. ($CH_2Cl_2$): 2052 and 1994br $cm^{-1}$. Yield of (35a,b): 98%. Calc. for $C_{32}H_{38}BF_4FeO_4P$: C, 58.2; H, 5.80. Found: C, 58.21; H, 6.05%. I.r. ($CH_2Cl_2$): 2052 and 1995br $cm^{-1}$.

(e) Separation of diastereoisomers (32a,b)

The mixture of (32a,b) (9.0 g) was dissolved in $CH_2Cl_2$ (75 $cm^3$) and, after filtration, diethyl ether (30 $cm^3$) was added dropwise with stirring until precipitation began to occur. More $CH_2Cl_2$ (20 $cm^3$) was added to redissolve the precipitate, and the solution was cooled for 1 day at -30°C. Filtration yielded 2.89 g of the phosphonium salt showing an 8:1 enrichment in one diastereoisomer. Isolation of further fractions, followed by repeated crystallization, gave a total yield of 3.17 g (70%) of the less soluble diastereoisomer (32a) shown to be pure by $^{31}P$ n.m.r. spectroscopy. Later fractions gave a smaller yield, 1.83 g (41%) of the more soluble diastereoisomer (32b) of ca. 90% purity as judged by $^{31}P$ n.m.r. spectroscopy.

(f) Preparation of tricarbonyl(5-exo-Nα dimethylbenzylaminecyclohexa-1,3-diene)iron (39a,b)

To a stirred suspension of compound (4) (1.73 g, 5.66 mmol) in $CH_2Cl_2$ (40 $cm^3$) was added (-)NH(Me)[CH(Me)Ph] (0.804 g, 5.94 mmol). After stirring for 10 mins at room temperature, a clear yellow solution was formed. A small excess of $NEtPr^i{}_2$ (0.842 g, 6.51 mmol) was added and the solution was stirred for 30 mins. After the removal of the solvent under reduced pressure, the residue was extracted with light petroleum (100 $cm^3$) to give a pale yellow solid (1.96 g) which was dried under vacuum. Yield: 98%. Calc. for $C_{18}H_{19}FeNO_3$: C, 61.2; H, 5.45; N, 3.95. Found: C, 61.3; H, 5.60; N, 3.70. I.r. (hexane): 2042 and 1984br $cm^{-1}$. Complexes (40a,b) were prepared in an identical fashion and isolated as a yellow oil. Yield: 98%. Calc. for $C_{19}H_{21}FeNO_4$: C, 59.55; H, 5.55; N, 3.65. Found: C, 59.5; H, 5.85; N, 3.50. I.r. (hexane): 2040 and 1983br $cm^{-1}$.

(g) Separation of diastereoisomers (39a,b)

The mixture of isomers (39a,b) (2.3 g) was dissolved in light petroleum (40 $cm^3$) and kept at 4°C overnight. Filtration yielded 0.47 g of pure diastereoisomer (39a), and further fractions eventually yielded a total of 0.74 g (64% yield) of pure (39a). Later fractions gave 1.08 g (94% yield) of the more soluble isomer (39b) of ca. 80% purity as judged by $^{13}C$ n.m.r. spectroscopy.

Attempted separation of diastereoisomers (39a,b) by chromatography on silica gel plates using diethyl ether as eluant yielded only (17) as the sole product recovered from the single band which developed. Chromatography of (40a,b) gave the alcohol (42) and a small amount of the dimeric complex (43a,b).

(h) Preparation of tricarbonyl(5α-hydroxy-2-methoxycyclohexadiene)-iron (42) and the dimeric complex (43a,b)

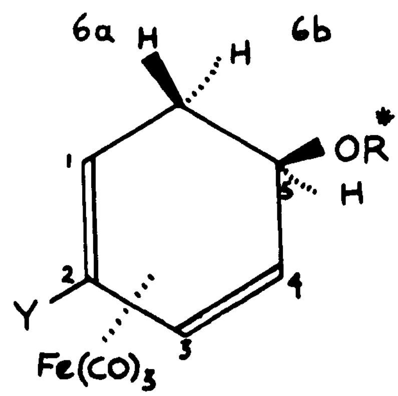
To a stirred solution of 2.58 g (7.67 mmol) of complex (3) dissolved in water (40 $cm^3$), was added an excess of $NaHCO_3$ (3.0 g). After the elution of $CO_2$ had ceased, the solution was extracted with diethyl ether, to give 2.0 g of yellow crystals in 98% yield. Sublimation of the crude reaction material (55°-62°C, ca. 0.03 mm Hg) resulted in the decomposition of the dimer (43a,b) to give pure (42).

Calc. for $C_{10}H_{10}FeO_5$: C, 45.14; H, 3.80. Found: C, 45.42; H, 3.83%. I.r. (hexane) 2042, 1988br $cm^{-1}$.

Chromatography of the crude reaction mixture on Grade II alumina using diethyl ether as the eluant gave the dimer (43a,b) as the initial less polar band, which was crystallized from light petroleum. (Chromatography resulted in the partial conversion of (42) to the dimeric complex). Calc. for $C_{20}H_{18}Fe_2O_9$: C, 46.72; H, 3.54. Found: C, 46.75; H, 3.53%; $M^+$, 514. I.r. (hexane) 2042, 1988br $cm^{-1}$.

TABLE 3 n.m.r. Spectra of Complexes (27) to (30)

Braces indicate resonances due to diastereoisomeric pairs




| COMPLEX | $^{13}$C ASSIGNMENT | | $^{1}$H ASSIGNMENT | |
|---|---|---|---|---|
| (29) | 2,3 | 87.3 | 2,3 | 5.48 (M) |
| R* = Me | | 84.9 | 5 | 3.81 (M) |
| Y = H | 1,4 | 56.3 | OMe | 3.18 (S) |
| | | 55.7 | 4 | 3.06 (M) |
| | 5 | 75.9 | 1 | 2.89 (M) |
| | 6 | 30.4 | 6b | 2.25 (M) |
| | OMe | 59.3 | 6a | 1.46 (M) |

TABLE 3 (continued)

| COMPLEX | $^{13}$C ASSIGNMENT | | $^{1}$H ASSIGNMENT | |
|---|---|---|---|---|
| (27a,b) | 2,3 | 87.2 | 2,3 | 5.47 (M) |
| R* = $CH_2CH(Me)Et$ | | 85.1 | 5 | 3.88 (M) |
| Y = H | 1,4 | 55.9 | $OCH_2$,CH,4 | 3.05 (M) |
| | | 55.8 | 1 | 2.85 (M) |
| | | 60.2 | 6b | 2.19 (M) |
| | 5 | 76.9 | 6a,Me,Et | 0.85-1.50 |
| | 6 | 30.9 | | |
| | $OCH_2$ | 74.4 | | |
| | CH | 35.2 | | |
| | Et | 26.2,11.2 | | |
| | Me | 16.6 | | |
| (28a) | | | | |
| R* = $C_{10}H_{19}$(menthyl) | 2,3 | 87.1 | (complexes 28a,b) 2,3 | 5.47 (M) |
| Y=H | | 84.9 | 5 | 3.97 (M) |
| | 1,4 | 62.2 | 4 | 3.02 (M) |
| | | 55.6 | 1 | 2.87 (M) |
| | 5 | 75.7 | $OC_{10}H_{19}$,6a,b | 0.62-2.87 |
| | 6 | 31.7 | | |

TABLE 3 (continued)

| COMPLEX | | $^{13}C$ ASSIGNMENT | | | | 1H ASSIGNMENT |
|---|---|---|---|---|---|---|
| (28a) | | | | | | |
| | $OC_{10}H_{19}$ | 16.0 | 31.3 | | | |
| | | 21.3 | 34.4[b] | | | |
| | | 22.4[b] | 42.4 | | | |
| | | 23.1 | 48.4 | | | |
| | | 25.1 | 78.9 | | | |
| (28b) | 2,3 | 87.3 | | | | |
| | | 84.7 | | | | |
| | 1,4 | 60.9 | | | | |
| | | 56.1 | | | | |
| | 5 | 75.1 | | | | |
| | 6 | 32.8 | | | | |
| | $OC_{10}H_{19}$ | 16.3 | 31.7 | | | |
| | | 21.2 | 34.4[b] | | | |
| | | 22.4[b] | 41.6 | | | |
| | | 23.3 | 48.2 | | | |
| | | 25.4 | 78.1 | | | |
| (30a) | 2,3 | 66.3 | | (com- | 3 | 5.13 (M) |
| R* = $C_{10}H_{19}$(menthyl) | | a | | plexes 30a,b) | 5 | 3.81 (M) |
| Y = OMe | 1,4 | 51.6 | | | OMe | 3.63 (S) } |
| | | 49.1 | | | | 3.62 (S) } |
| | 5 | 75.8 | | 1,4,6a,b,$OC_{10}H_{19}$ | | 0.61-3.11 |
| | 6 | 34.5 | | | | |
| | OMe | 54.3[b] | | | | |
| | $OC_{10}H_{19}$ | 16.1 | 31.8 | | | |
| | | 21.3 | 32.7 | | | |
| | | 22.4[b] | 42.5 | | | |
| | | 23.2 | 48.4 | | | |
| | | 25.2 | 79.1 | | | |

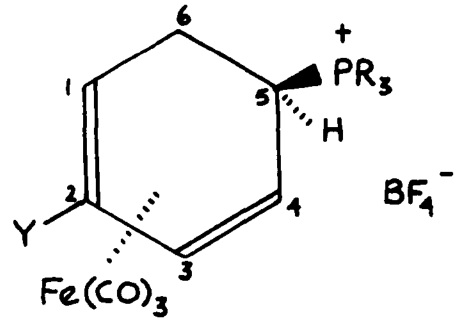
TABLE 3 (continued)

| COMPLEX | $^{13}C$ ASSIGNMENT | | | $^{1}H$ ASSIGNMENT |
|---|---|---|---|---|
| (30b) | 2,3 | 66.2 | | |
| | | a | | |
| | 1,4 | 50.3 | | |
| | | 49.3 | | |
| | 5 | 75.2 | | |
| | 6 | 34.0 | | |
| | OMe | 54.3[b] | | |
| | $OC_{10}H_{19}$ | 16.3 | 31.7 | |
| | | 21.2 | 34.5 | |
| | | 22.4[b] | 41.6 | |
| | | 23.3 | 48.3 | |
| | | 25.4 | 78.3 | |

a quaternary carbon not detected

b resonance common to the two diastereoisomers

TABLE 4 N.m.r. Spectra of Complexes (31) to (35)



| COMPLEX | $^{13}$C ASSIGNMENT | (Jp-c) Hz | $^{31}$P$^{b}$ |
|---|---|---|---|
| (34) | 2,3 | 84.6 (4.7) | 27.6 |
| $PR_3 = PMe_2Ph$ | | 86.0 | |
| Y = H | 1,4 | 58.9 (8.6) | |
| | | 51.7 (8.5) | |
| | 5 | 33.0 (40.3) | |
| | 6 | 25.4 (3.7) | |
| | Me | 6.2 (12.2) | |
| | | 4.3 (12.2) | |
| | Ph | 127-134 | |
| (31a,b) | 2,3 | 84.8 | 31.7 |
| $PR_3$ = PMePrPh | | 86.2 | 31.2 |
| Y = H | 1,4 | 59.0 (6.8) | |
| | | 58.9 (6.8) | |
| | | 51.8 (8.8) | |
| | 5 | 32.7 (39.1) | |
| | | 33.1 (39.1) | |
| | 6 | 26.1 (1.9) | |
| | | 25.4 (1.9) | |
| | Me | 3.2 (10.7) | |
| | | 1.2 (10.7) | |
| | Pr | 14.8-22.9 | |
| | Ph | 129-134 | |

TABLE 4 (continued)

| COMPLEX | $^{13}C$ ASSIGNMENT | | $(J_{P-C})$ Hz | $^{31}P$ |
|---|---|---|---|---|
| (32a,b) | 2,3 | 84.2 | | 34.2 |
| $PR_3=PPh_2(C_{10}H_{19})$ | | 85.7 | (3.8) | 32.4 |
| Y=H | | 85.6 | (3.8) | |
| | 1,4 | 58.0 | (7.8) | |
| | | 51.0 | (8.8) | |
| | | 50.7 | (8.8) | |
| | 6 | 26.2 | (2.9) | |
| | | 25.8 | (2.9) | |
| | $C_{10}H_{19}$,5 | 20-43.5 | | |
| | Ph | 128-134 | | |
| (32a) | | | | |
| Pure diastereoisomer | 2,3 | 84.2 | | 32.4 |
| isolated by fractional | | 85.6 | (3.8) | |
| crystallization | 1,4 | 58.0 | (7.8) | |
| | | 50.7 | (8.8) | |
| | 6 | 25.8 | (2.9) | |
| | $C_{10}H_{19}$,5 | 20-43.5 | | |
| | Ph | 128-134 | | |
| (33a,b) | 2,3 | 85.3 | | 30.8 |
| $PR_3=PPh_2(C_5H_{11})$ | | 85.1 | | 30.6 |
| Y=H | 1,4 | 58.7 | (7.8) | |
| | | 51.2 | (7.8) | |
| | 5 | 32.9 | (36.2) | |
| | 6 | 26.7 | (3.9) | |
| | $C_5H_{11}$ | 10.7-31.1 | | |
| | Ph | 128-134 | | |
| (35a,b) | 2,3 | 66.4 | (2.4) | 33.7 |
| $PR_3=PPh_2(C_{10}H_{19})$ | | a | | 31.7 |
| Y=OMe | 1,4 | 50.9 | | |
| | | 40.9 | (9.7) | |
| | | 40.8 | (9.7) | |

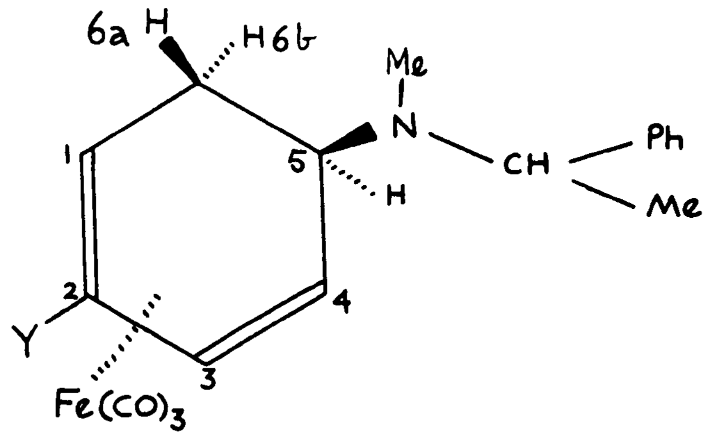
TABLE 4 (continued)

| COMPLEX | $^{13}C$ ASSIGNMENT | | (Jp-c)Hz | $^{31}P$ |
|---|---|---|---|---|
| (35a,b)(cont.) | 6 | 27.4 | (4.8) | |
| | OMe | 54.7 | | |
| | $C_{10}H_{19}$,5 | 18.9-43.8 | | |
| | Ph | 129-235 | | |

a quaternary carbon not detected

b $^{31}P$ p.p.m. relative to 85% $H_3PO_4$

TABLE 5 N.m.r. Spectra of Complexes (39a,b) to (43a,b)



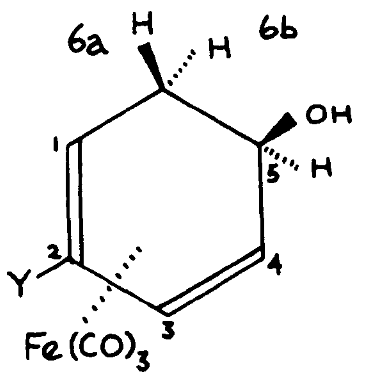

| COMPLEX | $^{13}$C ASSIGNMENT | | $^{1}$H ASSIGNMENT | | (Jp-c)Hz |
|---|---|---|---|---|---|
| (39a,b) | 2,3 | 86.3 | 2,3 | 5.40 (M) | |
| Y = H | | 86.1 | 5,CHMe | 3.51 (M) | |
| | | 84.7 | 4 | 2.90 (M) | |
| | | 84.5 | 1 | 2.75 (M) | |
| | 1,4 | 60.1 | NMe | 1.97 (S) | |
| | | 59.6 | 6b | 1.84 (M) | |
| | | 58.9 | 6a | 1.40 (M) | |
| | 5 | 62.2 | CHMe | 1.35 (d) | 6.8 |
| | | 62.6 | Ph | 7.24 (M) | |
| | 6 | 25.2 | | | |
| | | 24.8 | | | |
| | CHMe | 57.6 | | | |
| | NMe | 32.6 | | | |
| | CHMe | 20.9 | | | |
| | | 20.4 | | | |
| | Ph | 126-128 | | | |

TABLE 5 (continued)

| COMPLEX | $^{13}$C ASSIGNMENT | | $^{1}$H ASSIGNMENT | | (Jp-c) Hz |
|---|---|---|---|---|---|
| (39a) | 2,3 | 86.1 | | | |
| Pure diastereoisomer | | 84.7 | | | |
| isolated by fractional | 1,4 | 60.1 | | | |
| crystallization | | 58.9 | | | |
| | 5 | 62.2 | | | |
| | 6 | 24.8 | | | |
| | CHMe | 57.6 | | | |
| | NMe | 32.6 | | | |
| | CHMe | 20.4 | | | |
| | Ph | 126-128 | | | |
| (39b) | 2,3 | 86.3 | | | |
| Separated diastereo- | | 84.5 | | | |
| isomer ca. 80% pure | 1,4 | 59.6 | | | |
| major resonances | | 58.9 | | | |
| given | 5 | 62.6 | | | |
| | 6 | 25.2 | | | |
| | CHMe | 57.6 | | | |
| | NMe | 32.6 | | | |
| | CHMe | 20.9 | | | |
| | Ph | 126-128 | | | |
| (40a,b) | 2,3 | 68.3 | 3 | 5.21 (M) | |
| Y = OMe | | 68.1 | OMe | 3.62 (S) | |
| | | a | 5,CHMe | 3.40 (M) | |
| | 1,4 | 50.7 | 1 | 3.16 (M) | |
| | | 48.9 | 4 | 2.34 (M) | |
| | | 48.5 | NMe | 1.99 (S) | |
| | 5 | 62.5 | | 1.94 (S) | |
| | | 62.1 | CHMe | 1.26 (d) | 6.6 |
| | 6 | 26.5 | | 1.30 (d) | 6.6 |
| | | 26.4 | 6a,b | 1.30-1.70 (M) | |
| | OMe | 54.3 | Ph | 7.24 (M) | |
| | CHMe | 58.7 | | | |

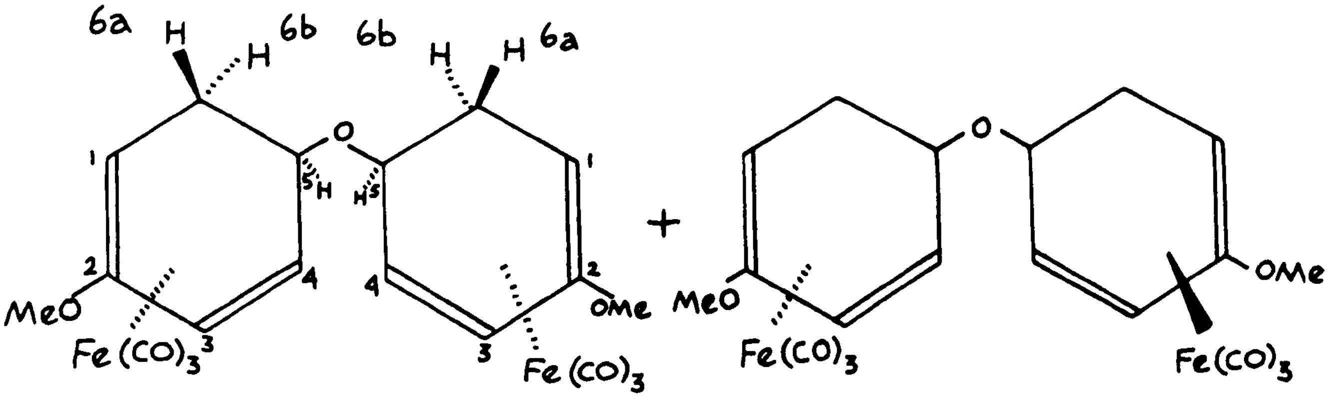
TABLE 5 (continued)

| COMPLEX | $^{13}C$ ASSIGNMENT | | $^{1}H$ ASSIGNMENT | | (Jp-c) Hz |
|---|---|---|---|---|---|
| (40 a,b) (cont) | NMe | 32.8 | | | |
| | CHMe | 20.7 | | | |
| | | 20.2 | | | |
| | Ph | 127-129 | | | |



| COMPLEX | $^{13}C$ ASSIGNMENT | | $^{1}H$ ASSIGNMENT | |
|---|---|---|---|---|
| (41) | 2,3 | 87.3 | 2,3 | 5.5 |
| Y = H | | 84.2 | 1,4 | 2.94 |
| | 1,4,5 | 69.3 | 5 | 4.34 |
| | | 63.1 | 6b | 2.34 |
| | | 55.5 | 6a | 1.40 |
| | 6 | 33.5 | OH | 1.57 |
| (42) | 2,3 | 69.3 | | |
| Y = OMe | | a | | |
| | 1,4 | 52.4 | | |
| | | 48.9 | | |
| | 5 | 65.4 | | |
| | 6 | 35.1 | | |
| | MeO | 54.4 | | |

TABLE 5 (continued)




| COMPLEX | $^{13}$C ASSIGNMENT | | $^{1}$H ASSIGNMENT | |
|---|---|---|---|---|
| (43a,b) | 2,3 | 66.2} 66.1} | 3 | 5.09 |
| | | a | 1,4 | 3.10 |
| | | | | 2.57 |
| | 1,4 | 50.2} 50.1} | 6b | 2.22 |
| | | | 6a | 1.57 |
| | | 48.9} 48.8} | MeO | 3.62 (S) |
| | 5 | 76.0} 75.5} | | |
| | 6 | 33.3} 32.7} | | |
| | MeO | 54.3 | | |

a quaternary carbon not detected

Braces indicate resonances due to diastereoisomeric pairs.

FIG I. $^{13}C$ N.M.R. SPECTRUM OF DIASTEREOISOMERS (28a,b)

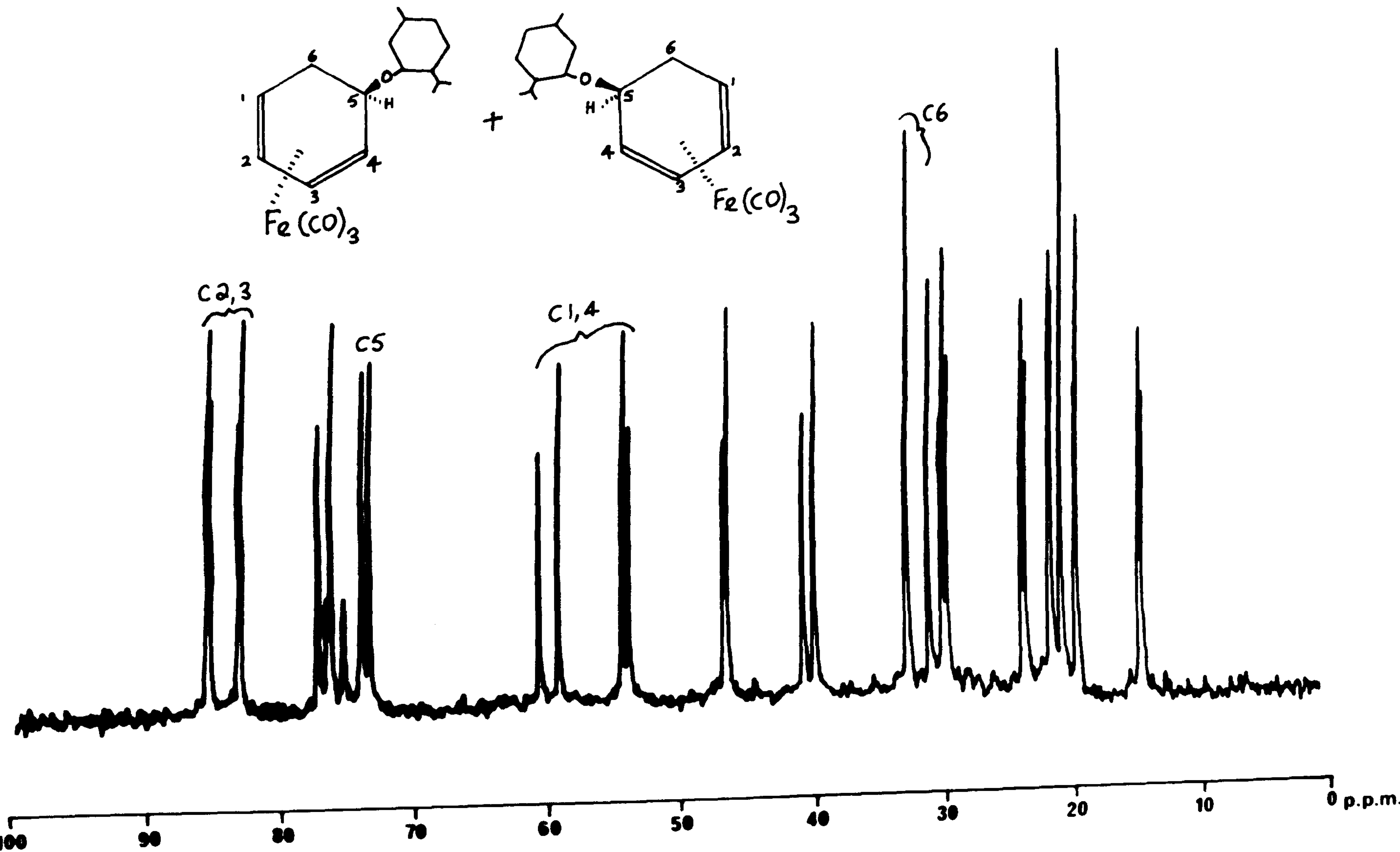
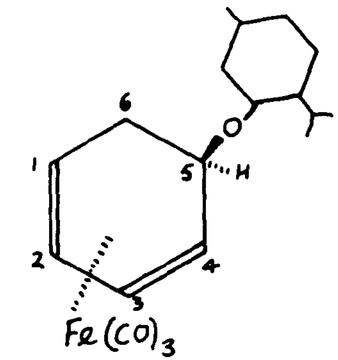


FIG. II $^{13}C$ NMR SPECTRUM OF SEPARATED DIASTEREOISOMER (28a)

(CONFIGURATION ARBITRARY)



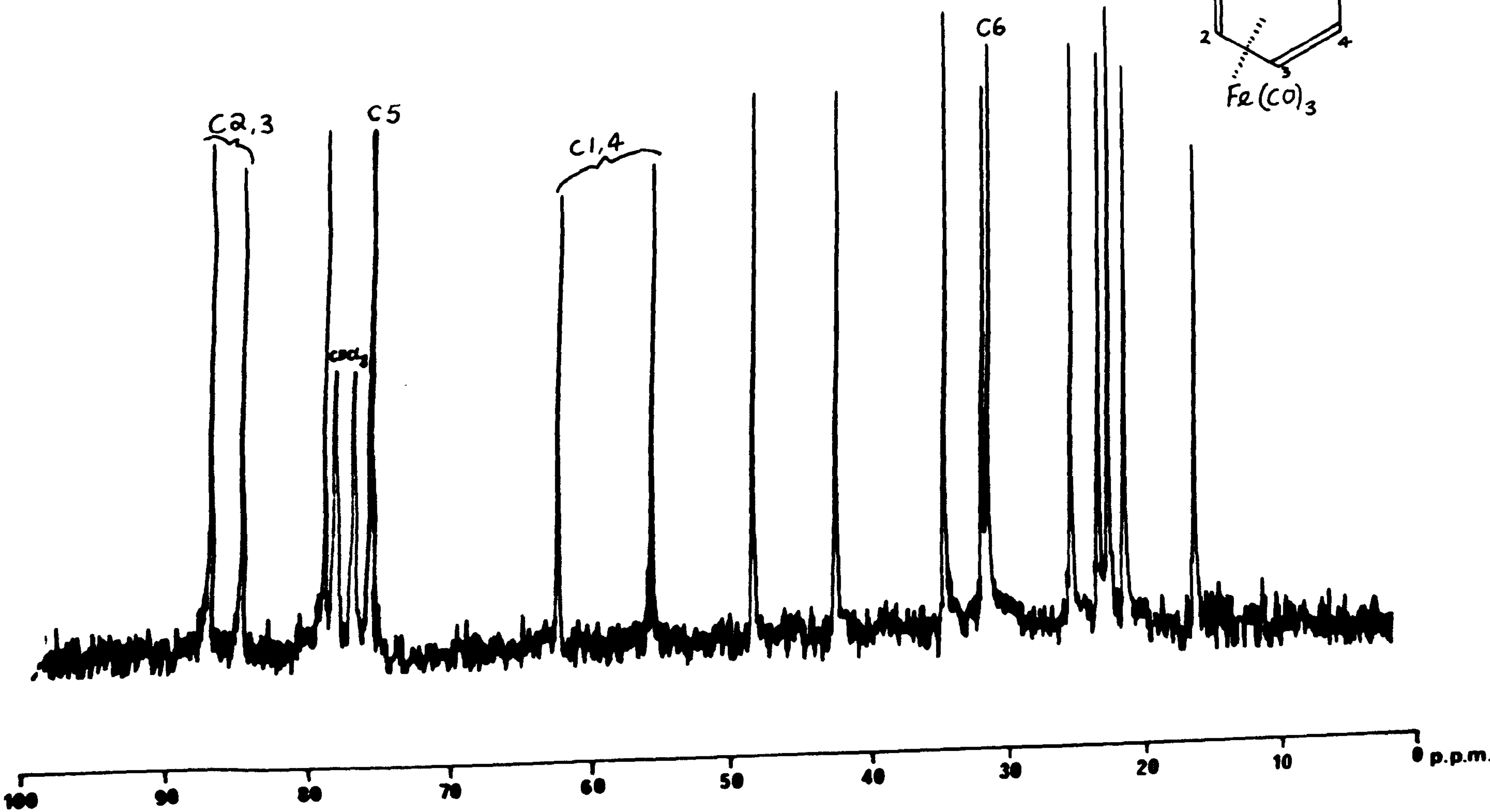
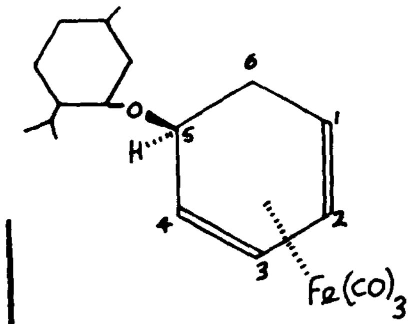



FIG III $^{13}$C NMR SPECTRUM OF SEPARATED DIASTEREOISOMER (28b)

(CONFIGURATION ARBITRARY)



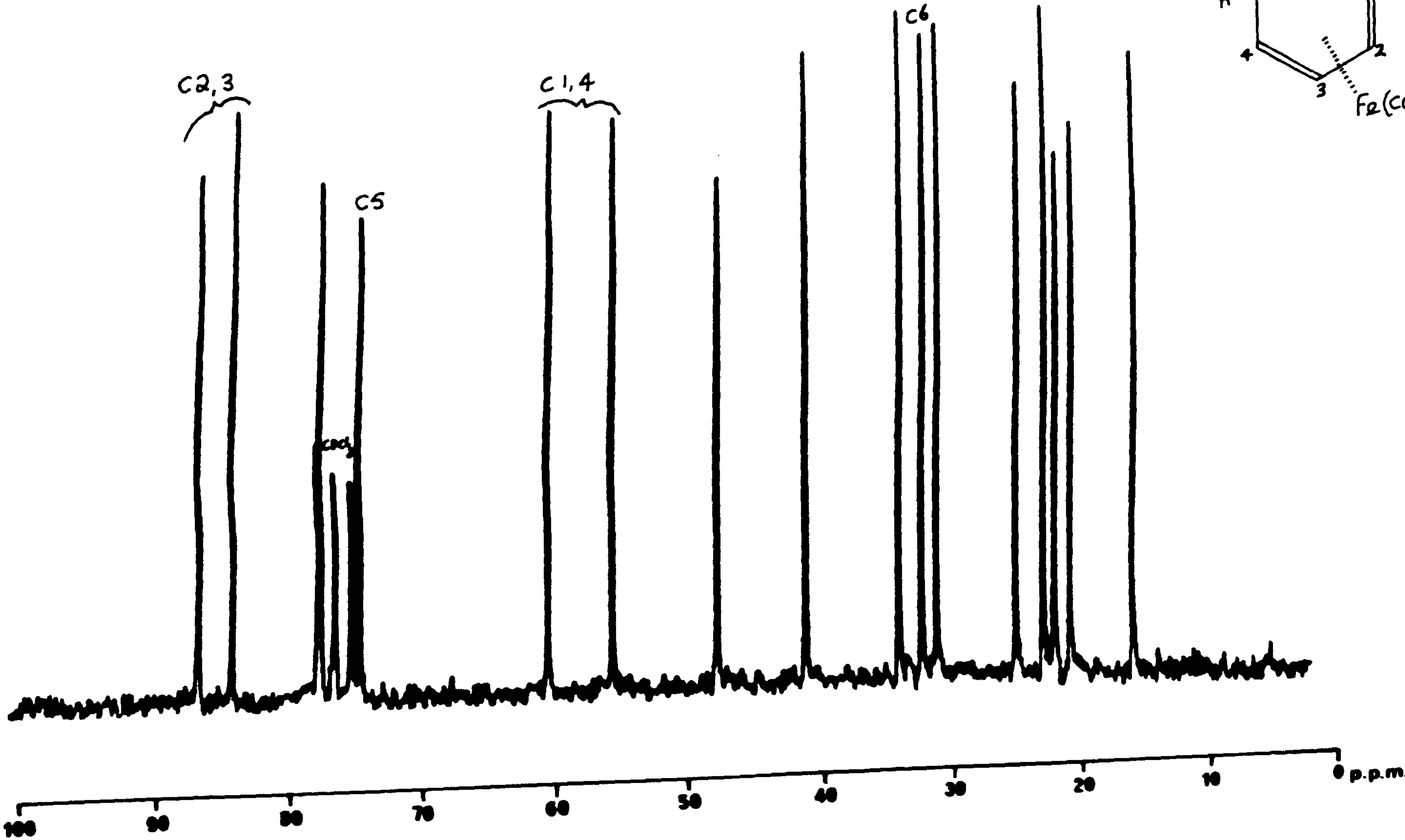



FIG IV $^{13}C$ NMR SPECTRUM OF DIASTEREOISOMERS (30a,b)

