ASYMMETRIC SYNTHESIS OF CYCLOPROPANES

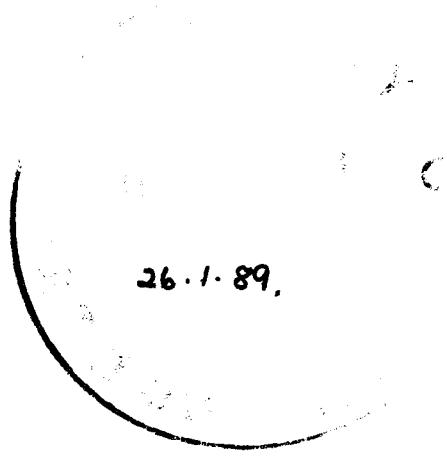
A thesis submitted in partial fulfilment of

the requirements for the degree of

Doctor of Philosophy

by

P.W. Ambler, B.A.



Exeter College

Oxford

September 1988

ASYMMETRIC SYNTHESIS OF CYCLOPROPANES

P.W. Ambler
Exeter College, Oxford.

D.Phil
September, 1988

Abstract

This thesis is concerned with the asymmetric synthesis of cyclopropyl derivatives via the use of chiral iron acyl complexes of the type $(\eta^5\text{-}C_5H_5)Fe(\overline{CO})(PPh_3)(COCH{=}CR'R)$. Chapter 1 reviews previous routes to optically active cyclopropyl derivatives and reviews the use of the chiral auxiliary $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)$ for asymmetric synthesis.

Chapter 2 describes the synthesis of the complexes $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(COCH{=}CRR')$ and presents a conformational analysis of the α,β-unsaturated acyl ligand.

Chapter 3 describes the diastereoselective synthesis of cis-substituted cyclopropyl complexes via the reaction of Z-α,β-unsaturated iron acyl complexes with electrophilic alkylidene species. Decomplexation, to give the corresponding cyclopropyl esters, occurred without epimerisation of the cyclopropane ring. By the use of homochiral iron acyl complexes the enantioselective synthesis of cyclopropyl derivatives was achieved. Section A describes methylene addition and Section B isopropylidene addition reactions. Section C describes attempts to synthesise pyrethroid insecticide precursors which occurred with good diastereoselectivity but poor regioselectivity. Section D describes electrophilic ethylidene addition reactions in which the chiral auxiliary exerts good stereochemical control over three new chiral centres.

Chapter 4 describes the diastereoselective synthesis of trans-substituted cyclopropyl complexes via the reaction of E-α,β- unsaturated iron acyl complexes with nucleophilic alkylidene transfer reagents. Section A describes methylene transfer reagents. Whilst α-lithiosulphides and α-lithiosulphoxides were of limited use, iodomethyllithium (generated in situ) resulted in highly diastereoselective syntheses of the cyclopropyl complexes. Decomplexation, to give the corresponding cyclopropyl esters, occurred without epimerisation of the cyclopropane ring. By the use of homochiral iron acyl complexes the enantioselective synthesis of cyclopropyl derivatives was achieved. Section B describes the generation of 1-iodoethyllithium and 1-iodobutyllithium and their reactions as nucleophilic alkylidene transfer reagents. The stereochemistry at two of the new chiral centres is controlled by the iron chiral auxiliary, whilst that at a third is controlled by a number of factors.

For my Father

ACKNOWLEDGEMENTS

I would like to thank my supervisor Dr. S.G. Davies for his help and enthusiasm over the past three years.

I would also like to thank other members of the group, in particular Kevin and Martin for obtaining the X-ray crystal structures presented in this thesis, and Brent, Jon, Shirley and Paul for the hours spent proof-reading.

A special thanks goes to Sue for her love and support throughout the last three years and her gallant efforts in proof-reading this thesis.

Thanks to all the technical staff at the Dyson Perrins Laboratory, especially Mrs. E. McGuinness and Dr. R.T. Aplin, for their help.

Finally, thanks to Lesley Woods for typing this thesis so efficiently.

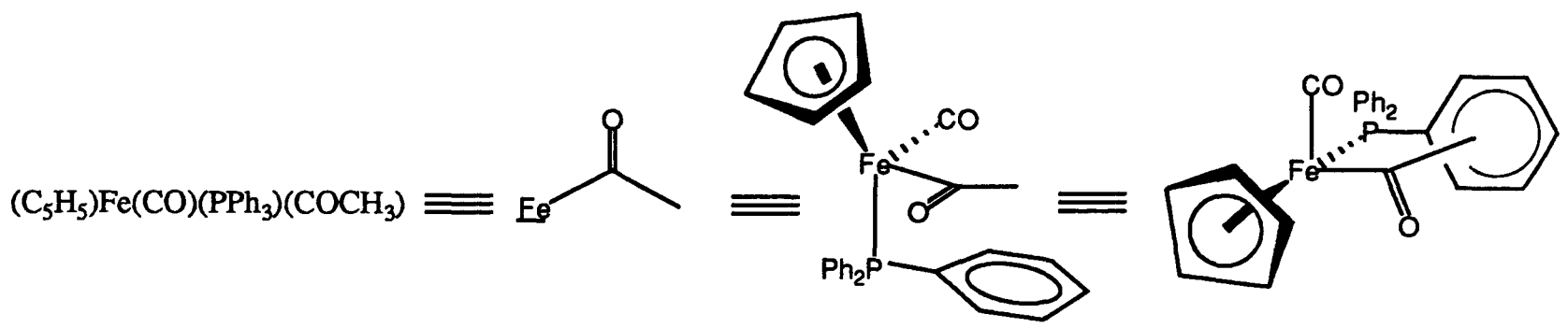
CONTENTS

List of Figures

Abbreviations

E^+	=	electrophile
L.A.	=	Lewis acid
B^-	=	base
Me	=	CH_3
Et	=	CH_2CH_3
^{n}Pr	=	$CH_2CH_2CH_3$
^{n}Bu(n-Bu)	=	$CH_2CH_2CH_2CH_3$
^{i}Pr	=	$CH(CH_3)_2$
^{t}Bu	=	$C(CH_3)_3$
Ph	=	C_6H_5
p-tolyl	=	p-$C_6H_4CH_3$
Bn	=	$CH_2C_6H_5$
Tf	=	triflate
THF	=	tetrahydrofuran
LDA	=	lithium diisopropylamide
NBS	=	N-bromosuccinimide
ν_{max}	=	infrared absorption peak
s	=	strong
vs	=	very strong
n.m.r.	=	nuclear magnetic resonance
br	=	broad
s	=	singlet
d	=	doublet
t	=	triplet
q	=	quartet
qn	=	quintet
m	=	multiplet
[^{1}H]	=	proton decoupled
m/z	=	mass to charge ratio

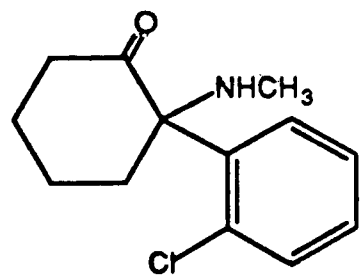
Å	=	Angstrom
d.e.	=	diastereoisomeric excess
e.e.	=	enantiomeric excess



CHAPTER 1

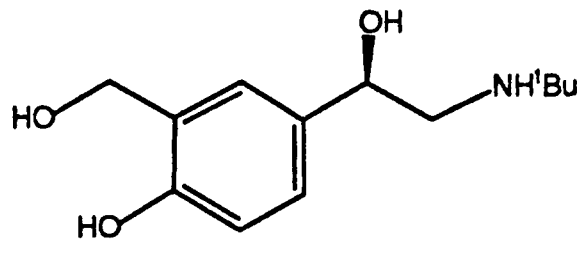
INTRODUCTION

The frequent observation that enantiomers of bioactive molecules interact differently with living systems is a direct consequence of the natural chirality inherent within these systems. The interaction is based on a chemical and steric complementarity of one enantiomer of the molecule with a specific receptor site. The less reactive enantiomer (distomer) can disrupt the action of the more reactive one (eutomer) by a number of effects including competitive antagonist action.[1] For example, the (+)-enantiomer of ketamine 1 is predominantly hypnotic and analgesic in action, whilst the (-)-enantiomer causes unwanted side effects such as central nervous system stimulation.[2]

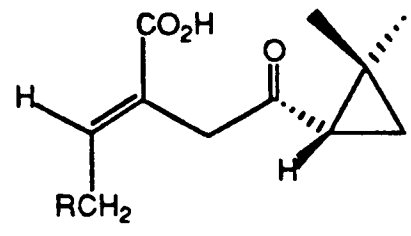


1

Alternatively, the distomer may have no biological activity. In such cases administration of the racemate is wasteful. The R(-)-enantiomer of the anti-asthmatic drug Salbutamol 2 is sixty-eight times more active than its distomer.[3] Similarly the S-enantiomers of the β-lactamase renal dipeptidase inhibitors 3 are typically more than one hundred times as active as the R-enantiomers.[4]

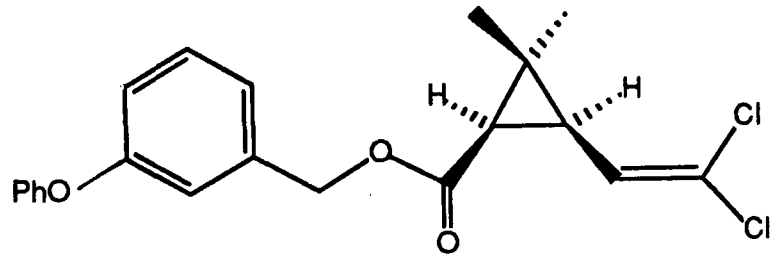


R(-)-2



S-3

These effects are common to all biological systems. For example, the insecticidal activity of the 1R,3R(+)-isomer of the synthetic pyrethroid Permethrin 4 is twenty times that of its enantiomer.[5] The need for synthetic chemists to make bioactive molecules of high enantiomeric purity is therefore clear.



1R,3R(+)-4

For compounds 3 and 4 the asymmetry within the molecule arises from the stereochemistry of the substituted cyclopropane ring. As exemplified by 3 and 4, it is frequently observed that the biological activity of a molecule containing a substituted cyclopropane ring is dependent upon the relative and absolute stereochemistry of the ring.[6] In order to study these structure/activity relationships methods for controlling the relative and absolute stereochemistry of a substituted cyclopropane ring must be used. In addition, the use of cyclopropyl derivatives as synthetic intermediates is common,[7] and again control of the ring stereochemistry is important. Previously reported approaches leading to cyclopropyl derivatives of high enantiomeric purity are outlined below, and their limitations discussed.

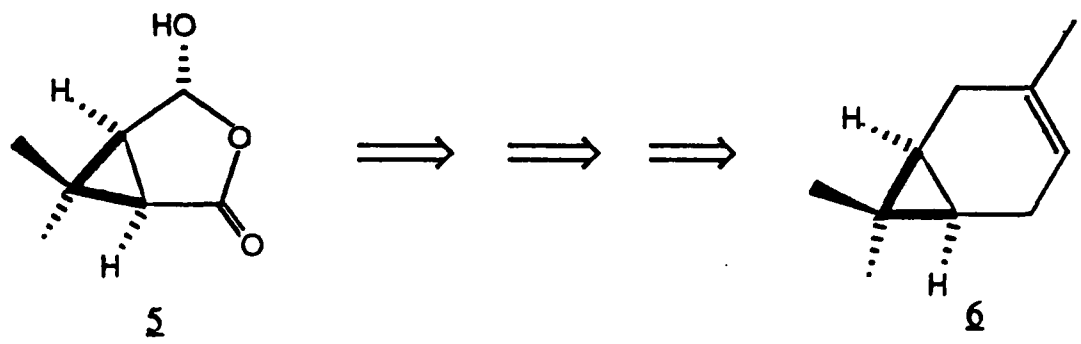
1. Methods for obtaining Optically Active Cyclopropyl Derivatives.

Although the methods outlined in the following sections are discussed mainly with reference to cyclopropyl derivatives, they also categorise the general approaches by which molecules of high

enantiomeric purity may be obtained.

a) From the Chiral Pool.[8]

Enantioselective modification of a suitable, naturally occurring, homochiral molecule can produce a desired target molecule. For example, the precursor to a range of synthetic pyrethroid insecticides, 1R-cis-caronaldehyde 5, has been made from the naturally occurring hydrocarbon (+)-3-carene 6.[9]



5 6

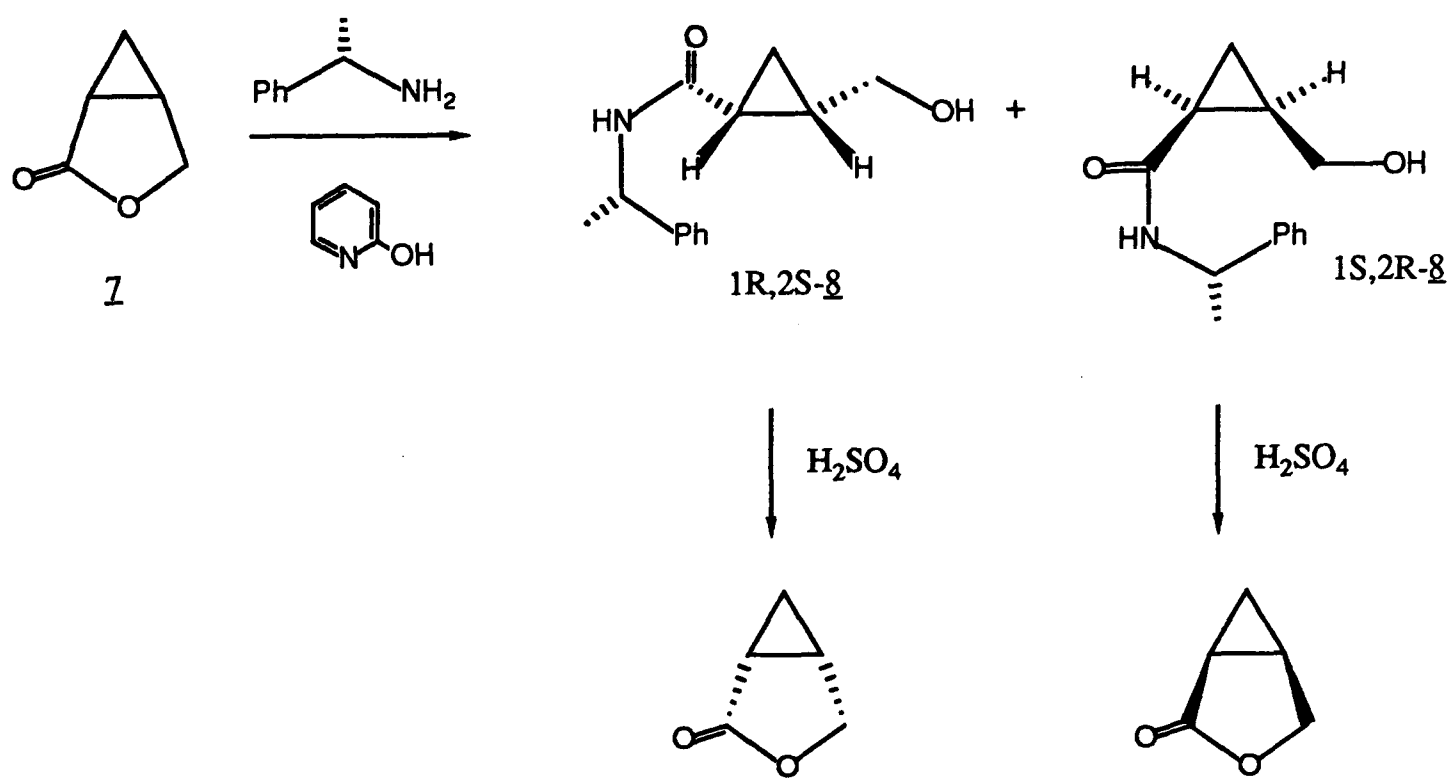
Both carbohydrates[10] and amino-acids[11] are also frequently used as precursors in this type of synthetic approach. The versatility of this method is limited by the availability of suitable starting materials. The syntheses can be long, requiring several protection/deprotection steps, and often result in the destruction of most of the chiral centres in the molecule.

b) Resolution Techniques.[12]

i) Resolution of racemic modifications by the physical separation of intermediate diastereoisomers.

Racemic modifications can be transformed into diastereoisomeric mixtures by reaction with a homochiral reagent. The diastereoisomers can be separated chromatographically or by fractional crystallisation. The key intermediates in Jaenicke's[13] synthesis of both enantiomers of Dictyopterene C were the homo-

chiral lactones 7. Treatment of racemic 7 with S(-)-phenylethylamine in base gave the diastereoisomers 8, which were separated by chromatography. Subsequent acid hydrolysis gave the homochiral lactones 7.

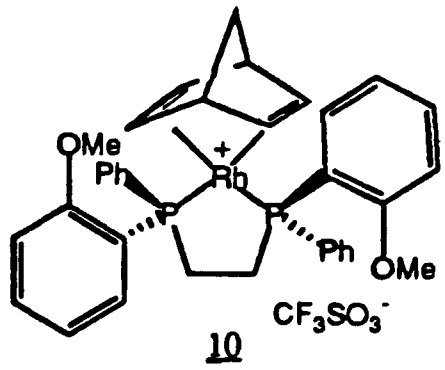


7 1R,2S-8 1S,2R-8

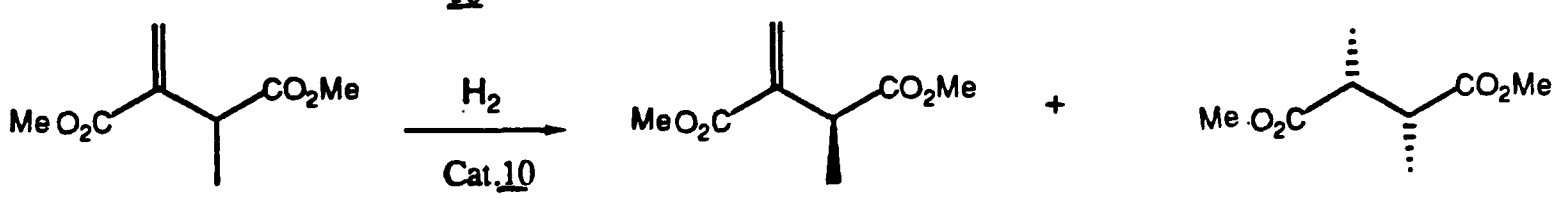
1R,2S-7 1S,2R-7

ii) Kinetic resolutions.[14]

The enantioselective reaction of a homochiral reagent with one enantiomer of a racemic modification can lead to an efficient kinetic resolution providing that the relative rates of reaction of the enantiomeric pairs are sufficiently large. Sharpless[15] has demonstrated the kinetic resolution of racemic β-hydroxy amines by enantioselective N-oxide formation. Brown[16] has shown that in the enantioselective hydrogenation of the racemic itaconate ester 9, catalysed by the optically active rhodium complex 10, the R-enantiomer reacts at ten times the rate of the S-enantiomer. After 65% reaction, recovered 9 was shown to be the enantiomerically pure S-enantiomer, whilst the product 11 was predominantly the R,R-enantiomer (53% e.e.).



10



9 S-9 11

Resolution often involves laborious separation techniques and is inherently inefficient if only one enantiomer is of interest. Direct resolution of enantiomers on columns containing homochiral stationary phases has been demonstrated[17] but the systems can be expensive and of limited application.

c) Asymmetric Synthesis.[18]

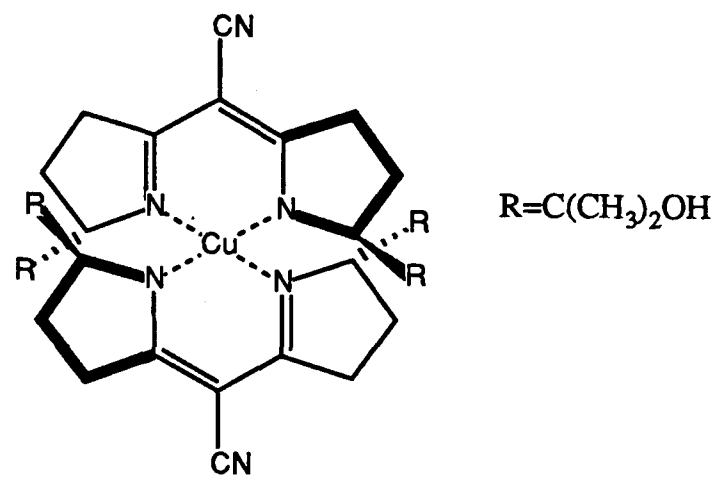
Asymmetric synthesis has the greatest potential utility of the methods described, due to the wide range of syntheses to which it can be applied. Transfer of chirality occurs from a chiral auxiliary of high enantiomeric purity to an associated substrate *via* a highly diastereoselective reaction. Dissociation from the auxiliary gives the product which, in an efficient process, will be isolated in high chemical yield and enantiomeric purity. Ideally, efficient recovery of the auxiliary without loss of enantiomeric purity is desirable. There are two general categories of reaction:

i) Catalytic reactions.[19]

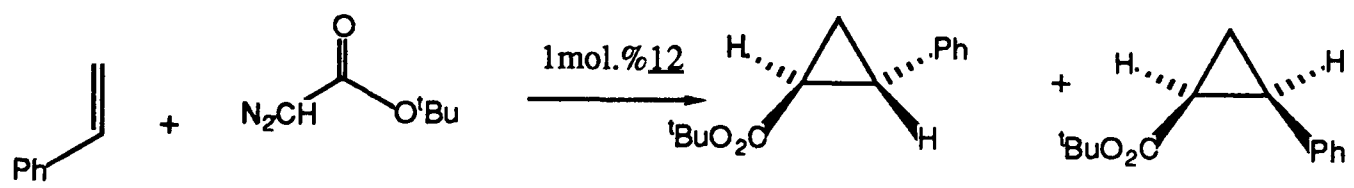
As well as enzyme catalysed reactions,[20] there are many examples of asymmetric syntheses being catalysed by homochiral reagents, especially highly stereoselective oxidation and hydrogenation reactions.[19] For example, the enantioselective epoxidation of allylic alcohols (Sharpless epoxidation),[21] in which

olefin oxidation occurs with high facial selectivity via the formation of an asymmetric diethyl tartrate/titanium(IV) complex in the presence of t-butyl hydroperoxide.

The decomposition of alkyl diazoacetates catalysed by transition metal complexes of high enantiomeric purity generates asymmetric carbenoid species which, in the presence of olefins, give cyclopropanecarboxylic esters enantioselectively.[22] For example, the decomposition of t-butyl diazoacetate in the presence of styrene, catalysed by the homochiral copper catalyst 12, gave the corresponding esters with high enantioselectivity.[23]



12



84:16

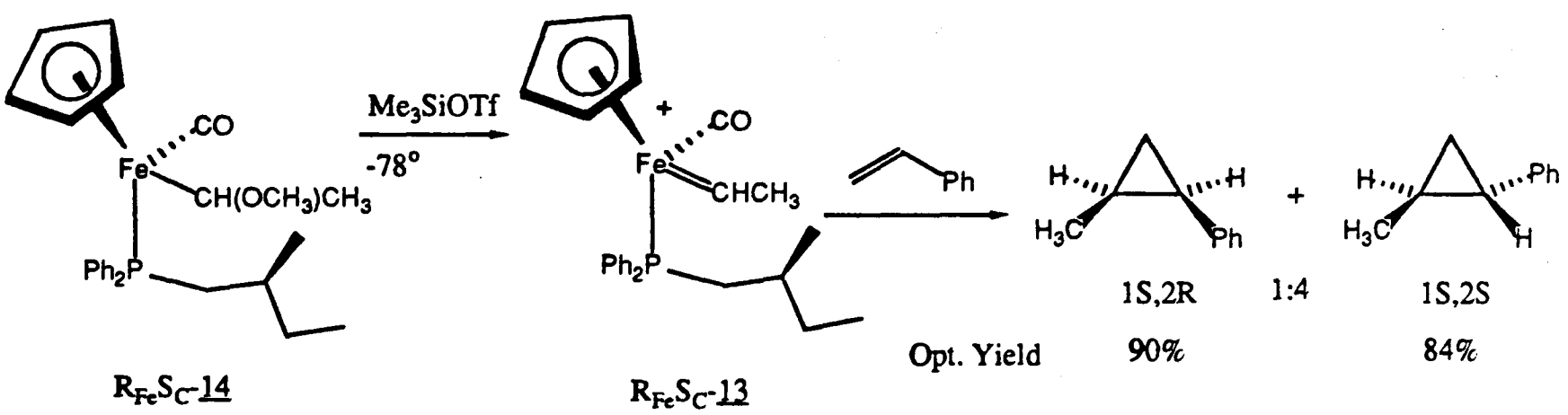
% e.e. 93 92

A drawback of this approach is that the poor control over the relative stereochemistry (i.e. trans v. cis) necessitates the chromatographic separation of the resulting diastereoisomeric products.

ii) Stoicheiometric reactions.

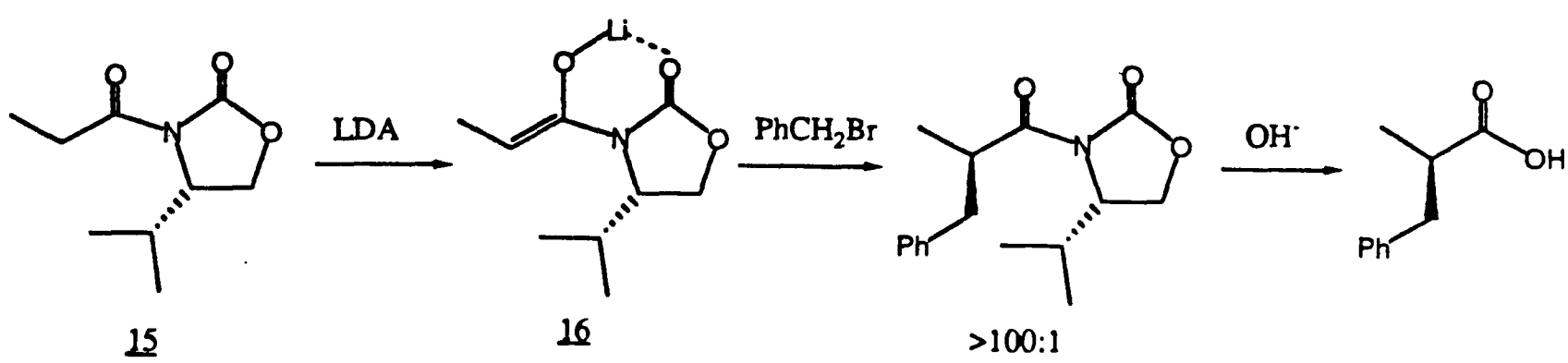
In these reactions the chiral auxiliary is attached stoicheiometrically to the substrate molecule. After elaboration of the substrate the auxiliary is removed and the optically active product

isolated. The enantioselective syntheses of cyclopropyl derivatives via the use of transition metal carbene species of high enantiomeric purity, in which the metal complex is stoicheiometrically bonded to the carbene, have been reported.[24] Brookhart[25] generated the metal carbene species 13 (from complex 14) in the presence of styrene, resulting in the enantioselective synthesis of the corresponding cyclopropyl products.

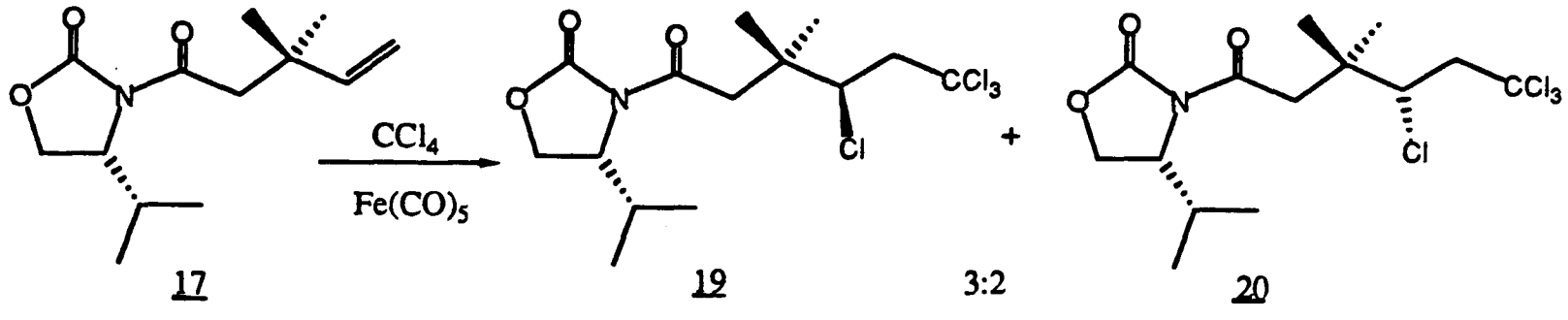


Control of the relative stereochemistry is again poor, necessitating chromatographic separation of diastereoisomers.

Evans[26] has developed homochiral oxazolidinones such as 15 (derived from S-valine) and demonstrated their use as chiral auxiliaries. Deprotonation of the imide produces enolate 16 which is maintained as a ring system via chelation to the metal counter-ion, the Z-enolate geometry being preferred on steric grounds. Subsequent alkylation is highly diastereoselective (>100:1) with the electrophile approaching from the unhindered face of the enolate. Mild hydrolysis yields the product.

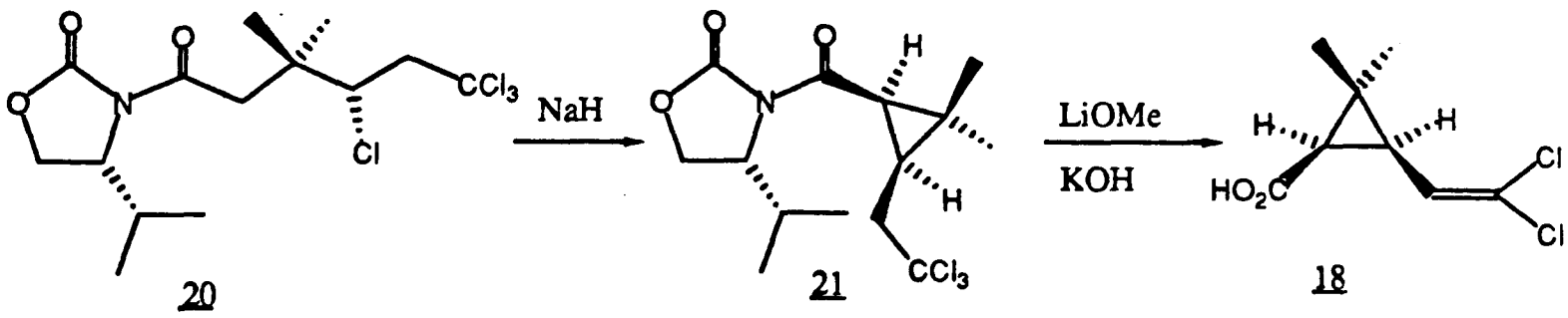


In a development of this work Kleschick[27] used the imide 17 (derived from R-valine) in the enantioselective synthesis of 1R,3R-3-(2,2-dichlorovinyl)-2,2-dimethyl cyclopropanecarboxylic acid 18. Radical addition of carbon tetrachloride across the vinylic bond gave the diastereoisomeric intermediates 19 and 20, which were separated by chromatography.



17 19 20

Subsequent treatment of the minor diastereoisomer 20 with base resulted in ring closure, giving the cyclopropanated product in 70% yield of which 92% was the diastereoisomer 21.



20 21 18

The highly stereoselective formation of 21 is due to the favourable approach of the internal electrophile to the unhindered face of the Z-enolate, ring closure occurring by an SN2 displacement of chloride. Subsequent hydrolysis and dehydrohalogenation of 21 gave the product 18.

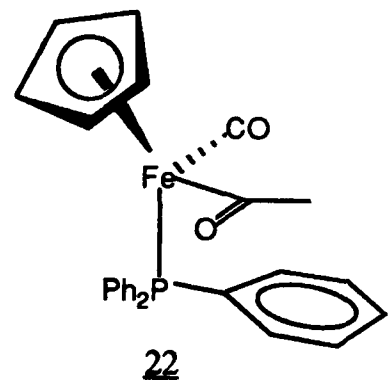
In recent years Davies et al. have developed the chiral auxiliary $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)$* and demonstrated its use in the

* The descriptor η^5 for the cyclopentadienyl ligand is omitted, henceforth, for clarity.

preparation of homochiral compounds (vide infra). We anticipated that by the use of this chiral auxiliary, highly diastereoselective and enantioselective syntheses of cyclopropyl derivatives could be developed which would overcome some of the problems outlined above for the previous approaches.

2. The Chiral Auxiliary $(C_5H_5)Fe(CO)(PPh_3)$.

The use of organometallic reagents in organic synthesis has developed rapidly.[28] Iron acyl complexes of the type $(C_5H_5)Fe(CO)(PPh_3)(COCH_2R)$ have been shown to undergo highly stereoselective reactions[29,30] and have been used in the syntheses of several homochiral biologically active compounds.[31] The parent complex $(C_5H_5)Fe(CO)(PPh_3)(COCH_3)$ 22 is shown below.

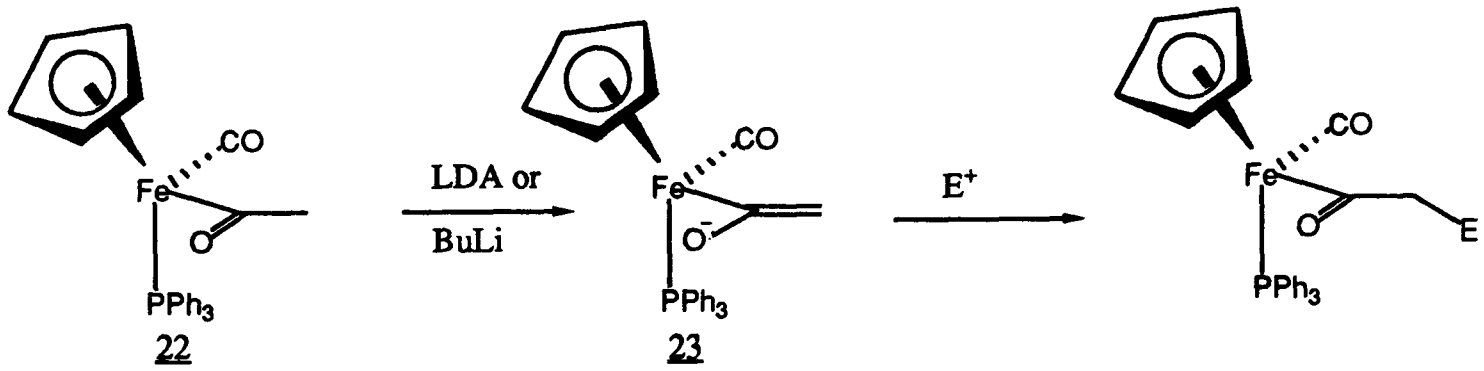


22

The arrangement of the ligands about the iron centre is essentially octahedral.[32] Three adjacent coordination sites are occupied jointly by the cyclopentadienyl ligand, whilst the remaining three are occupied by the triphenylphosphine, carbon monoxide and acetyl ligands. The line between the centroid of the cyclopentadienyl ligand and the iron subtends an angle of approximately 125° to each of the bonds between the iron and the other three ligands. In turn, these three bonds are approximately orthogonal to each other. The complex 22 is chiral and is commercially available[33] either as a racemate or in the enantio-

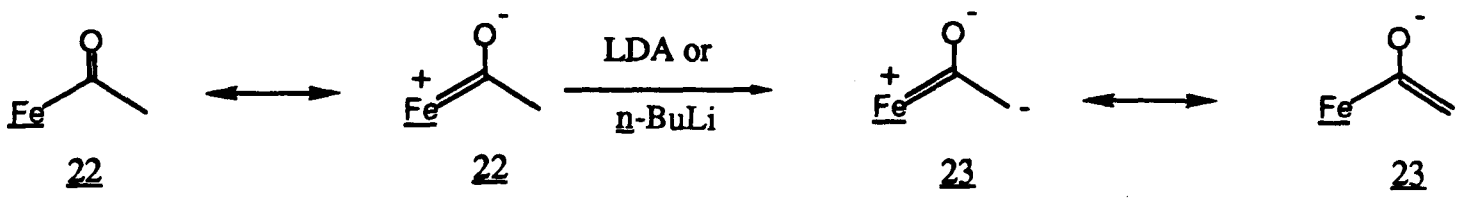
merically pure R(-) and S(+) forms.* Configurational stability has been demonstrated[35] and racemisation, resulting in loss of enantiomeric purity, has not been observed.

The acetyl ligand has some similarities to a methyl ketone. Treatment of complex 22 with base gives the enolate 23 which can be trapped by a range of electrophiles.[36]



22 23

However, the α-protons are less acidic, and the acyl group less electrophilic, than for the corresponding methyl ketones due to dπ-pπ electron back-donation by the iron moiety. This is manifested by both the low frequency infra-red absorption of the carbonyl group at 1608 cm^{-1}, and the necessity of using strong bases such as LDA or butyllithium to form enolate 23.



22 22 23 23

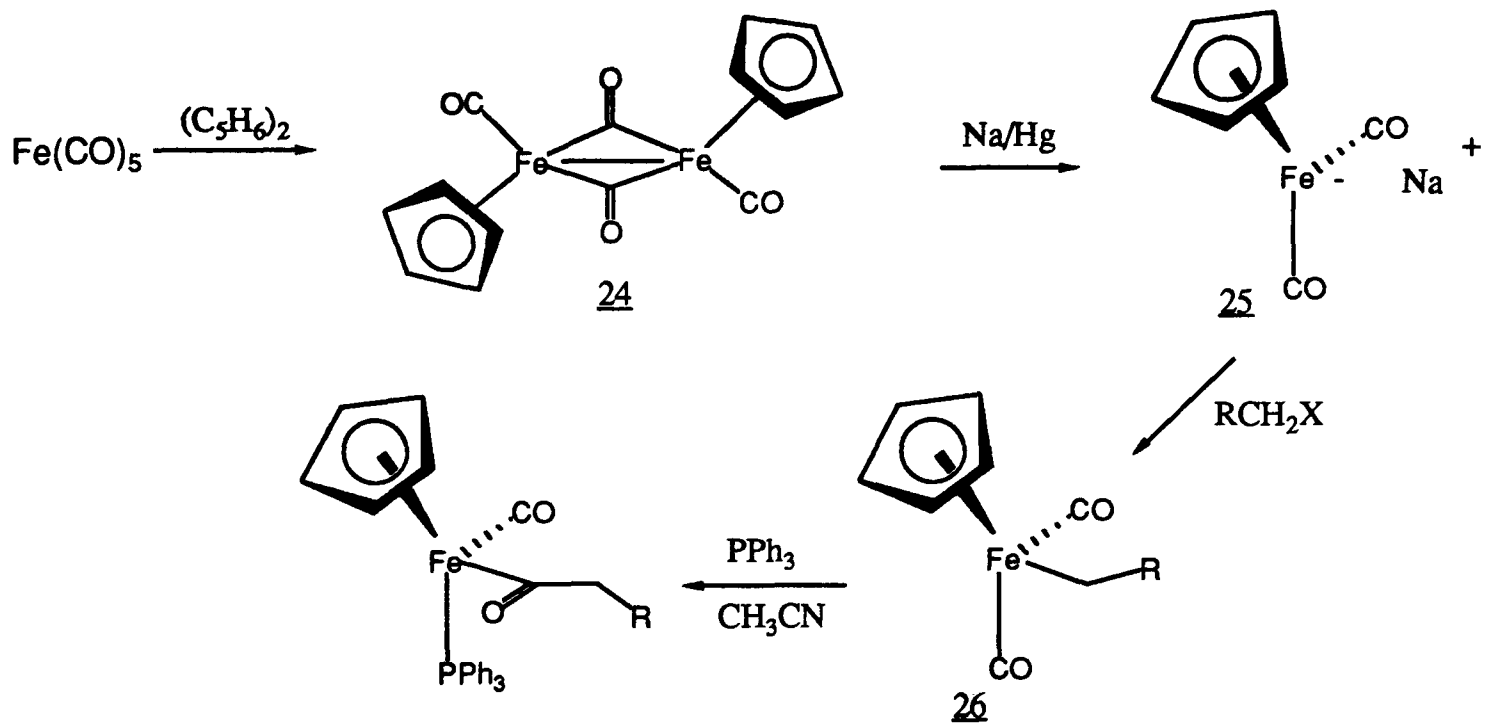
An appropriate analogy for the acetyl complex 22 is the monoanion of methyl acetoacetate which also requires the use of butyllithium to generate the bis-anion.

Consistent with this analogy, the bis-anion and enolate 23 both undergo C-silylation.[36,37]

* Ligand priority order $(C_5H_5)>(PPh_3)>(CO)>(COCH_2R)$.[34] Unless otherwise stated all iron complexes reported in this thesis are racemic. For the purposes of clarity, only complexes with the R-configuration at iron are shown.

a) Synthesis of the Iron Acyl Complexes $(C_5H_5)Fe(CO)(PPh_3)(COCH_2R)$

One synthetic approach to the above complexes is outlined below.



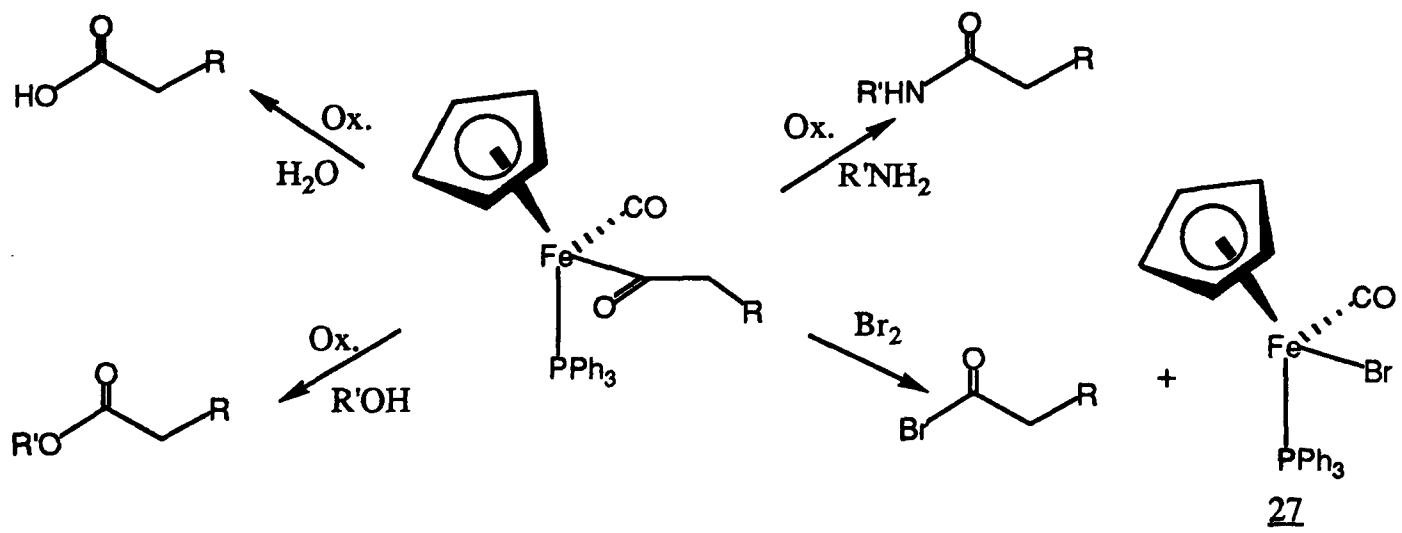
The iron dimer 24 is formed by heating iron pentacarbonyl with dicyclopentadiene.[38] Cleavage of 24 with sodium amalgam gives the anionic species 25, which is trapped by a range of alkyl halides to give the corresponding iron alkyl species 26.[39] Treatment of 26 with triphenylphosphine in acetonitrile at reflux gives the corresponding iron acyl product (see Experimental Section).[40]

Alternatively, iron acyl complexes are prepared from the iron bromide 27 which, in turn, is prepared from the iron dimer 24. Treatment of 27 with lithium acetylides gives the corresponding acetylide complexes 28 which, on mild hydrolysis, give the desired acyl complexes.[41]

Small scale syntheses of the enantiomerically pure complexes have been achieved *via* the resolution of diastereoisomeric menthyl ester derivatives which, on treatment with alkyllithiums, gave the desired homochiral iron acyl complexes.[35] However, this approach has proved to be unreliable, particularly for large scale syntheses.[42]

b) Decomplexation of Iron Acyl Complexes.

Following stereoselective elaboration of the acyl ligand (*vide infra*) its decomplexation must proceed with retention of stereochemistry at every chiral centre present. This can be achieved by using a mild one-electron oxidant such as bromine or cerium (IV) salts.[43] A range of the corresponding carboxylic acid derivatives can be formed depending on the reaction conditions.



27

The use of bromine as the oxidant generates the iron bromide species 27. Since this is an intermediate in one synthesis of iron acyl complexes (see p. 11), a route is provided for the recycling of the iron chiral auxiliary.[44]

c) Conformational Analysis of Acyl Ligands attached to the Chiral Auxiliary $(C_5H_5)Fe(CO)(PPh_3)$.

Davies *et al.* have developed a detailed conformational

analysis of $(C_5H_5)Fe(CO)(PPh_3)$(alkyl) complexes based on X-ray crystal structure data, theoretical modelling studies and ^1H n.m.r. data.[45,46] This analysis has been extended to include the corresponding iron acyl complexes.[47,48]

The X-ray crystal structure[29,49] of the iron acetyl complex 22 (figure 1) shows clearly the pseudo-octahedral geometry of the ligands about the iron centre, and reveals that in the solid state the acyl oxygen lies close to antiperiplanar to the carbon monoxide ligand.

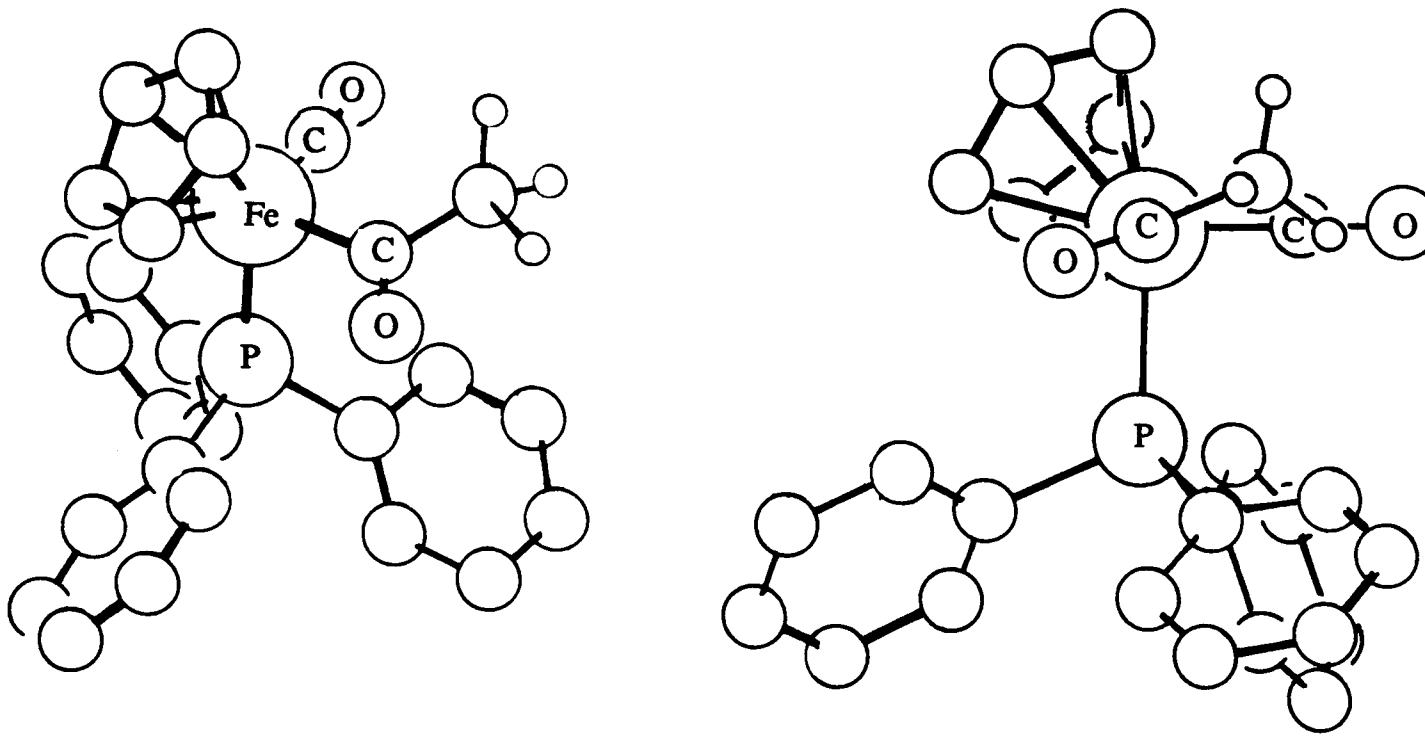
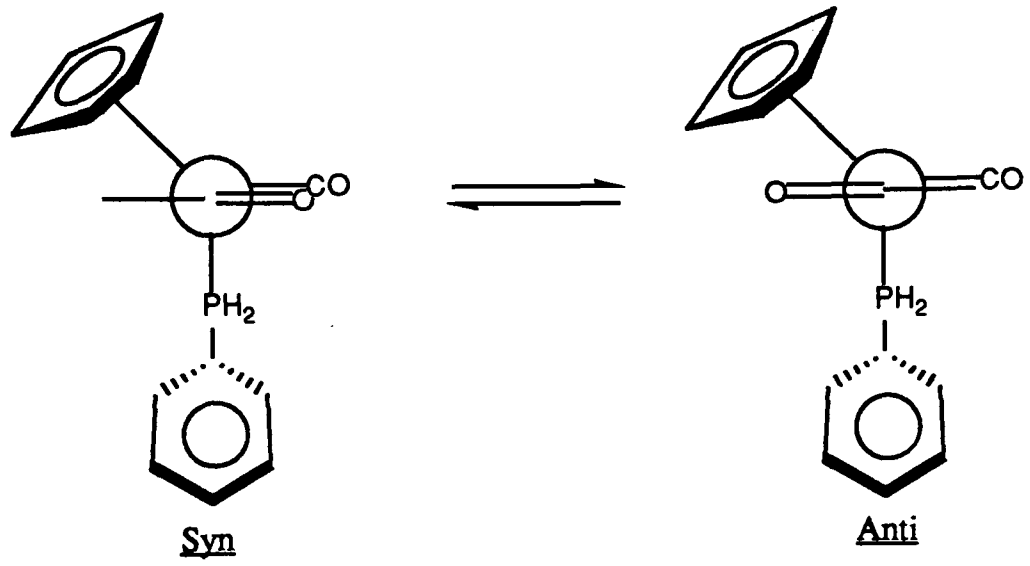


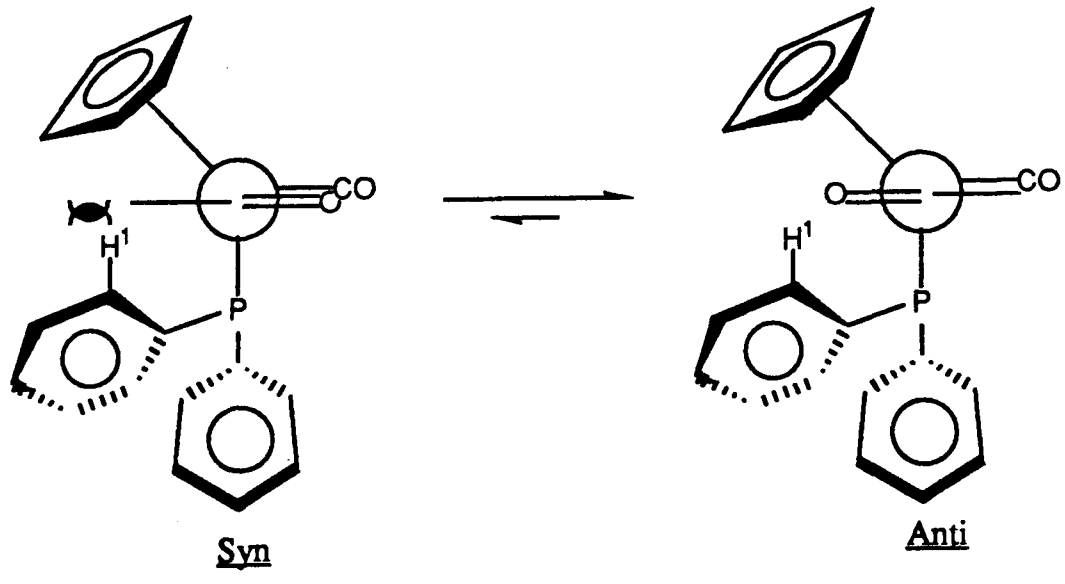
Figure 1. X-ray crystal structure for $(C_5H_5)Fe(CO)(PPh_3)(COCH_3)$ 22. Selected protons are removed for clarity.

Davies showed that the conformational preferences of the acetyl ligand are determined by steric effects,[47] the nature of these effects being calculated by a series of modelling studies.[48] The triphenylphosphine ligand will rotate about the Fe-P bond, but in order to determine the interaction between the acetyl ligand and the phenyl ring directly below, calculations were performed on the model system $(C_5H_5)Fe(CO)(PPhH_2)(COCH_3)$ where rotation about the Fe-P bond was restricted such that the $Fe-C(O)CH_3$ bond and the $P-C_{ipso}$ bond were eclipsed.



Syn Anti

The results of the calculation for this model system showed that steric interactions are minimised when the acyl ligand lies planar to the phenyl ring, the syn- and anti-(acyl oxygen to carbon monoxide ligand) conformations being energetically degenerate. Further calculations[48] showed that steric interactions between the methyl substituent and the ortho-proton (H^1) on the leading edge of a second proximate phenyl ring destabilises the syn-conformation relative to the anti-conformation.

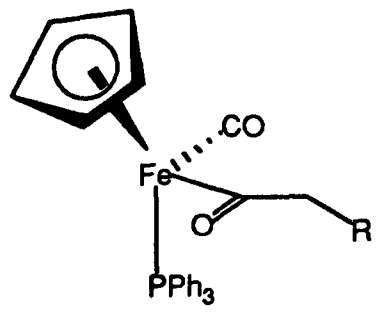


Syn Anti

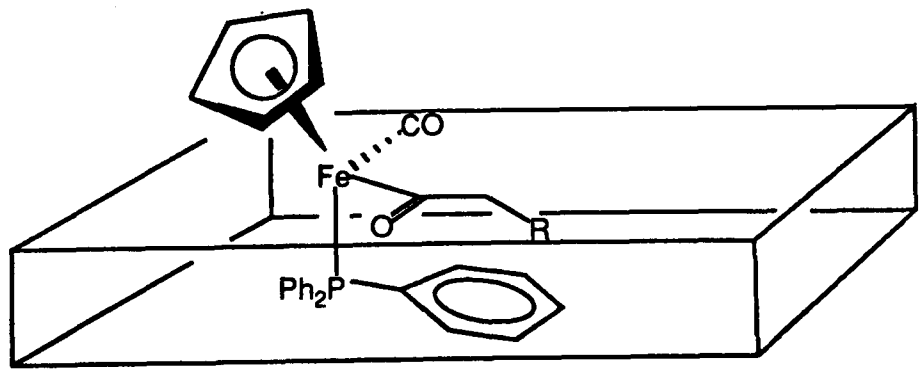
The overall conclusion from these calculations is that, in terms of steric considerations, the most stable conformation for the acetyl complex 22 is essentially that seen in the solid

state (figure 1).

The same steric properties discussed for the complex 22 will persist in complexes with longer alkyl chains. Furthermore, the alkyl chain will preferentially lie cis to the acyl oxygen, i.e. trans to the large iron moiety.[50]



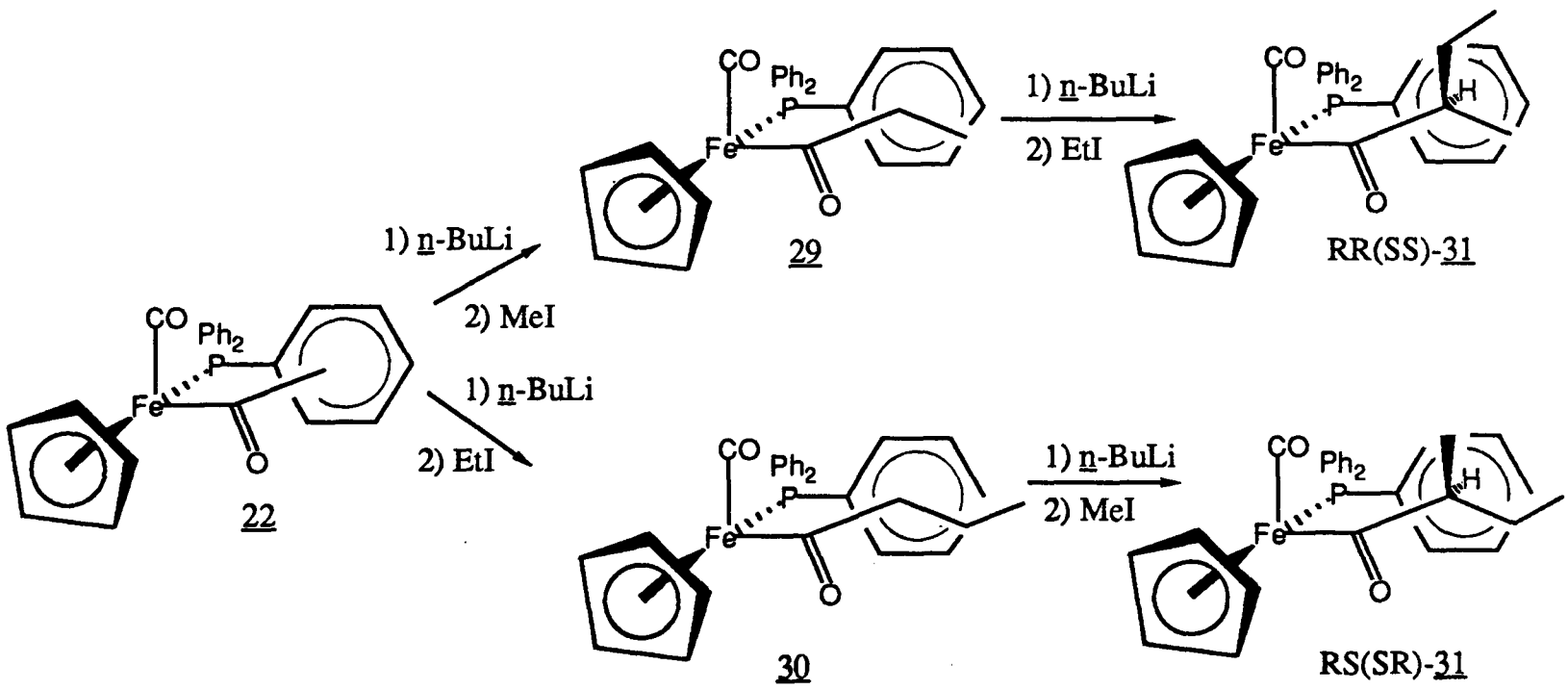
The plane containing the acyl oxygen, the iron and the carbon monoxide ligand is approximately parallel to one containing the phenyl ring directly beneath the acyl ligand. The planes may be considered as the upper and lower faces, respectively, of a box which represents an "excluded volume" to potential reagents. The bulk of the triphenylphosphine blocks the lower face of the acyl ligand and this, combined with the conformational preferences discussed above, account for the high stereoselectivity observed in reactions of the iron acyl complexes (vide infra).



d) Stereoselective Reactions of $(C_5H_5)Fe(CO)(PPh_3)(COCH_2R)$.

i) Alkylation reactions.

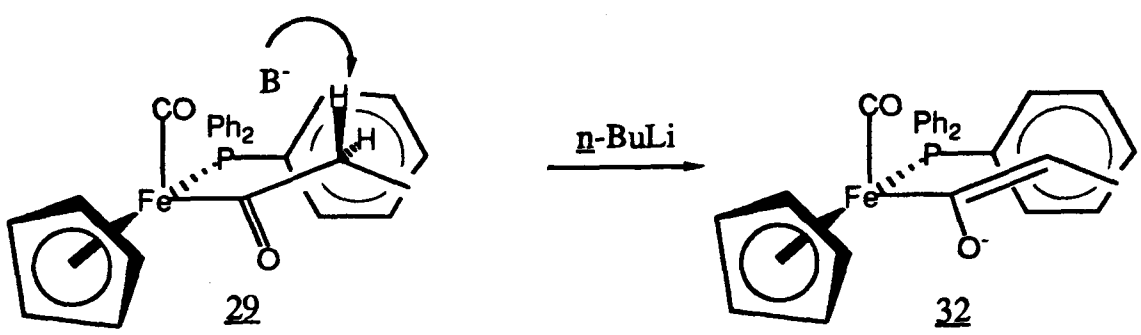
Treatment of the iron acetyl complex 22 with butyllithium generated the enolate 23, which, on trapping with methyl or ethyl iodide, gave the ethyl or propyl acyl complexes 29 and 30 respectively.[51] Deprotonation of 30 and methylation gave the s-butyl complex RS(SR)-31, the relative stereochemistry between the iron and α-centres being determined by X-ray crystallography.[51] Deprotonation of 29 and ethylation gave the diastereoisomeric product RR(SS)-31. Subsequently the alkylation reactions were shown to proceed with a diastereoselectivity of >200:1,[50] the ^{13}C satellites in the ^{1}H n.m.r. spectrum providing an internal standard for the assessment of diastereoisomeric purity.



The appearance of the methyl doublet for RR(SS)-31 at δ0.17 p.p.m. in the ^{1}H n.m.r. spectrum reflects its shielded position over the proximate phenyl ring of the triphenylphosphine ligand

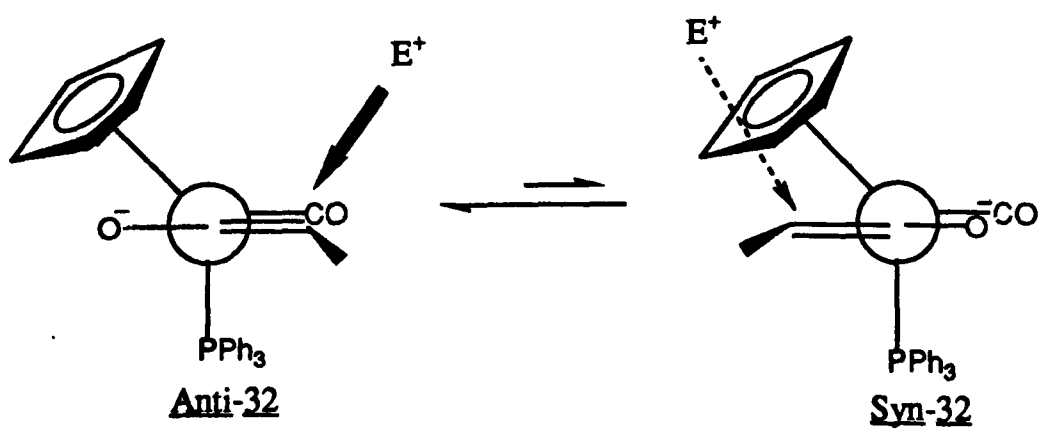
(cf the corresponding signal at δ 1.01 p.p.m. for the diastereoisomeric RS(SR)-31). This difference is common to all complexes with an α-methyl substituent and constitutes an important method of assigning the stereochemistry at this centre.[52]

The high degree of stereoselectivity in the alkylation reactions can be explained in terms of the previous conformational analysis (section 2.c)). Since the alkyl chain of the acyl ligand in 29 must lie trans to the large iron moiety, then only one of the two α-protons is accessible to the base, approach to the other one being blocked by the triphenylphosphine ligand, and the E-enolate 32 will be formed exclusively.[50]



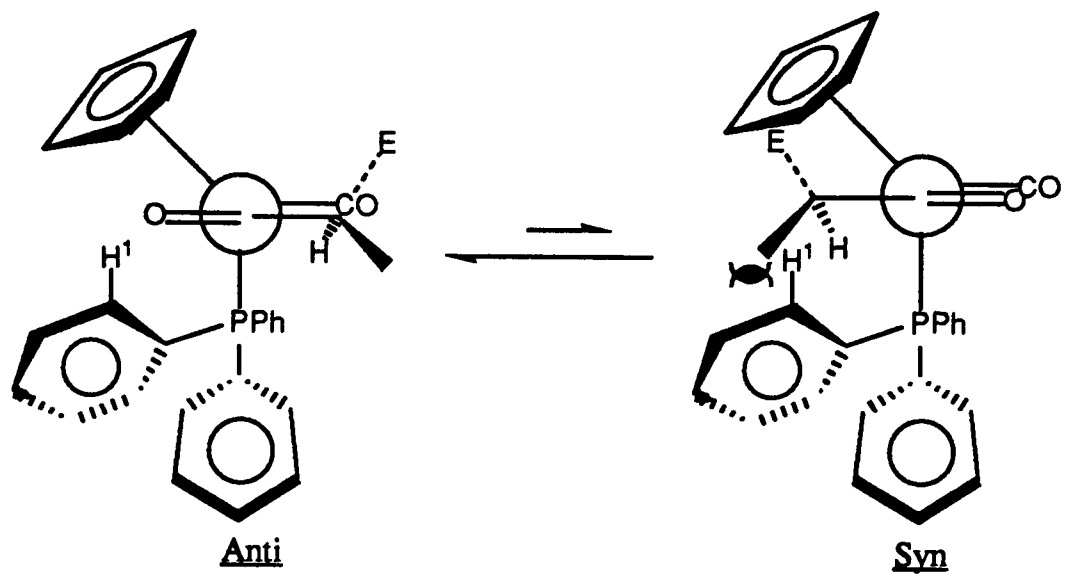
29 32

Since the α-carbon in 32 is sp^2 hybridised, then the steric interaction with the second proximate phenyl ring (see p. 14) would be expected to be greatly reduced and the syn-and anti-enolates to both be sterically accessible.[50] If the stereochemistry is determined by the ease of approach of the electrophile (early transition state), then reaction via the anti-conformation is expected to be preferred since approach of the electrophile in the syn-conformation is hindered by the cyclopentadienyl ligand.