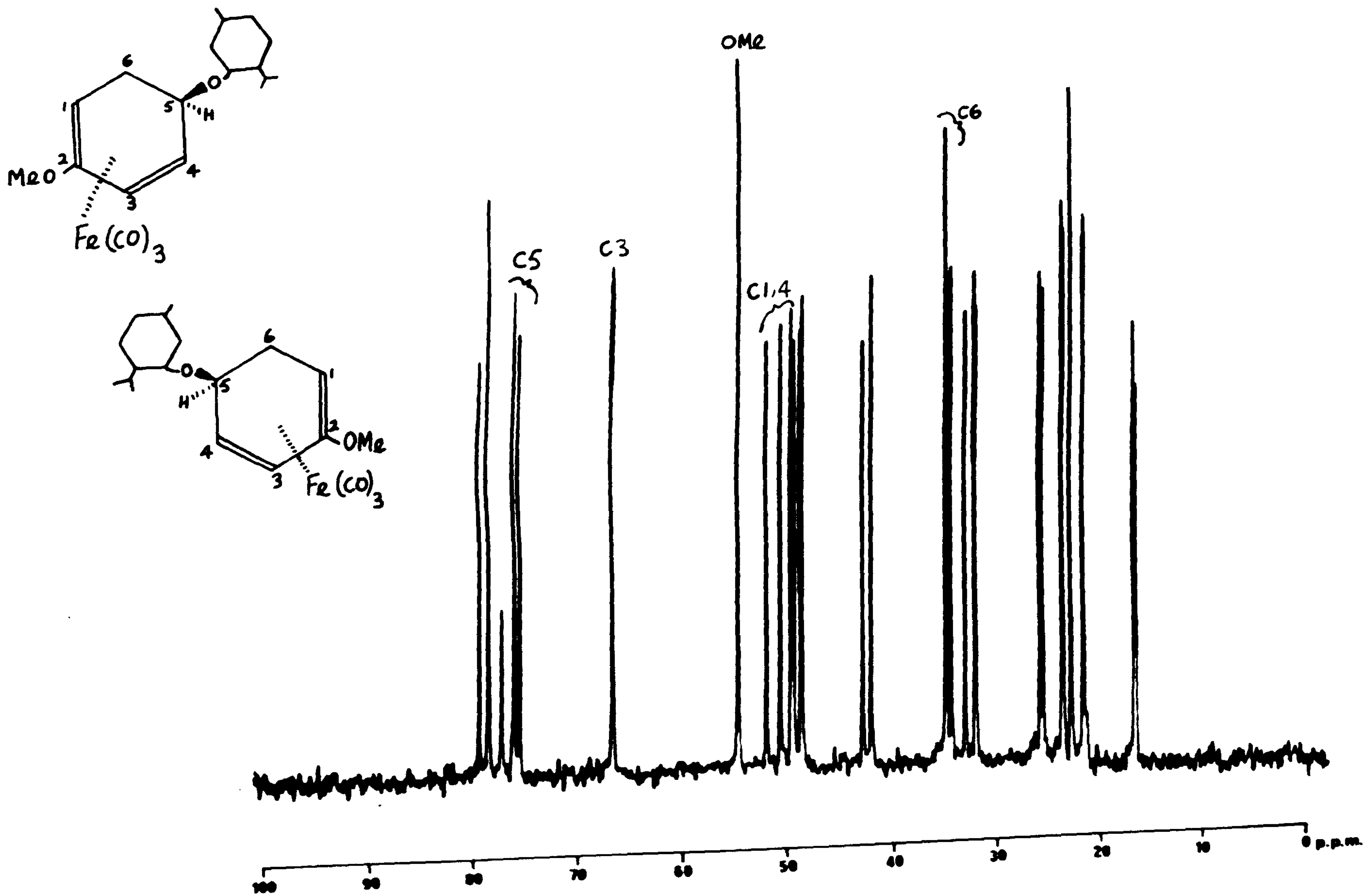


FIG V $^{13}C$ NMR SPECTRUM OF SEPARATED DIASTEREOISOMER (30a)

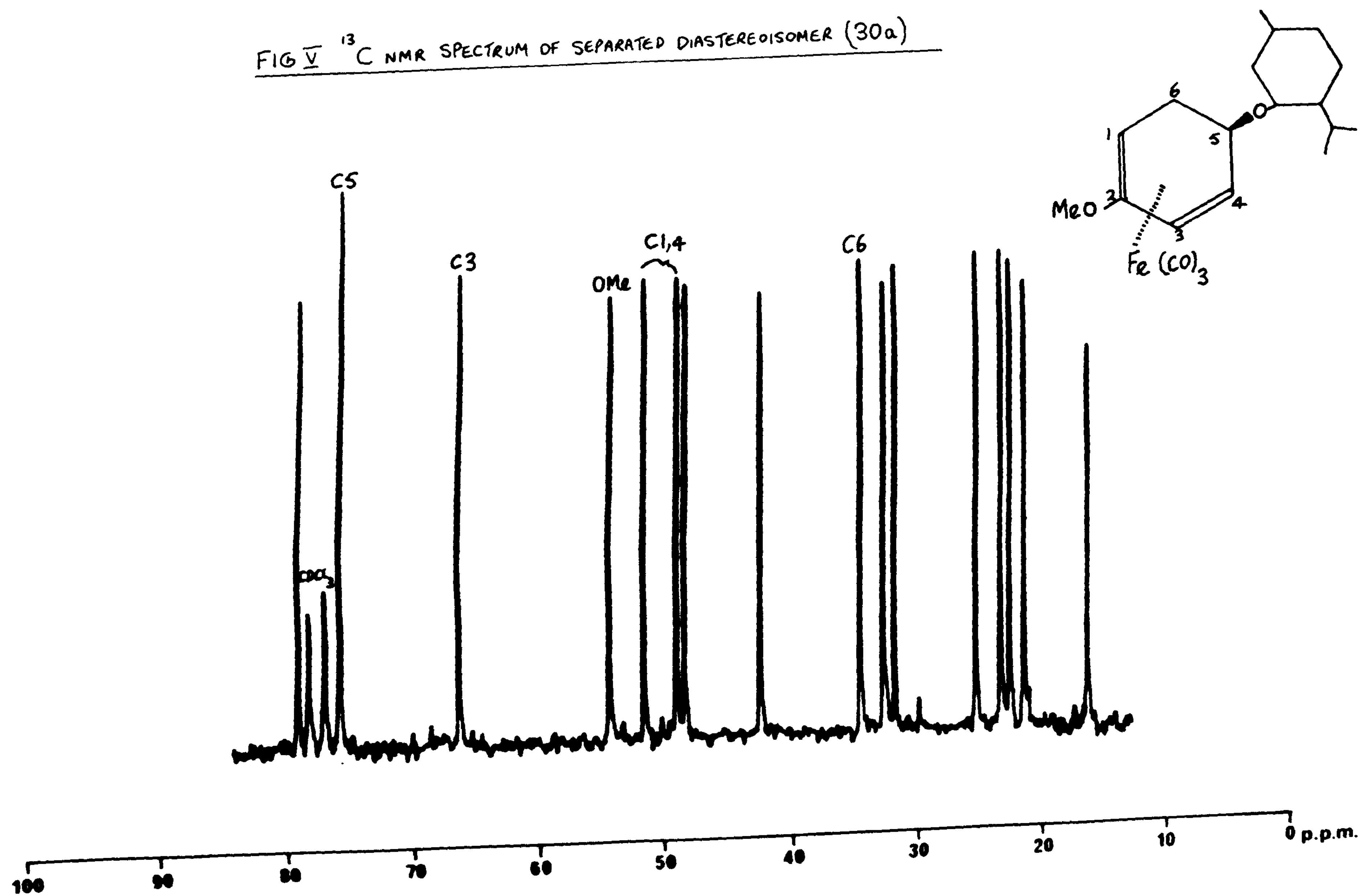
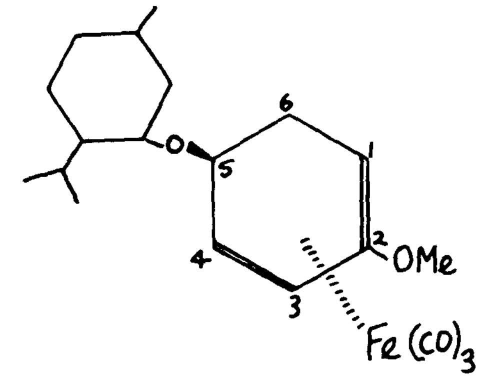


FIG. VI $^{13}C$ NMR SPECTRUM OF SEPARATED DIASTEREOISOMER (30b)



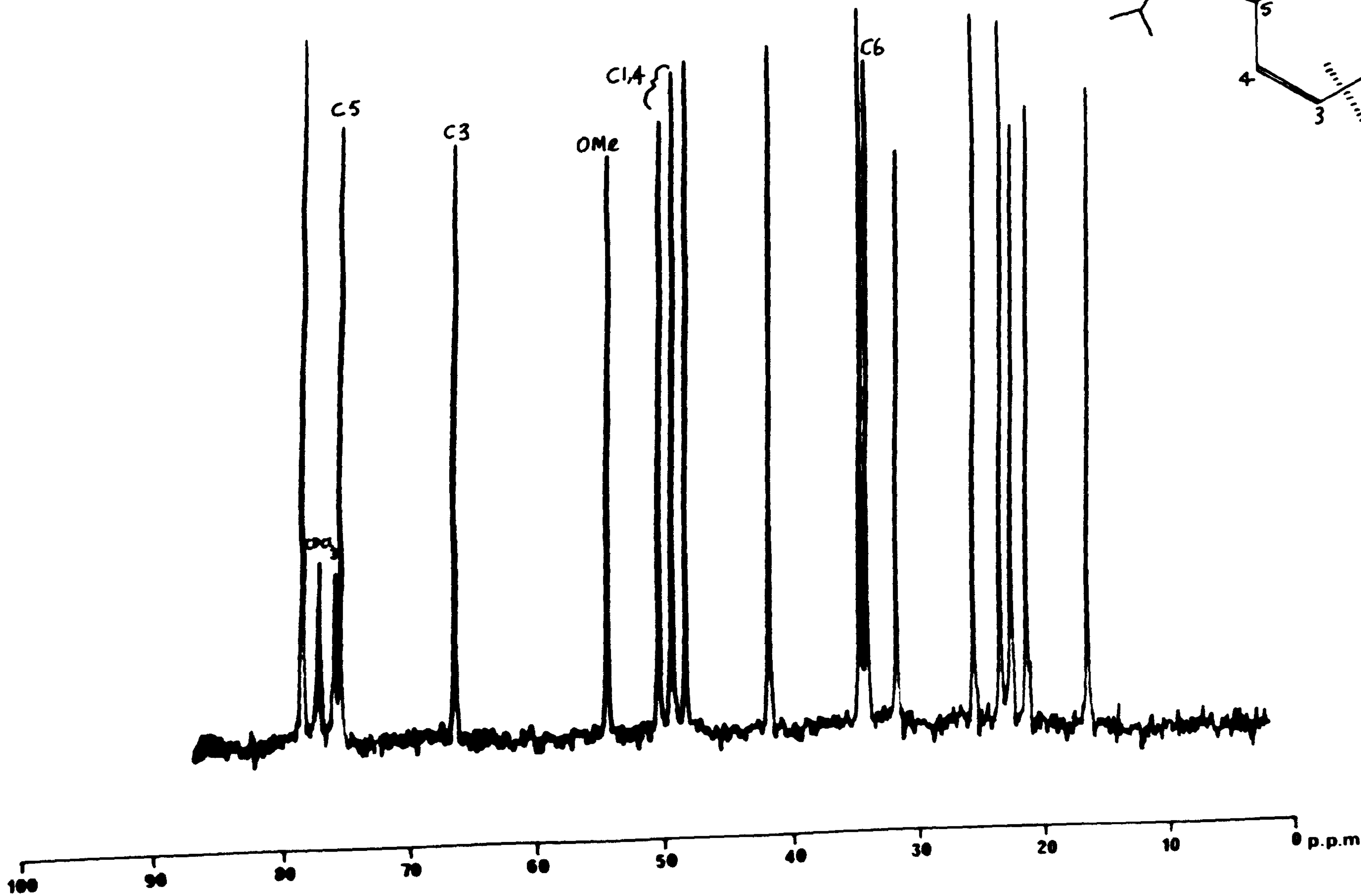



FIG XII $^{13}C$ NMR SPECTRUM OF DIASTEREOISOMERS (39a,b)

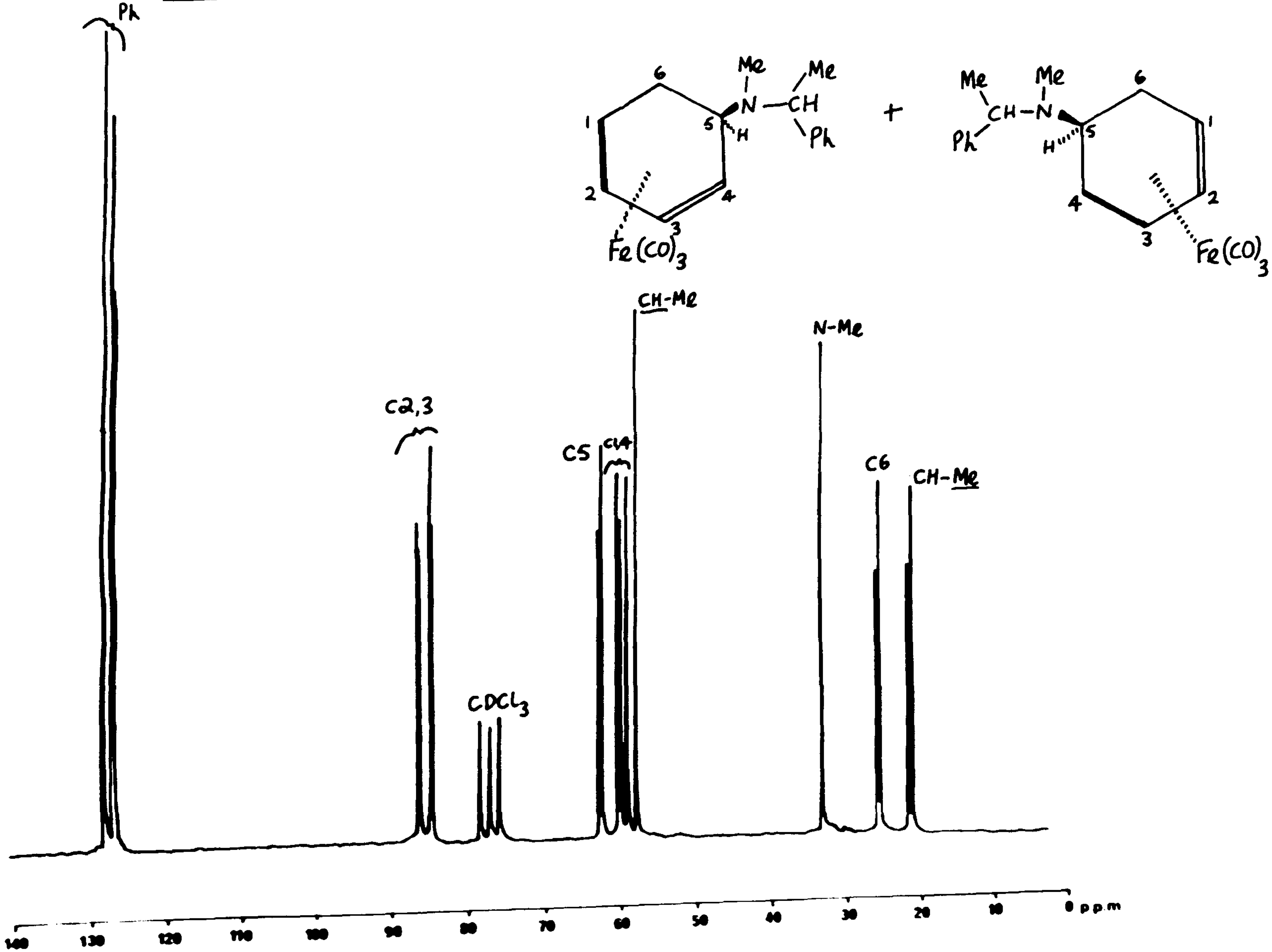


FIG. XIII $^{13}$C NMR SPECTRUM OF SEPARATED DIASTEREOISOMER (39a)

(CONFIGURATION ARBITRARY)

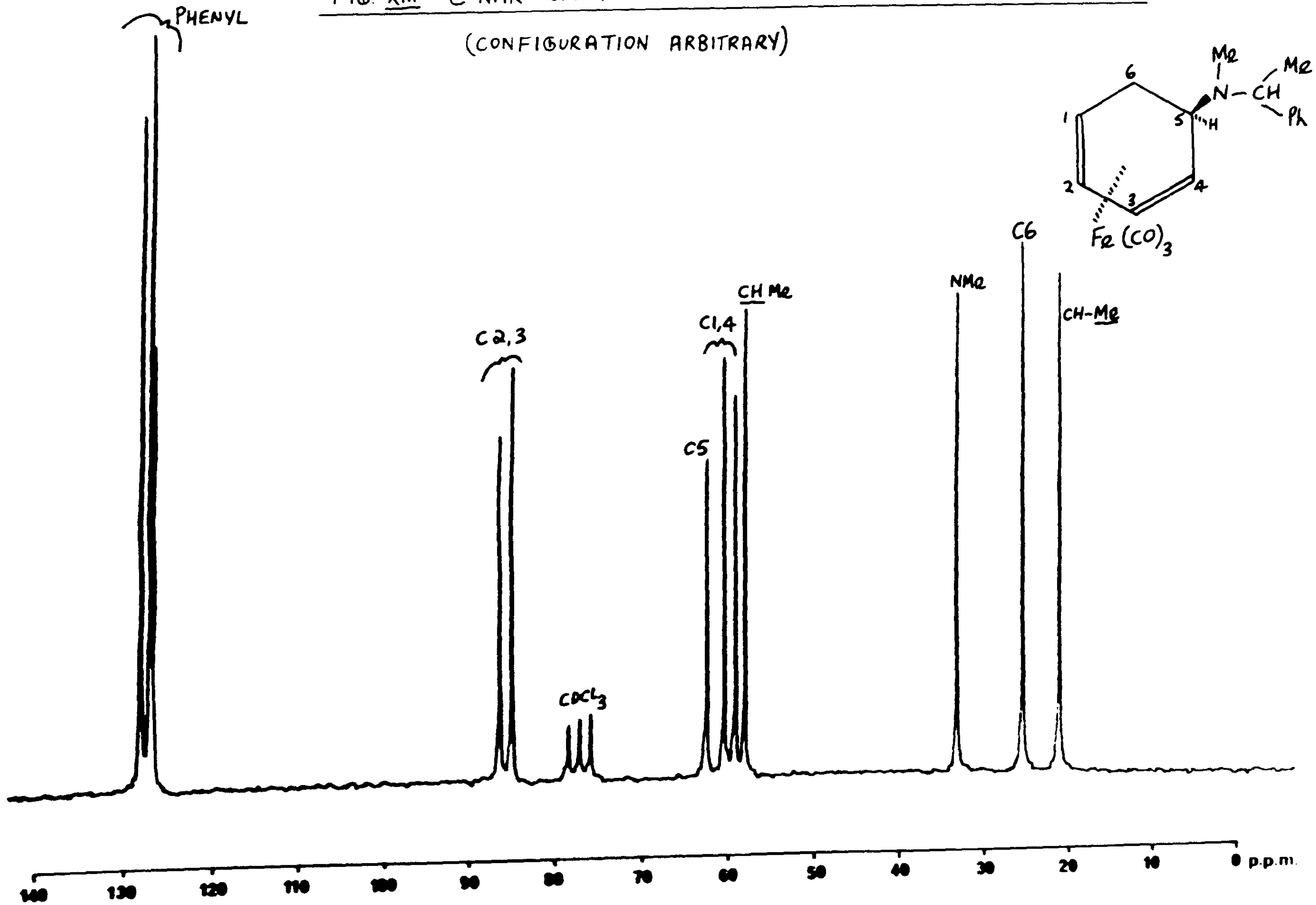


FIG XIV $^{13}C$ NMR SPECTRUM OF SEPARATED DIASTEREOISOMER (39b)

(CONFIGURATION ARBITRARY)

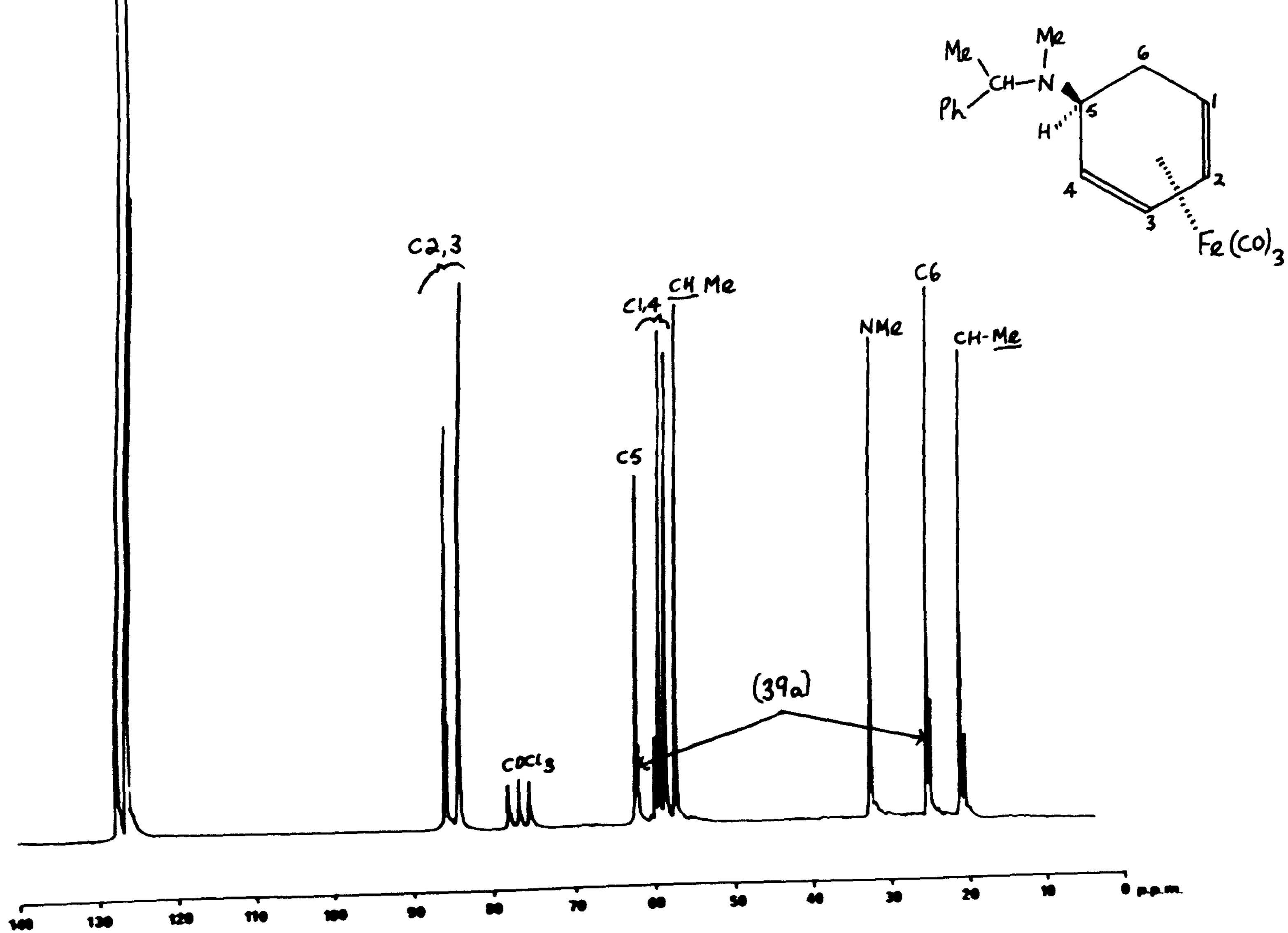
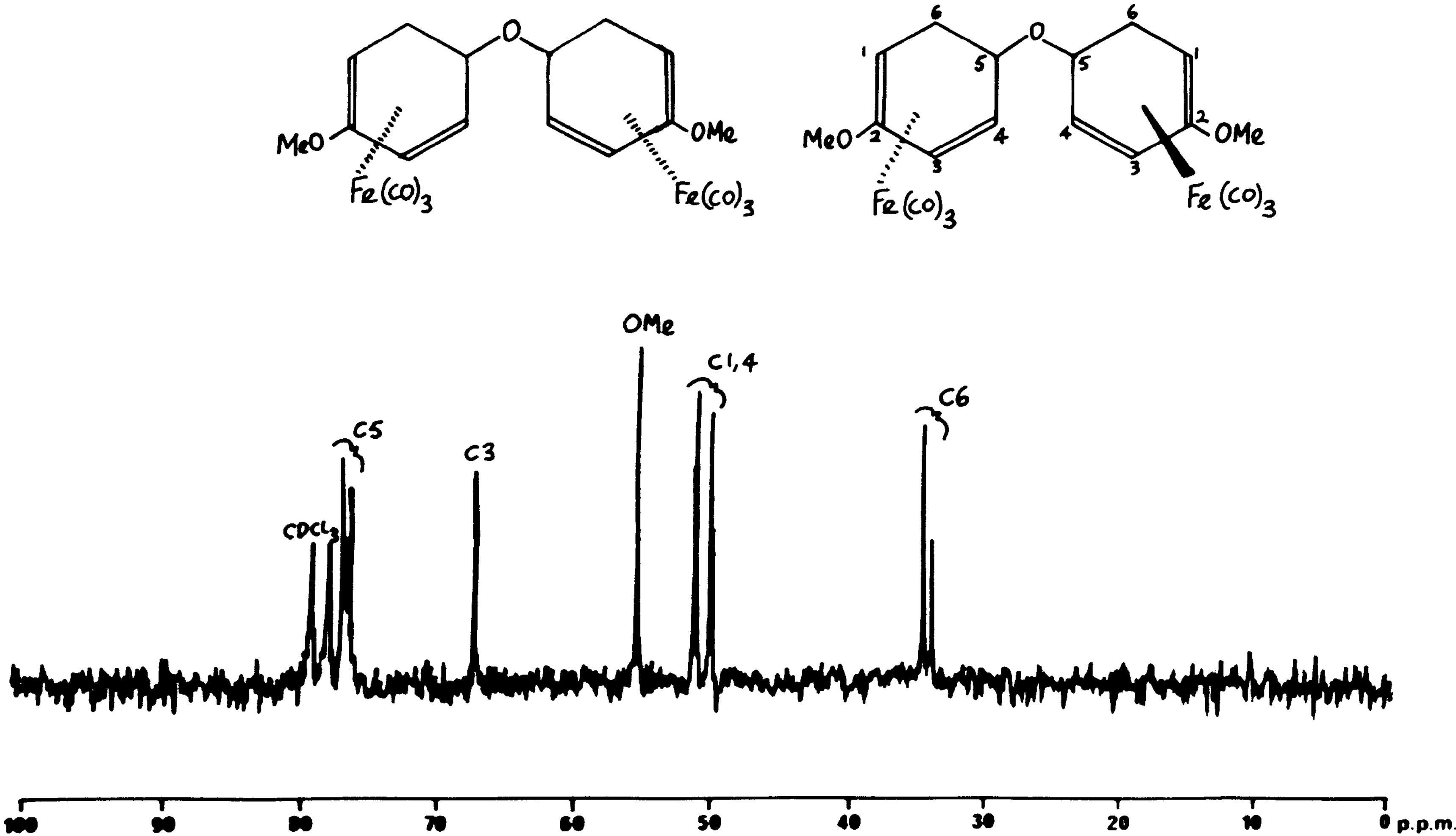


FIG. XVI $^{13}C$ NMR SPECTRUM OF COMPLEX (43a,b)



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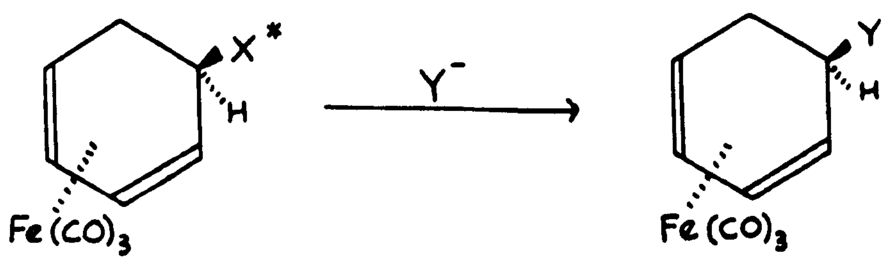
# CHAPTER 3

## REACTIONS OF ENANTIOMERICALLY PURE TRICARBONYL DIENE AND DIENYL IRON COMPLEXES

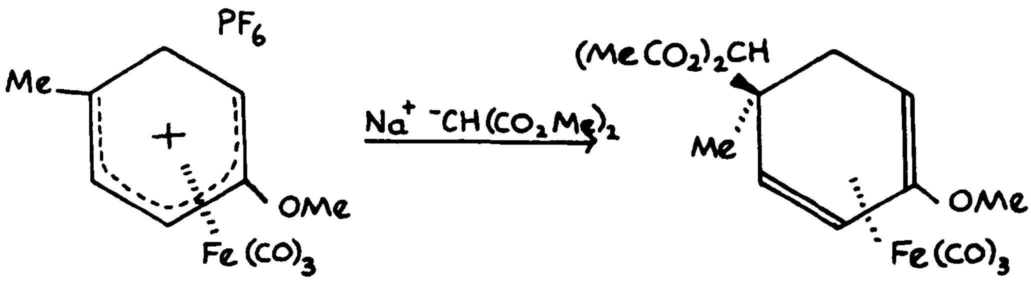
The work of Chapter 2 has described the separation of the enantiomers of $[(2MeO\text{-cyclohexadienyl})Fe(CO)_3]^+$ (1a,b) via the resolution of their menthoxy diastereoisomers, and the separation of the diastereoisomers of the unsubstituted derivatives (2) where X*=(-)-N(Me)CH(Me)Ph or (+)-$PPh_2$menthyl. This chapter describes the further elaboration of (1a,b) to enantiomerically pure samples of $[(2MeO\text{-}5Me\text{-}C_6H_5)Fe(CO)_3]^+$ (3a), together with attempts at the elimination of the resolving chiral reagent from (2), whilst retaining the configuration at the quaternary carbon.



(2)

### 3.1 The Preparation of Enantiomerically Pure $[(2\text{-}MeO\text{-}5\text{-}Me\text{-}C_6H_5)Fe(CO)_3]$-$[PF_6]$ (3a)

The recent synthetic work of Pearson[1] has shown that the $[(2\text{-}MeO\text{-}5\text{-}Me\text{-}C_6H_5)Fe(CO)_3]^+$ cation is a useful precursor in the synthesis of some advanced intermediates in natural product chemistry (Chapter 1.3). The para directing effect of the 2-methoxy substituent, results in nucleophilic addition to complex (3) occurring exclusively at the methylated terminus of the dienyl ring, to give the disubstituted derivative (4). Such derivatives are a useful means of ring connection, and have been used as precursors in approaches to the synthesis of trichothecenes, aspidosperma and spirocyclic compounds.

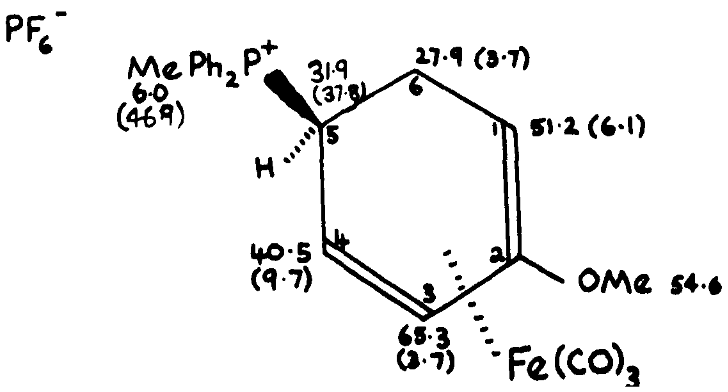



(3) (4)

Thus enantioselective natural product synthesis may be accomplished if enantiomerically pure samples of (3) are available. To date only the (-)-isomer has been isolated by fractional crystallization of an enantiomerically enriched sample, obtained by asymmetric induction in complexation.[2] (3) cannot be resolved by the methods described in Chapter 2, as deprotonation rather than addition occurs on the reaction with alkoxides or amines, and no stable products are observed on reaction with chiral phosphines (vide infra).

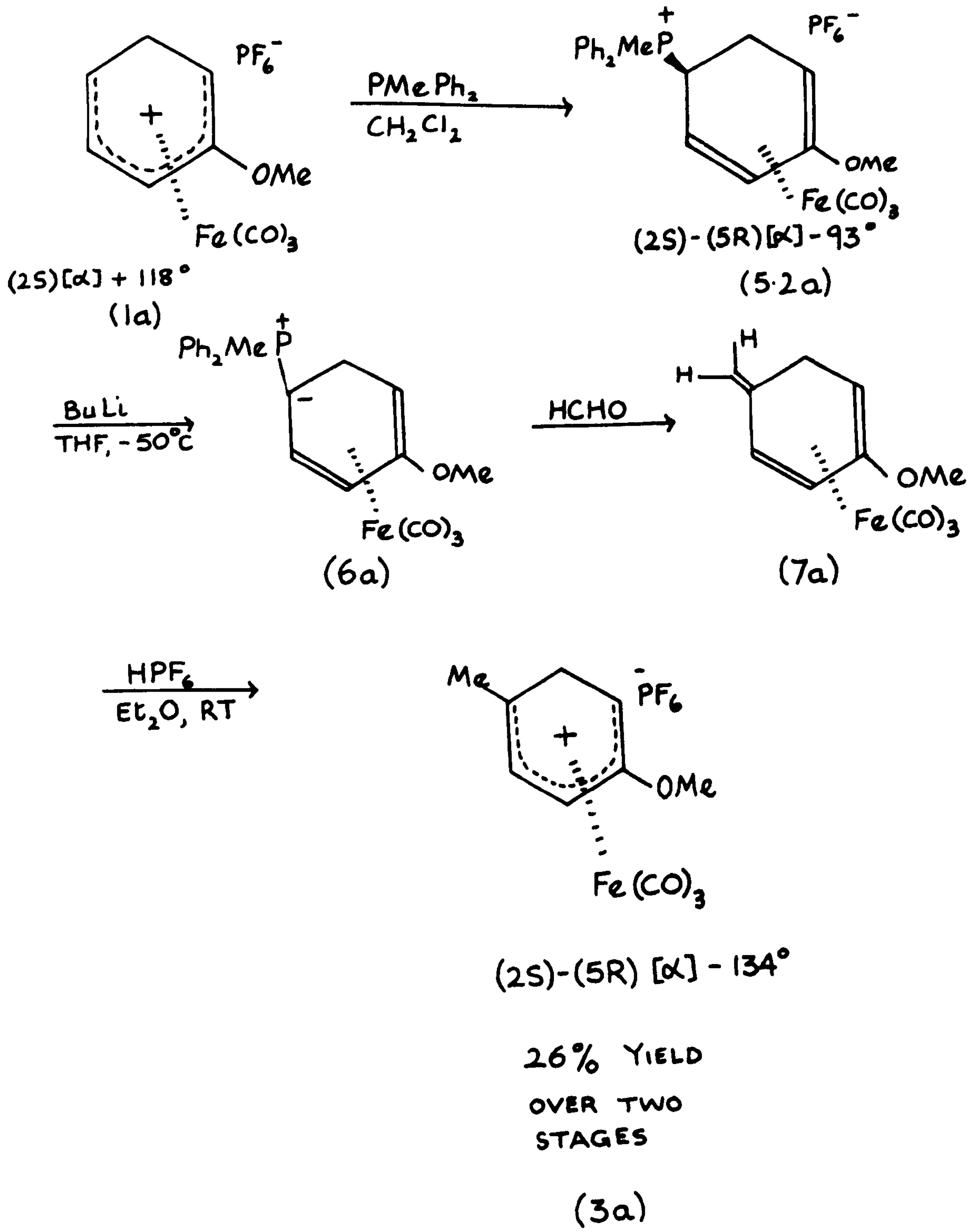
We wish to describe here the conversion of enantiomerically pure 2-methoxy cation (1a) into (3a) using the Wittig method recently described by Lewis et al.[3] The reaction of $[(2MeO-C_6H_6)Fe(CO)_3]$-$[PF_6]$ (1a) ((2S; [$\alpha$]+118°) with $PMePh_2$ (Scheme 1), gives a 97% yield of the phosphonium salt (5.2a)((2S)-(5R); [$\alpha$]-93°). Assignment of the $^{13}C$ n.m.r. spectrum of complex (5.2a) was made on the basis of comparison with $[(5\alpha-PMe_2Ph-C_6H_7)Fe(CO)_3][PF_6]$.[4]

$^{13}C$ n.m.r. Data of Complex (5.2a)
(JP-C)couplings in Hz given in brackets)



Carbon-4 was assigned on the basis of larger (JP-C) coupling compared with C-1. The assignment of C-5, C-6 and MeO were made with the aid of the off-resonance decoupled spectrum, the methoxy group being furthest downfield at 54.6 p.p.m. and appearing as a quartet; C-5 showing a large (JP-C) coupling of 37.8 Hz, was observed as a doublet at 31.9 p.p.m., whilst the methylene carbon (C-6) appeared as a triplet at 27.9 p.p.m.

Proton abstraction by treatment of (5.2a) with BuLi in THF at -50°C gives in situ the deep red phosphorus ylid (6a) (Scheme 1). Treatment with anhydrous formaldehyde yields the methylene cyclodexadiene complex (7a). Attempts at isolation of pure (7a) have been unsuccessful, as polymerization occurs and only traces of $Fe_3(CO)_{12}$ are isolated. (A satisfactory specific rotation value, and CHN analysis were unobtainable). However, complex (7a) was readily characterised on the basis of its $^{13}C$ n.m.r. data (figure 1), which was assigned by comparison with the completely stable phenyl derivative (8a) (Scheme II - vide infra). The i.r. spectrum (carbonyl stretching region) shows three bands at 2041, 1993 and 1982 $cm^{-1}$, consistent with the values obtained for (8a). Thus, once (7a) had been isolated, protonation was rapidly carried out using aqueous $HPF_6$ to give enantiomerically pure (3a) ((2S)-(5R); [$\alpha$] +134°) ($^{13}C$ spectrum at figure II).

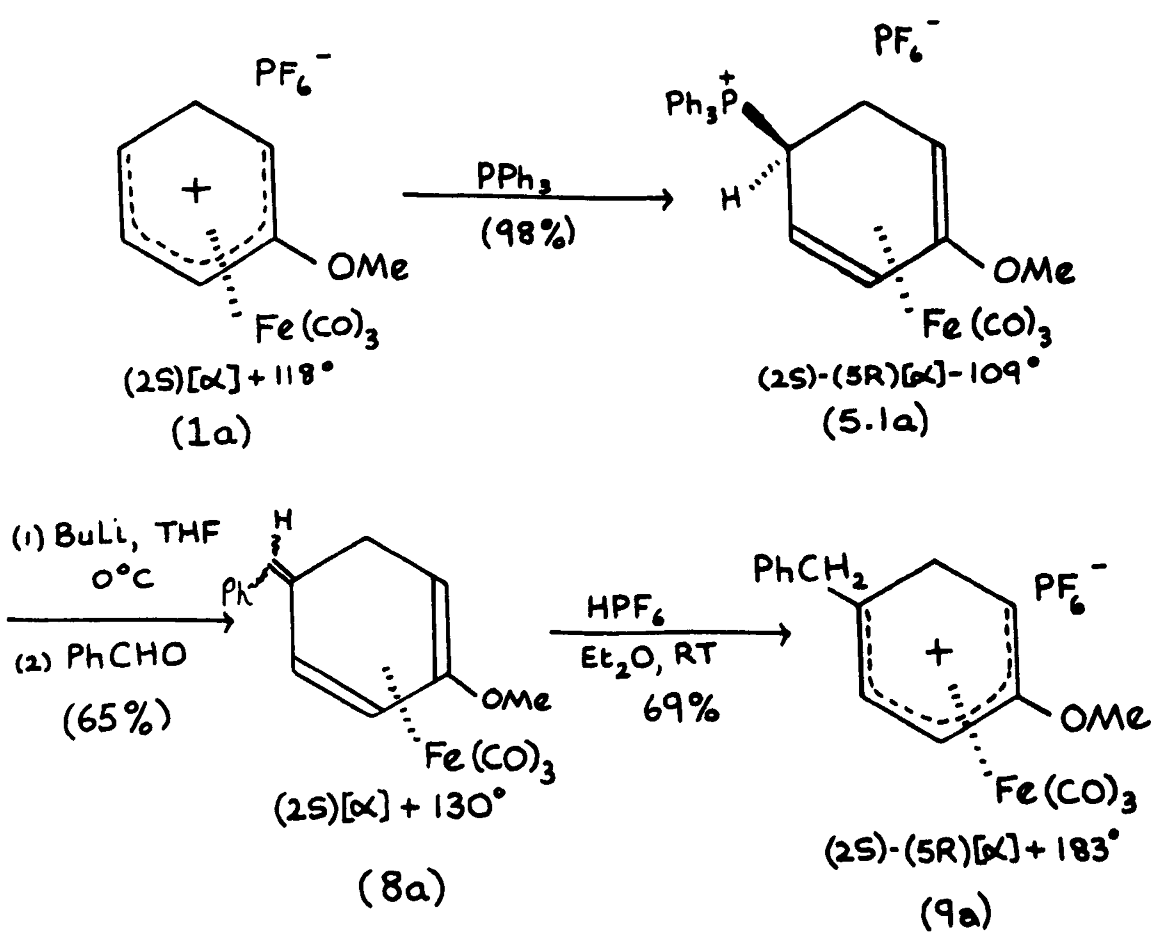



SCHEME I

The absolute configurations shown in Scheme I can be written with confidence, since the configurations of (1a) and (1b) have been determined by conversion of enantiomerically enriched samples (<10%)

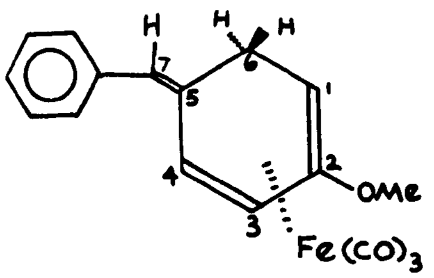
obtained from asymmetric complexation procedures, into natural products of known configuration[5] (Chapter 2.1). Since the reactions of (1a) are both regio- and stereospecific, the absolute configurations of (3a), (5.2a) and (7a) are also known.[6] In addition, the specific rotation value of (3a)([$\alpha$]+134°) is in agreement with the value obtained by Stephenson for the (2R)-(5S) enantiomer ([$\alpha$]-138°), complex (3b).[2]

The reaction may also be extended to benzaldehyde, to give the enantiomerically pure benzyl substituted dienyl salt (9a) as the final product ($^{13}$C n.m.r. spectrum at figure III).

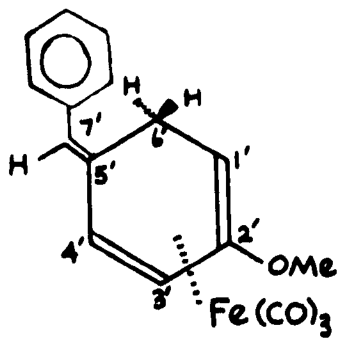



SCHEME II

In contrast to the substituted methylene cyclohexadiene derivative (7a), the phenyl substituted complex (8a) is a completely stable, sublimable yellow solid. Both $^{1}H$ and $^{13}C$ n.m.r. spectra show clearly the presence of the two possible geometric isomers ($\gtrsim$90:10) depending on the phosphonium salt used (vide infra), although attempts to separate them chromatographically have been unsuccessful. Although the configuration of the isomers cannot be assigned from the n.m.r. data (figures IV and V), the major isomer is more likely to be the less sterically congested structure as drawn.



(8a) PROBABLE STRUCTURE OF MAJOR ISOMER



(8a) PROBABLE STRUCTURE OF MINOR ISOMER

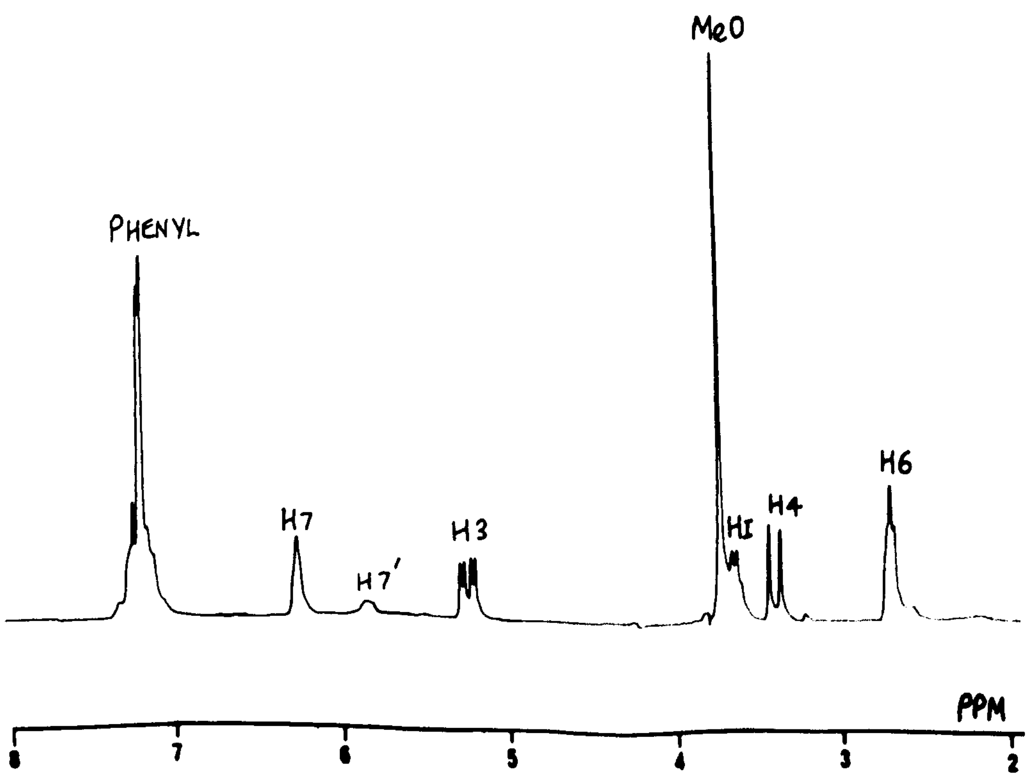



FIG.IV $^{1}H$ n.m.r. Spectrum of Complex (8a)

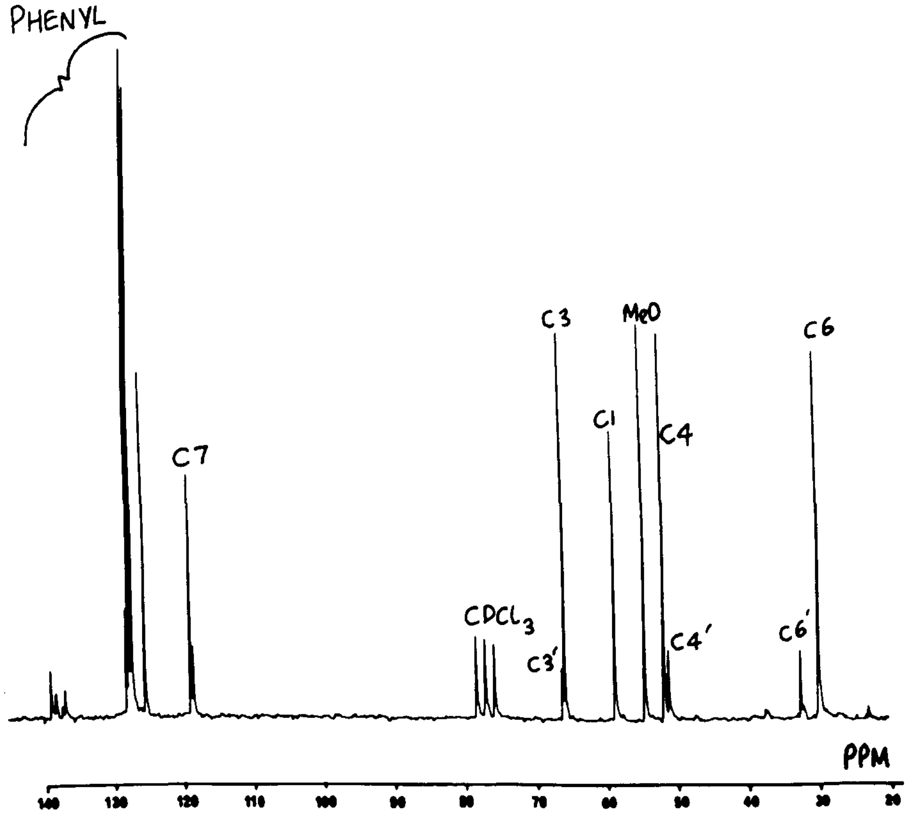
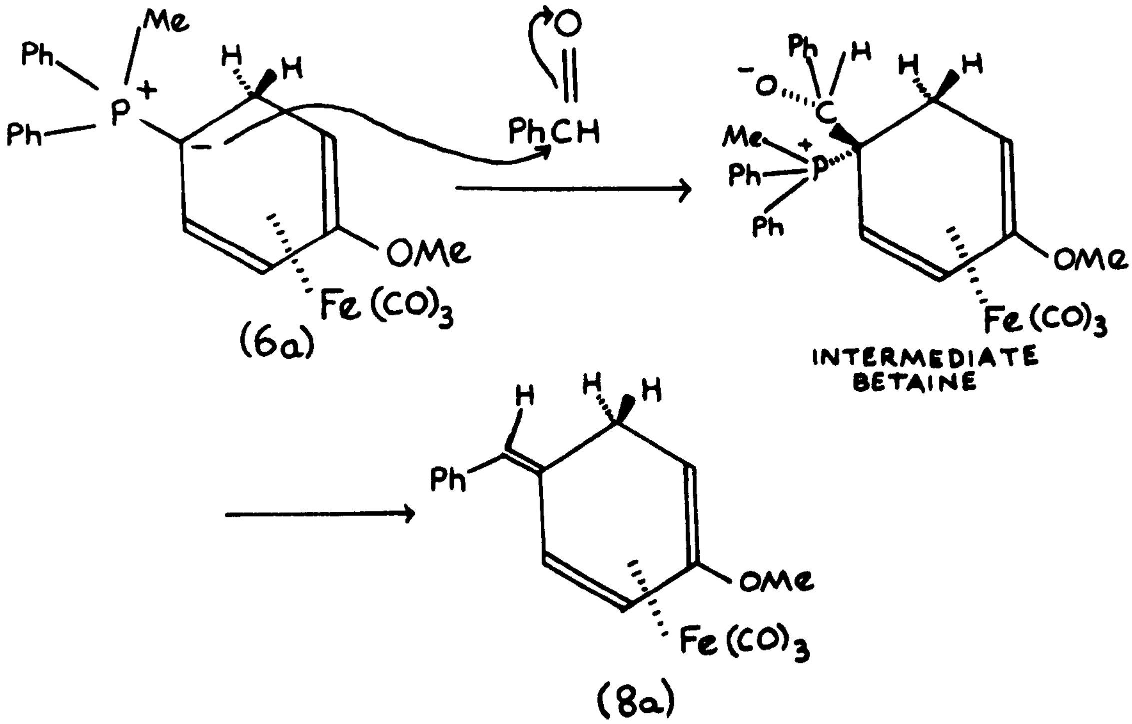



FIG. V $^{13}$C n.m.r. Spectrum of Complex (8a)

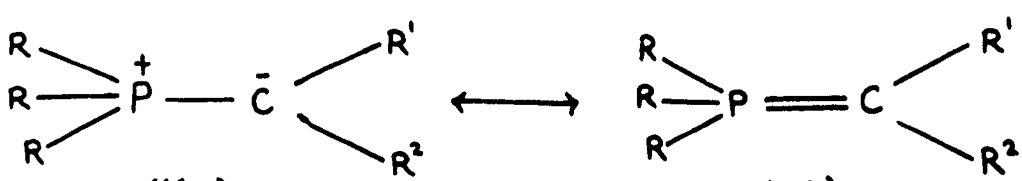
The assignment of the $^{1}$H n.m.r. spectrum (figure IV) was made by comparison with (2-MeO-cyclohexadiene)$Fe(CO)_3$ (10) (data given in ref [7]). The vinyl proton H-7 was observed as a singlet at 6.25 p.p.m., with H-7′ of the minor isomer appearing as a small singlet at 5.82 p.p.m. The ratio of the two isomers present, was most accurately determined by integration of the two vinyl proton signals. The $^{13}$C n.m.r. spectra (figure V) was similarly assigned by comparison with (2-MeO-cyclohexadiene)$Fe(CO)_3$ (10). The resonances of C-1, C-3, C-4 and OMe for complex (8a) are very similar to those for complex (10).[8] The assignment of C-7 and the methylene carbon C-6, was made with the aid of the off-resonance decoupled spectrum, C6 was observed as a triplet, with C-7 appearing at lower field. Individual resonances appear for the minor isomer at C-3′, C-4′, and C-6′.

The final configuration of (8a) depends on the initial orientation adopted by the aldehyde in the intermediate betaine complex. From steric considerations, the vinyl hydrogen adjacent to the methylene group is less strained and would therefore be expected to predominate.



We have examined the influence of the phosphonium salt used on the ratio of the two isomers produced. The reaction of the phosphonium salts (5.2a) ($PMePh_2$) or (5.3a) ($PMe_2Ph$) with BuLi and benzaldehyde in THF at low temperature gives the two geometric isomers of (8a) in the ratio of 90:10. However, when (5.1a) ($PPh_3$) is used as the starting material for the Wittig reaction with benzaldehyde, the amount of minor isomer obtained is barely detectable, the major isomer being present in the ratio of 99:1. Thus $PPh_3$ appears to be a more sterically demanding ligand than $PMePh_2$ or $PMe_2Ph$. Crystallographic observations show that $PMePh_2$ and $PMe_2Ph$ are better able to align the phenyl rings to minimise steric repulsions than is $PPh_3$ which has a more inflexible structure.[9] Interestingly, when [(2-MeO-5-α-benzyl-$C_6H_5$)Fe$(CO)_3$][$PF_6$] complex (9a) is deprotonated on treatment with the hindered base $NEtPr^i_2$, complex (8a) is regenerated in the isomeric ratio of 90:10. Deprotonation by the base must occur preferentially at the sterically less hindered orientation of the benzyl group. Lewis et al found that when the unsubstituted phosphonium salt [(5α $PMe_2Ph$-$C_6H_7$)Fe$(CO)_3$][$BF_4$] was used for the Wittig reaction with benzaldehyde, a 4:1 ratio of geometric isomers was produced.[3] This implies some degree of steric interaction between the methoxy substituent and the incoming benzaldehyde or between the methoxy group and the carbonyl ligands. The latter will affect the orientation adopted by the benzaldehyde group in the intermediate betaine complex.

We have also examined the influence of the phosphine used on the yield of complex (8a). When [(2-MeO-5α $PPh_3$-$C_6H_6$)Fe$(CO)_3$][$PF_6$] (5.1a) was used, the yield was 65%; for (5.2a) ($PMePh_2$) a 39% yield was obtained, whilst (5.3a) ($PMe_2Ph$) gave only a 22% yield. It is known that the reactivity of the phosphorus ylid depends not only on the distribution of the negative charge onto groups $R^1$ and $R^2$, but also on the nature of the groups attached to the phosphorus.[10]

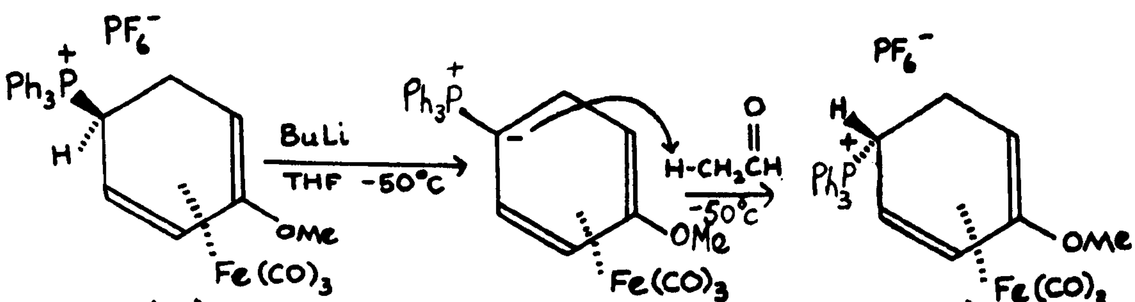


(11a) (11b)

The R groups on the phosphorus are capable of increasing or decreasing the extent of the phosphorus d-orbital participation and consequently the relative importance of form (11b). The presence of electron donating R groups (for instance alkyl) on the phosphorus, results in a reduction in the formal positive charge, thus decreasing the phosphorus d-orbital participation and increasing the importance of the form (11a), leading to the increased reactivity of the ylid. However, the effect of substituting $PR_3$=$PMe_2Ph$ for the less electron donating $PR_3$=$PPh_3$, is to increase the positive charge on the phosphorus atom, resulting in an increase in the d-orbital participation. The resonance hybrid form (11b) assumes greater importance and therefore the ylid is slightly stabilised and not so reactive. Thus for complex (5.3a) ($PMe_2Ph$) the low yield obtained indicates that its increased Wittig reactivity does not counterbalance its increased instability, resulting in decomposition, whilst for (5.1a) ($PPh_3$) the increased stability compensates for the decrease in reactivity.

Lewis et al found that when the unsubstituted phosphonium salt [(5-exo-PMePh-$C_6H_7$)Fe$(CO)_3$][$BF_4$] was treated with NaH in $CH_2Cl_2$, it readily underwent proton $\alpha$ abstraction.[3] However, due to increased electron donation to the cyclohexadiene ring from the 2-MeO substituent, we found that [(2-MeO-5$\alpha$ $PMePh_2$-$C_6H_6$)-Fe$(CO)_3$][$PF_6$] will not undergo $\alpha$ proton abstraction with NaH. Using the stronger base, butyl lithium proton abstraction is achieved; however, lithium salts are thought to form stable complexes with ylids, which dissociate only at elevated temperatures.[11] These complexes could interfere with the course of the reaction, and might account for the moderate to low yields obtained.

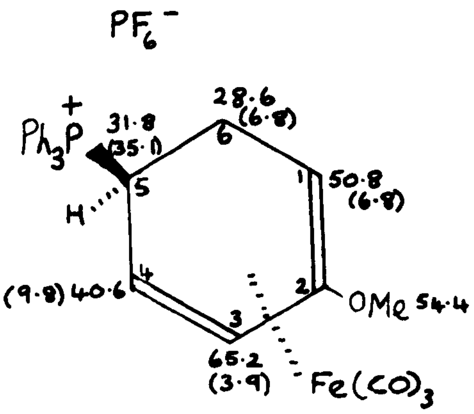
The strongly basic ylids formed are extremely unstable, decompose above -15°C, and react only with benzaldehyde and formaldehyde to give olefinic products. We have also examined the reaction of ketones and aliphatic aldehydes with the ylid (6) formed in situ. Only decomposition of the ylid was observed on reaction with ketones, consistent with the generally lower reactivity of ketones in the Wittig reaction. In contrast, addition of aliphatic aldehydes to the deep red solution of the ylid results in an immediate colour change to light yellow and the product isolated exhibits similar carbonyl stretching bands in the i.r. spectrum to those of the starting phosphonium salt. Thus the strongly basic ylid deprotonates aldehydes possessing an acidic hydrogen $\alpha$ to the carbonyl group (such as acetaldehyde), to regenerate the phosphonium salt. However, from the $^{13}C$ n.m.r. spectrum, it is clear that proton addition had occurred on the opposite face of the diene to that complexed to the metal, to give an endo substituted product (12).



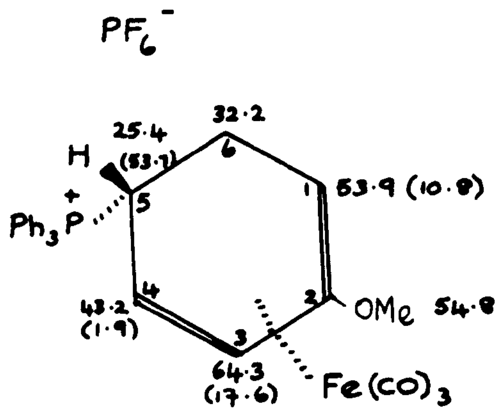

(5.1) (12)

(12) was prepared in an analytically pure form by protonation of the ylid with aqueous $HPF_6$. However, it is clear from the $^{13}C$ n.m.r. spectrum (figure VI) that (12) is not entirely pure but contaminated with a minor amount of exo 5.1. Assignment of the $^{13}C$ n.m.r. spectrum for complex (12) was made on the basis of comparison with (5.1) (figure VII).

$^{13}$C n.m.r. Data of Complexes (5.1) and (12)
(JP-C)couplings in Hz given in brackets)




(5·1)

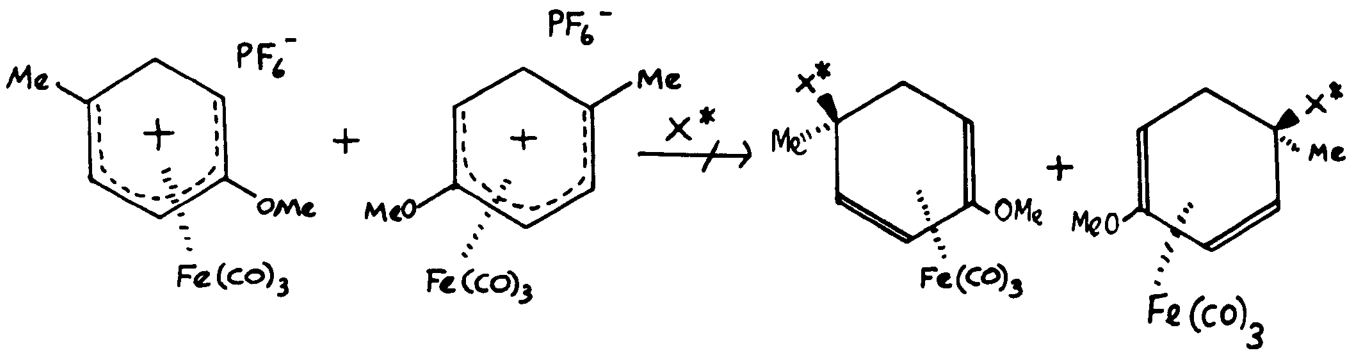



(12)

The presence of the bulky endo $PPh_3$ group, probably results in the distortion of the $sp^2$ carbon C-5 away from the plane of the diene, to minimise steric repulsions from the $Fe(CO)_3$ moiety. Thus changes in the dihedral angles between the phosphorus and the carbon atoms will lead to quite different (JP-C) being observed in the endo complex, compared with the exo complex. The (JP-C) found for C-1, C-3 and C-4 of complex (12), show considerable variation with those of (5.1), whilst the chemical shifts are quite similar. C-5 and C-6 of complex (12) were assigned with the aid of the off-resonance decoupled spectrum. C-5 (JP-C) 53.7 Hz appears as a doublet of doublets at 25.4 p.p.m., whilst C-6, with no (Jp-c), is observed as a triplet at 32.3 p.p.m.

Thus a useful method has been found for changing the stereochemistry of the asymmetric carbon atom, if a resolved chiral phosphonium salt is used as the starting exo-isomer.

Attempts to convert a racemic mixture of (3) into diastereoisomers using the methods described in Chapter 2 were unsuccessful.




(3a,b)

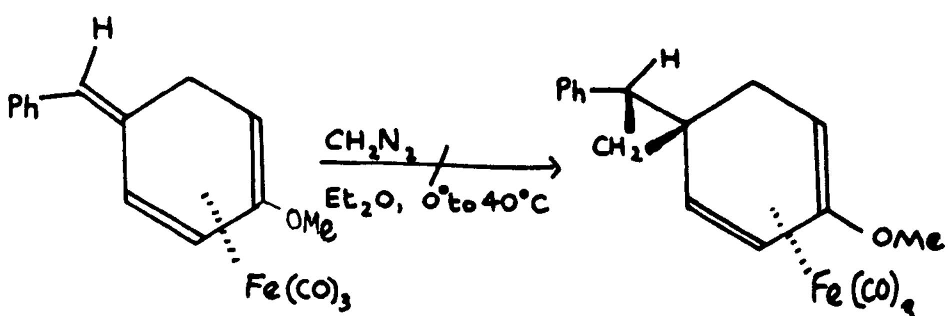
X*= (-)$OC_{10}H_{19}$ (menthoxy)

(+)$PPh_2$menthyl

Treatment of (3a,b) with the menthoxide anion generated by the addition of $NEtPr^i_2$ to (-)menthol resulted in deprotonation to give the methylene complex (7). The addition of (+)$PPh_2$menthyl to (3a,b) appeared to be an equilibrium reaction. Treatment of (3a,b) with a 5-fold excess of the chiral phosphine gave a yellow/brown solution with $\nu$ CO spectrum of 2045 and 1988br $cm^{-1}$. However, attempted isolation of the product by precipitation with diethyl ether yielded only (3a,b).

Finally, two attempts at cycloaddition to the phenyl substituted derivative (8) may be described.

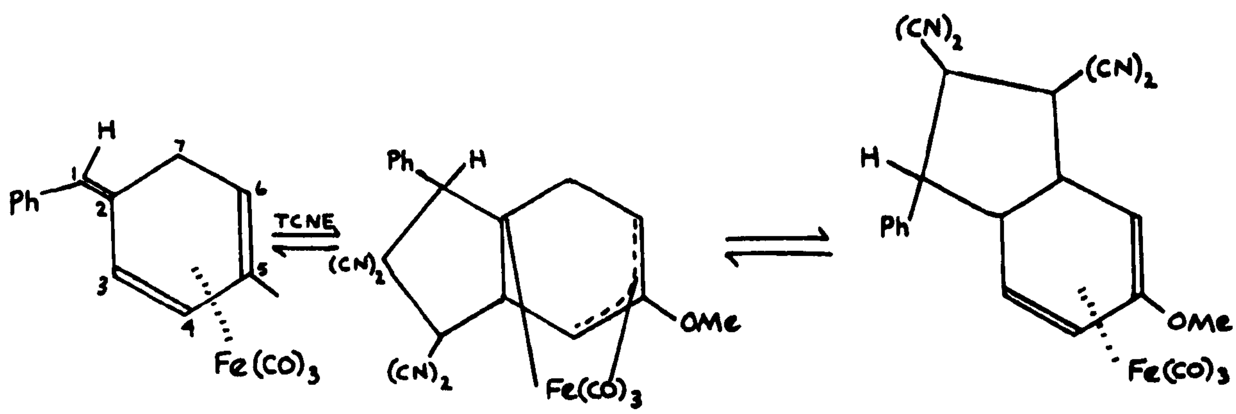
(a) Reger has shown that methylene carbene can be added to ($\eta^4$-cycloheptatriene)$Fe(CO)_3$ to generate a cyclopropyl ring.[12]




(8) (13)

However, our attempts at carbene addition to the uncomplexed double bond of (8) to form (13) were unsuccessful, giving only starting material. Diazomethane in $Et_2O$ (generated from the treatment of N-nitrosomethylurea with 40% KOH at 5°C),[13] failed to react with complex (8), even when present in a five fold excess at a temperature range between 0° to 40°C.

(b) The reaction of TCNE with ($\eta^4$-diene)$Fe(CO)_3$ complexes is well known, and occurs via 1,3-cycloaddition to give novel $\sigma$, $\pi$ bonded complexes. Tricarbonyl(7-phenylmethylenecycloheptatriene)iron has been shown to undergo initial 1,3-cycloaddition, followed by isomerization to give the 1,8-adduct (see Chapter 1.2.4). On this basis, TCNE addition to (8) may occur to give the $\sigma$, $\pi$ complex (14) which may possibly isomerize to the 1,8-adduct (15).




(8) (14) (15)

We have found that the adduct formation [either (14) or (15)] is an equilibrium reaction; addition of a 2.8 fold excess of TCNE to complex (8) in $CH_2Cl_2$ is required to give 80% of (14) or (15) over the amount of starting material remaining in solution (as judged by i.r. spectroscopy).