Anti-32 Syn-32

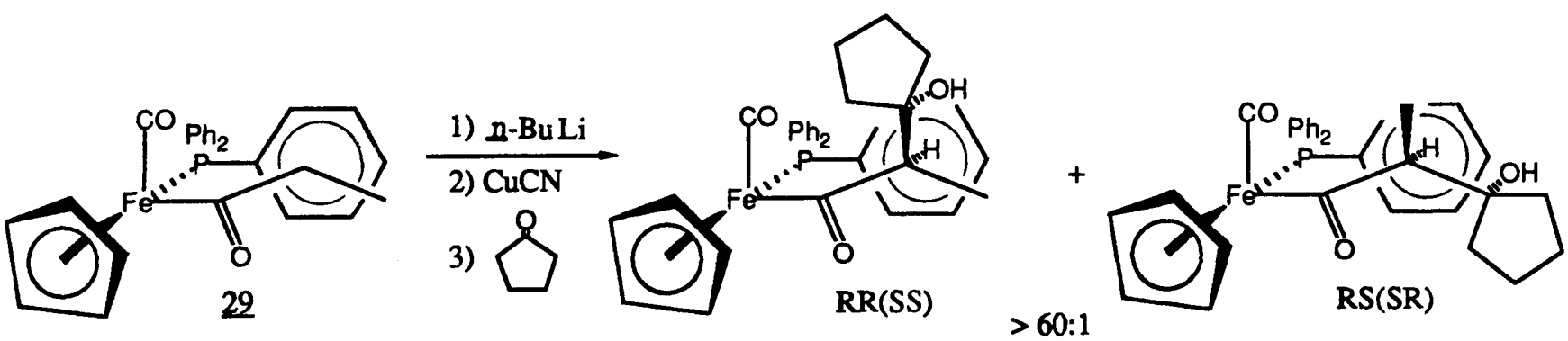
Alternatively, if the reaction is under product development control (late transition state) then generation of the secondary alkyl centre will be favoured in the more sterically accessible position i.e. away from the ortho-proton (H^1).[50]



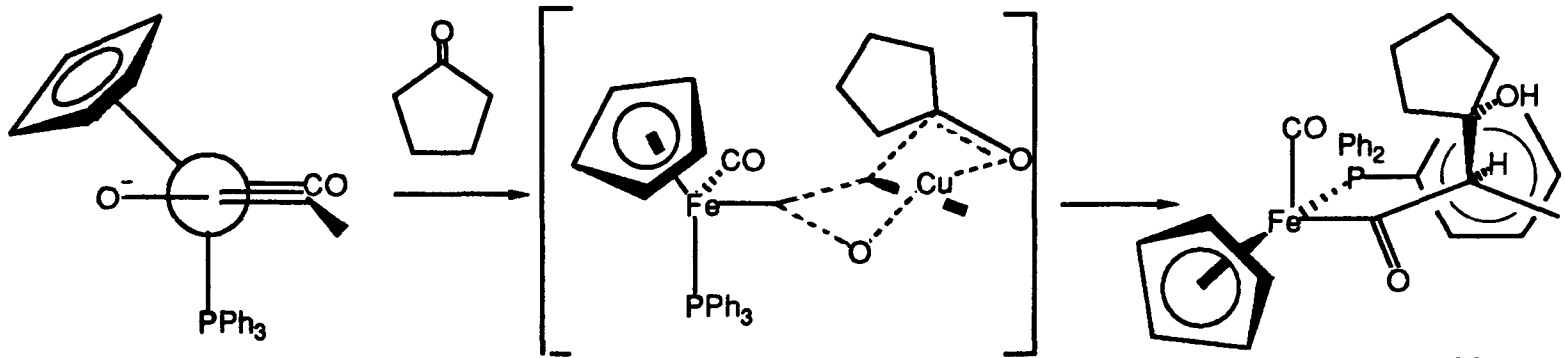
Both approaches account for the stereochemistry of the product RR(SS)-31.

ii) Aldol reactions.

Similarly high diastereoselectivity at the α-centre is observed when the copper enolate derived from 29 is treated with symmetrical ketones.[53]



The high diastereoselectivity arises due to the favourable approach of the ketone to the anti E-enolate 32 and the formation of the relatively unhindered chair-like transition state 33.[54]



32 33 RR(SS)

By the use of aldehydes in this type of aldol reaction, the iron chiral auxiliary has been shown to exert stereochemical control over the β- as well as the α-centre.[55,56]

iii) Other reactions.

Highly diastereoselective Michael additions to α,β-unsaturated iron acyl complexes (see Chapter 4) have been reported[57] and these complexes also undergo stereoselective Diels-Alder reactions.[58] The generation and alkylation of chiral dienolates has also been reported.[59]

The ability of the chiral auxiliary $(C_5H_5)Fe(CO)(PPh_3)$ to exert high stereochemical control over associated ligands has therefore been demonstrated. Furthermore, the wide range of mild oxidative decomplexation techniques make the iron acyl complexes attractive reagents for the asymmetric synthesis of organic molecules.

The importance of cyclopropyl derivatives of high diastereoisomeric and enantiomeric purity has been described above. Despite a number of methods for the preparation of such compounds (vide supra), few general procedures are available. Our aims were to utilise the strong stereochemical influence of the chiral auxiliary $(C_5H_5)Fe(CO)(PPh_3)$ to devise highly stereoselective syntheses of such compounds in which both the relative and absolute stereochemistry of the substituted cyclopropane ring was controlled.

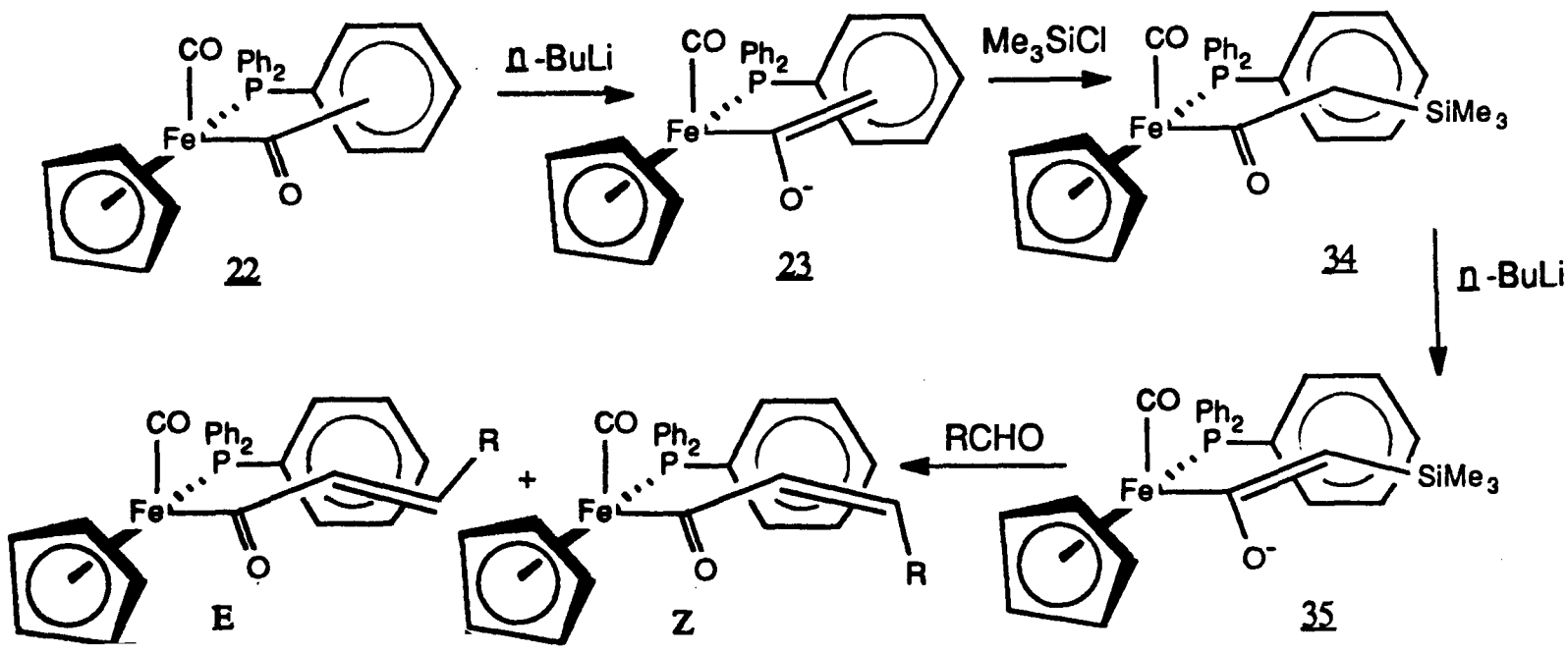
CHAPTER 2

PREPARATION OF α,β-UNSATURATED IRON ACYL COMPLEXES AND CONFORMATIONAL ANALYSES OF THE ACYL LIGANDS

Cyclopropyl derivatives are frequently prepared from olefinic starting materials, either by reaction with carbenes (or carbenoid species)[22-25,60,61] (see Chapter 3) or with ylids (see Chapter 4).[62] Davies et al. have reported the preparation [59,63] and stereoselective elaboration[57-59] of α,β-unsaturated iron acyl complexes of the type $(C_5H_5)Fe(CO)(PPh_3)(COCH=CRR')$ and have demonstrated their utility in the preparation of enantiomerically pure molecules.[57c,57d,58] By the use of existing methodology for cyclopropane ring formation, and by the development of new techniques, we sought to utilise the strong stereochemical influence of the chiral auxiliary $(C_5H_5)Fe(CO)(PPh_3)$ on the α,β-unsaturated acyl ligand, for the asymmetric synthesis of cyclopropyl derivatives.

1. Preparation of the α,β-Unsaturated Iron Acyl Complexes $(C_5H_5)Fe(CO)(PPh_3)(COCH=CRR')$.

According to the literature method,[36,63] a solution of $(C_5H_5)Fe(CO)(PPh_3)(COCH_3)$ 22 in THF at -78°C was treated with butyllithium, generating enolate 23 which was quenched with trimethylsilyl chloride. The resulting complex 34 was treated with butyllithium, as before, forming the enolate 35 which, on treatment with a range of aldehydes, underwent a Peterson reaction[64] to give mixtures of E- and Z-isomers of the corresponding α,β-unsaturated iron acyl complexes.



After work up the isomers were easily separated chromatographically, the Z-isomer eluting first in every case. Double bond geometries were assigned from the ^{1}H n.m.r. spectra on the basis of the observed coupling constants between olefinic protons, typically in the range 11.1-11.4 Hz for the Z-isomers and 14.9-15.2 Hz for the E-isomers. The results are summarised in table 1. The majority of products had been synthesised previously and the structures were confirmed by comparison of the spectroscopic data with that reported in the literature.[59,63] The novel complexes 50 and 51 were characterised satisfactorily.*

R	Compound E:Z	Ratio E:Z	Yield %
Me	36:37	2:1	79
Et	38:39	2:1	60
^{n}Pr	40:41	3:2	87
^{n}Bu	42:43	3:2	83
^{i}Pr	44:45	4:3	92
^{t}Bu	46:47	—[a]	50
$CH=CH_2$	48:49	3:2	85
$CH=C(CH_3)_2$	50:51	5:2	67

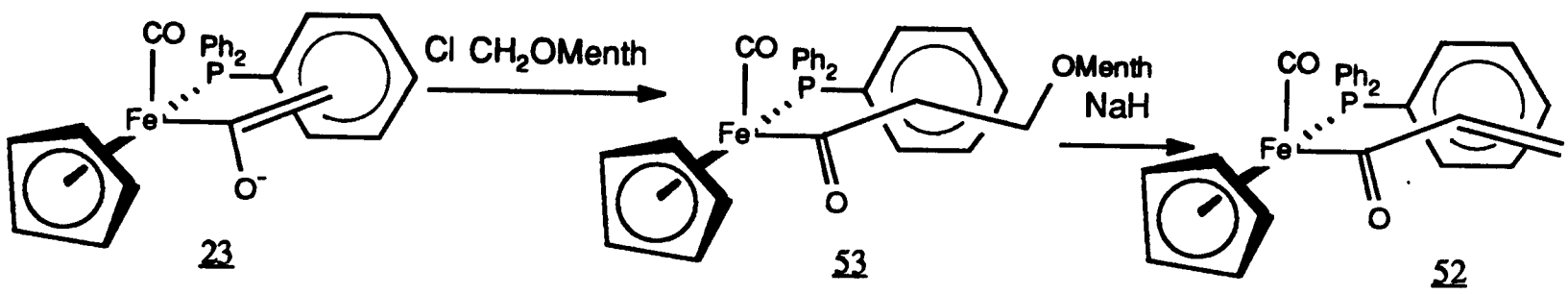
a) A single isomeric product was obtained which was identified as the E-isomer 46.

Table 1. Overall yield and E:Z isomer ratio for the preparation of $(C_5H_5)Fe(CO)(PPh_3)(COCH=CHR)$.

* Throughout this thesis, unless otherwise stated, novel complexes were characterised by ^{1}H, ^{13}C and ^{31}P (where applicable) n.m.r. spectroscopy, mass spectrometry, infra-red spectroscopy and by combustion analysis.

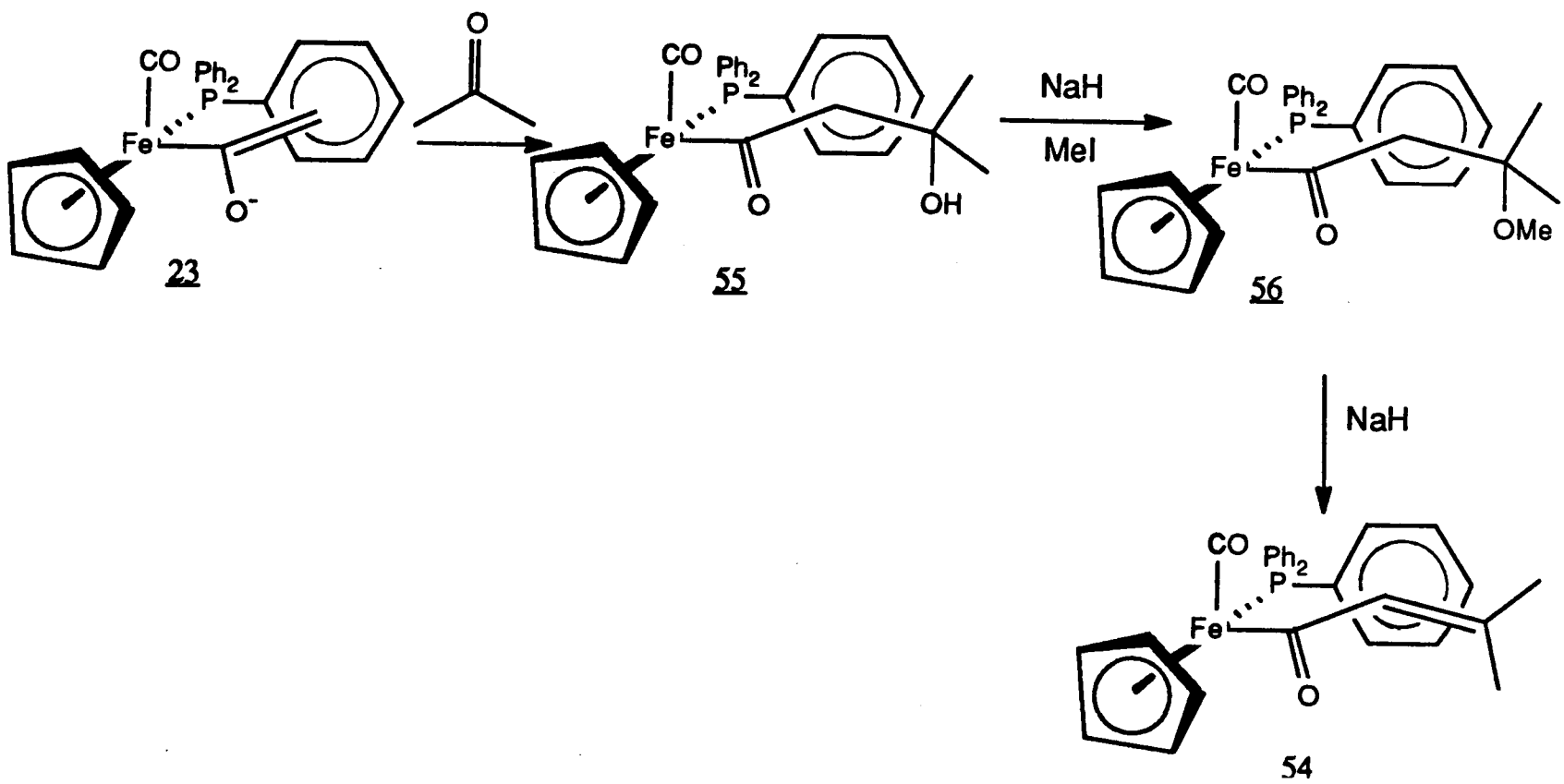
Enantiomerically pure complexes 36 and 37 were synthesised in the same way by the use of homochiral R(-)- or S(+)-22.[33] The enantiomeric purity of the products was confirmed by comparing their optical rotations with the published data.[29]

Reaction of enolate 35 with formaldehyde results in base promoted polymerisation.[63] An alternative route to the parent acryloyl complex 52 is shown below.[29]



Enolate 23 was quenched with chloromethyl R-menthyl ether[65] generating the diastereoisomeric β-menthoxy complexes 53. Crude 53 was treated with base, elimination of menthol giving the product 52 in 44% isolated yield.

Reaction of enolate 35 with ketones gives only recovered starting material 34.[59] Instead, the β-dialkylated α,β-unsaturated iron acyl complexes are prepared from the corresponding β-methoxy complexes. For example, the β-dimethylated complex 54 was prepared as outlined below.[59]

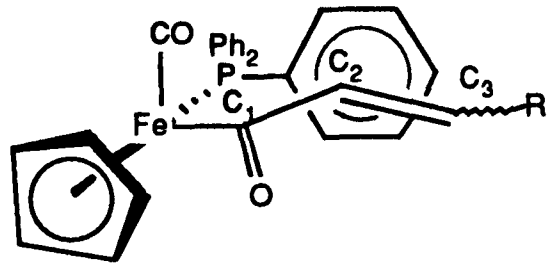


Quenching enolate 23 with acetone gave the β-hydroxy complex 55, which was O-methylated giving the β-methoxy complex 56. Treatment of 56 with base resulted in elimination of methanol to give, on work up, the product 54 in 46% isolated yield.

2. Conformational Analyses of the α,β-Unsaturated Acyl Ligands Attached to the Iron Chiral Auxiliary $(C_5H_5)Fe(CO)(PPh_3)$.

Davies et al. have reported a detailed conformational analysis for alkyl and acyl ligands bound to the chiral auxiliary $(C_5H_5)Fe(CO)(PPh_3)$.[29,45-48] By use of the ChemX[66] computer modelling system we hoped to develop the previous work to obtain more detailed conformational analyses for a range of α,β-unsaturated acyl ligands bound to the same chiral auxiliary.

The calculations were performed, where possible, on the basis of X-ray crystal structure data. Where no data was available, the structures were generated from the X-ray crystal structure data of either E-$(C_5H_5)Fe(CO)(PPh_3)(COCH{=}CHCH_3)$ 36[57c] (for 52 and 46) or Z-$(C_5H_5)Fe(CO)(PPh_3)(COCH{=}CHCH_3)$ 37[67] (for 45 and 47). Since conformational properties of the saturated acyl ligands have been shown to be determined by steric effects,[47] the calculations performed on the unsaturated acyl ligands were qualitative empirical force-field ones using default parameters which only took into account Van der Waal's interactions. For each complex the α,β-unsaturated ligand was allowed to rotate about both the Fe-C1 and C1-C2 bonds with the relative energy being calculated at 15° intervals.



In order to make the calculations feasible no other bond rotations within the complexes were allowed. The relative energies calculated are plotted as conformational energy maps, the

energy being plotted against the O-C1-Fe-P (abscissa) and O-C1-C2-C3 (ordinate) torsional angles. For each axis the 0^{o} torsional angle represents eclipsed bonds, and negative angles represent anticlockwise rotations. The calculations are not intended to predict the absolute energy of the barrier to rotation, but rather to provide insight into the inherent steric forces present in these complexes. The additional stability afforded to conformations in which planarity of the α,β-unsaturated acyl ligands results in resonance stabilisation will not be apparent from this calculation, but will be discussed (vide infra).

a) $(C_5H_5)Fe(CO)(PPh_3)(COCH{=}CH_2)$ 52

The results of the calculation for 52 are shown in figure 2. Newman projections along the C1-Fe and C2-C1 bonds are highlighted on the abscissa and ordinate respectively. At 0^{o} the bonds defining the torsional angles (i.e. O-C1 and Fe-P (abscissa), and O-C1 and C2-C3 (ordinate)) are eclipsed, whilst at $\pm 90^{o}$ the bonds, are orthogonal. The dark regions are areas of minimum energy, and each contour represents an approximately 5kcal mol^{-1} increase in energy from these regions.

The contour map shows energy minima corresponding to conformations in which the carbon-oxygen (C1-O) bond of the acyl group is approximately anti or syn to the carbon monoxide ligand. These conformations would minimise steric interactions of the acyl ligand with the proximate phenyl ring. Similar conformational preference is seen for the parent iron acyl complex $(C_5H_5)Fe(CO)(PPh_3)(COCH_3)$ 22. (see Chapter 1, section 2.c)). For complex 22 the syn-conformation is of higher energy than the anti due to unfavourable steric interaction between the methyl group and the ortho-proton (H^1) of the leading edge of a second phenyl ring.

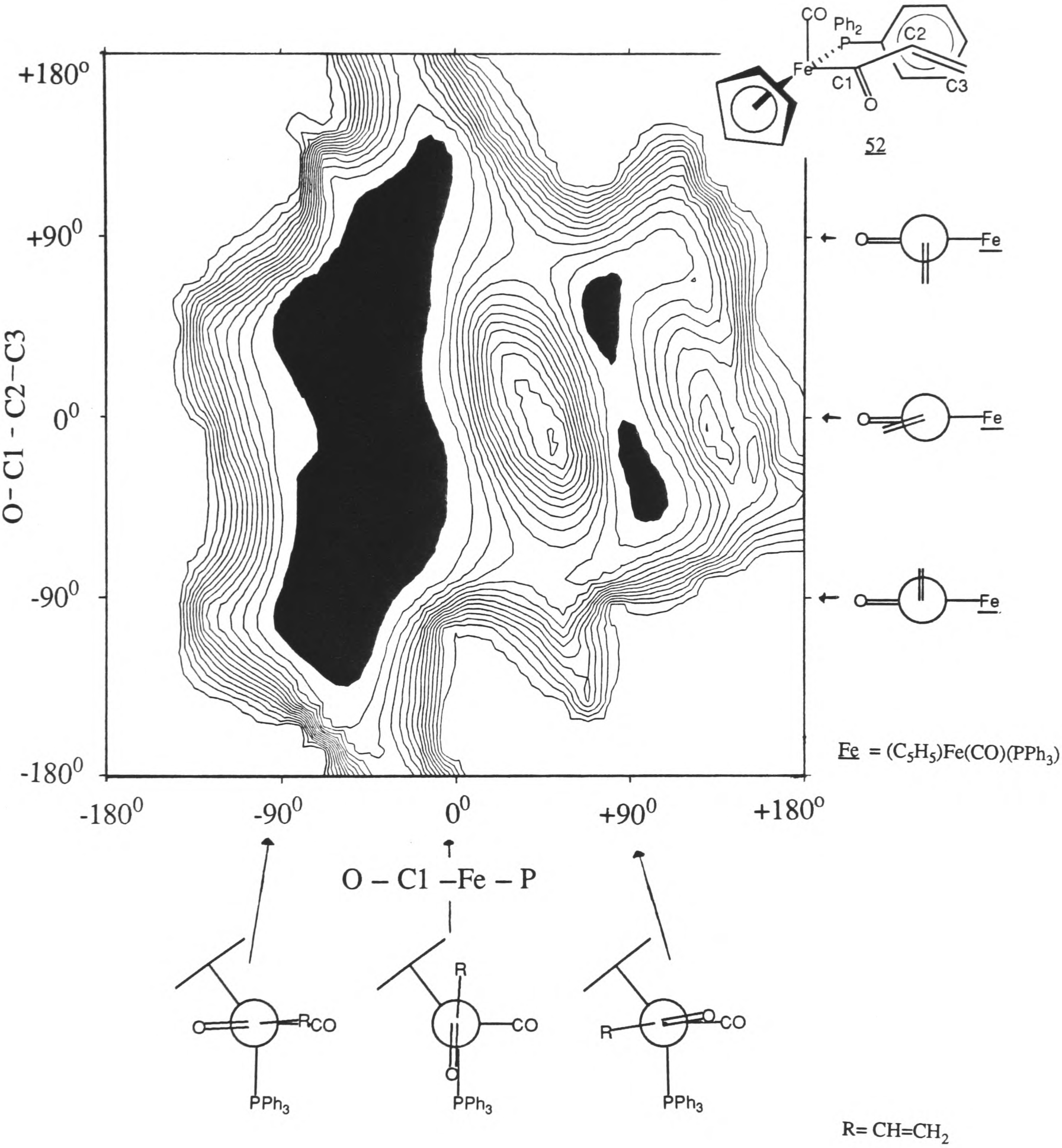
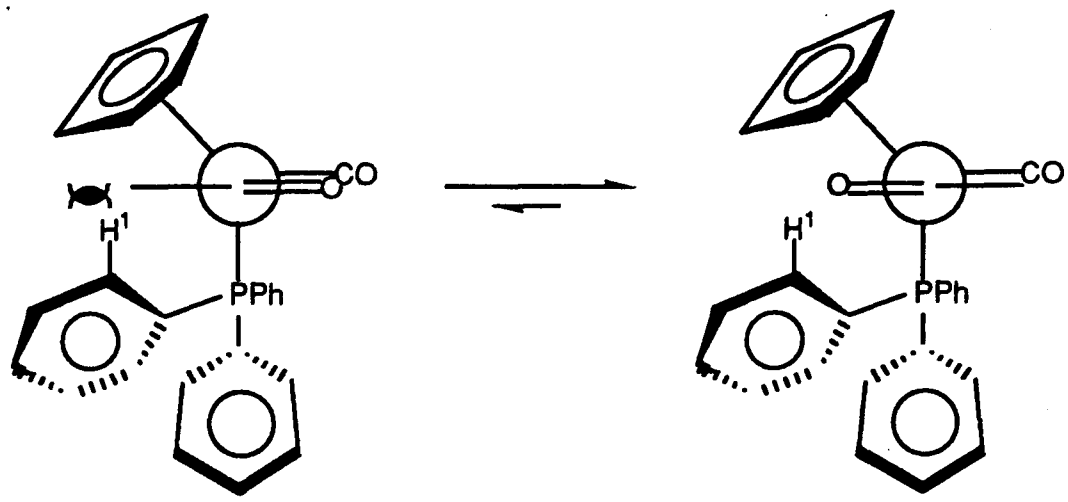
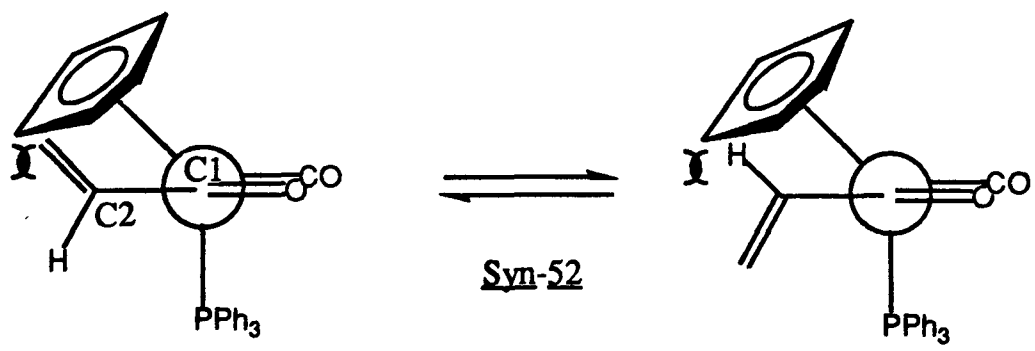


Figure 2. Conformational energy map for $(C_5H_5)Fe(CO)(PPh_3)(COCH=CH_2)$ 52



Syn -22 Anti -22

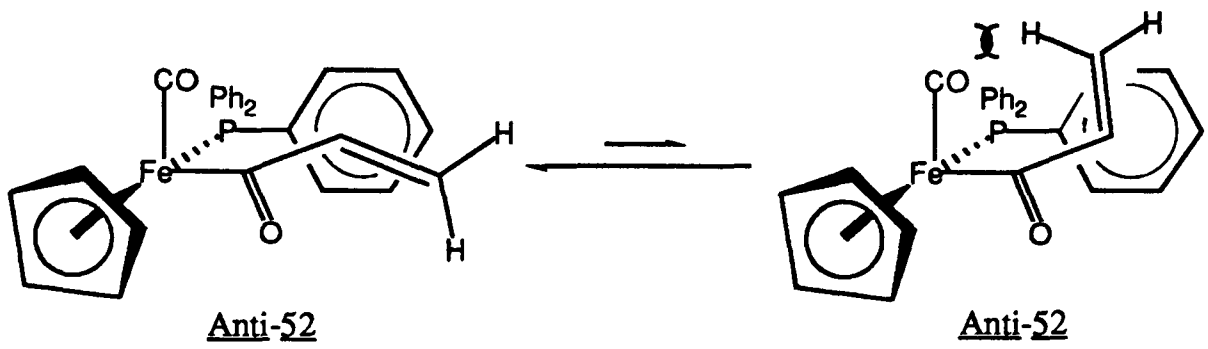
In the acryloyl complex 52, the α-carbon is sp^2 hybridised, and the interaction described above will be less severe. However, the result of the calculation for 52 (figure 2) shows that the syn-conformations are still of slightly higher energy than the anti-ones. Models show that in syn-conformations, the substituents on the α-carbon interact with the cyclopentadienyl ligand. In addition to raising the energies of syn-conformations, these interactions decrease rotational freedom about the acyl-vinyl (C1-C2) bond.



Syn-52

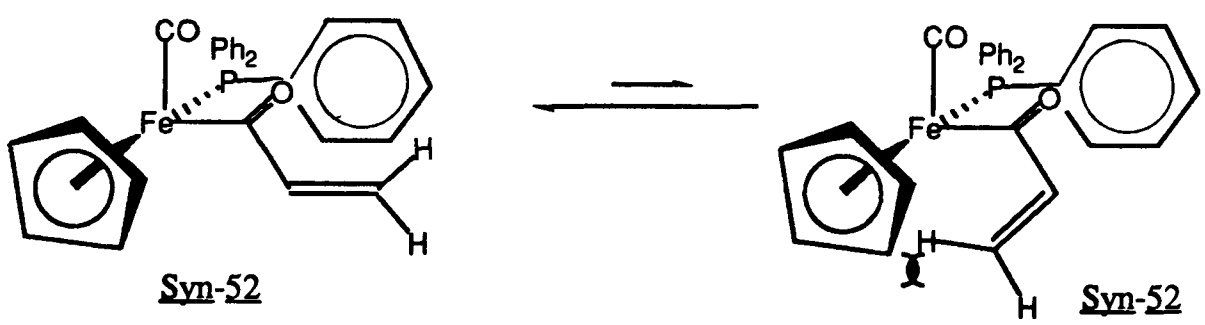
For both syn and anti cases, S-trans conformations (i.e. vinyl trans to acyl) are sterically less favourable since these place the vinyl group cis to the large iron moiety. Models show that in any S-trans conformation the cis-β-proton will be proximate to

one or more of the ligands about the iron centre, resulting in increased steric hindrance relative to the corresponding S-cis conformation.



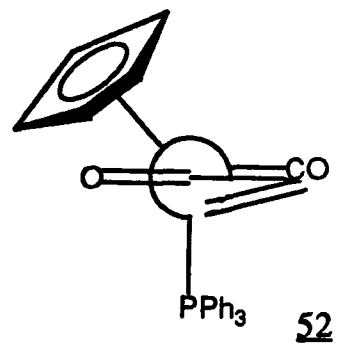
Anti-52 Anti-52

S-cis S-trans

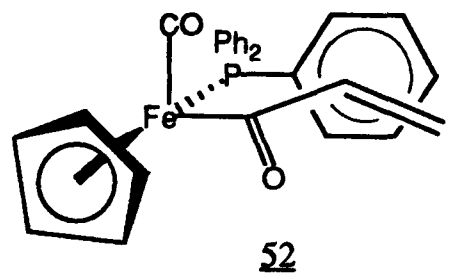


Syn-52 Syn-52

The calculation performed considered solely steric effects acting on the acryloyl ligand. An additional factor affecting its conformational properties will be π-resonance stabilisation, which is maximised in the planar S-cis or S-trans conformations. The lowest energy conformations will therefore be ones of minimum steric hindrance and maximum π-orbital overlap. These are expected to be conformations in which the acyl bond is approximately anti to the carbon monoxide ligand, and the acyl ligand adopts the sterically accessible and electronically favourable S-cis conformations, the S-trans conformations being less favourable on steric grounds (vide supra).



52



52

The conformational properties of both E- and Z-isomers of α,β-unsaturated iron acyl complexes are investigated in the following sections.

b) E-(C_5H_5)Fe(CO)(PPh_3)(COCH=CHR) (R=CH_3-36 or R=$C(CH_3)_3$-46).

The results of the calculations for complexes 36 (R=CH_3) and 46 (R=$C(CH_3)_3$) are shown in figures 3 and 4 respectively. The energy contour map for each complex is essentially the same as for the parent acryloyl complex 52 (figure 2). From the result of the calculation performed on 52 it was concluded that the primary steric interaction experienced by the unsaturated acyl ligand was with the proximate phenyl ring of the triphenylphosphine ligand which favoured conformations placing the carbon-oxygen bond of the acyl group close to periplanar to the carbon monoxide ligand. A secondary interaction, between the substituents on the α-carbon and the cyclopentadienyl ligand, disfavoured the syn-relative to the anti-conformations. A third interaction between the cis-β-proton and the ligands about the iron centre disfavoured the S-trans relative to the S-cis conformations. The results of the calculations for complexes 36 and 46 indicate that no new major steric interactions occur when the trans-β-proton in complex 52 is replaced by an alkyl substituent. This

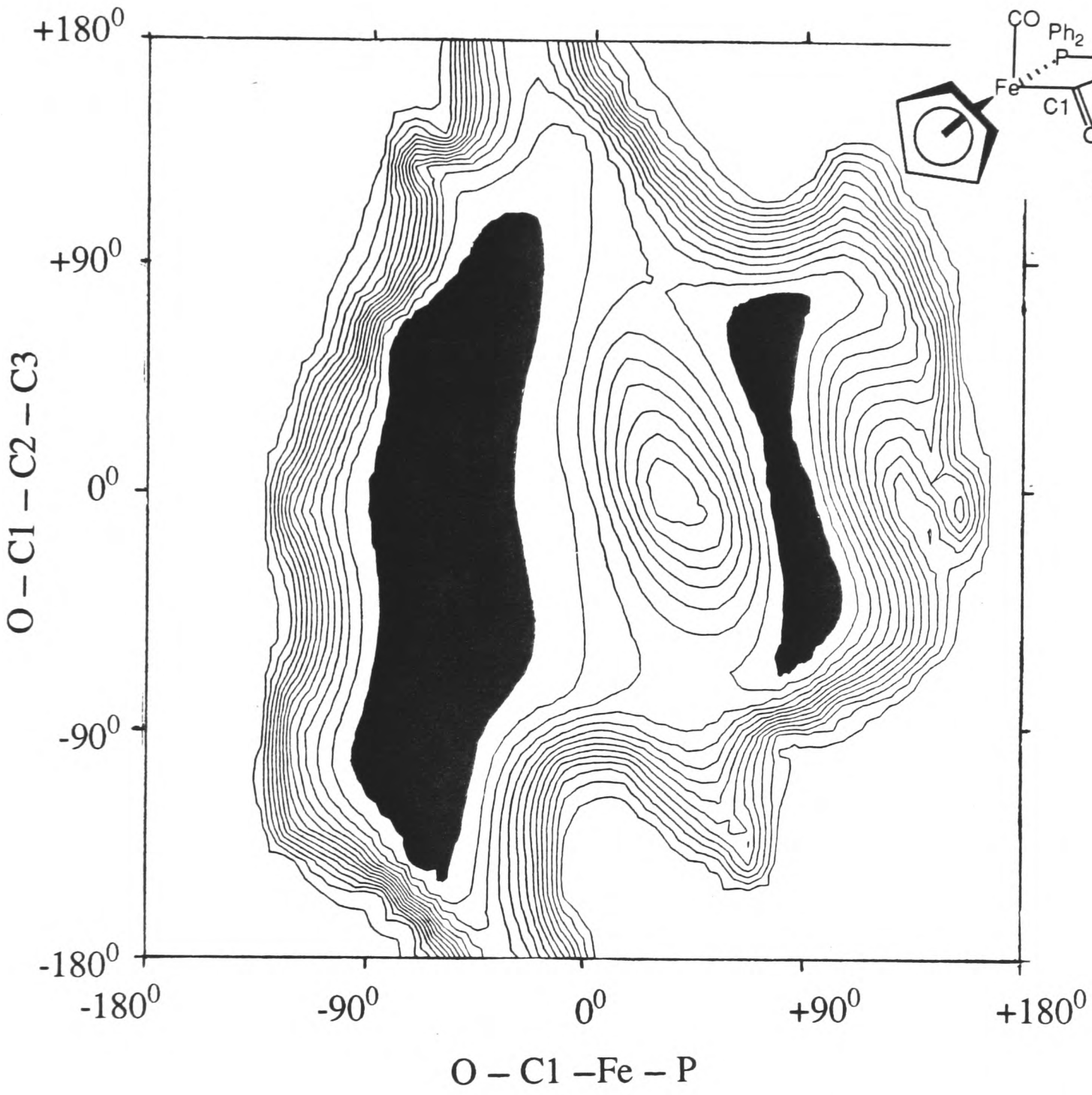


Figure 3. Conformational energy map for E-(C_5H_5)Fe(CO)(PPh_3)(COCH=$CHCH_3$) 36

is consistent with the previous analysis in which no steric effects on the conformational properties of the unsaturated acyl ligand were attributed to the trans-β-proton. Models show that any trans-β-substituent will be distant from the iron moiety, experiencing minimal steric interaction with it. The most stable conformations for the unsaturated acyl ligands in complexes 52, 36 and 46 will therefore be close to S-cis with the acyl bond

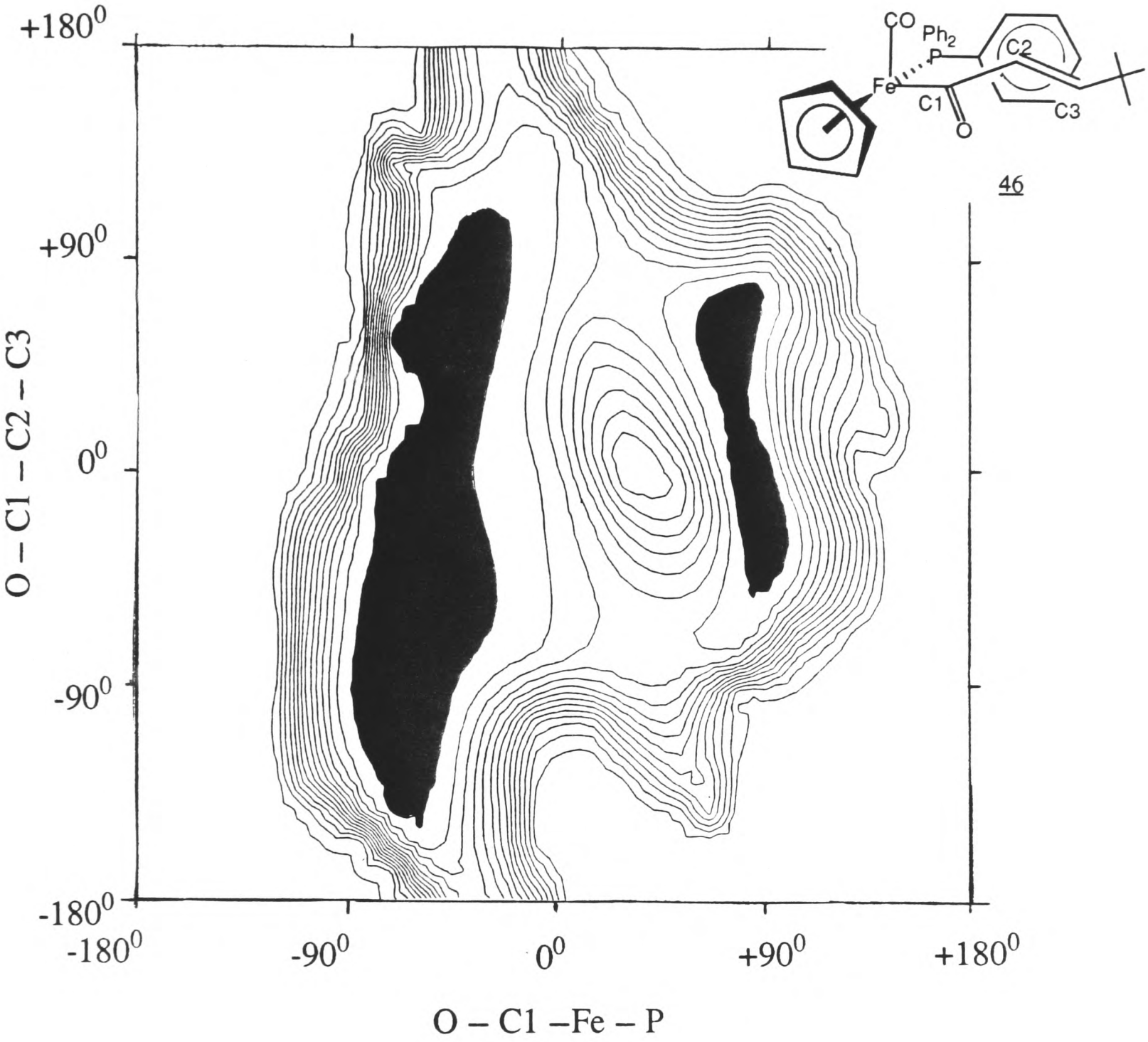
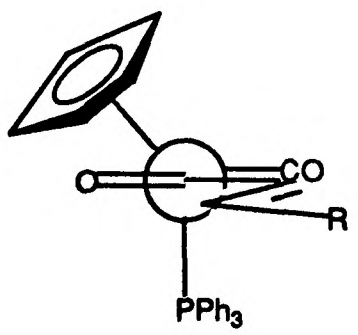


Figure 4. Conformational energy map for E-(C_5H_5)Fe(CO)(PPh_3)(COCH=CHC(CH_3)$_3$) 46

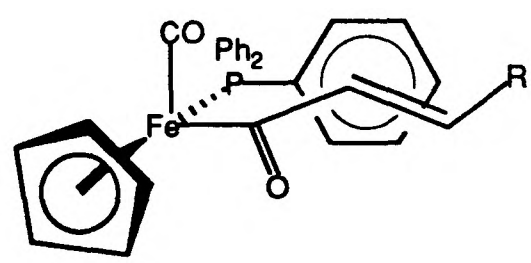
approximately anti to the carbon monoxide ligand since this will minimise steric interactions whilst maximising π-orbital overlap.



R = H 52

R = CH_3 36

R = $C(CH_3)_3$ 46



c) Z-(C_5H_5)Fe(CO)(PPh_3)(COCH=CHR) (R=CH_3-37 or R=$CH(CH_3)_2$-45 or R=$C(CH_3)_3$-47)

The results of the calculation for complex 37 (R=CH_3) are shown in figure 5.

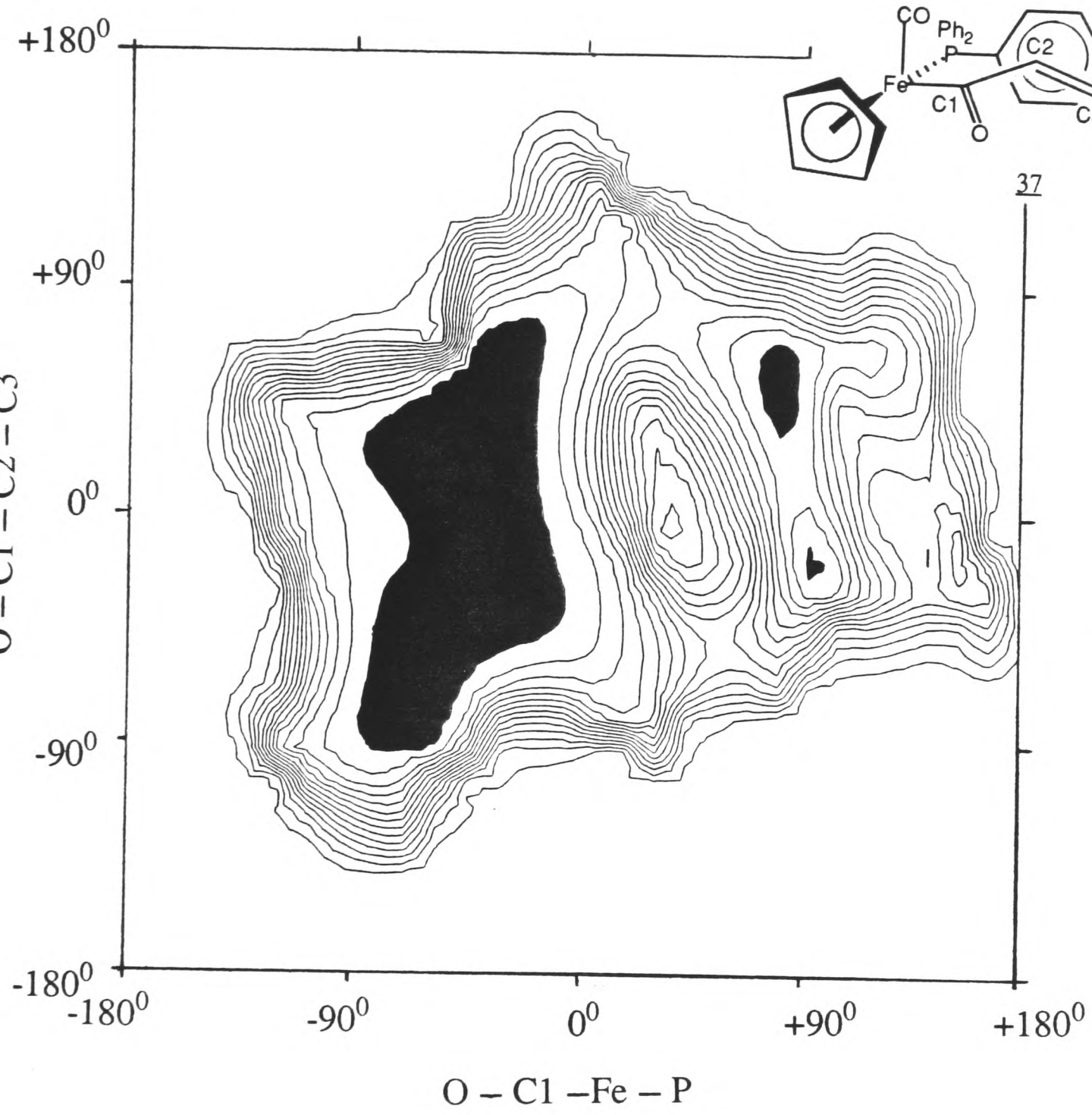


Figure 5. Conformational energy map for Z-(C_5H_5)Fe(CO)(PPh_3)(COCH=$CHCH_3$) 37.

The contour map shows again that conformations placing the C1-O bond of the acyl group approximately anti to the carbon monoxide ligand are the most favoured. In addition, the results show that replacement of the cis-β-proton of the acryloyl complex

52 with a methyl group introduces new steric interactions into the complex, the major restriction being placed on acyl-vinyl (C1-C2) bond rotation. For the acryloyl complex 52, the higher energy of the S-trans conformations relative to the S-cis conformations was attributed to unfavourable interactions between the cis-β-proton and the ligands about the iron (vide supra). The replacement of the cis-β-proton of 52 with the methyl group in 37 results in these interactions becoming more severe and, as a result, the S-trans conformations are no longer sterically accessible.

In order to determine the effect of larger cis-β-alkyl substituents, the calculations were repeated for the known complex 45 ($R=CH(CH_3)_2$) and the unknown complex 47 ($R=C(CH_3)_3$). (see table 1). The results are shown in figures 6 and 7 respectively. For complex 45, rotation about the β-carbon-γ-carbon (C3-C4) bond was also calculated, and in the conformational energy contour map the interactions of the isopropyl substituent are minimised in every conformation. The result for complex 45 (figure 6) shows essentially the same features as that for the cis-methyl complex 37 (figure 5), with acyl-vinyl (C1-C2) bond rotation being only slightly more restricted. Presumably rotation about the β-carbon-γ-carbon (C3-C4) bond will place the γ-proton in the most sterically hindered position in any particular conformation. The similarity of the results for complexes 45 and 37 suggests that the limits of the rotational freedom about the acyl-vinyl (C1-C2) bonds are defined by the interactions experienced by the γ-proton. The results of the calculations for 37 and 45 show that the most stable conformations for the unsaturated acyl ligands will be close to S-cis with the carbon-oxygen bond of the

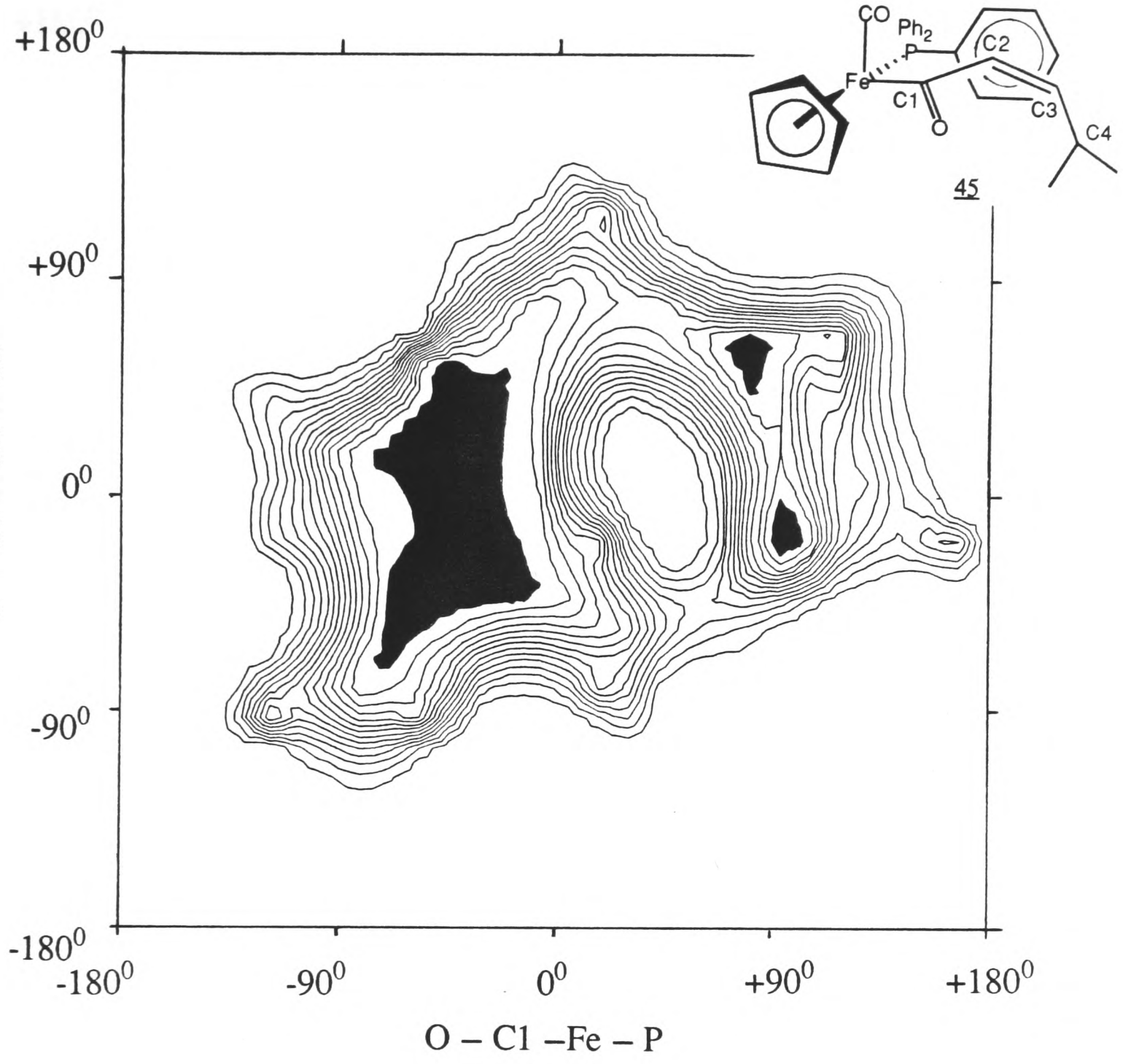
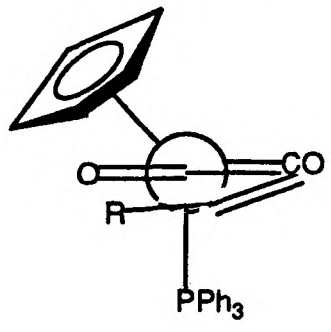


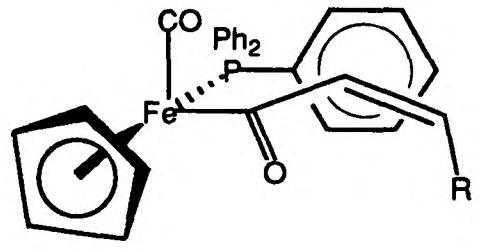
Figure 6. Conformational energy map for Z-(C_5H_5)Fe(CO)(PPh_3)(COCH=CHCH(CH_3)$_2$) 45.

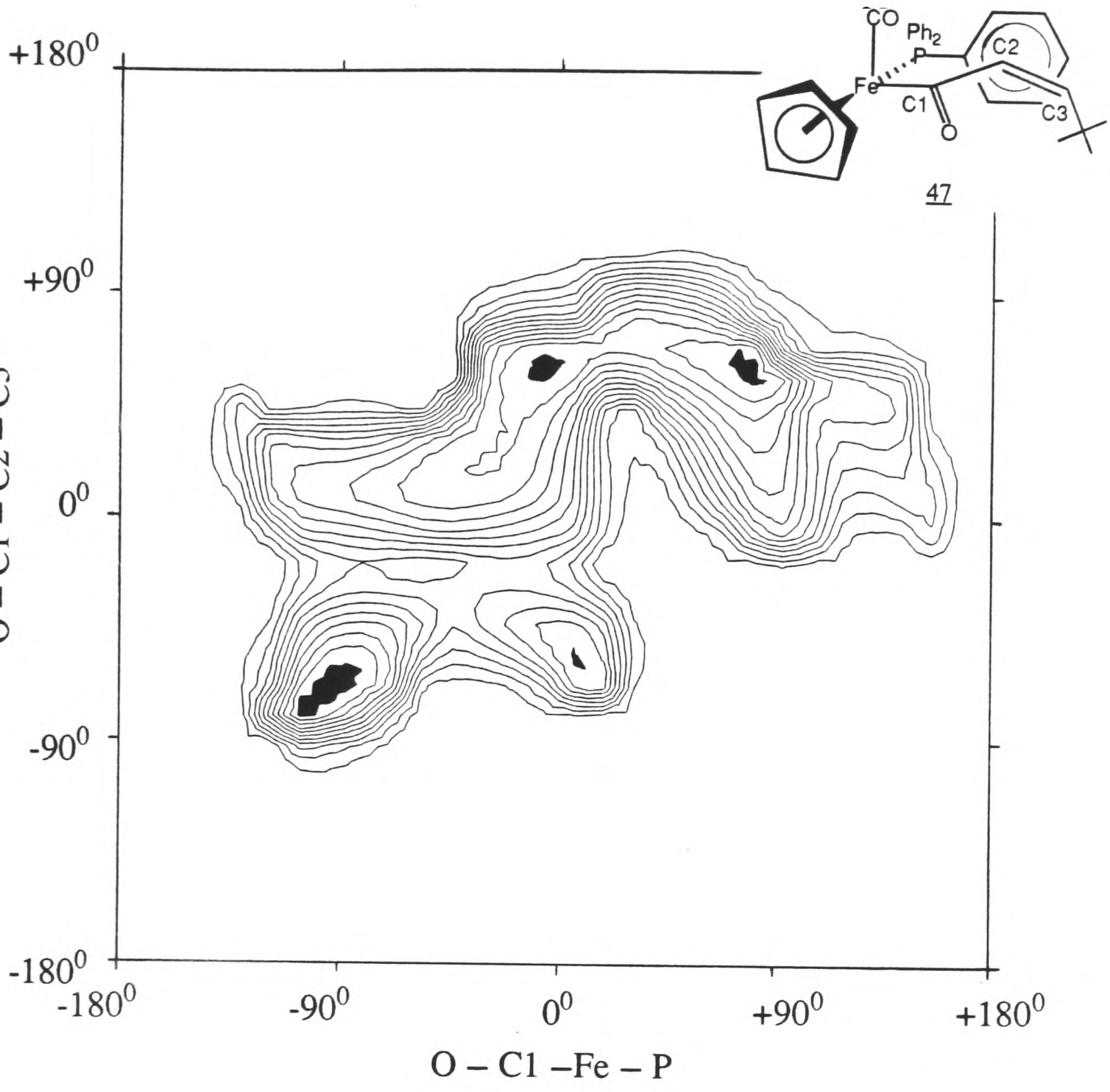
acyl group approximately anti to the carbon monoxide ligand, thus minimising steric interactions whilst maximising π-orbital overlap.



R = CH_3 37

R = $CH(CH_3)_2$ 45

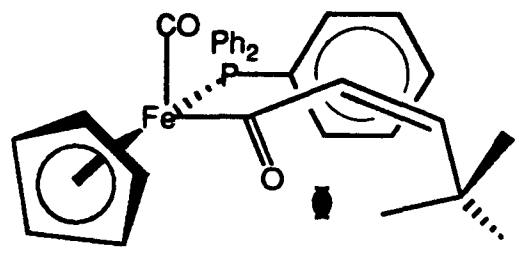




47

Figure 7. Conformational energy map for Z-(C_5H_5)Fe(CO)(PPh_3)(COCH=CHC(CH_3)$_3$) 47.

The result of the calculation for the cis-t-butyl complex 47 (figure 7) shows that the acyl ligand would experience extreme steric interactions in virtually every conformation. The preferred conformations for complexes 37 and 45 (see above) will not be accessible for 47 because the methyl group proximate to the acyl oxygen will experience severe steric interactions.



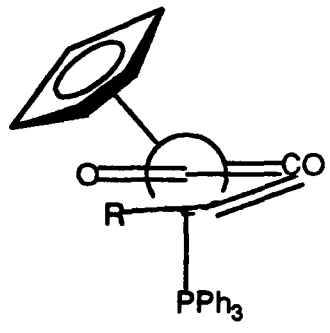
47

Only conformations placing the vinyl group approximately orthogonal to the acyl group would be accessible (see figure 7). However, complex 47 cannot be synthesised by any of the methods described in section 1 and this probably reflects the severe steric strain calculated to exist within the molecule.

From this study of the conformational preferences of the α,β-unsaturated acyl ligands attached to the chiral auxiliary $(C_5H_5)Fe(CO)(PPh_3)$ the following conclusions can be drawn:

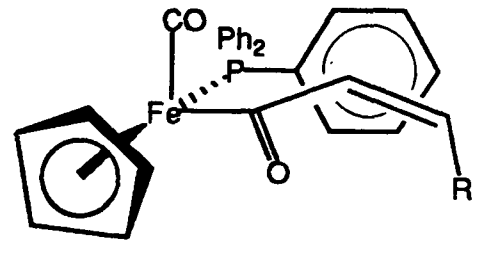
1) The primary steric interaction for the ligand is with the proximate phenyl ring of the triphenylphosphine ligand such that the carbon-oxygen bond of the acyl group lies close to periplanar to the carbon monoxide ligand.
2) Steric interactions between the substituents on the α-carbon and the cyclopentadienyl ligand disfavour the syn-conformations relative to the anti-ones.
3) Steric interactions between the cis-β-substituent and the ligands about the iron disfavour S-trans conformations relative to S-cis ones. The extent of the interaction reflects, to some degree, the bulk of the substituent. Hence, for the cis-t-butyl complex 47, virtually all conformations (including S-cis) are extremely hindered. For smaller substituents the preferred conformations will be close to

S-cis with the acyl bond approximately anti to the carbon monoxide ligand since these conformations minimise steric interaction whilst maximising π-orbital overlap.

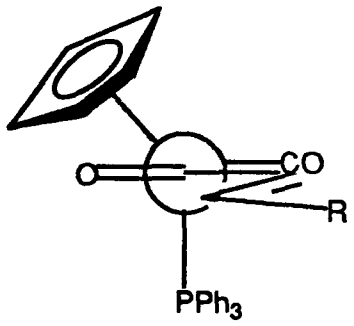


R = CH_3 37

R = $CH(CH_3)_2$ 45



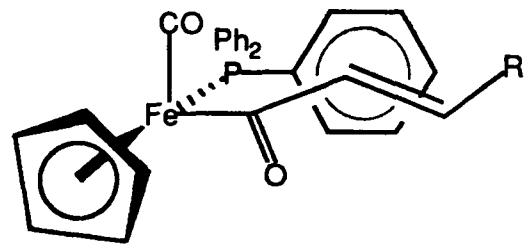
4) A trans-β-substituent has minimal effect on the conformational properties of the ligand. The preferred conformation will again be S-cis with the acyl bond approximately anti to the carbon monoxide ligand.



R = H 52

R = CH_3 36

R = $C(CH_3)_3$ 46

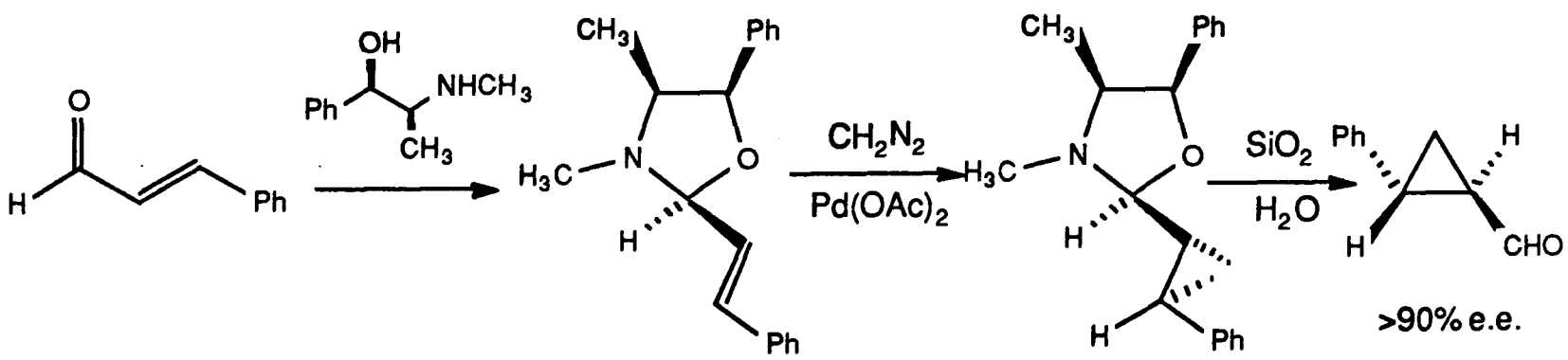


In the following chapters the syntheses of cyclopropyl derivatives from α,β-unsaturated iron acyl complexes are investigated.

CHAPTER 3

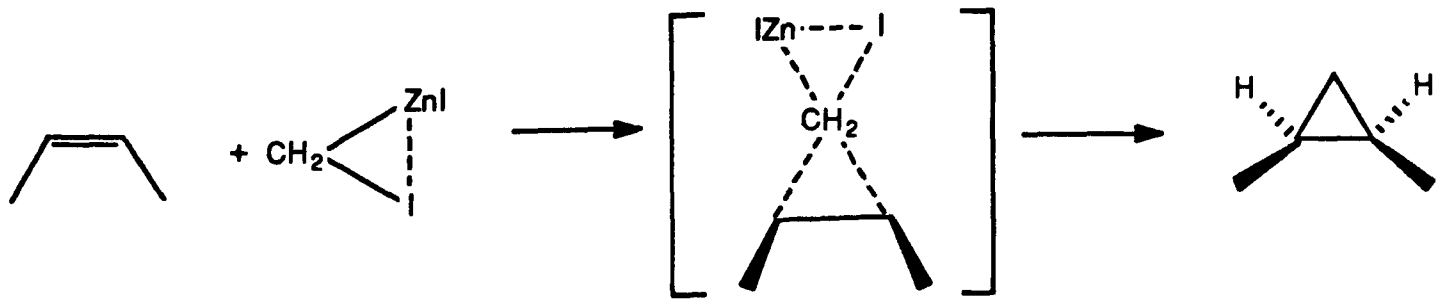
REACTIONS OF COMPLEXES $(C_5H_5)Fe(CO)(PPh_3)(COCH=CRR')$ WITH ELECTROPHILIC ALKYLIDENE SPECIES

The synthesis of optically active cyclopropyl derivatives *via* the addition of asymmetric carbenoid species to olefinic bonds has been reported[22-25] and was described previously (see Chapter 1 section 1c)). An alternative approach is *via* carbene addition to olefinic bonds bound to a chiral auxiliary of high enantiomeric purity. For example, Carrié[68] demonstrated the synthesis of formyl cyclopropanes of high enantiomeric excess *via* methylene addition to intermediates derived from (-)-ephedrine and α,β-unsaturated aldehydes.