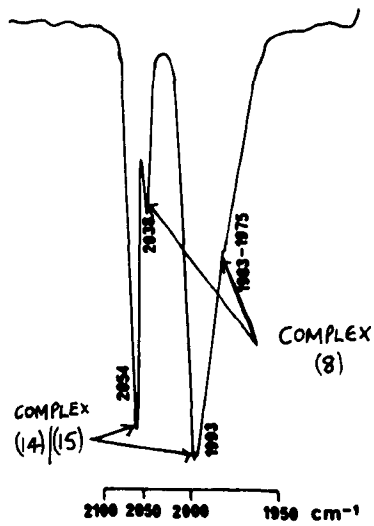



FIG. VIII I.r. ($\nu$CO) Spectrum of Complexes (14)/(15) and (8) in $CH_2Cl_2$ after the Addition of a 2.2 Excess of TCNE

However, attempted isolation of the adduct by precipitation with hexane yielded only complex (8) and free TCNE. The stoichiometry of adduct formation may be shown to be 1:1 using Job's method or the method of continuous variation.[14] Solutions with identical concentrations of complex (8) and TCNE were mixed in such a way that the total volume of each mixture remained the same. The amount of adduct formed in each mixture was measured from the sharp carbonyl stretching band at 2054 $cm^{-1}$. Maximum absorbance due to the formation of the adduct was reached when the mole fraction of complex (8) to TCNE was 1:1. (See following page).

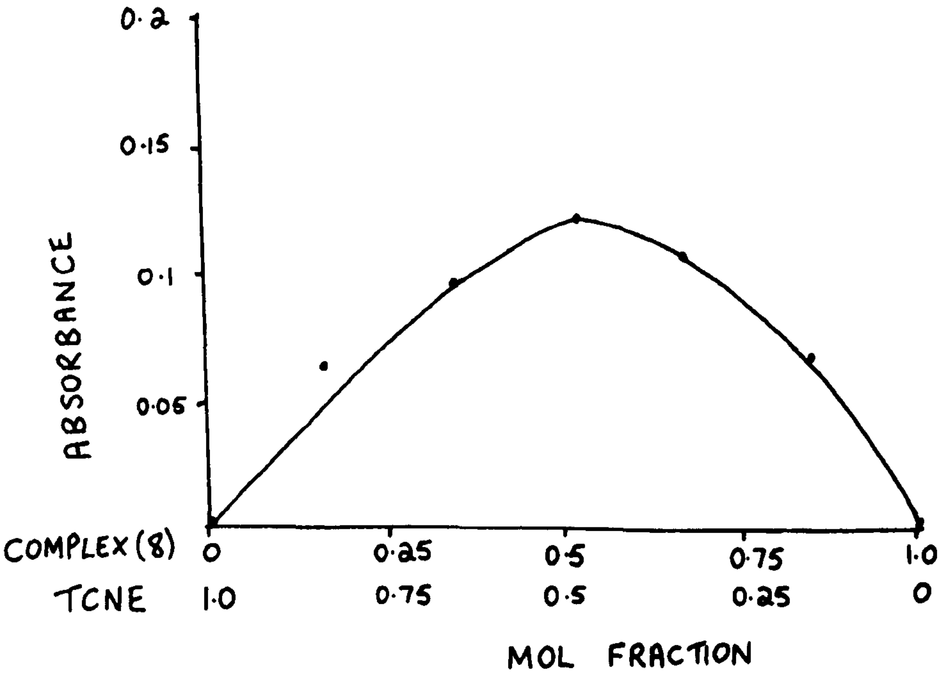
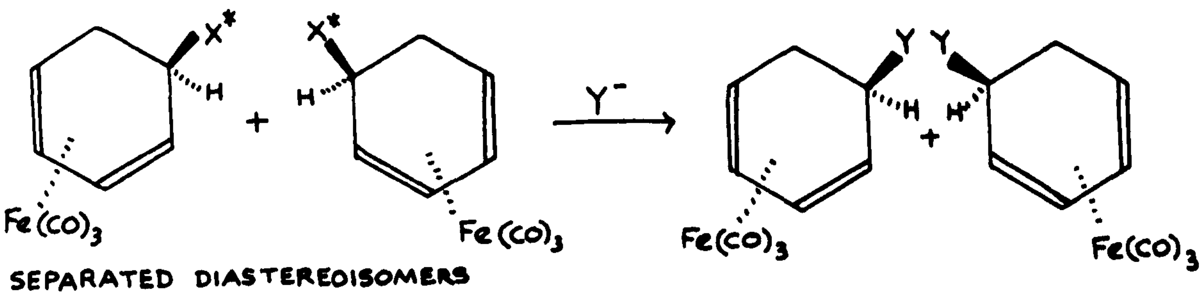



FIG. IX Plot of absorbance against mol fraction for the formation of the adduct by addition of TCNE to complex (8)

## 3.2 Attempts at the Elimination of the Chiral Residue from the Menthoxy and Amine Derivatives



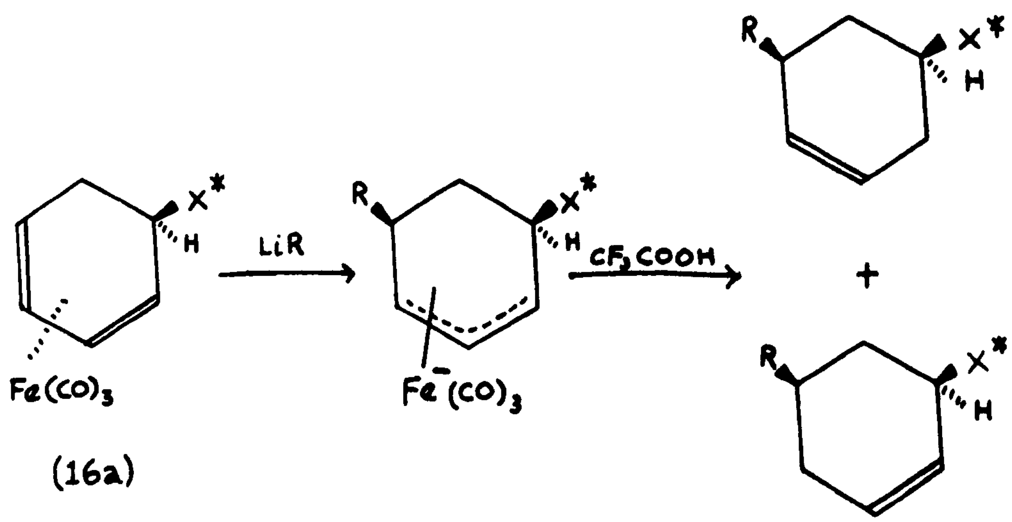

$X^*$

(16a,b)=(-)$OC_{10}H_{19}$(menthoxy)

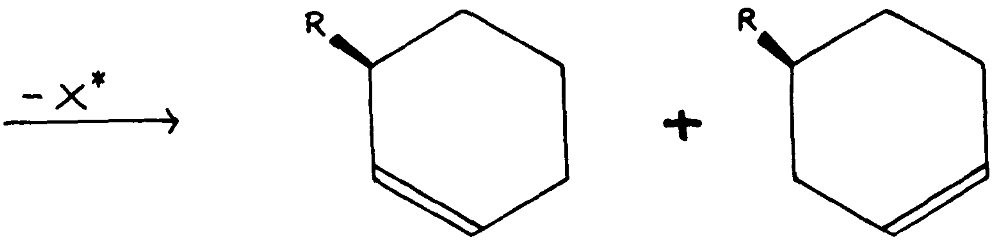
Y=nucleophile

(17a,b)=(-)N(Me)CH(Me)Ph

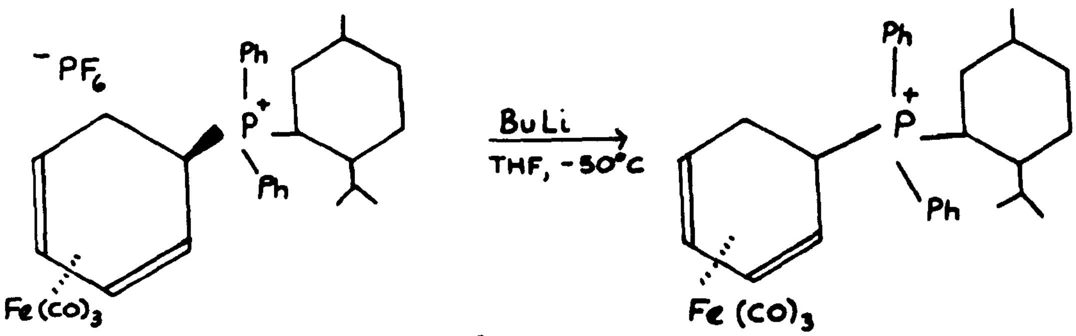
We have attempted the nucleophilic displacement of the resolving centre of (16a,b) and (17a,b) in order to maintain the stereochemistry of the resolved quaternary carbon. The methylation of (16a) was attempted using lithium dimethylcuprate,[15] generated by the addition of methyllithium to a suspension of cuprous iodide in diethyl ether at 0°C. On addition of (16a) much decomposition occurred to give a brown solution, and the expected less polar product was not observed by thin layer chromatography on silica gel. Similarly the attempted nucleophilic displacement of the chiral amine group from separated diastereoisomer (17a) by methylation with lithium dimethylcuprate, resulted in decomposition with no clear reaction products. Further work is needed in this area especially in view of Semmelhack's recent report of reactive carbanion addition to ($\eta^4$-cyclohexadiene)$Fe(CO)_3$[16] (see Chapter 1.2.2.4). The resulting stable $\eta^3$-allyl intermediates can be protonated with trifluoroacetic acid to produce substituted cyclohexene isomers in a 1:1 ratio. If a resolved diastereoisomer (16a) or (17a) were used as starting material, separation of the isomeric cyclohexenes followed by elimination of the chiral residue, would give enantiomerically pure products.




(16a)

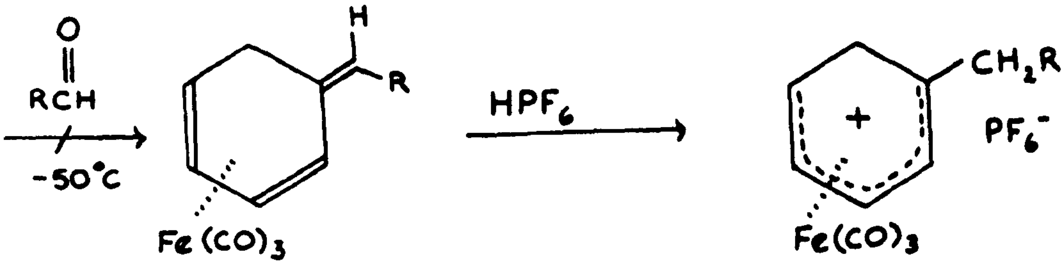



## 3.3 Chiral Phosphonium Salts




SEPARATED DIASTEREOISOMER

(18a) (19)

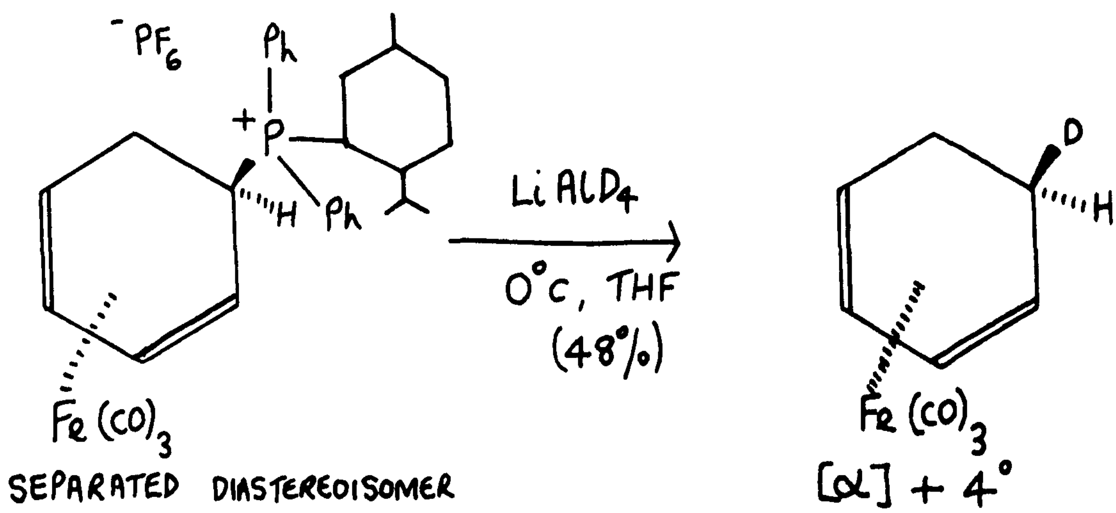



(20) (21)

R=H,Ph

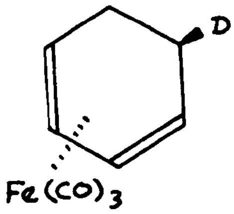
We hoped to transform the readily available pure diastereoisomer (18a) (Chapter 2.2.2) into the enantiomerically pure (20) via the Wittig reaction, and by protonation of (20) into (21). This would provide a useful route to enantiomerically pure (21 R=Me) which is not available by any other means. Treatment of (18a) with an excess of BuLi in THF at -50°C, results in the slow formation of the deep red phosphorus ylid (19). Unfortunately, on the addition of benzaldehyde to (19) only decomposition was observed on warming to room temperature. In order to ensure that the lack of ylid reactivity was not due to the formation of stable lithium salts, the reaction was repeated with a variety of strong bases; sodium hydride in $CH_2Cl_2$ failed to abstract the $\alpha$ proton to give the ylid (19). The use of sodium amide in liquid ammonia or sodium methyl sulfinyl carbanion in dimethyl sulphoxide[10] gave the ylid (19), but again no olefinic products (20) were formed on the addition of benzaldehyde or formaldehyde. The lack of Wittig reactivity must be due to steric rather than electronic factors; the steric bulk of the menthyl group must severely hinder attack of the ylid carbanion on the aldehyde carbonyl group.

Phosphonium salts are known to undergo reduction with lithium aluminium hydride, to give tertiary phosphines and hydrocarbons.[17] We have found that (+)-$PPh_2$menthyl can be eliminated from the pure diastereoisomer (18a) with $LiAlD_4$ to give (22).

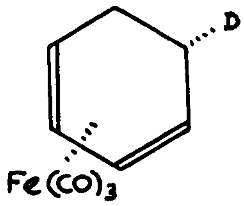



(18a) (22)

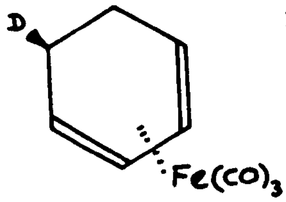
Although complex (22) exhibits only a small optical rotation, this is to be expected since the asymmetry of the chiral carbon atom is associated with two different isotopes. However, in theory, four distinct isomeric products (A to D) are possible for the reduction of (18a) with $LiAlD_4$.



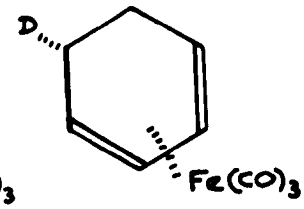

(A)




(B)




(C)




(D)

Isomer (A) results from the direct deuteride attack on the phosphorus atom, to give the exo substituted product; isomer (B) is the endo product of direct phosphorus attack. Alternatively, deuteride attack may occur at carbon-1 of the diene, leading to expulsion of the phosphine to give isomers C and D as the exo or endo derivatives. Isomers A/C and B/D are enantiomeric pairs, thus if the reaction was proceeding to give both pairs of enantiomers racemization would occur, leading to a small optical rotation. Isomers A/B and C/D however, are diastereoisomers. From the $^{13}C$ n.m.r. spectrum of complex (22), it is clear that only one diastereoisomer is present, since only one set of resonances is observed.

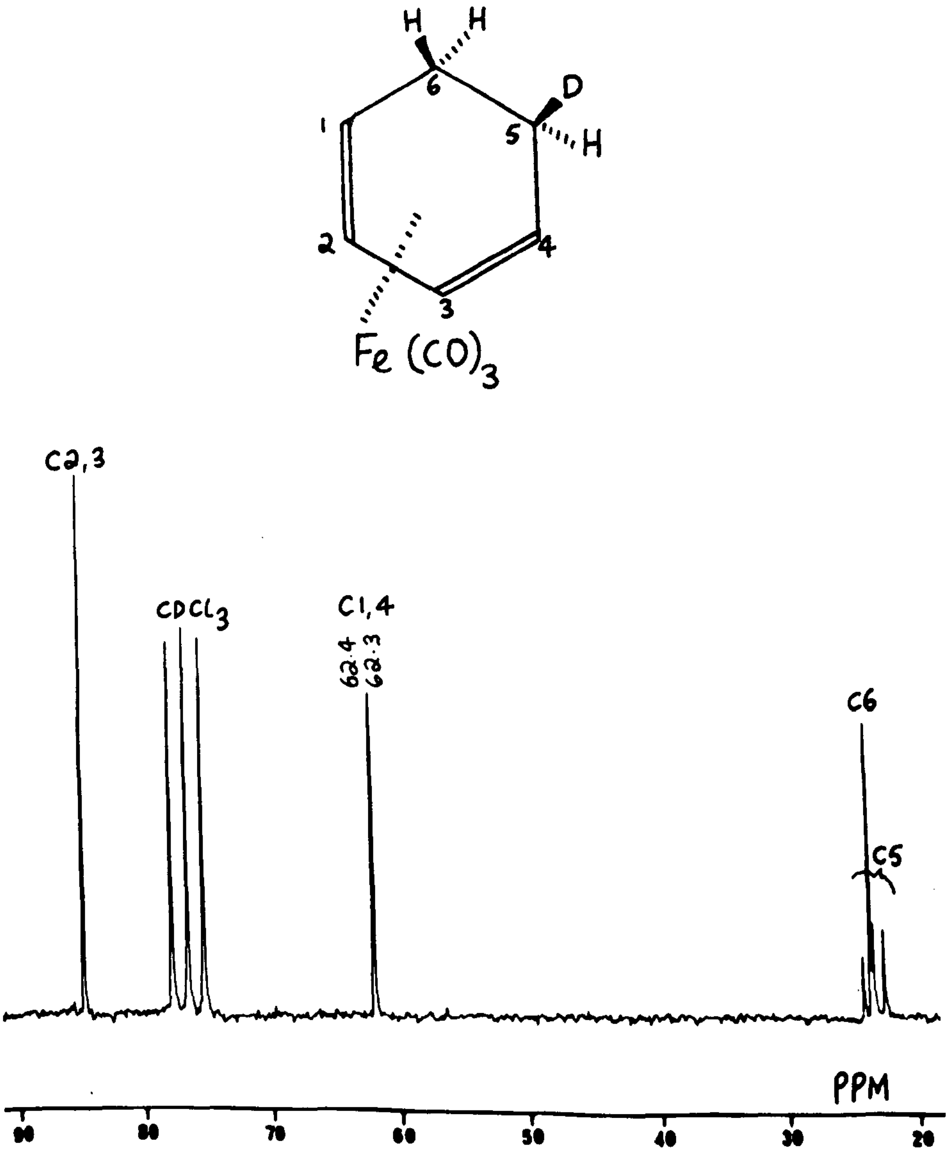
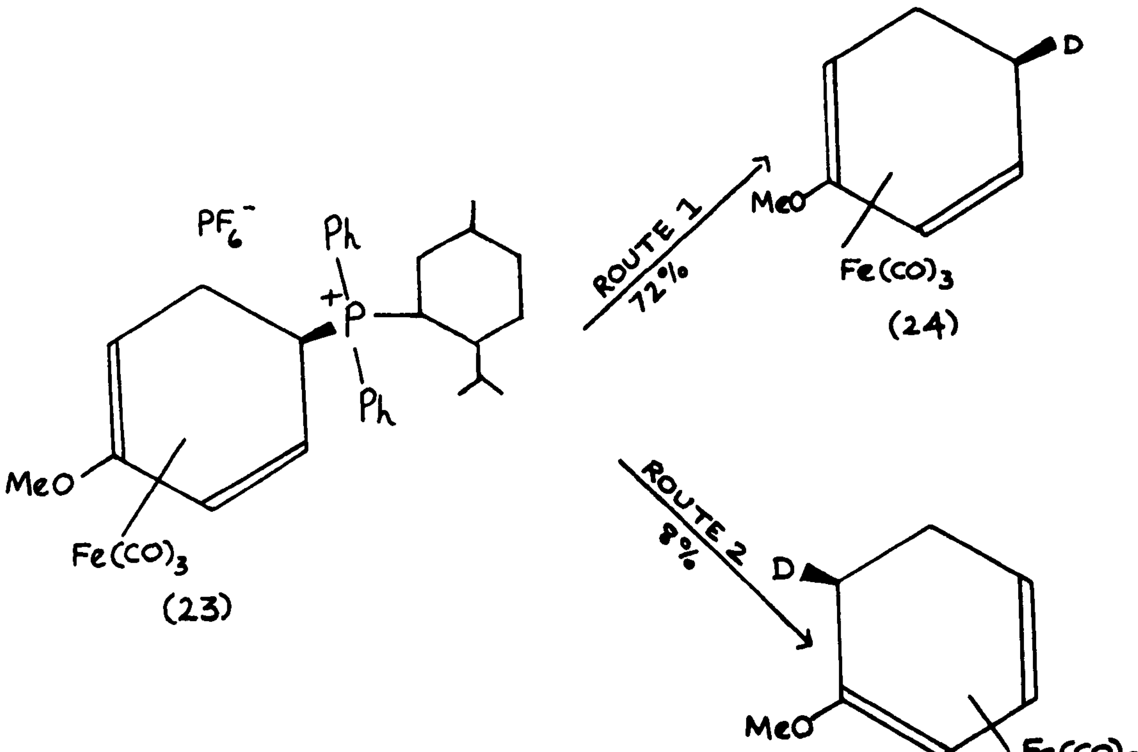



FIG. X $^{13}$C n.m.r. Spectrum of Complex (22)

C-5 appears as a triplet due to the carbon-deuterium spin coupling. The outer diene carbons (C-1 and C-4) are no longer chemically equivalent and have separate resonances, because of the asymmetric centre in the molecule.

In order to confirm that deuteride attack had occurred exclusively exo to carbon-5, the 2-MeO substituted phosphonium salt (complex 23) (racemic mixture) was reduced with $LiAlD_4$.




(23)

(24)

(25)

A mixture of products was obtained; a 72% yield of complex (24), the product of direct phosphine displacement (Route 1), and 8% of complex (25), the product of deuteride attack on carbon-1, resulting in expulsion of the phosphine (Route 2). The ratio of complex (24) to (25) present was confirmed by $^{13}C$ n.m.r. spectroscopy (figures XI and XII - see following page).

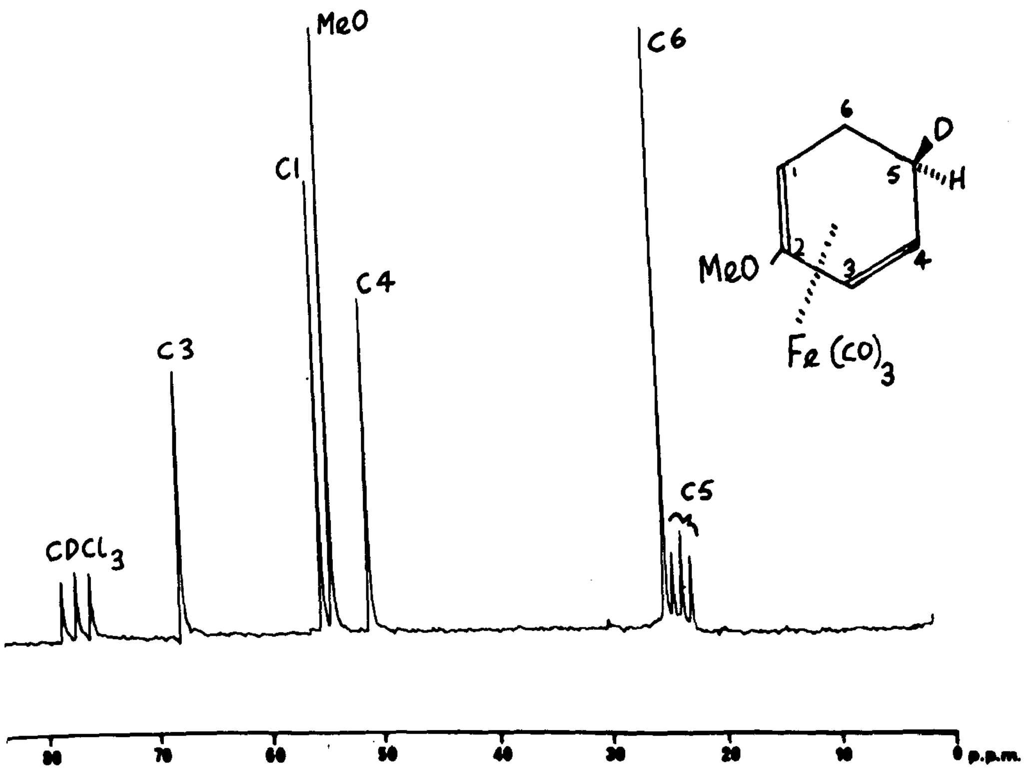



FIG. XI $^{13}$C n.m.r. Spectrum of Complex (24)

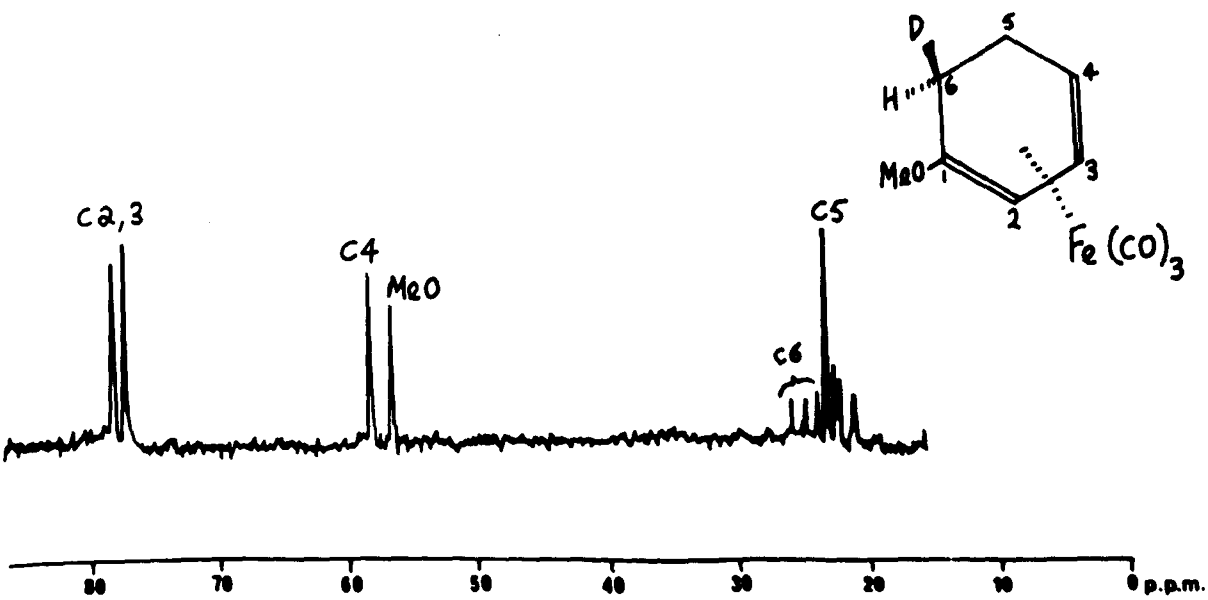



FIG. XII $^{13}$C n.m.r. Spectrum of Complex (25)

The $^{13}$C n.m.r. data of complexes (24) and (25) were assigned on the basis of comparison with (2-MeO-cyclohexadiene)$Fe(CO)_3$ [8] and (1-MeO-cyclohexadiene)$Fe(CO)_3$ and with the aid of the off-resonance decoupled spectra. Thus reduction of (18a) with $LiAlD_4$

may be occurring via two possible routes, to give enantiomers, thus resulting in partial racemization. The introduction of a resolved chiral centre into the molecule, by displacing a carbonyl ligand with (+)$PPh_2$menthyl, would confirm whether an enantiomeric mixture was present or if (18a) was optically pure.

## 3.4 Experimental

The same reaction conditions and instrumentation were used as specified in Chapter 2.3, except that optical rotations were measured automatically on an AA100 polarimeter supplied by Optical Activity Ltd. The concentration of butyl lithium in hexane was determined by titration of a solution of 2,5-dimethoxybenzyl alcohol in diethyl ether.[18] Formaldehyde was generated externally from the Wittig reaction vessel by heating paraformaldehyde (previously dried over $P_2O_5$ for 24 hours at 0.01 mm Hg) to 160-180°C. The formaldehyde was bubbled into the reaction flask via a wide tube to prevent clogging due to polymerisation.[19] THF was purified by distillation over sodium and benzophenone. Benzaldehyde was purified by dissolving in $Et_2O$, washing with $Na_2CO_3$ followed by $H_2O$, drying over $MgSO_4$ and distillation.[20]

(a) Preparation of (2S)(5R)(-)-[(2-MeO-5α$PPh_3$-$C_6H_6$)Fe(CO)$_3$]-[$PF_6$] complex (5.1a)

To a stirred suspension of (2S)(+)-[(2-MeO-$C_6H_6$)Fe(CO)$_3$][$PF_6$] ([α]=+118°) (0.30 g, 0.76 mmol) in $CH_2Cl_2$ (20 $cm^3$) was added $PPh_3$ (0.22 g, 0.84 mmol). Immediate dissolution occurred to give a yellow solution. Removal of the solvent under reduced pressure gave a yellow gum, which solidified on standing in diethyl ether (50 $cm^3$) for 1 hour at 0 C. The pale yellow solid was filtered and washed repeatedly with diethyl ether to give 0.46 g of product. Yield: 98%. $[\alpha]_D^{20}$ -108.8° ± 1° (MeCN, C=5.0). Calc. for $C_{28}H_{24}F_6FeO_4P_2$: C, 51.24; H, 3.69. Found: C, 51.00; H, 3.73%. I.r. ($CH_2Cl_2$) 2050, 1993br $cm^{-1}$.

Complexes (5.2a) and (5.3) were prepared in an identical manner. Yield of (2S)(5R)(-)-[(2-MeO-5α-$PPh_2Me$-$C_6H_6$)$Fe(CO)_3$]-[$PF_6$] (5.2a): 97%. $[\alpha]_D^{17}$ = -92° ± 3° (acetone, C=2.9). Calc. for $C_{23}H_{22}F_6FeO_4P_2$: C, 46.48; H, 3.74. Found: C, 45.95; H, 3.61%. I.r. ($CH_2Cl_2$) 2048, 1993br $cm^{-1}$. Yield of [(2-MeO-5α$PPhMe_2$-$C_6H_6$)$Fe(CO)_3$][$PF_6$] (5.3): 99%. Calc. for $C_{18}H_{20}F_6FeO_4P_2$: C, 40.62; H, 3.80. Found: C, 40.59; H, 3.74%. I.r. ($CH_2Cl_2$) 2051, 1993br $cm^{-1}$.

(b) <u>Preparation of [(2-MeO-5β-$PPh_3$-$C_6H_6$)$Fe(CO)_3$][$PF_6$] complex (12)</u>

A stirred suspension of racemic (5.1) (0.86 g, 1.31 mmol) in tetrahydrofuran (30 $cm^3$) under a dinitrogen atmosphere, was cooled to -60°C in an acetone/liquid $N_2$ bath. An excess of BuLi (2.0 mmol) in hexane was added in two portions over 1 hour. The stirred mixture was kept at -60°C throughout, and the phosphonium salt gradually dissolved to give a deep red solution. A small excess of $HPF_6$ (75% aqueous, 1.7 mmol) was added dropwise, to give a yellow solution which was allowed to warm to room temperature. After stirring for a further 1 hour, the solvent was removed under reduced pressure. The yellow gum was redissolved in $CH_2Cl_2$ (10 $cm^3$), filtered and precipitated by the addition of diethyl ether. The small quantity of less soluble exo-isomer (5.1) was removed by redissolving the the crude reaction mixture in acetone (10 $cm^3$). On the addition of light petroleum (10 $cm^3$), (5.1) separated out as a small amount of brown oil, from which the more soluble endo isomer (12) was readily decanted. (12) was isolated by the addition of an excess of light petroleum (50 $cm^3$) followed by filtration to give 0.61 g of yellow solid. Yield: 71%. Calc. for $C_{28}H_{24}F_6FeO_4P_2$: C, 51.24; H, 3.69. Found: C, 51.20; H, 4.07%. I.r. ($CH_2Cl_2$) 2047, 1991br $cm^{-1}$.

(c) Preparation of (2S)-(5R)-(+)-[(2-MeO-5-Me-$C_6H_5$)Fe(CO)$_3$][$PF_6$] (2a)

The (2S)-(5R)-(-)-enantiomer of (5.2a) [$\alpha$]-92° (0.48 g, 0.8 mmol) was suspended in THF under an atmosphere of dinitrogen and cooled to -60°C. BuLi (1.12 mmol) in hexane was added, and the suspension stirred for 1½ hours at between -60°--40°C until the phosphonium salt had completely dissolved to give a deep red solution. Formaldehyde generated externally was bubbled through the solution, which was stirred vigorously and allowed to gradually warm up to room temperature, to give a yellow solution. After hydrolysis, the product was extracted with diethyl ether (3 x 50 $cm^3$), the organic layer dried over $MgSO_4$, and the solvent evaporated. Chromatography on silica gel using light petroleum/diethyl ether 80/20 gave 0.108 g of a yellow gum, complex (7a), which was found to slowly decompose in a pure state. CHN analysis and a specific rotation value were unobtainable. I.r. (hexane) 2041, 1993 and 1982 $cm^{-1}$.

Complex (7a) was immediately converted into complex (2a). 0.108 g (0.41 mmol) of (7a) was dissolved in diethyl ether (20 $cm^3$), addition of an excess of $HPF_6$ (75% aqueous, 0.82 mmol) precipitated a yellow solid which was kept at 0°C for 12 hours, filtered and washed with diethyl ether. Recrystallization from acetone/diethyl ether gave 84 mg of product $[\alpha]_D^{20}$+134°$\pm$ 2° (MeCN, C=0.34). Yield over two stages: 26%. Calc. for $C_{11}H_{11}F_6FeO_4P$: C, 32.38; H, 2.72.

Found: C, 31.95; H, 2.54%. I.r. (acetone) 2099, 2047 $cm^{-1}$.

(d) Preparation of (2S)-(+)-(2-MeO-5-benzylidene-$C_6H_5$)Fe$(CO)_3$ complex (8a)

A stirred suspension of (2S)-(5R)-(-) (5.1a) ([$\alpha$]-109°) (0.47 g, 0.72 mmol) in THF was cooled to -60°C. An excess of BuLi (1.0 mmol) in hexane was added, and the mixture was stirred between -60° and -40°C for 1½ hours until the phosphonium salt had dissolved to give a deep red solution. An excess of benzaldehyde (2.16 mmol) was added and the cooling bath removed; the solution was stirred for 3 hours and gradually became orange. The product was hydrolysed, extracted with diethyl ether (3 x 50 $cm^3$), the organic layer dried over $MgSO_4$ and the solvent evaporated. Chromatography on silica gel using light petroleum/benzene 50/50 gave 157 mg of a yellow crystalline material which was shown by $^{13}C$ n.m.r. to exist almost entirely as one geometric isomer (99:1). Yield: 65%. An analytically pure sample was obtained by sublimation (79-88°C, ca. 0.015 mm Hg).

Calc. for $C_{17}H_{14}FeO_4$: C, 60.38; H, 4.18. Found: C, 60.83; H, 3.88%

$[\alpha]_D^{18}$ +130° ± 1° ($CHCl_3$, C=4.8). I.r. (hexane) 2042, 1992, 1981 $cm^{-1}$.

Yield using complex (5.2) as starting material: 39%. Ratio of isomers 10:1. Yield using complex (5.3) as starting material: 22%. Ratio of isomers 10:1.

(e) Preparation of (2S)-(5R)-(+)-[(2-MeO-5benzyl-$C_6H_5$)Fe$(CO)_3$][$PF_6$] (9a)

140 mg (0.414 mmol) of complex (8a) ([$\alpha$]+130°) were dissolved in diethyl ether (20 $cm^3$). On the addition of an excess of $HPF_6$ (75% aqueous, 1.6 mmol), a yellow solid precipitated, which was kept at 0°C for 12 hours, filtered and washed with diethyl ether. Recrystallization from $CH_2Cl_2/Et_2O$ gave 138 mg of product. Yield: 69% $[\alpha]_D^{20°}$ +183° ± 1° (MeCN, C=4.2). Calc. for $C_{17}H_{15}F_6FeO_4P$: C, 42.17;

H, 3.13. Found: C, 42.97; H, 3.23%. I.r. ($CH_2Cl_2$) 2100, 2045 $cm^{-1}$.

Complex (8a) could be easily regenerated by the deprotonation of complex (9a) with hindered base. 100 mg (0.21 mmol) of (9) were dissolved in $Et_2O$, and an excess of $EtNPr^i_2$ (0.42 mmol) added until the reaction was complete (as judged by i.r. spectroscopy). After filtration and removal of the solvent under reduced pressure, the crude reaction mixture was chromatographed on silica gel using light petroleum/benzene 50/50, to give 72 mg of complex (8a). Yield: 72%. $^{13}C$ n.m.r. showed the ratio of geometric isomers to be 10:1.

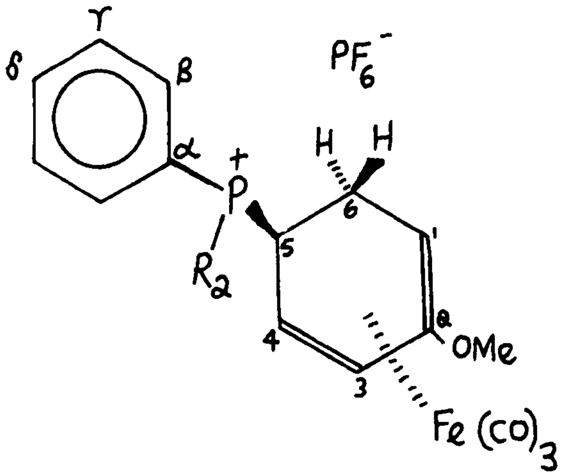
(f) Attempted Cycloaddition of Tetracyanoethylene (TCNE) to Complex (8)

A small excess of freshly sublimed TCNE (86 mg, 0.67 mmol) was added to a stirred solution of complex (7) (190 mg, 0.56 mmol), in $CH_2Cl_2$ (25 $cm^3$) at 0°C. The solution became brown and after stirring for 30 mins, the reaction was found to be about 55% complete, from examination of the carbonyl stretching bands in the i.r. spectrum. Several further additions of TCNE (200 mg, 1.56 mmol in total) were made over a five hour period, after which time the reaction appeared 80% complete from the i.r. spectrum. Removal of the solvent under reduced pressure, followed by attempted precipitation with hexane, gave a yellow-brown solid, and yellow solution. The solid had no carbonyl stretching bands in the i.r. and was thought to be iron oxide and TCNE. However, evaporation of the hexane gave the starting material, complex (8) - (74% recovery). I.r. of TCNE adduct in $CH_2Cl_2$: 2054, 1993br $cm^{-1}$. A satisfactory $^1H$ n.m.r. spectrum could not be obtained.

(g) Reduction of pure diastereoisomer $[(5\alpha\text{-}PPh_2C_{10}H_{19}\text{-}C_6H_7)Fe(CO)_3][BF_4]$ (18a) with $LiAlD_4$

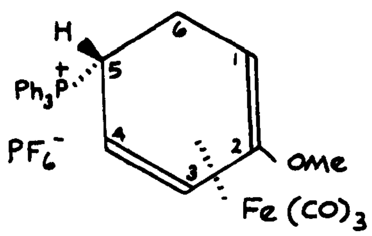
Finely powdered pure diastereoisomer (18a) (0.80 g, 1.27 mmol) was suspended in dry tetrahydrofuran (40 $cm^3$) at 0°C, and $LiAlD_4$ (0.092 g, 2.2 mmol) was added in three portions. The reaction mixture was stirred at 0°C until the i.r. spectrum indicated the consumption of the starting material (6 hours). The reaction mixture was treated cautiously with 20% sodium potassium tartate solution (50 $cm^3$) and extracted with diethyl ether (30 $cm^3$ x 3). Drying over $MgSO_4$, followed by removal of solvent and chromatography of the residue on Grade II alumina using light petroleum as eluant gave $(\eta^4\text{-}C_6H_7D)Fe(CO)_3$ (0.135 g, 48% yield) complex (22), identified by a comparison of its i.r. and $^1H$ n.m.r. spectra with those of an authentic sample of $(\eta^4\text{-}C_6H_8)Fe(CO)_3$. $[\alpha]_D$ + 4.3° ± 1.5° ($CHCl_3$ , C=3.3) $M^+$, 221. Reduction of a racemic mixture of $[(2\text{-}MeO\text{-}5\alpha PPh_2C_{10}H_{19}\text{-}C_6H_6D)Fe(CO)_3][BF_4]$ (23) with $LiAlD_4$ was carried out in a similar manner. The reaction was complete after 1½ hours to give a mixture of $(2\text{-}MeO\text{-}C_6H_6D)Fe(CO)_3$ (24) and $(1\text{-}MeO\text{-}C_6H_6D)Fe(CO)_3$ (25) in 72% and 8% yields respectively. The mixture was separated by chromatography on silica gel preparative plates using light petroleum as eluant.

## Table of $^{1}H$, $^{13}C$ and $^{31}P$ n.m.r. Spectra

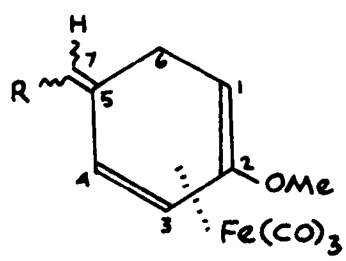



| COMPLEX | $^{13}C$ ASSIGNMENT | | $(J_{P-C})$ Hz | $^{31}P$ ASSIGNMENT |
|---|---|---|---|---|
| (5.1) | 3 | 65.2 | (3.9) | 26.4 |
| $PPhR_2=PPh_3$[a] | 2 | b | | |
| | 1 | 50.8 | (6.8) | |
| | 4 | 40.6 | (9.8) | |
| | 5 | 31.8 | (35.1) | |
| | 6 | 28.6 | (2.0) | |
| | MeO | 54.4 | | |
| | Phα | 117.7[c] | (d) | |
| | β or γ | 130.0 | (d) | |
| | β or γ | 133.6 | (d) | |
| | δ | 135.0 | (s) | |
| (5.2) | 3 | 65.3 | (3.7) | 25.9 |
| $PPhR_2=PPh_2Me$ | 2 | b | | |
| | 1 | 51.2 | (6.1) | |
| | 4 | 40.5 | (9.7) | |
| | 5 | 31.9 | (37.8) | |
| | 6 | 27.9 | (3.7) | |
| | MeO | 54.6 | | |
| | Ph | 136-117 | | |
| | Me | 6.0 | (46.9) | |

| COMPLEX | $^{13}$C ASSIGNMENT | | (Jp-c) Hz | $^{31}$P ASSIGNMENT |
|---|---|---|---|---|
| (5.3) | 3 | 65.8 | (2.9) | 26.8 |
| $PPhR_2$=$PPhMe_2$ | 2 | b | | |
| | 1 | 51.2 | (7.8) | |
| | 4 | 40.9 | (8.8) | |
| | 5 | 33.2 | (39.1) | |
| | 6 | 26.8 | (2.6) | |
| | MeO | 54.8 | | |
| | Ph | 136-117 | | |
| | Me | 6.24 | (53.7) | |
| | | 5.20 | (53.7) | |




| COMPLEX | $^{13}$C ASSIGNMENT | | (Jp-c) Hz | $^{31}$P ASSIGNMENT |
|---|---|---|---|---|
| (12) | 3 | 64.3 | (17.6) | 25.4 |
| | 2 | b | | |
| | 1 | 53.9 | (10.8) | |
| | 4 | 43.2 | (1.9) | |
| | 5 | 25.4 | (53.7) | |
| | 6 | 32.2 | | |
| | MeO | 54.8 | | |
| | Ph | 135-116 | | |




| COMPLEX | $^{13}$C ASSIGNMENT | |
|---|---|---|
| (7a) | 3 | 66.1 |
| R=H | 2 | b |
| | 1 | 55.9 |
| | 4 | 51.7 |

COMPLEX

(7a) (cont)

| $^{13}C$ ASSIGNMENT | |
|---|---|
| 5 | b |
| 6 | 29.8 |
| 7 | 102.9 |
| MeO | 54.5 |

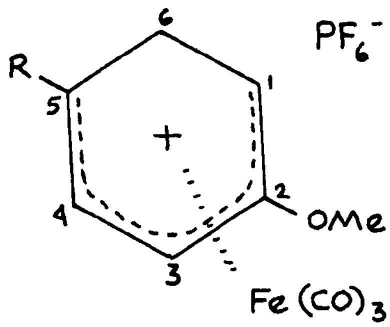
COMPLEX

(8a)

R=Ph

| $^{13}C$ ASSIGNMENT | |
|---|---|
| 3 | 65.9 |
| | 66.2[d] |
| 2 | b |
| 1 | 58.7 |
| 4 | 51.7 |
| | 51.1[d] |
| 5 | b |
| 6 | 29.9 |
| | 32.4[d] |
| 7 | 119.1 |
| MeO | 54.5 |
| Ph | 139-118 |

| $^{1}H$ ASSIGNMENT | |
|---|---|
| 3 | 5.21 (d of d) |
| 1 | 3.59 (m) |
| 4 | 3.37 (d) |
| 6 | 2.66 (m) |
| vinyl H | 6.25 (s) |
| | 5.82[d] (s) |
| MeO | 3.67 |
| Ph | 7.28-7.11 |



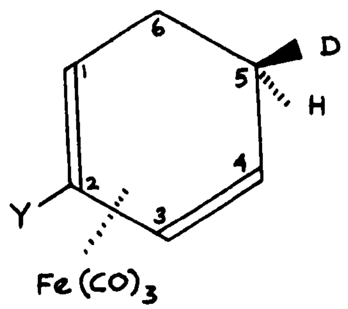

COMPLEX

(3a)

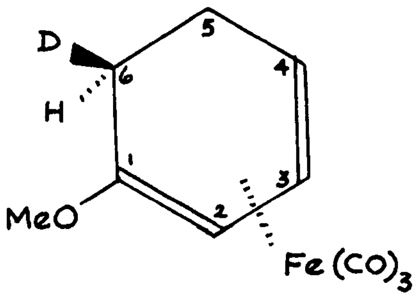
R = Me

| $^{13}C$ ASSIGNMENT | |
|---|---|
| 2 | 150.4[e] |
| 4 | 95.6 |
| 3 | 71.7 |
| 1 | 41.2 |
| 5 | b |
| 6 | 33.2 |
| MeO | 57.1 |
| Me | 23.2 |

| COMPLEX | $^{13}C$ ASSIGNMENT | |
|---|---|---|
| (9a) | 2 | 150.1[e] |
| $R=CH_2Ph$ | 4 | 94.0 |
| | 3 | 71.4 |
| | 1 | 41.3 |
| | 5 | b |
| | 6 | 32.3 |
| | $CH_2$ | 42.5 |
| | MeO | 57.1 |
| | Ph | 133-128 |




| COMPLEX | $^{13}C$ ASSIGNMENT | | $(J_{C-D})$Hz | |
|---|---|---|---|---|
| (22) | 2,3 | 85.3 | | |
| Y=H | 1,4 | 62.4 | | |
| | | 62.3 | | |
| | 5 | 23.6 | (20.5) | (triplet) |
| | | | | |
| (24) | 3 | 67.6 | | |
| Y=OMe | 2 | b | | |
| | 1 | 55.1 | | |
| | 4 | 50.9 | | |
| | 5 | 23.3 | (20.5) | (t) |
| | 6 | 24.8 | | |
| | MeO | 54.0 | | |



| COMPLEX | $^{13}$C ASSIGNMENT | | |
|---|---|---|---|
| (25) | 2,3 | 78.5 | |
| | | 77.6 | |
| | 1 | b | |
| | 4 | 58.3 | |
| | 5 | 23.2 | |
| | 6 | 24.9 | (t) |
| | MeO | 56.7 | |

a phosphonium salts run in $CDCl_3/CH_2Cl_2$ solvent mixture

b quaternary carbon not detected

c assignment made on basis of ref 2

d resonance of minor geometric isomer present in the ratio of 10:1

e complexes (2a) and (9a) run in $CF_3CO_2D/CDCl_3$

FIG. I $^{13}C$ NMR Spectrum of Complex (7a)

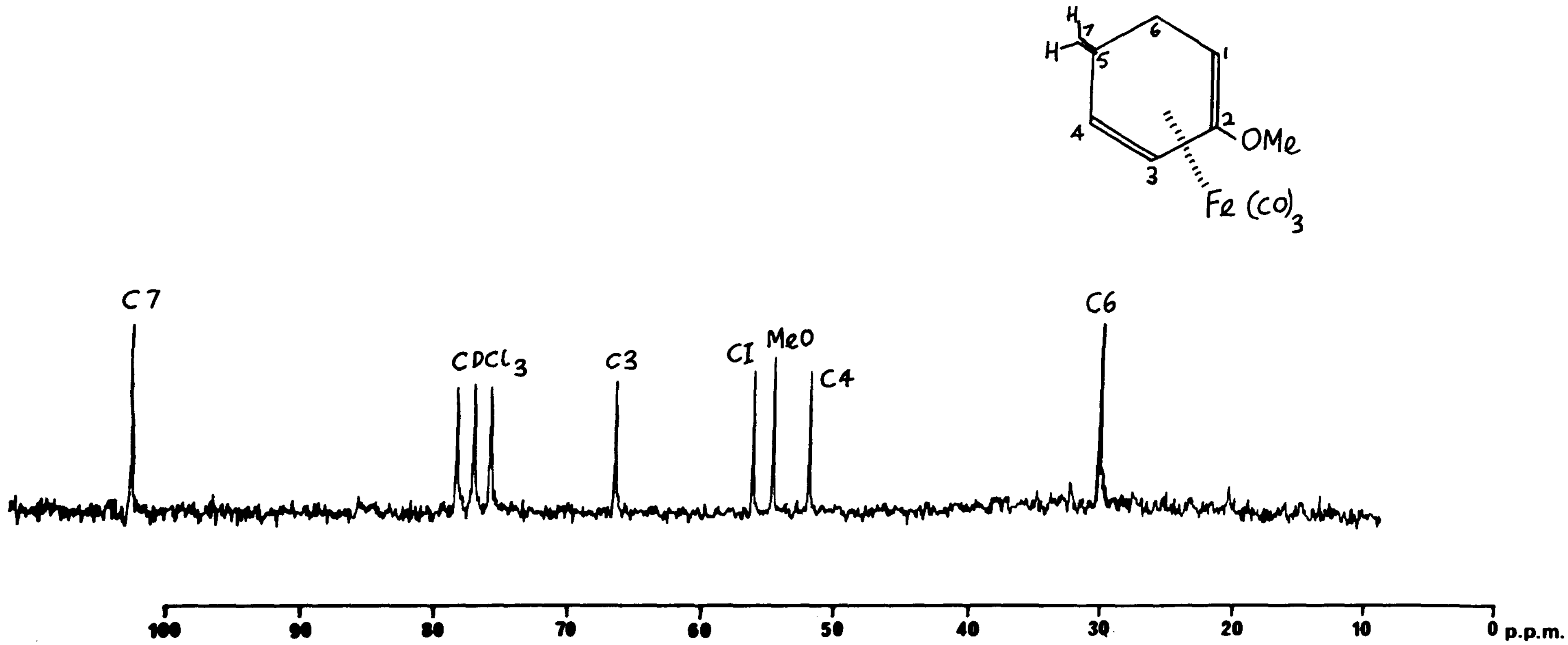


FIG II $^{13}$C NMR SPECTRUM OF COMPLEX (3a)

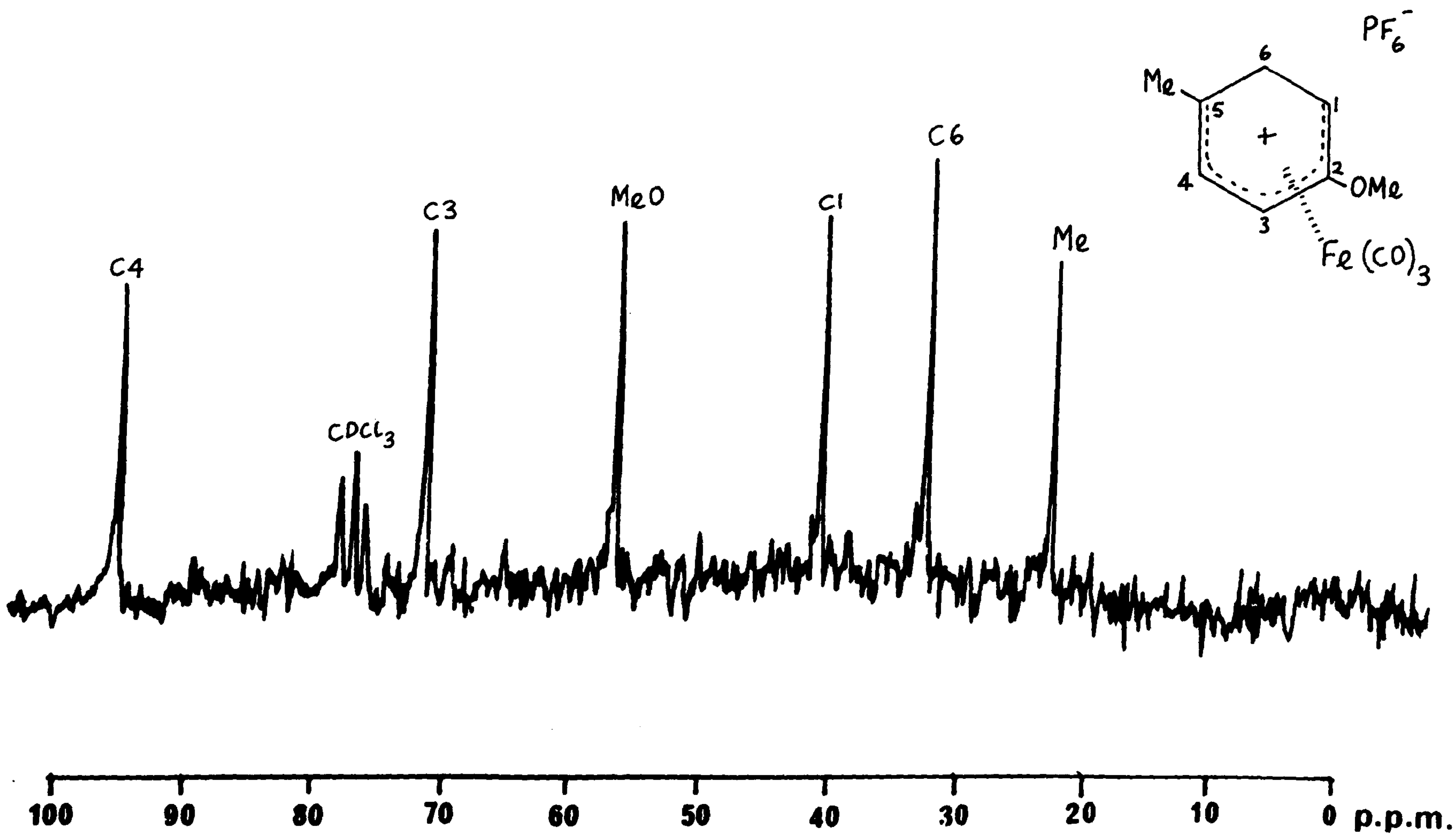


FIG III $^{13}$C NMR SPECTRUM OF COMPLEX (9a)

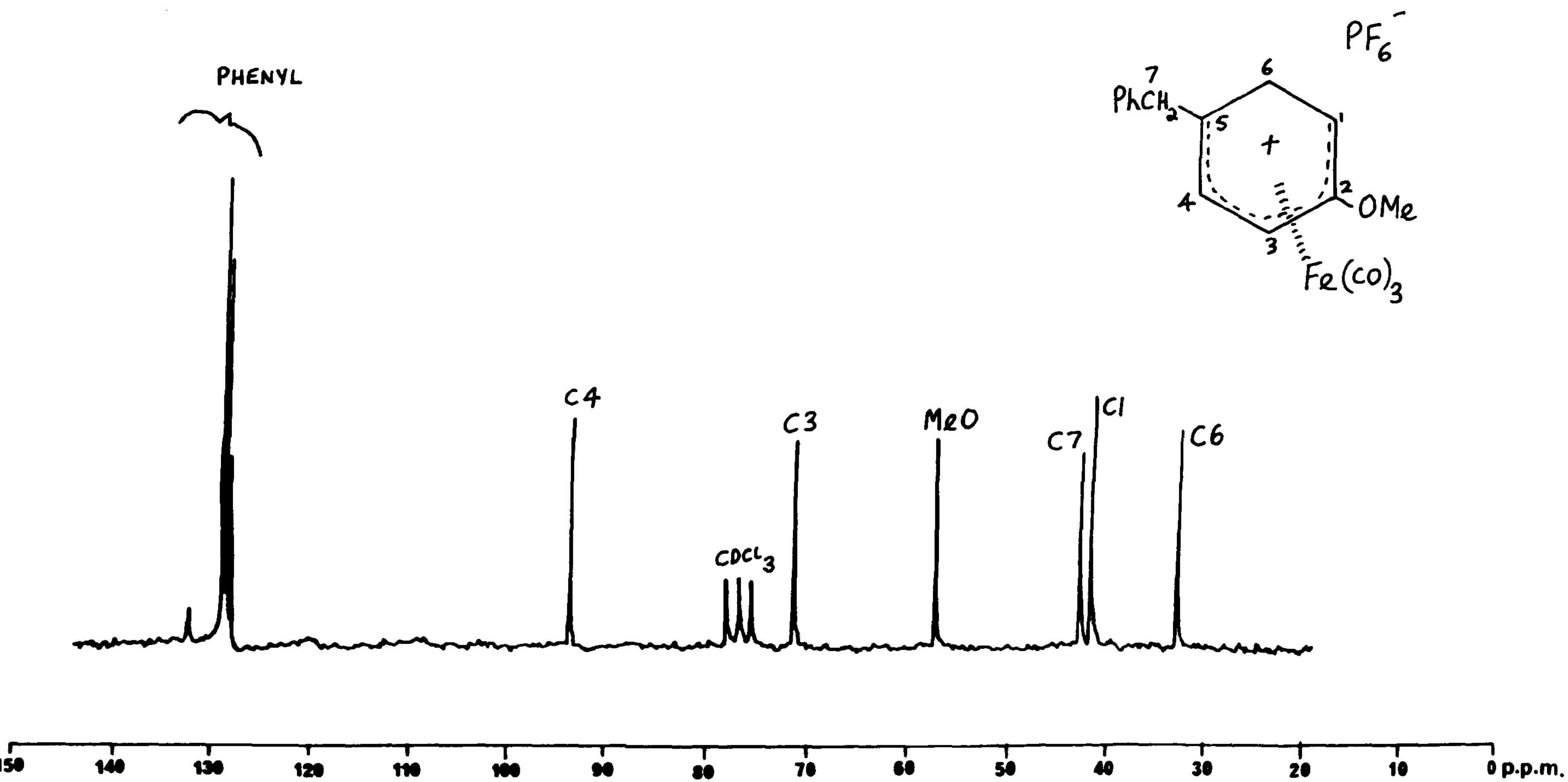


FIG. VI $^{13}$C NMR Spectrum of Complex (12)

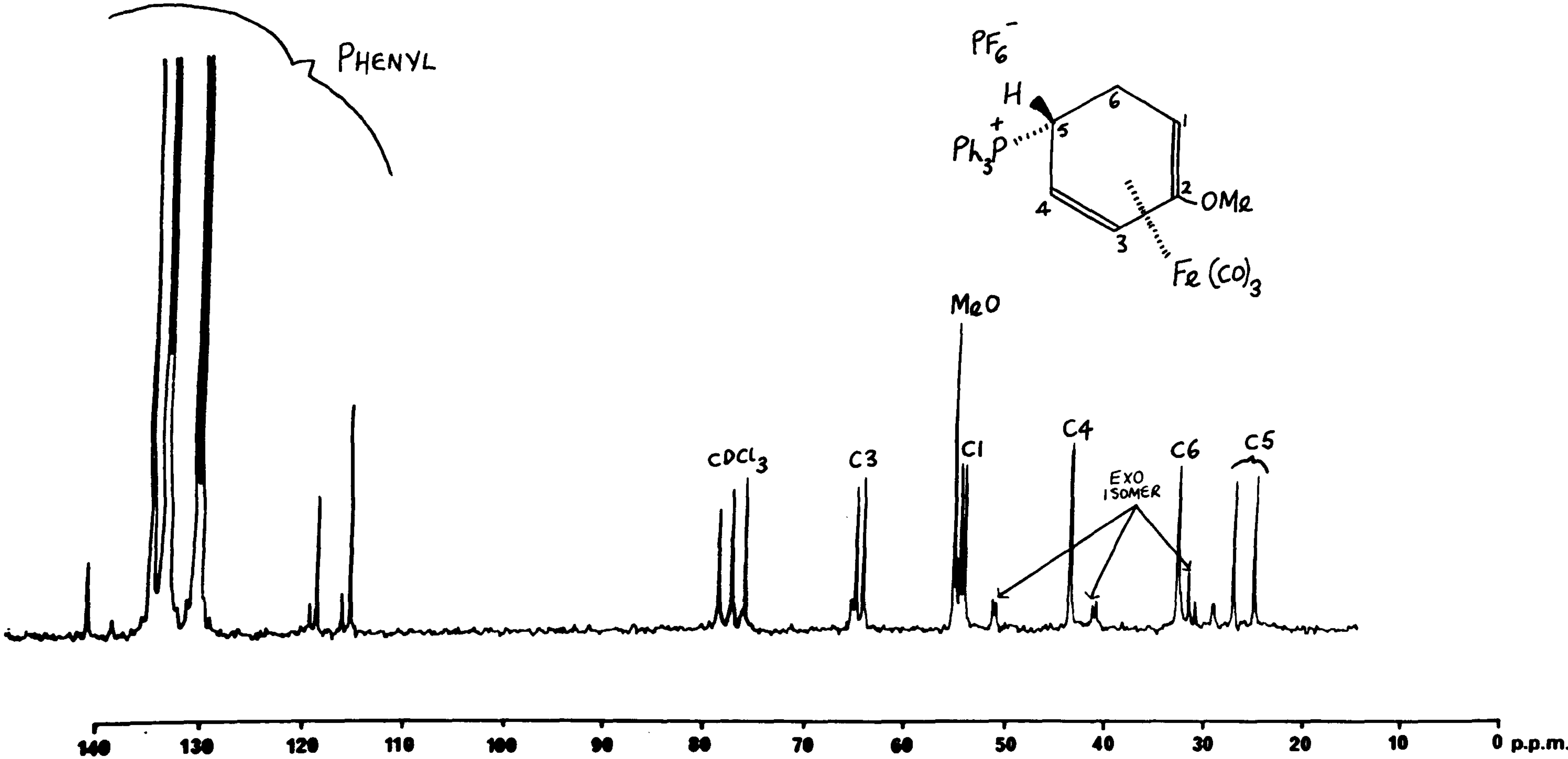
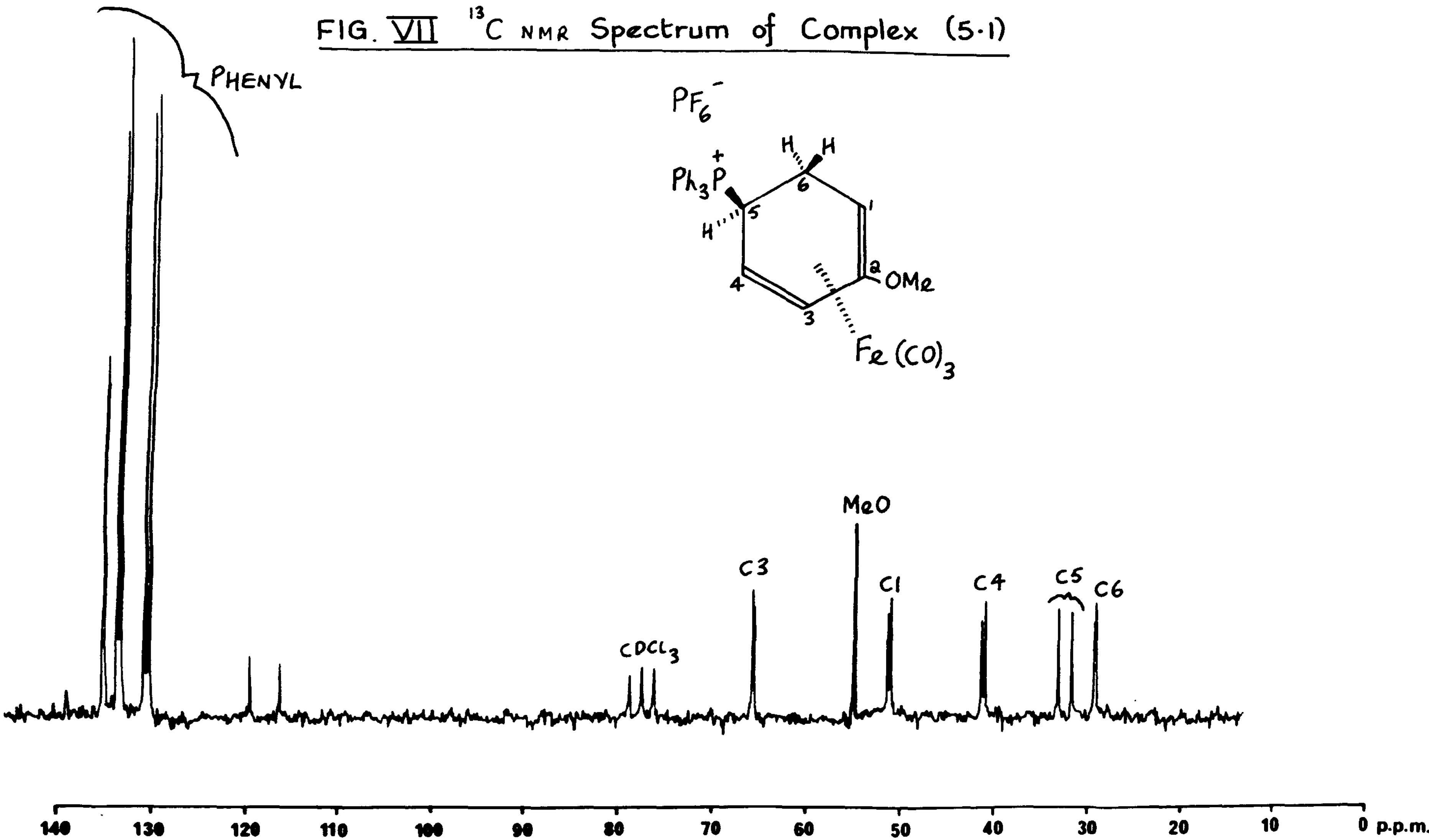


FIG. VII $^{13}C$ NMR Spectrum of Complex (5·1)



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# CHAPTER 4

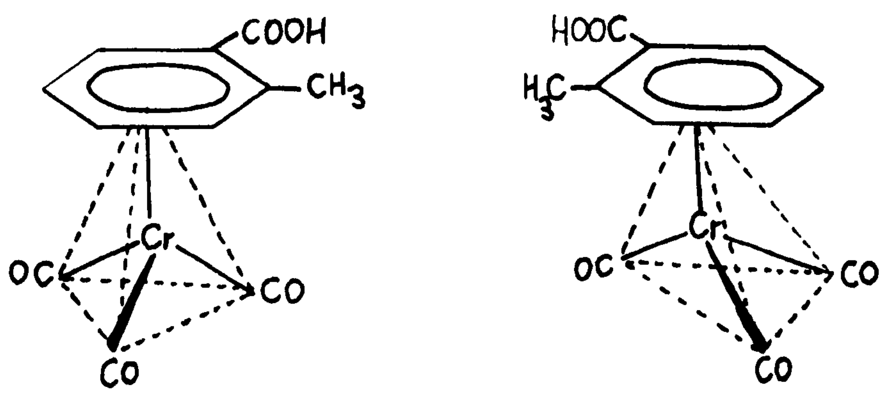
## ASYMMETRIC INDUCTION INVOLVING METAL-CENTRED CHIRAL LIGANDS

### 4.1 Introduction

A variety of chiral organometallic complexes have been prepared by the introduction of a resolved chiral centre into the molecule, thus converting the enantiomers of a racemic mixture into a pair of diastereoisomers. Separation by fractional crystallization or chromatography, followed by elimination of the chiral reagent, gives the resolved enantiomers.

| | | | | |
|---|---|---|---|---|
| A + A<br>(+) (-) | $\xrightarrow{2B(+)}$ | A B + A B<br>(+) (+) (-) (+) | $\xrightarrow{-2B(+)}$ | A + A<br>(+) (-) |
| ENANTIOMERIC MIXTURE | CHIRAL RESOLVING AGENT | SEPARATION | | RESOLVED ENANTIOMERS |

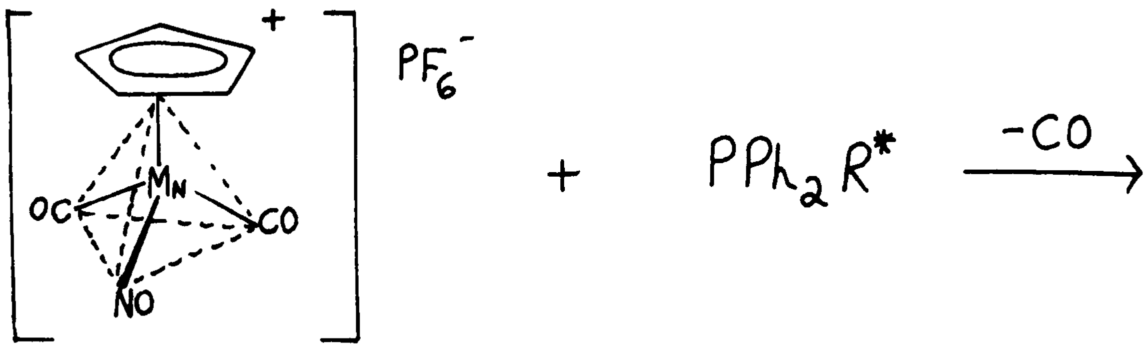
In many of the resolved chiral complexes, chirality has resided in the molecule as a whole. For instance, the enantiomers of tricarbonylchromium-O-toluic acid (1a,b) have been resolved via the diastereoisomeric (S)-(-)-phenylethylamine salts.[1] The optical activity of these complexes is due to the dissymmetry of the ligands; the plane of symmetry that is still present in the free ligands is lost on complexation to $Cr(CO)_3$.