In the preceding examples, the carbenes (or carbenoid species) were generated by decomposition of diazo-compounds. An alternative approach is seen in the Simmons-Smith reaction which has found widespread use in the synthesis of cyclopropyl derivatives.[60,69] In this reaction, treatment of olefins with methylene iodide in the presence of a zinc/copper couple affords the corresponding cyclopropane in good yield.

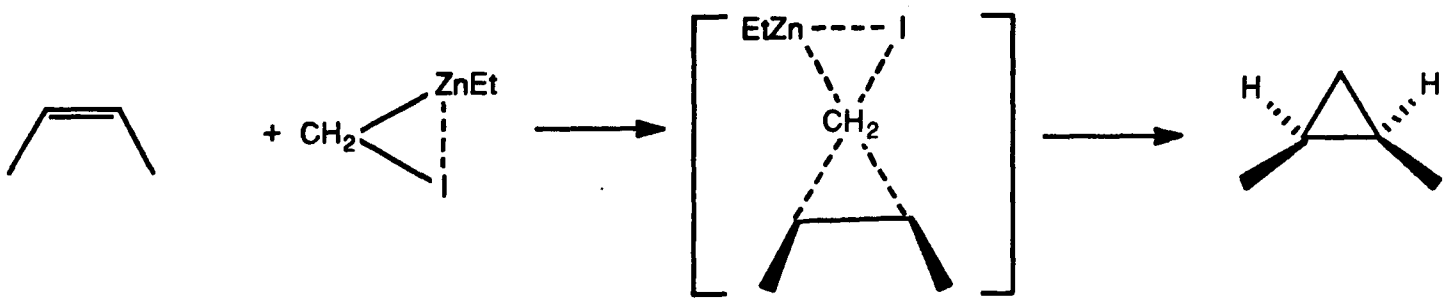
A weakly electrophilic carbenoid species is generated, *in situ*, with a probable stoicheiometry of (ICH_2ZnI), the exact nature of the active species being unknown.[60,69] The reaction is believed to occur by *cis*-addition of the methylene group to the olefinic bond *via* transition state *57*, both new carbon-carbon bonds being formed simultaneously.[60]



57

The stereospecificity of the reaction, with E- and Z-olefins, giving trans- and cis-substituted cyclopropyl rings respectively, is evidence for a concerted rather than non-concerted mechanism since, in the latter case, bond rotation might be expected to compete with ring closure resulting in some loss of stereochemistry.

Furukawa et al.[70] have described a similar reaction in which diethylzinc replaces the zinc/copper couple. The species ICH_2ZnEt is generated in situ, although the exact nature of the reactive species is unknown.[69] The stereospecificity of the reaction indicates concerted addition via a transition state such as 58.

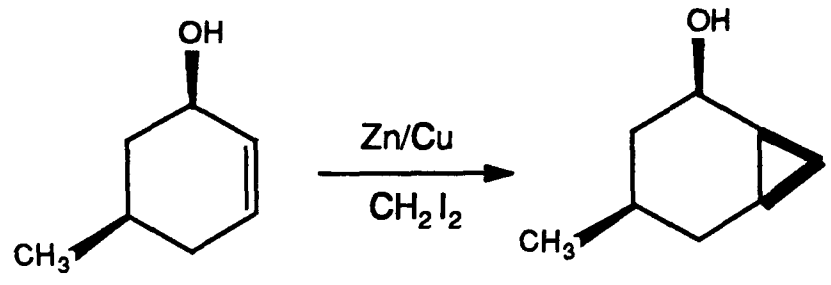


58

The homogeneous reaction with diethylzinc is more rapid than the heterogeneous reaction with the zinc/copper couple.[69,70] A further advantage is the efficient reaction with ethylidene[70b] and benzylidene iodides,[70d] allowing syntheses of more highly substituted cyclopropane rings (see section D).

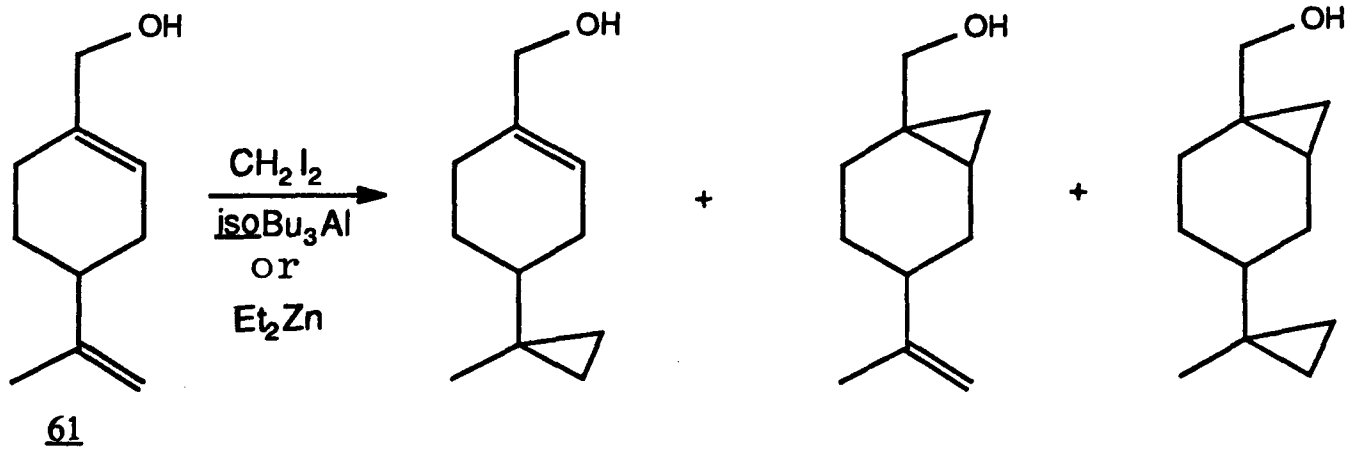
Miller[71a] and, more recently, Yamamoto[71b] have reported a related reaction in which diethylzinc is replaced by a trialkyl aluminium. In this case the active species is believed to be ICH_2AlR_2 and the stereospecificity of the reaction again indicates a concerted methylene addition mechanism.

Prior coordination of zinc carbenoid species to an allylic or homoallylic hydroxyl or ether oxygen can facilitate and direct methylene addition reactions. In molecules where the faces of the olefinic bond are diastereotopic the product can be obtained with high stereoselectivity, especially when steric factors favour conformational rigidity within the system.[60] For example, the reaction with cis-5-methyl-cyclohex-2-enol 59 gives exclusively the corresponding cis-cyclopropyl derivative 60.[72]



59 60

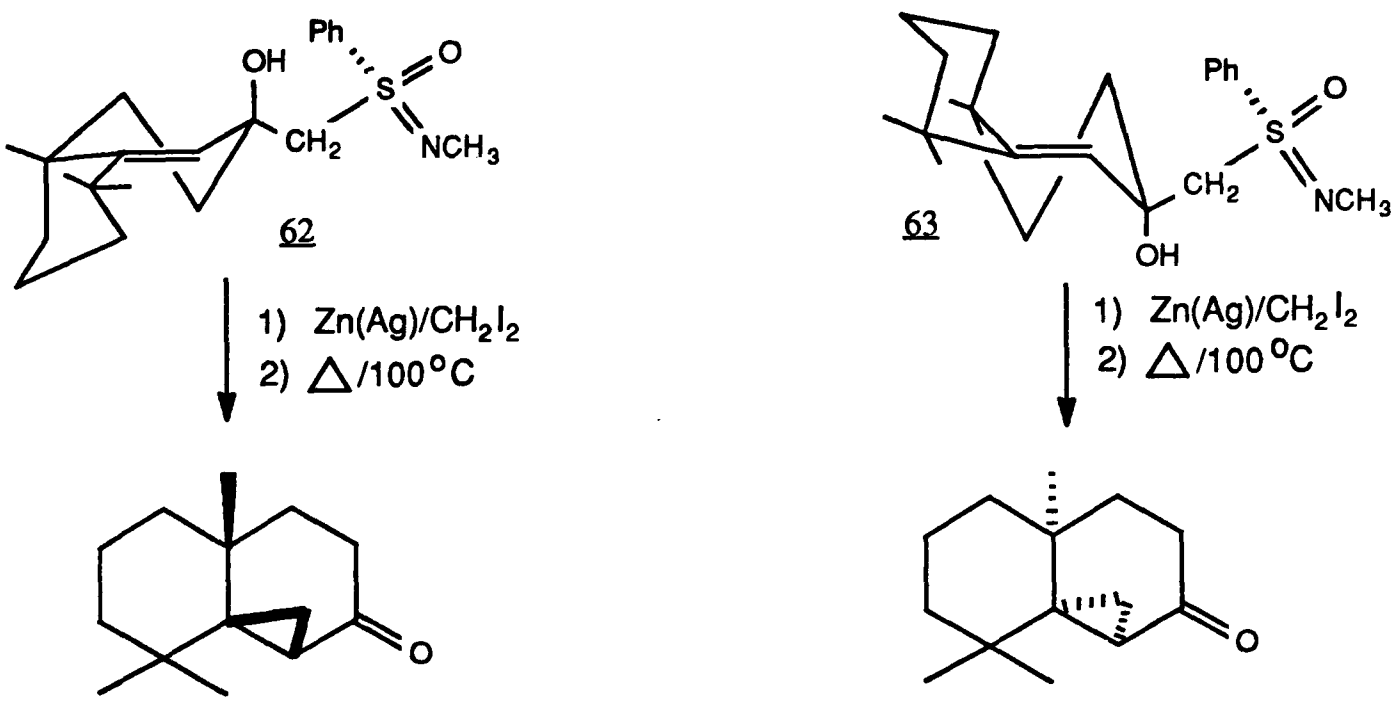
Interestingly, Yamamoto[71b] reported that the carbenoid species generated from triisobutyl aluminium and methylene iodide reacts exclusively at the isolated olefinic bond of perillyl alcohol 61, whilst the corresponding zinc carbenoid species reacts, as expected, regioselectively at the allylically hydroxylated olefin.



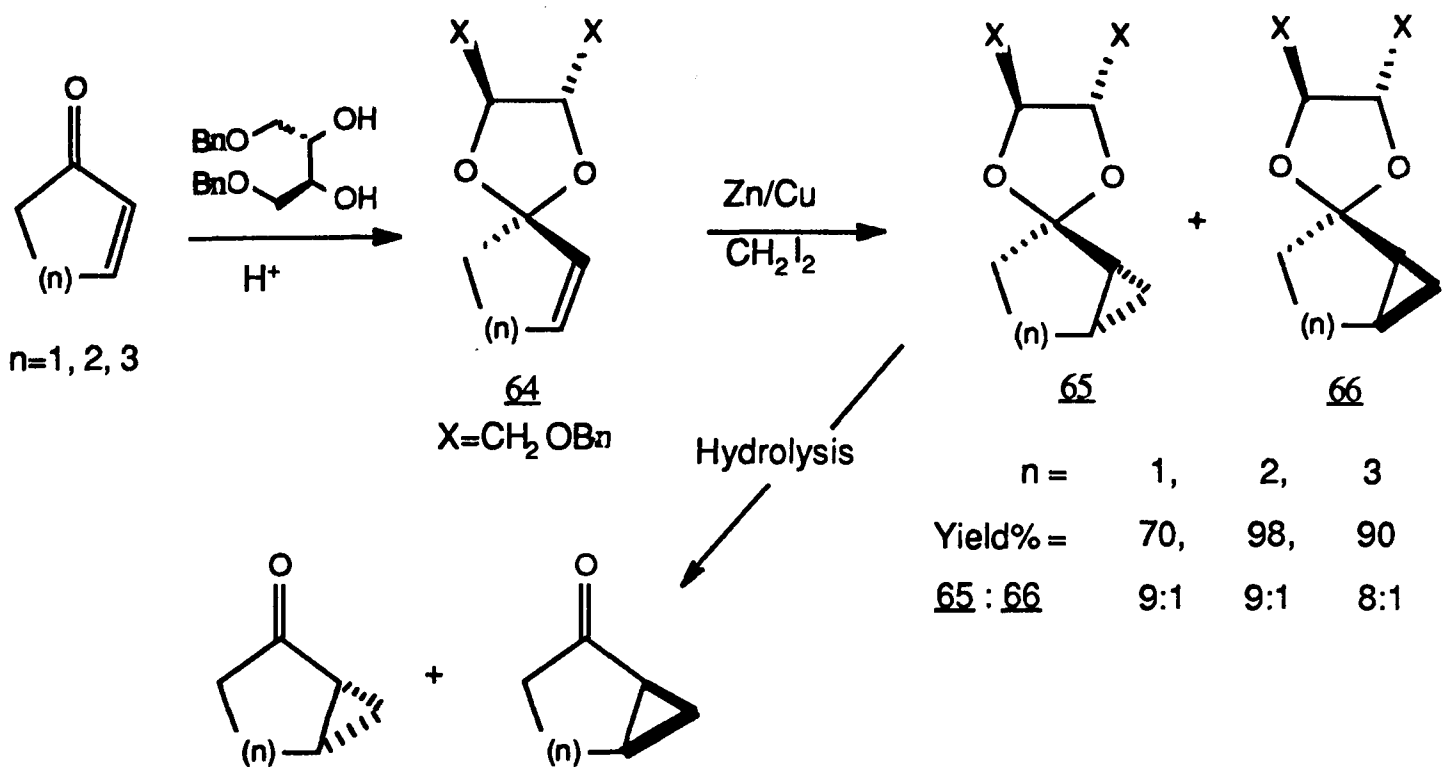
61

isoBu$_3$Al/CH$_2$I$_2$	%	79	0	0
Et$_2$Zn/CH$_2$I$_2$	%	3	49	8

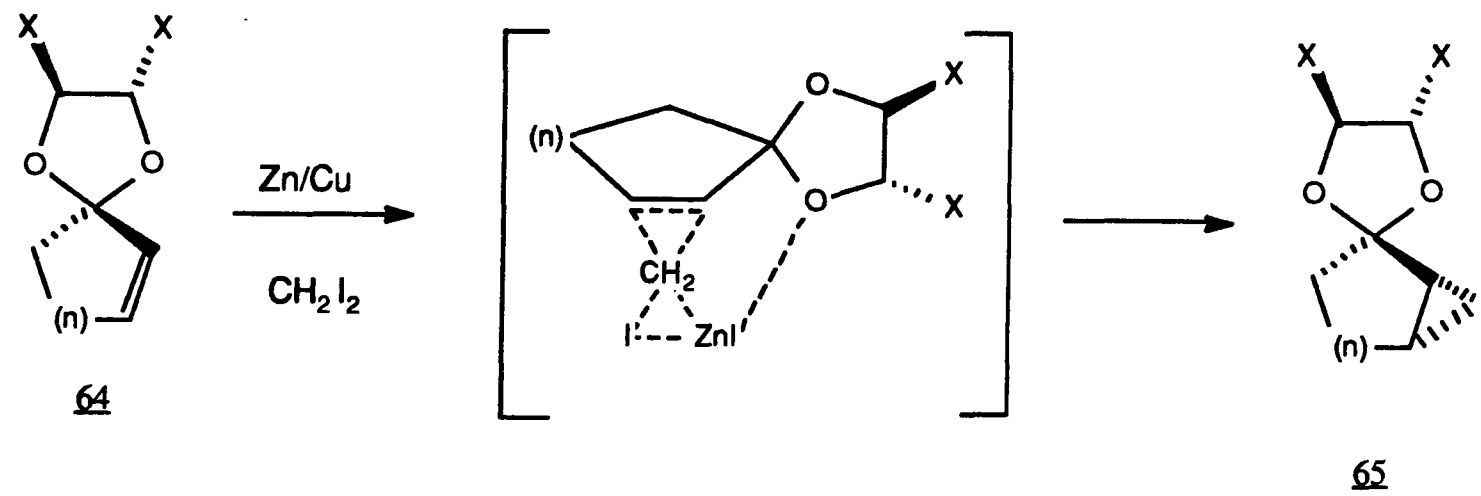
Although these methods for cyclopropane ring formation are widely used, there are relatively few examples of asymmetric syntheses of cyclopropyl derivatives *via* alkylidene-transfer reactions from electrophilic carbenoid species. Simmons-Smith reactions, either in the presence of (-)-menthol[73] or with (-)-menthyl esters of unsaturated carboxylic acids,[74] have been reported to give products with low enantioselectivity (<3.4% and <9.3% optical yield respectively). Johnson[75] reported that prior coordination of the carbenoid species to the hydroxyl groups of the diastereoisomeric allylic β-hydroxysulphoximines 62 and 63 resulted in stereospecific addition *cis* to the hydroxyl groups in both cases.



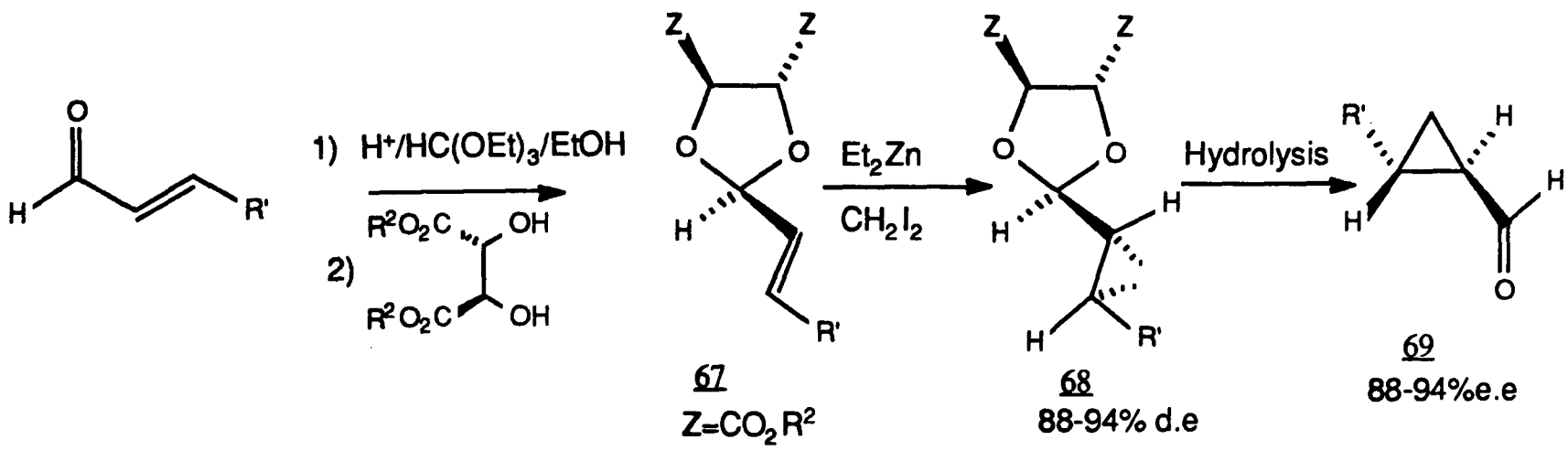
Recently, Mash[76] and Yamamoto[77] independently reported asymmetric Simmons-Smith type reactions using homochiral α,β-unsaturated ketals and acetals respectively. Mash[76] treated a series of cyclic enones with 1,4-di-*O*-benzyl-L-threitol to give the ketals 64. Methylene addition to 64 occurred diastereoselectively, the corresponding cyclopropyl ketones being generated by hydrolysis of the ketals 65 and 66.



The diastereoselectivity probably arises due to coordination of the carbenoid species to the only sterically accessible dioxolane oxygen lone pair of electrons which are directed towards the olefin, prior to intramolecular methylene transfer.[76c]



Yamamoto[77] utilised homochiral acetals 67, derived from α,β-unsaturated aldehydes and homochiral dialkyl tartrates. Reaction with the carbenoid species resulted in the highly diastereoselective formation of the cyclopropyl acetal 68 which, on hydrolysis, gave the corresponding cyclopropyl aldehyde 69. The high diastereoselectivity presumably arises from prior coordination of the carbenoid species to a ring oxygen, and subsequent intramolecular methylene transfer.



67 68 69

These two approaches are the most generally applicable of the available methods for the asymmetric synthesis of cyclopropyl derivatives *via* alkylidene transfer from electrophilic carbenoid species. However, the reaction described by Mash[76] is restricted to cyclic enones, whilst that described by Yamamoto[77] is limited to E-α,β-unsaturated aldehydes.

The high degree of stereochemical control exerted by the iron chiral auxiliary $(C_5H_5)Fe(CO)(PPh_3)$ over associated acyl ligands was described previously (see Chapter 1). It was anticipated that reaction of the α,β-unsaturated iron acyl complexes (see Chapter 2) with electrophilic alkylidene species would allow the stereoselective synthesis of the corresponding cyclopropyl derivatives.

A. Methylene Addition Reactions

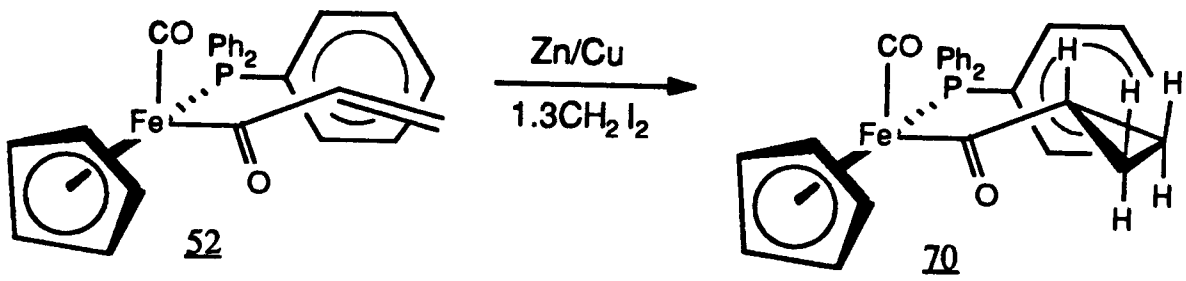
1. Addition to $(C_5H_5)Fe(CO)(PPh_3)(COCH=CH_2)$ 52.

The complex 52 and methylene iodide were added to a zinc/copper couple[78] in ether, and heated at reflux for three hours. After work up and chromatography a single band, drying to an orange solid, was collected with no other iron acyl species being detected.

The ^1H n.m.r. spectrum* of the product showed resonances

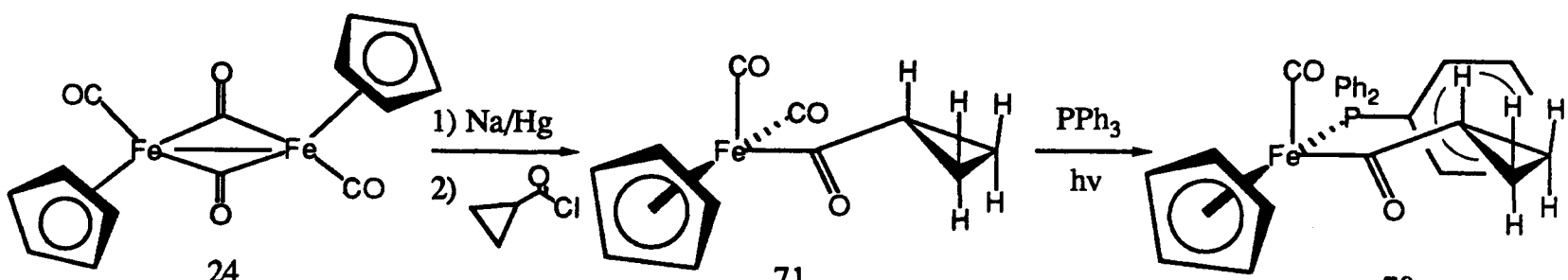
*Throughout this thesis, unless otherwise stated, ^1H n.m.r. experiments were performed in chloroform-d_1.

characteristic of the iron chiral auxiliary at δ 7.6-7.3 (PPh_3) and 4.46 (C_5H_5). In addition there were resonances at δ 2.85 (1H), 0.8 (1H), 0.36 (2H) and 0.24(1H), the high-field shifts being characteristic of protons substituted on a cyclopropane ring.[79] On the basis of the ^1H n.m.r. spectrum the product was assigned as the cyclopropyl complex 70 (30%).



52 70

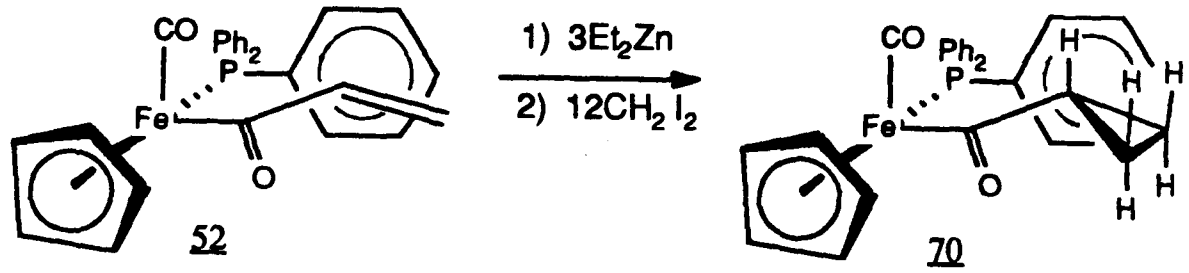
The assignment of 70 was confirmed by its independent synthesis via the literature route outlined below.[80]



24 71 70

The anion (25), formed on cleavage of the iron dimer 24 by sodium amalgam, was trapped with cyclopropanecarboxylic acid chloride to give the iron complex 71. Photolysis of 71, in the presence of triphenylphosphine, resulted in the displacement of a carbon monoxide ligand by the phosphine. The reaction was monitored by infra-red spectroscopy, stretches at 2020, 1965 (C≡O) and 1630 cm^{-1} (C=O) for complex 71 being replaced by ones at 1915 (C≡O) and 1585 cm^{-1} (C=O) for complex 70. After work up and chromatography a single band, drying to an orange solid, was collected the ^1H n.m.r. spectrum of which was identical to that of the product formed in the Simmons-Smith reaction. The cyclopropyl complex 70 (16%), synthesised from the iron dimer 24, was characterised satisfactorily.

The yield of 70 from the Simmons-Smith reaction was low (30%), no other iron acyl species being present. This indicated substantial decomposition, possibly reflecting the vigorous reaction conditions. The carbenoid species generated from diethylzinc and methylene iodide has been reported[69,70] to be more reactive than that described above, and this methodology was utilised in an alternative synthesis of the cyclopropyl complex 70. A solution of complex 52 in toluene at 0°C was treated with diethylzinc and methylene iodide. The solution was stirred (0°C; 20mins. and 20°C; 40mins) and the reaction monitored by TLC, the product 70 being less polar than starting material 52. After work up the ^{1}H n.m.r. spectrum of the product confirmed it as 70 (63% yield). In addition, starting material 52 was recovered (24%).



52 70

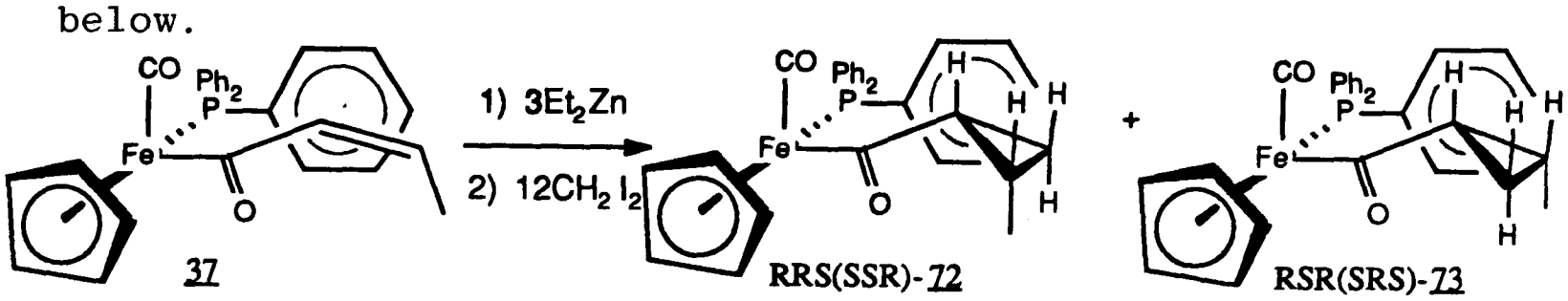
In order to determine the stereochemistry of methylene addition, the reactions were repeated on Z- and E-α,β-unsaturated iron acyl complexes.

2. Addition to Z-(C_5H_5)Fe(CO)(PPh_3)(COCH=CHR) and to (C_5H_5)Fe(CO)(PPh_3)(COCH=C(CH_3)$_2$) 54.

a) By use of the diethylzinc derived carbenoid

A solution of Z-(C_5H_5)Fe(CO)(PPh_3)(COCH=CHCH_3) 37 in toluene at 0°C was treated with diethylzinc and methylene iodide. By TLC the reaction appeared to have gone to completion in ten minutes, the product being less polar than the starting material 37. After work up the molecular ion in the mass spectrum of the product indicated addition of methylene to 37. The ^{1}H n.m.r.

spectrum showed two sets of signals, consistent with the diastereoisomeric cis-substituted cyclopropyl complexes 72 and 73 (89%). The ^{1}H n.m.r. data of the acyl ligands for 72 and 73 are summarised in table 2. The major diastereoisomer was assigned as RRS(SSR)-72, the basis of this assignment being discussed below.



Complex	COCH(J/Hz)[a]	$CH_2CH(CH_3)$	CH_3
72	2.83 (7.8, 7.8, 5.4)	0.35, 0.48, 1.12	1.04
73[c]	2.93 (8.1, 8.1, 5.4)	0.64 0.75[b]	0.51

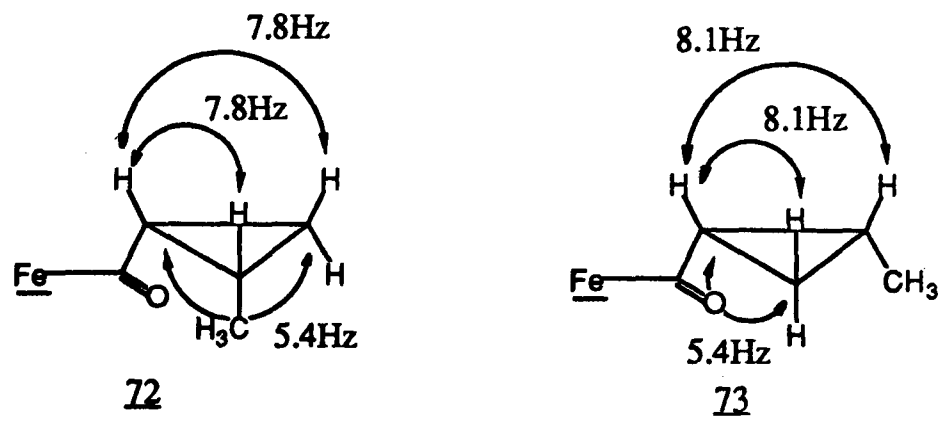
a) Coupling constants to ring protons in parenthesis

b) Remaining resonances obscured by those of 72.

c) Ratio of 72:73=3:1, measured from the integrals of the α-protons (COCH).

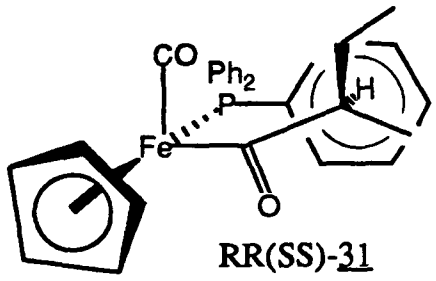
Table 2. The chemical shifts (δ) of the acyl ligands in the ^{1}H n.m.r. spectrum of 72 and 73.

It has been reported[81] that within any cyclopropane ring system, in accord with the Karplus rule, cis-couplings of protons are always larger than trans-couplingsthe cis-protons being essentially eclipsed. On this basis the relative stereochemistry of the ring in each diastereoisomer was assigned as cis.

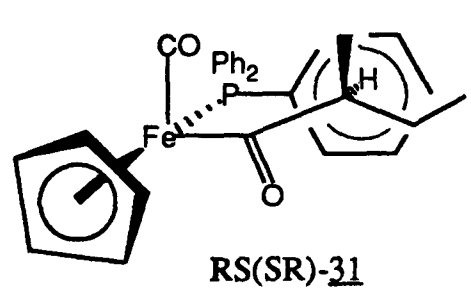


The subsequent synthesis of the corresponding trans-substituted cyclopropyl complexes (section 3.) confirmed that in this reaction the cis-isomers had been formed stereospecifically.

The diastereoselectivity of the reaction was 3:1 (see table 2), the diastereoisomers being chromatographically inseparable. The major diastereoisomer was assigned as RRS(SSR)-72 on the basis of the chemical shifts of the methyl groups for the major and minor diastereoisomers (δ 1.04, 0.51ppm respectively). The high-field shift of the α-methyl resonance of the s-butyl complex RR(SS)-31 in the ^{1}H n.m.r. spectrum relative to that of the α-methyl group in RS(SR)-31 reflects the shielding, in the former instance, of the methyl group by the proximate phenyl ring (see p.16).[51,52]

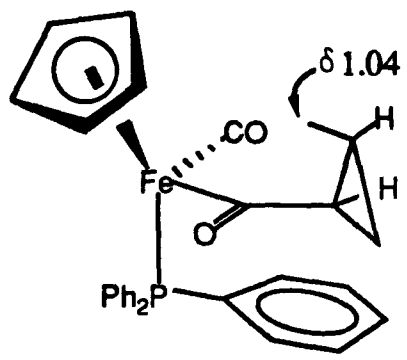


RR(SS)-31

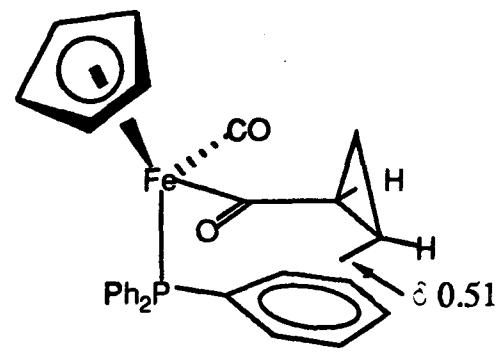


RS(SR)-31

In the same way, the high-field shift in the ^{1}H n.m.r. spectrum, for the methyl group of the minor cis-substituted cyclopropyl complex (vide supra), indicated its proximity to the phenyl ring. Assuming the acyl bond to be approximately anti to the carbon monoxide ligand, and the bond of the cyclopropane ring closest to the triphenylphosphine ligand to lie approximately cis to the acyl bond (see Chapter 1 section 2.c)), then it was apparent that the methyl group in RSR(SRS)-73 would experience greater shielding by the proximate phenyl ring than the same group in RRS(SSR)-72. Hence the minor diastereoisomer was assigned as RSR(SRS)-73 and the major as RRS(SSR)-72.



RRS(SRR) -72



RSR(SRS) -73

Subsequently, the X-ray crystal structure determination of a related product confirmed this stereochemical assignment (see p.95).

The reaction was repeated under a variety of conditions in an attempt to improve the stereoselectivity. The results are summarised in Table 3.

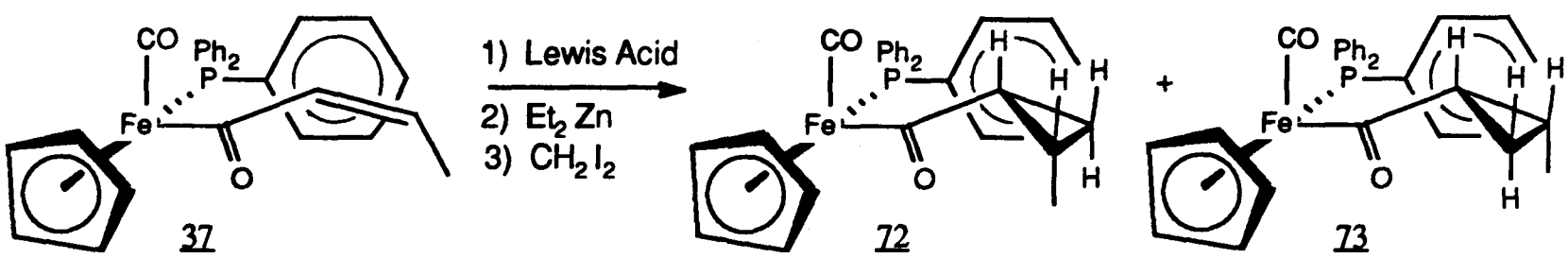
Equiv. of Et_2Zn	Equiv. of CH_2I_2	T/^oC	t/mins.	Yield %	Ratio 72:73
3	12	20	8	94	2:1
3	12	0	10	89	3:1
3	12	-78	180	70	3:1
3	4	0	25	73	4:1
1.5	2	20	50	71	4:1
1.5	4	20	15	78	4.5:1

Table 3. The diastereoisomeric ratio of 72:73 and the overall yields under a range of conditions.

The diastereoselectivity of the reaction appeared to show little temperature dependence and remained low over a range of conditions.

The prior coordination of organometallic reagents to the acyl oxygen of iron acyl species has been invoked to rationalise

subsequent highly stereoselective reactions (see p102).[57] The facilitation of methylene addition to olefinic bonds in Simmons-Smith types of reaction by prior coordination of the carbenoid species to an allylic or homoallylic oxygen atom has been discussed (vide supra).[60] The possibility of directed attack occurring by coordination of the carbenoid species to the acyl oxygen in the reactions described here was investigated. A range of other Lewis acids were added to the complex 37 in toluene and stirred, prior to addition of diethylzinc and methylene iodide. Coordination of these Lewis acids to the acyl oxygen should block any directing influence it might have on the carbenoid species, resulting in a change in the reaction diastereoselectivity.

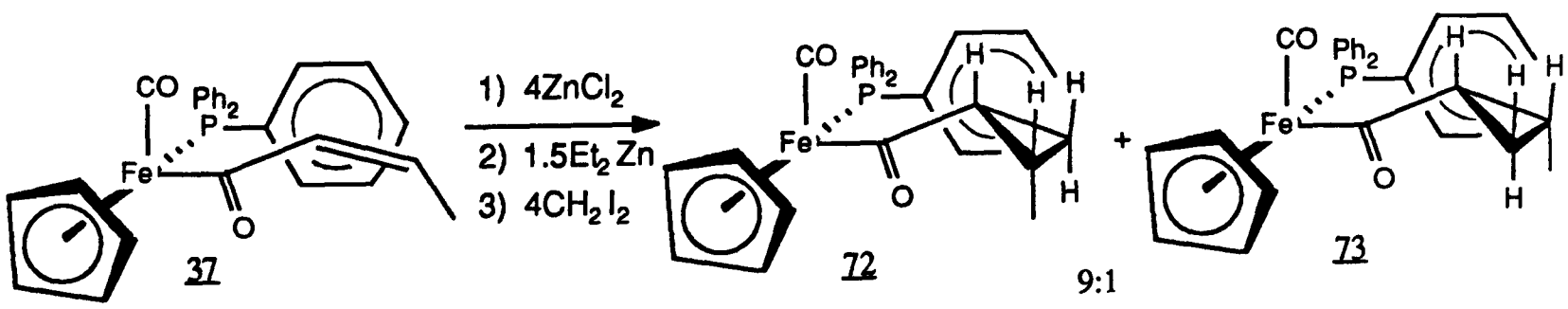


The conditions and results are summarised in table 4.

The results are discussed below (see Discussion) but it is clear that the diastereoselectivity of the reaction was affected by prior addition of the Lewis acids. For optimum results (highlighted in table 4), four equivalents of zinc dichloride were added to the complex 37 in toluene at room temperature. After stirring, the addition of diethylzinc and methylene iodide resulted in rapid reaction, going to completion in less than ten minutes. On work up a 9:1 mixture of 72:73 was isolated (91%), a single crystallisation from dichloromethane/hexane increasing the diastereoisomeric ratio to 12:1.

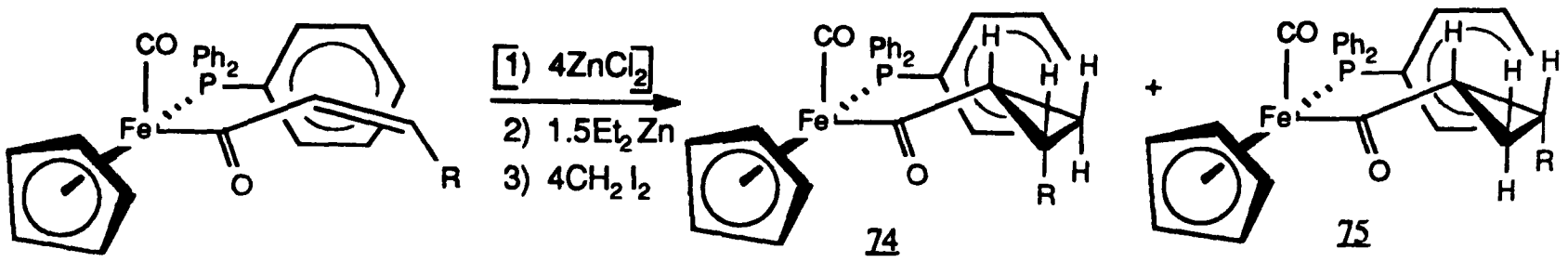
Equiv. of Lewis acid	Equiv. of Et_2Zn	Equiv. of CH_2I_2	T/°C	t/mins.	Yield %	Ratio 72:73
Et_2AlCl						
1	1.5	2	0	300	40	7:1
2	1.5	2	0	360	15	6:1
1	1.5	2	20	240	55	6:1
1	1.5	4	20	30	65	6:1
iso-Bu_2AlCl						
1	1.5	4	0	120	57	6:1
$BF_3.Et_2O$						
4	1.5	4	-40	120	58	1.5:1
1	1.5	2	0	60	90	3:1
$ZnCl_2$						
2	1.5	4	-40	180	55	3:1
2	1.5	4	0	45	92	5:1
2	1.5	4	20	<10	85	7.5:1
4	1.5	4	20	<10	91	9:1
4	1.5	4	50	5	43	4.5:1

Table 4. The diastereoisomeric ratio of 72:73 and the overall yields after prior addition of a range of Lewis acids.



Repeating the reaction with the omission of diethylzinc gave only unreacted starting material 37, indicating that the reactive carbenoid species was not formed from methylene iodide and zinc dichloride.

The reaction was repeated with, and without, prior addition of zinc dichloride on a range of Z-α,β-unsaturated iron acyl complexes. The results are summarised in table 5.

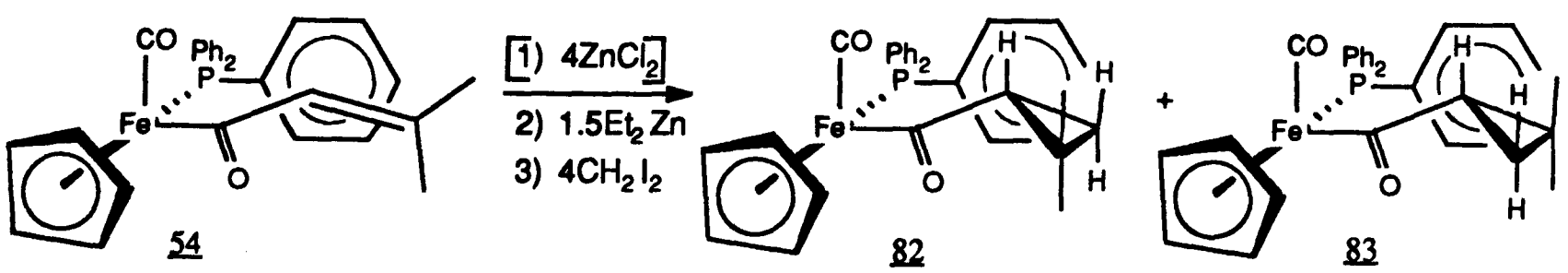


R		Without addition of $ZnCl_2$ Yield %	Ratio 74:75	With addition of $ZnCl_2$ Yield %	Ratio 74:75	Products
Me	37	78	4.5:1	91	9:1	72:73
^{n}Pr	41	91	4:1	91	14:1	76:77
^{n}Bu	43	83	4:1	95	16:1	78:79
^{i}Pr	45	60	4:1	93	24:1	80:81

Table 5. The diastereoisomeric ratios 74:75 and overall yields in the reactions of Z-(C_5H_5)Fe(CO)(PPh_3)(COCH=CHR) with methylene iodide and diethylzinc.

The diastereoisomeric ratios were obtained from the integrals of the resonances of the α-protons (COCH) in the ^{1}H n.m.r. spectra. In each case this resonance was up-field for the major, relative to the minor, diastereoisomer. By comparison with 72 and 73 (vide supra) the major diastereoisomer was assigned as 74, the diastereoisomers being chromatographically inseparable.

The reactions were repeated on the complex 54 and the results are shown in the following scheme.



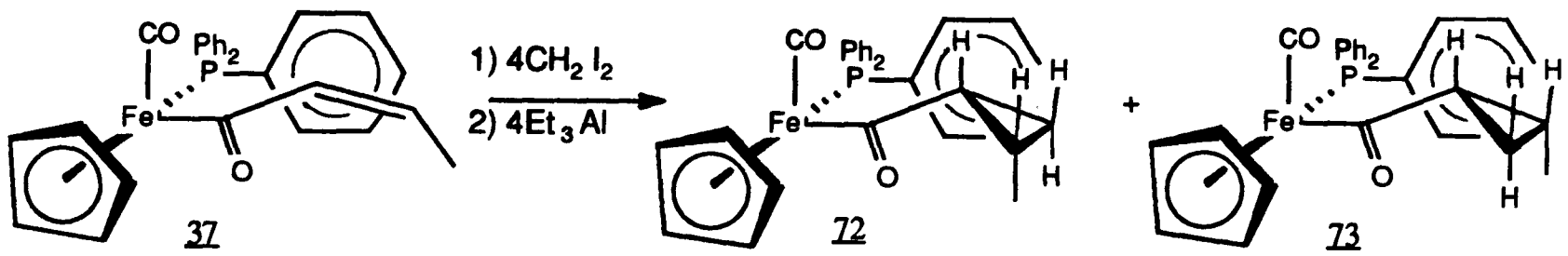
Without $ZnCl_2$ 4:1 (72%)

With $ZnCl_2$ 11:1 (89%)

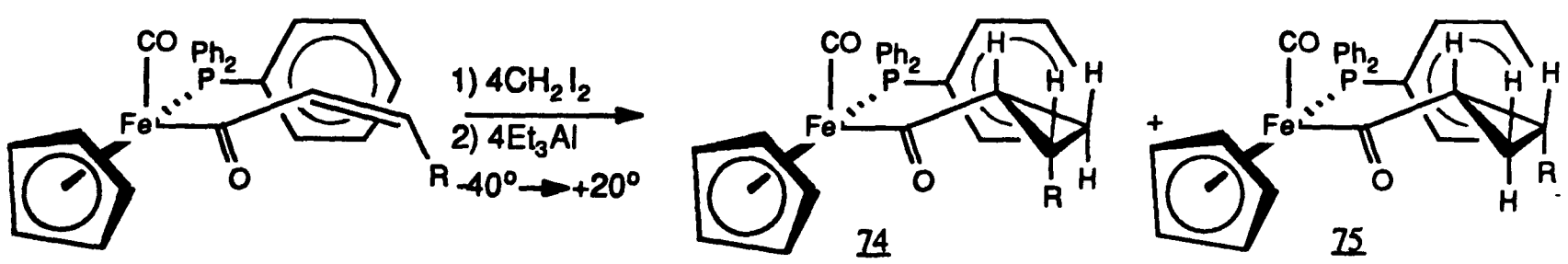
The basis for the good diastereoselectivity seen in these reactions is discussed elsewhere (vide infra). The use of trialkyl aluminium reagents to generate carbenoid species has been reported (see p. 38),[71] and the application of this methodology to the Z-α,β-unsaturated iron acyl complexes was investigated.

b) By use of triethylaluminium derived carbenoids.

Methylene iodide and triethylaluminium were added to a solution of 37 in toluene at room temperature. The reaction was monitored by TLC and was shown to go to completion in less than fifteen minutes. After work up, the ^1H n.m.r. spectrum of the product identified it as an 8:1 mixture of the diastereoisomeric cis-substituted cyclopropyl complexes 72 and 73 (88%), showing that 72 was formed diastereoselectively in the reaction of 37 with either the diethylzinc or triethylaluminium derived carbenoid species.



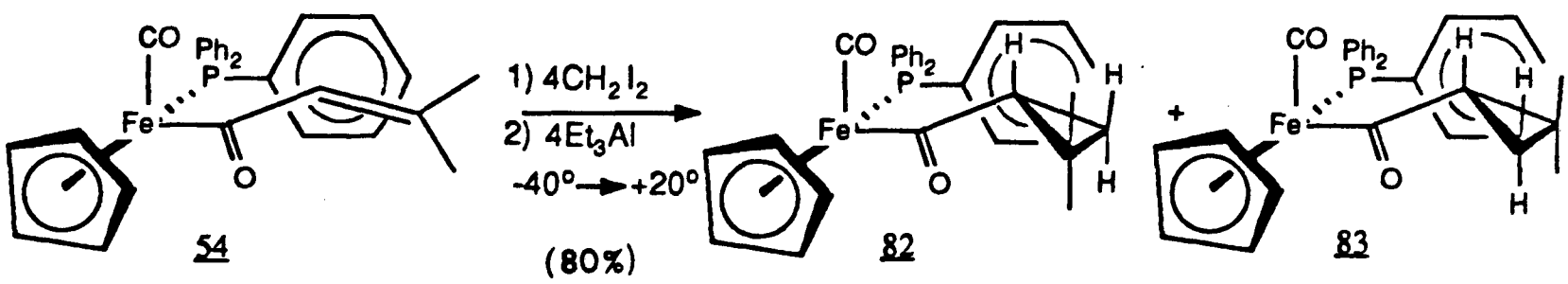
Prior addition of zinc dichloride to complex 37 did not result in increased diastereoselectivity. Instead, the conditions were optimised by addition of the reagents at -40°C, stirring for one hour, then allowing the reaction to warm to room temperature over two hours. The experiment was repeated on a range of Z-α,β-unsaturated iron acyl complexes and the results are summarised in table 6.



R	Yield %	Ratio 74:75	Products
Me 37	74	16:1	72:73
^{n}Pr 41	86	18:1	76:77
^{n}Bu 43	62	19:1	78:79
^{i}Pr 45	49	24:1	80:81

Table 6. The diastereoisomeric ratios 74:75 and overall yields in the reactions of Z-(C_5H_5)Fe(CO)(PPh_3)(COCH=CHR) with methylene iodide and triethylaluminium.

The reaction was repeated with the complex 54 and the result is shown in the following scheme.

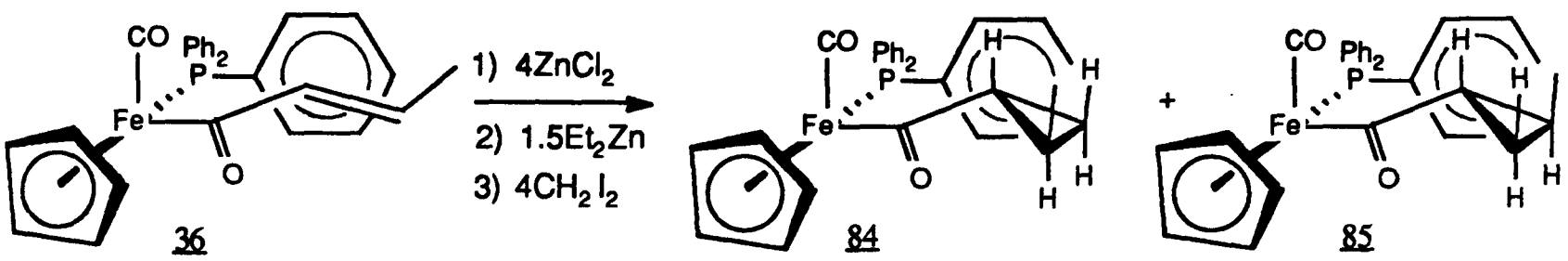


Having demonstrated the efficient and diastereoselective addition of methylene to the Z-α,β-unsaturated iron acyl complexes, reactions with the corresponding E-isomers were investigated.

3. Addition to E-(C_5H_5)Fe(CO)(PPh_3)(COCH=CHR).

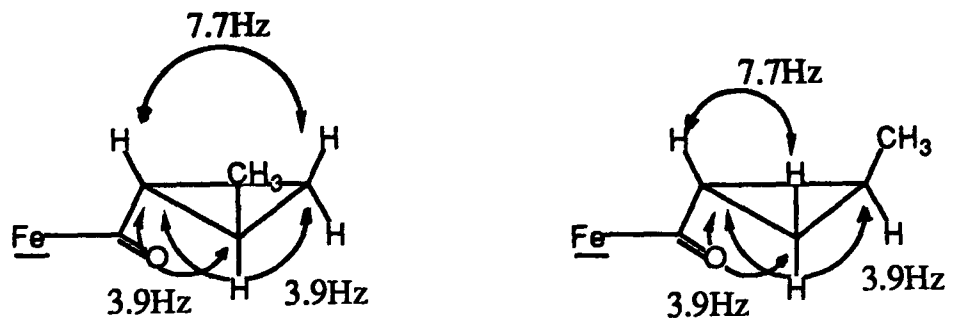
Diethylzinc and methylene iodide were added to a solution of E-(C_5H_5)Fe(CO)(PPh_3)(COCH=CHCH_3) 36 in toluene. In contrast to the rapid reaction of the Z-isomer 37 (< 10 mins., p. 48) the E-isomer 36 reacted only slowly. The reaction was monitored by TLC, the product spot being less polar than the starting material 36. After one hour the reaction was quenched with methanol and, after work up and chromatography, two bands drying to orange solids were isolated. The material from the second band was identified by ^{1}H n.m.r. spectroscopy as unreacted complex 36 (30%).

The molecular ion in the mass spectrum of the product from the first band indicated the incorporation of a methylene unit onto 36. The ^1H n.m.r. spectrum (chloroform-d_1) showed high-field resonances at δ 0.56 and 0.26, characteristic of protons substituted on a cyclopropane ring.[79] No resonances for the cis-substituted cyclopropyl complexes 72 and 73 were present and the products were assigned as the corresponding trans-substituted diastereoisomeric complexes 84 and 85 (62%).



Overlapping doublets at δ 0.98 and 0.96 ($CHC\underline{H}_3$) in the ^1H n.m.r. spectrum suggested that both diastereoisomers had been formed, but the coincidence of the remaining resonances prevented determination of the diastereoisomeric ratio. The ^1H n.m.r. spectrum, in toluene-d_8, showed the resonances assigned to the methyl groups at δ 1.00 and 0.95 in a ratio of 1:1.3, indicating minimal selectivity in the formation of the diastereoisomeric complexes. The major diastereoisomer was assigned arbitrarily as RRR(SSS)-84 by assuming the same stereochemistry at the α-centre as in the major cis-substituted cyclopropyl complex RRS(SSR)-72. Subsequently, this stereochemical assignment was confirmed by the X-ray crystal structure determination of the minor diastereoisomeric product RSS(SRR)-85 made by an alternative, highly diastereoselective route (see p.122).

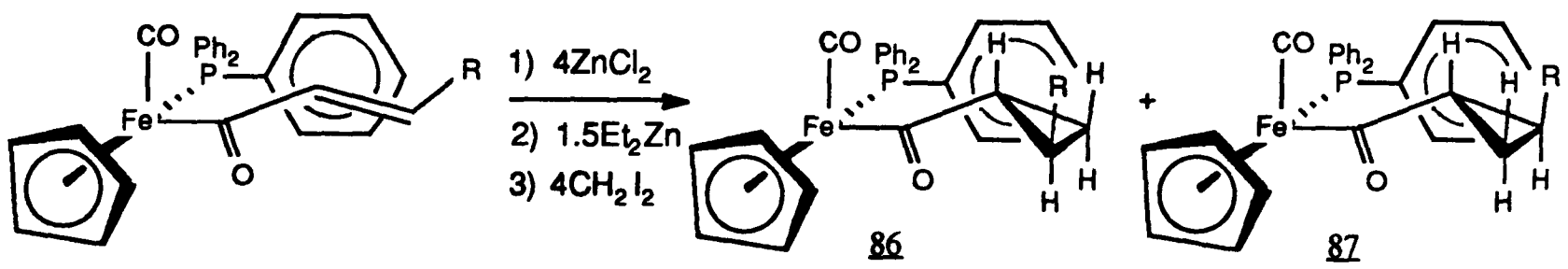
The resonances for the α-protons (COCH) of 84 and 85 were coincidental at δ 2.75. The coupling pattern showed one cis-coupling of 7.7 Hz, and two trans-couplings of 3.9 Hz each, which provided further evidence for the assigned trans-stereochemistry about the cyclopropane ring.[81]



84 85

Fe = $(C_5H_5)Fe(CO)(PPh_3)$

The reaction was repeated on a range of E-α,β-unsaturated iron acyl complexes to determine whether this poor diastereoselectivity was general. The results are summarised in table 7



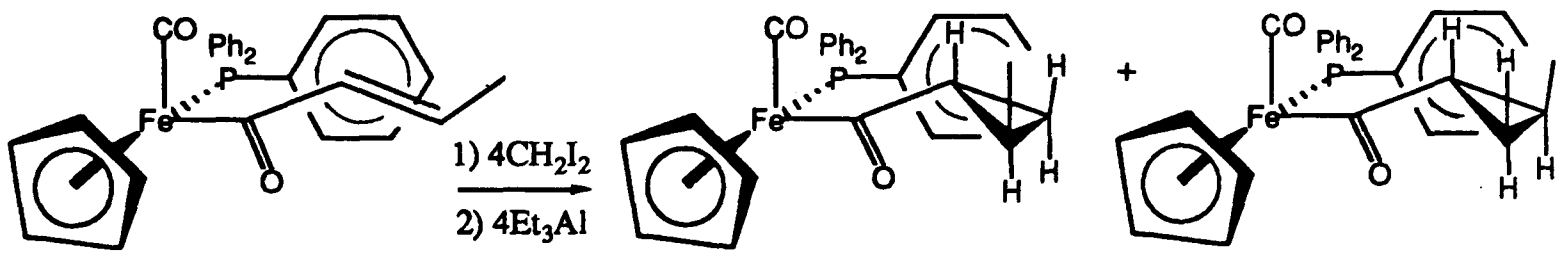
86 87

R	Yield %	Ratio 86:87	Products
Me 36	62	1.3:1	84:85
^{n}Pr 40	47	2:1	88:89
^{n}Bu 42	43	2:1	90:91
^{i}Pr 44	45	2:1	92:93
^{t}Bu 46	31	6:1	94:95

Table 7. The diastereoisomeric ratios 86:87 and overall yields in the reactions of E-$(C_5H_5)Fe(CO)(PPh_3)(COCH{=}CHR)$ with methylene iodide and diethylzinc.

The diastereoisomeric ratios were determined by the integration of whichever resonances for both diastereoisomers could be clearly identified in the ^{1}H n.m.r. spectra. No pairs of diastereoisomers were chromatographically separable. The major diastereoisomer in each case was assigned as 86 and subsequent results (see Chapter 4) confirmed this assignment.

Reaction of 36 with the carbenoid species generated from triethylaluminium and methylene iodide gave a 1:1 mixture of the diastereoisomeric trans-substituted cyclopropyl complexes 84 and 85 (11%), as well as recovered starting material 36 (63%).



36 11% 84 1:1 85

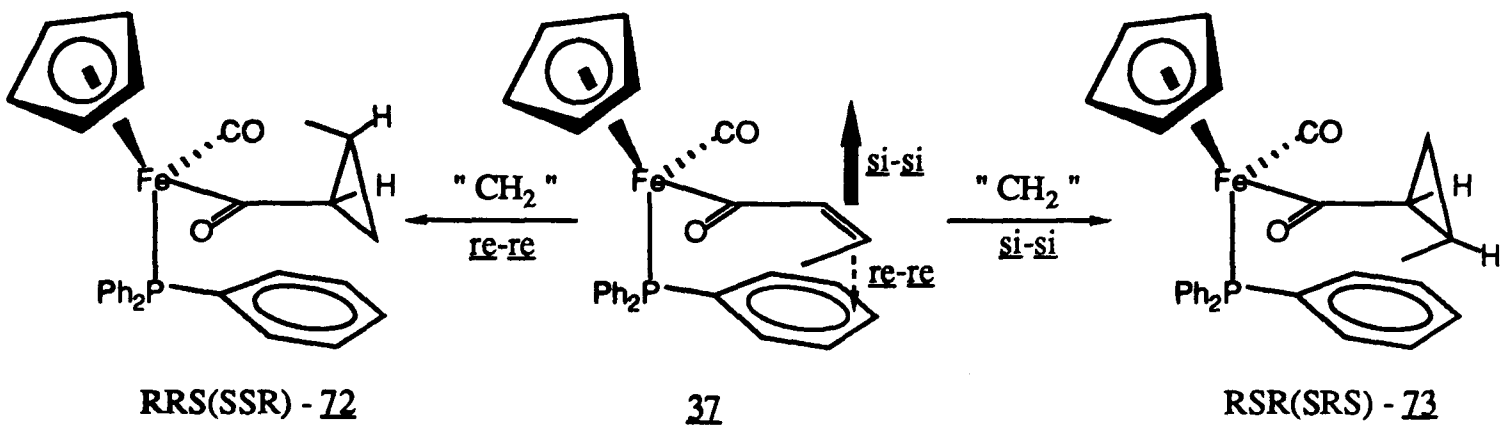
In contrast to the reactions of Z-α,β-unsaturated iron acyl complexes with carbenoid species, the corresponding reactions of the E-isomers give cyclopropyl complexes in low yield and with poor diastereoselectivity. Reasons for these differences are discussed in the following section

Discussion

From the conformational analyses of the α,β-unsaturated acyl ligands attached to the chiral auxiliary $(C_5H_5)Fe(CO)(PPh_3)$, (Chapter 2), it was concluded that the most stable conformations were close to S-cis with the acyl bond approximately anti to the carbon monoxide ligand (the one exception being the computer simulated complex $Z-(C_5H_5)Fe(CO)(PPh_3)(COCH=CHC(CH_3)_3)$ 47), these conformations minimising steric interaction whilst maximising π-orbital overlap. Considering, for example, the complex $Z-(C_5H_5)Fe(CO)(PPh_3)(COCH=CHCH_3)$ 37, then in these conformations the si-si face of the olefinic bond is sterically accessible whilstthe re-re face is blocked by the triphenylphosphine ligand.* The major diastereoisomeric cyclopropyl complex 72, produced from the reaction of 37 with carbenoid species, results from addition to the re-re face of the olefinic bond (vide supra). Therefore

* Throughout this thesis the terms si and re[82] will be used with respect to those complexes with the R-configuration at iron, unless otherwise stated.

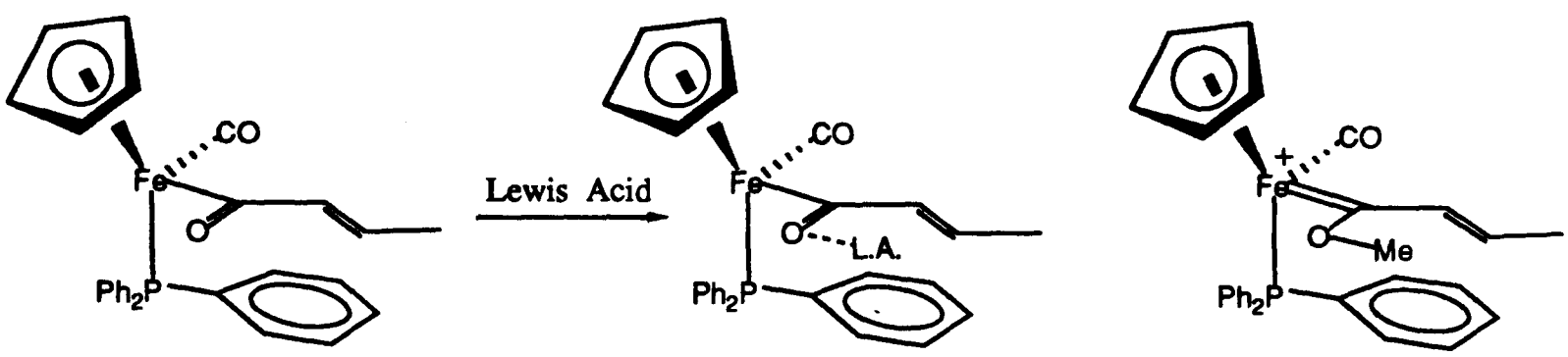
the reactive conformations, resulting in the synthesis of the major diastereoisomeric product 72, cannot be the ones calculated previously to be the most stable since in these the re-re face is sterically inaccessible.



RRS(SSR) - 72 37 RSR(SRS) - 73

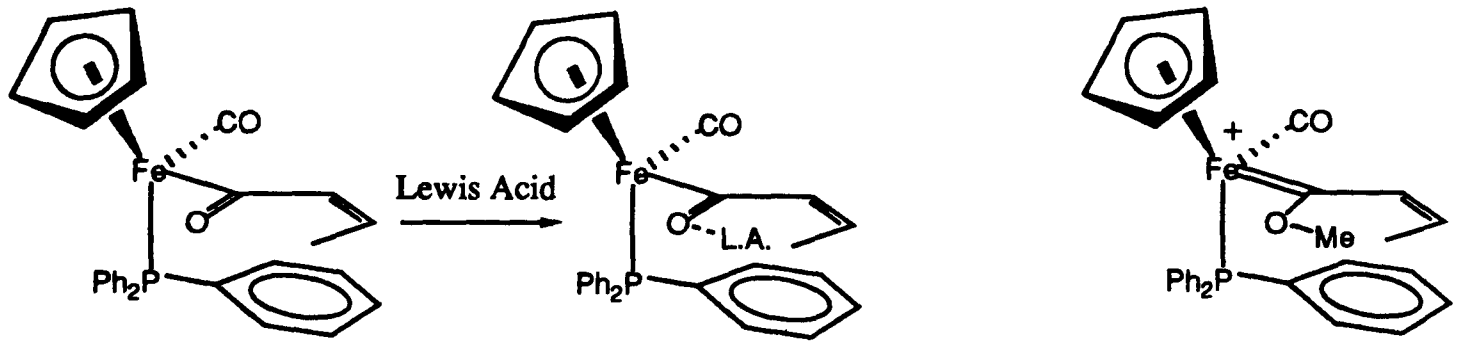
The ability of the acyl oxygen in iron acyl species to coordinate to Lewis acids, and thus direct the stereochemical course of subsequent reactions, has been reported,[52,57] and the possibility of this effect influencing the stereochemical outcome of the reactions with the zinc carbenoid species was investigated (see table 4, p.49). Literature reports[71b] show that the carbenoid species generated from a trialkyl aluminium and methylene iodide do not react with olefinic bonds via prior coordination to allylic oxygen functionalities. That this species reacts diastereoselectively with Z-α,β-unsaturated iron acyl complexes, and that the corresponding zinc carbenoid reacts with the same degree of diastereoselectivity, indicates that prior coordination of the carbenoid species to the acyl oxygen, with subsequent intramolecular transfer of methylene, is not necessary for the diastereoselective addition to occur. Even in those cases where external Lewis acids are not added to the starting material prior to reaction, the nature of the reagents and the species generated in solution should result in some coordination of unreactive species to the acyl oxygen, such that the conformational properties of both the Z- and E- α,β-unsaturated acyl ligands might be altered.