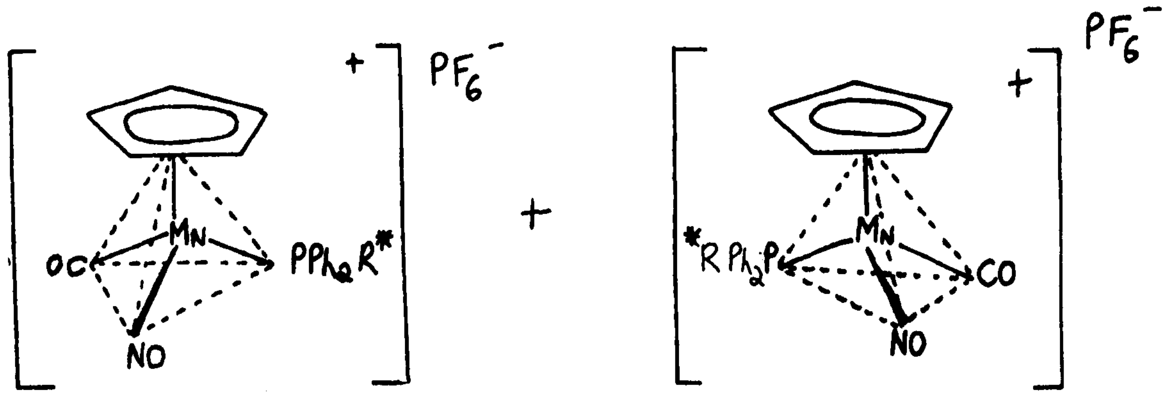

(1a,b)

Conversion of an enantiomeric racemic mixture into a diastereoisomeric pair has also been achieved by the introduction of a chiral ligand containing an asymmetric carbon centre. Examples of chiral ligands include the mentholate ion $OC_{10}H_{19}^-$,[2] and the isocyanide CNCH(Me)Ph.[3]

There are a few examples of complexes which owe their optical activity to the chiral metal centre alone. The reaction of (S)(+)-$PPh_2$[N(Me)CH(Me)Ph] with (2) displaces one of the enantiotopic CO groups to give the diastereoisomeric pair (3a,b) which have been separated by fractional crystallization.[4]



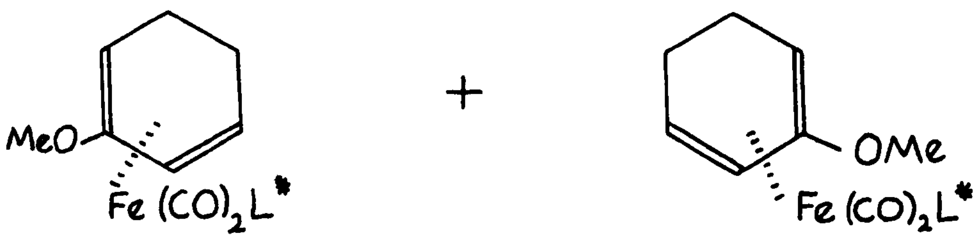

(2)




(3a,b)

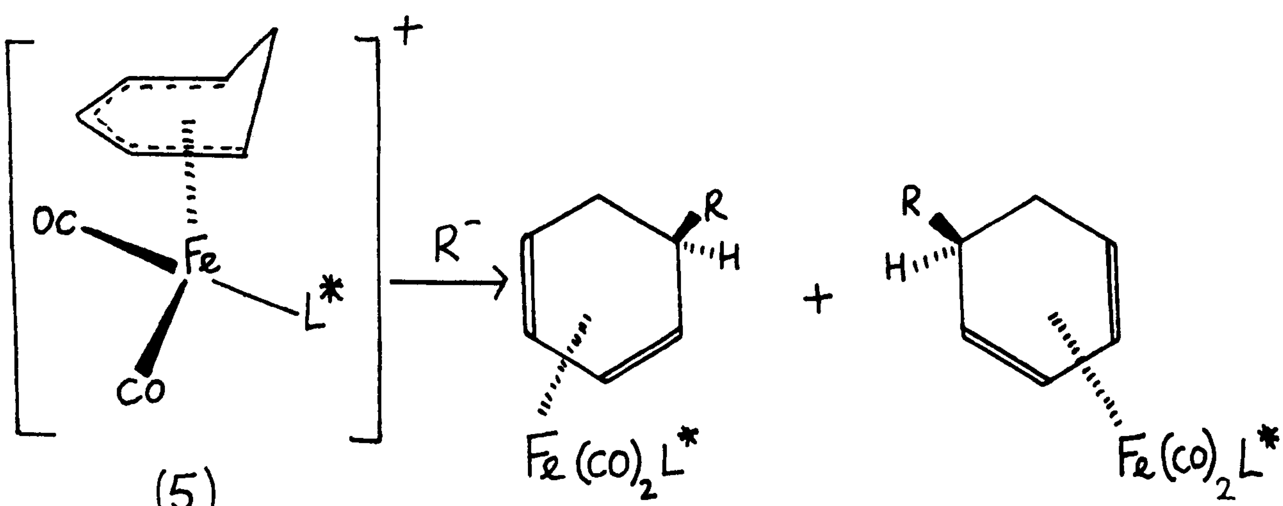
R*═N(Me)CH(Me)Ph

Complexes of the type ($\eta^4$-diene)$Fe(CO)_2L$ and [($\eta^5$-dienyl)-$Fe(CO)_2L]^+$ (L=phosphine,[5,6,7] arsine[6] or isocyanide[8]) may be readily synthesized. Thus incorporation of chiral ligands (L*) presents the possibility of a potential method for the resolution of dia-stereoisomeric pairs in the case of substituted diene complexes such as (4a,b).



(4a,b)

Also in the case of the complex [($\eta^5$-dienyl)$Fe(CO)_2L^*$] (5), because of the presence of the resolved chiral centre, the terminal $sp^2$ carbons are no longer chemically equivalent. Therefore the potential for asymmetric induction exists; attack by an achiral nucleophile may give an enrichment of one diastereoisomer over the other.



(5)

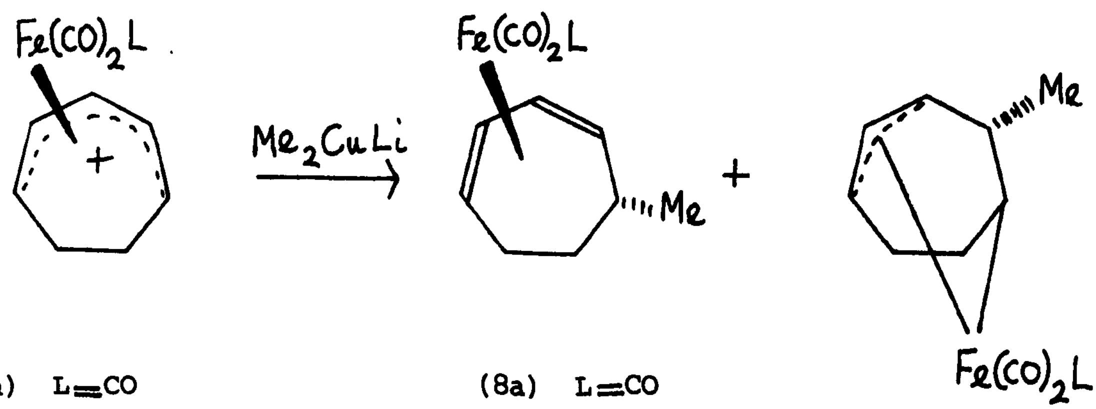
(6a,b)

After separation of the diastereoisomeric pairs, to complete the resolution, the optically active resolving agent L* must be eliminated. When the ligand L* has a resolved chiral centre, as in (6a,b), metal oxidation using $Me_3NO$ [9] may be carried out to give chiral substituted cyclohexadienes. However, when chirality is associated with the molecule as a whole and there is a plane of symmetry present in the free organic ligand, as in (4a,b), L* must be eliminated or transformed without destroying the asymmetry conferred by complexation. The displacement of L* (where L* = chiral phosphine) to give the $Fe(CO)_3$ analogue, might be carried out by carbonylation, possibly in the presence of an alkylating agent to remove the phosphine as a quaternary phosphonium salt.

The auxiliary ligands present in a complex exert an influence on the reactivity through steric effects and through differences in their $\sigma$ donor and $\pi$ acceptor capabilities. For instance, the substitution of a carbonyl group by triphenylphosphine leads to a two-fold decrease in the rate of nucleophilic attack on $[(\eta^5\text{-dienyl})Fe(CO)_2L]^+$.[10] $PPh_3$ is more electron donating than CO (better $\sigma$ donor, poorer $\pi$ acceptor), resulting in a smaller effective positive charge on the dienyl ring, making it less susceptible to nucleophilic attack. Substitution with a weaker $\pi$ acceptor leads to increased back donation from the metal to CO, the Fe—C bond becomes stronger and the C≡O bond weaker, thus causing a drop in the CO vibrational frequency observed by i.r. spectroscopy. However, from X-ray evidence, the CO bond lengths are not appreciably altered by substitution with a weaker $\pi$

acceptor. Surprisingly, the $^{13}$C n.m.r. spectra of (4a,b) and related complexes (where L=$PPh_3$) have been interpreted in terms of the depopulation of the diene LUMO as the $\pi$ acceptor strength of L decreased rather than the expected enhanced population of the orbital.[11]

From the fragmentary studies carried out, it appears that the reactivity of ($\eta^4$-diene)$Fe(CO)_2L$ complexes can be significantly different from $Fe(CO)_3$ analogues. For instance, Friedel-Crafts acylation of (chd)$Fe(CO)_3$ occurs in 45% yield, but by the use of the less electron-withdrawing $Fe(CO)_2PPh_3$, the product is formed in 75% yield.[12] The position of nucleophilic attack at ($\eta^5$-cycloheptadienyl)$Fe(CO)_2PPh_3{}^+$ (7a) is modified relative to its $Fe(CO)_3$ analogue (7b). Addition of nucleophiles to (7a) results in a mixture of product from attack at C1/5 or C-2 to give (8a) and (9a).[6] Thus, treatment of (7b) with lithium dimethylcuprate gives exclusively (8b) in 85-90%.[13]




(7a) L=CO
(7b) L=$PPh_3$

(8a) L=CO
(8b) L=$PPh_3$

(9a) L=CO

Several routes exist for the preparation of [($\eta^4$-diene)$Fe(CO)_2$-$PPh_3$] complexes. U.v. photolysis or the thermal reaction of (chd)$Fe(CO)_3$

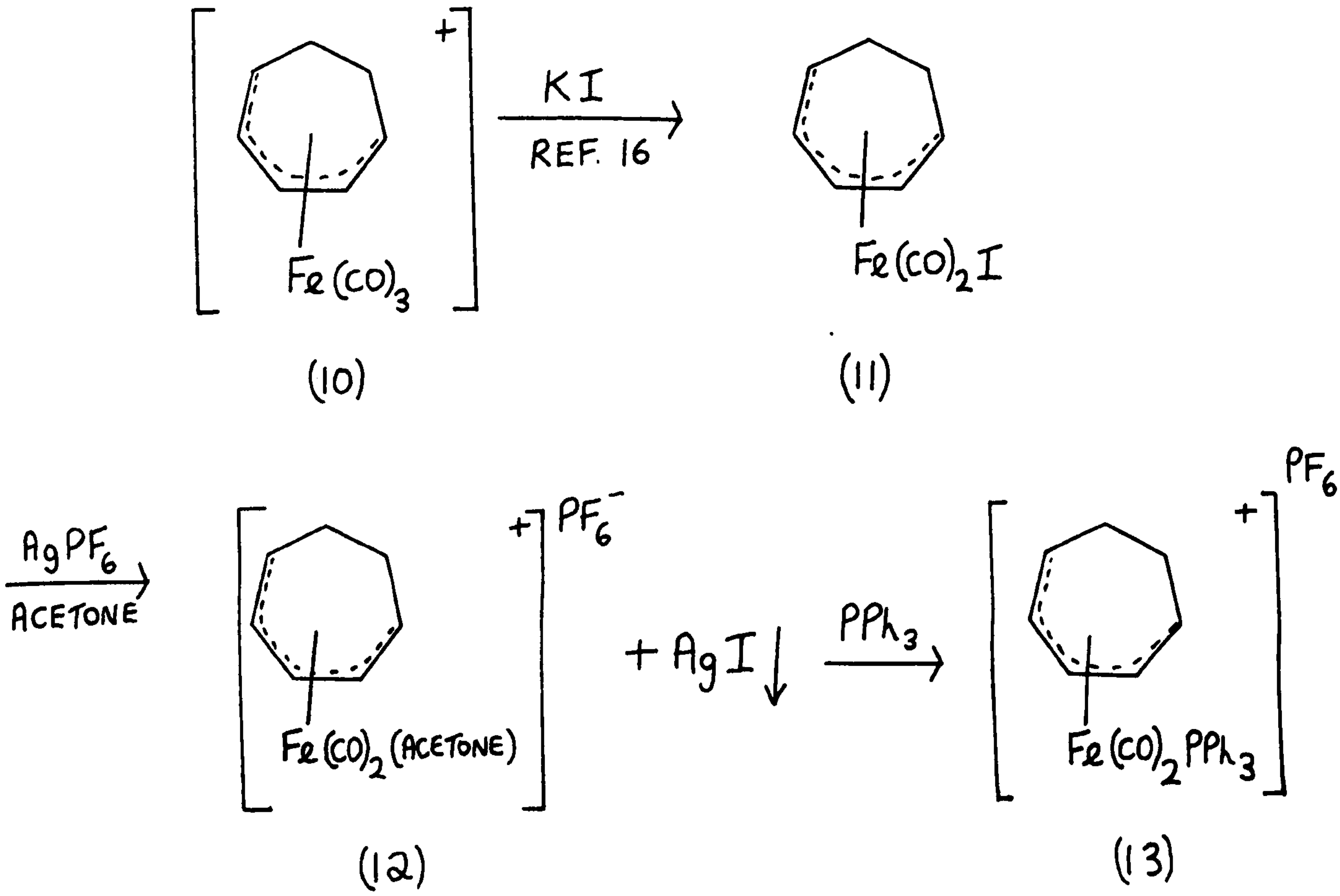
with $PPh_3$ gives (chd)$Fe(CO)_2PPh_3$ in low yield, together with some (chd)$Fe(CO)(PPh_3)_2$.[5] In contrast to the six-membered ring system (cycloocta-1,3-diene)$Fe(CO)_3$ reacts with excess $PPh_3$ to form $Fe(CO)_3(PPh_3)_2$.[14] The olefin is readily displaced under mild conditions by $PPh_3$, whilst cyclohexa-1,3-diene and cyclohepta-1,3-diene complexes are generally inert to olefin displacement.

$[(\eta^5$-cycloheptadienyl$)Fe(CO)_2PPh_3]^+$ has also been prepared by nucleophilic displacement of iodide by $PPh_3$ from the complex $[(\eta^5$-cycloheptadienyl$)Fe(CO)_2I]$.[6] Recently, (chd)$Fe(CO)_2PPh_3$ has been synthesized in good yields via the exchange reaction with $[(\eta^4$-benzylideneacetone$)Fe(CO)_2L]$ and cyclohexadiene.[7]

## 4.2 Results and Discussion

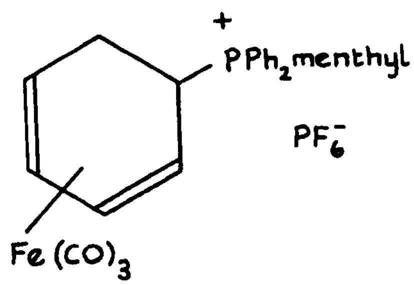
### 4.2.1 $[(\eta^5$-dienyl$)Fe(CO)_2PPh_2R^*]^+$ complexes via $[(\eta^5$-dienyl$)Fe(CO)_2I]$

Lewis et al have shown that the direct reaction of $PPh_3$ with $[(\eta^5$-cycloheptadienyl$)Fe(CO)_3]^+$ (10) leads to nucleophilic attack on the dienyl system in preference to substitution at the metal.[15] However, $[(\eta^5$-cycloheptadienyl$)Fe(CO)_2PPh_3]^+$ (13) has been prepared by utilising the weaker nucleophilicity of iodide for the dienyl fragment and its greater nucleophilicity for the metal. The addition of an acetone solution of silver(I)hexafluorophosphate to a solution of the neutral iodide complex (11) in dichloromethane generates the intermediate acetone adduct (12), from which the weakly bound acetone may readily be displaced by the addition of $PPh_3$.[6]




This represents a route to the formation of $[(\eta^5$-cyclohexadienyl$)Fe(CO)_2L^*]^+$, where L* is a chiral phosphine. We have found that iodide is displaced from $(\eta^5$-cyclohexadienyl$)Fe(CO)_2I$ ($\nu$ CO 2037,1997 $cm^{-1}$ in $CH_2Cl_2$) on the addition of silver(I) hexafluorophosphate in acetone to give some silver(I) iodide precipitate. The addition of (+)$PPh_2$menthyl yielded a yellow solid on precipitation with diethyl ether, showing two carbonyl bands of equal intensity at 2046 and 2004 $cm^{-1}$. The wavenumbers were ca. 50 $cm^{-1}$ lower than for the $Fe(CO)_3$ analogue, and consistent with the poor $\pi$ acceptor capabilities of the phosphine ligand.

However, the $^{31}P$ n.m.r. spectrum clearly showed that the yellow solid contained less than 10% of the expected product (63.6 p.p.m., see section 4.2.3), the major complex had a chemical shift further up field than expected at 7.95 p.p.m. In addition the phosphonium adduct (14) was also present (ca. 20%, 34.2 and 32.4 p.p.m., see Chapter 2.2.2).



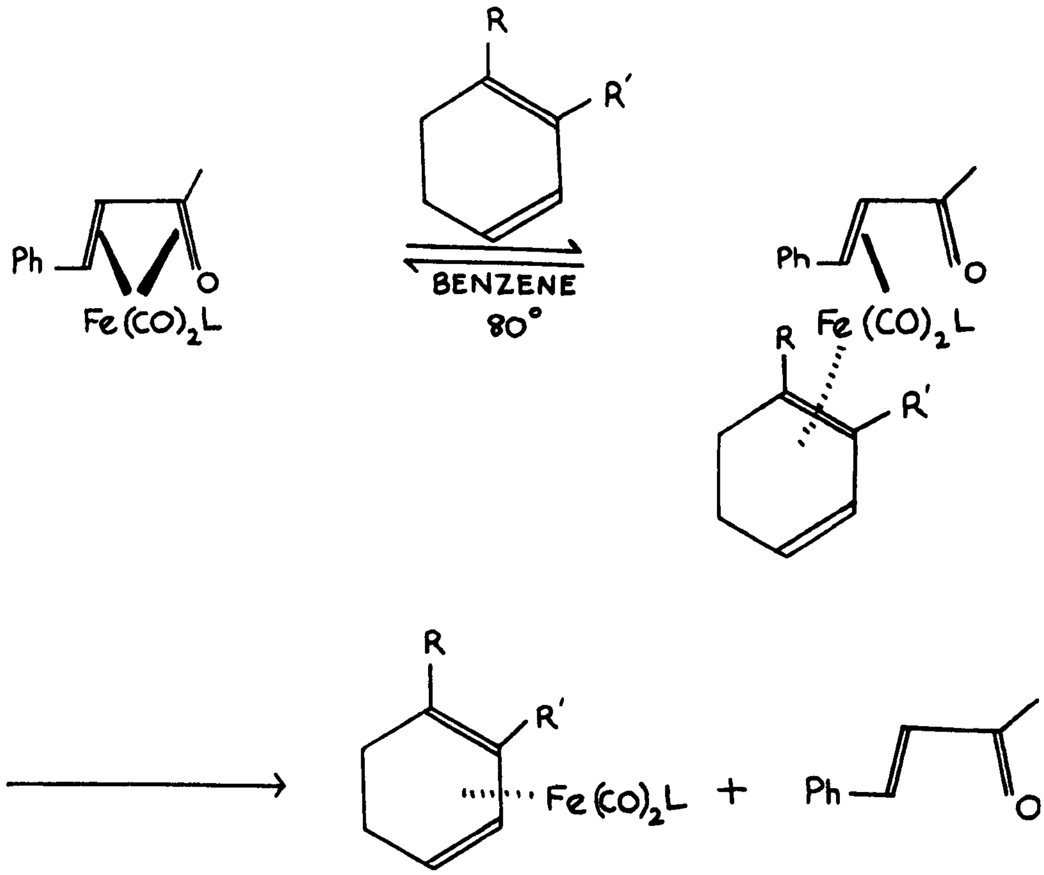

(14)

The $^{13}C$ spectrum showed that the major complex present did not contain an olefinic ligand indicating that (cyclohexadienyl)Fe-$(CO)_2I$ undergoes decomposition rather than iodide displacement, so that very little of the intermediate acetone adduct (cyclohexadienyl)Fe$(CO)_2$(acetone) is formed. Alternatively, the latter may be formed but readily decompose, due to its instability compared with the cycloheptadienyl adduct (12). The major product formed may be a silver phophine complex. Similar results were obtained using (S)(+)$PPh_2CH_2CH(Me)Et$.

4.2.2 <u>[($\eta^4$-diene)Fe$(CO)_2PPh_2R^*$] via [(bda)Fe$(CO)_2PPh_2R^*$]</u>

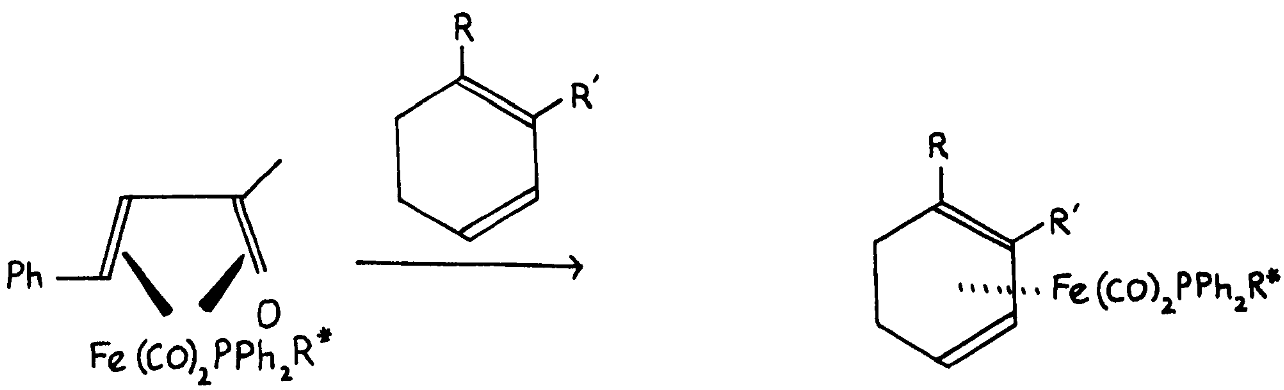
Labile ($\eta^4$-heterodiene)Fe$(CO)_3$ complexes have been used as Fe$(CO)_3$ donors in the synthesis of ($\eta^4$-diene)Fe$(CO)_3$ compounds,[17] thereby providing an alternative to the high temperatures (>100°C) or u.v. photolysis needed in the use of Fe$(CO)_5$. Recently, related

[($\eta^4$-benzylideneacetone)$Fe(CO)_2L$] complexes ($L = PPh_3$, $P(OPh)_3$) have been prepared by the irradiation of $Fe(CO)_4L$ in the presence of benzylideneacetone, and have been shown to undergo exchange reactions with cyclohexa-1,3-diene to give (chd)$Fe(CO)_2L$.[7] The stereochemical outcome of the exchange reaction is determined by the first approach of the diene to [(bda)-$Fe(CO)_2L$]. Displacement is thought to proceed by dechelation of the ketone group and partial co-ordination to the diene[18] (Scheme I).




SCHEME I

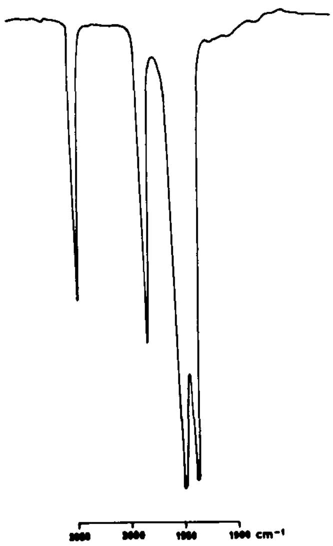
Since the exchange reaction occurs with the retention of configuration, the introduction of a chiral phosphine to give [(bda)Fe(CO)$_2$PPh$_2$R*] (15) provides a possible route for the preparation of optically active 1,3-diene complexes. Separation of the diastereoisomeric pair (15), followed by bda displacement with a substituted 1,3-diene complex should yield one of the diastereoisomers of (16) in a pure form, or the diastereoisomeric pair of (16) which may be separated after exchange with the unseparated pair of (15).

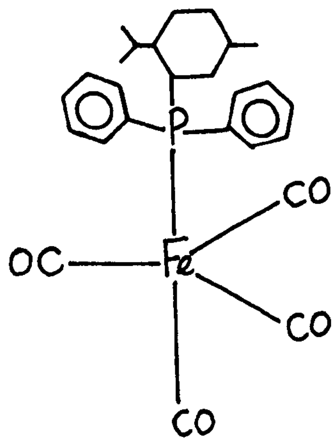



SEPARATED DIASTEREOISOMER (15)

ENRICHMENT OF ONE DIASTEREOISOMER (16)

We have found that CoCl$_2$ - catalysed substitution of Fe(CO)$_5$ [19] with chiral phosphine L* [L* = (+)PPh$_2$(C$_{10}$H$_{19}$= menthyl) and (S)(+)-PPh$_2$CH$_2$CH(Me)Et] gives Fe(CO)$_4$L* complexes (17) and (18) respectively. The i.r. spectrum of complex (17) shows <u>four</u> carbonyl stretching bands at 2042, 1977, 1947 and 1937 cm$^{-1}$ (in hexane). Similar values are recorded for complex (18) (2051, 1987, 1954 and 1947 cm$^{-1}$).






(17)

FIG. I $\nu$(CO) Spectrum of (17) in Hexane

However, when L = $PPh_3$ only three carbonyl peaks are observed (2052, 1978, 1940 $cm^{-1}$; data from ref.[19])

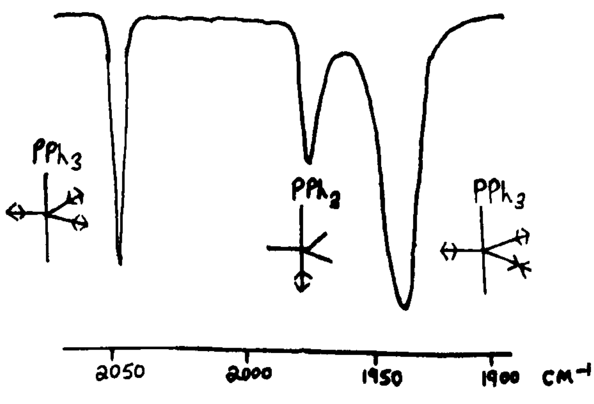
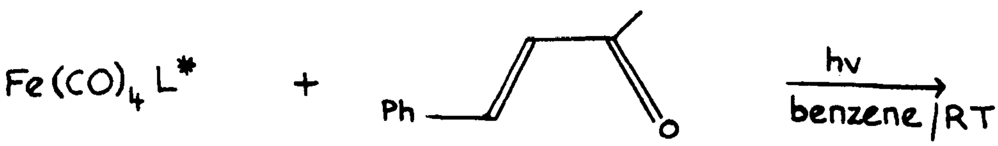


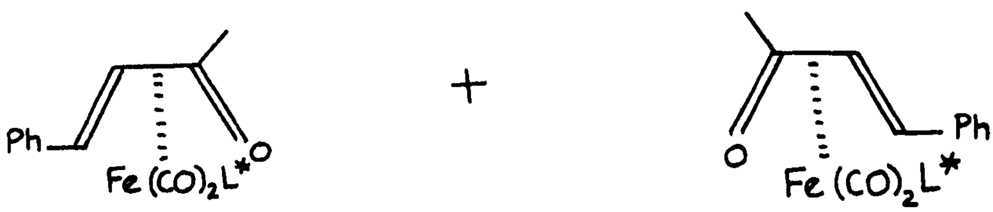

FIG. II $\nu$ (CO) Spectrum of $Fe(CO)_4PPh_3$ in $CHCl_3$

The presence of an additional carbonyl stretching band in the i.r. spectra of complexes (17) and (18) may reflect the non-degeneracy of the asymmetric CO stretching frequencies in the case where L contains an asymmetric centre. Complexes of the type $Fe(CO)_4L$ are known to adopt a trigonal bipyramid structure in the solid state, where L occupies the axial position. However, the $^{13}C$ n.m.r. spectra of (17) and (18) (see Table 3) shows a single phosphorus-coupled carbonyl resonance at 212 p.p.m., indicating the fluctional behaviour of these molecules in solution.

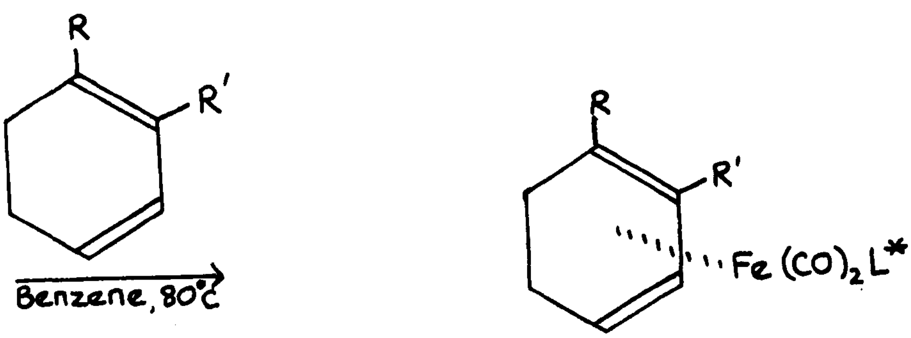
Irradiation of (17) or (18) in the presence of benzylideneacetone leads to the elimination of CO and the formation of the diastereoisomeric pairs (20a,b) and (21a,b).




(17) (+)$PPh_2(C_{10}H_{19})$
(18) (+)(S)$PPh_2(CH_2CH(Me)Et)$



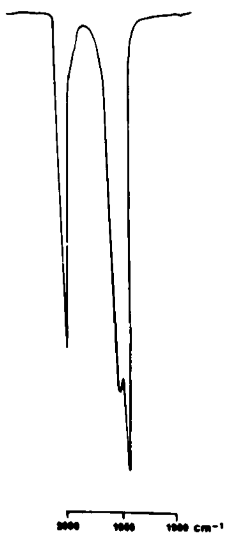

(20a,b) (+)$PPh_2(C_{10}H_{19})$
(21a,b) (S)(+)$PPh_2(CH_2CH(Me)Et)$

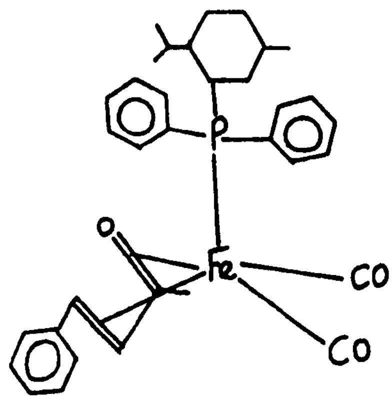



R=R'=H

(22) (+)$PPh_2(C_{10}H_{19})$
(23) (S)(+)$PPh_2(CH_2CH(Me)Et)$

As characteristic for enones complexed to a transition metal, [(bda)Fe(CO)$_2$L*] exhibits no ketonic absorption in the range 1900-1600 cm$^{-1}$. <u>Three</u> carbonyl stretching bands are observed in the i.r. spectra of complex (20a,b) (1997, 1947 and 1939 cm$^{-1}$) and complex (21a,b) (1997, 1949 and 1941 cm$^{-1}$). When L is an achiral ligand such as PPh$_3$, only <u>two</u> carbonyl peaks are present (1999 and 1939 cm$^{-1}$).[7] From crystal structure determinations of related complexes such as ($\eta^4$-bda)Fe(CO)$_2$PPhMe$_2$ [20] and (cinnemaldehyde)Fe(CO)$_2$PPh$_3$,[21] diastereoisomers (20a,b) and (21a,b) would be expected to have a distorted square pyramidal structure, with the chiral phosphine ligand occupying the axial site.