In order to examine the nature of this effect, the known E-α,β-unsaturated carbene complex 96[83] was used to model qualitatively, the coordination complex 97 in which a Lewis acid was assumed to coordinate to the acyl oxygen in complex 36.



36 97 96

Similarly, the Z-α,β-unsaturated carbene complex 98 (vide infra) was used to model the coordination complex 99 in which a Lewis acid was assumed to coordinate to the acyl oxygen in complex 37.



37 99 98

By use of the ChemX[66] computer modelling system it was hoped to probe the effect of Lewis acid coordination on the conformational properties of the α,β-unsaturated acyl ligands. The calculation was performed on the basis of the known X-ray crystal structure for 96 (figure 8.),[83] the Z-isomer 98 being generated from this.

Qualitative empirical force-field calculations were performed using default parameters which considered only Van der Waal's forces. Assuming the acyl bond to remain approximately anti to the carbon monoxide ligand, only rotations about C1-C2 were considered with the relative energies being calculated at 5^{o} intervals. The calculations are not intended to predict absolute barriers to rotation but to provide insight into the steric

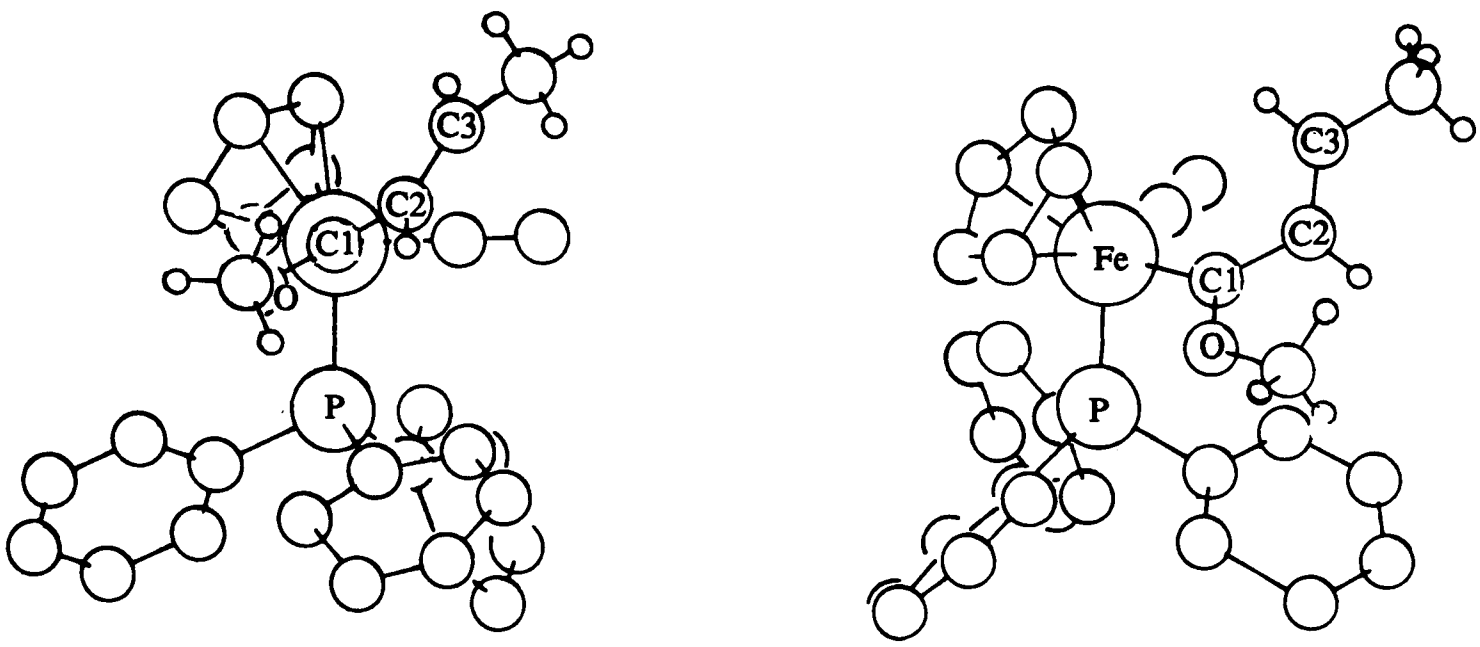


Figure 8. X-ray crystal structure of E-$(C_5H_5)Fe(CO)(PPh_3)(=C(OCH_3)CH=CHCH_3)^+$ 96. Selected protons are removed for clarity.

factors exhibited within these complexes. The conformational energy profiles for 98 and 96 are shown in figures 9 and 10 respectively. The relative energies (kcal mol^{-1})(ordinate) are plotted against the O -C1-C2-C3(abscissa) torsional angle. Newman projections along C1-Fe are highlighted for the energy minima.

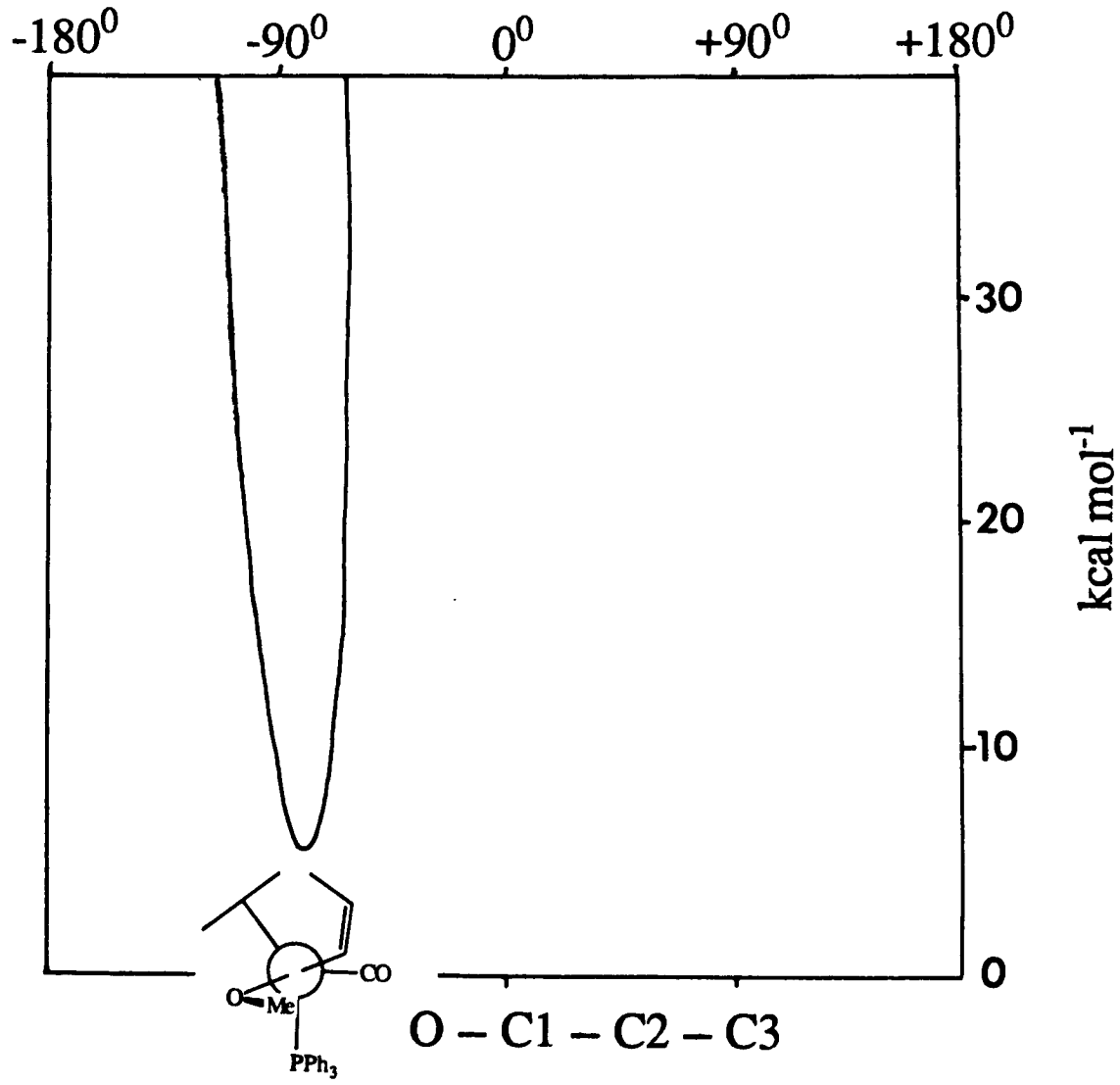


Figure 9. Conformational energy profile for Z-$(C_5H_5)Fe(CO)(PPh_3)(=C(OCH_3)CH=CHCH_3)^+$ 98.

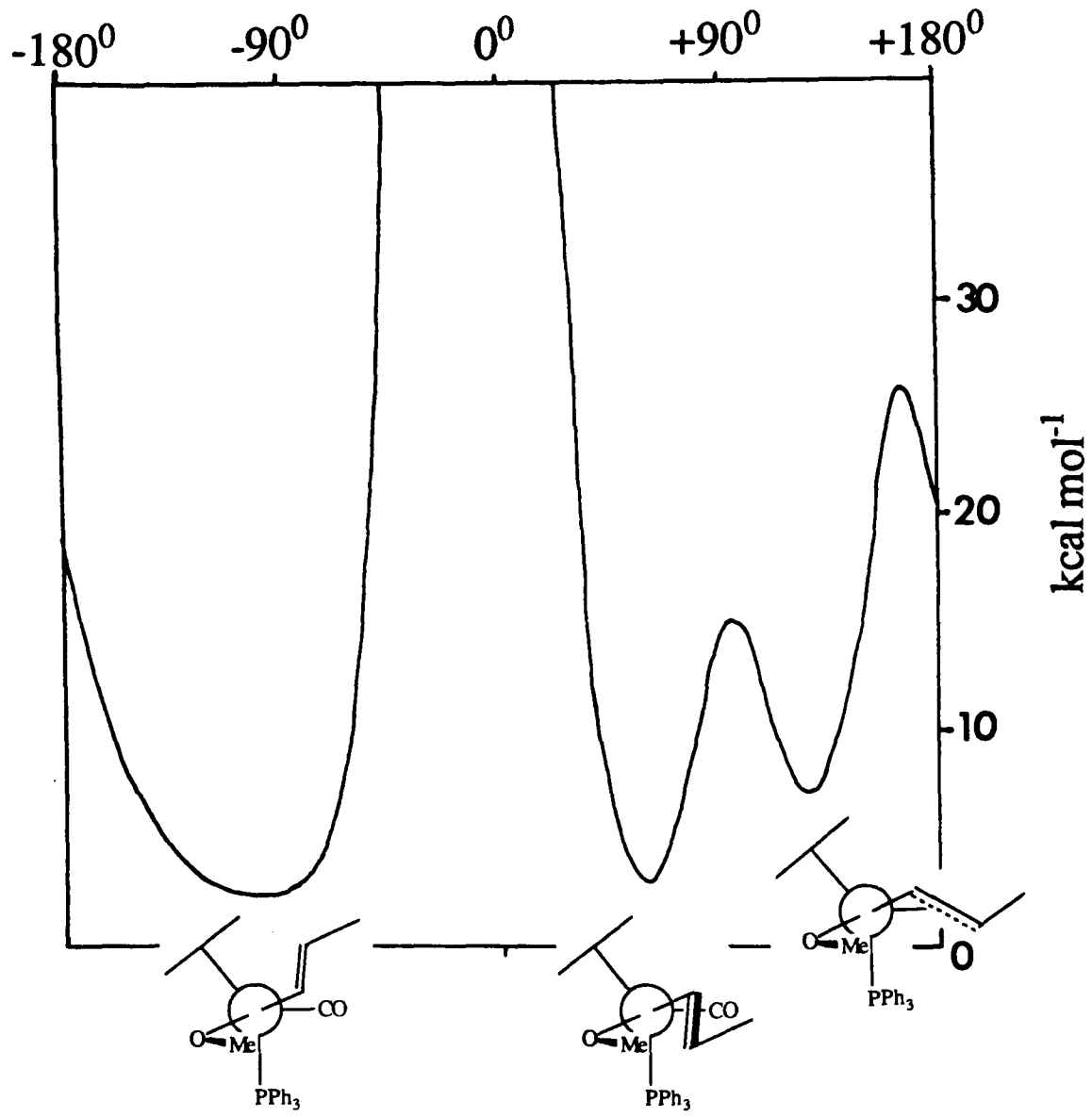
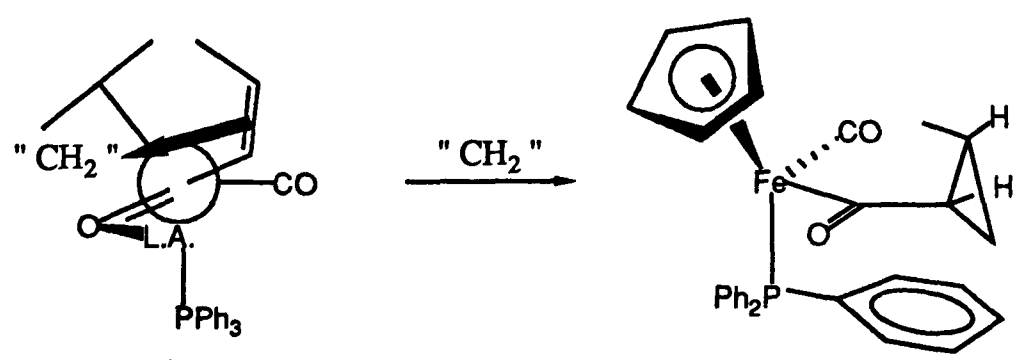


Figure 10. Conformational energy profile for E-$(C_5H_5)Fe(CO)(PPh_3)(=C(OCH_3)CH=CHCH_3)^+$ 96.

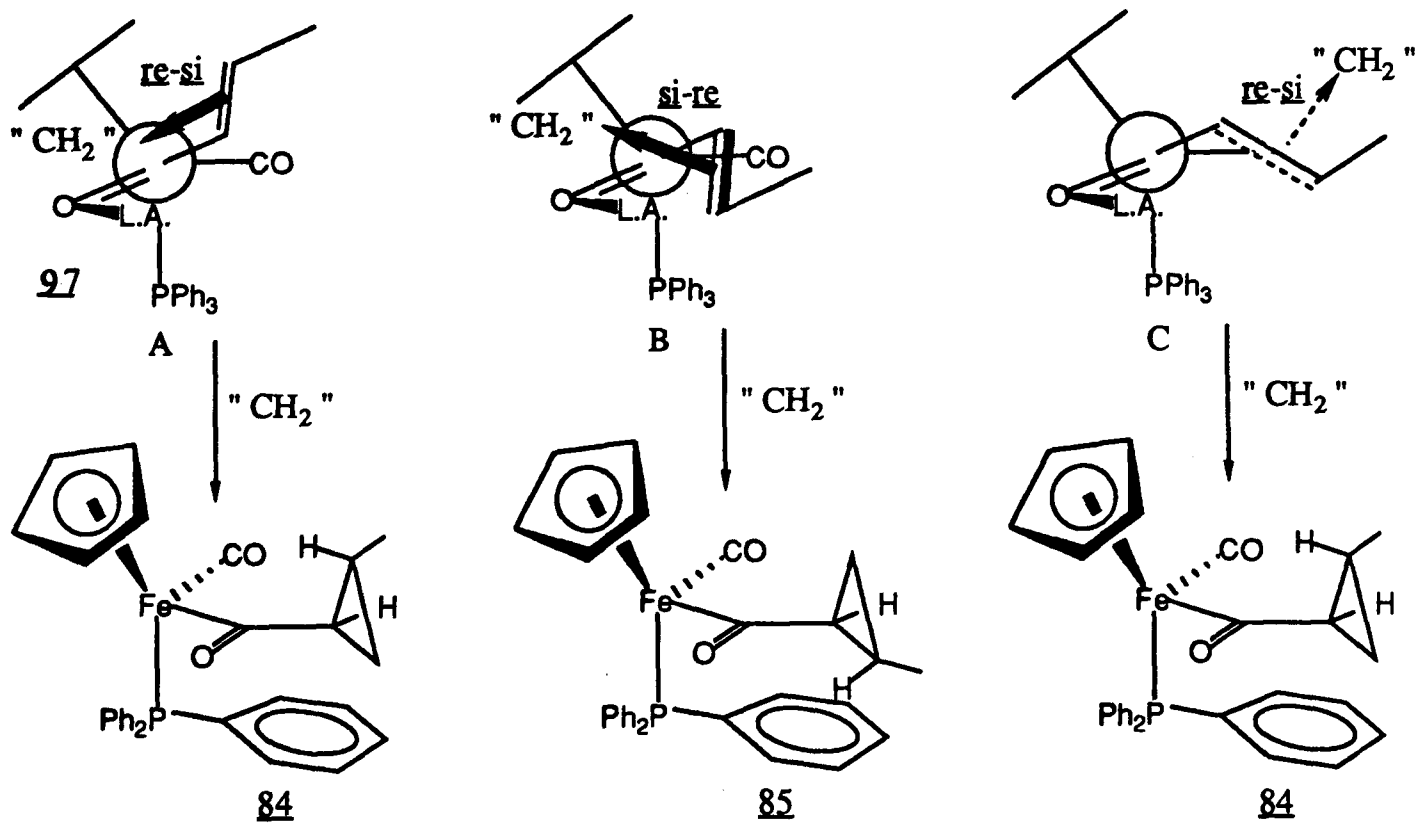
The conformational energy profile for 98 (figure 9) indicates a single sterically accessible conformation, interactions between the olefinic methyl substituent and the ligands about the iron preventing any other conformations being adopted. If 98 models accurately the assumed Lewis acid coordination complex 99, then the latter might be expected to adopt, and react via, the conformation shown below.



99 72

The si-si face of the olefinic bond is blocked by the cyclopentadienyl and carbon monoxide ligands and therefore the carbenoid species approaches the re-re face preferentially, in agreement with the experimentally observed diastereoselectivity. Furthermore, since the olefinic bond is orthogonal to the acyl group then no π-orbital overlap occurs, resulting in maximum electron density on the olefinic bond leading to the observed rapid reaction with the electrophilic carbenoid species. The β-dimethyl substituted α,β-unsaturated complex 54 resembles 37 in its reactions with the carbenoid species. Presumably the cis-β-methyl substituent in 54 affords the acyl ligand the same conformational properties as those of the ligand in 37, and the reactions of 54 can thus be accounted for in the same way.

The conformational energy profile for carbene 96 (figure 10) shows three regions of energy minima. If 96 models accurately the assumed Lewis acid coordination complex 97 then the latter might be expected to adopt, and react via, conformations A→C shown below.

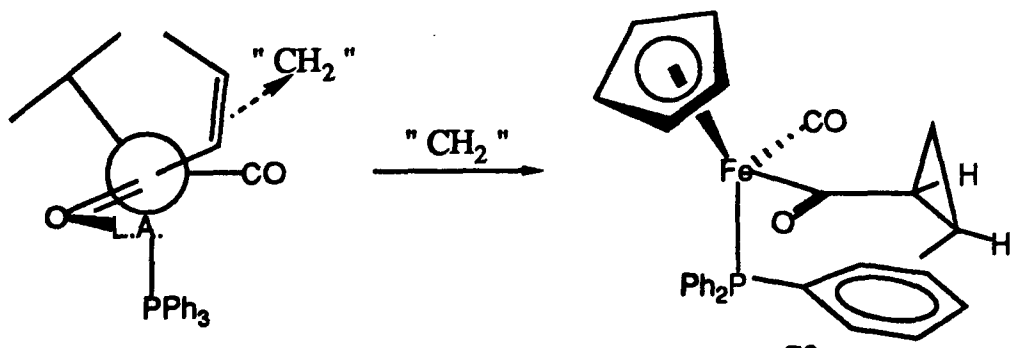


For conformations A and C the re-si face of the olefinic bond is exposed, the si-re face being shielded, whilst for

conformation B this situation is reversed. Hence the carbenoid species can react at either face of the olefinic bond, a conclusion consistent with the experimentally observed poor diastereoselectivity. That poor diastereoselectivity is observed indicates that the rate of reaction via each conformation will be similar. Furthermore, since in conformations A→C the olefinic bond is not orthogonal to the acyl group then some π-orbital overlap can occur, making the E-isomers less reactive towards the electrophilic carbenoid species than the corresponding Z-isomers, a conclusion consistent with experimental observations.

By assuming that, in the reaction of carbenoids with α,β-unsaturated iron acyl complexes, a Lewis acid species coordinates to the acyl oxygen, and that such a coordination complex can be modelled by the known carbene complex 96, a series of conclusions have been reached which account, qualitatively, for the experimental observations.

For the Lewis acid complex 99, the minor diastereoisomeric product 73 might arise by approach of the carbenoid species to the si-si face of the olefinic bond if the cyclopentadienyl and carbon monoxide ligands do not completely block this face.



99 73

Alternatively, reaction might also occur via a minor pathway in which no Lewis acid coordinates to the acyl oxygen. The conformational analysis of Z-(C_5H_5)Fe(CO)(PPh_3)($COCH{=}CHCH_3$) 37 (Chapter 2) indicated considerable rotational freedom about the acyl-vinyl bond, and presumably conformations in which either the si-si or re-re faces of the olefinic bond are exposed can

be adopted, thus reducing the diastereoselectivity of the reaction. Prior addition of an external Lewis acid might be expected to favour the former pathway (vide supra) over the latter, thus increasing the diastereoselectivity of the reaction. Consistent with this is the experimental observation that prior addition of zinc dichloride to Z-α,β-unsaturated iron acyl complexes increases the diastereoselectivity of the subsequent reactions with the zinc carbenoid species. Alternatively, the action of zinc dichloride might be due to interaction with the carbenoid species itself.

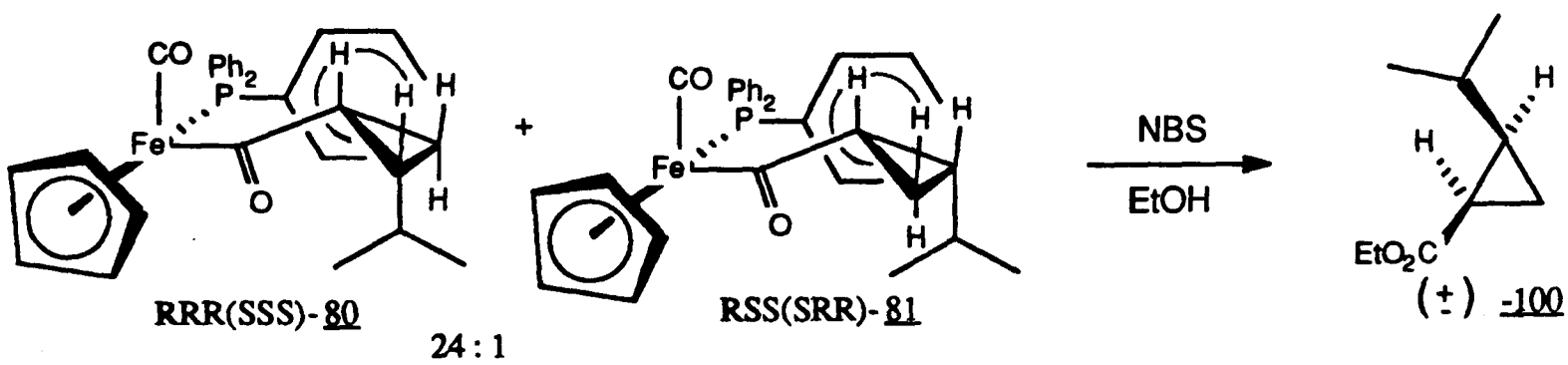
Having developed a diastereoselective synthesis of cis-substituted cyclopropyl iron acyl complexes, the decomplexation of the acyl ligands to give the corresponding cyclopropyl derivatives was investigated.

4. Decomplexation of cis-$(C_5H_5)Fe(CO)(PPh_3)(COCH\!-\!\overset{CH_2}{\diagup\diagdown}\!-CHR)$

For the previously described diastereoselective syntheses of cis-substituted cyclopropyl derivatives to be synthetically useful it was necessary to show that the cyclopropyl acyl ligands could be decomplexed efficiently and with complete retention of stereochemistry. The use of one-electron oxidants in the decomplexation of acyl ligands bound to the iron chiral auxiliary has been demonstrated[43] (see Chapter 1 section 2b)) but it has also been reported that these oxidants can catalyse cis/trans epimerisations of substituted cyclopropane rings.[84] Hence, decomplexation of the cis-substituted cyclopropyl complexes might give the corresponding trans-substituted cyclopropyl derivatives via epimerisation of the ring. Alternatively, the isolation of only the cis-substituted cyclopropyl derivative would show not only that epimerisation does not occur, but would provide further evidence that the cis-stereochemistry had been correctly assigned

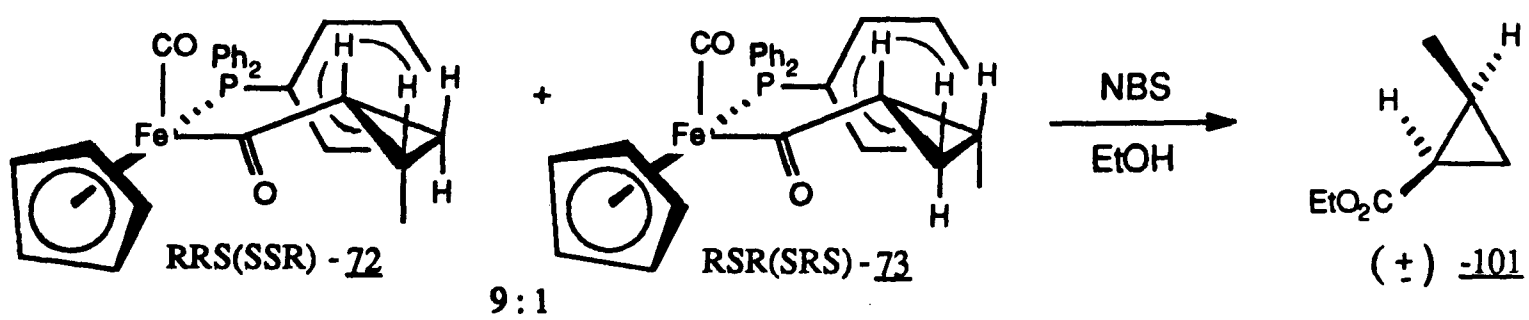
in the original complex.

N-bromosuccinimide was added to a 24:1 mixture of diastereoisomers RRR(SSS)-80 and RSS(SRR)-81 in dichloromethane:ethanol (1:1) at -40°C. After stirring (-40°C; 10mins., 20°C, 40mins.), the reaction was worked up and a single product band isolated by chromatography, no other products being seen. The product was isolated as a yellow oil and identified as (±)-100 (60% -unoptimised) by ^{1}H n.m.r. spectroscopy.



The ^{1}H n.m.r. spectrum (chloroform-d_1) of 100 showed resonances for the ring protons at δ 1.69 (COCH) and 1.03-0.82 ($CHCH_2$) and all signals were consistent with those given in the literature for 100.[85] Further evidence for cis-stereochemistry of the ring was the coupling pattern for the α-proton (COCH) in the ^{1}H n.m.r. spectrum (toluene-d_8), one trans-coupling of 5.5 Hz and two cis-couplings of 8.3 Hz each being consistent with the assigned stereochemistry.[81] That no cis/trans epimerisation had occurred was subsequently confirmed by the synthesis of the corresponding trans-substituted ester (see p.124), none of which was isolated from this reaction.

The reaction was repeated on a 9:1 mixture of the diastereoisomers RRS(SSR)-72 and RSR(SRS)-73, a single product being isolated from the reaction and identified by ^{1}H n.m.r. spectroscopy as (±)-101 (65%-unoptimised).[86]



The ^{1}H n.m.r. spectrum (benzene-d_6) of 101 showed resonances for the ring protons at δ 1.52 (COCH), 0.90 (HC<u>H</u>), 0.84 (C<u>H</u>CH_3) and 0.62 (<u>H</u>CH), the coupling pattern for the α-proton (COCH) confirming the assigned cis-stereochemistry. Subsequent synthesis of the corresponding trans-isomer (see p.125) confirmed that no epimerisation had occurred in this reaction.

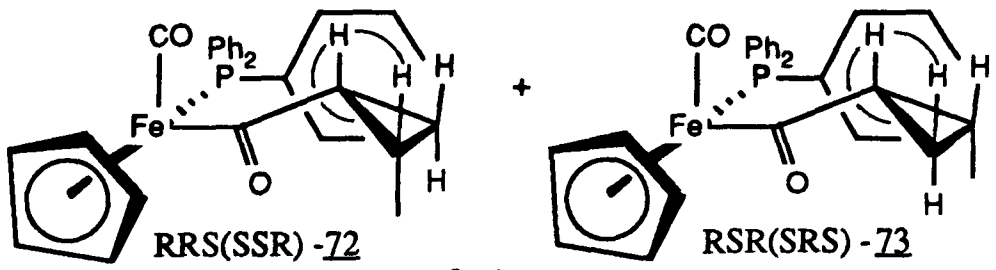
These reactions demonstrate that no cis/trans epimerisation occurs on the decomplexation of the cyclopropyl acyl ligands. The preparation of the cis-alkylated cyclopropanecarboxylic esters is the first such synthesis in which the relative stereochemistry of the ring is controlled stereospecifically. Other preparative routes produce cis/trans epimeric mixtures which must be separated chromatographically.[85-87]

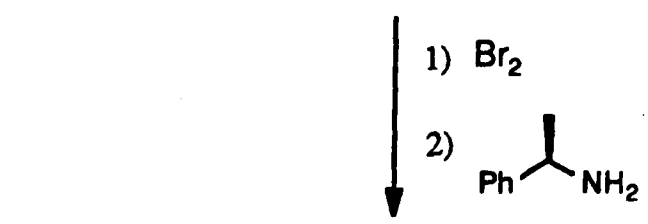
The diastereoselectivity of cyclopropane ring formation was not reflected in the decomplexed product since racemic materials were used. By the use of homochiral iron acyl complexes, the asymmetric synthesis of cyclopropanecarboxylic esters should be possible. It was anticipated, having demonstrated that the cyclopropane ring does not epimerise on decomplexation (vide supra), that racemisation on decomplexation would not occur. The enantioselectivity of ester formation should therefore equal the degree of diastereoselectivity of the intermediate cyclopropyl acyl complex synthesis. However, no data existed by which the enantiomeric purity of any of the cis-substituted cyclopropanecarboxylic esters accessible by this synthetic route could be measured. Furthermore, attempts to separate the resonances due to each enantiomer of (±)-101, in the ^{1}H n.m.r. spectrum, by the use of Pirkle's chiral shift reagent, R-(-)-2,2,2,-trifluoro-1-(9-anthryl)ethanol,[88] were unsuccessful.

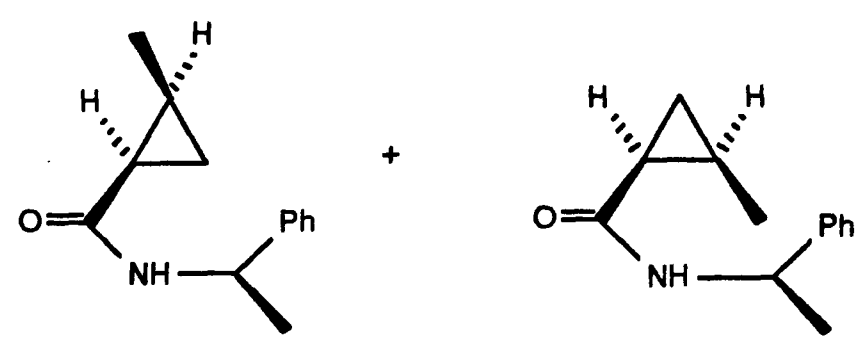
An alternative approach was adopted in which a homochiral compound was introduced into the cyclopropyl derivative on decom-

plexation, resulting in diastereoisomeric products. This new chiral centre acts as an internal standard against which the enantiomeric purity of the cyclopropane ring can be measured. The commercially available amine R(+)-2-phenylethylamine was chosen as the homochiral reagent, its enantiomeric purity being confirmed by ^{1}H n.m.r. experiments with Pirkle's chiral shift reagent.[88] Decomplexation of the cyclopropyl complexes in the presence of the amine should result in the synthesis of the corresponding cyclopropyl amides.

A 9:1 mixture of RRS(SSR)-72 and RSR(SRS)-73 in dichloromethane at -40°C was treated successively with bromine and R(+)-2-phenylethylamine. After work up the product was isolated as a white solid, the mass spectrum and ^{1}H n.m.r. spectrum of which indicated the formation of the novel diastereoisomeric amides RRS-102 and RSR-103 (52%-unoptimised).



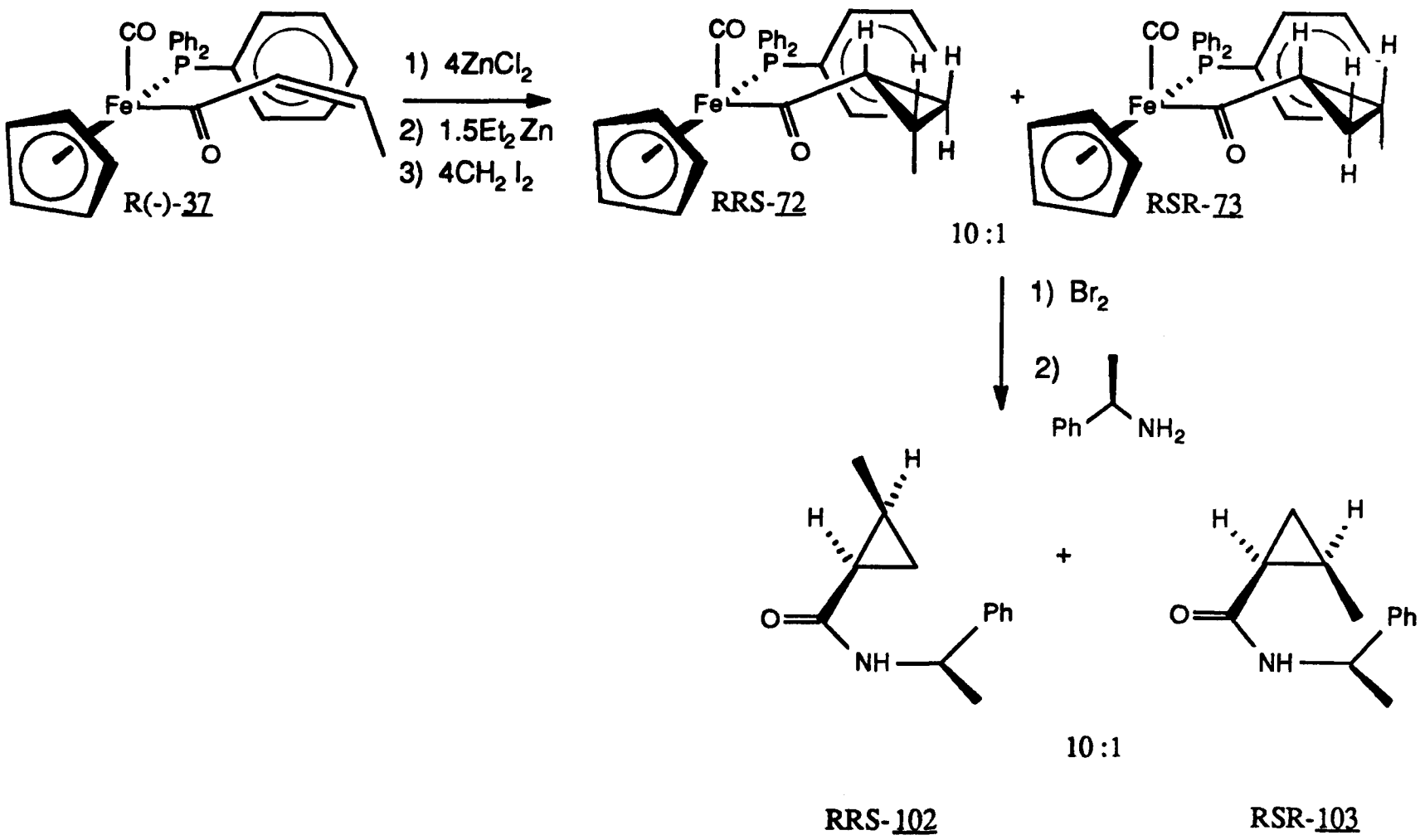




RRS-102 RSR-103

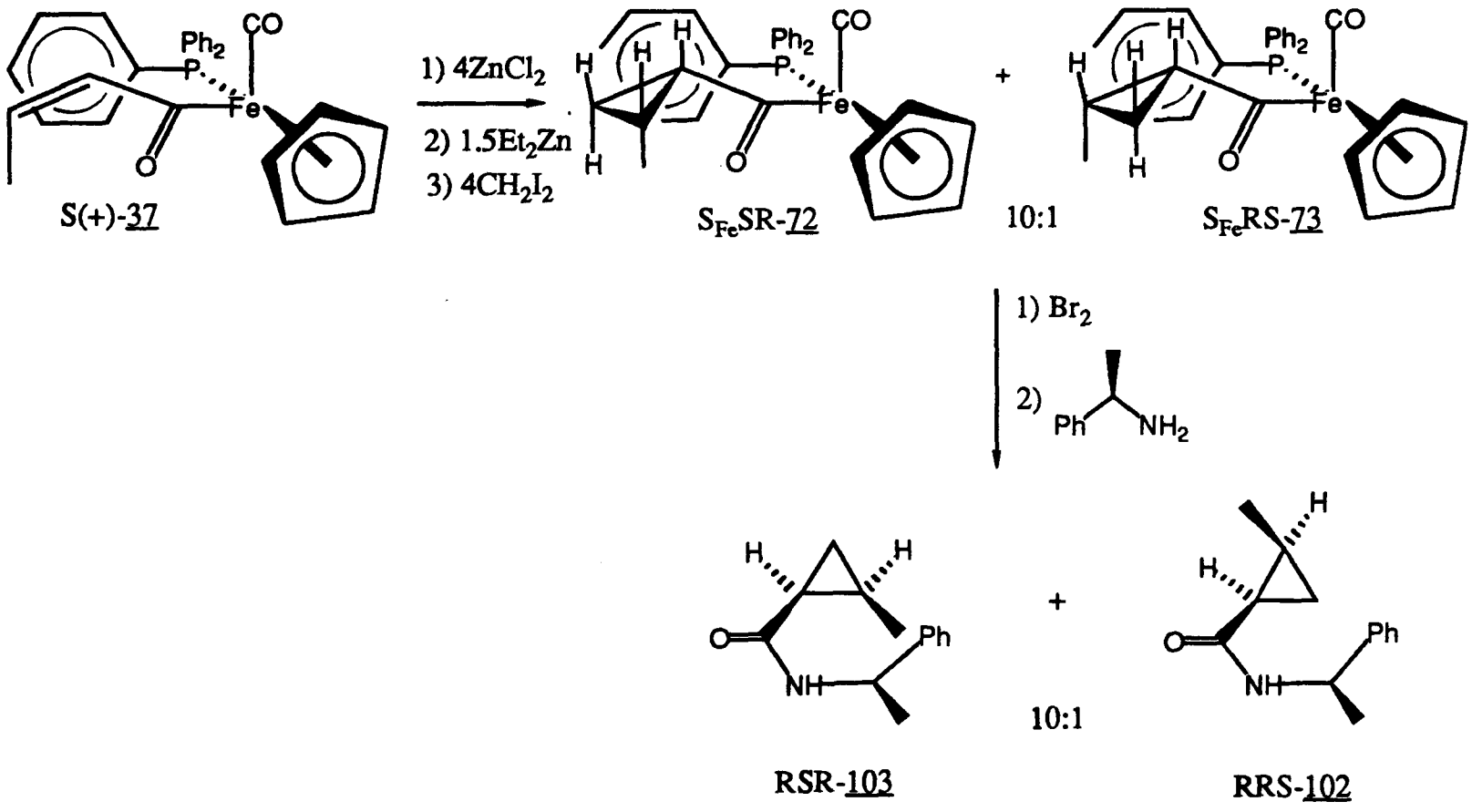
The majority of resonances in the ^1H n.m.r. spectrum for the two diastereoisomers overlapped or were coincidental. However, in chloroform-d_1:benzene-d_6 (1:1), the signals for the methyl groups substituted on the cyclopropane rings appeared at δ 1.03 and 1.11, although assignment to either 102 or 103 was not possible at this stage. The resonances were of equal intensity, the 1:1 ratio of diastereoisomers reflecting the use of racemic 72 and 73, and that no diastereoisomeric separation had occurred on work up. To show that the rates of diastereoisomer formation were equal, the reaction was repeated using one-half equivalent of amine. Again a 1:1 mixture of diastereoisomers was isolated (18%).

The reaction was then repeated with the homochiral complex R(-)-Z-$(C_5H_5)Fe(CO)(PPh_3)(COCH{=}CHCH_3)$ 37 which was treated with zinc dichloride, diethylzinc and methylene iodide as before (vide supra). The diastereoisomeric ratio of the products RRS-72:RSR-73 was 10:1 after a single crystallisation. Decomplexation in the presence of R(+)-2-phenylethylamine, as before, gave the diastereoisomers RRS-102 and RSR-103 in 61% isolated yield.



The ^{1}H n.m.r. spectrum in chloroform-d_1:benzene-d_6 (1:1) showed resonances in common with those observed previously in the ^{1}H n.m.r. spectrum of the product from the racemic series (vide supra). Resonances due to the methyl groups substituted on the cyclopropane ring at δ1.03 and 1.11, which were of relative intensity 10:1, demonstrated that the diastereoisomeric ratio of amides 102 and 103, equalled the degree of diastereoselectivity observed in the formation of the intermediates 72 and 73. The major diastereoisomer was assigned as RRS-102 by comparison with the major diastereoisomeric starting material RRS-72.

The reaction was repeated with S(+)-Z-(C_5H_5)Fe(CO)(PPh_3)(COCH=$CHCH_3$) 37 and the results are outlined in the following scheme.



Decomplexation of a 10:1 mixture of S_{Fe}SR-72 and S_{Fe}RS-73 gave the corresponding amides in 77% isolated yield. The ^{1}H n.m.r. spectrum in chloroform-d_1:benzene-d_6 (1:1) showed the resonances due to the methyl groups substituted on the cyclopropane ring at δ1.11 and 1.03. The relative intensity of 10:1

showed that the diastereoisomeric ratio of the amides 103 and 102 equalled the degree of diastereoselectivity observed in the formation of the intermediates 72 and 73. The major diastereoisomer was assigned as RSR-103 by comparison with the stereochemistry of S_{Fe}SR-72.

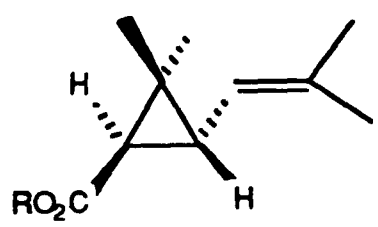
The results from these experiments show that by the use of homochiral R(-) or S(+) starting material 37 the cis-substituted cyclopropyl amides 102 and 103 respectively, can be synthesised with good control over the absolute stereochemistry of the substituted cyclopropane ring. The diastereoselectivity observed in the formation of the intermediate cyclopropyl complexes is maintained totally on decomplexation, proving that no racemisation of the cyclopropane ring occurs.

The efficient and stereoselective synthesis of cis-substituted cyclopropyl complexes via the reactions of Z-α,β-unsaturated iron acyl complexes with electrophilic carbenoid species have been demonstrated. Decomplexation gives the corresponding cis-substituted cyclopropanecarboxylic esters diastereospecifically, the first such synthesis of these compounds. By the use of homochiral starting material the decomplexed cyclopropyl derivatives are synthesised with complete control over the relative stereochemistry and good control over the absolute stereochemistry of the substituted cyclopropane ring.

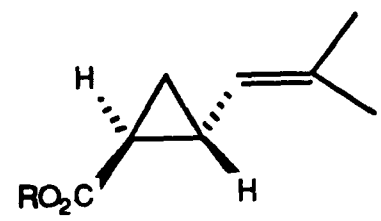
Having demonstrated this novel method for the asymmetric synthesis of cis-substituted cyclopropanecarboxylic acid derivatives, we sought to develop this approach to include the synthesis of more highly substituted cyclopropane rings whilst maintaining the high degree of stereochemical control described above.

B. Isopropylidene Addition Reactions

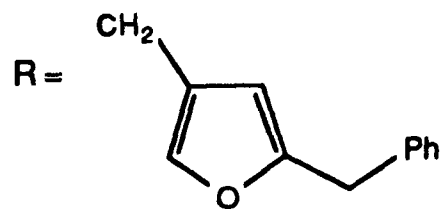
Essential structural features of all active pyrethroid insecticides are the geminal methyl substituents on the cyclopropane ring.[6b] The absence of these substituents results in little or no insecticidal activity. For example, the 5-benzyl-3-furylmethyl ester of trans-(±)2,2-dimethyl-3-(2,2-dimethylvinyl)-cyclopropanecarboxylic acid 104 is more than one thousand times as toxic to houseflies as the same ester of trans-(±)3-(2,2-dimethylvinyl)-cyclopropanecarboxylic acid 105.[89]



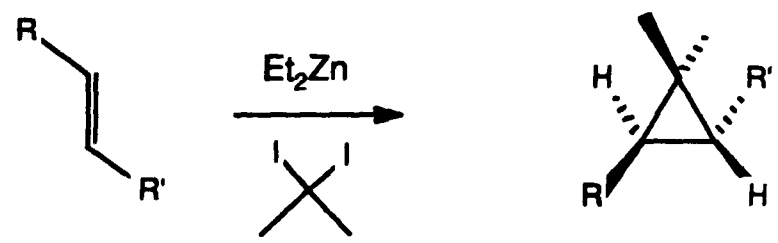
104



105



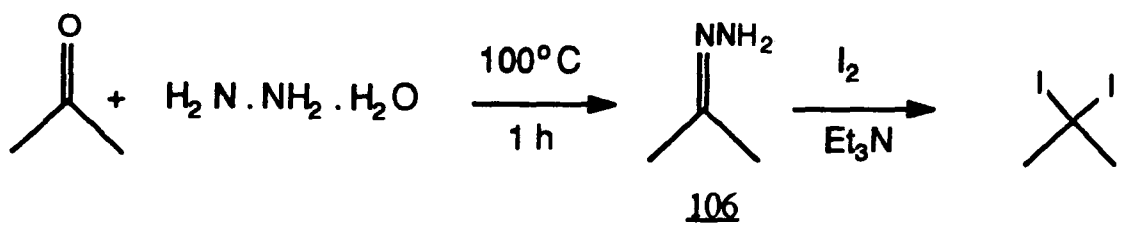
A possible synthetic approach to gem-dimethyl substituted cyclopropane rings might be via the reaction of olefinic bonds with the carbenoid species generated from isopropylidene iodide, although no literature precedent exists for such a reaction.



In the previous section a stereoselective synthesis of cis-substituted cyclopropyl derivatives was demonstrated via the transfer of methylene from a carbenoid species, generated from methylene iodide, to the olefinic bond of Z-α,β-unsaturated iron acyl complexes. It was anticipated that if a similar carbenoid species could be generated from isopropylidene iodide, then stereoselective syntheses of gem-dimethyl substituted cyclopropyl derivatives might be achieved.

1. Preparation of Isopropylidene Iodide.

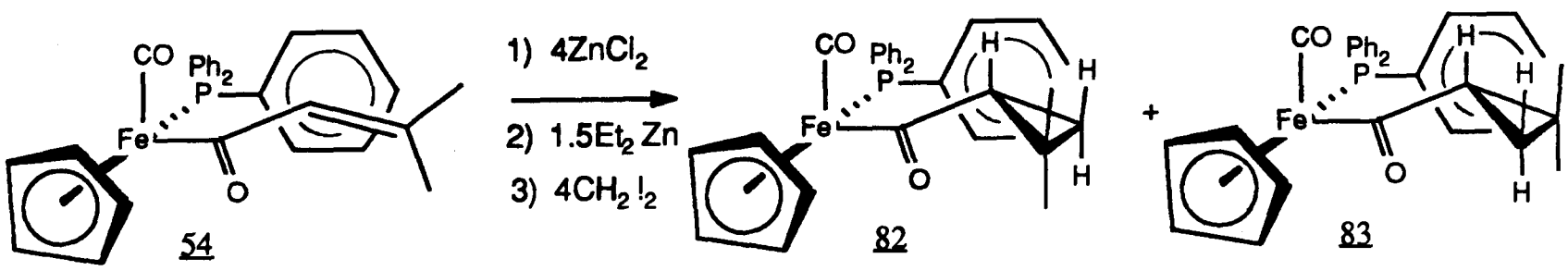
According to the literature procedure,[90] acetone was added slowly to hydrazine hydrate and the mixture refluxed. The crude hydrazone 106 was dissolved in dichloromethane and triethylamine and iodine added. After work up, isopropylidene iodide was isolated as a dark oil (14%).



106

2. Addition to $(C_5H_5)Fe(CO)(PPh_3)(COCH=CH_2)$ 52 and to E-$(C_5H_5)Fe(CO)(PPh_3)(COCH=CHR)$

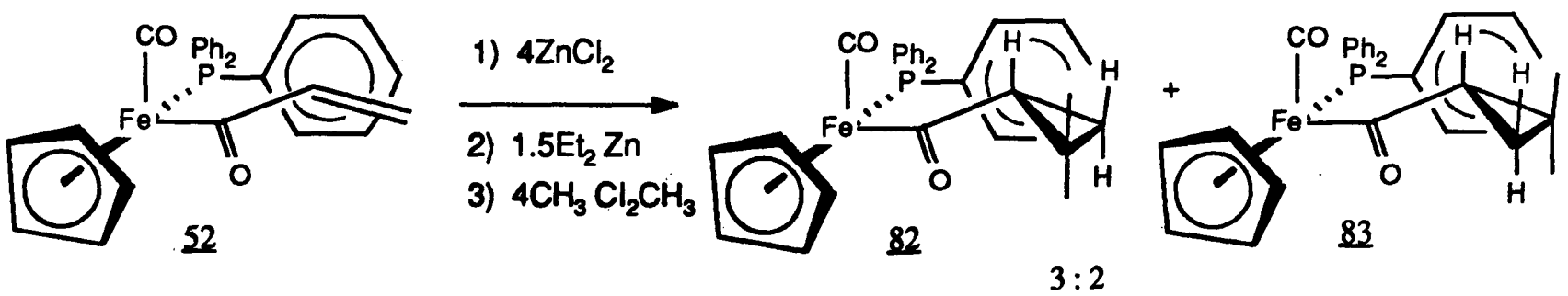
Initially the reaction with the unsubstituted complex 52 was investigated since the anticipated diastereoisomeric products 82 and 83 had been synthesised previously via the diastereoselective addition of methylene to complex 54 (see p.50 and p.52).



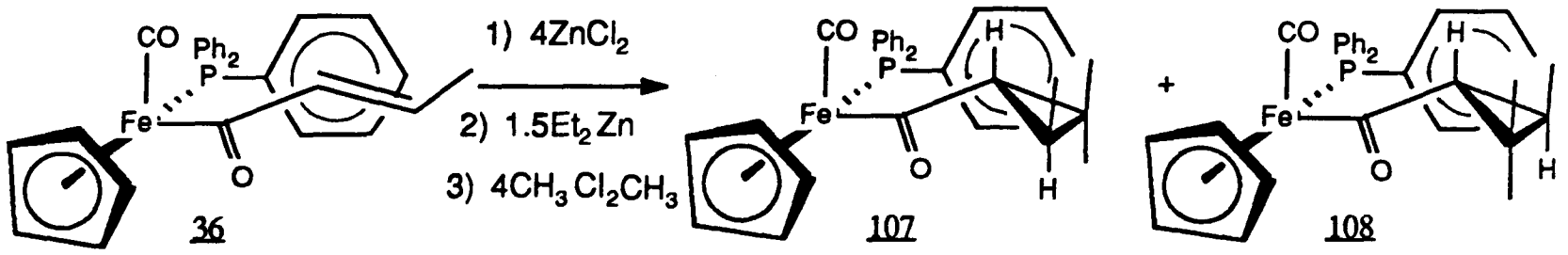
54 82 83

11:1

After stirring a solution of 52 with zinc dichloride in toluene at room temperature, diethylzinc and isopropylidene iodide were added and the mixture stirred. After work up, chromatography gave two bands, each drying to an orange solid. The material from the second band was identified by ^1H n.m.r. spectroscopy as starting material 52 (40%). The ^1H n.m.r. spectrum of the product from the first band identified it as the cyclopropyl complexes 82 and 83 (27%). The diastereoisomeric ratio of 82: 83 was 3:2 indicating that there had been minimal facial selectivity at the olefinic bond during the reaction.

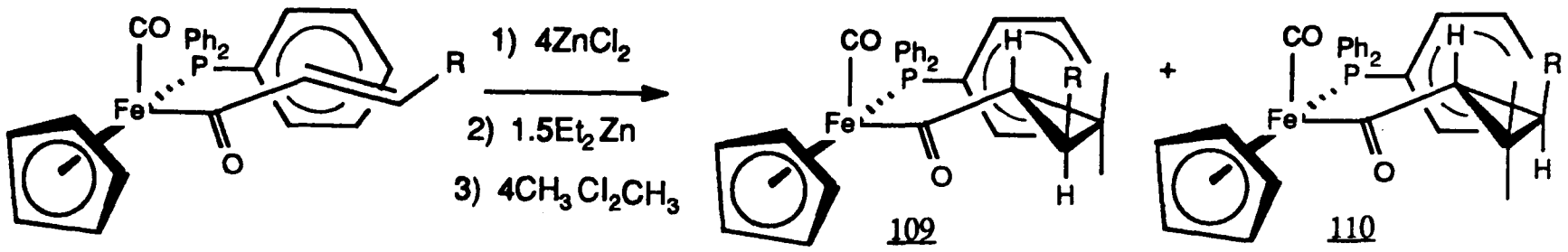


The reaction was repeated on the complex E-(C_5H_5)Fe(CO)(PPh_3)($COCH{=}CHCH_3$) 36 and after two hours was worked up, chromatography giving two orange bands drying to orange solids. The material from the second, larger band was identified by ^1H n.m.r. spectroscopy as unreacted starting material 36 (42%). The molecular ion in the mass spectrum of the product from the first band indicated incorporation of isopropylidene into 36. The ^1H n.m.r. spectrum showed two sets of resonances, consistent with the diastereoisomeric trans-substituted cyclopropyl complexes 107 and 108 (9%).



The ^1H n.m.r. spectrum of the product showed distinct resonances at δ2.45 (COCH), 2.34 (COCH), 1.11 (CCH_3), 1.05 (CCH_3), 1.03 (CCH_3), 0.94 ($CHC\underline{H}_3$), 0.79 ($CHC\underline{H}_3$) and 0.56 (CCH_3). The resonances due to the α-protons (COCH), at δ2.45 and 2.34, were of equal intensity indicating a non-diastereoselective reaction whilst the coupling constants of 5.3 Hz and 5.4 Hz respectively were consistent with the assigned trans-stereochemistry.[81] The diastereoisomers were chromatographically inseparable but a subsequent diastereoselective synthesis of 107 (vide infra) allowed its further characterisation.

The reaction was repeated on other E-α,β-unsaturated iron acyl complexes, and the results are summarised in table 8. In each case the diastereoisomeric ratio was measured from the integrals of the α-protons (COCH).



R	Yield %	Ratio 109:110	Products
Me 36	9	1:1	107:108
Et 38	29	1:1	111:112
^{n}Pr 40	10	1:1	113:114

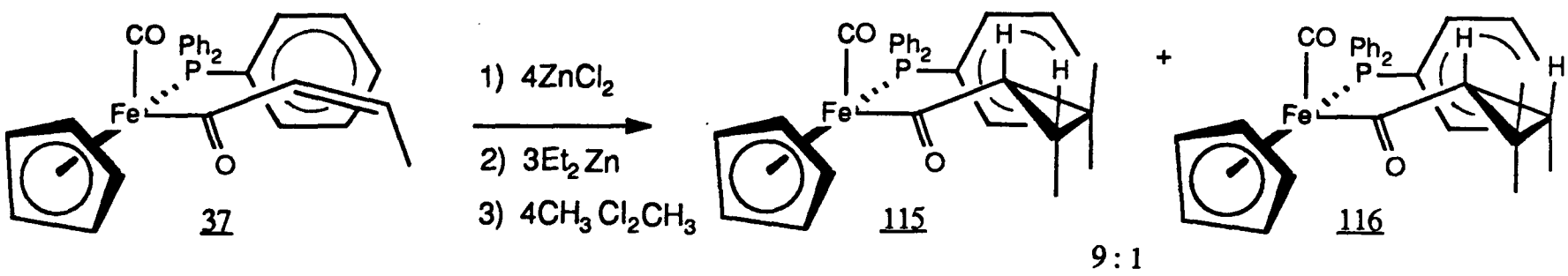
Table 8. The diastereoisomeric ratios 109:110 and overall yields in the reactions of E-(C_5H_5)Fe(CO)(PPh_3)(COCH=CHR) with isopropylidene iodide and diethylzinc.

The results of these reactions show that the low stereoselectivity and reactivity observed previously between the E-α,β-unsaturated iron acyl complexes and the species generated from diethylzinc and methylene iodide (see table 7, p.54) are general to the reactions with other electrophilic alkylidene species. The results of the isopropylidene addition reactions are consistent with, and can be explained in terms of, the previous discussion accounting for the results of methylene addition to E-α,β-unsaturated iron acyl complexes (see p. 55). The poor facial selectivity of isopropylidene addition to the acryloyl complex 52 is consistent with the previous conformational analysis (Chapter 2), which showed the acryloyl and E-α,β-unsaturated acyl ligands to have similar conformational properties when bound to the iron chiral auxiliary. The poor diastereoselectivity of isopropylidene addition to E-α,β-unsaturated iron acyl complexes is therefore reflected in the reaction with the acryloyl complex 52.

In the following section the reaction is repeated with Z-α,β-unsaturated iron acyl complexes.

3. Addition to Z-$(C_5H_5)Fe(CO)(PPh_3)(COCH=CHR)$ and to $(C_5H_5)Fe(CO)(PPh_3)(COCH=C(CH_3)_2)$ 54.

Under the optimum reaction conditions, a solution of complex 37 was stirred in toluene at room temperature with four equivalents of zinc dichloride. Three equivalents of diethylzinc were then added, followed by four equivalents of isopropylidene iodide over fifteen minutes, by which time only trace amounts of the starting material 37 could be seen by TLC. After work up, chromatography gave three bands, each drying to an orange solid. The ^1H n.m.r. spectrum of the material from the final band showed it to be starting material 37 (6%). The molecular ion in the mass spectrum of the product from the first band indicated isopropylidene addition to 37, and the product was identified as the diastereoisomeric cis-substituted cyclopropyl complexes 115 and 116 (85%) from the ^1H n.m.r. spectral data.



The ^1H n.m.r. data for the acyl ligands of 115 and 116 are summarised in table 9. The major diastereoisomer was assigned as RSR(SRS)-115, the basis of this assignment being discussed below, and the diastereoisomeric ratio of 115:116 was 9:1, the diastereoisomers being chromatographically inseparable.

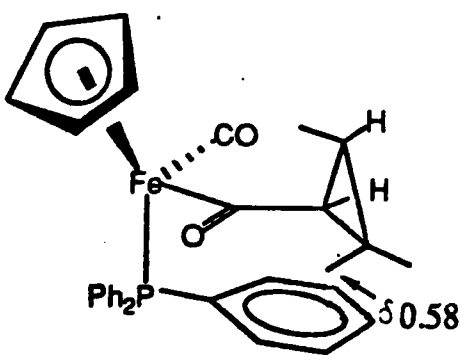
Product	COCH(J/Hz)[a]	CH	$CHCH_3$-	$C(CH_3)_2$-
115	2.79 (8.0)	1.03	1.03	0.94, 0.58
116	2.80 (8.3)	—[b]	0.63	1.08, —[b]

a) Coupling constant to remaining ring proton in parenthesis.

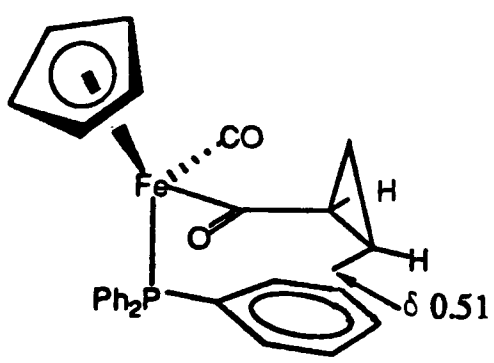
b) Remaining resonances obscured by those of 115.

Table 9. The chemical shifts (δ) of the acyl ligands in the ^1H n.m.r. spectrum of 115 and 116.

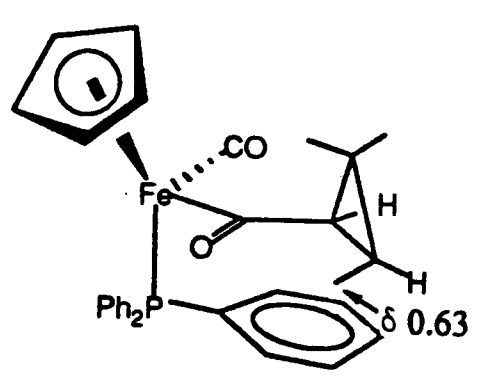
The coupling constants for the α-protons (COCH) are consistent with each diastereoisomer having cis-substituted ring stereochemistry (cf 5.3 Hz and 5.4 Hz for the corresponding trans-isomers p. 71). The stereochemistry of the major diastereoisomer was assigned as RSR(SRS)-115 on the basis of the high-field shift of the singlet due to one of the gem-dimethyl substituents in the ^1H n.m.r. spectrum (δ 0.58). By analogy with RSR(SRS)-73 (p. 46), the high-field shift was attributed to the proximity of the methyl group to the phenyl ring directly beneath the acyl ligand.



RSR(SRS)-115



RSR(SRS)-73



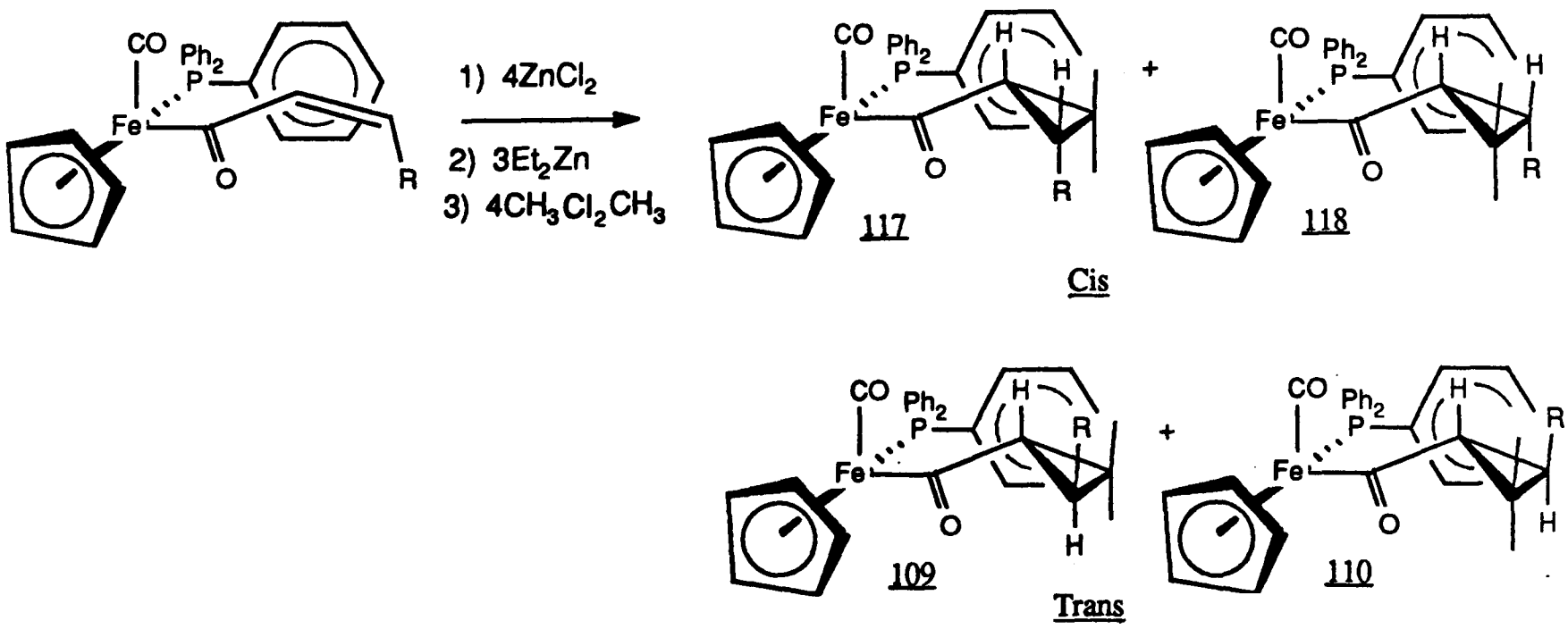
RRS(SSR)-116

The high-field shift of the methyl doublet ($CHCH_3$) of the minor diastereoisomer 116 in the ^1H n.m.r. spectrum (δ 0.63) can be attributed to the same effect, and is further evidence for this stereochemical assignment.

The product from the second band collected, on chromatography of the crude reaction mixture (vide supra), was identified by ^{1}H n.m.r. spectroscopy as a mixture of the diastereoisomeric trans-substituted cyclopropyl complexes 107 and 108, the non-diastereoselective synthesis of which had been demonstrated previously (see p. 71). In this instance the ratio of 107:108 was greater than 30:1, the isolated yield being 3%. The major diastereoisomer was assigned as RSS(SRR) 107 on the basis of the high-field singlet in the ^{1}H n.m.r. spectrum at δ 0.56, assigned to one of the gem-dimethyl substituents (vide supra), and 107 was also characterised by infra-red spectroscopy and mass spectrometry.

The isolation of 107 from this reaction was unusual in that carbenoid additions to olefinic bonds are generally stereospecific, Z-olefins giving only the corresponding cis-substituted cyclopropyl derivatives.[60] The origin of 107 is unclear, but it is unlikely to arise by an initial isomerisation of the starting material Z-37 to E-36, followed by isopropylidene addition, since this latter reaction has been shown to be non-diastereoselective (vide supra). The diastereoselectivity is more likely to occur via a non-concerted addition of isopropylidene to complex 37 (see discussion).

The reaction was repeated with other Z-α,β-unsaturated iron acyl complexes and the results are summarised in table 10.



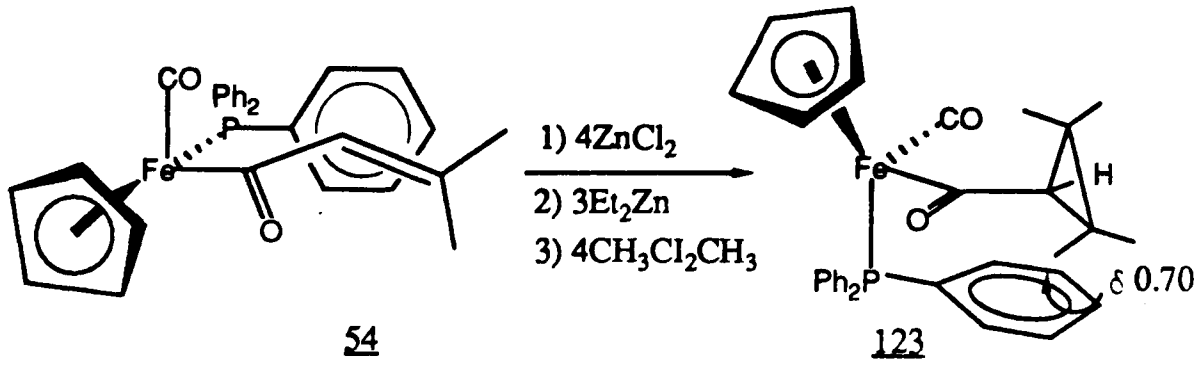
R	Yield %	Ratio cis:trans	Ratio trans 109:110	Ratio cis 117:118
Me 37	88	28:1	>30:1 107:108	9:1 115:116
Et 39	87	15:1	>30:1 111:112	13:1 119:120
^{n}Pr 41	87	15:1	>30:1 113:114	14:1 121:122
^{i}Pr 45	– [a]	–	– –	– –

a) Only starting material 45 isolated from reaction.

Table 10. The diastereoisomeric ratios 117+118:109+110, 109:110 and 117:118, and the overall yield in the reactions of Z-(C_5H_5)Fe(CO)-(PPh_3)(COCH=CHR) with isopropylidene iodide and diethylzinc.

In each case, small amounts of the trans-substituted cyclopropyl complexes were isolated. Since these had previously been synthesised non-stereoselectively (see table 8 p. 72), the diastereoisomeric ratio could be determined from the integrals of the α-protons in the ^{1}H n.m.r. spectra. The diastereoisomeric ratios for the cis-substituted cyclopropyl complexes were measured from the integrals of suitable resonances in the ^{1}H n.m.r. spectra (see Experimental). The major cis- and trans-isomers were assigned as RSR(SRS)-117 and RSS(SRR)-109 respectively, on the basis of the high-field shift of a resonance assigned to one of the gem-dimethyl substituents (vide supra).

The reaction was also performed on the complex 54, producing the tetra-methyl substituted cyclopropyl complex 123 (89%).



54 123

In the ^{1}H n.m.r. spectrum of 123, the resonances for the methyl substituents appear at δ 1.11, 1.07, 1.00 and 0.70, the

latter being due to the methyl substituent closest to, and shielded by, a phenyl ring of the triphenylphosphine ligand (vide supra).

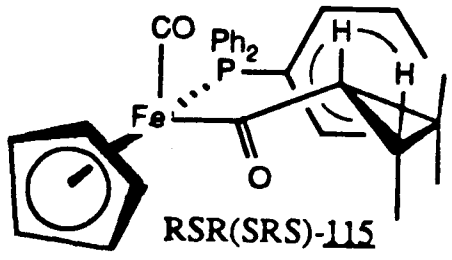
Discussion

We have demonstrated the generation of a novel carbenoid species from isopropylidene iodide, and have shown that its addition to Z-α,β-unsaturated iron acyl complexes occurs efficiently and with good stereoselectivity. The major diastereoisomeric product results from reaction at the re-re face of the olefinic bond, a result consistent with the previously described methylene addition reactions (see Section A). The explanation offered for the stereoselectivity of the previous reactions (see p. 55) will be equally valid in this instance. Similarly, the low reactivity and stereoselectivity on reaction with the corresponding unsubstituted and E-α,β-unsaturated complexes is consistent with the previous discussion.

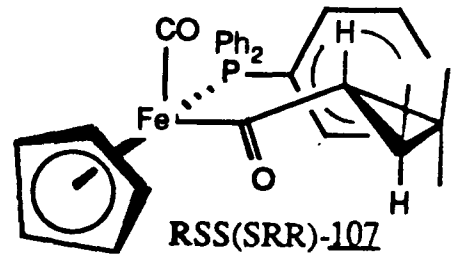
An unusual aspect of the reaction with the Z-α,β-unsaturated complexes is the isolation of small amounts (3-7%) of the trans-substituted cyclopropyl products. The stereoselective synthesis of one diastereoisomer (>30:1) discounts a mechanism by which olefinic bond isomerisation is followed by isopropylidene addition to the E-isomer, this addition being non-stereoselective (vide supra). An alternative mechanism could be a non-concerted, diastere facially selective addition of isopropylidene to the Z-isomer of the starting material, forming an intermediate species in which bond rotation can compete with ring closure. This type of mechanism has been invoked to account for the isolation of trans-substituted cyclopropyl diesters from the addition of arylchlorocarbenes to diethylmaleate.[91]

The stereochemistry of the major cis- and trans-products

from the reaction with Z-$(C_5H_5)Fe(CO)(PPh_3)(COCH{=}CHCH_3)$ 37 show that both are formed by addition to the re-re face of the olefinic bond.

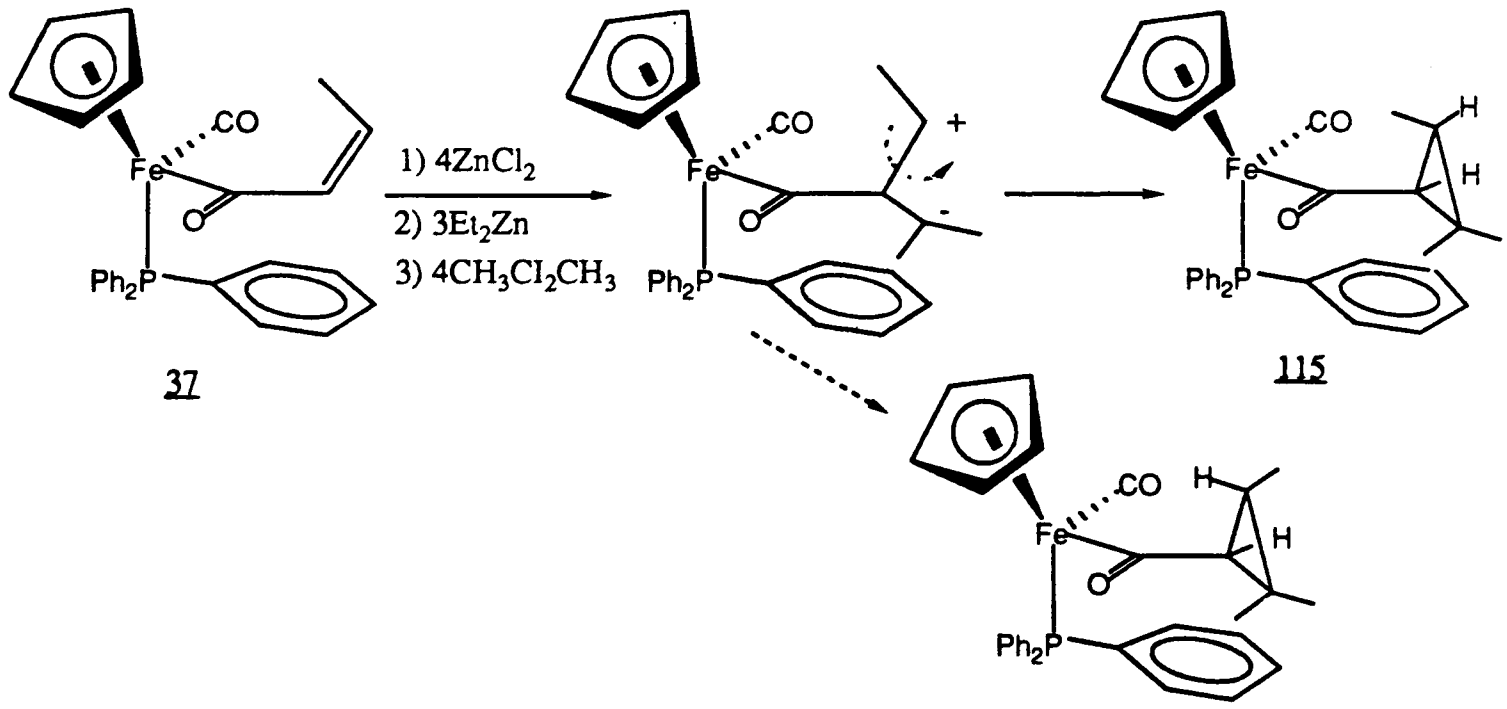


RSR(SRS)-115



RSS(SRR)-107

The stereochemistry at the α-carbon is the same for both 115 and 107 suggesting that initial bond formation occurs to the α-centre and that some type of intermediate is formed in which bond rotation can compete with ring closure. An idealised scheme for this mechanism is shown below although complete charge separation in the intermediate is unlikely.



37 115 107

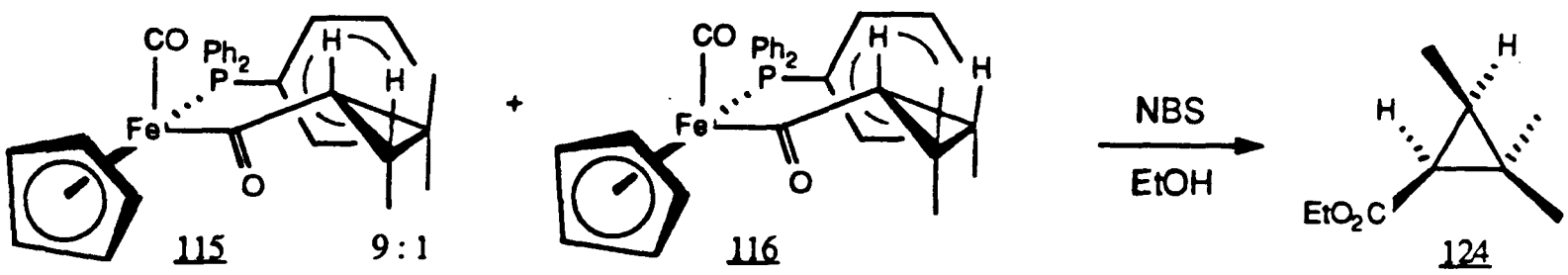
The minor cis-substituted cyclopropyl complex 116 arises from reaction at the si-si face of the olefinic band. The greater diastereoselectivity in the formation of the trans-substituted complexes (107:108 = >30:1), relative to the cis-substituted complexes (115:116 = 9:1) indicates that in reaction at the si-si face, bond rotation does not compete with ring closure to the same extent as on reaction at the re-re face.

No trans-substituted cyclopropyl complexes were produced on methylene addition to Z-α,β-unsaturated iron acyl complexes (see section A), indicating either concerted addition, or non-concerted addition in which bond rotation did not compete with ring closure. That bond rotation does occur on addition of isopropylidene indicates a slower rate of ring closure, possibly reflecting the greater bulk of the isopropylidene group.

In the following section the decomplexation of a diastereoisomeric mixture of the cis-methyl substituted cyclopropyl complexes 115 and 116 is described.

4. Decomplexation of cis-$(C_5H_5)Fe(CO)(PPh_3)(COCH\text{-}CHCH_3^{C(CH_3)_2})$ 115 and 116

A 9:1 mixture of the diastereoisomeric cis-substituted cyclopropyl complexes 115 and 116 was treated with N-bromosuccinimide in ethanol, as previously described (see p.63). The corresponding ester (±)-124 was isolated as a yellow oil (46%-unoptimised), no other cyclopropyl derivatives being seen.

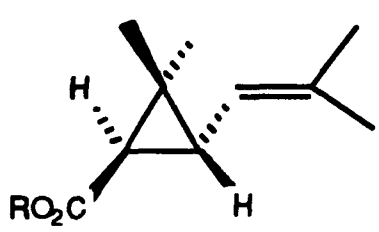


The ^1H n.m.r. spectrum of 124 in benzene-d_6 had resonances at δ 1.42 (COCH), 1.29 ($CHCH_3$), 1.29 (CCH_3), 0.90 ($CHCH_3$) and 0.87 (CCH_3). The coupling of the α-proton (COCH, J_{cis} 8.8 Hz) was consistent with the assigned cis-stereochemistry.[81] However, in the literature,[85] the cyclopropanecarboxylic ester with the same chemical shifts in the ^1H n.m.r. spectrum as those described above, has been reported as having trans-, and not cis-, stereochemistry. Subsequently (see p.97) we synthesised the corresponding trans-isomer and proved that the stereochemistry had been wrongly assigned in the literature.

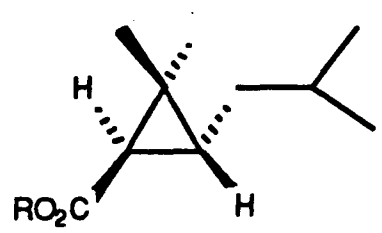
Hence, we have demonstrated that decomplexation of these cis-substituted cyclopropyl complexes occurs without epimerisation, and the corresponding cis-substituted cyclopropanecarboxylic esters with gem-dimethyl substituents can be synthesised efficiently and with good stereochemical control. The synthesis utilises the novel carbenoid generated from isopropylidene iodide, for which no literature precedent exists. In the following section the utilisation of this methodology in attempts to synthesise the acid components of some pyrethroid insecticides is discussed.

C. Attempted Syntheses of Pyrethroid Insecticide Precursors

The importance of gem-dimethyl substituents on the cyclopropyl ring of a pyrethroid insecticide to its overall biological activity was described previously (p. 69). A further important structural feature is an unsaturated substituent at the third ring carbon .[88] The 5-benzyl-3-furylmethyl ester of trans-(±)-2,2-dimethyl-3-(2,2-dimethylvinyl) -cyclopropanecarboxylic acid 104 is more than ten times as toxic to houseflies as the same ester of trans-(±)-2,2-dimethyl-3-(2-methylpropyl)-cyclopropane-carboxylic acid 125.[89]

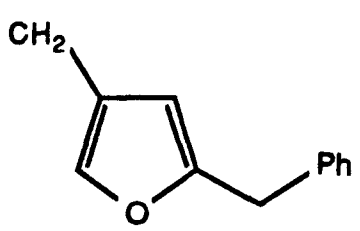


104



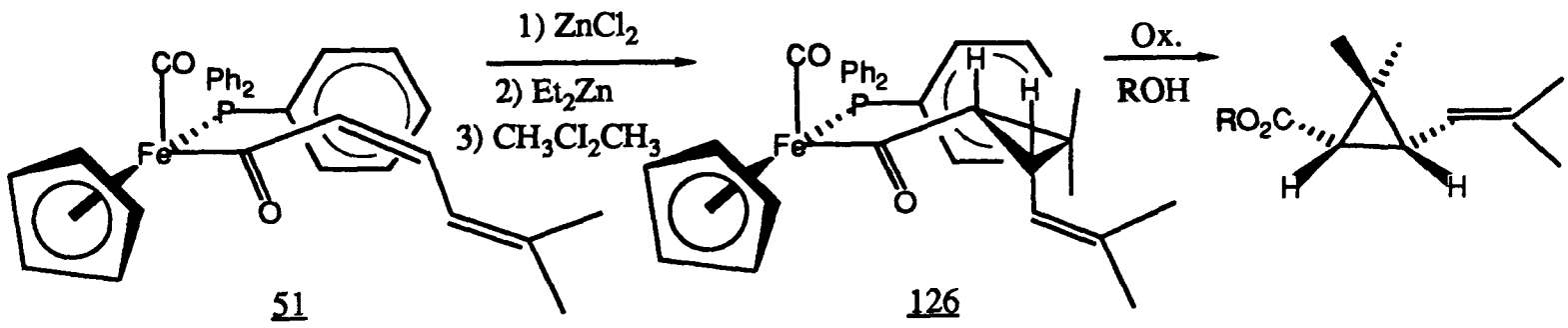
125

R=



The corresponding cis-isomer of 104 is slightly less toxic,[89] but in other cases, such as Permethrin 4 (see p. 2)[5], the cis-

isomers are more toxic. It was anticipated that by the use of Z-α,β-γ,δ-unsaturated iron acyl complexes, highly regioselective and stereoselective reactions with carbenoid species at the α,β-olefinic bond would allow the efficient syntheses of precursors to the pyrethroid insecticides.

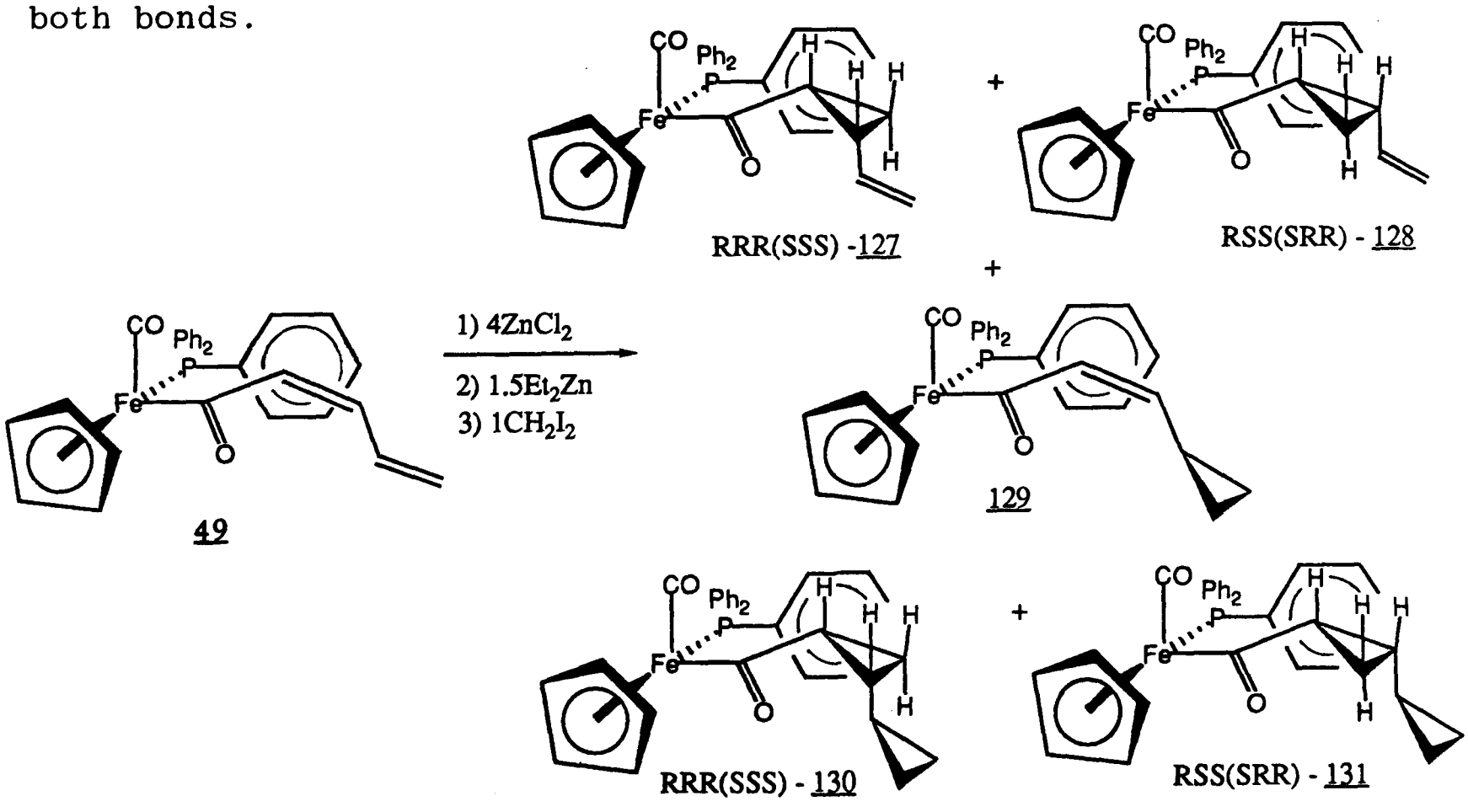


51 126

Initial studies were performed on a model system and this is outlined below.

1. Methylene Addition to Z-(C_5H_5)Fe(CO)(PPh_3)(COCH=CHCH=CH_2) 49

Complex 49 in toluene was treated with zinc dichloride, diethylzinc and methylene iodide as before. Methylene addition to the γ,δ-olefinic bond would give a single diastereoisomeric product, whilst addition to the α,β-olefinic bond could give two. Hence, a non-regioselective and non-stereoselective reaction would give five products, 130 and 131 arising from addition to both bonds.



RRR(SSS) -127 RSS(SRR) - 128

49 129

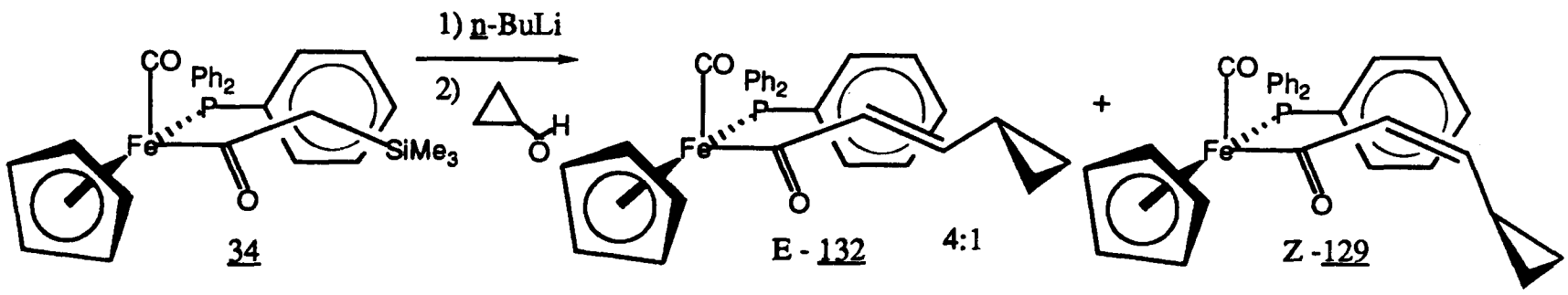
RRR(SSS) - 130 RSS(SRR) - 131

Only one equivalent of methylene iodide was added in an attempt to prevent over-reaction. On work up and chromatography two bands, each drying to orange solids, were eluted. The ^1H n.m.r. spectrum of the material from the second, larger band showed two sets of resonances, the larger being due to unreacted starting material 49. A smaller set of resonances were assigned to the product 129, including signals for vinylic protons at δ 6.62 and 3.93 (COCH=CH) and for cyclopropyl ring protons at δ 1.70, 0.62, 0.50 and 0.17. The ratio of 49:129 was approximately 2:1.

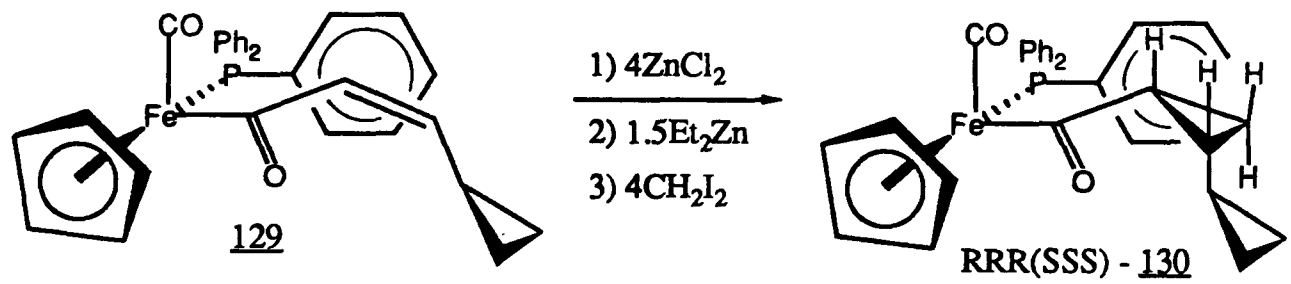
The ^1H n.m.r. spectrum of the product from the first band showed two sets of resonances, the smaller of which was assigned to the product 127. Vinylic signals at δ 5.75, 5.09 and 4.89 were consistent with this product assignment, as was the coupling pattern of the α-proton (COCH).[81] The product was assigned the stereochemistry RRR(SSS) by assuming preferential carbenoid addition at the re-re face of the olefinic bond (vide supra). The presence, or otherwise, of the minor diastereoisomer RSS(SRR)-128 could not be determined from the ^1H n.m.r. spectrum. The major series of resonances were assigned to the product 130, a multitude of high-field signals in the region δ 0.13-0.85 being consistent with this assignment. The stereochemistry was assigned as RRR(SSS) as above, and the presence, or otherwise, of the diastereoisomer RSS(SRR)-131 could not be determined. The ratio of 130:127 was 2:1 and the approximate distribution of starting material to products in the reaction was 49:129:130:127, 4:2:2:1.

The structural assignment of 129 was confirmed by its synthesis via an alternative route. By treatment of the trimethylsilyl complex 34 with base and cyclopropanecarboxaldehyde (obtained by Swern oxidation[92] of cyclopropyl carbinol), a 4:1 mixture of

the E- and Z-vinylic complexes, 132 and 129 respectively, was obtained, the isomers being separated chromatographically.



The ^{1}H n.m.r. spectrum of 129 was identical to that synthesised previously and isolated as a mixture with the starting material 49. Furthermore, treatment of 129 with zinc dichloride, diethylzinc and methylene iodide gave the product 130 (86%), identical by ^{1}H n.m.r. spectroscopy with that synthesised previously as a mixture with 127. The ^{1}H n.m.r. and ^{13}C n.m.r. spectra were consistent with the formation of a single diastereoisomer.



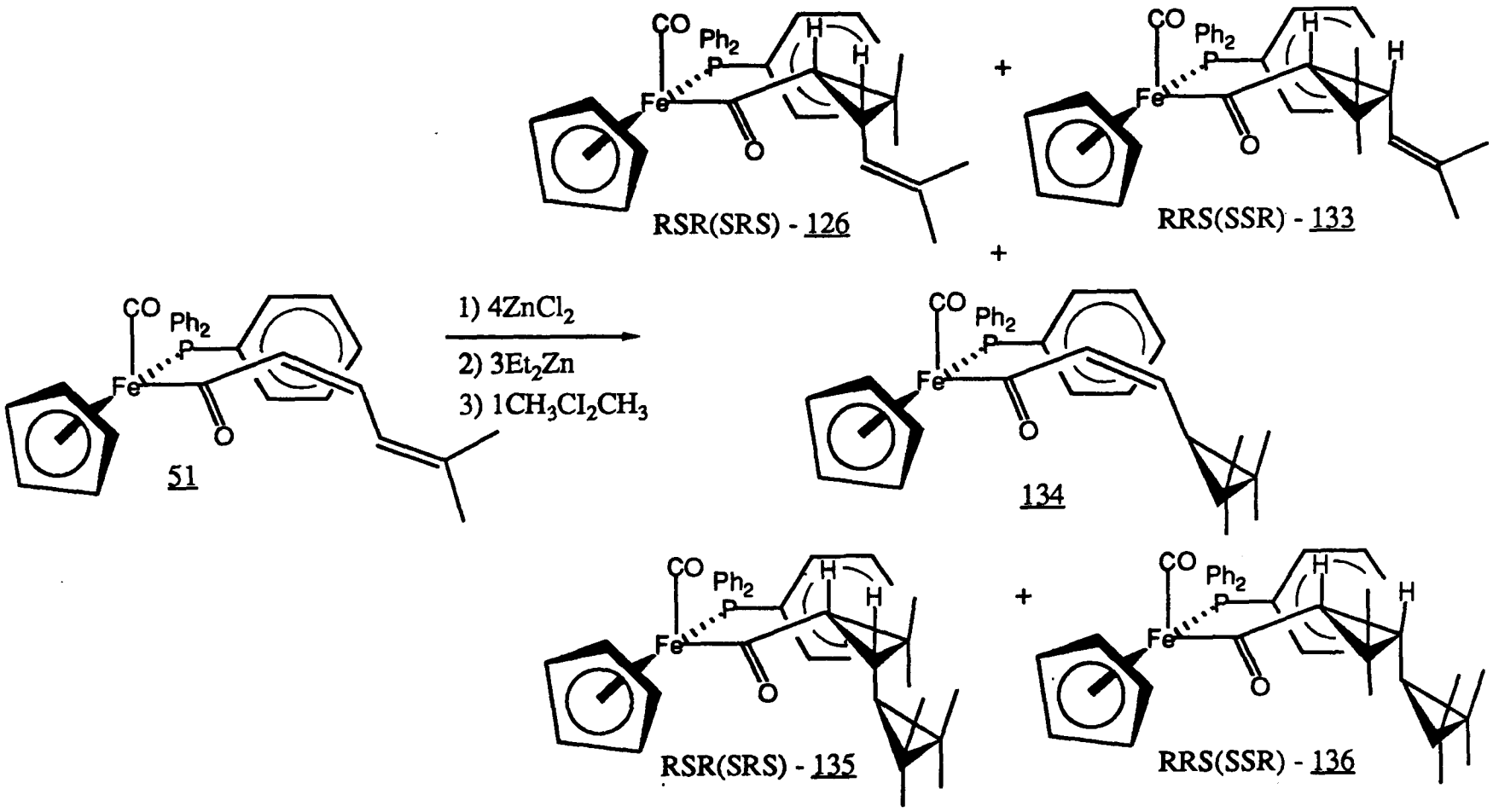
Treatment of 49 with excess methylene iodide also gave the product 130, apparently as a single diastereoisomer (82%).

The conclusion from these preliminary studies is that carbenoid addition to the α,β-γ,δ-unsaturated complex 49 occurs with low regioselecivity. In the following section the reaction is developed to examine the possible synthesis of pyrethroid insecticides.

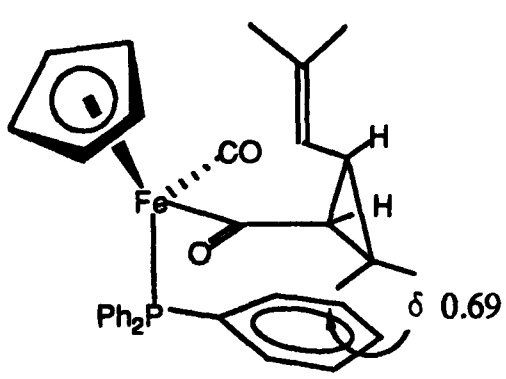
2. Isopropylidene Addition to Z-(C_5H_5)Fe(CO)(PPh_3)(COCH=CHCH=$C(CH_3)_2$) 51.

The Z-isomer of the γ-dimethylated α,β-γ,δ-unsaturated iron acyl complex 51 was treated with zinc dichloride, diethylzinc and

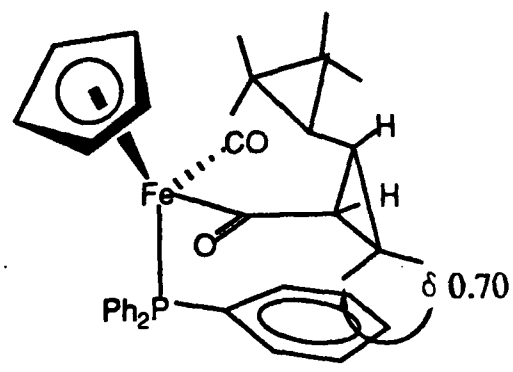
isopropylidene iodide (one equivalent). The reaction is stereochemically similar to that described in the preceding section and potentially five products might be formed.



After work up, chromatography gave four separate bands, the final one being identified by ^{1}H n.m.r. spectroscopy as unreacted starting material 51 (23%). The ^{1}H n.m.r. spectra of the remaining bands, and their assignments, are summarised in table 11. No products with trans-stereochemistry about the cyclopropane ring α- to the acyl group were detected. For the products 126 and 135, only a single diastereoisomer could be detected and the stereochemistry was assigned as RSR(SRS) by assuming reaction to occur at the re-re face of the olefinic bond. Consistent with this assignment were the high-field shifts in the ^{1}H n.m.r. spectra of the gem-dimethyl substituents on the ring α- to the acyl group (vide supra).



RSR(SRS) - 126



RSR(SRS) - 135

	Product[a]	^{1}H n.m.r.[b]
Band 1	135[c,d] (10%)	2.89(COCH, J_{cis} 9 Hz), 1.10, 1.04, 0.91, 0.85, 0.70 ($6CH_3$), 0.75 (CH), 0.56 (CH)
Band 2	126[c,d,e] (7%)	5.28 ($C\underline{H}$=$C(CH_3)_2$), 2.98 (COCH, J_{cis} 8.9 Hz) 1.74, 1.67 (CH=$C(C\underline{H}_3)_2$), 0.96, 0.69 ($C(CH_3)_2$)
Band 3	134 (53%)	6.58 (COCH, J_{cis} 11.3 Hz), 4.39 (COCH=C$\underline{H}$). 1.45 ($C\underline{H}C(CH_3)_2$), 1.05, 0.98, 0.97, 0.96 ($4CH_3$)

a) Assigned from ^{1}H n.m.r. spectrum and molecular ion in mass spectrum.

b) Chemical shift (δ).

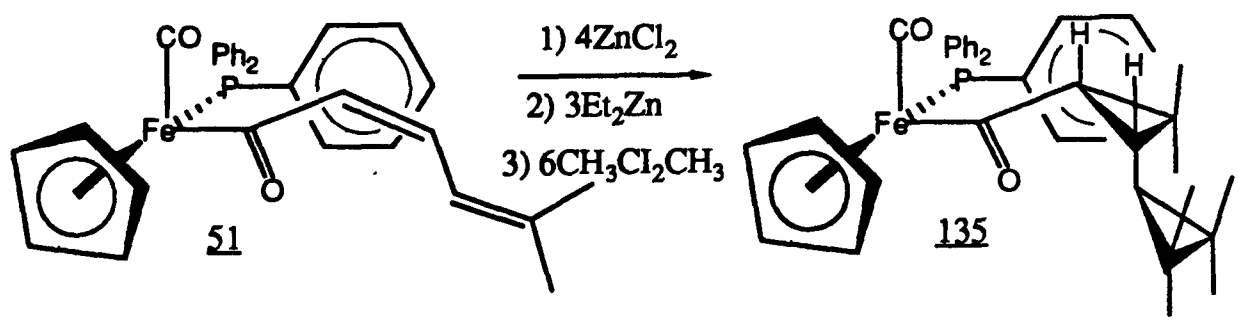
c) Reaction assumed to occur selectively at re-re face of α,β-olefinic bond.

d) Resonances for minor diastereoisomer not seen.

e) Could not be fully purified.

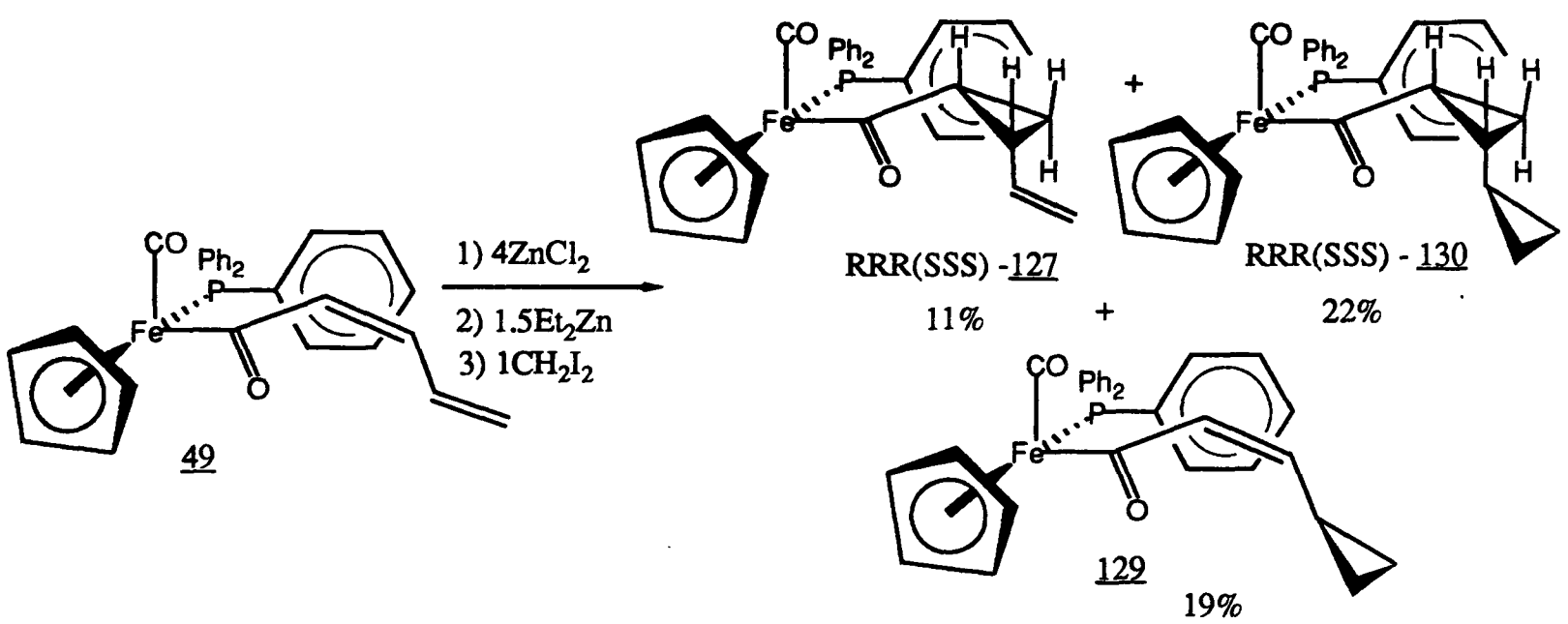
Table 11. The ^{1}H n.m.r. data of the acyl ligands of the products isolated from the reaction between Z-$(C_5H_5)Fe(CO)(PPh_3)$(COCH=CH-CH=$C(CH_3)_2$) 51, diethylzinc and isopropylidene iodide.

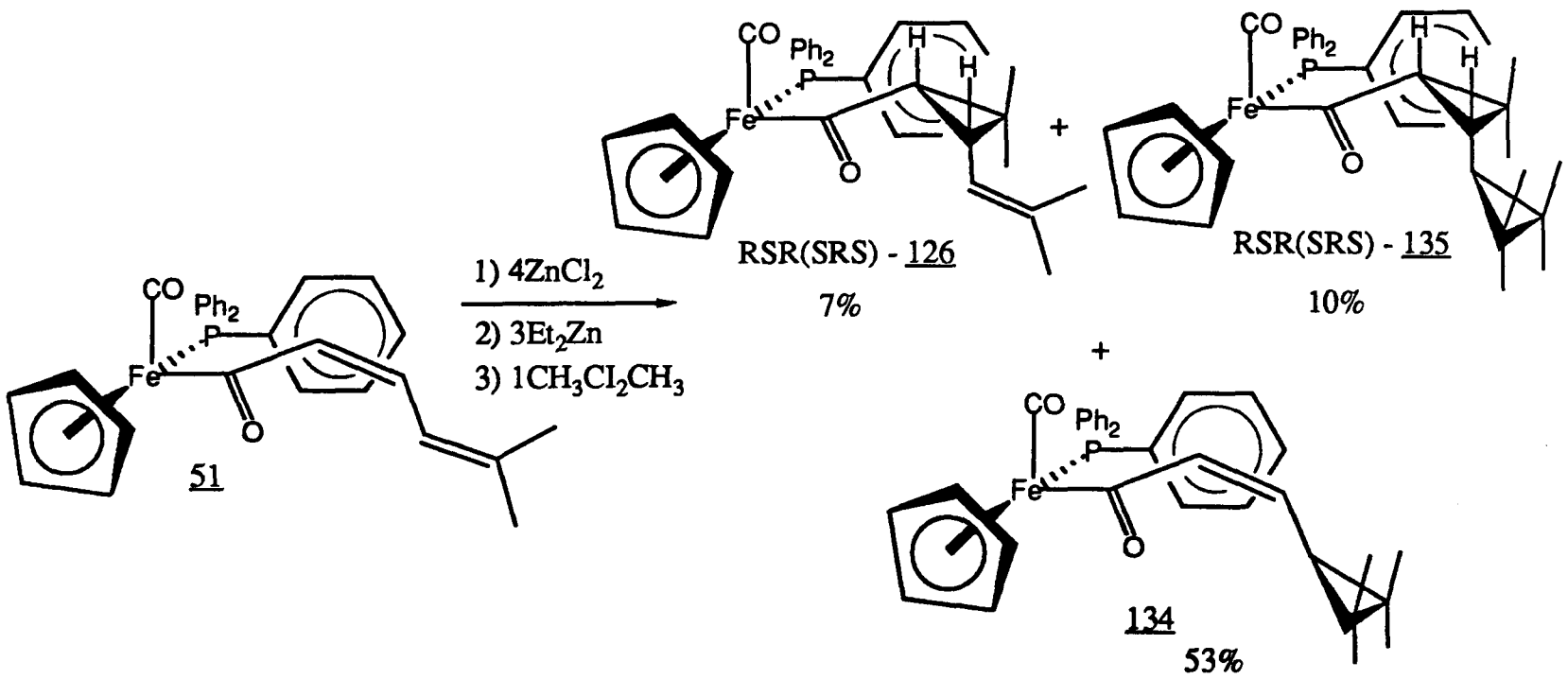
Treatment of 51 with excess isopropylidene iodide gave the product 135 (77%), the ^{1}H n.m.r. and ^{13}C n.m.r. spectra of which indicated a single diastereoisomer, the same as that synthesised above.



Discussion

The product distribution in the reactions of 49 with the methylene iodide derived carbenoid (calculated from the ^1H n.m.r. spectra) and of 51 with the isopropylidene iodide derived carbenoid are summarised below.





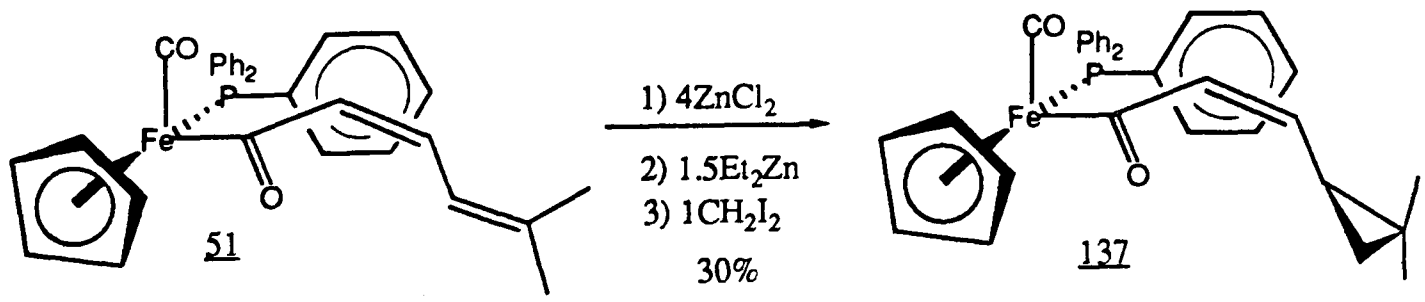
In each case, reaction occurs regioselectively at the γ,δ-olefinic bond. Presumably this bond is more sterically accessible, being distant from the iron chiral auxiliary. For the bulky isopropylidene this effect will be greater, favouring the formation of 134. The results confirm the previous observation that carbene transfer need not necessarily occur via prior coordination of the

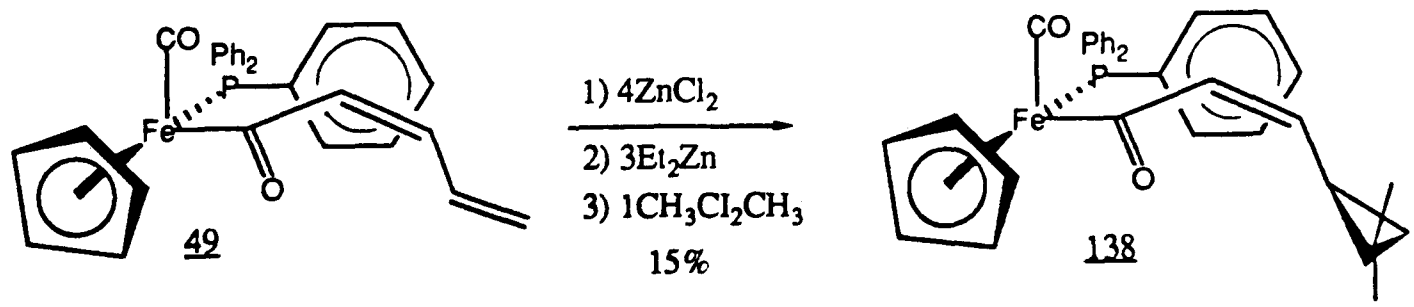
carbenoid species to the acyl oxygen (p. 56), since this would favour attack at the α,β-olefinic bond. An additional factor favouring attack on the γ,δ-bond in 51 will be its greater electron density and hence more rapid reaction with the electrophilic carbenoid species.

The preparation of pyrethroid insecticide precursors via this synthetic route was unsuccessful due to reaction occurring regioselectively at the wrong bond. However, it was of interest to determine the extent of stereochemical influence over the γ,δ-olefinic bond exerted by the iron chiral auxiliary, and this is described below.

3. Synthesis of Z-(C_5H_5)Fe(CO)(PPh_3)(COCH=CHCH-C(CH_3)$_2$)

If the iron chiral auxiliary exerts a stereochemical influence over the γ,δ-olefinic bond then the reaction between complex 49 and the isopropylidene species, and the reaction between complex 51 and the methylene species should give diastereoisomeric products on reaction at the γ,δ-olefinic bond.





The reaction was performed under standard conditions (vide supra) on 51. One major product band was isolated from the reaction mixture and identified by ^{1}H n.m.r. spectroscopy and mass spectrometry as 137 (30%) (see table 12), the stereochemistry being arbitrarily assigned. The reaction with 49 gave several products, as seen by TLC, presumably due to reaction occurring at either or both olefinic bonds. The product band with identical polarity to 137 was isolated and identified as 138 (15%) (see table 12).

Product	COCHCH	$CHCH_2$	$C(CH_3)_2$
137	6.63, 4.33	1.82, 0.65, 0.24	1.05, 0.92
138	6.58, 4.24	1.78, 0.54, 0.21	1.04, 0.97

Table 12. The chemical shifts (δ) of the acyl ligands in the ^{1}H n.m.r. spectrum of 137 and 138.

The stereochemistry of 137 and 138 was necessarily arbitrarily assigned. The ^{1}H n.m.r. spectrum of 137 showed a minor set of resonances corresponding to 138, the ratio of 137:138 being 5:1. Similarly the ^{1}H n.m.r. spectrum of 138 showed the presence of 137, the ratio 138:137 being 5:1. These two experiments demonstrate that the iron chiral auxiliary does influence the stereochemical properties of the γ,δ-olefinic bond although the nature of this influence cannot be determined since the stereochemistry of the products is unknown.

All of the reactions described previously have consisted of the addition of symmetrical carbenoid species to the olefinic bonds of α,β-unsaturated iron acyl complexes. Good stereochemical control over the formation of up to two new chiral centres has been demonstrated. In the final section the reactions of these iron acyl complexes with a non-symmetrical carbenoid species are described in which up to three new chiral centres are formed.

D. Ethylidene Addition Reactions

Benzylidene [70d] and ethylidene[70b] iodides have been shown to react rapidly with olefinic bonds, in the presence of diethylzinc, to give the corresponding cyclopropyl derivatives.

In the preceding sections we have demonstrated efficient and stereoselective addition of symmetrical alkylidene species to Z-α,β-unsaturated iron acyl complexes, the stereochemistry of up to two new chiral centres being controlled. It was anticipated that on reaction with the non-symmetrical ethylidene species, the cis/trans alignment of the methyl group relative to the iron moiety would be influenced by the iron chiral auxiliary itself, resulting in stereochemical control over a third chiral centre.

1. Preparation of Ethylidene Iodide.

According to the literature procedure,[93] acetaldehyde was added dropwise to hydrazine hydrate at 0°C and stirred. The resulting hydrazone 139 was treated with iodine and, after work up, ethylidene iodide was isolated in 31% overall yield.

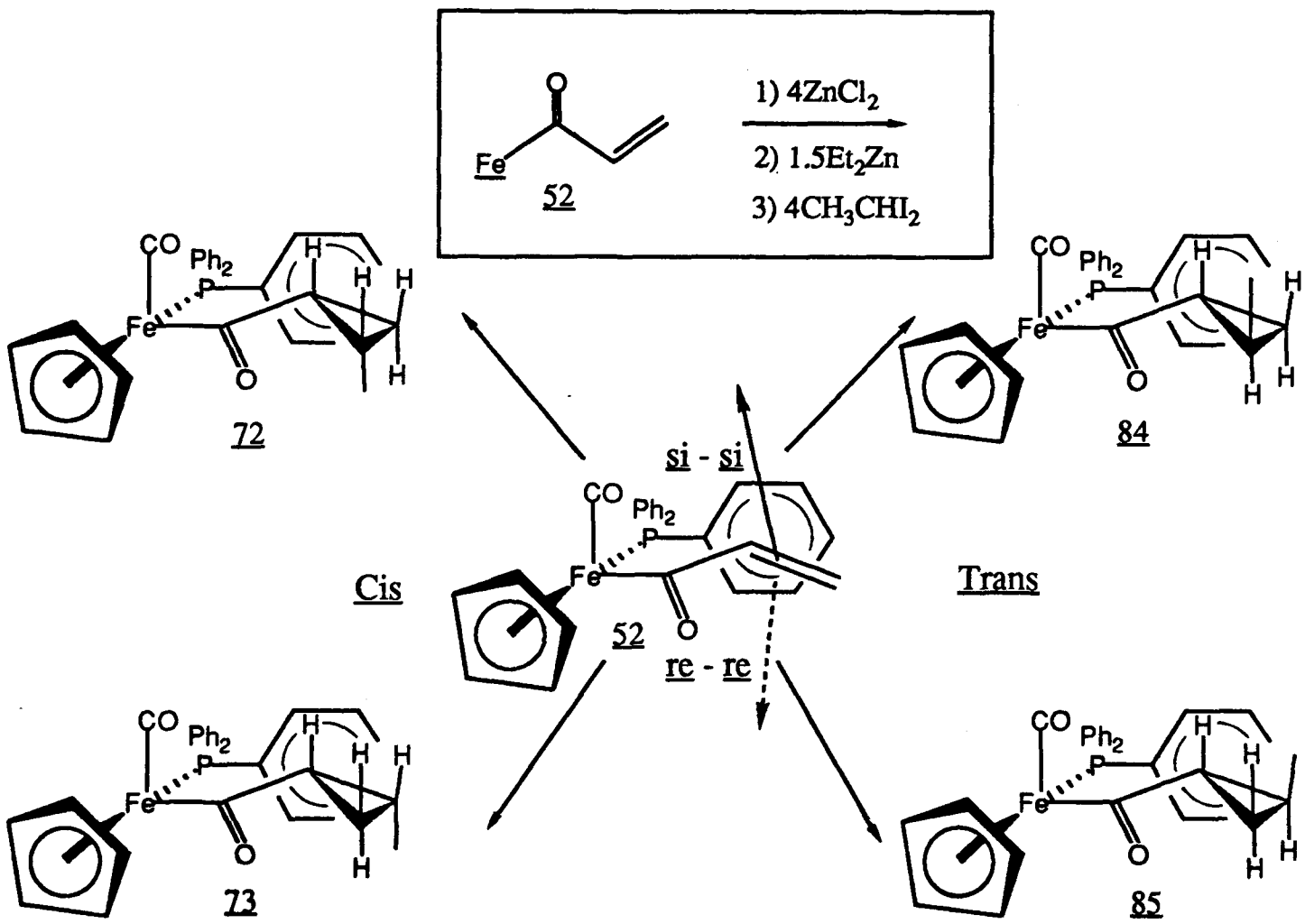
139

2. Addition to $(C_5H_5)Fe(CO)(PPh_3)(COCH=CH_2)$ 52 and $(C_5H_5)Fe(CO)(PPh_3)(COCH=C(CH_3)_2)$ 54

To determine the extent to which the iron chiral auxiliary might control the cis/trans (methyl to iron) stereochemistry of the ethylidene group on addition to α,β-unsaturated iron acyl complexes, reactions with the complexes 52 and 54 were studied initially. In each complex the β-carbon of the unsaturated acyl ligand is symmetrically substituted, and thus the stereochemistry

of the new centre will be determined solely by interaction with the chiral auxiliary.

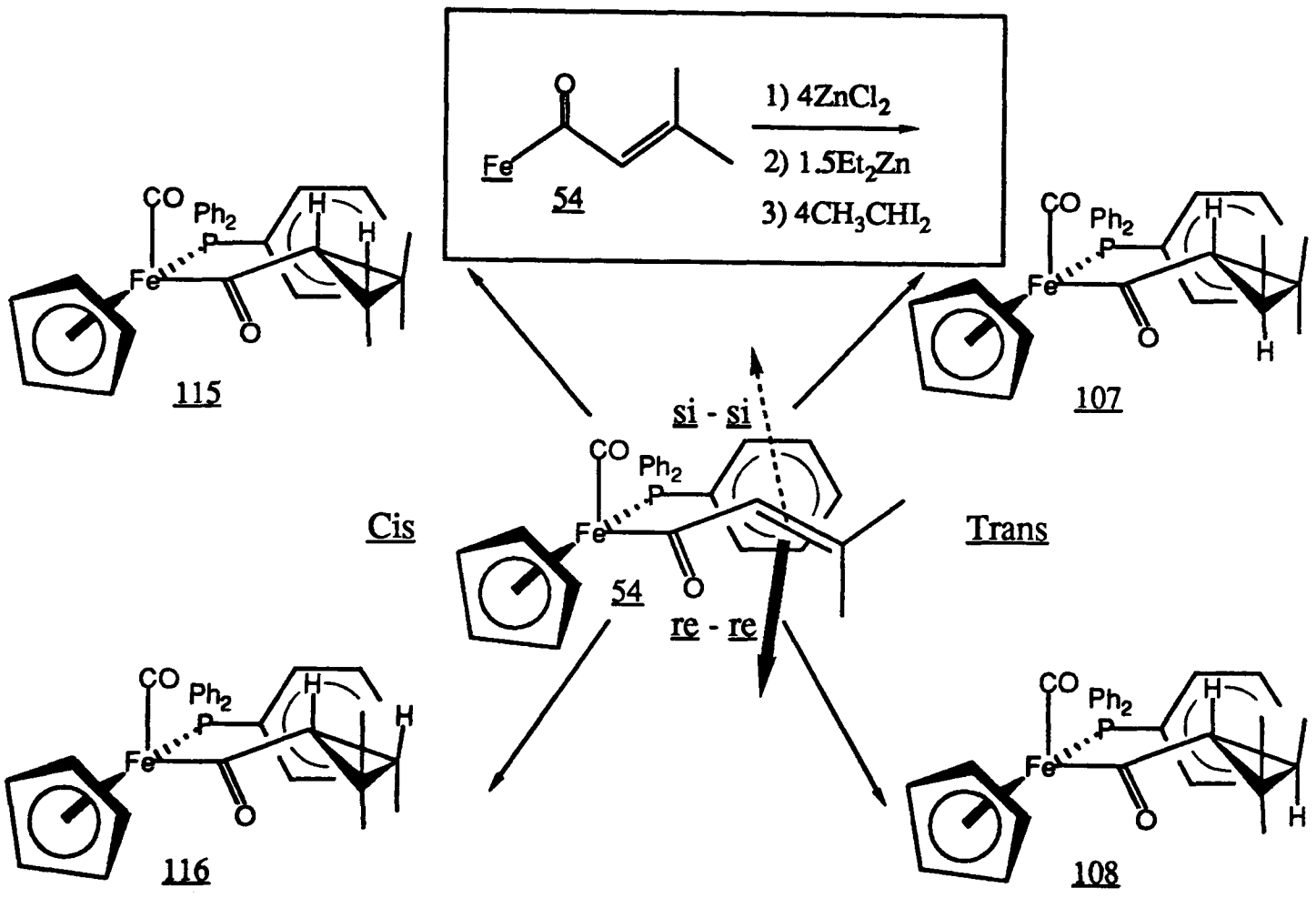
A solution of 52 in toluene was treated with zinc dichloride, diethylzinc and ethylidene iodide and stirred for two hours. After work up, chromatography gave three bands each drying to an orange solid. The material from the final band was identified as unreacted starting material 52 (23%). The product from the first band consisted of a 3:1 mixture of the known cis-substituted cyclopropyl complexes 72:73 (7%), and that from the second band of a 2:1 mixture of the corresponding known trans-isomers 84:85 (64%).



The results show that carbene addition to 52 occurs with minimal diastereofacial selectivity, consistent with previous results (see p.70). The predominance of the trans-substituted cyclopropyl complexes indicates that the chiral auxiliary directs the approach of the carbenoid species such that the methyl group

lies preferentially trans to the iron centre, steric factors presumably favouring this alignment.

The reaction was repeated with the complex 54, going to completion in under fifteen minutes. After work up and chromatography two bands, drying to orange solids, were isolated. The ^1H n.m.r. spectrum of the product from the minor, first band showed it to be an 8:1 mixture of the known diastereoisomeric cis-substituted cyclopropyl complexes 116 and 115 (7%) (see p. 73). The ^1H n.m.r. spectrum of the product from the major, second band showed it to be an 8:1 mixture of the known trans-substituted cyclopropyl complexes 108 and 107 (80%)(see p.71 and p.75).



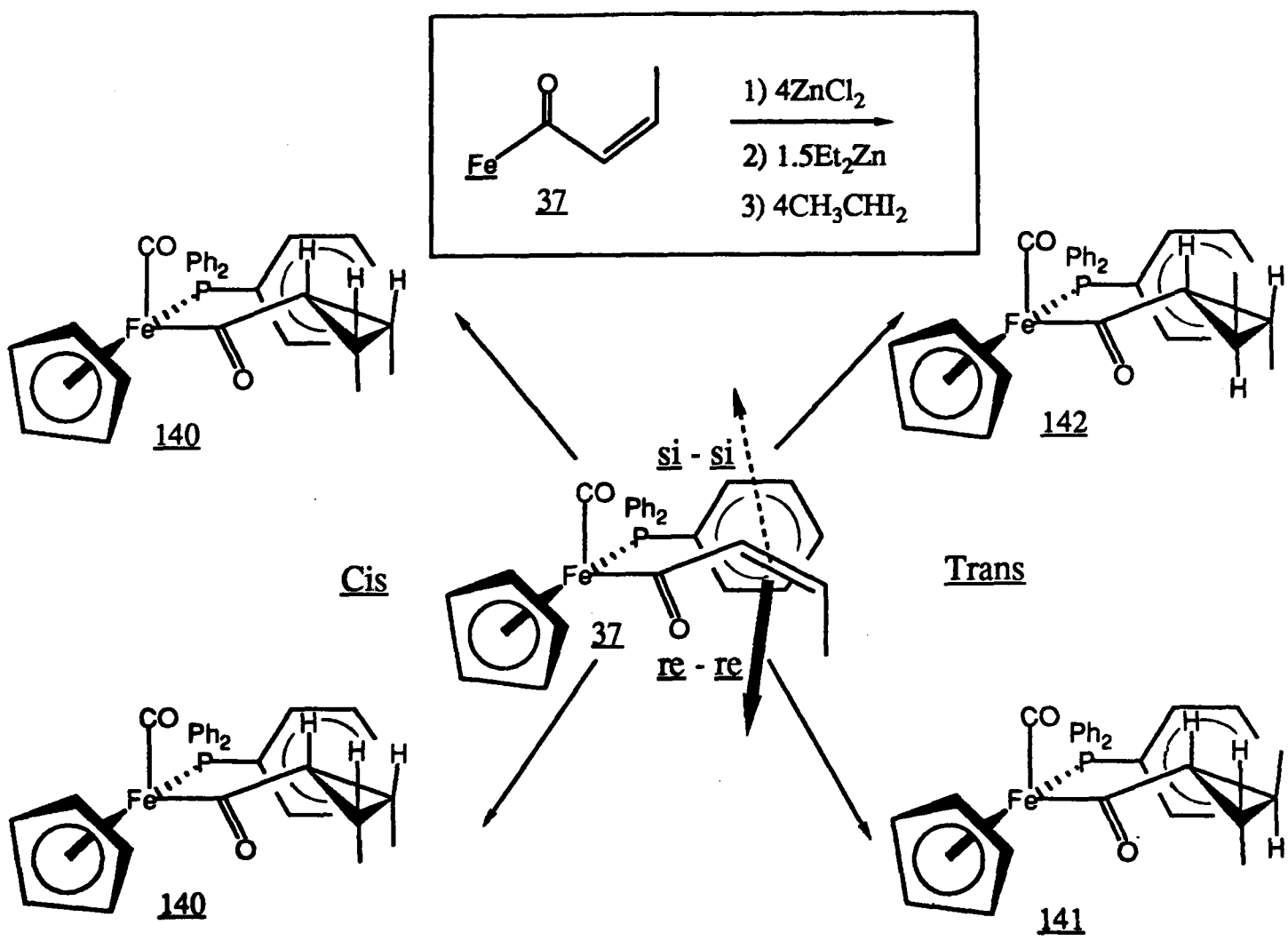
The ratio of trans:cis products (10:1) shows again that the methyl group of the ethylidene species minimises steric interactions when aligned trans to the iron moiety. The favourable reaction at the re-re face of 54 is consistent with previous results (vide supra). This reaction complements that described previously (p.73), in which isopropylidene addition to Z-(C_5H_5)Fe(CO)(PPh_3)($COCH{=}CHCH_3$) 37 gave 115 and 107 as the major cis-and

trans-substituted cyclopropyl complexes respectively. In the reaction described above the diastereoselectivity is reversed, and 116 and 108 are the major cis-and trans-isomers respectively.

These reactions demonstrate that the methyl group of the ethylidene species preferentially aligns itself trans to the iron chiral auxiliary, the latter therefore controlling the stereochemistry at this chiral centre. In the following section, ethylidene additions to Z-α,β-unsaturated iron acyl complexes are described.

3. Addition to Z-(C_5H_5)Fe(CO)(PPh_3)(COCH=CHR).

Complex 37 was treated with zinc dichloride, diethylzinc and ethylidene iodide under standard conditions (vide supra), the reaction going to completion in under fifteen minutes. In this reaction only three diastereoisomeric products can be synthesised since ethylidene addition with the methyl group aligned cis to the iron will give the product 140, whichever face of the olefinic bond reacts.



Work up and chromatography gave one minor and one major orange band, each drying to an orange solid. From the ^{1}H n.m.r. spectra (table 13) the product from the first band was assigned as 140 (5%), and that from the second band as a diastereoisomeric mixture of 141 and 142 (90%).

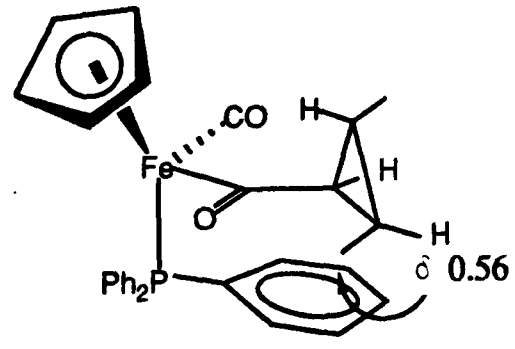
Product	COCH(J/Hz)[a]	CHCH	CH_3,CH_3–
140	2.96(8.5, 8.5)	1.09-0.97	1.01, 0.56
141	2.62(8.4, 4.3)	1.00-0.80	1.05, 0.85
142	2.68(8.5, 4.6)	—[b]	0.95, 0.56

a) Coupling constants to ring protons in parenthesis.

b) Remaining resonances obscured by those of 141.

Table 13. The chemical shifts (δ) of the acyl ligands in the ^{1}H n.m.r. spectra of 140, 141 and 142.

The coupling constants of the α-protons (COCH) for 141 and 142 confirm the assigned cis/trans stereochemistry.[81] The minor diastereoisomer was assigned as 142 on the basis of the high field shift of one of the methyl doublets in the ^{1}H n.m.r. spectrum (vide supra), and the ratio of 141:142 was 9:1.