(20a,b)

ONLY ONE DIASTEREOISOMER DRAWN

<u>FIG. III</u> <u>$\nu$(CO) Spectrum of (20a,b) in Hexane</u>

The additional carbonyl stretching bands in the i.r. spectra of complexes (20a,b) and (21a,b) are not due to the presence of diastereoisomers (vide infra); the appearance of three bands must be attributed to the internal rotation of the chiral phosphine resulting in the formation of rotameric isomers.

The $^{31}P$ n.m.r. spectrum of (21a,b) shows that the diastereo-isomers exist in a nearly equimolar ratio.

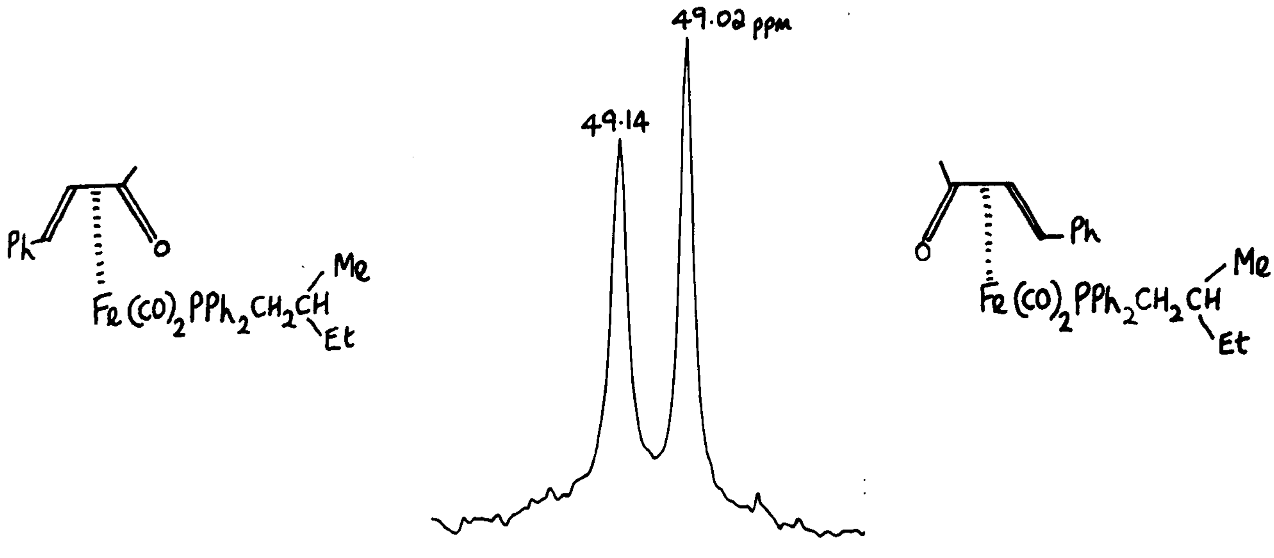



FIG. IV $^{31}P$ n.m.r. of Diastereoisomers (21a,b)
(configurations are arbitrarily drawn)

Attempts to separate diastereoisomers (21a,b) were unsuccessful; however, racemic (21a,b) underwent bda displacement in the presence of cyclohexa-1,3-diene to give (23);R=R$'$=H. The $^{31}P$ n.m.r. spectrum of diastereoisomers (20a,b) gave a single coincident resonance at 59.02 p.p.m. However, preparative thin layer chromatography using dichloromethane/light petroleum 70/30 as eluant, gave two yellow bands of equal intensity, with identical carbonyl stretching bands of 1997, 1947 and 1939 $cm^{-1}$ (in hexane). Unfortunately, both bands were found to decompose partially to give free phosphine and benzylideneacetone, consequently $^{31}P$, $^{13}C$ n.m.r. spectra and pure samples for CHN analysis were not obtained. The separated bands were, however, reacted <u>independently</u> with cyclohexa-1,3-diene to give (cyclohexadiene)$Fe(CO)_2$-$PPh_2$menthyl (22), implying that they were the separated diastereoisomers (20a) and (20b).

Thus the preparation of complexes (22) and (23) provides a synthetically useful route to $[(\eta^4\text{-diene})Fe(CO)_2L^*]$ complexes and via them to $[(\eta^5\text{-dienyl})Fe(CO)_2L^*]^+$ salts.

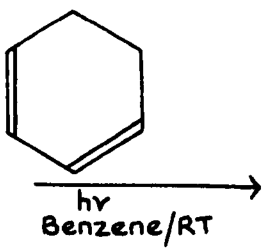
4.2.3 <u>[(chd)Fe(CO)$_2$L*] via Photolysis of Fe(CO)$_4$L* and chd</u>

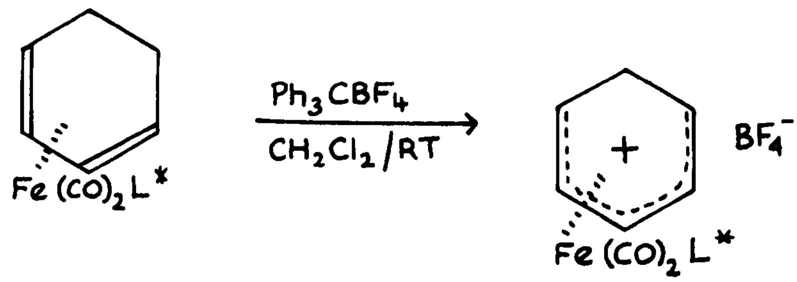
Although the u.v. photolysis of (chd)$Fe(CO)_3$ with $PPh_3$ gives (chd)$Fe(CO)_2PPh_3$,[5] our attempts to prepare (chd)$Fe(CO)_2L^*$ (L* = (+)$PPh_2$menthyl) (22) or its 2-MeO derivative by the same procedure resulted in a mixture of products in poor yields. However, we found that photolysis of $Fe(CO)_4L^*$ (L* = (+)$PPh_2$menthyl, (S)-(+)$PPh_2CH_2CH$(Me)Et, $PPh_2N$(Me)CH(Me)Ph) complexes (17), (18) and (19) in the presence of cyclohexa-1,3-diene produces (chd)$Fe(CO)_2L^*$ complexes (22), (23) and (24). Hydride abstraction on (22) and (23) using $Ph_3CBF_4$ gives the dienyl salts (25) and (26). (See following page).

$$Fe(CO)_5 + L^* \xrightarrow[\text{Toluene } 110^\circ]{CoCl_2 \cdot 2H_2O} Fe(CO)_4L^*$$

<u>L*</u>

(17) (+)$PPh_2C_{10}H_{19}$
(18) (+)$PPh_2CH_2CH(Me)Et$
(19) (+)$PPh_2N(Me)CH(Me)Ph$



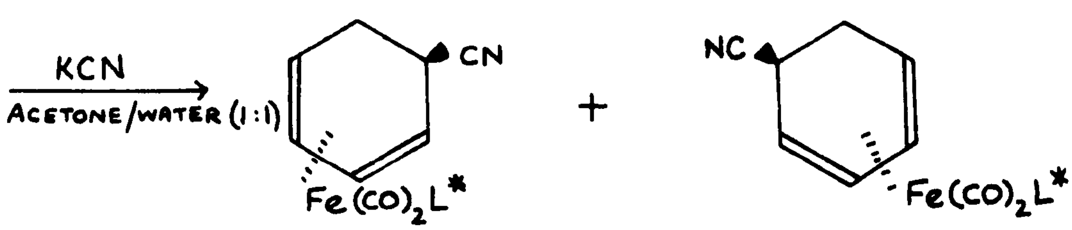




<u>L*</u>

(22) (+)$PPh_2C_{10}H_{19}$
(23) (+)$PPh_2CH_2CH(Me)Et$
(24) (+)$PPh_2N(Me)CH(Me)Ph$

<u>L*</u>

(25) (+)$PPh_2C_{10}H_{19}$
(26) (+)$PPh_2CH_2CH(Me)Et$




| <u>L*</u> | | <u>RATIO OF ISOMERS</u> |
|---|---|---|
| (27a,b) | (+)$PPh_2C_{10}H_{19}$ | 2 : 1 |
| (28a,b) | (+)$PPh_2CH_2CH(Me)Et$ | 1 : 1 |

Although $Fe(CO)_4[PPh_2N(Me)CH(Me)Ph]$ (19) and ($\eta^4$-cyclohexadiene)-$Fe(CO)_2[PPh_2N(Me)CH(Me)Ph]$ (24) can be easily prepared, attempts to isolate the dienyl salt were unsuccessful. Treatment of (24) with $Ph_3CBF_4$ in $CH_2Cl_2$ gave the expected carbonyl stretching bands of 2039 and 1998 $cm^{-1}$. However, the dienyl salt was found to be unstable in solution; decomposition resulted in the liberation of free phosphine, which subsequently underwent nucleophilic addition to the unreacted dienyl cation to generate the phosphonium adduct.

The X-ray crystal structure of ($\eta^4$-cyclohexadiene)$Fe(CO_2)PPh_3$ (29) has been determined by Pearson.[11] The overall molecular geometry closely resembles that of the tricarbonyl analogue, with the phosphine ligand occupying a basal position. However, Pearson found that the $^{13}C$ n.m.r. spectrum of (29) was completely symmetrical, with no change being observed down to -70°C. Thus, the molecule exhibits a facile diene rotation in solution. Complexes (22) and (23) probably adopt a similar conformation to complex (29) in the solid state and are probably fluxional in solution. However, the presence of a resolved chiral centre on the phosphine results in the chemical non-equivalence of the diene carbons even in the presence of rapid diene rotation. Consequently, the six carbon atoms are observed as separated resonances in the $^{13}C$ n.m.r. spectra (Table 1).

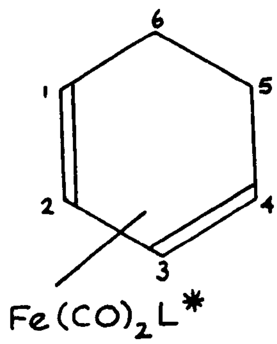



TABLE 1 $^{13}$C n.m.r. Data for (chd)Fe(CO)$_2$L Complexes

| COMPLEX L | C2/3 | C1/4 | C5/6 |
|---|---|---|---|
| L = CO | 85.5 | 62.5 | 24.5 |
| L = $PPh_3$ [a] | 84.6 | 61.0 (3.7)[b] | 24.7 |
| (22) L* = (+)$PPh_2$menthyl (see FIG. V) | 86.5, 85.6 | 61.0, 60.5 (2.0) (2.9) | 24.9, 24.4 |
| (23) L* = (+)$PPh_2CH_2CH$(Me)Et | 84.8, 84.7 | 61.1, 60.5 (3.9) | 24.9, 24.6 |

a data from ref[11]
b spin-spin couplings (Jp-c) in Hz

Due to the poor π acceptor capabilities of the phosphine ligand, it would be expected that the diene carbon resonances would be shifted to a slightly higher field, indicating a small increase in electron density on the diene π orbitals or at the metal.[11] However, this effect is not clearly found at Table 1. Small spin-spin couplings are observed between C-1, C-4 and phosphorus, whilst the central carbon atoms C-2 and C-3 show no coupling. This effect has also been observed for (chd)Fe(CO)$_2$PPh$_3$,[11] and it is suggested that it is due to a non-zero contact term because in six membered ring complexes there appears to be a small amount of s character at the terminal carbon atoms. However, the JP-C coupling is not observed in acyclic or analogous ring systems indicating that the constraint on the diene due to ring size induces a slight rehybridisation at the terminal carbon which is reflected in the n.m.r. spectrum. The carbonyl stretching frequencies of complexes (22) and (23) show the expected shift to a lower wavenumber; complex (22), for example, has carbonyl stretching bands at 1978 and 1975 $cm^{-1}$, due to the weaker $\pi$ acceptor capabilities of L*.

The $^{13}C$ n.m.r. spectra of complexes (25) and (26) [($\eta^5$-cyclohexadienyl)$Fe(CO)_2L^*]^+$ also show individual resonances for all six carbon atoms of the dienyl system (Table 2).

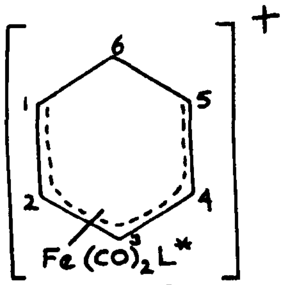


TABLE 2 $^{13}C$ n.m.r. Data for [($\eta$-cyclohexadienyl)$Fe(CO)_2L^*]^+$ Complexes

| COMPLEX L+ | C1/5 | C2/4 | C3 | C6 |
|---|---|---|---|---|
| L=CO | 65.4[a] | 103.2 | 89.9 | 24.7 |
| (25) L*=(+)$PPh_2$menthyl (see FIG. VI) | 60.6<br>57.79 | 101.9<br>100.8 | 89.0 | 23.6 |
| (26) L*=(+)$PPh_2CH_2CH(Me)Et$ | 58.7[b]<br>58.3 | 100.8<br>100.5 | 88.4 | 23.7 |

a data from ref 23
b in $CH_2Cl_2/CDCl_3$

The dienyl carbon resonance of complexes (25) and (26) are shifted to a higher field compared to ($\eta^5$-cyclohexadienyl)$Fe(CO)_3$, due to the decrease in the $\pi$ acceptor strength of $PPh_2R^*$ resulting in a smaller effective positive charge on the dienyl ring. The chemical shifts of complex (26) ($L^* = PPh_2CH_2CH(Me)Et$) are slightly further up-field than complex (25) ($L^* = PPh_2$menthyl) consistent with the slightly greater electron donating capacity of primary alkyl groups compared with secondary alkyl groups.[24] Nucleophilic attack on (25) with $^{-}CN$ was found to proceed with some degree of asymmetric induction to yield the 5-exo-cyano-complex (27a,b) which $^{13}C$ (figure VII) and $^{31}P$ n.m.r. studies show clearly to exist as a mixture of two diastereoisomers present in the ratio of ca. 2:1.

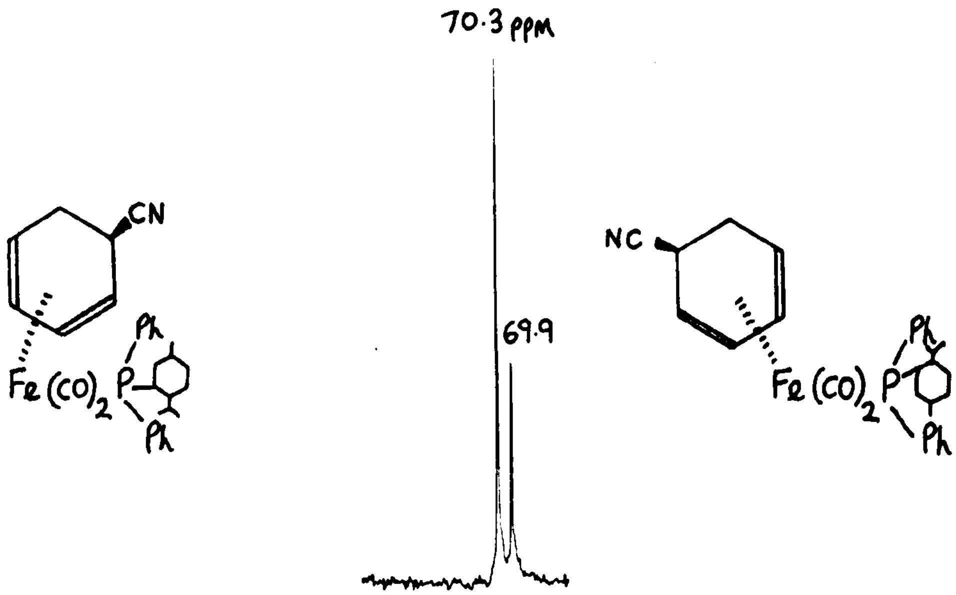
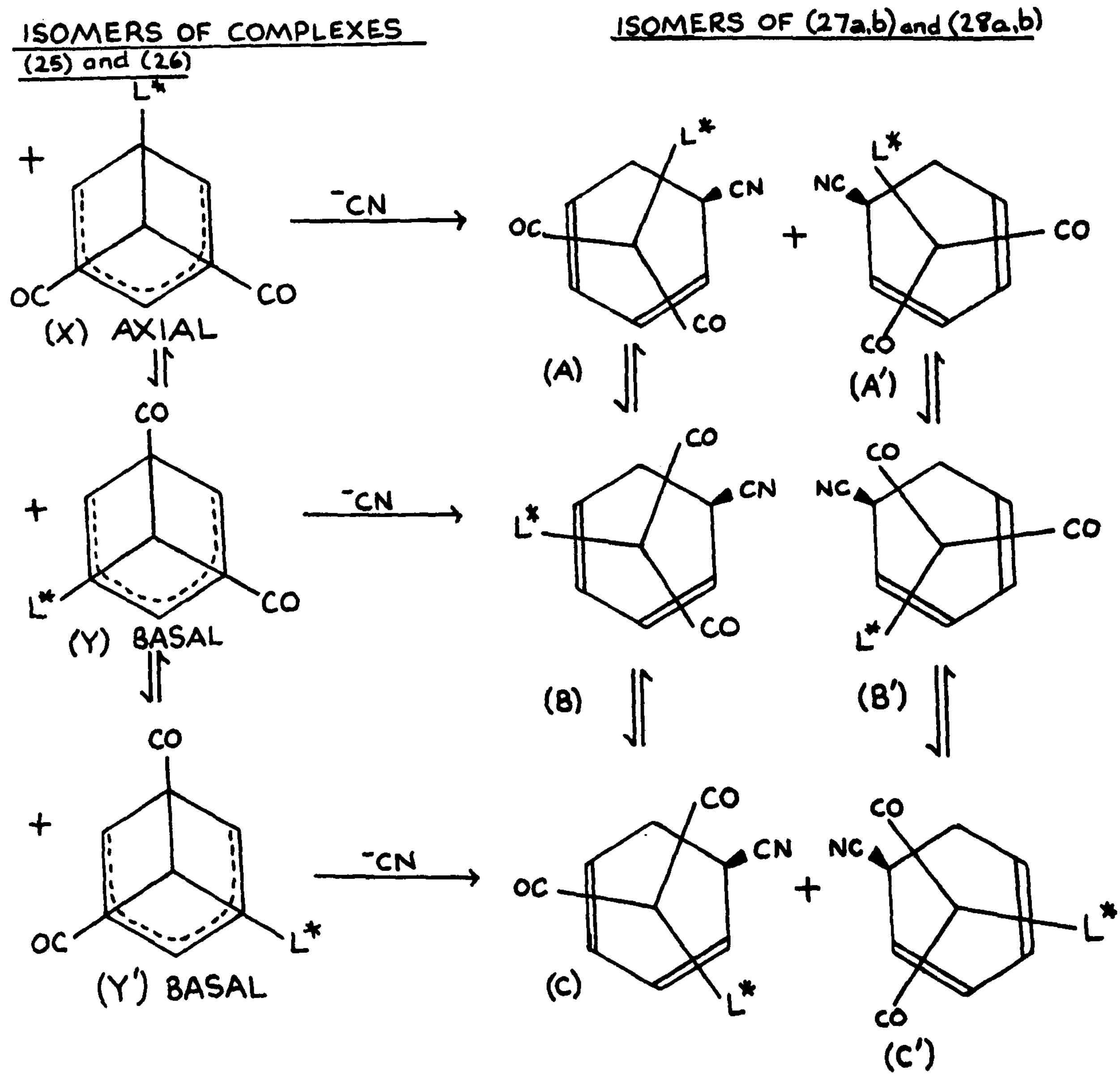



FIG VIII $^{31}P$ n.m.r. spectrum of diastereoisomers (27a,b)
(configurations drawn are arbitrary)

$^{31}P$ n.m.r. analysis of the crude material before chromatography showed the same diastereoisomeric excess of the pure product after chromatography. Nucleophilic attack on (26) with $^{-}CN$ gave (28a,b), which were found to exist as an equimolar mixture of diastereoisomers. A scheme which summarises the possible isomeric structures is shown below (Scheme I). On the basis of a distorted square pyramidal structure, the $[(\text{dienyl})Fe(CO)_2L^*]^+$ salt may adopt either the axial structure (X) or the basal structure which in the case where L* possesses a resolved centre exists as the pair of diastereoisomers (Y) and ($Y^1$). Interconversion is easily accomplished by dienyl rotation, thus accounting for the single $^{31}P$ resonance at room temperature. To our knowledge, no crystallographic studies have established the solid state structure of $[(\text{dienyl})Fe(CO)_2L]^+$ complexes. Thus, in the axial structure (X), the terminal $sp^2$ carbons of the dienyl system are rendered non-equivalent by the resolved carbon of the chiral phosphine, whereas in the pair (Y)($Y^1$) non-equivalence is a consequence of both the resolved carbon centre and the position of the phosphine itself.



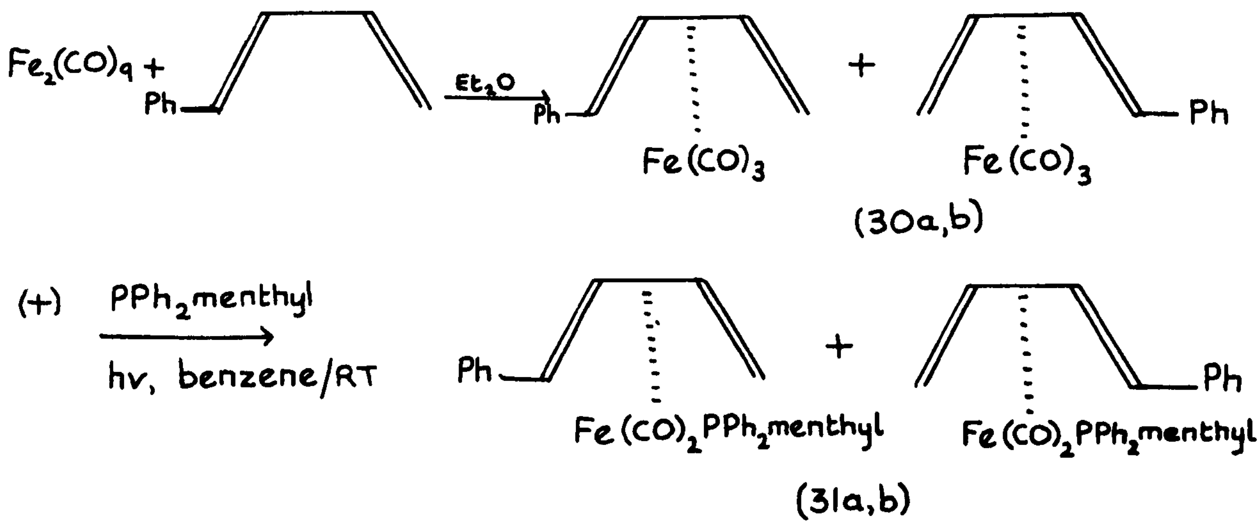

SCHEME I

Nucleophilic attack can thus proceed in principle to yield the six diastereoisomers. Regardless of the kinetic product of the reaction, facile diene rotation will allow the establishment of the thermodynamic equilibrium between ($A \rightleftharpoons B \rightleftharpoons C$) and ($A' \rightleftharpoons B' \rightleftharpoons C'$). Based on the crystal structure of (chd)$Fe(CO)_2PPh_3$,[11] this most probably consists of ($B \rightleftharpoons C$) and ($B' \rightleftharpoons C'$). However, interconversions of the type ($N \rightleftharpoons N'$)($N \equiv A,B,C$) cannot occur by diene rotation and it can be noted that all (N)/(N′) pairs differ in the configuration of the 5-substituted carbon atom of the cyclohexadiene ring. Thus, two sets of resonances are observed, the relative intensities depending on the degree of asymmetric induction in the initial nucleophilic attack. The degree of asymmetric induction is much greater for complex (27a,b) ($L^* \equiv$ (+)$PPh_2$menthyl) than for complex (28a,b) ($L^* \equiv$ (+)$PPh_2CH_2CH$(Me)Et). It might appear that the distance from the metal of the resolving centre is crucial in determining the degree of asymmetric induction.

Thus a route has been found to the synthesis of enantiomerically enriched 5-substituted cyclohexa-1,3-diene. The degree of asymmetric induction could be further investigated by reactions with other nucleophiles and by varying the choice of L*.

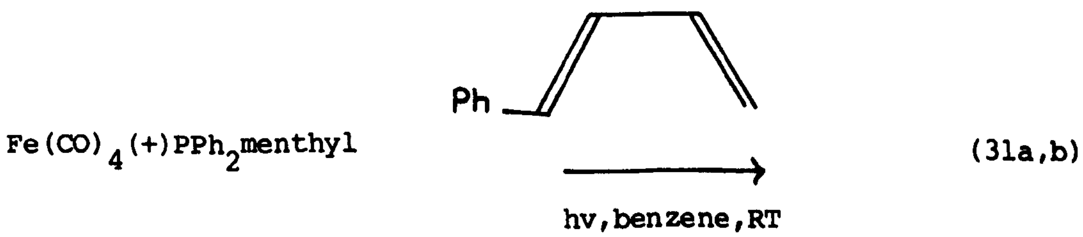
### 4.2.4 (1-phenylbutadiene)$Fe(CO)_2L^*$)

($\eta^4$-diene)$Fe(CO)_3$ compounds which have no hydrogens $\alpha$ to the olefinic carbons cannot form dienyl salts. Consequently, the only method of introducing a resolved chiral centre into the molecule leading to the formation of a diastereoisomeric pair is by displacement of CO by a chiral ligand. We have prepared (trans-1-phenylbutadiene)-$Fe(CO)_2PPh_2$menthyl (31a,b) by two routes. The asymmetric diene trans-1-phenylbutadiene is stirred with $Fe_2(CO)_9$ in diethyl ether to give the enantiomeric pair (trans-1-phenylbutadiene)$Fe(CO)_3$ (30a,b). U.v. photolysis of (30a,b) in the presence of (+)$PPh_2$-menthyl gives the diastereoisomers (31a,b) (Route A).




ROUTE A

Alternatively (31a,b) can be synthesized by the u.v. photolysis of $Fe(CO)_4$(+)$PPh_2$menthyl (17) in the presence of trans-1-phenylbutadiene (Route B).




ROUTE B

We found that (31a,b) was more easily prepared via route A, since route B gave some minor contaminants which were difficult to separate from the product. The $^{31}P$ n.m.r. spectra of (31a,b) from <u>both</u> methods of synthesis clearly shows that asymmetric induction has occurred on complexation or substitution to give an enrichment of one diastereoisomer over the other in a ratio of ca. 2:1.

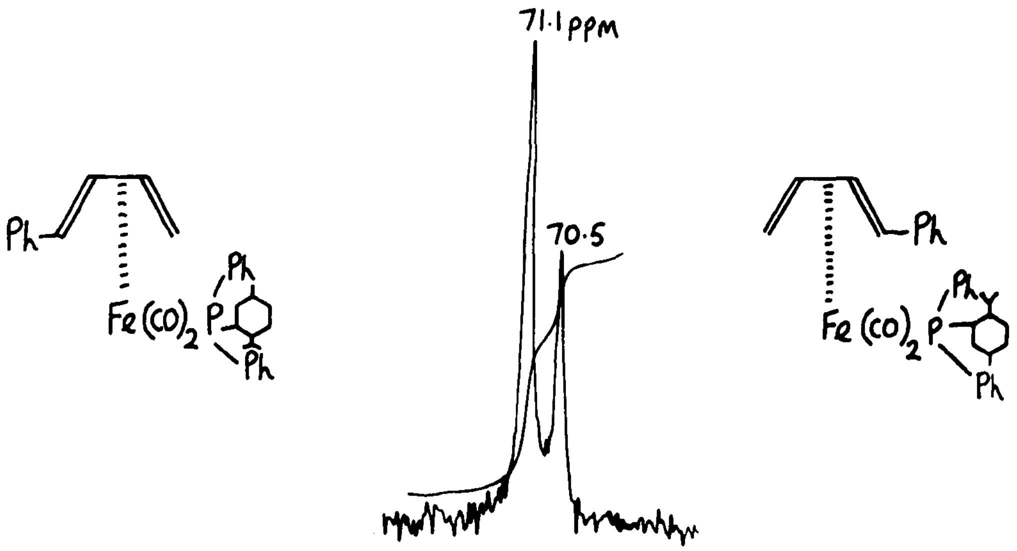



FIG. IX $^{31}P$ n.m.r. spectrum of diastereoisomers (31a,b)
(the configurations are arbitrarily drawn)

The major diastereoisomer present will be the one where the sterically demanding chiral phosphine is less hindered by the phenyl substituent of the diene. Although (31a,b) have been produced by two different mechanisms, carbonyl substitution by the chiral ligand in route A and carbonyl substitution by the asymmetric diene in route B, the steric preferment of the chiral phosphine results in the same degree of asymmetric induction. In route A, the enantiomers (30a,b) are chemically equivalent and must exist as an equimolar mixture; therefore carbonyl substitution by (+)$PPh_2$menthyl must occur at different rates, and the reaction not allowed to reach completion for an enrichment of one diastereoisomer of (31a,b) to be produced.

This route to the synthesis of enantiomerically enriched complexes of acyclic dienes, is particularly useful in cases where the absence of $\alpha$-hydrogens means that they cannot be resolved by diene- or dienyl-centred methods.

## 4.3 Experimental

The same reaction conditions and instrumentation were used as specified in Chapter 2.3. Trans-1-phenylbutadiene was prepared by the Grignard reaction of $CH_3MgI$ with cinnamaldehyde.[25] (S)(+)$PPh_2$[N(Me)CH(Me)Ph][26,27] and $Fe_2(CO)_9$[28] were synthesized by literature methods. $CoCl_2 \cdot 2H_2O$ was obtained by drying $CoCl_2 \cdot 6H_2O$ under vacuum (0.01 mm Hg) at 40°C for 1 hour. Irradiations were carried out in a quartz reactor, using a 90-W medium pressure lamp.

(a) Preparation of $Fe(CO)_4(+)PPh_2(C_{10}H_{19})$ (complex 17)

$(+)PPh_2(C_{10}H_{19})$ (2.45 g, 7.55 mmol) and $CoCl_2 \cdot 2H_2O$ (0.04 g, 0.24 mmol) were added to toluene (30 $cm^3$) and the stirred solution brought to reflux. $Fe(CO)_5$ (2.96 g, 15.1 mmol) was added and the reaction mixture was refluxed until the i.r. spectrum indicated the reaction was complete (ca. 4.5h). The catalyst and excess ligand were removed by eluting the cold reaction mixture through a $CoCl_2 \cdot 6H_2O$-alumina-silica gel (5g:20g:20g) column with benzene. Solvent and excess $Fe(CO)_5$ were removed on a rotary evaporator using a cold finger to trap the $Fe(CO)_5$. The residue was chromatographed on a silica gel column using light petroleum-dichloromethane (90:10) as eluant, to give a yellow oil (2.9 g) which solidified on cooling. An analytical sample was obtained by sublimation (130°C, ca. 0.01 mm Hg). Yield: 78%. Calc. for $C_{26}H_{29}FeO_4P$: C, 63.4; H, 5.95. Found: C, 63.35; H, 5.85%. I.r. (hexane): 2042, 1977, 1947 and 1937 $cm^{-1}$.

Complexes $Fe(CO)_4[PPh_2CH_2CH(Me)Et]$ (18) and $Fe(CO)_4$-$[PPh_2N(Me)CH(Me)Ph]$ (19) were prepared in a similar manner.

Yield of (18): 73%. An analytical sample was obtained by sublimation (105-115°C, ca. 0.02 mm Hg). Calc. for $C_{21}H_{21}FeO_4P$: C, 59.45; H, 5.00. Found: C, 59.34; H, 4.90%. I.r. (hexane) 2051, 1987, 1954, 1947 $cm^{-1}$. Complex (19) was sparingly soluble in light petroleum. Small quantities of a highly coloured unknown red contaminant were removed by extracting with light petroleum leaving the product. Sublimation (120-130°C, 0.02 mm Hg) gave a yellow solid. Yield: 46%. Calc. for $C_{25}H_{22}FeNO_4P$: C, 61.62; H, 4.56; N, 2.88; C, 61.78; H, 4.76; N, 2.62. I.r. (hexane) 2042, 1986, 1953, 1944 $cm^{-1}$.

(b) Preparation of (chd)Fe$(CO)_2$[$PPh_2(C_{10}H_{19})$] complex (22)

Cyclohexa-1,3-diene (0.65 g, 8.12 mmol) and complex (17) (2.0 g, 4.06 mmol) were dissolved in dry benzene (250 $cm^3$) and the resulting solution irradiated for 22 hours until the reaction had gone to completion (as judged by i.r.). Removal of the solvent gave the product as a red oil, contaminated by small quantities of complex (17), (chd)Fe$(CO)_3$ and $Fe(CO)_3(PPh_2C_{10}H_{19})_2$. The red oil is chromatographed on Grade I alumina using light petroleum-ethyl acetate (97.5:2.5) as eluant. The initial yellow band (chd)Fe$(CO)_3$ was discarded, the middle band gave 1.2 g of product isolated as a yellow oil (est. purity 95%), which solidified on drying in a vacuum. Later fractions were contaminated by complex (17) and were discarded. An analytical sample was purified by sublimation to separate (22) from the small amounts of (chd)Fe$(CO)_3$ and $Fe(CO)_4L^*$ still remaining (150°C, 0.05 mm Hg). Yield: 57%. Calc. for $C_{30}H_{37}FeO_2P$: C, 69.75; H, 7.25. Found: C, 69.95; H, 7.45%. I.r. (hexane): 1978 and 1925 $cm^{-1}$. A later attempt to prepare (22) resulted in a yellow oil contaminated by

(+)$PPh_2$menthyl. Separation of the free phosphine from the product proved difficult and attempted hydride abstraction with $Ph_3CBF_4$ gave the dienyl salt which underwent nucleophilic addition with the free phosphine, to generate the phosphonium adduct. It is thus vital to obtain (22) free of unreacted phosphine.