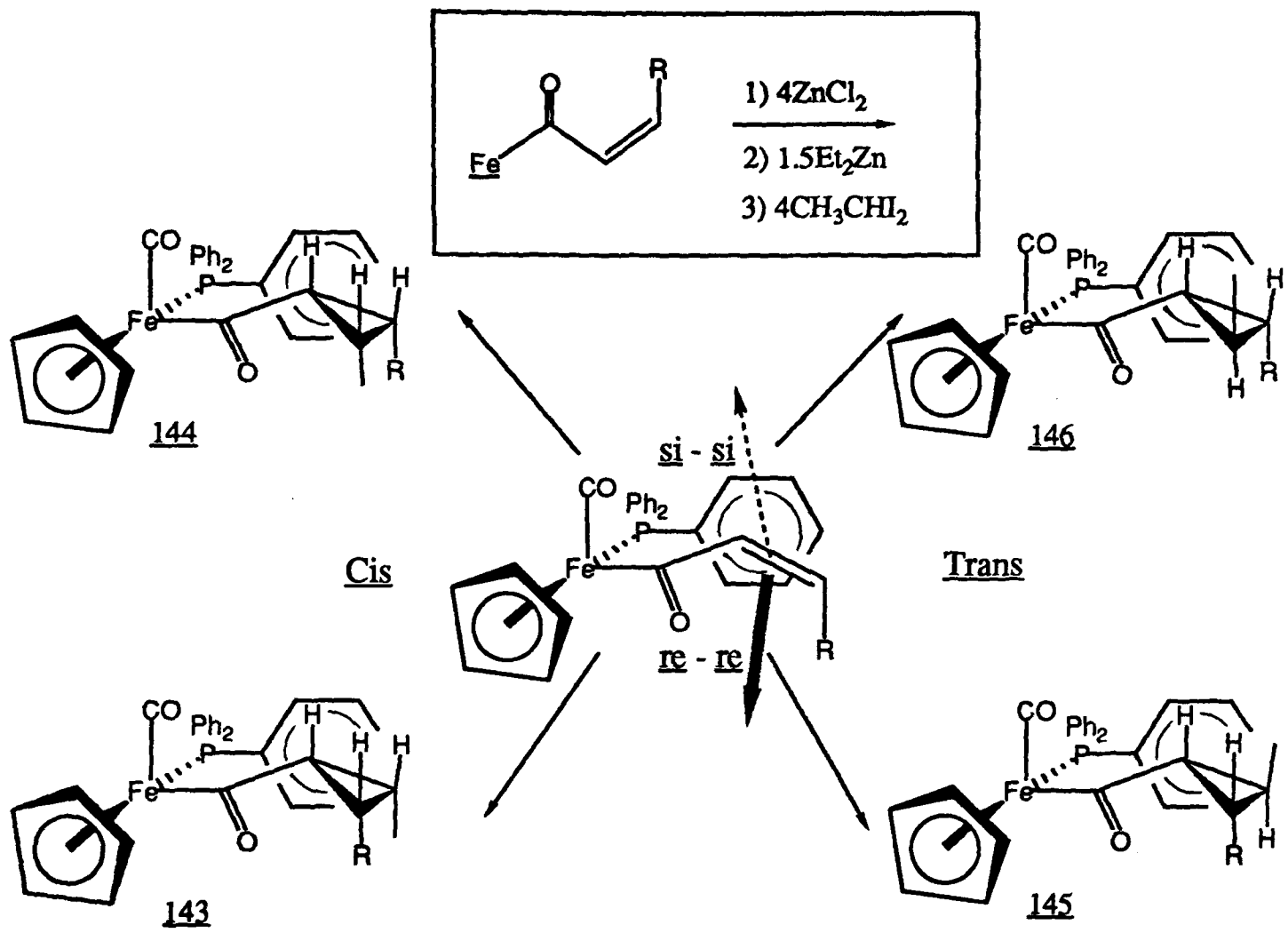


142

Similarly, the coupling constants of the α-protons (COCH) for 140, and the high-field resonance of one of the methyl substituents confirms the assigned stereochemistry. The ratio of 141 and 142:140 was 19:1 reflecting the methyl group from the carbenoid species lying trans to both the iron moiety and the

methyl substituent on the original olefinic bond.

The reaction was repeated on other Z-α,β-unsaturated iron acyl complexes and the results are summarised in table 14.



R	Yield %	Ratio Trans:Cis	Ratio Cis 143:144		Ratio Trans 145:146	
Me 37	95	19:1	—[a]	140	9:1	141:142
^{n}Pr 41	87	28:1	10:1[b]	147:148	12:1	149:150
^{n}Bu 43	86	21:1	10:1	151:152	15:1	153:154
^{i}Pr 45	95	—[c]	—[c]		28:1	155:156

a) Only one diastereoisomeric product (vide supra).

b) Ratio based on integral of overlapping resonances for the α-protons(COCH).

c) No cis-isomers formed.

Table 14. The diastereoisomeric ratios 145+146:143+144, 145:146 and 143:144 and the overall yields in the reactions of Z-(C_5H_5)Fe-(CO)(PPh_3)(COCH=CHR) with ethylidene iodide and diethylzinc.

After chromatographic separation of the cis/trans products, the diastereoisomeric ratio within each was measured from the ^1H n.m.r. spectrum. The cis and trans-stereochemistries were assigned on the basis of the coupling constants of the α-protons (COCH),[81] the stereochemistries in each on the basis of previous results.

Crystallisation of the 28:1 diastereoisomeric mixture of 155 and 156 gave red crystals of the former as a single diastereoisomer. An X-ray crystal structure analysis of 155 was undertaken[94] (see Appendix 1), and the structure solution consisted of two chemically identical but crystallographically distinguishable molecules which are shown in figure 11. The structure with the R-configuration at iron is shown in figures 12 (with selected X-ray data) and 13.

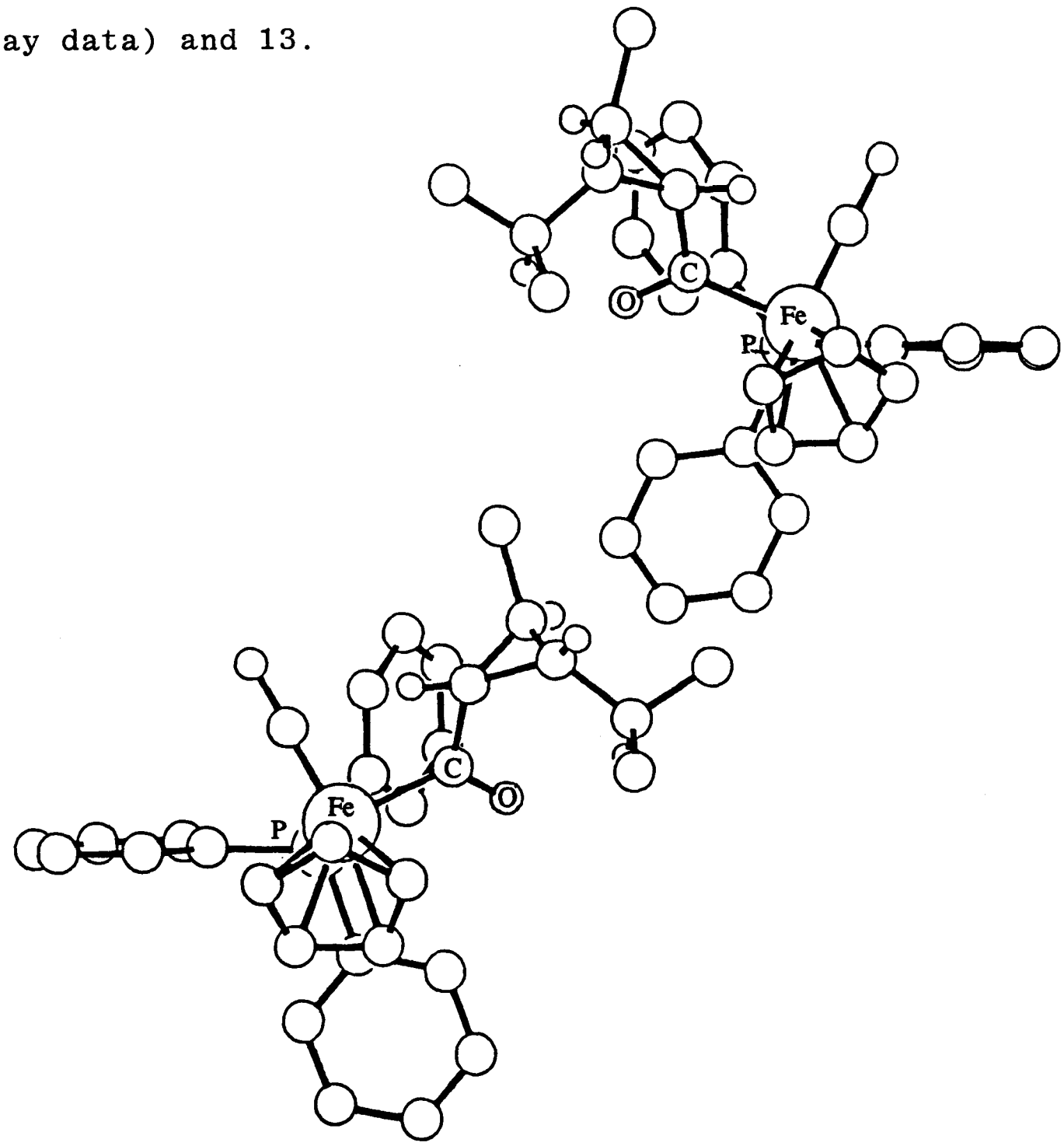
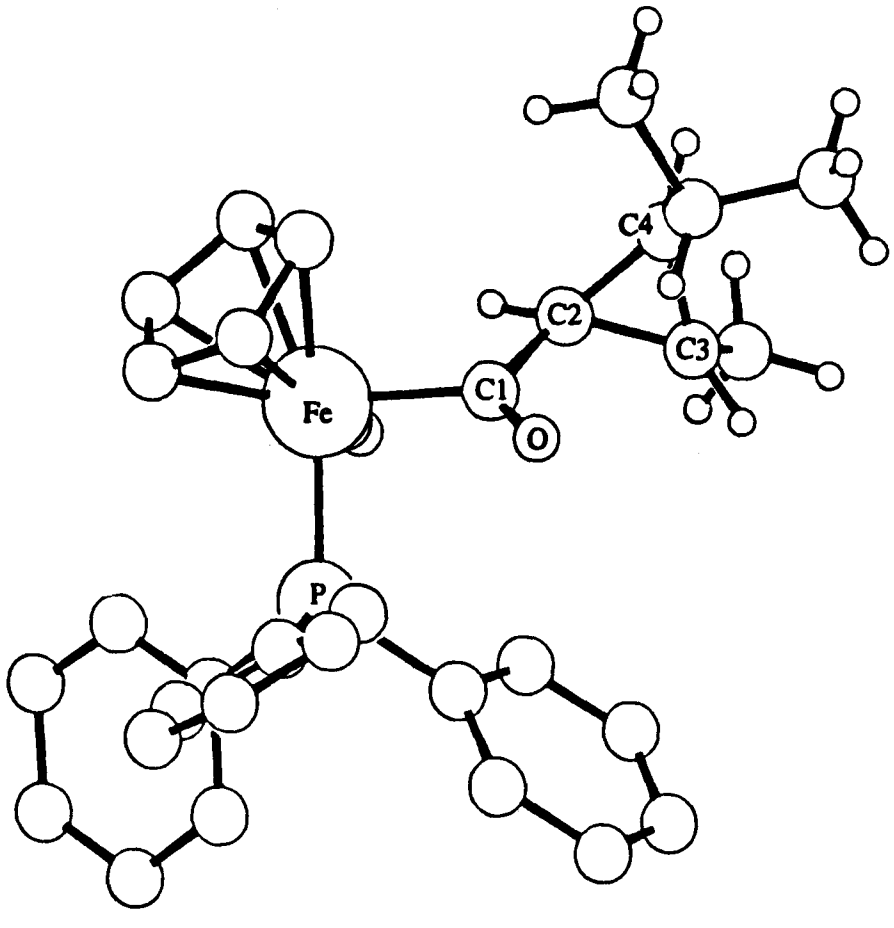


Figure 11. The X-ray crystal structure solution for RRSS(SSRR)-$(C_5H_5)Fe(CO)(PPh_3)(COCH(CH(CH_3)_2)-CHCH_3)$ 155. Selected protons are removed for clarity.



Fe-C1 1.976 Fe-P 2.187 C1-O 1.220 C1-C2 1.499

P-Fe-C1 92.42 Fe-C1-O 123.05 O-C1-Fe-P -48.30

O-C1-C2-C4 -31.33 O-C1-C2-C3 37.35

Figure 12. X-ray crystal structure and selected bond lengths (Å), angles and torsional angles (°) for RRSS-$(C_5H_5)Fe(CO)(PPh_3)$ $(COCH(CH_3)_2-CHCH_3)$ 155. Selected protons are removed for clarity.

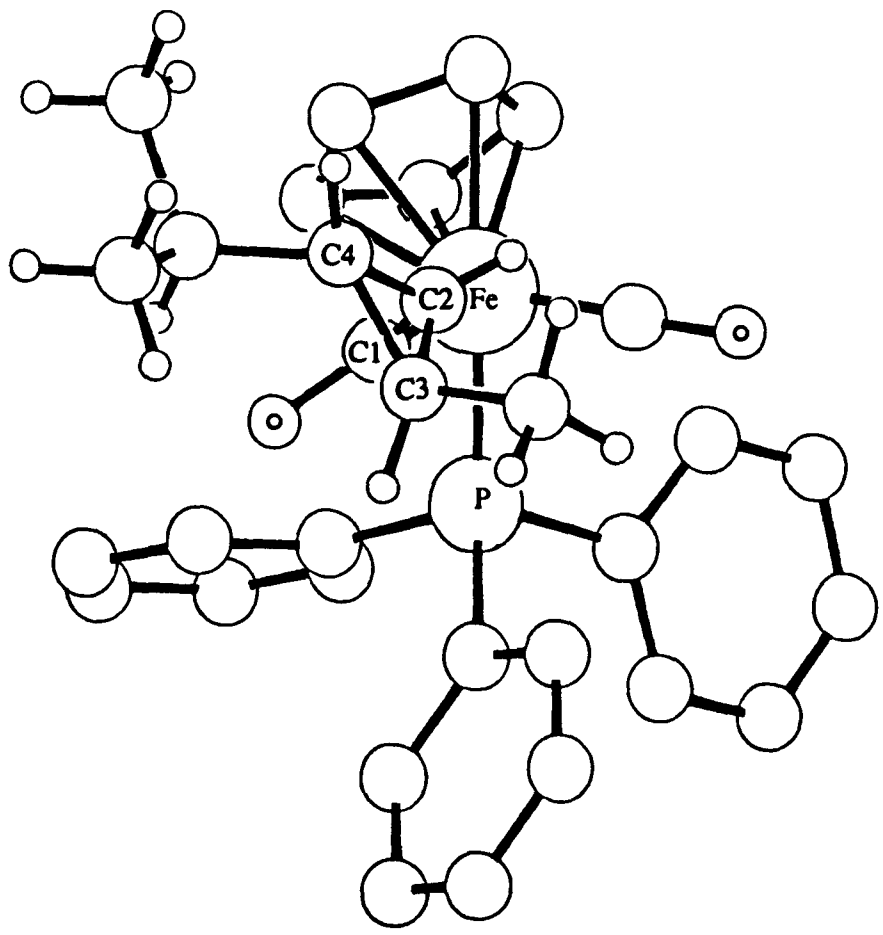


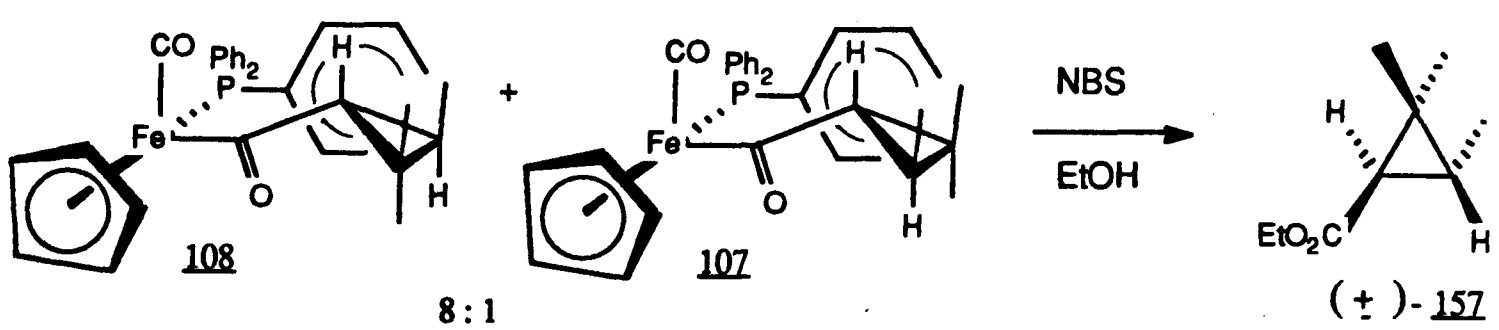
Figure 13. X-ray crystal structure for RRSS-$(C_5H_5)Fe(CO)(PPh_3)$ $(COCH(CH_3)_2-CHCH_3)$ 155. (View approximately along C2-Fe). Selected protons are removed for clarity.

The X-ray crystal structure confirms that the methyl group from the ethylidene species is aligned *trans* to the iron moiety and the isopropyl substituent in the product 155, thus minimising the steric interactions. The X-ray crystal structure also shows that ethylidene addition occurs to the re-re face of the olefinic bond in R-45. The favourable reaction of carbenoid species at the re-re face of olefinic bonds was assumed previously (p. 46), based on the high-field shift of the methyl substituent in RSR(SRS)-73, relative to that in RRS(SRR)-72. This effect was thought to arise from shielding of the methyl group in 73 by a proximate phenyl ring. Hence the X-ray crystal structure for 155 indicates that stereochemistries of the products described throughout this chapter have been correctly assigned.

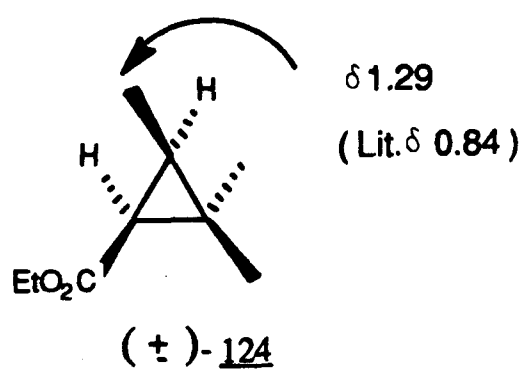
We have demonstrated that in addition of ethylidene to α,β-unsaturated iron acyl species, the iron chiral auxiliary can exert good stereochemical control over up to three new chiral centres. The decomplexation of the products is described in the following section.

4. Decomplexation of $(C_5H_5)Fe(CO)(PPh_3)(COCH(CRR')CHCH_3)$

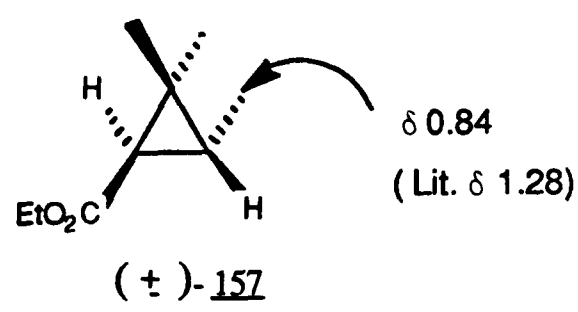
An 8:1 mixture of the diastereoisomeric *trans*-substituted cyclopropyl complexes 108:107 were treated with N-bromosuccinimide in ethanol as described previously (see p. 63). The corresponding ester (±)-157 was isolated as a yellow oil (39% -unoptimised), no other cyclopropyl derivatives being observed.



The ^{1}H n.m.r. spectrum of 157 in benzene-d_6 showed resonances at δ 1.50 ($C\underline{H}CH_3$), 1.30 (CCH_3), 1.16 (COCH), 0.88 (CCH_3) and 0.84 ($CHC\underline{H}_3$). The coupling of the α-proton (COCH, J_{trans} 5.4 Hz) was consistent with the assigned trans-stereochemistry. However, in the literature,[85] the cyclopropanecarboxylic ester with the same chemical shifts in the ^{1}H n.m.r. spectrum as those described above has been reported as having cis-, not trans-, stereochemistry. The coupling constants measured by us of the α-protons (COCH) for the esters 124, synthesised previously (p. 79), and 157 of 8.8 Hz and 5.4 Hz respectively indicated that the cis/trans isomers had been wrongly assigned in the literature[85] and that ours was the correct stereochemical assignment. Further evidence for this is provided by the relative chemical shifts of the methyl substituents ($CHC\underline{H}_3$) for 124 and 157 in the ^{1}H n.m.r. spectra. Wharton[95] reported that for methyl substituted cyclopropanecarboxylic esters, methyl groups cis to the ester are always deshielded relative to those trans to the ester, in the ^{1}H n.m.r. spectrum, due to differential solvation of the methyl groups by benzene. Our stereochemical assignments of cis-124 and trans-157 are consistent with this report, whilst the literature[85] assignment is contradictory.

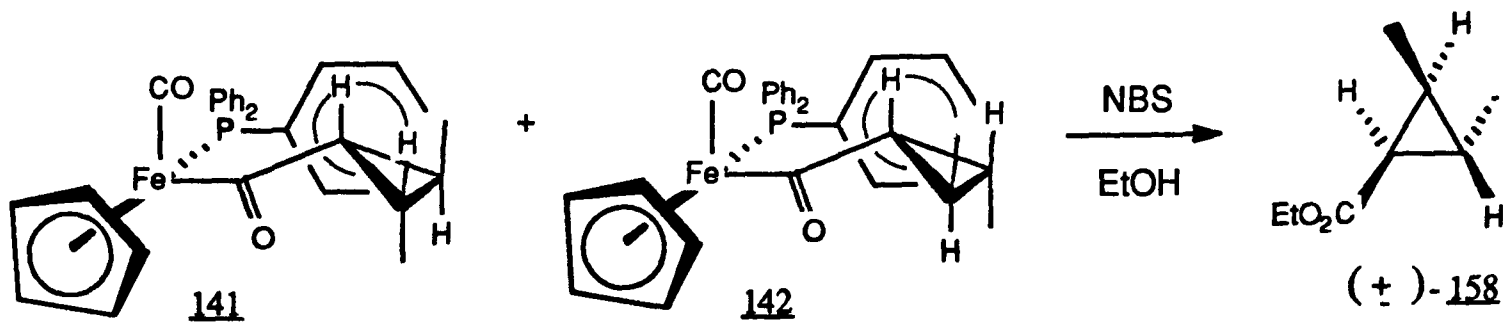


(±)-124



(±)-157

A 9:1 mixture of 141:142 was treated with N-bromosuccinimide in ethanol as before. On work up a single product was isolated drying to a yellow oil, and identified as 158 (45%-unoptimised).[96]



The coupling constants for the α-proton (COCH) in the ^1H n.m.r. spectrum were consistent with the assigned cis/trans stereochemistry of 158 and all resonances were consistent with those given in the literature.[96]

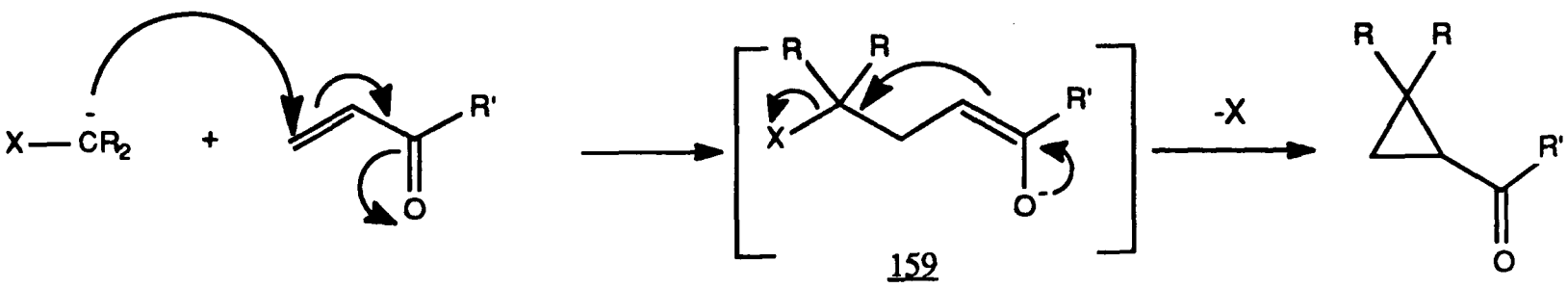
We have demonstrated that Z-α,β-unsaturated iron acyl complexes undergo highly diastereoselective reactions with electrophilic carbenoid species generated from alkylidene iodides and diethylzinc to give cyclopropyl acyl complexes in good yield. Decomplexation, to give the corresponding cyclopropanecarboxylic acid derivatives, occurs with complete retention of the stereochemistry of the cyclopropane ring. By the use of homochiral starting materials the absolute stereochemistry of the cyclopropane ring can also be controlled. Highly substituted cyclopropane rings have been synthesised by the use of ethylidene and isopropylidene iodides, the latter being the first reported example of addition of isopropylidene, generated in this manner, to an olefinic bond.

The reactions with E-α,β-unsaturated iron acyl complexes showed poor diastereoselectivity. In the following chapter alternative, stereoselective routes to trans-substituted cyclopropyl complexes are described.

CHAPTER 4

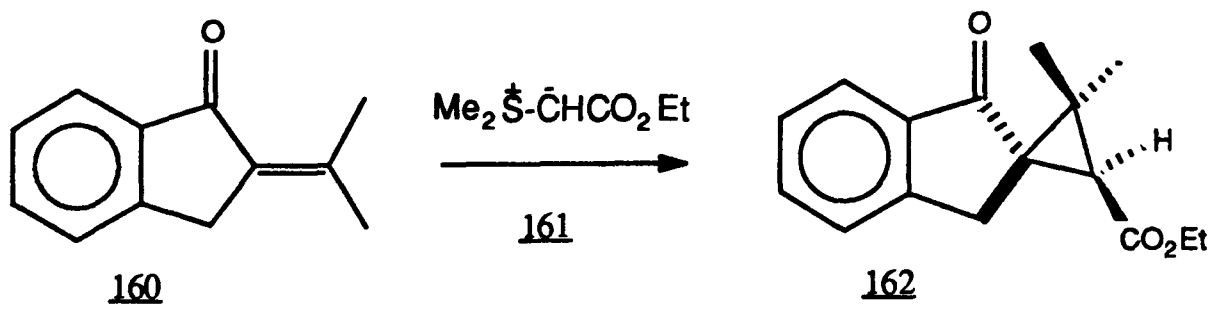
REACTIONS OF COMPLEXES $(C_5H_5)Fe(CO)(PPh_3)$ (COCH=CHR) WITH NUCLEOPHILIC ALKYLIDENE TRANSFER REAGENTS.

The syntheses of cyclopropyl derivatives via addition of electrophilic carbenoid species to olefinic bonds were described in the preceding chapter. An alternative approach to these compounds is via the reaction of α,β-unsaturated carbonyl compounds with nucleophilic alkylidene transfer reagents. A generalised scheme for this type of synthetic approach is illustrated below.

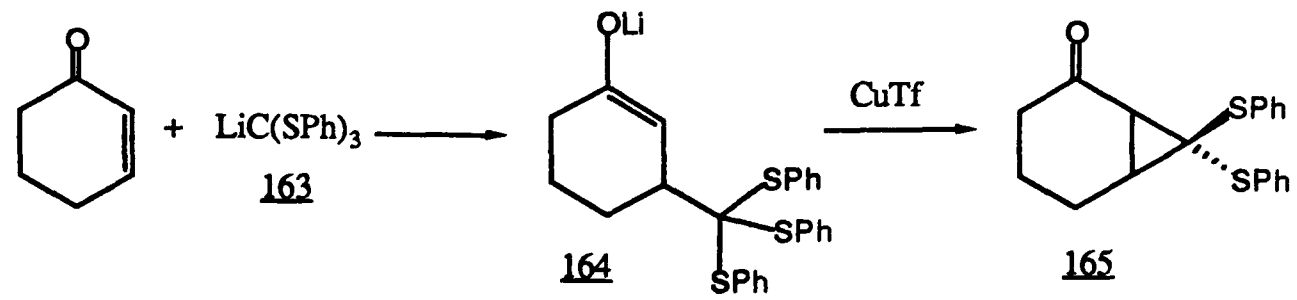


The Michael addition of a nucleophile, with a leaving group substituted on the nucleophilic carbon, to an α,β-unsaturated carbonyl compound, gives an intermediate enolate 159. Ring closure, via the intramolecular displacement of the leaving group, can then occur to give the cyclopropyl derivative.

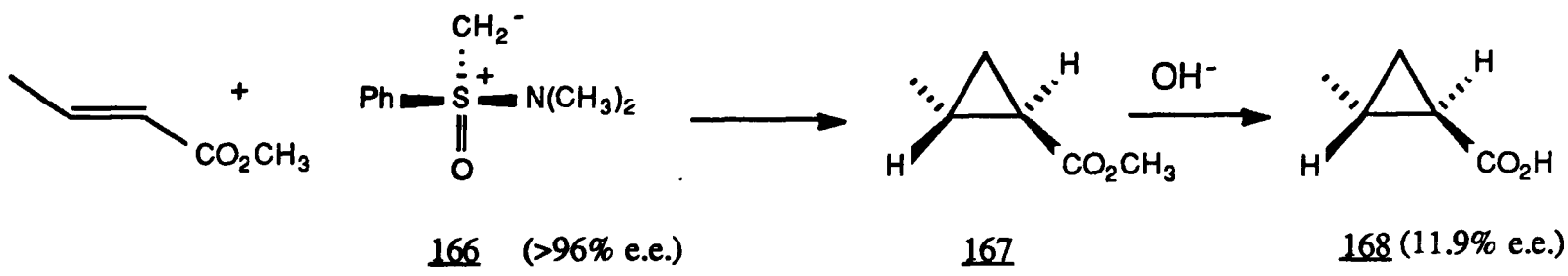
The utilisation of ylids, usually sulphur[62] but occasionally phosphorus ylids[97], in this type of synthesis has been widely reported. For example, reaction of the enone 160 with the ylid 161 gave the spiro-fused compound 162 quantitatively.[98]



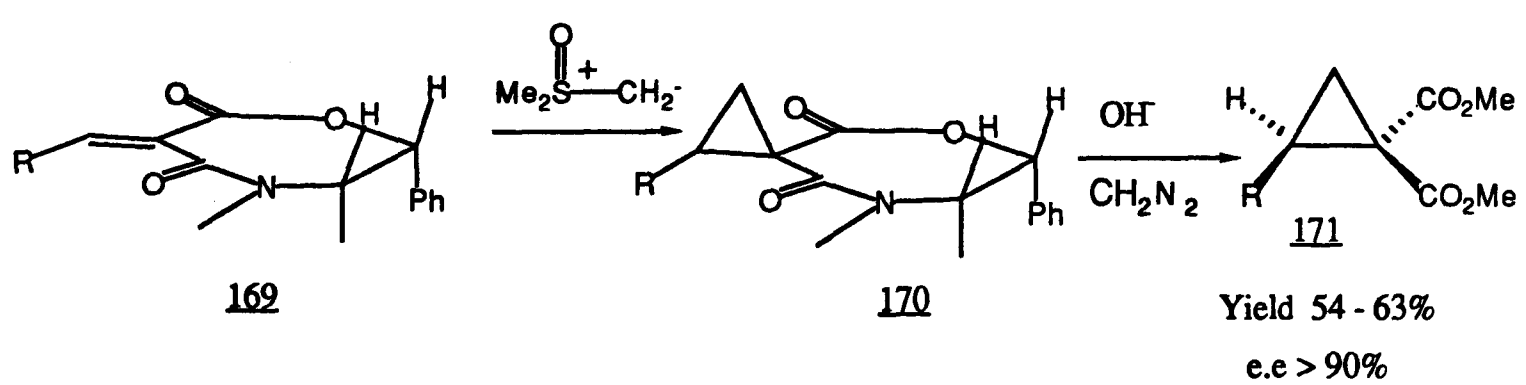
The utilisation of other suitably substituted nucleophilic species in this type of reaction have also been reported.[99] For example, Michael addition of the anion 163 to cyclohexenone gave the enolate 164 from which thiophenoxide displacement gave the corresponding cyclopropyl derivative 165.[99a]



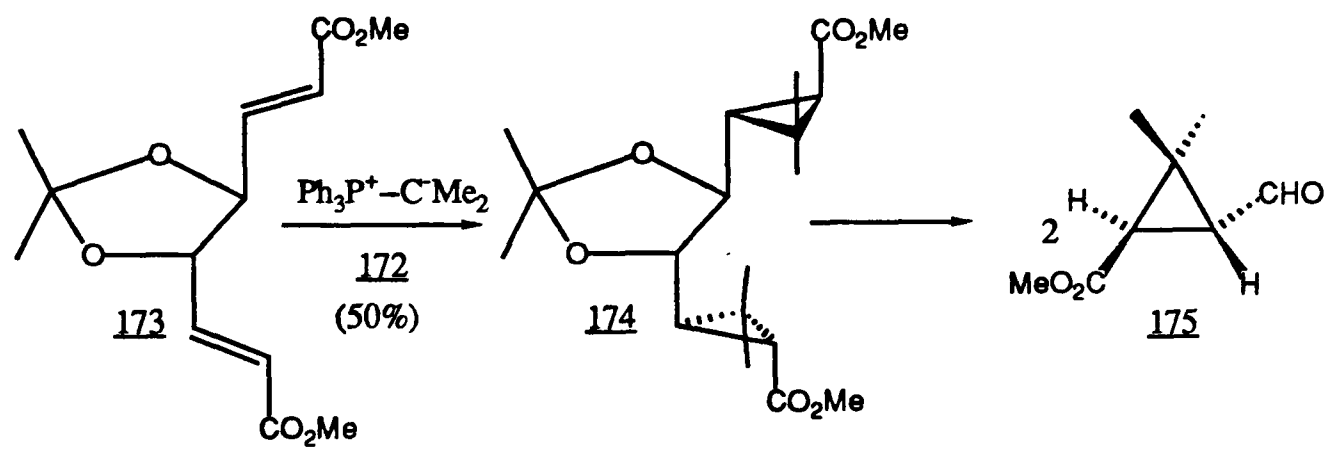
The asymmetric syntheses of cyclopropyl derivatives via this type of Michael addition-ring closure reaction have been reported (vide infra). Johnson et al. have demonstrated the use of optically active sulphoximines[100] and oxosulphonium ylids[101] as asymmetric nucleophilic alkylidene transfer reagents. For example, the reaction of S-(dimethylamino)phenyloxosulphonium methylide 166 (>96% e.e.) with methyl crotonate gave the cyclopropanecarboxylic ester 167, which on base hydrolysis gave the corresponding acid 1R,2R-168 (11.9% e.e.).



Alternatively, the use of optically active α,β-unsaturated acyl compounds can result in highly enantioselective syntheses of cyclopropyl derivatives. Treatment of the enones 169 with dimethylsulphoxonium methylide gave the intermediates 170, which on cleavage gave the corresponding diesters 171,[102] the synthesis being highly enantioselective (>90% e.e.).

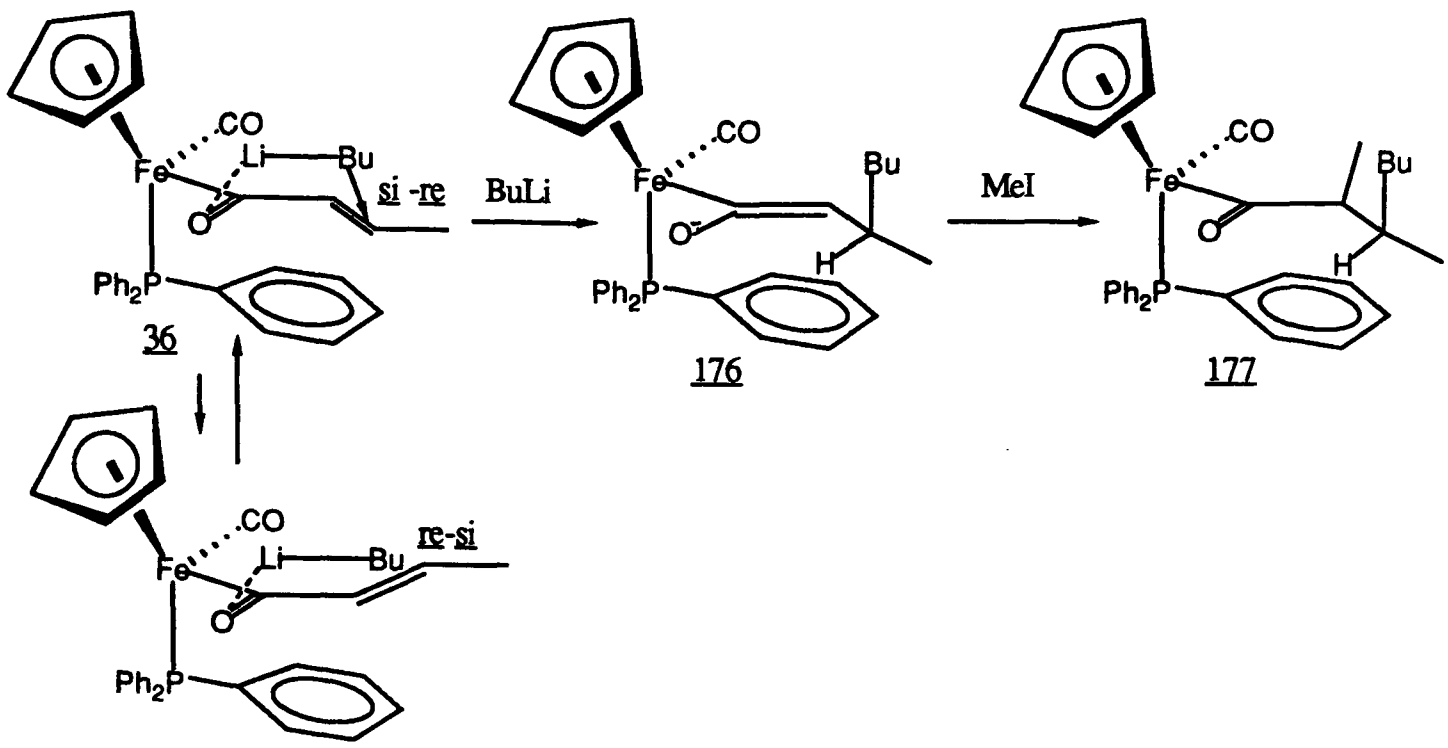


Krief et al. reported moderate diastereoselectivity in the reaction of triphenylphosphonium isopropylide 172 with dimenthyl fumarate[103] and, more recently, the highly stereoselective addition of ylid 172 to the α,β-unsaturated ester 173, derived from dimethyl 2R,3R-O-isopropylidene tartrate.[104] The di-adduct 174 was subsequently cleaved to give methyl-trans-1R,3R-hemicaronic aldehyde 175 (98% e.e.).



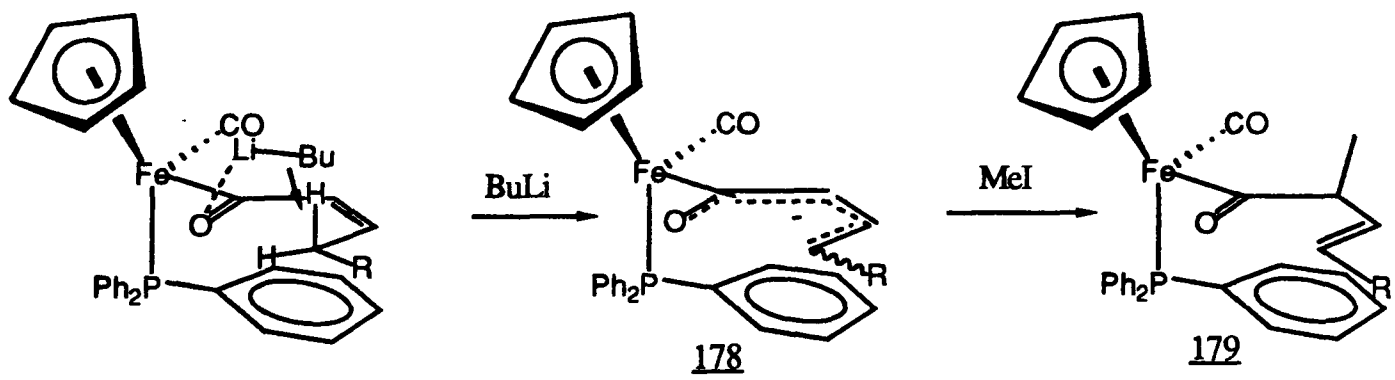
Davies et al.[29,57] have demonstrated highly diastereoselective tandem Michael addition-alkylation reactions of E-α,β-unsaturated iron acyl complexes. For example, addition of butyllithium to E-$(C_5H_5)Fe(CO)(PPh_3)(COCH{=}CHCH_3)$ 36, and trapping the resulting enolate 176 with methyl iodide, generates the diastereoisomer RSS(SRR)-177 with >100:1:1:1 selectivity.[57c] The reaction is regiospecific, no products arising from 1,2-addition being isolated. The diastereoselective Michael addition is believed to occur via prior coordination of the alkyllithium species to the acyl oxygen in a conformation in which the acyl bond is approximately anti to the carbon monoxide ligand.[57c] The nucleophile is then delivered exclusively to the si-re* face of the olefinic bond in the S-cis conformation. The S-trans conformations place the olefinic bond distant from the nucleophile, and have been shown to be disfavoured (Chapter 2).

*The si-re[82] face is that face of the olefinic bond not shielded by the proximate phenyl ring when the acyl ligand adopts the anti (acyl bond to carbon monoxide ligand) S-cis conformation, the iron ~~centre having~~ The R-configuration.

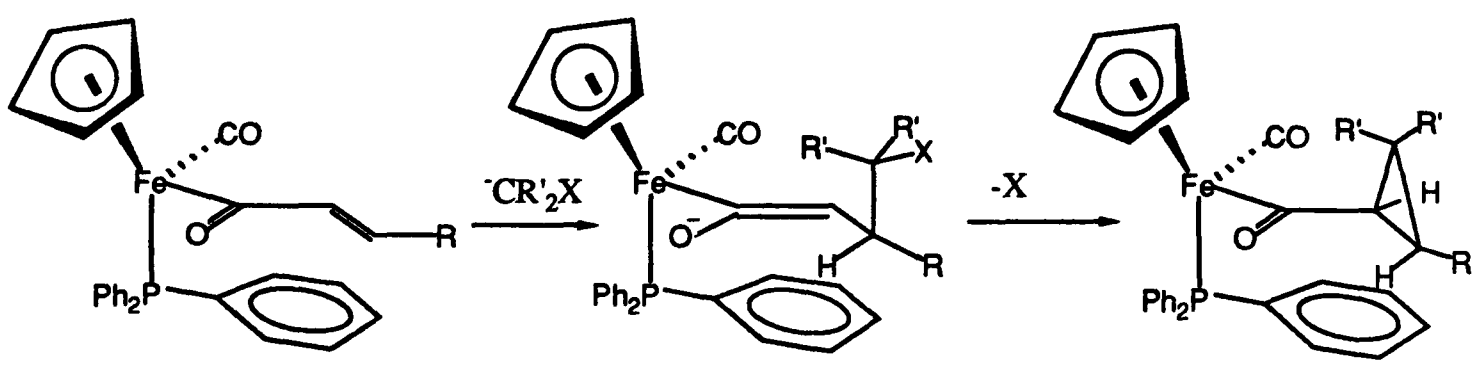


Subsequent methylation occurs exclusively away from the proximate phenyl ring (see Chapter 1, section 2d(i)).

The corresponding Z-α,β-unsaturated iron acyl complexes do not act as Michael acceptors to alkyllithium reagents. Instead, directed deprotonation to give the dienolate species 178 occurs, with subsequent highly regioselective and stereoselective trapping to give the corresponding β,γ-unsaturated complex 179.



It was anticipated that reaction of E-α,β-unsaturated iron acyl complexes with nucleophilic alkylidene transfer reagents would result in highly diastereoselective syntheses of the corresponding cyclopropyl complexes.



A. Methylene Addition Reactions.

1. Reactions With Ylids.

According to the literature procedure,[105] diphenylsulphonium methylide 180 was generated by treatment of the salt 181[106] with t-butyllithium. A solution of E-$(C_5H_5)Fe(CO)(PPh_3)(COCH{=}CHCH_3)$ 36 in THF at -78°C was added and the reaction stirred. After work up only recovered 36 was isolated.

$$(Ph_2SCH_3)^+BF_4^- \xrightarrow{t\text{-BuLi}} Ph_2S^+\text{-}CH_2^- \xrightarrow{36} \text{No Reaction}$$

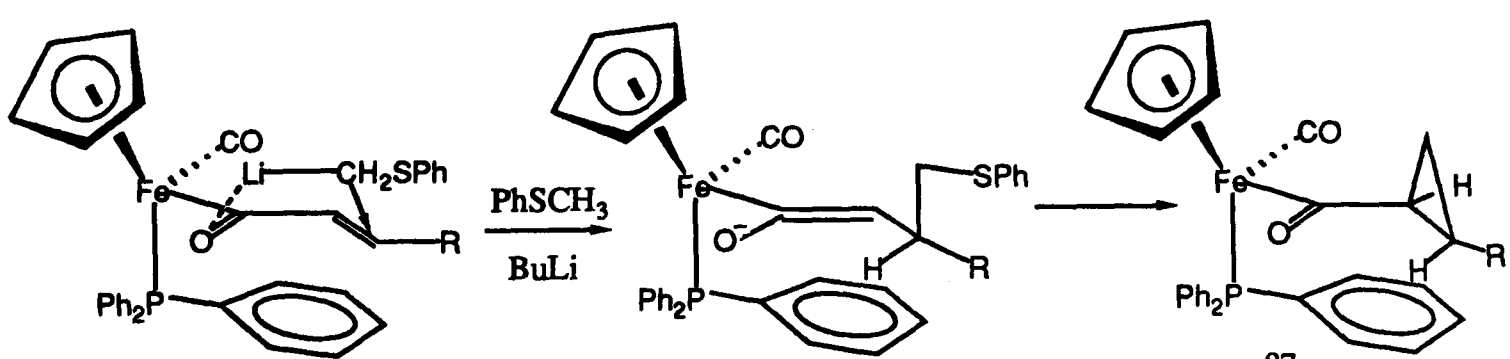
181 180

Similarly, no reaction of triphenylphosphonium methylide[97] with 36 occurred, only starting material being recovered.

The E-α,β-unsaturated iron acyl complexes are relatively unreactive towards nucleophiles and only addition of reactive alkyllithium species have been reported.[29,30,57] Presumably the ylids described here are insufficiently reactive towards the iron acyl complexes. In the following sections the additions of more reactive nucleophiles are described.

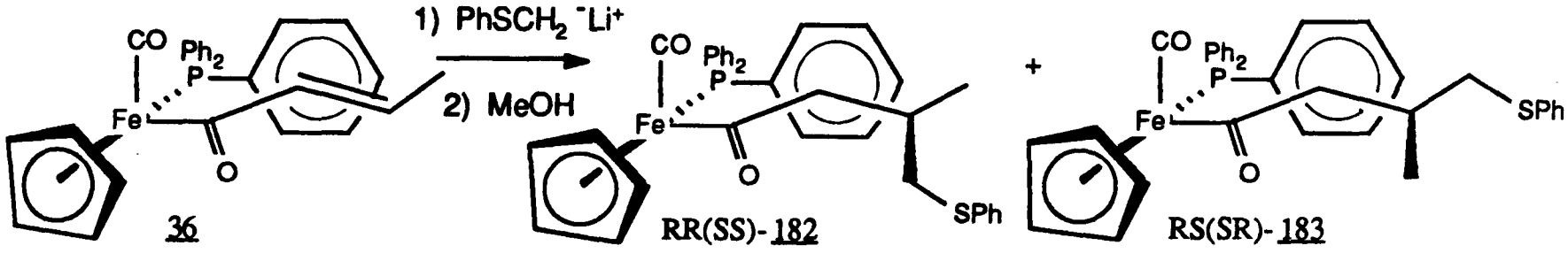
2. Reactions With α-Lithiosulphides and Sulphoxides.

On the basis of literature reports[107,108] it was anticipated that the α-lithiosulphide, formed on treatment of thioanisole with butyllithium, would act as a nucleophilic methylene transfer reagent.



87

Butyllithium was added dropwise to a solution of thioanisole in THF at 0°C. After stirring, a solution of E-(C_5H_5)Fe(CO)(PPh_3)($COCH{=}CHCH_3$) 36 in THF at -78°C was added and the reaction was stirred at -40°C for two hours. Addition of methanol, work up and chromatography gave a single band drying to an orange solid which, on the basis of the ^1H n.m.r. spectrum and the mass spectrum, was assigned as a mixture of the diastereoisomeric sulphenyl complexes 182 and 183 (82%).



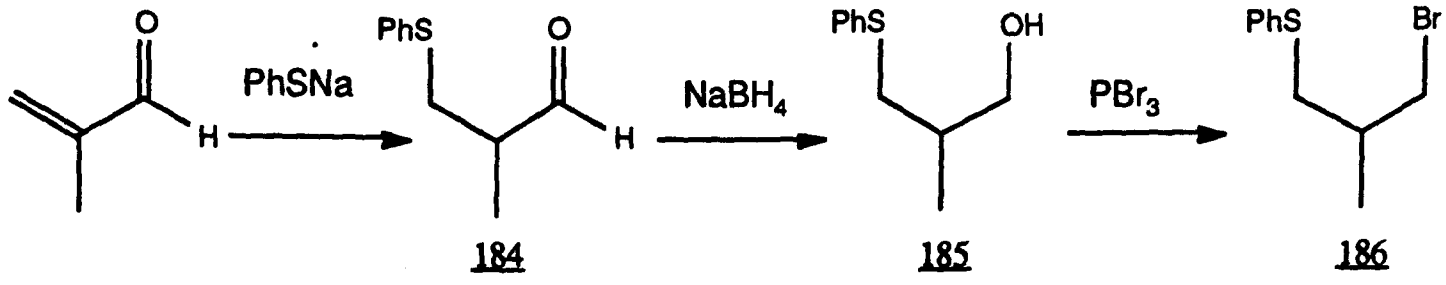
36 RR(SS)-182 RS(SR)-183

19 : 1

The ^1H n.m.r. spectrum of the product showed a major series of resonances at δ 3.15, 2.49 (ABX, $COCH_2$), 2.76, 2.67 (ABX, CH_2SPh), 1.95 (CH) and 0.57 (CH_3). In addition a minor doublet at δ 0.84 (CH_3) was tentatively assigned to a second diastereoisomer. The major diastereoisomeric product was assigned as RR(SS)-182, assuming favourable attack on the si-re face of the olefinic bond in 36 (vide supra). Subsequently, this was confirmed by the X-ray crystal structure determination of a related complex (p.111). The diastereoisomeric ratio of 182:183 was 19:1, crystallisation giving the diastereoisomerically pure 182.

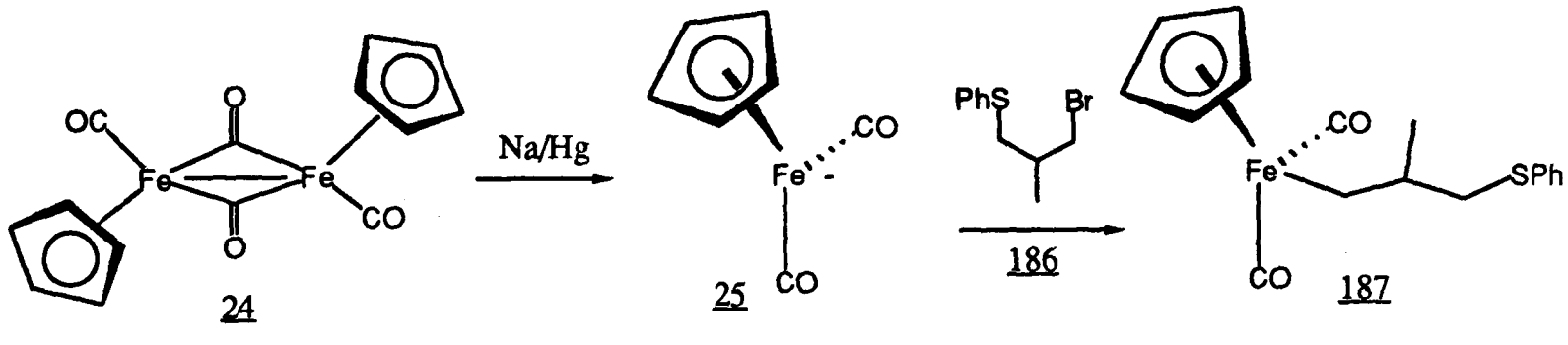
To confirm the gross structural assignment of 182 and 183, and that the minor resonance at δ 0.84 in the ^1H n.m.r. spectrum had been correctly assigned to 183, a non-stereoselective synthesis of the complexes, via an independent route, was undertaken. Michael addition of thiophenoxide to methacrolein gave the β-sulphenylated aldehyde 184.[109] Reduction to the alcohol 185[109] and

treatment with phosphorus tribromide[110] gave the corresponding bromide 186, the overall yield being 15%.

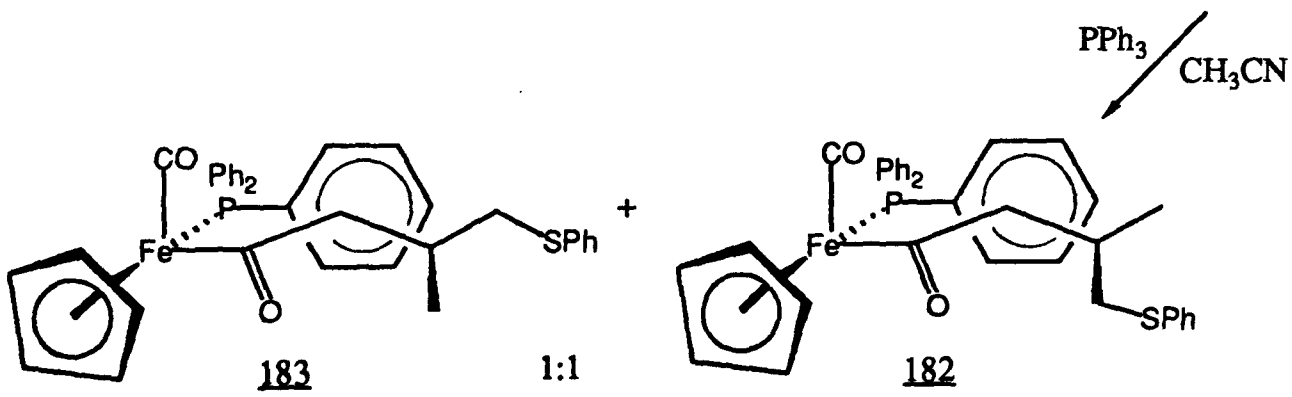


184 185 186

Treatment of the anion 25 (formed by cleavage of the iron dimer 24 with sodium amalgam) with 186 gave the iron alkyl species 187 which began to decompose rapidly and could not be isolated. Crude 187 was heated with triphenylphosphine at reflux in acetonitrile for four hours, and the reaction was then worked up, a single product band being isolated.



24 25 187

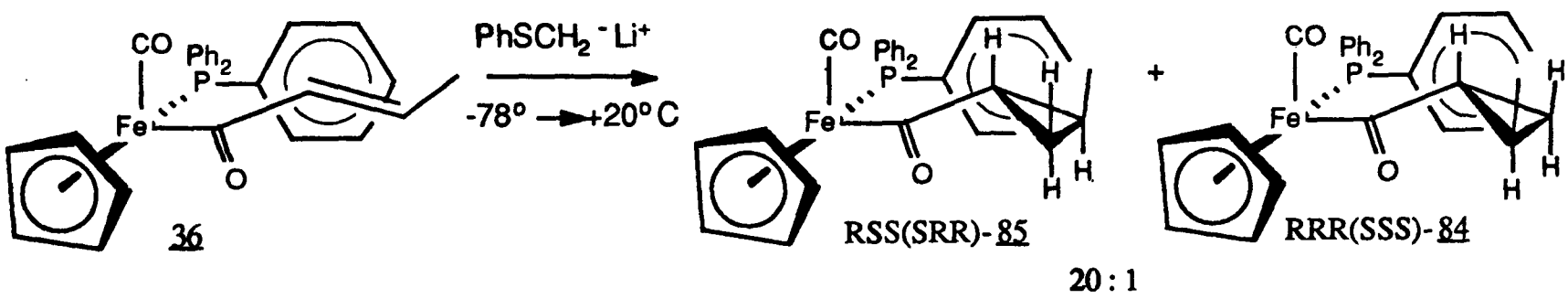


183 1:1 182

The $^{1}_{H}$ n.m.r. spectrum of the product showed a 1:1 diastereoisomeric mixture of the complexes 182 and 183 (31%) and confirmed the previous result.

The isolation of only the Michael adducts in the previous reaction indicated that ring closure was not occurring under the reaction conditions. The experiment was repeated, but after stirring (-40°C; 2h) was allowed to warm rapidly to room temperature and stirred (20°C; 20mins.). Work up and chromatography gave a

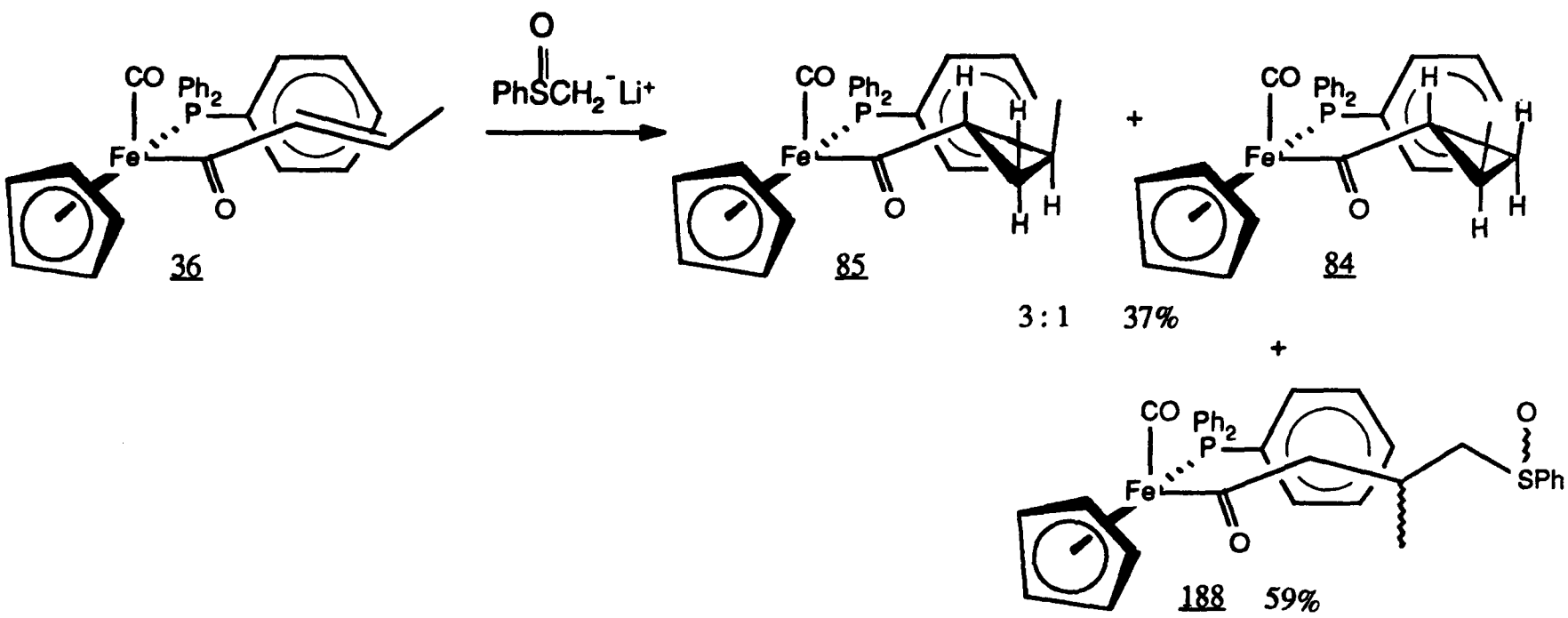
single band drying to an orange solid, the ^1H n.m.r. spectrum of which indicated the formation of the trans-substituted cyclopropyl complexes 84 and 85 (42%). A non-stereoselective synthesis of these complexes was described previously (p. 52), and the diastereoisomeric ratio could therefore be determined as 20:1. The major diastereoisomer was assigned as RSS(SRR)-85 by assuming directed Michael addition to the si-re face of 36 (vide supra). Subsequently, an X-ray crystal structure analysis of another sample of 85 confirmed this assignment (p. 122).



The relatively low yield for the reaction, and the absence of other iron acyl complexes, indicated substantial enolate decomposition under these conditions. The iron acyl enolates have been shown to only be indefinitely stable at temperatures below approximately -35°C.[111] However, ring closure in the reaction described here only occurs at temperatures greater than this, thus limiting the effectiveness of this approach. It was anticipated that by utilisation of α-lithiosulphoxides, in place of the corresponding sulphides, ring closure would be more favoured.

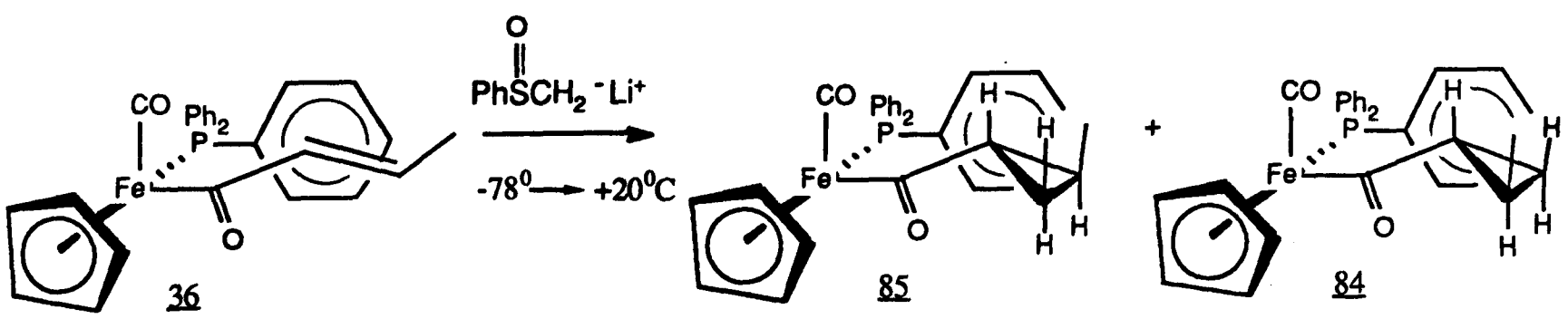
Methyllithium was added dropwise to a solution of phenyl methyl sulphoxide in THF at -78°C.[112] After stirring, a solution of E-$(C_5H_5)Fe(CO)(PPh_3)(COCH{=}CHCH_3)$ 36 (0.25 equivs.) in THF at -78°C was added and the reaction stirred (-78°C; 30mins., -40°C; 6h). After addition of methanol work up and chromatography, two

bands drying to orange solids were collected. The ^{1}H n.m.r. spectrum of the material from the first band showed it to be a 3:1 diastereoisomeric mixture of the cyclopropyl complexes 85 and 84 (37%). On the basis of the molecular ion in the mass spectrum, the material from the second band was assigned the gross structure 188 (59%), the stereochemistry of which will be discussed below.



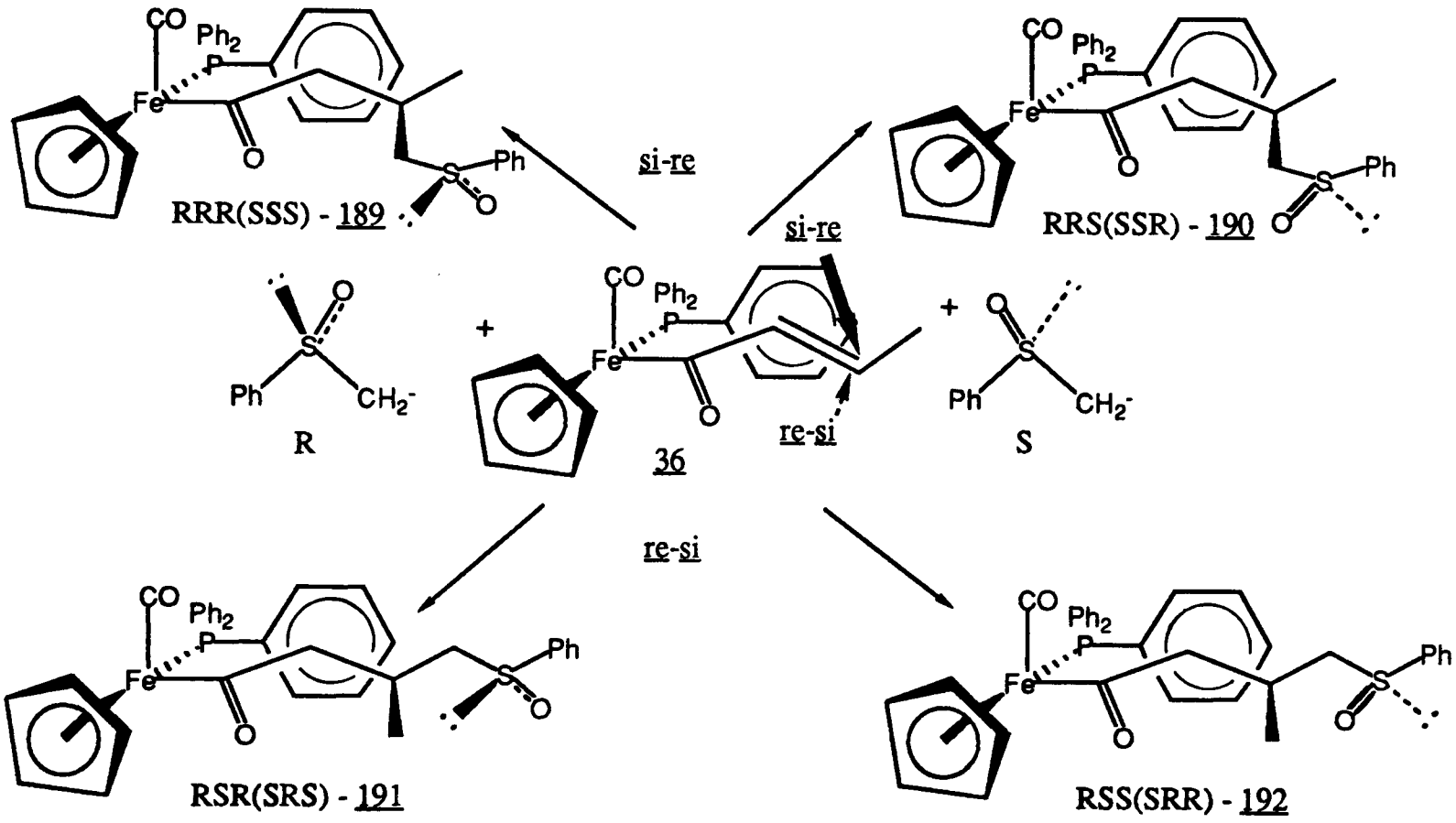
When either a smaller excess of the α-lithiosulphoxide was used, or when the reaction was run for a shorter time period, the product yields were reduced and starting material 36 was recovered, indicating low reactivity of the nucleophile.

The previous reaction was repeated, but after stirring (-40°C; 6h) was allowed to warm rapidly to room temperature. After fifteen minutes the reaction was worked up as before. A single product band was isolated which was identified, by ^{1}H n.m.r. spectroscopy, as an 8:1 mixture of diastereoisomers 85 and 84 (90%).



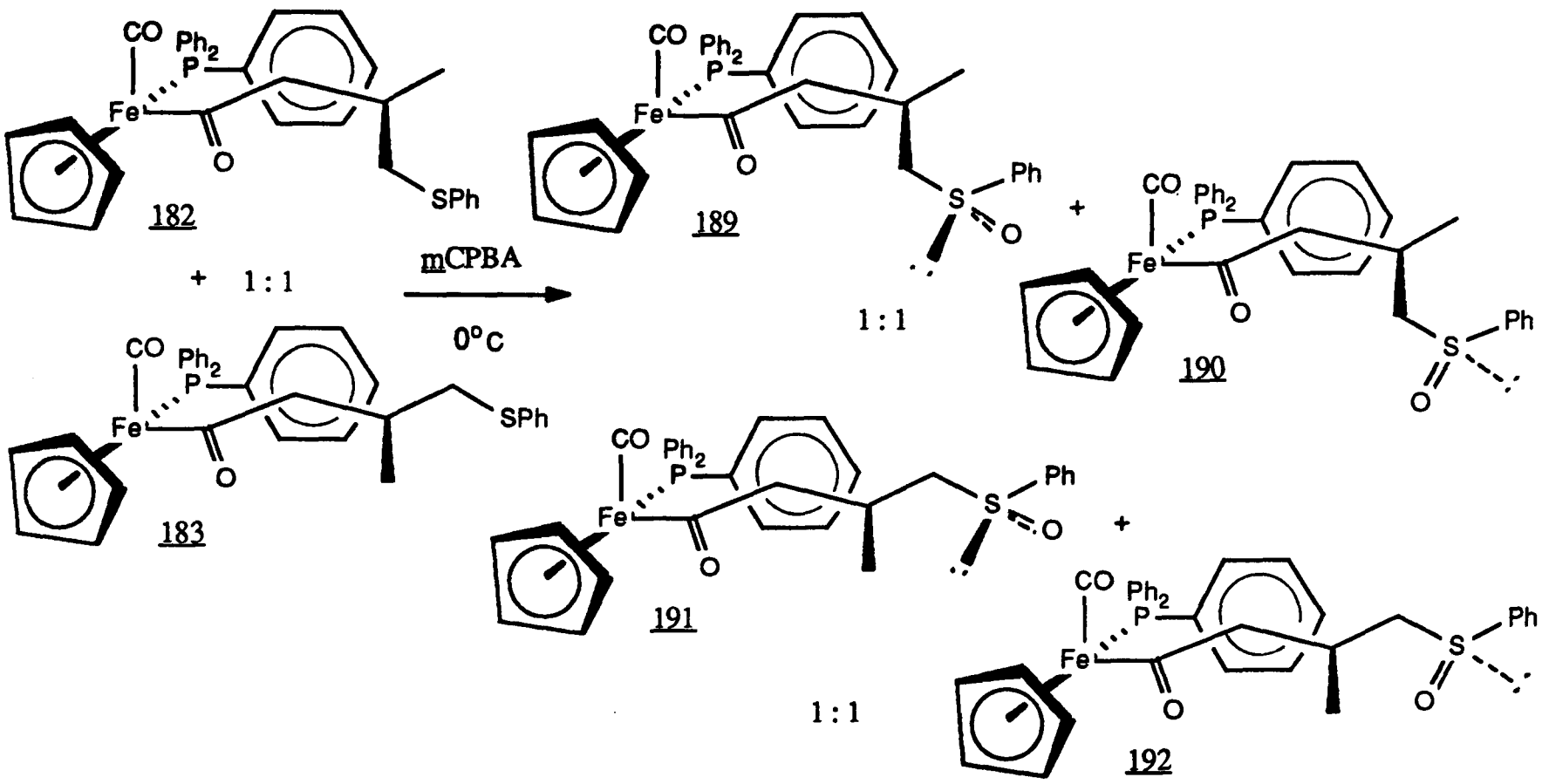
Hence, ring closure at -40°C is slow, but on warming to room temperature occurs more rapidly than enolate decomposition. The relatively low diastereoselectivity indicates lower diastereofacial selectivity in this Michael addition than has been reported in the literature.[29,57] Possible reasons for this will be discussed below.

The sulphinyl complex isolated in the initial reaction, and assigned the gross structure 188, could consist of up to four diastereoisomers resulting from attack of either enantiomer of the α-lithiosulphoxide onto either face of the olefinic bond of 36.



In order to determine the degree of diastereoselectivity in the formation of the sulphinyl complexes, a non-stereoselective synthesis of 189-192 was undertaken. The 1:1 diastereoisomeric mixture of the sulphenyl complexes 182 and 183, synthesised previously (p.106), was dissolved in chloroform and treated with m-chloroperbenzoic acid at 0°C.[113] On work up and chromatography a very polar band, drying to an orange solid, was collected. The mass spectrum confirmed the formation of the sulphinyl complexes

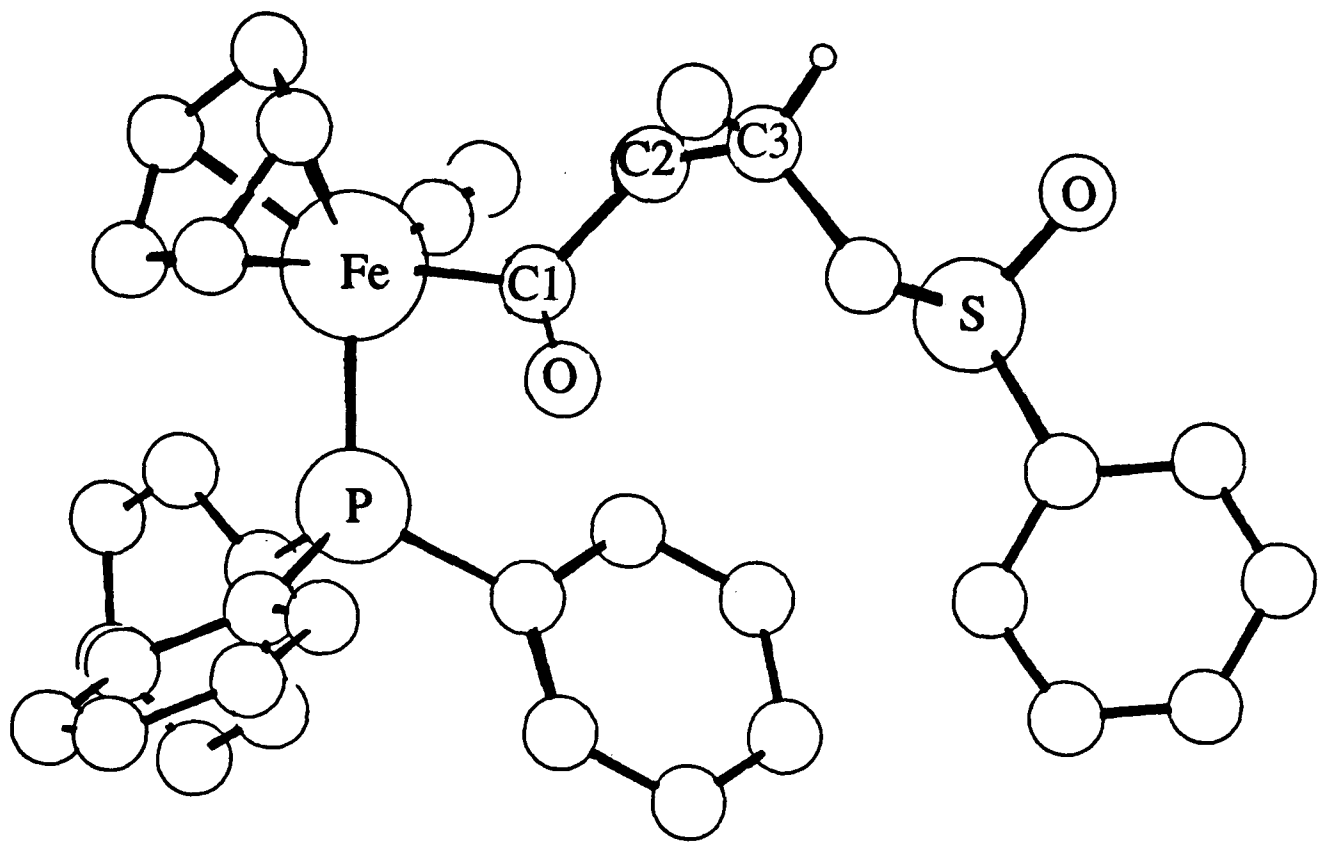
and the ^{1}H n.m.r. spectrum showed that 189-192 had been formed non-selectively (78%), the diastereoisomers being chromatographically inseparable.



The ^{1}H n.m.r. spectrum showed a series of resonances. Of particular interest were four doublets of equal intensity, at δ 0.94, 0.91, 0.76 and 0.67, which were assigned to the β-methyl groups of 189-192. Subsequently (vide infra), these characteristic shifts were used to determine relative and absolute stereochemistries of these and related products. The formation of 189-192 shows that oxidation of the sulphenyl complex 182 to the sulphinyl complexes 189 and 190 occurs non-selectively, as does the oxidation of 183 to 191 and 192.

The ^{1}H n.m.r. of the sulphinyl complex isolated in the previous reaction showed a major series of resonances at δ 3.20, 2.60 (ABX, $COCH_2$), 2.60 (m, $CH_2S(O)Ph$), 2.11 (CH) and 0.67 (CH_3), consistent with the formation of one major diastereoisomer. In addition, a minor doublet at δ 0.91 (CH_3) was assigned to a second diastereoisomer, the ratio being 20:1. Crystallisation from dichloromethane/hexane gave crystals of the major diastereo-

isomer on one of which an X-ray crystal structure analysis was performed.[94] The major diastereoisomeric sulphinyl complex was identified as RRR(SSS)-189 (see Appendix 2). The X-ray crystal structure is shown in figure 14.



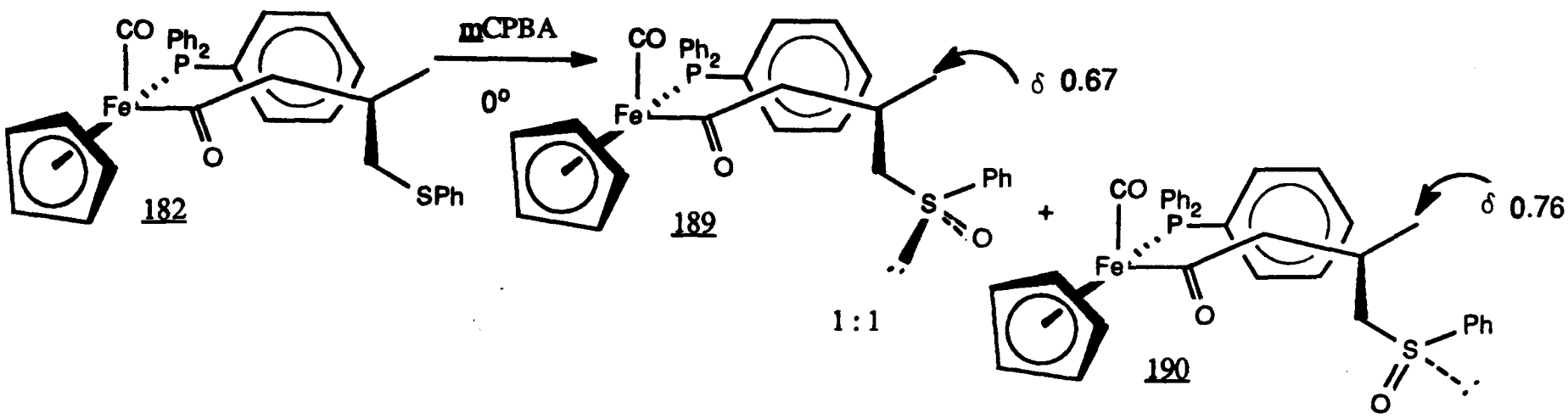
Fe-C1 1.964 Fe-P 2.205 C1-O 1.207 C1-C2 1.537 P-Fe-C1 90.61

Fe-C1-O 124.23 O-C1-Fe-P - 45.19 O -C1-C2-C3 -19.74

Figure 14. X-ray crystal structure and selected bond lengths (Å), angles and torsional angles (°) for RRR(SSS)-$(C_5H_5)Fe(CO)(PPh_3)$ $(COCH_2CH(CH_3)CH_2S(O)Ph)$ 189. Selected protons are removed for clarity.

The previously synthesised sulphenyl complex 182 (p.105) was oxidised to the sulphinyl complexes 189 and 190 as described above. The ^1H n.m.r. spectrum showed resonances assigned to the β-methyl substituents at δ 0.76 and 0.67 and of equal intensity. The latter arises from RRR(SSS)-189 (vide supra), and hence the former could be unambiguously assigned to RRS(SSR)-190 since the stereochemistry

at the β-centre was known.

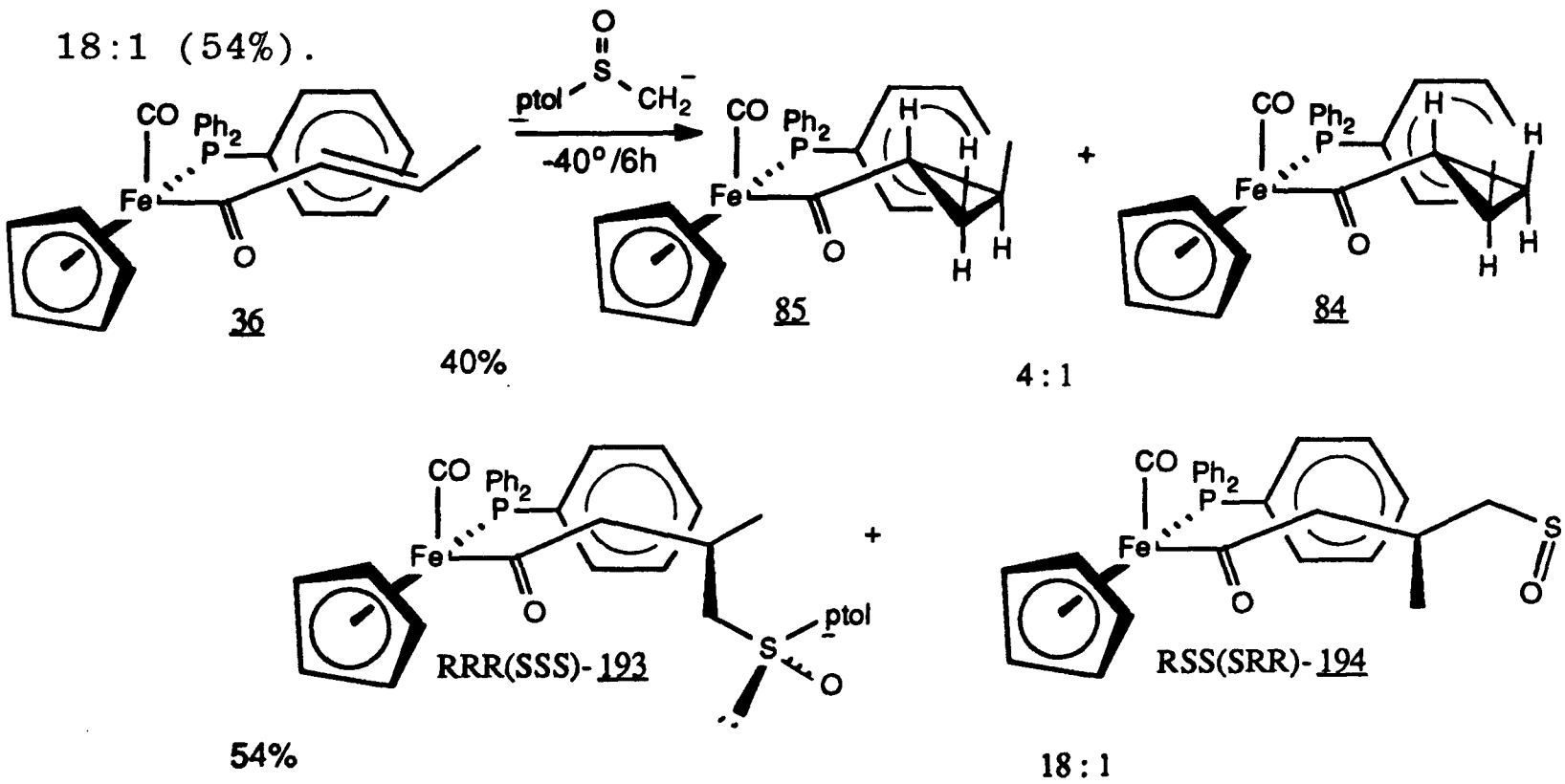


From this result it was apparent that none of the diastereoisomer 190 had been synthesised in the previous reaction (vide supra), since no resonance at δ 0.76 in the ^{1}H n.m.r. spectrum had been observed. Subsequently the minor diastereoisomer from that reaction was identified as RSS(SRR)-192 (vide infra).

The absence of RRS(SSR)-190 and RSR(SRS)-191 from the reaction might arise in a number of ways. Considering 190, then inversion of the sulphur centre in the enolate precursor to 190 would give 189, but is unlikely under these reaction conditions.[114] Chiral recognition between the iron and sulphur centres may result in the exclusive reaction of the α-lithiosulphoxide with the R-configuration at sulphur, with R-36 (and the corresponding S-sulphoxide with S-36). A third possibility is that ring closure in the enolate precursor to RRS(SSR)-190 is more rapid than in the precursor to RRR(SSS)-189, resulting in the selective destruction of the former. Attempts were made to generate the enolates of 189 and 190 by treatment of a 1:1 diastereoisomeric mixture with methyllithium. However, apparent preferential deprotonation α- to the sulphoxide occurred and so the relative rates of ring closure could not be determined by this method.

It was anticipated that by the use of homochiral materials the nature, and relative importance, of these effects might be determined. Since homochiral p-tolyl methyl sulphoxide was readily available (vide infra), this was utilised in preference to

phenyl methyl sulphoxide. To determine that the anion from p-tolyl methyl sulphoxide reacted in the same way as that from phenyl methyl sulphoxide, the reaction described previously (p.107) was repeated with racemic p-tolyl methyl sulphoxide. After work up and chromatography two bands, drying to orange solids, were isolated. The first was identified by ^{1}H n.m.r. spectroscopy as a 4:1 mixture of the diastereoisomeric cyclopropyl complexes 85 and 84 (40%). The ^{1}H n.m.r. spectrum of the product from the second, more polar band showed one major diastereoisomeric product which was identified as RRR(SSS)-193 by comparison with RRR(SSS)-189 (see table 15). A minor diastereoisomer, with a resonance attributed to the β-methyl substituent at δ 0.90, was present and assigned as RSS(SRR)-194. The ratio of 193:194 was 18:1 (54%).



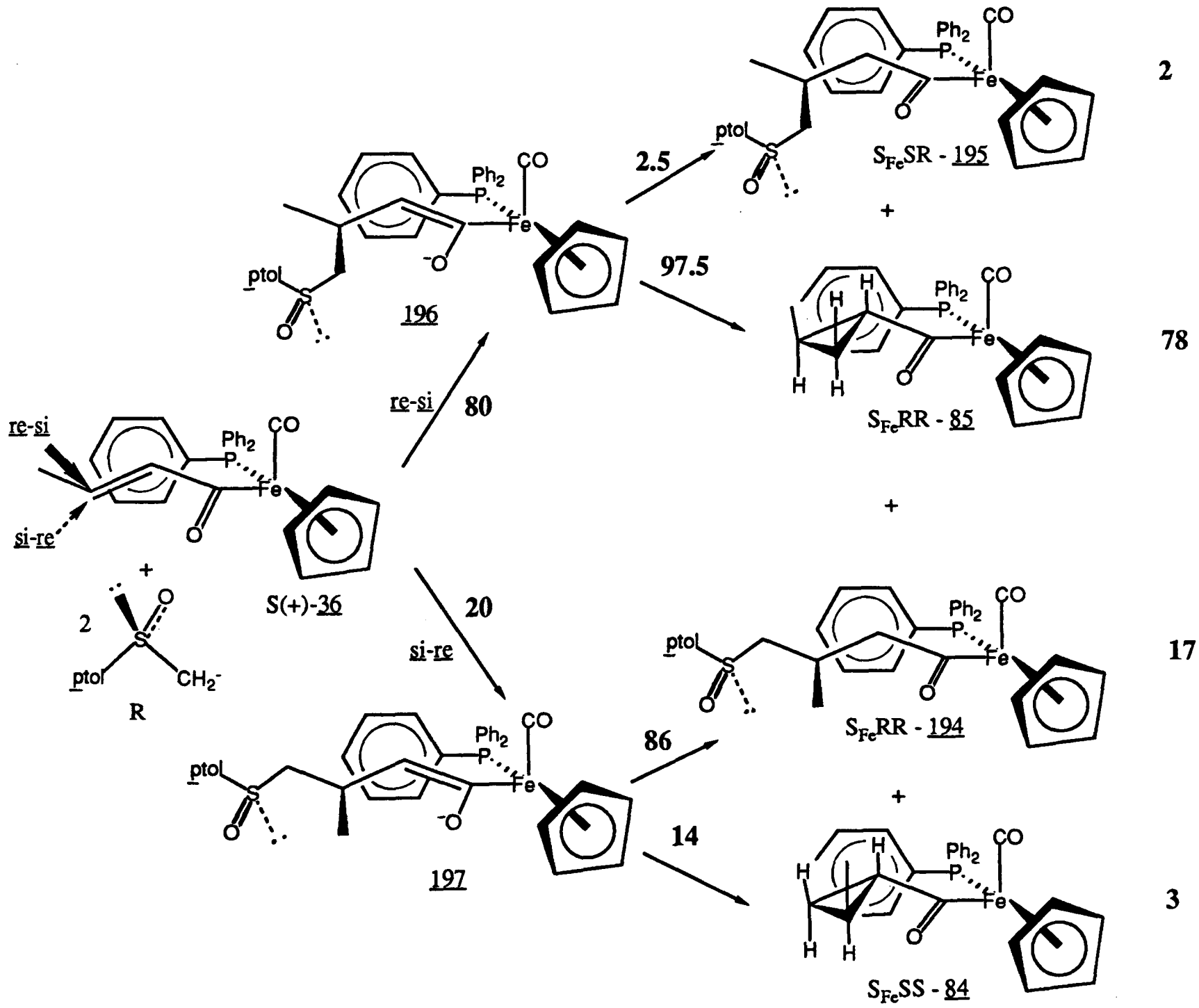
Some of the ^{1}H n.m.r. data for RRR(SSS)-193 and for RRR(SSS)-189 is given in table 15.

Product	$COCH_2$(ABX)	CH_2S(m)	CH	CH_3
193	3.18, 2.61	2.61	2.08	0.64
189	3.20, 2.60	2.60	2.11	0.67

Table 15. The chemical shifts (δ) of the acyl ligands (except aromatics) in the ^{1}H n.m.r. spectrum of 193 and 189.

The result confirmed that the anions from phenyl and p-tolyl methyl sulphoxide react similarly on addition to 36.

R(+)-p-tolyl methyl sulphoxide (>98% e.e.) was synthesised as described in the literature.[115] After deprotonation (as before) homochiral S(+)-36 (0.5 equivs.) was added and the reaction stirred (-40°C; 6h). After work up and chromatography the products were identified and their approximate distribution is summarised in the following scheme. The figures represent ratios not absolute yields.



The overall yields of cyclopropyl and sulphinyl complexes were 71% and 18% respectively. By comparison with RRS(SSR)-190

(p.111), the minor sulphinyl complex was assigned as S_{Fe}SR-195 on the basis of the resonance at δ 0.72 ($CHC\underline{H}_3$) in the ^{1}H n.m.r. spectrum. The major diastereoisomer was therefore S_{Fe}RR-194 with a characteristic resonance at δ 0.90 ($CHC\underline{H}_3$). Hence the assignments of RSS(SRR)-194 (p.113) and RSS(SRR)-192 (p.112) were confirmed.

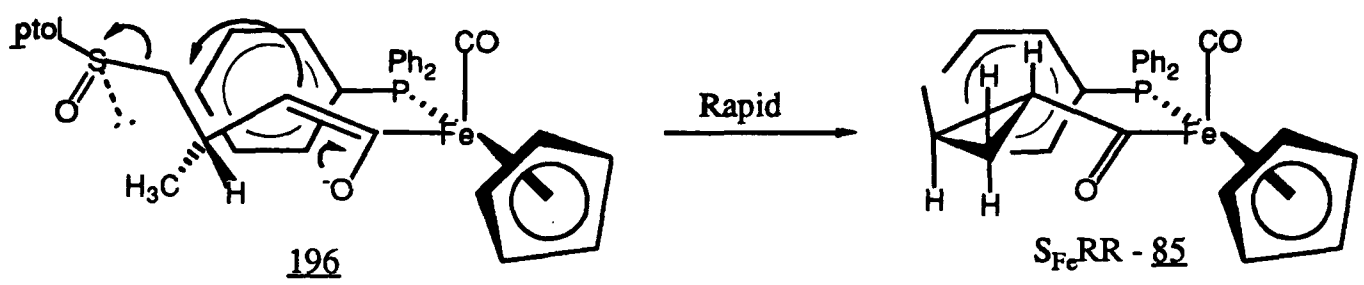
The complexes 195 and 85 are derived from enolate 196, which is formed by Michael addition to the re-si* face of the olefinic bond. Similarly, complexes 194 and 84 are formed from enolate 197, resulting from si-re face addition. Hence, from the product distribution the re-si:si-re diastereofacial selectivity can be determined as approximately 4:1. Furthermore, it is clear that ring closure in enolate 197, to give the cyclopropyl complex 84, is slow whilst ring closure in enolate 196 is more rapid. Hence, the product distribution depends both on the diastereofacial selectivity of the Michael addition, and the subsequent rate of ring closure in the enolate intermediates.

Considering, initially, the diastereofacial selectivity then it is apparent that this is lower than that reported previously for the Michael addition of alkyllithium reagents to E-α,β-unsaturated iron acyl complexes.[29,57] This may reflect the previous observation that the α-lithiosulphoxide reagents were of low reactivity (vide supra), resulting in non-directed Michael additions of lower selectivity. Alternatively, the result may be as a consequence of double asymmetric induction[116] between the "mis-matched" iron and sulphur chiral centres. It has been reported[117] that allylic sulphoxide anions can show high diastereofacial selectivity on Michael addition to cyclic enones.

*Since 36 has the S-configuration at iron, the face of the olefinic bond to which directed Michael addition is expected to occur is now labelled the re-si face.

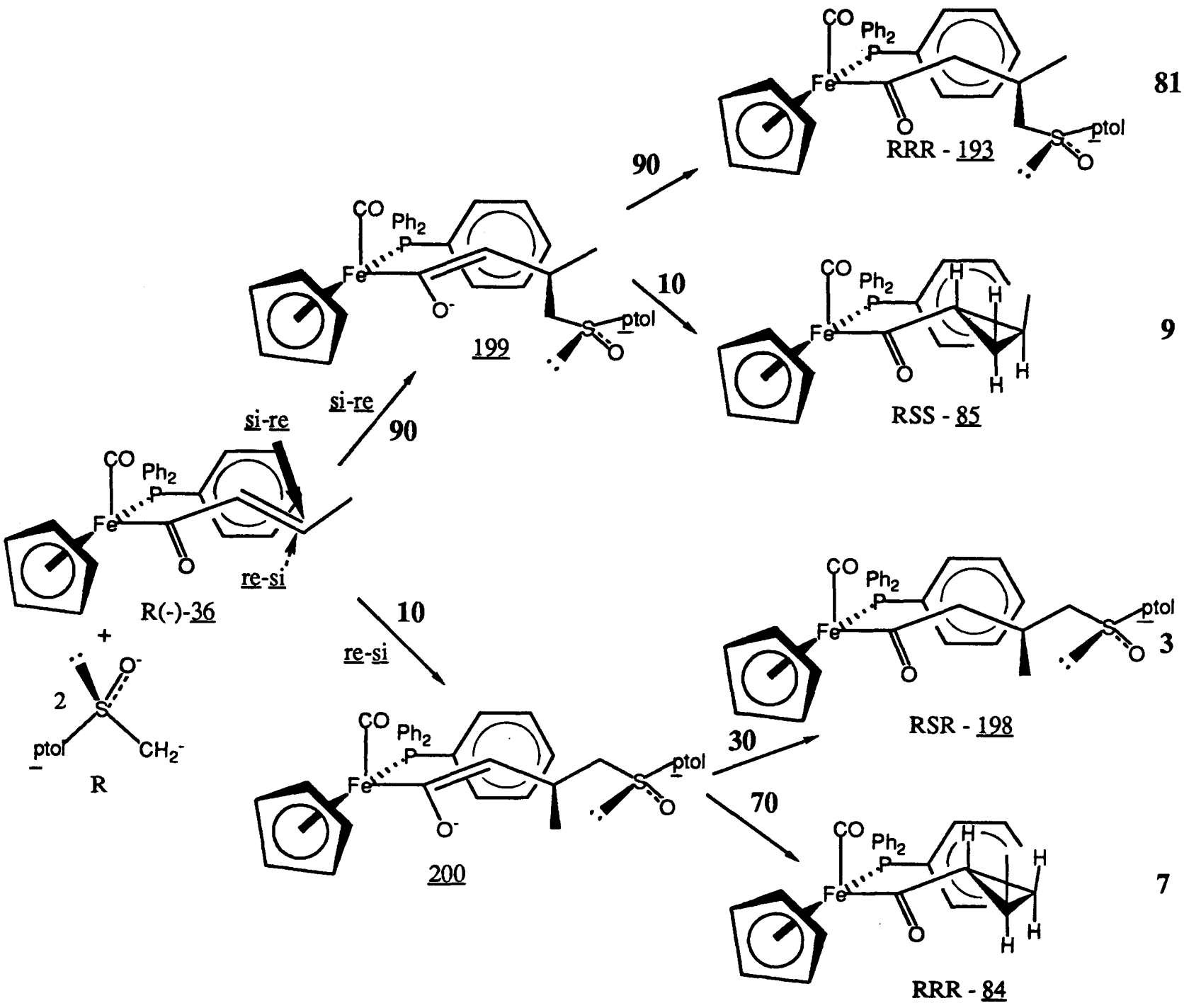
Similar facial discrimination by the α-lithiosulphoxide in this reaction may result in the iron and sulphur centres directing attack to opposite faces of the olefinic bond, resulting in low diastereofacial selectivity and reactivity.

Ring closure from enolates 196 and 197 will occur via an intramolecular SN2 displacement of the p-tolyl sulphinate leaving group. A conformation must be adopted in which the γ-carbon-sulphur bond must lie along the line of the enolate bond to allow SN2 displacement to occur.



It is apparent from the results that ring closure in enolate 196 is more favourable than in 197. Considering enolate structures similar to these shown here, if bond rotation about the γ-carbon-sulphur bond is unrestricted then it is not apparent, from models, why the different rates in ring closure should arise. Presumably the conformations in which ring closure can occur are not readily accessible for enolate 197, but the origins and nature of these restraints are unclear.

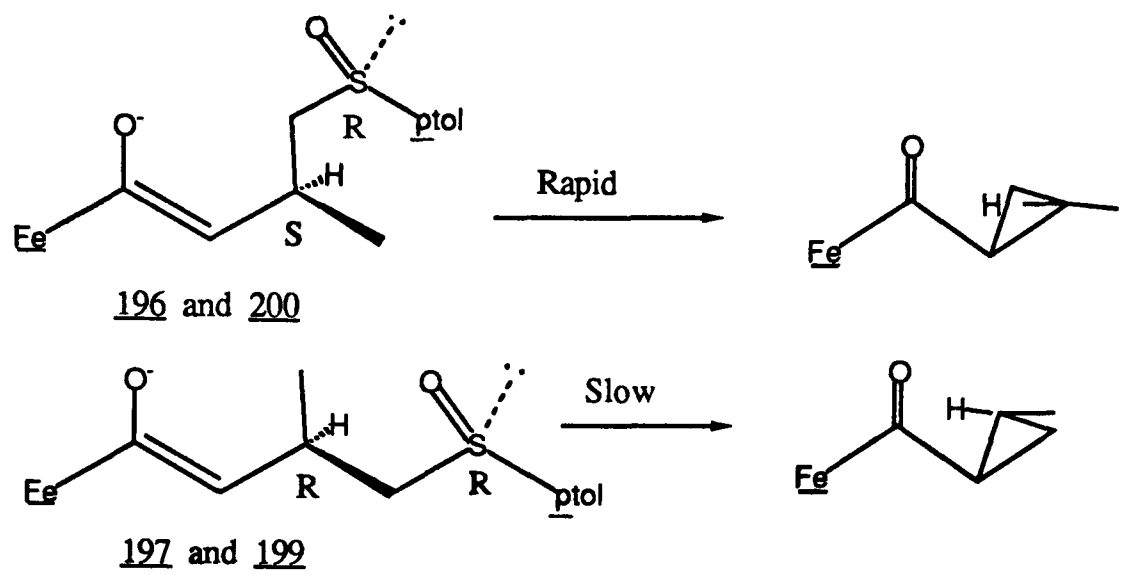
The reaction was repeated with homochiral R(+)-p-tolyl methyl sulphoxide and R(-)-36 (0.5 equivs.). The approximate product distributions are shown in the following scheme, the figures representing ratios not absolute yields.



The overall yields of cyclopropyl and sulphinyl complexes were 13% and 72% respectively. The major sulphinyl complex was RRR-193, and the minor was assigned as RSR-198, characterised by the resonance in the ^{1}H n.m.r. spectrum at δ 0.94($CHCH_3$).

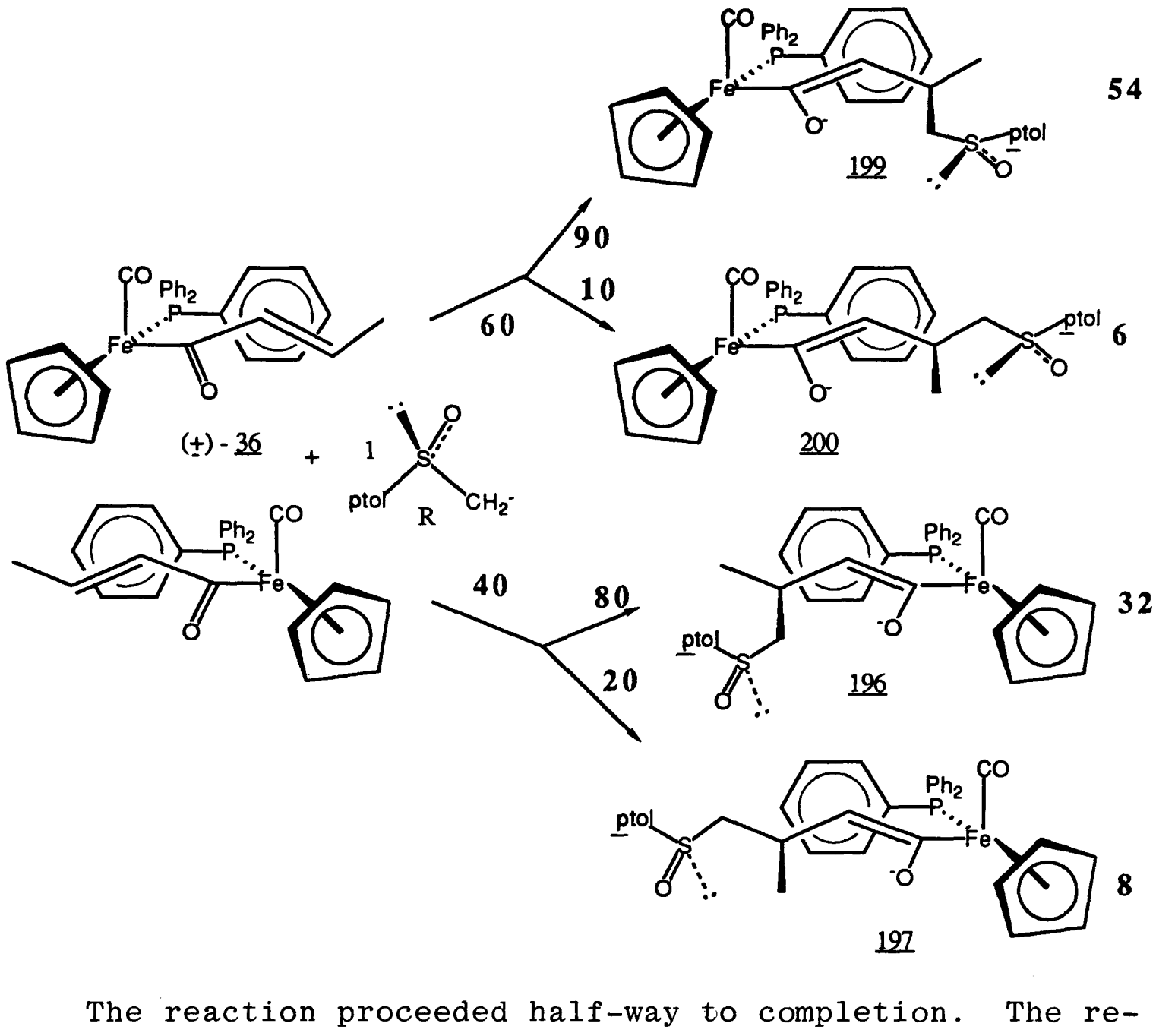
The ratio of si-re to re-si diastereofacial selectivity in the Michael addition can be calculated as approximately 9:1, slightly greater than in the previous reaction (labels reversed), possibly reflecting the "matching" of the iron and sulphur chiralities.[116] Ring closure in enolate 200 is more rapid than in 199 although again the factors affecting this are unclear. However, from the results of this and the preceding reaction it is apparent that ring closure is more rapid in those enolates with

the S_CR_S configuration on the acyl ligand, irrespective of the absolute configuration at iron.



This indicates that some steric interaction in enolates 197 and 199, possibly of the sulphoxide with the β-methyl substituent, prevents the conformations in which ring closure can occur from being easily adopted.

To determine whether chiral recognition between the iron and sulphur centres had occurred, the anion from R(+)-p-tolyl methyl sulphoxide was treated with one equivalent of racemic 36. After work up, the products were separated chromatographically. All of the sulphoxide complexes could be identified by the characteristic shifts of the β-methyl substituents in the ^1H n.m.r. spectrum (vide supra). The major enantiomer of the cyclopropyl complex 85 was determined from the ^1H n.m.r. spectrum by the use of a chiral shift reagent.[88] The minor cyclopropyl complex 84 was assumed to have predominantly the R-configuration at iron. The distribution of products is given in the experimental section, and from these the relative concentrations of the enolates 196, 197, 199 and 200 could be determined and are shown in the following scheme. Subsequent reactions of the enolates reflected closely the previous reactions in which homochiral R(-)- and S(+)-36 had been used.



The reaction proceeded half-way to completion. The recovered starting material 36 was shown, by the use of a chiral shift reagent, to be enriched in the S-enantiomer (S:R = 3:2) indicating a small degree of chiral recognition between the α-lithiosulphoxide with the R-configuration at sulphur and R-36, resulting in some kinetic resolution of racemic 36 (see Chapter 1 section 1b)ii)). However, the minimal chiral recognition and the complex nature of the α-lithiosulphoxide reagent in solution[118] prevent the origins of this effect from being determined.

From these experiments, it has been demonstrated that the product distributions in the reactions of α-lithiosulphoxides with E-$(C_5H_5)Fe(CO)(PPh_3)(COCH{=}CHCH_3)$ 36 are dependent upon:

1) Chiral recognition between the iron and sulphur centres.
2) The extent of diastereofacial selectivity, which may be

determined by double asymmetric induction between the iron and sulphur centres.

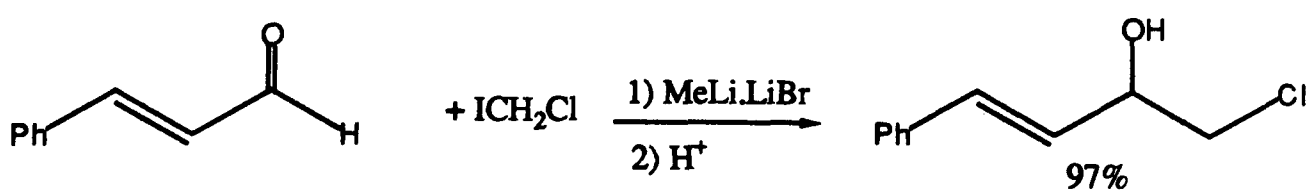
3) The rate of ring closure in the enolate intermediates which appears, to some extent, to be determined by the relative configurations at the sulphur centre and the β-centre on the acyl ligands.

The origin of these effects are unclear and cannot be determined at this time.

As a synthetic route to trans-substituted cyclopropyl complexes this method is complicated by the use of a chiral methylene transfer reagent which appears to exert its own stereochemical influence on the reaction. A simple, achiral reagent should be more effective as the stereochemical outcome will then be determined solely by the iron chiral auxiliary. The utilisation of such a reagent is described in the following section.

3. Reactions With Iodomethyllithium

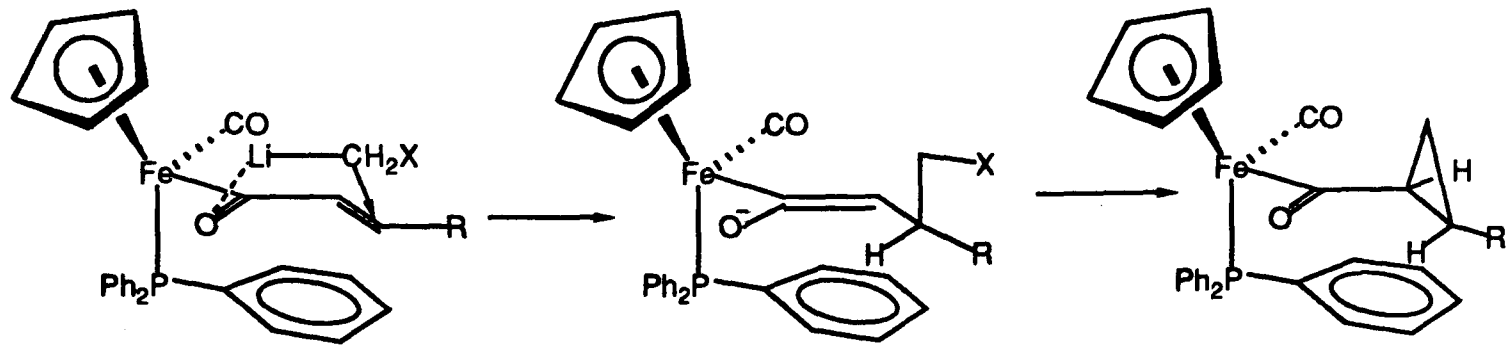
The generation of halomethyllithium reagents has been reported [119] and their potential utility as nucleophilic methylene transfer reagents described. However, this utility is limited by their extreme instability.[119] Recently the in situ generation of chloromethyllithium has been reported,[120] subsequent reaction with aldehydes giving the corresponding chlorohydrins or epoxides.



The efficiency of the reaction demonstrates that iodine/lithium exchange, to generate chloromethyllithium, occurs at a faster rate than methyllithium addition to the aldehyde substrate.

It was anticipated that the generation of a halomethyllithium reagent in the presence of an E-α,β-unsaturated iron acyl complex would result in the highly diastereoselective synthesis

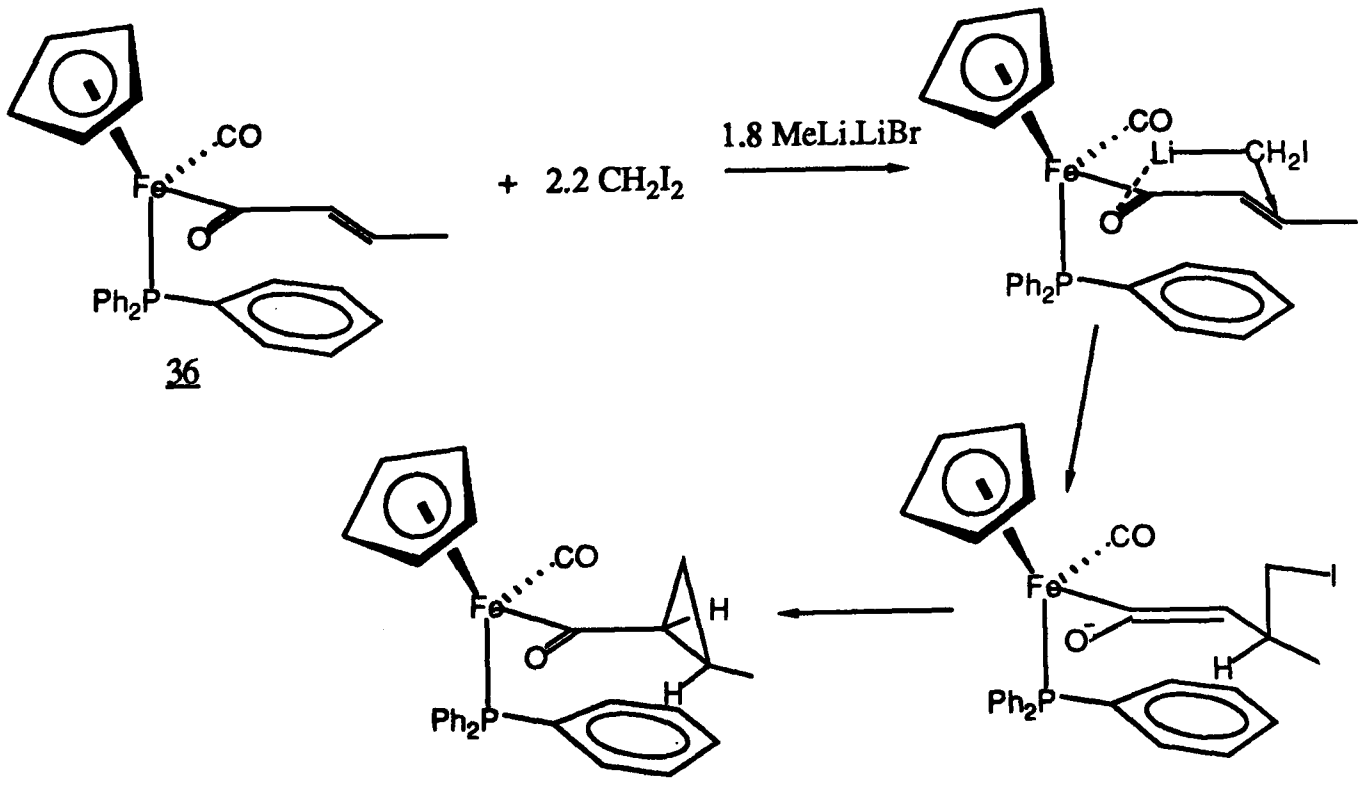
of the corresponding cyclopropyl complex *via* the mechanism outlined below. On the basis of previous results,[29,57] it was clear that 1,2-addition would not be a competing reaction.



87

In the literature report,[120] chloromethyllithium was generated *via* iodine/lithium exchange from chloroiodomethane and methyllithium. It was anticipated that by the use of methylene iodide and methyllithium, iodine/lithium exchange would generate iodomethyllithium in the same way.

Methyllithium was added to a solution of E-(C_5H_5)Fe(CO)(PPh_3)($COCH{=}CHCH_3$) 36 and methylene iodide in THF at -78°C and stirred for two hours. After work up and chromatography, the *trans* methyl substituted cyclopropyl complexes 85 and 84 were isolated in 10% yield (85:84 = >50:1), together with recovered starting material 36 (73%). Repeating the reaction, but working up immediately after methyllithium addition, gave similar results indicating a rapid reaction. The highly diastereoselective synthesis of 85 is consistent with Michael addition being directed by prior coordination of the haloalkyllithium to the acyl oxygen.

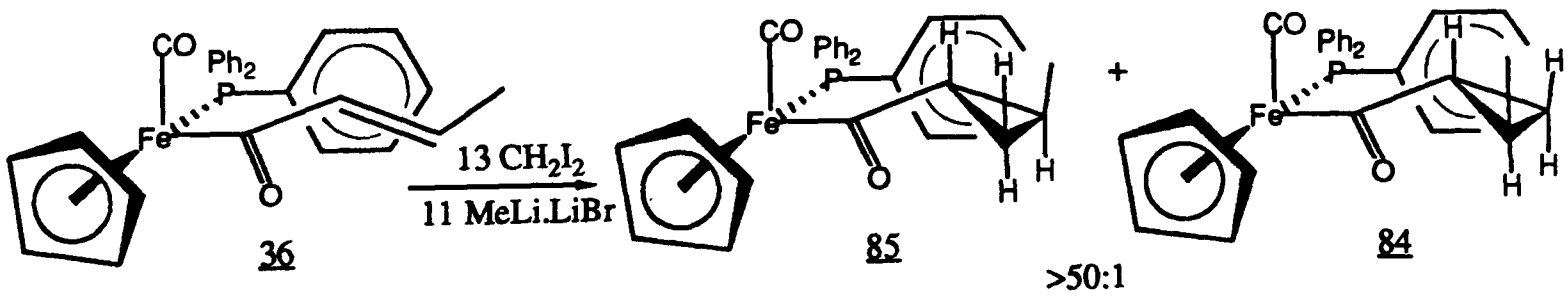


36

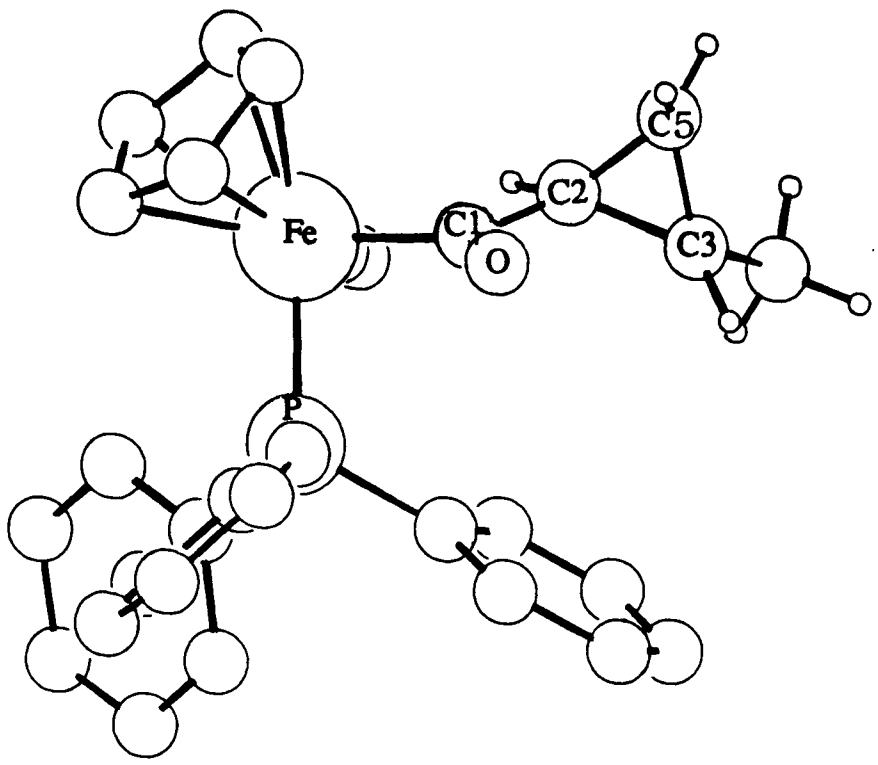
85

That no product arising from methyllithium addition to 36 was isolated indicated that iodine/lithium exchange, to form iodomethyllithium, was occurring but the low yield suggested rapid decomposition of the reagent. It was found that simply increasing the amounts of reagents did not increase the overall yield of cyclopropyl complexes. However, consecutive additions of small amounts of methylene iodide and methyllithium did increase the yield. A further experimental observation was that the yield, in terms of iodomethyllithium, decreased as the relative concentration of 36 decreased. Halomethyllithium reagents are known to be unstable, experiencing rapid decomposition the exact nature of which is unclear.[119] It has also been reported[119a] that these reagents can homologise the alkyllithium reagents used to generate them. Hence, if decomposition and/or homologisation are alternative reaction pathways for iodomethyllithium, in competition with the desired Michael addition, then as the concentration of 36 decreases the latter will become less favourable.

Under the optimum reaction conditions a total of a thirteen-fold excess of methylene iodide and an eleven-fold excess of methyllithium were added over thirty consecutive additions, resulting in an 85% isolated yield of 85 and 84 (85:84 = >50:1).



Crystallisation from dichloromethane/hexane gave orange crystals of 85, on one of which an X-ray crystal structure determination was undertaken.[121] The results are shown in figures 15 and 16 (see also Appendix 3). The structure of 85 is consistent with the mechanism shown previously in which Michael addition is directed to the si-re face of 36 (vide supra).



Fe-C1 1.961 Fe-P 2.194 C1-O 1.214 C1-C2 1.493

P-Fe-C1 89.31 Fe-C1-O 122.83 O-C1-Fe-P -67.09

O-C1-C2-C5 -32.53 O-C1-C2-C3 33.67

Figure 15. X-ray crystal structure and selected bond lengths (Å), angles and torsional angles (°) for RSS(SRR)-(C_5H_5)Fe(CO)(PPh_3)(COCH-CH_2-$CHCH_3$) 85. Selected protons are removed for clarity.

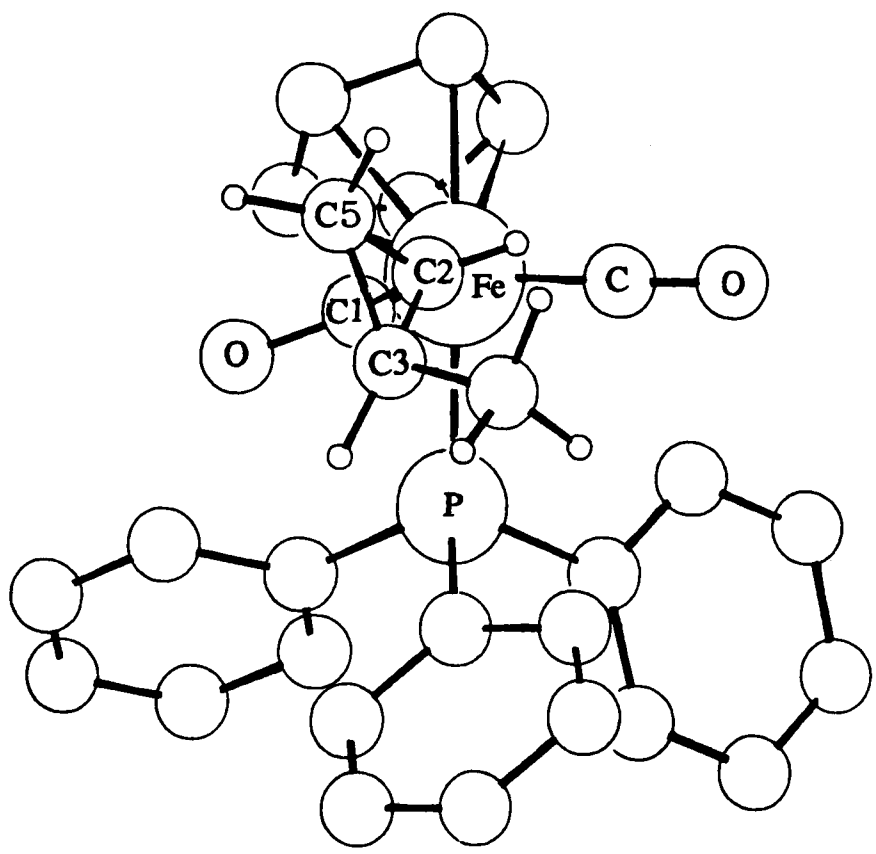
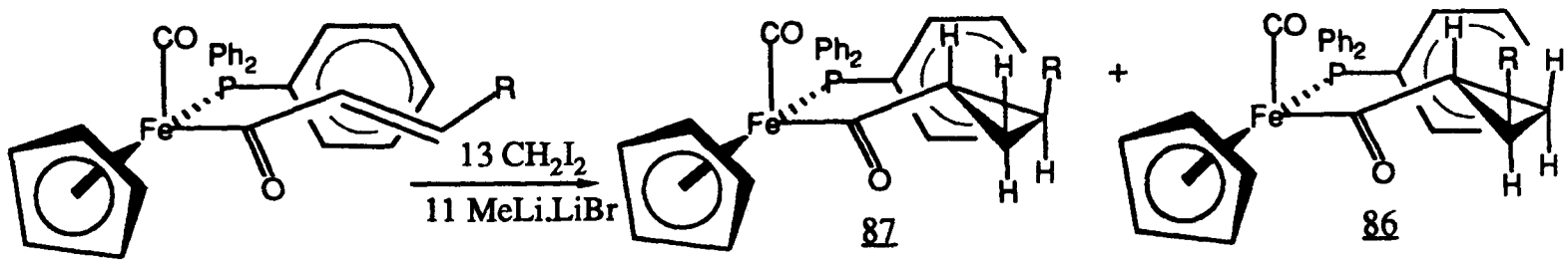


Figure 16. X-ray crystal structure for RSS(SRR)-C_5H_5)Fe(CO)(PPh_3)(COCH-CH_2-$CHCH_3$) 85 (view approximately along C2-Fe). Selected protons are removed for clarity.

The reaction was repeated on a range of other E-α,β-unsaturated iron acyl complexes and the results are shown in table 16. Each of the minor diastereoisomers 86 had been synthesised diastereoselectively in previous reactions (see table 7), and so diastereoisomeric ratios could be determined from the ^{1}H n.m.r. spectra.



R		Yield %	Ratio 87:86	Products
Me	36	85	>50:1	85:84
^{n}Pr	40	89	>50:1	89:88
^{n}Bu	42	82	>50:1	91:90
^{i}Pr	44	82	>50:1	93:92
^{t}Bu	46	22	>50:1	95:94

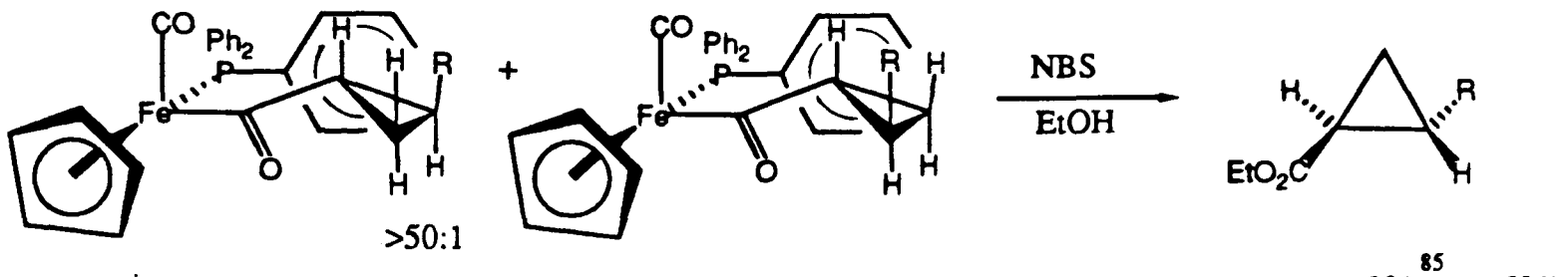
Table 16. The diastereoisomeric ratios 87:86 and overall yields in the reactions of E-(C_5H_5)Fe(CO)(PPh_3)(COCH=CHR) with iodomethyllithium.

In the following section the decomplexation of the acyl ligands is described.

4. Decomplexation of Trans-(C_5H_5)Fe(CO)(PPh_3)(COCH-CH_2-CHR)

N-bromosuccinimide was added to a solution of the diastereoisomeric complexes 93 and 92 (93:92 = >50:1) in dichloromethane:ethanol (1:1) as described previously (p. 63). On work up and chromatography a single cyclopropyl product was isolated, identified as the trans-isopropyl substituted cyclopropanecarboxylic

ester 201.[85] In a similar manner, the diastereoisomeric complexes 85 and 84 (85:84 = >50:1) were decomplexed. The results for this and the previous reaction are summarised below.

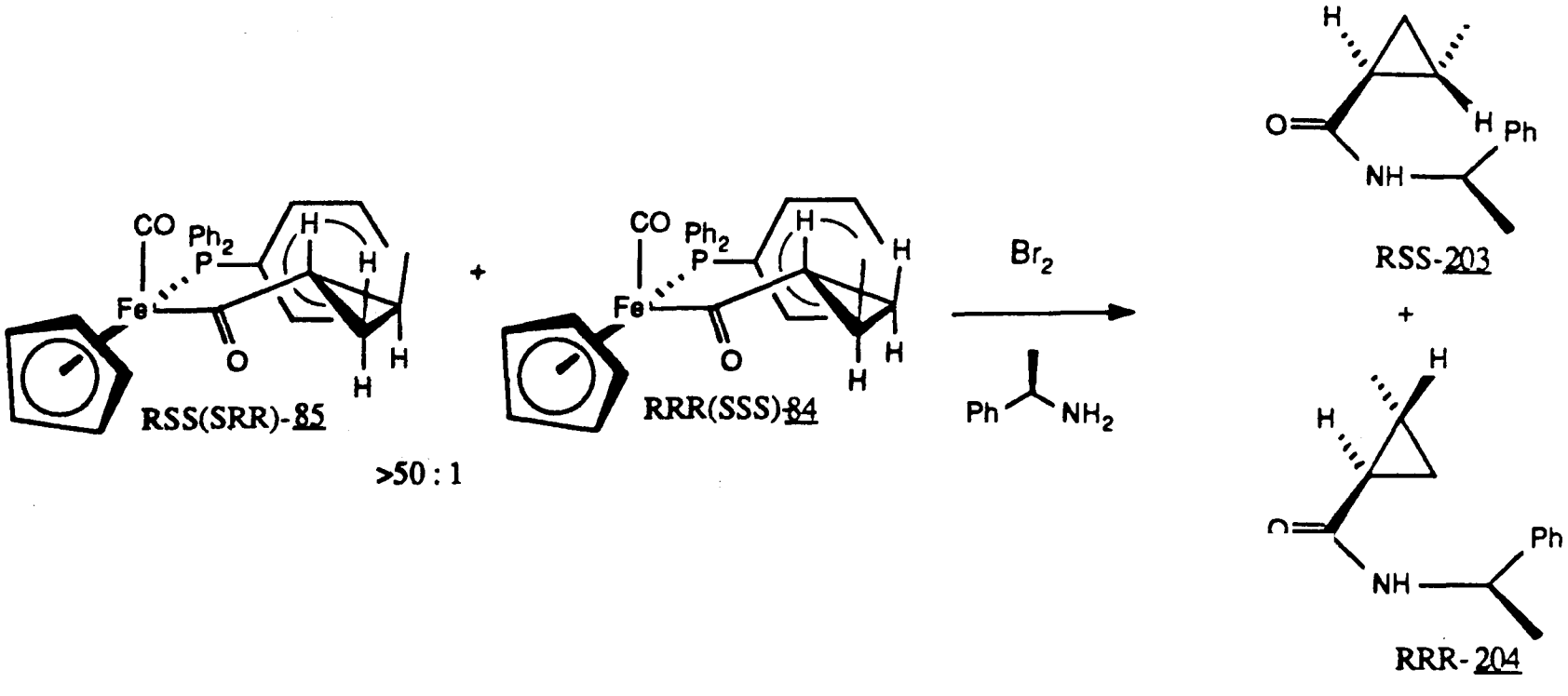


R = ^{i}Pr	93	92	201[85]	60%
R = Me	85	84	202[86]	50%

In each case none of the corresponding cis-isomers (p. 63) were detected, indicating that no epimerisation had occurred on decomplexation.