Complexes (chd)$Fe(CO)_2[PPh_2CH_2CH(Me)Et]$ (23) and (chd)-$Fe(CO)_2[PPh_2N(Me)CH(Me)Ph]$ (24) were prepared in a similar manner. Complex (23) was prepared by the irradiation of cyclohexa-1,3-diene with $Fe(CO)_4[PPh_2CH_2CH(Me)Et]$ in benzene for 10 hours. The red oil was chromatographed on Grade I alumina using light petroleum-ethyl acetate (95:5) as eluant to give a yellow oil (est. 95% pure). An analytical sample was purified by sublimation (130°C, 0.01 mm Hg) to give yellow crystals. Yield: 40%. Calc. for $C_{25}H_{29}FeO_2P$: C, 66.97; H, 6.53. Found: C, 67.19; H, 6.70. I.r. (hexane) 1982, 1927 $cm^{-1}$. Complex (24) was purified by chromatography on silica gel preparative plates using light petroleum-dichloromethane (90:10) as eluant to give a yellow-brown oil (est. 90% pure). Yield: 53%. I.r. (hexane) 1978, 1974 $cm^{-1}$. No satisfactory CHN analysis was obtained.

(c) Preparation of (bda)$Fe(CO)_2$ $PPh_2CH_2CH(Me)Et$ diastereoisomers (21a,b)[7]

$Fe(CO)_4[PPh_2CH_2CH(Me)Et]$ complex (18) (0.658 g, 1.55 mmol) and benzylideneacetone (0.226 g, 1.55 mmol) were dissolved in benzene (200 $cm^3$) and irradiated for 22 hours. After removal of the solvent, the orange-red oil was chromatographed on 200 g $SiO_2$.

Elution with benzene gave small amounts of $Fe(CO)_4[PPh_2CH_2CH(Me)Et]$, the product was obtained as a red oil by eluting with benzene-ethyl acetate (90:10). The last fractions were discarded because of contamination with free benzylideneacetone. An analytical sample was purified by sublimation (120-130°C, 0.03 mm Hg) to separate the product from small amounts of free benzylideneacetone and $(bda)Fe(CO)_3$ to give a red crystalline solid. Yield: 56%. Calc. for $C_{29}H_{31}FeO_3P$: C, 67.71; H, 6.09. Found: C, 67.90; H, 6.06%. I.r. (hexane) 1997, 1949, 1941 $cm^{-1}$.

$(Bda)Fe(CO)_2(PPh_2C_{10}H_{19})$ diastereoisomers (20a,b) were prepared in the same way. Yield: 65%. I.r. (hexane) 1997, 1947, 1939 $cm^{-1}$. Preparative thin layer chromatography of the crude mixture, using $CH_2Cl_2$/light petroleum 70/30 as eluant, gave two yellow bands which were thought to be the separated diastereoisomers (yield ca. 60%). Unfortunately, both bands were found to decompose in solvent to give free phosphine and benzylideneacetone. Therefore $^{13}C$ n.m.r. data and pure samples for CHN analysis were unobtainable.

(d) <u>Preparation of $(chd)Fe(CO)_2L^*$ via $(bda)Fe(CO)_2L^*$</u>

$(Chd)Fe(CO)_2L^*$ [$L^* = (+)PPh_2(C_{10}H_{19})$ and (S)$(+)PPh_2CH_2CH(Me)Et$] complexes (22) and (23) were prepared by the reaction of (bda)-$Fe(CO)_2L^*$ complexes (20a,b) and (21a,b) with cyclohexa-1,3-diene.[7] Complex (21a,b) (0.38 g, 0.739 mmol) and cyclohexadiene (0.59 g, 7.39 mmol) were dissolved in benzene and refluxed for 8 hours until the reaction had gone to completion as judged by i.r. Removal of the solvent and chromatography on $SiO_2$ using benzene as eluant gave 0.265 g of complex (23) as a yellow oil. Yield: 82%.

(e) Preparation of $[(\eta^5\text{-cyclohexadienyl})Fe(CO)_2PPh_2C_{10}H_{19})]$ $[BF_4]$ complex (25)

$Ph_3CBF_4$ (0.679 g, 2.06 mmol) was added to a solution of (cyclohexadiene)$Fe(CO)_2(PPh_2C_{10}H_{19})$ complex (22) (1.12 g, 2.17 mmol) in $CH_2Cl_2$ (20 $cm^3$). After stirring at room temperature for 15 min, the solution was filtered and diethyl ether was added to the filtrate to precipitate the product as a yellow solid. Cooling to 0°C, followed by filtration and washing with diethyl ether, gave complex (25) (0.75 g, yield 60%). Calc. for $C_{30}H_{36}BF_4FeO_2P$: C, 59.8; H, 6.05. Found: C, 59.7; H, 6.25%. I.r. ($CH_2Cl_2$): 2037 and 1997 $cm^{-1}$.

Complex (26) $L^* = PPh_2CH_2CH(Me)Et$ was prepared in an identical manner. Yield: 69%. Calc. for $C_{25}H_{28}BF_4FeO_2P$: C, 56.21; H, 5.29. Found: C, 56.08; H, 5.57%. I.r. ($CH_2Cl_2$) 2035 and 1996 $cm^{-1}$.

(f) Preparation of $[(5\text{-exo-cyanocyclohexadiene})Fe(CO)_2PPh_2C_{10}H_{19})]$ complexes (27a,b)

Potassium cyanide (0.345 g, 5.31 mmol) was added slowly to a solution of complex (25) (0.64 g, 1.06 mmol) in acetone-water (1:1, 25 $cm^3$). The mixture was stirred at room temperature until the i.r. spectrum indicated complete reaction (ca. 20 mins). Water (40 $cm^3$) was added and the solution was extracted with diethyl ether (3 x 75 $cm^3$). After drying with $MgSO_4$ and removal of solvent, the residue was chromatographed on a Grade II alumina column using light petroleum-ethyl acetate (0.43 g) which was dried under vacuum to give a yellow solid. $^{31}P$ n.m.r. spectrum (figure VII) of the product showed an excess of one diastereoisomer over the other in a ratio of 2:1. Yield: 75%. Calc. for $C_{31}H_{36}FeNO_2P$: C, 68.75; H, 6.71; N, 2.59. Found: C, 68.62, H, 7.35; N, 2.40%. I.r. (hexane): 1983 and 1932 $cm^{-1}$.

Complexes (28a,b) [(5exo-cyanocyclohexadiene)Fe$(CO)_2$-$PPh_2CH_2CH(Me)Et$] were prepared in an identical manner. $^{31}P$ n.m.r. spectra showed an equimolar amount of both diastereoisomers. Yield: 72%. I.r. (hexane): 1986 and 1933. No satisfactory CHN analysis was obtained

(g) Preparation of (trans-1-phenylbutadiene)Fe$(CO)_2(PPh_2C_{10}H_{19})$ complexes (31a,b)

Complexes (31a,b) were prepared by the photolysis of (trans-1-phenylbutadiene)Fe$(CO)_3$ in the presence of (+)$PPh_2(C_{10}H_{19})$.

(g.1) (1-phenylbutadiene)Fe$(CO)_3$ complex (30a,b), 1.0 g (7.7 mmol) of trans-1-phenylbutadiene with 3.4 g (9.2 mmol) of $Fe_2(CO)_9$ and diethyl ether (30 $cm^3$) were stirred for two days and refluxed for 2 hours. The cold reaction mixture was filtered and the solvent and $Fe(CO)_5$ were removed on a rotary evaporator with a liquid nitrogen trap. The residue was chromatographed using Grade II alumina with light petroleum as eluant, to give 0.91 g (44% yield) of compound (30), an orange oil. An analytical sample was purified by sublimation (52-60°C, ca. 0.005 mm Hg). Calc. for $C_{13}H_{10}FeO_3$: C, 57.81; H, 3.74. Found: C, 58.86; H, 3.73%. I.r. (hexane) 2042, 1992 and 1983 $cm^{-1}$.

(g.2) (trans-1-phenylbutadiene)Fe$(CO)_2(PPh_2C_{10}H_{19})$ (31a,b) 0.19 mg (0.7 mmol) of complex (30a,b) and 240 mg (0.75 mmol) of (+)$PPh_2C_{10}H_{19}$ (+ neomenthyldiphenylphosphine) were dissolved in 250 mls of benzene and irradiated for 7 hours. Chromatography on silica gel preparative plates using light petroleum-dichloromethane (90:10) as eluant gave 0.28 g of an orange-yellow solid in 70% yield. Calc. for $C_{34}H_{39}FeO_2P$: C, 72.07; H, 6.95. Found: C, 71.84; H, 7.23%. I.r. (hexane) 1987 and 1927 $cm^{-1}$.

Complexes (31a,b) were also prepared by photolysis of $Fe(CO)_4(PPh_2C_{10}H_{19})$ (17) with trans-1-phenylbutadiene. The $^{31}P$ n.m.r. spectra (figure VIII) was identical for both methods of synthesis, and showed an excess of one diastereoisomer over the other in a ratio of 2:1.

(h) Preparation of (S)(+)$PPh_2$[N(Me)CH(Me)Ph] (32)

A solution of freshly distilled diphenylchlorophosphine (4.0 g, 18.1 mmol) in diethyl ether (50 $cm^3$) was added dropwise at 0°C to a stirred solution of (S)(-)NH(Me)CH(Me)Ph [$\alpha$]-74° in diethyl ether (100 $cm^3$). The addition took 1 hour and was carried out in an inert atmosphere. The reaction mixture was refluxed for 4 hours with continued stirring. After filtration of the amine hydrochloride salt, the solvent was removed and the residue extracted with light petroleum. The solution was then concentrated and distilled (141-167°, 0.02 mm Hg) to give 4.07 g (70% yield) of a clear colourless oil, which solidified to a white crystalline solid. $[\alpha]^{20}_{589}$ + 81.7°($CH_2Cl_2$, C=5.0). This value disagrees with the literature specific rotation of $[\alpha]^{25}_{589}$ + 57° ($CH_2Cl_2$, C=1.5) [26] where the product was not purified by distillation. The $^1H$ n.m.r. spectrum obtained was identical to the values given in the literature. Calc. for $C_{21}H_{22}NP$: C, 78.96; H, 6.96; N, 4.39. Found: C, 79.22; H, 7.16; N, 4.29%.

TABLE 3 N.m.r. Spectra of Complexes (17) to (31)

| COMPLEX | $^{13}C$ ASSIGNMENT | | $(J_{P-C})$ Hz | $^{1}H$ ASSIGNMENT | |
|---|---|---|---|---|---|
| $Fe(CO)_4L^*$ | $C_{10}H_{19}$ | 17.5 | | $C_{10}H_{19}$ | 0.45-3.06 |
| (17) $L^* = PPh_2C_{10}H_{19}$ | | 20.8 | | Ph | 7.34-7.90 (m) |
| ($C_{10}H_{19}$= menthyl) | | 21.4 | (12.6) | | |
| | | 23.9 | | | |
| | | 28.3 | ( 7.7) | | |
| | | 28.4 | | | |
| | | 30.2 | ( 3.9) | $^{31}P$ ASSIGNMENT | |
| | | 31.0 | ( 6.8) | 73.9 | |
| | | 39.1 | | | |
| | | 41.4 | (22.4) | | |
| | Ph | 128-135 | | | |
| | | | $J_{P-Fe-C}$ | | |
| | CO[a] | 212.6 | (15.7) | | |

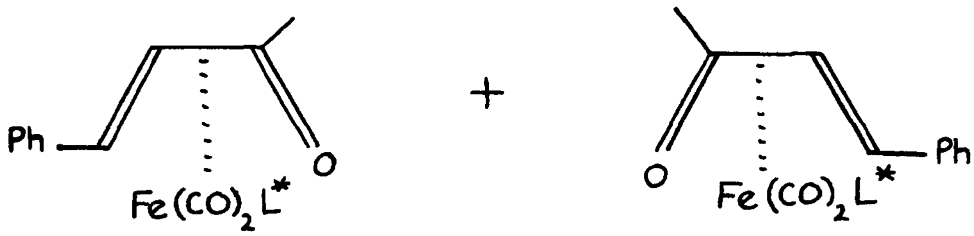
| COMPLEX | $^{13}C$ ASSIGNMENT | | $(J_{P-C})$ Hz | $^{1}H$ ASSIGNMENT | |
|---|---|---|---|---|---|
| $Fe(CO)_4L^*$ | $P-CH_2$ | 39.0 | (28.4) | $C_5H_{11}$ | 0.81-2.44 |
| (18) $L^* = PPh_2[CH_2CH(Me)Et]$ | CH | 31.7 | | Ph | 7.41 (m) |
| | Et | 31.4, 11.1 | | | |
| | Me | 21.1 | ( 5.8) | $^{31}P$ ASSIGNMENT | |
| | Ph | 128-135 | $J_{P-Fe-C}$ | 66.4 | |
| | CO[a] | 212.6 | (17.6) | | |

| COMPLEX | $^{13}C$ ASSIGNMENT | | $(J_{P-C})$ Hz | $^{1}H$ ASSIGNMENT | | $J_{P-H}$ z | |
|---|---|---|---|---|---|---|---|
| $Fe(CO)_4L^*$ | CH | 57.3 | (10.8) | CH | 5.31 | (11.3) | (m) |
| (19) $L^* = PPh_2[N(Me)CH(Me)Ph]$ | NMe | 31.5 | ( 7.8) | NMe | 2.39 | ( 8.6) | (d) |
| | CH<u>Me</u> | 17.0 | | CH<u>Me</u> | 1.46 | ( 7.0) | (m) |
| | Ph | 127-132 | $J_{P-Fe-C}$ | Ph | 7.23-7.74 | | |
| | CO[a] | 213.1 | (19.5) | | | | |

a $^{13}C$ spectra in the Fe-CO region were run in the presence of $Cr(acac)_3$ as a relaxing agent.

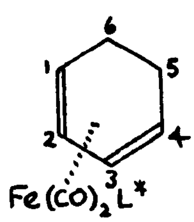
| COMPLEX | $^{13}C$ ASSIGNMENT | | $(J_{P-C})$ Hz | $^{31}P$ ASSIGNMENT |
|---|---|---|---|---|
| (32) | CH | 63.3 | (59.1) | 60.3 |
| $PPh_2[N(Me)CH(Me)Ph]$ | NMe | 31.6 | ( 9.7) | |
| | CH<u>Me</u> | 19.1 | ( 9.2) | |
| | Ph | 127-143 | | |

TABLE 3 (continued)



| COMPLEX | $^{31}$P ASSIGNMENT |
|---|---|
| (20a,b) | 59.02 |
| $L^* = PPh_2(C_{10}H_{19})$ | |

| COMPLEX | $^{31}$P ASSIGNMENT |
|---|---|
| (21a,b) | 49.14 |
| $L^* = PPh_2[CH_2CH(Me)Et]$ | 49.02 |

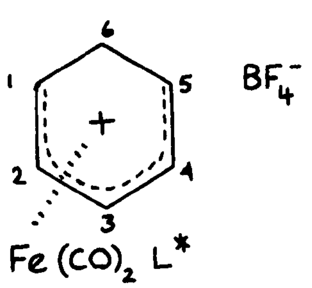


| COMPLEX | $^{13}$C ASSIGNMENT | | (Jp-c) Hz | $^{1}$H ASSIGNMENT |
|---|---|---|---|---|
| (22) | C2,3 | 86.5 | | C2,3 4.32 (m) |
| $L^* = PPh_2(C_{10}H_{19})$ | | 85.6 | | C1,4,5,6;$C_{10}H_{19}$ 0.17-2.71 |
| | C1,4 | 61.0 | ( 2.0) | Ph 7.13-7.78 (m) |
| | | 60.5 | ( 2.9) | |
| | C5,6 | 24.9 | | |
| | | 24.4 | | |
| | $C_{10}H_{19}$ | 17.9 | | |
| | | 20.4 | | |
| | | 21.3 | (11.7) | |
| | | 24.0 | | |
| | | 28.0 | ( 5.8) | $^{31}$P ASSIGNMENT |
| | | 28.8 | | 72.3 |
| | | 30.3 | ( 3.9) | |
| | | 31.0 | ( 6.8) | |
| | | 38.9 | (20.5) | |
| | | 39.7 | ( 3.9) | |

TABLE 3 (continued)

| COMPLEX | $^{13}C$ ASSIGNMENT | | $(J_{P-C})$ Hz | $^{1}H$ ASSIGNMENT | |
|---|---|---|---|---|---|
| (23) | C2,3 | 84.8 | | C2,3 | 4.67 (m) |
| L* = $PPh_2[CH_2CH(Me)Et]$ | | 84.7 | | C1,4 | 2.28 (m) |
| | C1,4 | 61.1 | | C5,6,$C_5H_{11}$ | 2.14-0.6 |
| | | 60.5 | ( 3.9) | Ph | 7.32 (m) |
| | C5,6 | 24.9 | | | |
| | | 24.6 | ( 2.0) | | |
| | P-$CH_2$ | 39.2 | (23.5) | | |
| | CH | 31.9 | | $^{31}P$ ASSIGNMENT | |
| | Et | 31.5, 11.2 | | | 62.9 |
| | Me | 21.2 | ( 4.9) | | |
| | Ph | 127-132 | | | |

| COMPLEX | $^{13}C$ ASSIGNMENT | | $(J_{P-C})$ Hz |
|---|---|---|---|
| (24) | C2,3 | 84.7 | |
| L* = $PPh_2[N(Me)CH(Me)Ph]$ | | 84.6 | |
| | C1,4 | 62.6 | ( 3.0) |
| | | 61.2 | ( 4.3) |
| | C5,6 | 24.8 | |
| | <u>CH</u>Me | 57.5 | (17.1) |
| | NMe | 29.8 | |
| | CH<u>Me</u> | 17.1 | |



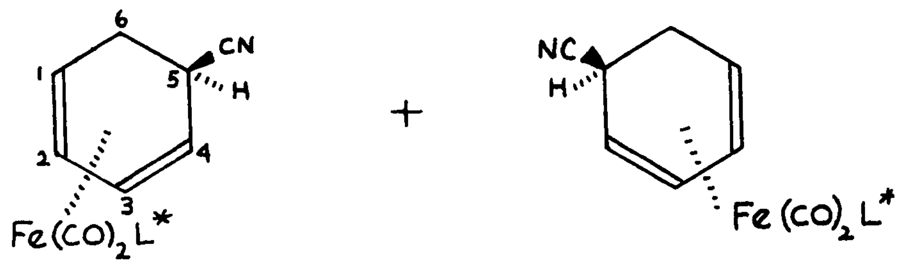

| COMPLEX | $^{13}C$ ASSIGNMENT | | $(J_{P-C})$ Hz | $^{31}P$ ASSIGNMENT |
|---|---|---|---|---|
| (25) | C2,4 | 101.9 | | 65.0 |
| L*=$PPh_2C_{10}H_{19}$ | | 100.8 | | |
| | C3 | 89.0 | | |
| | C1,5 | 60.6 | | |
| | | 57.9 | | |

TABLE 3 (continued)

| COMPLEX | $^{13}C$ ASSIGNMENT | | (Jp-c) Hz | $^{31}P$ ASSIGNMENT |
|---|---|---|---|---|
| (25) (continued) | C6 | 23.6 | | |
| | $C_{10}H_{19}$ | 17.7 | | |
| | | 20.1 | | |
| | | 21.0 | (12.7) | |
| | | 23.8 | | |
| | | 27.7 | | |
| | | 28.1 | ( 4.9) | |
| | | 30.8 | | |
| | | 31.2 | ( 6.9) | |
| | | 39.7 | (22.5) | |
| | | 40.5 | | |
| | Ph | 128-134 | | |

| COMPLEX | $^{13}C$ ASSIGNMENT | | (Jp-c) Hz | $^{31}P$ ASSIGNMENT |
|---|---|---|---|---|
| (26) | C2,4 | 100.8 | | 58.1 |
| L*=$PPh_2CH_2CH(Me)Et$ | | 100.5 | | |
| | C3 | 88.4 | | |
| | C1,5 | 58.7 | | |
| | | 58.3 | | |
| | C6 | 23.7 | | |
| | P-$CH_2$ | 38.0 | (27.4) | |
| | CH | 31.4 | | |
| | Et | 31.1, 10.6 | | |
| | Me | 20.2 | ( 5.9) | |
| | Ph | 129-132 | | |

TABLE 3 (continued)



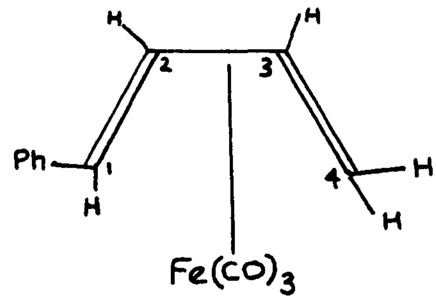

| COMPLEX | $^{13}$C ASSIGNMENT | | (Jp-c)Hz | $^{1}$H ASSIGNMENT | |
|---|---|---|---|---|---|
| (27a,b) | C2,3 | 88.5 | | C2 | 4.39 (m) |
| $L^*=PPh_2C_{10}H_{19}$ | | 87.9[a] | | C3 | 4.61 (m) |
| | | 85.3[a] | | C1,C4-6;$C_{10}H_{19}$ | 0.23-2.83 |
| | | 84.5 | | Ph | 7.30-7.05 (m) |
| | C1,4 | 57.3[a] | (2.5) | | |
| | | 56.7 | (3.7) | | |
| | | 55.6 | | | |
| | | 55.1[a] | (2.5) | | |
| | C6 | 26.4[a] | | | |
| | | 26.2 | | $^{31}$P ASSIGNMENT | |
| | C5,$C_{10}H_{19}$ | 17.8-39.9 | | | 70.5[a] |
| | Ph | 127-135 | | | 70.1 |

a resonance of major isomer present in ratio of 2:1

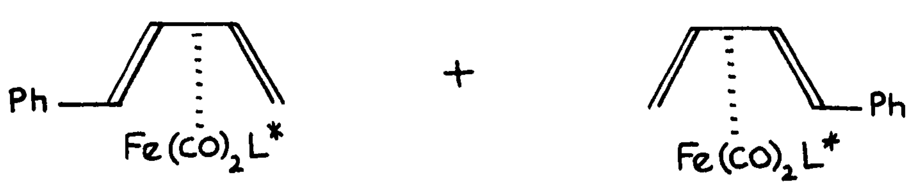
Braces indicate resonances due to diastereoisomeric pairs.

| COMPLEX | $^{31}$P ASSIGNMENT |
|---|---|
| (28a,b) | 61.3 |
| $L^* = PPh_2[CH_2CH(Me)Et]$ | 61.2 |

TABLE 3 (continued)




| COMPLEX | $^{13}$C ASSIGNMENT | | $^{1}$H ASSIGNMENT | |
|---|---|---|---|---|
| (30a,b) | C2 | 83.5 | 2 | 5.93 |
| | C3 | 81.2 | 3 | 5.41 |
| | C1 | 61.6 | 1 | 1.99 |
| | C4 | 39.6 | 4 | 0.66 |
| | Ph | 139.5-125.9 | Ph | 7.25 |




| COMPLEX | $^{31}$P ASSIGNMENT |
|---|---|
| (31a,b) | 71.1[a] |
| L* = (+)$PPh_2(C_{10}H_{19})$ | 70.5 |

[a] resonance of major isomer present in ratio of 2:1

FIG. V $^{13}$C n.m.r. Spectrum of Complex **(22)**

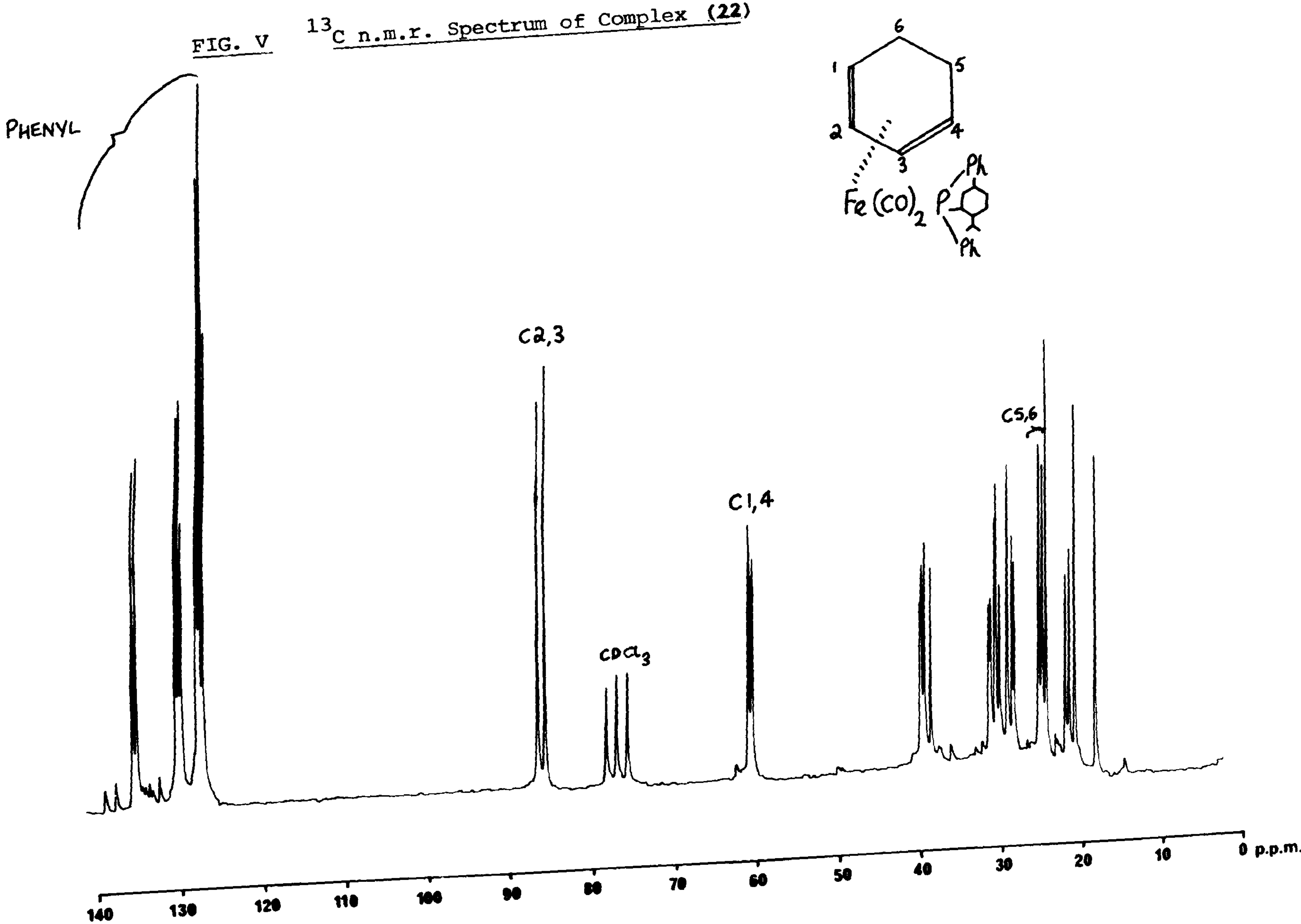


**FIG. VI** $^{13}C$ n.m.r. Spectrum Complex (25)

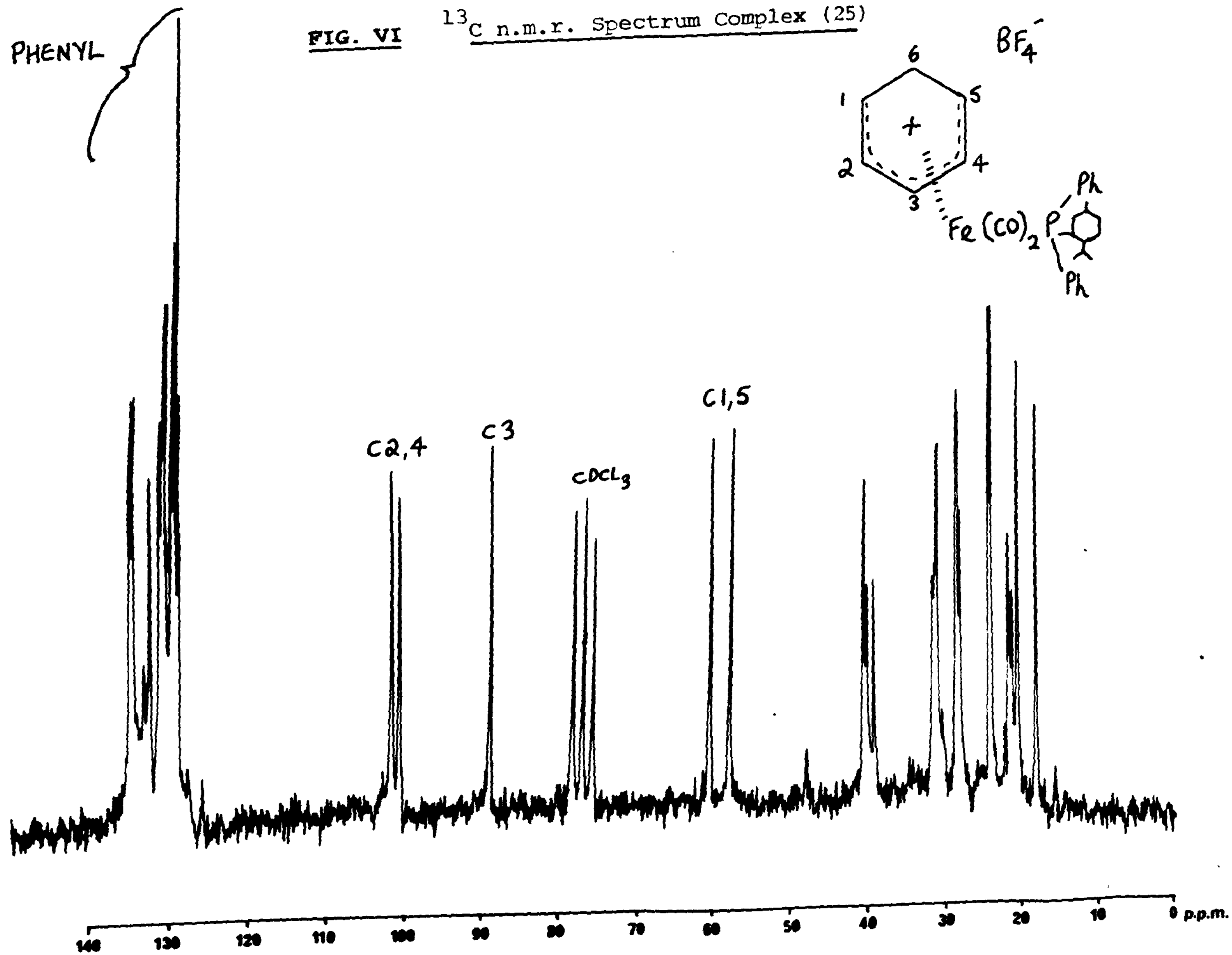
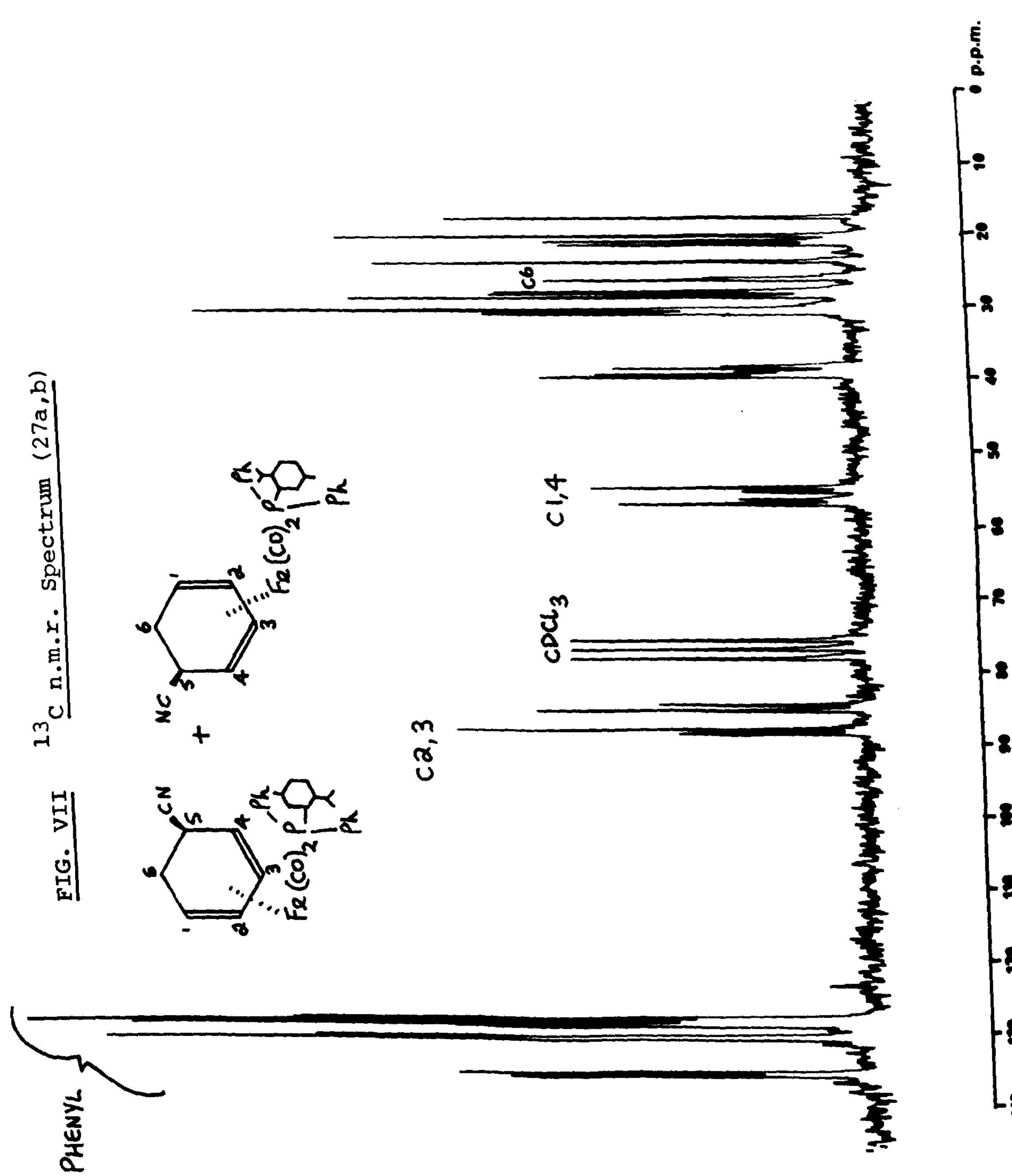


FIG. VII $^{13}$C n.m.r. Spectrum (27a,b)



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