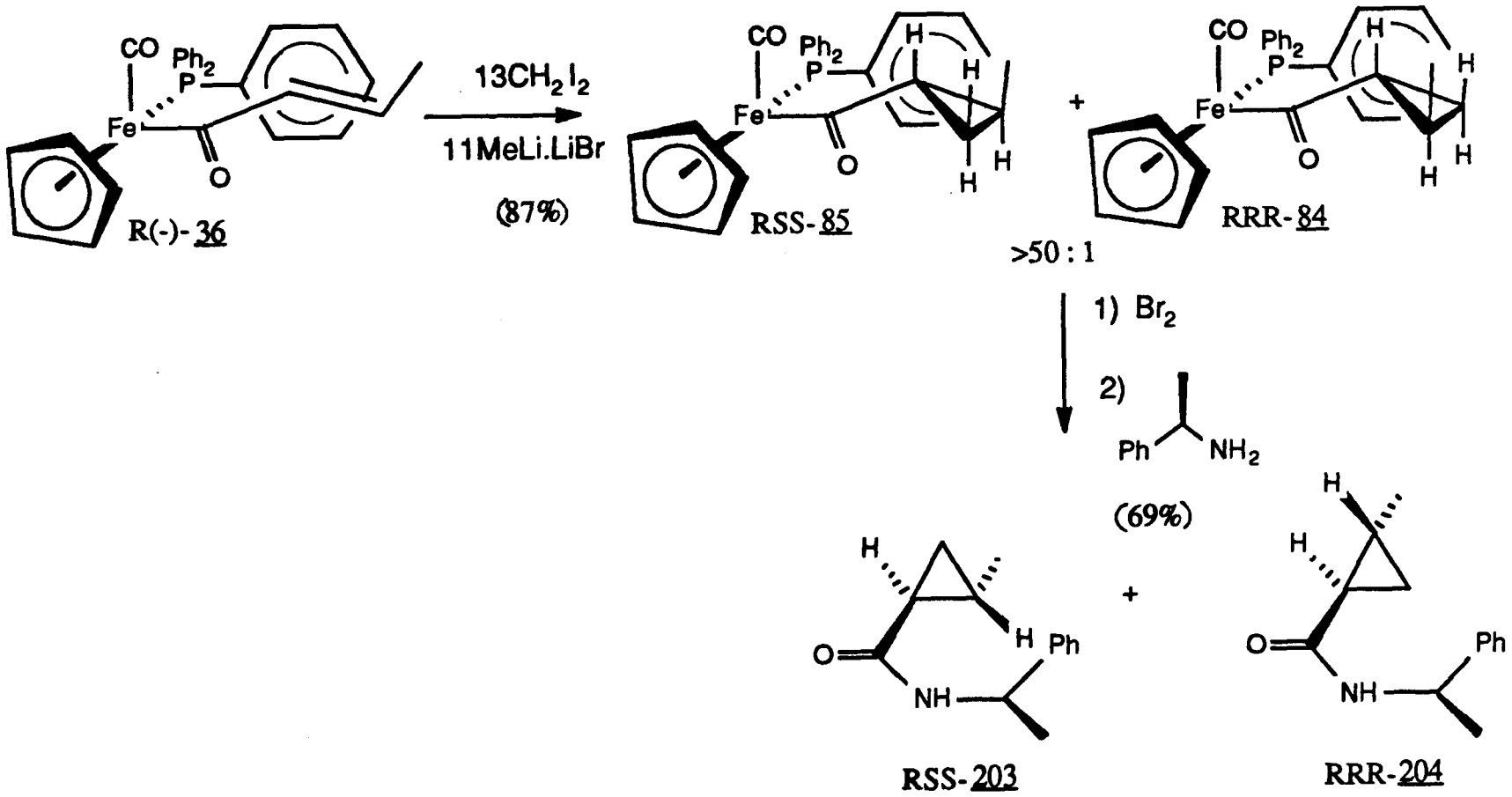
To demonstrate that this synthetic approach could be utilised in the asymmetric synthesis of cyclopropyl derivatives the reactions were repeated on homochiral R(-)-36 and S(+)-36. To determine the enantiomeric purity of the substituted cyclopropane ring in the decomplexed derivative, the decomplexations were performed in the presence of R(+)-2-phenylethylamine to give the corresponding diastereoisomeric amides (see p. 65).

Treatment of a solution of the racemates 85 and 84 (85:84 = >50:1) with bromine at -40°C, followed by addition of R(+)-2-phenylethylamine gave, on work up, a 1:1 mixture of the novel diastereoisomeric amides RSS-203 and RRR-204 (70%).



In the ^1H n.m.r. spectrum of 203 and 204 the majority of resonances overlapped or were coincidental. However, in chloroform-d_1:benzene-d_6 (3:1), the resonances for the methyl groups substituted on the cyclopropane ring could be clearly identified at δ 0.89 and 0.85, although assignment to either 203 or 204 was not possible at this time. The resonances were of equal intensity indicating no diastereoisomeric separation on work up. That the rates of the diastereoisomers formation were equal was demonstrated by repeating the reaction using one-half equivalent of amine. Again, a 1:1 mixture of diastereoisomers was isolated (12%).

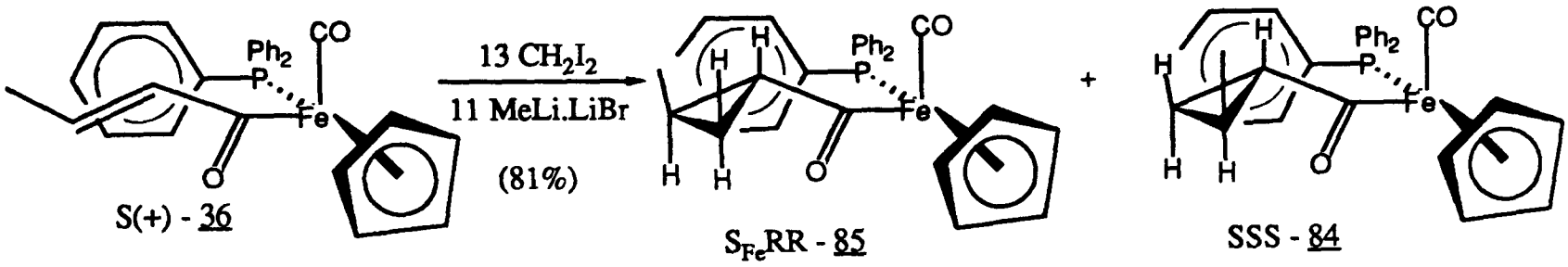
The reaction was repeated with R(-)-36 and the total synthetic scheme is outlined below.

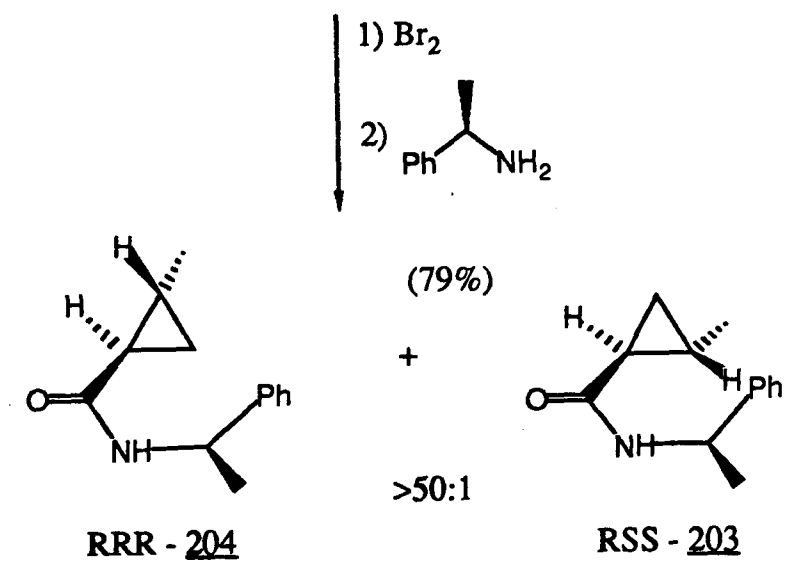


The ^1H n.m.r. spectrum (chloroform-d_1:benzene-d_6 (3:1)) of the product showed one major diastereoisomeric amide, consistent with highly diastereoselective formation of the preceding cyclopropyl iron acyl complex. In particular, resonances due to the methyl groups substituted on the cyclopropane ring, at δ 0.89

and 0.85 and of relative intensity >50:1, demonstrated that no loss of stereochemistry had occurred on decomplexation. The major diastereoisomer was assigned as RSS-203 by comparison with RSS-85.

The reaction was repeated with S(+)-36 and the results are outlined below.



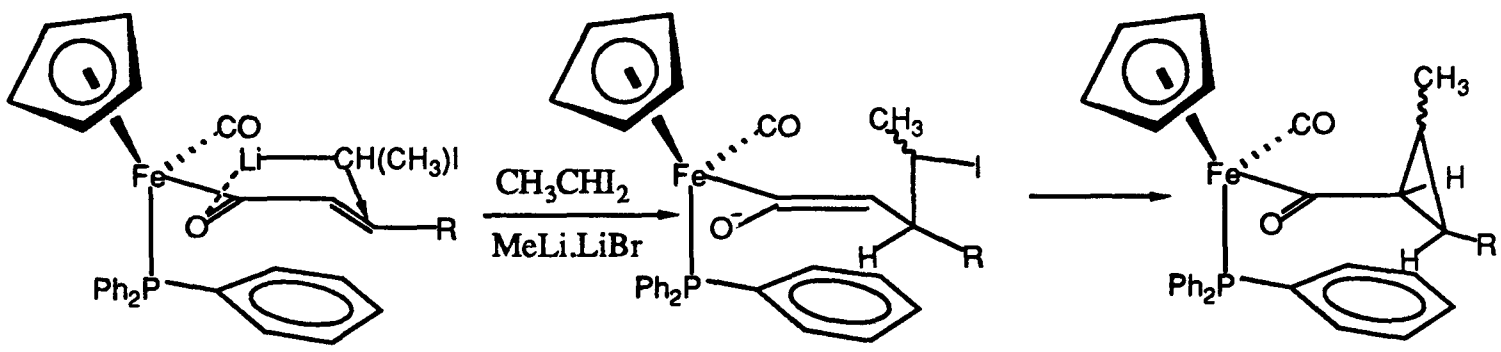


The ^1H n.m.r. spectrum (chloroform-d_1:benzene-d_6 (3:1)) was consistent with the highly diastereoselective synthesis of RRR-204. In particular, resonances assigned to the methyl substituents on the cyclopropane ring at δ 0.85 and 0.89 and with a relative intensity of >50:1, demonstrated that no loss of stereochemistry had occurred on decomplexation.

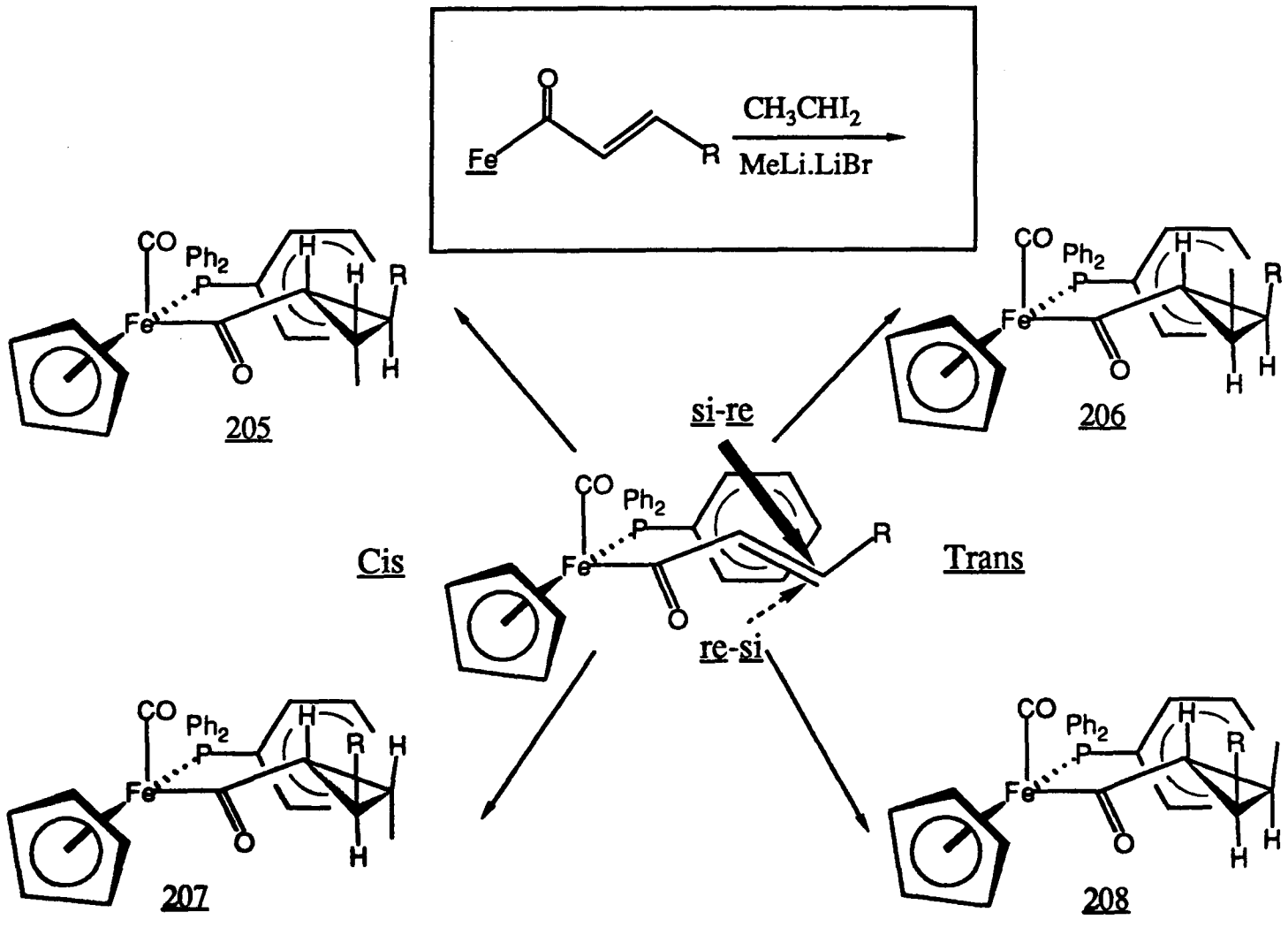
Having developed effective nucleophilic methylene transfer reagents, and demonstrated their use in the asymmetric synthesis of trans-substituted cyclopropyl derivatives, the syntheses of more highly substituted cyclopropyl derivatives were investigated.

B. Alkylidene Addition Reactions

The *in situ* generation, and subsequent reactions, of iodomethyllithium were described in the preceding section. It was anticipated that addition of methyllithium to ethylidene iodide in the presence of E-α,β-unsaturated iron acyl complexes might generate 1-iodoethyllithium which could then undergo Michael addition - ring closure reactions of the type described previously.

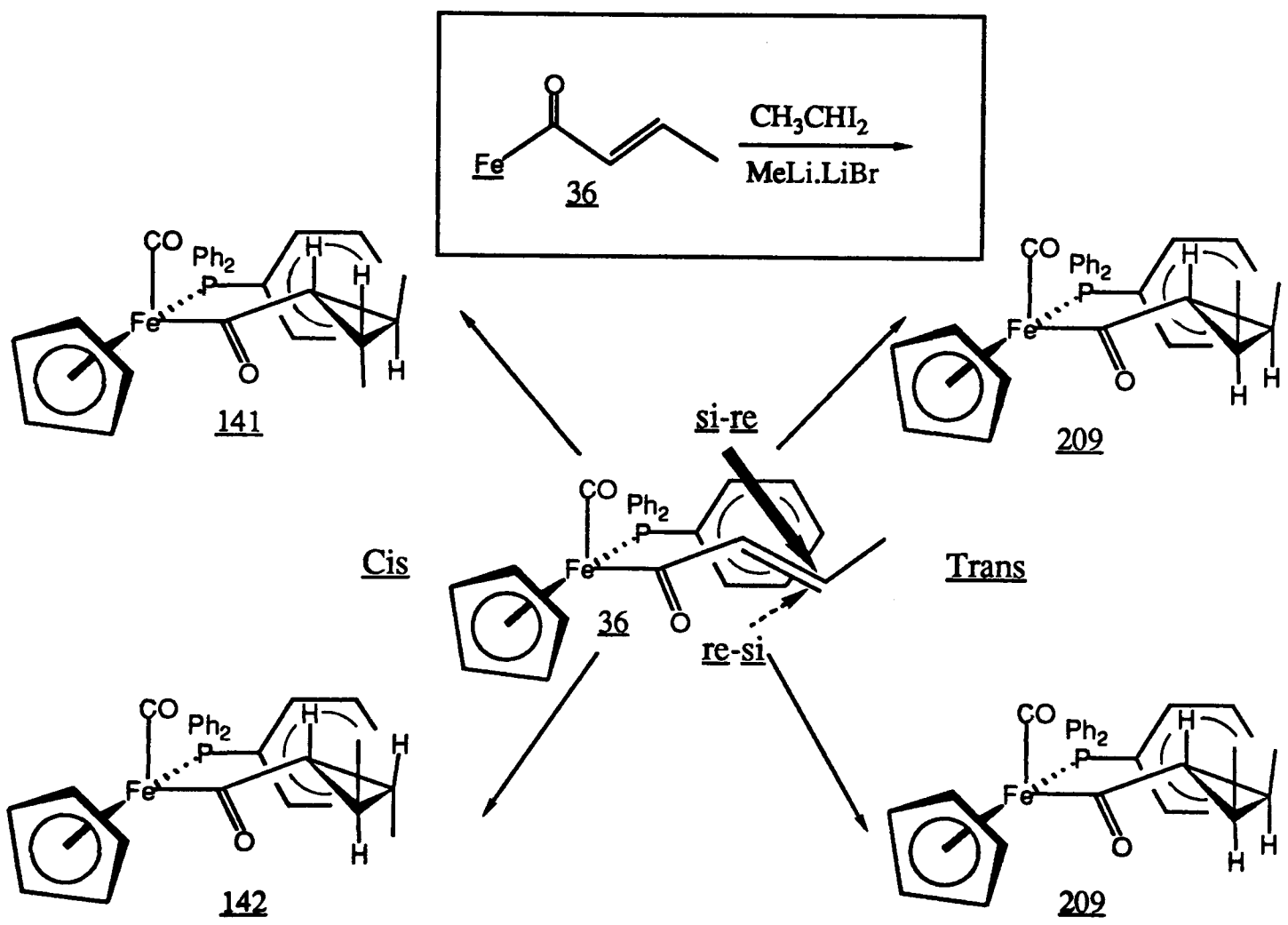


The diastereoselective reactions of Z-α,β-unsaturated iron acyl complexes with an electrophilic ethylidene transfer reagent were described previously (Chapter 3 section D). It was anticipated that the reaction of E-α,β-unsaturated iron acyl complexes with nucleophilic ethylidene transfer reagents would also occur diastereoselectively.



On the basis of previous results it would be anticipated that 205 and 206 would predominate, to the virtual exclusion of 207 and 208, due to directed Michael addition to the si-re face of the olefinic bond (vide supra). The cis/trans alignment of the methyl group, relative to the iron moiety, will be determined both by interactions with the chiral auxiliary and with the alkyl substituent on the olefinic bond.

Initially the reaction was studied with E-(C_5H_5)Fe(CO)(PPh_3)(COCH=$CHCH_3$) 36 in which up to three diastereoisomeric products might be synthesised.

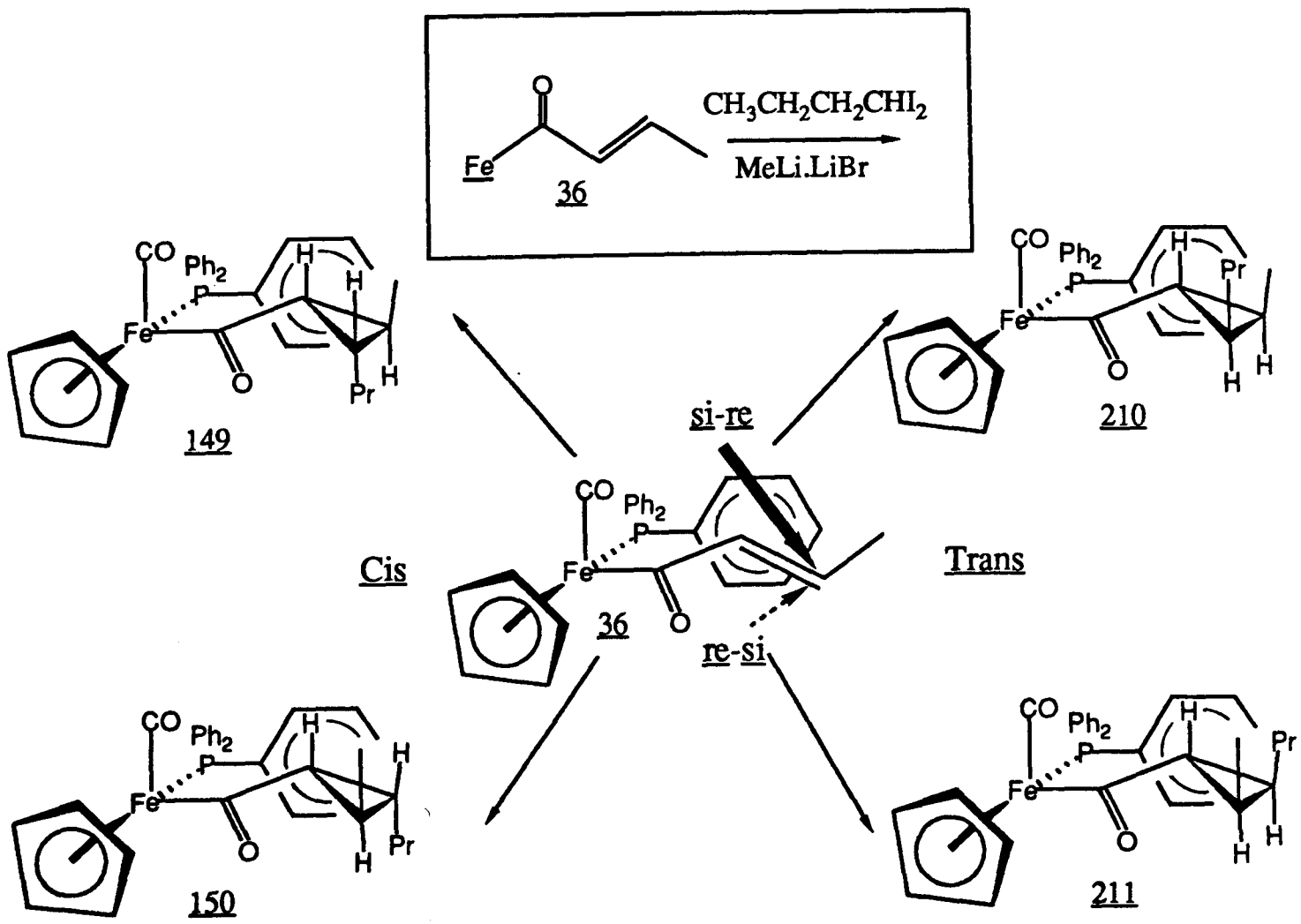


The complexes 141 and 142 had been synthesised previously (p.92). Attack on either face of the olefinic bond with the methyl group of ethylidene trans to the iron would give 209.

Ethylidene iodide and methyllithium were added consecutively to a solution of 36 in THF at -78°C in the same manner as described previously for methylene transfer reactions (p.122). On work up the major product band consisted of the chromatographically inseparable complexes 141 and 142 (47%). The ratio of 141:142 (>50:1) was consistent with directed Michael addition as

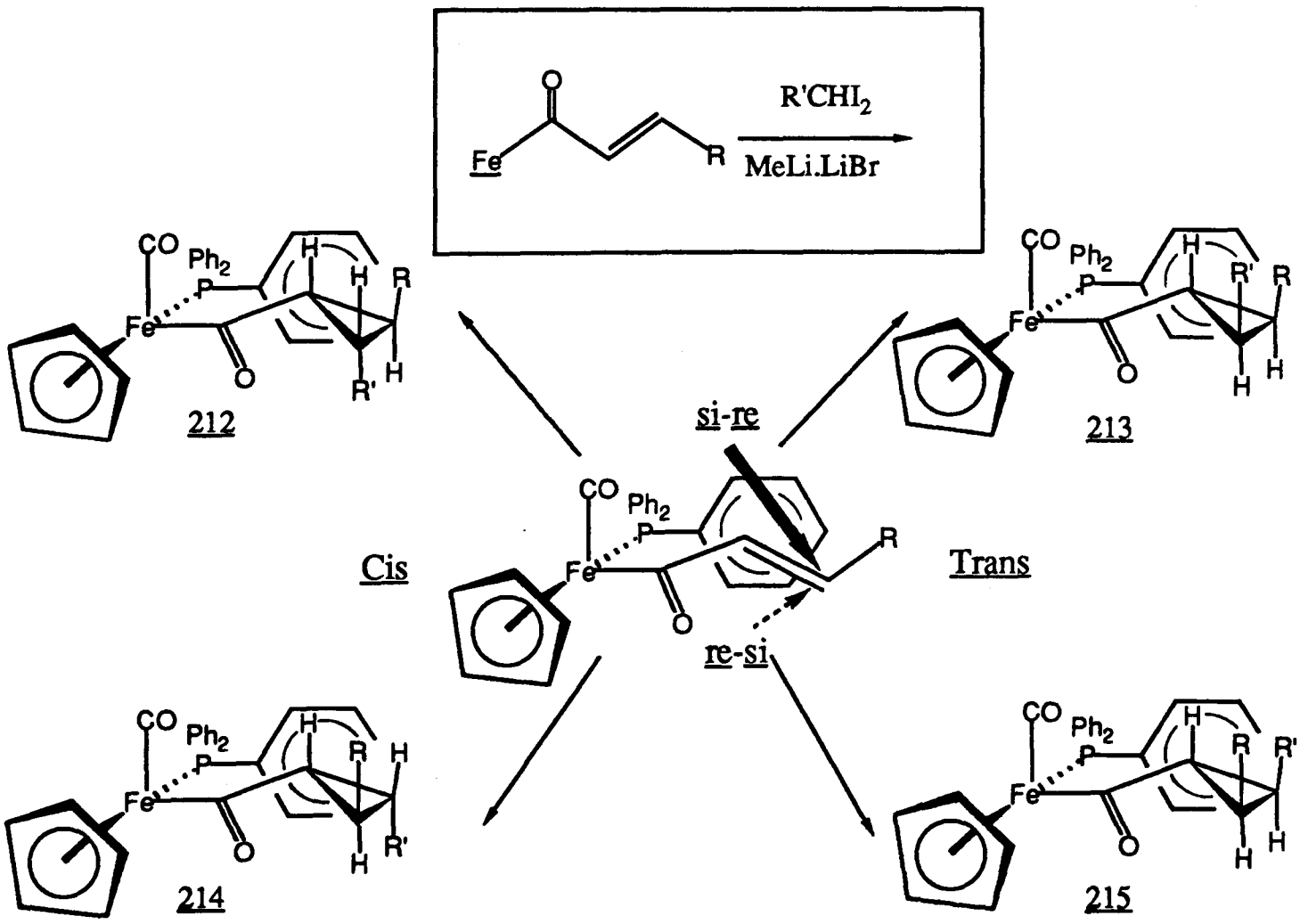
described previously. A minor product band was identified by ^1H n.m.r. spectroscopy and mass spectrometry as the complex 209 (22%). The coupling constants of the α-proton (COCH) in the ^1H n.m.r. spectrum, at δ 2.37, of 4.2 Hz each were consistent with the assigned trans stereochemistry.[81] In addition, starting material 36 (21%) was recovered. The results show that by a ratio of approximately 2:1, the methyl group from the ethylidene species is preferentially aligned cis to the iron moiety in the cyclopropyl complexes.

To determine whether other iodoalkyllithium species could be generated in situ, and would act as alkylidene transfer reagents, the reaction was repeated with isopropylidene iodide replacing ethylidene iodide. However, only starting material 36 was recovered from the reaction, indicating that no isopropylidene transfer had occurred. The reaction was then repeated with butylidene iodide (synthesised by the method described previously, p.89). Up to four diastereoisomeric products could result from butylidene addition to E-$(C_5H_5)Fe(CO)(PPh_3)(COCH{=}CHCH_3)$ 36.



The reaction was performed as described previously. After work up and chromatography, the major product band was identified as a diastereoisomeric mixture of the products 149 and 150 (68%) (149:150 = >50:1), a synthesis of which was reported previously (see table 14 p. 94). A second band consisted of the diastereoisomeric products 210 and 211 (25%) (210:211 = >50:1). Subsequently (see table 17) 210 and 211 were synthesised with reverse diastereoselectivity (211:210 = >50:1) which allowed the diastereoisomeric ratios in each reaction to be confirmed.

The reactions of 1-iodoethyllithium and 1-iodobutyllithium with other E-α,β-unsaturated iron acyl complexes were studied. The results are summarised in table 17, the diastereoisomeric ratios being determined from the ^{1}H n.m.r. or ^{31}P n.m.r. spectra and the stereochemistries of the major diastereoisomers by comparison with previous results.



R		R'	Yield %	Ratio Cis:Trans	Ratio Cis 212:214	Ratio Trans 213:215
Me	36	Me	69	2:1	>50:1 141:142	– [a] 209
^{n}Pr	40	Me	78	3:1	>50:1 216:217	>50:1 211:210
^{i}Pr	44	Me	60	8:1	– [b] 218:219	– [b] 220:221
Me	36	^{n}Pr	93	3:1	>50:1 149:150	>50:1 210:211
^{n}Pr	40	^{n}Pr	83	4:1	>50:1 222:223	– [a] 224
^{i}Pr	44	^{n}Pr	63	12:1	– [b] 225:226	– [b] 227:228

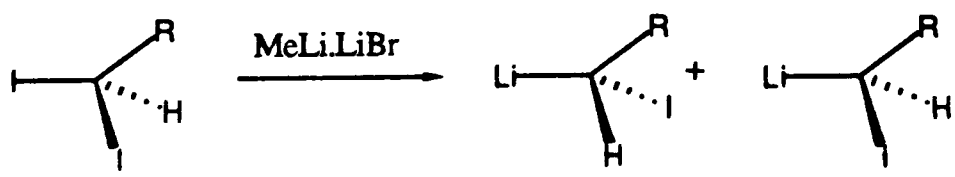
a) Only one diastereoisomeric product possible.

b) No trace of minor diastereoisomer.

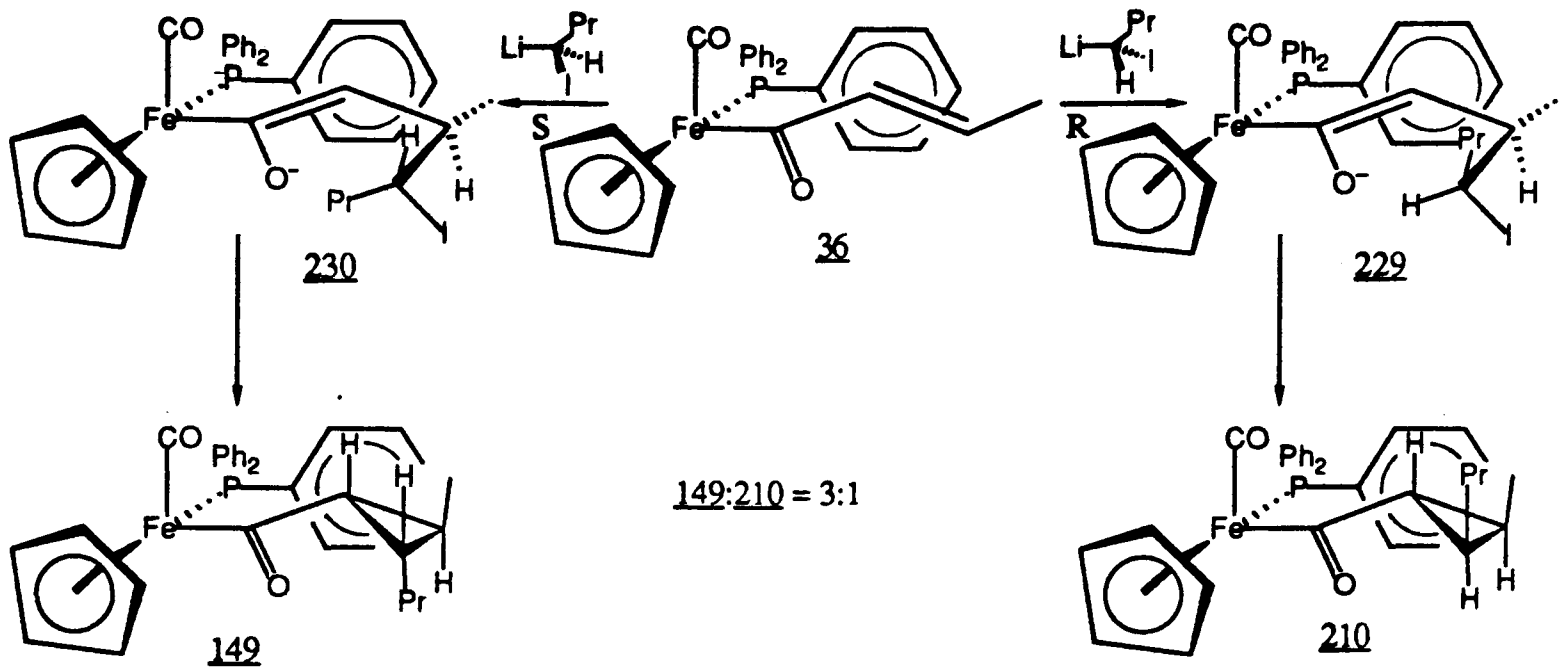
Table 17. The diastereoisomeric ratios 212+214:213+215, 212:214 and 213:215 and the overall yields in the reactions of E-(C_5H_5)Fe-(CO)(PPh_3)(COCH=CHR) with 1-iodoethyllithium and 1-iodopropyl-lithium.

The results show a trend in which the alkyl group from the iodoalkyllithium reagent increasingly favours cis-alignment to the iron moiety in the cyclopropyl product, as the size of the alkyl substituent on the olefinic bond in the starting material increases.

The iodoalkyllithium reagents are chiral, iodine/lithium exchange giving enantiomeric species.



Considering the reaction of 1-iodobutyllithium with E-(C_5H_5)-Fe(CO)(PPh_3)(COCH=$CHCH_3$) 36 then Michael addition of the R- or S-iodobutyllithium would give rise to enolates 229 and 230 respectively.

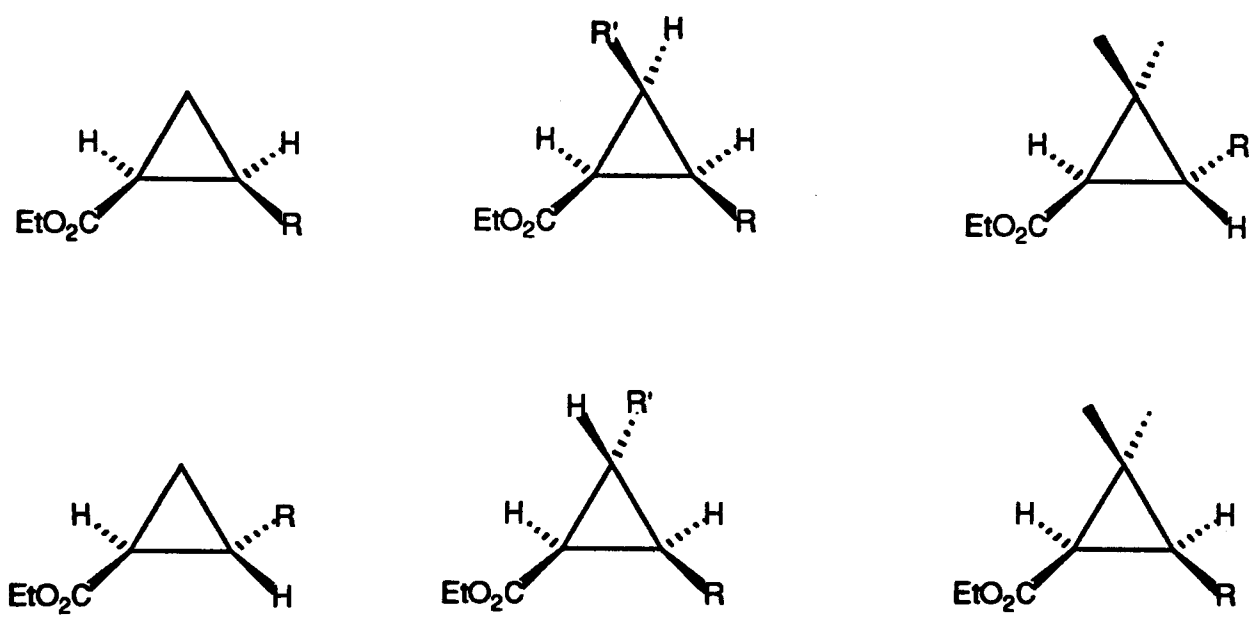


If ring closure occurs rapidly, and at the same rates, in these enolates then the product distribution of 149:210 (3:1) would reflect the relative populations of 230 and 229 respectively. This in turn would indicate a degree of chiral recognition between R-36 and S-1-iodobutyllithium. An alternative explanation might be that enolate 230 is kinetically favourable and/or its rate of ring closure is more rapid than that of enolate 229. Epimerisation, by iodide exchange, at the γ-carbon in 229 would then give the enolate 230 which would either be kinetically favoured, or would ring close before it could epimerise back to 229. In either case, 149 would be the major diastereoisomeric product. However, the origins and nature of the effects described above are unclear, and the relative importance of any or all of them cannot be determined at this time.

The generation of iodoalkyllithium reagents, and their subsequent reactions as nucleophilic alkylidene transfer reagents, have been demonstrated. Very high diastereofacial selectivity is observed, consistent with previous reports,[29,57] and the resulting diastereoisomeric products (cis/trans) are chromatographically separable giving essentially single diastereoisomers. Hence further diastereoselective and enantioselective routes to highly substituted cyclopropyl derivatives have been developed.

SUMMARY

The aim of this thesis was to utilise the strong stereochemical influence of the chiral auxiliary $(C_5H_5)Fe(CO)(PPh_3)$ to devise stereoselective syntheses of cyclopropyl derivatives. The highly diastereoselective syntheses of a wide range of substituted cyclopropanecarboxylic esters have been achieved, the range of accessible structures being shown below.



In addition, by the use of homochiral iron acyl complexes the asymmetric synthesis of the cyclopropyl derivatives was realised with good control over the absolute, and relative, stereochemistry about the cyclopropane ring.

EXPERIMENTAL

General Experimental Techniques

All experiments and purifications were carried out under an atmosphere of nitrogen (except when otherwise stated), all reaction solvents were deoxygenated (except when otherwise stated) and standard vacuum line and Schlenk tube techniques were used throughout.[122] Solvents were removed under reduced pressure.

Solvents. THF was distilled from sodium benzophenone ketyl under nitrogen. Dichloromethane was distilled from calcium hydride under nitrogen. Ethanol was distilled before use in decomplexation reactions. Petroleum ether refers to that fraction of light petroleum boiling between 40°C and 60°C and hexane refers to that fraction boiling between 67°C and 70°C.

Reagents. n-Butyllithium was used as a 1.6M solution in hexane. Methyllithium, as a complex with lithium bromide, was used as a 1.6M solution in diethyl ether. Diethylzinc was used either as a 2.5M or a 1.1M solution in toluene. Triethylaluminium was used as a 1.0M solution in hexanes. Diethylaluminium chloride was used as a 1.8M solution in toluene. Other Lewis acids were dried under vacuum prior to use. All aldehydes were dried over molecular sieves (4Å) prior to use. All other reagents were used as supplied.

Chromatography was performed on grade I alumina or grade I alumina deactivated with 10% by weight of water (grade V), under an atmosphere of nitrogen. In the cases where diastereoselectivities were to be determined, all coloured bands were collected. Flash chromatography was performed on silica gel (15 μm) according to the procedure of Still et al.[123]

Infrared spectra were obtained as solutions in dichloromethane on a Perkin-Elmer 297 instrument (calibrated against polystyrene 1601 cm^{-1}).

N.m.r. spectra. ^{1}H n.m.r. spectra were recorded on a Bruker WH 300 (300.13 MHz) spectrometer in $CDCl_3$ solutions unless otherwise stated. ^{13}C n.m.r. spectra were recorded on a Bruker AM 250 (62.90 MHz) spectrometer in $CDCl_3$ solutions. Both ^{1}H and ^{13}C n.m.r. spectra were referenced to tetramethylsilane using internal solvent peaks. ^{31}P n.m.r. spectra were recorded on a Bruker AM 250 (101.26 MHz) spectrometer in $CDCl_3$ solutions and were referenced to external 85% orthophosphoric acid. All chemical shifts are quoted as δ values.

Mass spectra were obtained by Dr. R.T. Aplin on a V.G. Micromass ZAB 1F instrument, using field desorption techniques unless otherwise stated.

Elemental microanalyses were carried out by Mrs. V. Lamburn (Oxford).

Preparation of $(C_5H_5)Fe(CO)(PPh_3)(COCH_3)$ 22.[39,40]

$[(C_5H_5)Fe(CO)_2]_2$ 24 (100g, 0.282mol) was added to 2% sodium amalgam (250g) in THF (750ml) and stirred (12h; 20°C). The resulting brown solution of the anion $[(C_5H_5)Fe(CO)_2]^-Na^+$ 25 was cooled to -78°C and methyl iodide (45ml, 0.725mol) in THF (50ml) was added over 45 minutes. The solution was stirred (12h; 20°C), and then the solvent removed under reduced pressure to give a brown solid, which was extracted with petroleum ether and filtered through celite. Removal of the solvent under reduced pressure gave $(C_5H_5)Fe(CO)_2(CH_3)$ as a red oil, which was dissolved in acetonitrile (500ml) and added to triphenylphosphine (148g, 0.565mol).

The solution was heated under reflux (44h), and the solvent was then removed under reduced pressure. The resulting brown solid was dissolved in dichloromethane and filtered through alumina (grade V) to give an orange solution. Evaporation of the solvent under reduced pressure gave the complex 22 as an orange, crystalline solid (154g, 60%); ν_{max} 1920 vs (C≡O), 1595 s (C=O) cm^{-1}; ^1H n.m.r. δ 7.6-7.3 (15H, m, Ph), 4.45 (5H, d, J_{PH} 0.9 Hz, C_5H_5), 2.32 (3H, s, CH_3). [Lit.,[40b] ^1H n.m.r. δ 7.59 (15H, m, Ph), 4.62 (5H, s, C_5H_5), 2.52 (3H, s, CH_3)]

Preparation of (±)-$(C_5H_5)Fe(CO)(PPh_3)(COCH_2Si(CH_3)_3)$ 34.[36,63]

Butyllithium (13.2ml, 33mmol) was added dropwise to a solution of (±)-$(C_5H_5)Fe(CO)(PPh_3)(COCH_3)$ 22 (9.7g, 21.4mmol) in THF (320ml) at -78°C giving a dark red solution of enolate 23. After stirring (-78°C; 1h), trimethylsilyl chloride (6.6ml, 52.1 mmol, freshly distilled from CaH_2) was added in one portion and the mixture stirred (-78°C; 1h) and then warmed to room temperature over 2h. Removal of the solvent gave a red oil which was dissolved

in dichloromethane (20ml) and filtered through alumina (grade I) eluting with diethyl ether. Removal of solvent gave $(C_5H_5)Fe(CO)(PPh_3)(COCH_2Si(CH_3)_3)$ 34 as an orange solid. On crystallisation from dichloromethane/hexane, orange crystals were formed (10.3g, 92%); ν_{max} 1915 vs (C≡O), 1580 s (C=O) cm^{-1}; ^1H n.m.r. δ 7.6-7.3 (15H, m, Ph), 4.42 (5H, d, J_{PH} 1.0 Hz, C_5H_5), 2.76 and 1.74 (2H, AB system, J_{AB} 11.5 Hz, CH_2), 0.02 (9H, s, $(CH_3)_3$); m/z 526(M^+) [Lit.[34], ^1H n.m.r. δ 7.6-7.3, (15H, m, Ph), 4.43 (5H, d, J_{PH} 1.1 Hz, C_5H_5), 2.76 and 1.73 (2H, AB system, J_{AB} 11.4 Hz, CH_2), 0.01 (9H, s, $(CH_3)_3$)].

The Peterson reaction between (±)-$(C_5H_5)Fe(CO)(PPh_3)(COCH_2Si(CH_3)_3)$ 34 and aldehydes.[59,63]

Typically, butyllithium (1.4ml, 2.28mmol) was added to a solution of $(C_5H_5)Fe(CO)(PPh_3)(COCH_2Si(CH_3)_3)$ 34 (1g, 1.90mmol) in THF (10ml) at -78°C giving a dark red solution. After stirring (-78°C; 1h) the aldehyde (2.7mmol, freshly distilled or dried) was added and the mixture was stirred (-78°C; 1h) and then warmed to room temperature over 2h. Removal of the solvent gave an orange oil which was dissolved in dichloromethane (10ml) and filtered through alumina (grade I), eluting with dichloromethane:ethyl acetate (4:1).

The overall yields and selectivities (E:Z) for the reactions are summarised in table 1 (page 21). The E-and Z-isomers were separated by chromatography on alumina (grade I), the Z-isomer eluting first in each case. The Z-isomers were crystallised to orange crystals from dichloromethane/hexane. The E-isomers were all oils, except for E-$(C_5H_5)Fe(CO)(PPh_3)(COCH=CHCH_3)$ 36 and E-$(C_5H_5)Fe(CO)(PPh_3)(COCH=CHCH=C(CH_3)_2)$ 50 which gave orange crystals

from dichloromethane/hexane.

Z-$(C_5H_5)Fe(CO)(PPh_3)(COCH=CHCH_3)$ 37.[63] Elution with diethyl ether gave complex 37 (28%); $\nu_{max.}$ 1915 vs (C≡O), 1610 s and 1570 s (C=O) cm^{-1}; ^1H n.m.r. δ 7.6-7.3 (15H, m, Ph), 6.56 (1H, dq, J_{cis} 11.2 Hz, $J_{1,3}$ 1.8 Hz, COCH), 4.74 (1H, dq, J_{cis} 11.1 Hz, $J_{1,2}$ 7.1 Hz, C$\underline{H}CH_3$), 4.43 (5H, d, J_{PH} 0.9 Hz, C_5H_5), 1.33 (3H, dd, $J_{1,2}$ 7.0 Hz, $J_{1,3}$ 1.8 Hz, CH_3); m/z 480 (M^+) [Lit.,[63] ^1H n.m.r. δ 7.5-7.3 (15H, m, Ph), 6.57 (1H, dq, J_{cis} 11.2 Hz, $J_{1,3}$ 1.7 Hz, COCH), 4.73 (1H, dq, J_{cis} 11.2 Hz, $J_{1,2}$ 7.0 Hz, C$\underline{H}CH_3$), 4.43 (5H, d, J_{PH} 1.3 Hz, C_5H_5), 1.33 (3H, dd, $J_{1,2}$ 7.0 Hz, $J_{1,3}$ 1.7 Hz, CH_3)].

E-$(C_5H_5)Fe(CO)(PPh_3)(COCH=CHCH_3)$ 36.[63] Elution with diethyl ether:ethyl acetate 4:1 gave complex 36 (52%); $\nu_{max.}$ 1920 vs (C≡O), 1615 s and 1575 s (C=O) cm^{-1}; ^1H n.m.r. δ 7.6-7.3 (15H, m, Ph), 6.51(1H, d, J_{trans} 15.0 Hz, COCH),5.49 (1H, dq, J_{trans} 15.0 Hz, $J_{1,2}$ 6.8 Hz, C$\underline{H}CH_3$), 4.42 (5H, d, J_{PH} 0.9 Hz, C_5H_5), 1.58 (3H, dd, $J_{1,2}$ 6.8 Hz, $J_{1,3}$ 1.4 Hz, CH_3); m/z 480 (M^+) [Lit.,[63] ^1H n.m.r. δ 7.5-7.3 (15H, m, Ph), 6.50 (1H, d, J_{trans} 15.0 Hz, COCH), 5.50 (1H, dq, J_{trans} 15.0 Hz, $J_{1,2}$ 6.8 Hz, C$\underline{H}CH_3$), 4.44 (5H, d, J_{PH} 1.0 Hz, C_5H_5), 1.57 (3H, dd, $J_{1,2}$ 6.8 Hz, $J_{1,3}$ 1.6 Hz, CH_3)].

Z-$(C_5H_5)Fe(CO)(PPh_3)(COCH=CHCH_2CH_3)$ 39.[63] Elution with diethyl ether gave complex 39 (20%); $\nu_{max.}$ 1910 vs (C≡O), 1615 s and 1570 s (C=O) cm^{-1}; ^1H n.m.r. δ 7.6-7.3 (15H, m, Ph), 6.50 (1H, dt, J_{cis} 11.1 Hz, $J_{1,3}$ 1.5 Hz, COCH), 4.60 (1H, dt, J_{cis} 11.1 Hz, $J_{1,2}$ 7.1 Hz, C$\underline{H}CH_2$), 4.42 (5H, d, J_{PH} 1.0 Hz, C_5H_5), 1.92-1.59 (2H, m, CH_2), 0.78 (3H, t, $J_{1,2}$ 7.0 Hz, CH_3); m/z 494 (M^+) [Lit.,[63] ^1H n.m.r. δ 7.6-7.3 (15H, m, Ph), 6.49 (1H, dt, J_{cis} 11.2 Hz, $J_{1,3}$ 1.5 Hz, COCH), 4.59 (1H, dt, J_{cis} 11.2 Hz, $J_{1,2}$ 7.0 Hz, C$\underline{H}CH_2$), 4.41

(5H, d, J_{PH} 1.0 Hz, C_5H_5), 1.92-1.59 (2H, m, CH_2), 0.78 (3H, t, $J_{1,2}$ 7.0 Hz, CH_3)].

E-$(C_5H_5)Fe(CO)(PPh_3)(COCH{=}CHCH_2CH_3)$ 38.[63] Elution with diethyl ether:ethyl acetate (4:1) gave complex 38 (40%); ν_{max} 1912 vs (C≡O), 1580 s and 1555 s (C=O) cm^{-1}; ^1H n.m.r. δ 7.6-7.3 (15H, m, Ph), 6.45 (1H, d, J_{trans} 15.2 Hz, COCH), 5.49 (1H, dt, J_{trans} 15.2 Hz, $J_{1,2}$ 6.6 Hz, $C\underline{H}CH_2$), 4.44 (5H, d, J_{PH} 1.3 Hz, C_5H_5), 1.97-1.88 (2H, m, CH_2), 0.95 (3H, t, $J_{1,2}$ 7.2 Hz, CH_3); m/z 494 (M^+) [Lit.,[63] ^1H n.m.r. δ 7.5-7.3 (15H, m, Ph), 6.44 (1H, dt, J_{trans} 15.1 Hz, $J_{1,3}$ 1.4 Hz, COCH), 5.49 (1H, dt, J_{trans} 15.1 Hz, $J_{1,2}$ 6.5 Hz, $C\underline{H}CH_2$), 4.43 (5H, d, J_{PH} 1.0 Hz, C_5H_5), 1.97-1.87 (2H, m, CH_2), 0.94 (3H, t, $J_{1,2}$ 7.5 Hz, CH_3)].

Z-$(C_5H_5)Fe(CO)(PPh_3)(COCH{=}CHCH_2CH_2CH_3)$ 41.[59] Elution with diethyl ether gave complex 41 (32%); $\nu_{max.}$ 1915 vs (C≡O), 1615 s and 1560 s (C=O) cm^{-1}; ^1H n.m.r. δ 7.6-7.3 (15H, m, Ph), 6.51 (1H, dt, J_{cis} 11.2 Hz, $J_{1,3}$ 1.5 Hz, COCH), 4.61 (1H, dt, J_{cis} 11.2 Hz, $J_{1,2}$ 7.0 Hz, $C\underline{H}CH_2$), 4.42 (5H, d, J_{PH} 1.0 Hz, C_5H_5), 1.87-1.56 (2H, m, $CHC\underline{H}_2$), 1.23-1.18 (2H, m, $C\underline{H}_2CH_3$), 0.79 (3H, t, $J_{1,2}$ 7.4 Hz, CH_3); m/z 508 (M^+) [Lit.,[59] ^1H n.m.r. δ 7.6-7.3 (15H, m, Ph), 6.52 (1H, d, J_{cis} 11.2 Hz, COCH), 4.62 (1H, dt, J_{cis} 11.2 Hz, $J_{1,2}$ 7.0 Hz, $C\underline{H}CH_2$), 4.42 (5H, d, J_{PH} 1.2 Hz, C_5H_5), 1.9-1.6 (2H, m, $CHC\underline{H}_2$), 1.20 (2H, m, $C\underline{H}_2CH_3$), 0.79 (3H, t, $J_{1,2}$ 7.4 Hz, CH_3).

E-$(C_5H_5)Fe(CO)(PPh_3)(COCH{=}CHCH_2CH_2CH_3)$ 40.[59] Elution with diethyl ether:ethyl acetate (4:1) gave complex 40 (45%); $\nu_{max.}$ 1718 vs (C≡O), 1625 s and 1570 s (C=O) cm^{-1}; ^1H n.m.r. δ 7.6-7.3 (15H, m, Ph), 6.48 (1H, dt, J_{trans} 15.1 Hz, $J_{1,3}$ 1.2 Hz, COCH), 5.49 (1H, dt, J_{trans} 15.1 Hz, $J_{1,2}$ 7.1 Hz, $C\underline{H}CH_2$), 4.44 (5H, d, J_{PH} 1.0 Hz, C_5H_5), 1.94-1.86 (2H, m, $CHC\underline{H}_2$), 1.42-1.34 (2H, m, $C\underline{H}_2CH_3$), 0.89 (3H, t, $J_{1,2}$ 7.3 Hz, CH_3); m/z 508 (M^+) [Lit.,[59] ^1H

n.m.r. δ 7.6-7.3 (15H, m, Ph), 6.47 (1H, d, J_{trans} 15.1 Hz, COCH), 5.49 (1H, dt, J_{trans} 15.1 Hz, $J_{1,2}$ 6.6 Hz, C<u>H</u>CH_2), 4.44 (5H, d, J_{PH} 1.2 Hz, C_5H_5), 1.89 (2H, m, $CHC\underline{H}_2$), 1.37 (2H, m, $C\underline{H}_2CH_3$), 0.88 (3H, t, $J_{1,2}$ 7.1 Hz, CH_3)].

<u>Z-(C_5H_5)Fe(CO)(PPh_3)(COCH=$CHCH_2CH_2CH_2CH_3$) 43.</u>[63] Elution with diethyl ether gave complex <u>43</u> (33%); $\nu_{max.}$ 1910 vs (C≡O), 1605 s and 1570 s (C=O) cm^{-1}; ^1H n.m.r. δ 7.6-7.3 (15H, m, Ph), 6.50 (1H, dt, J_{cis} 11.2 Hz, $J_{1,3}$ 1.6 Hz, COCH), 4.61 (1H, dt, J_{cis} 11.2 Hz, $J_{1,2}$ 7.1 Hz, COCHC<u>H</u>), 4.41 (5H, brs, C_5H_5), 1.87-1.66 (2H, m, $CHC\underline{H}_2$), 1.22-1.11 (4H, m, $C\underline{H}_2C\underline{H}_2CH_3$), 0.83 (3H, t, $J_{1,2}$ 6.7 Hz, CH_3); <u>m/z</u> 522 (M^+) [Lit.,[63] ^1H n.m.r. δ 7.6-7.3 (15H, m, Ph), 6.50 (1H, dt, J_{cis} 11.2 Hz, $J_{1,3}$ 1.7 Hz, COCH), 4.61 (1H, dt, J_{cis} 11.2 Hz, $J_{1,2}$ 7.1 Hz, COCHC<u>H</u>), 4.42 (5H, d, J_{PH} 1.1 Hz, C_5H_5), 1.90-1.63 (2H, m, $CHC\underline{H}_2$), 1.22-1.11 (4H, m, $C\underline{H}_2C\underline{H}_2CH_3$), 0.83 (3H, t, $J_{1,2}$ 6.7 Hz, CH_3)].

<u>E-(C_5H_5)Fe(CO)(PPh_3)(COCH=$CHCH_2CH_2CH_2CH_3$)42.</u>[63] Elution with dichloromethane:ethyl acetate (9:1) gave complex <u>42</u> (50%); $\nu_{max.}$ 1910 vs (C≡O), 1610 s (C=O) cm^{-1}; ^1H n.m.r. δ 7.6-7.3 (15H, m, Ph), 6.46 (1H, d, J_{trans} 15.1 Hz, COCH), 5.50 (1H, dt, J_{trans} 15.1 Hz, $J_{1,2}$ 7.6 Hz, COCHC<u>H</u>), 4.44 (5H, brs, C_5H_5), 1.94-1.88 (2H, m, $CHC\underline{H}_2$), 1.33-1.27 (4H, m, $C\underline{H}_2C\underline{H}_2CH_3$), 0.89 (3H, t, $J_{1,2}$ 7.0 Hz, CH_3); <u>m/z</u> 522 (M^+) [Lit.,[63] ^1H n.m.r. δ 7.6-7.3 (15H, m, Ph), 6.48 (1H, d, J_{trans} 15.2 Hz, COCH), 5.51 (1H, dt, J_{trans} 15.2 Hz, $J_{1,2}$ 7.0 Hz, C<u>H</u>CH_2), 4.44 (5H, d, J_{PH} 1.2 Hz, C_5H_5), 1.97-1.90 (2H, m, $CHC\underline{H}_2$) 1.36-1.28 (4H, m, $C\underline{H}_2C\underline{H}_2CH_3$), 0.90 (3H, t, $J_{1,2}$ 7.1 Hz, CH_3)].

<u>Z-(C_5H_5)Fe(CO)(PPh_3)(COCH=$CHCH(CH_3)_2$) 45.</u>[59] Elution with diethyl ether gave complex <u>45</u> (40%); $\nu_{max.}$ 1920 vs (C≡O), 1615 s and 1580 s (C=O) cm^{-1}; ^1H n.m.r. δ 7.6-7.3 (15H, m, Ph), 6.35 (1H,

d, J_{cis} 11.2 Hz, COCH), 4.42 (5H, d, J_{PH} 1.2 Hz, C_5H_5), 4.41 (1H, dd, J_{cis} 11.2 Hz, $J_{1,2}$ 9.2 Hz, COCHC<u>H</u>), 2.43 (1H, m, C<u>H</u>$(CH_3)_2$), 0.82 (3H, d, $J_{1,2}$ 6.6 Hz, CH_3), 0.72 (3H, d, $J_{1,2}$ 6.5 Hz, CH_3); <u>m/z</u> 508 (M^+) [Lit.,[59] ^{1}H n.m.r. δ 7.6-7.3 (15H, m, Ph), 6.37 (1H, d, J_{cis} 11.3 Hz, COCH), 4.41 (5H, d, J_{PH} 1.2 Hz, C_5H_5), 4.41 (1H, dd, J_{cis} 11.3 Hz, $J_{1,2}$ 9.6 Hz, COCHC<u>H</u>), 2.44 (1H, m, C<u>H</u>$(CH_3)_2$), 0.82 (3H, d, $J_{1,2}$ 6.6 Hz, CH_3), 0.72 (3H, d, $J_{1,2}$ 6.6 Hz, CH_3)].

<u>E-(C_5H_5)Fe(CO)(PPh_3)(COCH=CHCH$(CH_3)_2$) 44.</u>[59] Elution with dichloromethane:ethyl acetate (9:1) gave complex <u>44</u> (52%); $\nu_{max.}$ 1920 vs (C≡O), 1620 s and 1580 s (C=O) cm^{-1}; ^{1}H n.m.r. δ 7.6-7.3 (15H, m, Ph), 6.42 (1H, dd, J_{trans} 15.2 Hz, $J_{1,3}$ 1.3 Hz, COCH), 5.41 (1H, dd, J_{trans} 15.2 Hz, $J_{1,2}$ 6.7 Hz, COCHC<u>H</u>), 4.44 (5H, d, J_{PH} 0.9 Hz, C_5H_5), 2.15 (1H, m, C<u>H</u>$(CH_3)_2$), 0.94 (6H, d, $J_{1,2}$ 6.7 Hz, $(CH_3)_2$); <u>m/z</u> 508 (M^+) [Lit.,[59] ^{1}H n.m.r. δ 7.6-7.3 (15H, m, Ph), 6.42 (1H, dd, J_{trans} 15.3 Hz, $J_{1,3}$ 1.3 Hz, COCH), 5.40 (1H, dd, J_{trans} 15.3 Hz, $J_{1,2}$ 6.7 Hz, COCHC<u>H</u>), 4.44 (5H, d, J_{PH} 1.2 Hz, C_5H_5), 2.15 (1H, m, C<u>H</u>$(CH_3)_2$), 0.94 (6H, d, $J_{1,2}$ 6.7 Hz, $(CH_3)_2$)].

<u>E-(C_5H_5)Fe(CO)(PPh_3)(COCH=CHC$(CH_3)_3$) 46.</u>[63] Elution with dichloromethane:ethyl acetate (9:1) gave complex <u>46</u> (50%); $\nu_{max.}$ 1910 vs (C≡O), 1610 s and 1560 s (C=O) cm^{-1}; ^{1}H n.m.r. δ 7.6-7.3 (15H, m, Ph), 6.39 (1H, d, J_{trans} 15.4 Hz, COCH), 5.45 (1H, d, J_{trans} 15.4 Hz, COCHC<u>H</u>), 4.45 (5H, brs, C_5H_5), 0.97 (9H, s, $(CH_3)_3$); <u>m/z</u> 522 (M^+) [Lit.,[63] ^{1}H n.m.r. δ 7.5-7.3 (15H, m, Ph), 6.39 (1H, d, J_{trans} 15.5 Hz, COCH), 5.44 (1H, d, J_{trans} 15.5 Hz, COCHC<u>H</u>), 4.45 (5H, d, J_{PH} 1.2 Hz, C_5H_5), 0.96 (9H, s, $(CH_3)_3$)].

<u>Z-(C_5H_5)Fe(CO)(PPh_3)(COCH=CHCH=CH_2) 49.</u>[63] Elution with diethyl ether gave complex <u>49</u> (35%); $\nu_{max.}$ 1920 vs (C≡O) cm^{-1}; ^{1}H n.m.r. δ 7.6-7.3 (15H, m, Ph), 6.44 (1H, d, J_{cis} 11.4 Hz, COCH), 6.28-

6.15 (1H, m, C<u>H</u>CH$_2$), 5.22-4.95 (3H, m, C<u>H</u>CHC<u>H</u>$_2$), 4.44 (5H, d, J_{PH} 1.3 Hz, C_5H_5); <u>m/z</u> 492 (M^+) [Lit.,[63] ^{1}H n.m.r. δ 7.5-7.3 (15H, m, Ph), 6.43 (1H, d, J_{cis} 11.1 Hz, COCH), 6.27-6.14 (1H, m, C<u>H</u>CH$_2$), 5.21-4.94 (3H, m, C<u>H</u>CHC<u>H</u>$_2$), 4.43 (5H, d, J_{PH} 1.4 Hz, C_5H_5)].

<u>E-(C_5H_5)Fe(CO)(PPh_3)(COCH=CHCH=CH$_2$) 48.</u>[63] Elution with dichloromethane:ethyl acetate (19:1) gave complex <u>48</u> (50%); $\nu_{max.}$ 1915 vs (C≡O), 1590 s and 1555 s (C=O) cm^{-1}; ^{1}H n.m.r. δ 7.6-7.3 (15H, m, Ph), 6.52 (1H, d, J_{trans} 14.9 Hz, COCH), 6.24-6.12 (1H, m, C<u>H</u>CH$_2$), 5.79 (1H, dd, J_{trans} 14.9 Hz, $J_{1,2}$ 10.8 Hz, CHC<u>H</u>CH), 5.41-5.31 (2H, m, CH$_2$), 4.45 (5H, d, J_{PH} 0.9 Hz, C_5H_5); <u>m/z</u> 492 (M^+) [Lit.,[63] ^{1}H n.m.r. δ 7.5-7.3 (15H, m, Ph), 6.51 (1H, d, J_{trans} 14.4 Hz, COCH), 6.23-6.11 (1H, m, C<u>H</u>CH$_2$), 5.78 (1H, dd, J_{trans} 15.0 Hz, $J_{1,2}$ 10.8 Hz, CHC<u>H</u>CH), 5.40-5.30 (2H, m, CH$_2$), 4.45 (5H, d, J_{PH} 1.5 Hz, C_5H_5)].

<u>Z-(C_5H_5)Fe(CO)(PPh_3)(COCH=CHCH=C(CH$_3$)$_2$) 51.</u> Elution with diethyl ether gave complex <u>51</u> (19%); Found: C, 71.22, H, 5.87, $C_{31}H_{29}FePO_2$ requires: C, 71.55; H, 5.62%; $\nu_{max.}$ 1915 vs (C≡O), 1590 s (C=O) cm^{-1}; ^{1}H n.m.r. δ 7.6-7.3 (15H, m, Ph), 6.38 (1H, d, J_{cis} 11.2 Hz, COCH), 5.80 (1H, d, $J_{1,2}$ 11.7 Hz, C<u>H</u>=C(CH$_3$)$_2$), 5.36 (1H, dd, J_{cis} 11.4 Hz, $J_{1,2}$ 11.4 Hz, CHC<u>H</u>CH), 4.43 (5H, d, J_{PH} 0.9 Hz, C_5H_5), 1.70 (3H, s, CH$_3$), 1.65 (3H, s, CH$_3$); ^{13}C-[^{1}H] n.m.r. δ 220.5 (d, J_{PC} 31.8 Hz, C≡O), 141.0 (s, <u>C</u>(CH$_3$)$_2$), 139.5 (d, J_{PC} 3.8 Hz, CO<u>C</u>H), 136.4 (d, J_{PC} 42.9 Hz, PhC_{ipso}), 133.3 (d, J_{PC} 10.0 Hz, PhC_{ortho}), 129.5 (s, PhC_{para}), 127.9 (d, J_{PC} 9.8 Hz, PhC_{meta}), 122.8 (s, CH), 116.7 (s, CH), 85.4 (s, C_5H_5), 26.3 (s, CH$_3$), 17.9 (s, CH$_3$); ^{31}P-[^{1}H] n.m.r. δ73.1 ; <u>m/z</u> 520 (M^+).

<u>E-(C_5H_5)Fe(CO)(PPh_3)(COCH=CHCH=C(CH$_3$)$_2$) 50.</u> Elution with dichloromethane:ethyl acetate (19:1) gave complex <u>50</u> (48%); Found: C, 71.36, H, 5.76, $C_{31}H_{29}FePO_2$ requires: C, 71.55, H, 5.62%; $\nu_{max.}$

1915 vs (C≡O), 1600 s and 1550 s (C=O) cm^{-1}; ^{1}H n.m.r. δ 7.6-7.3 (15H, m, Ph), 6.52 (1H, d, J_{trans} 14.7 Hz, COCH), 6.18 (1H, dd, J_{trans} 14.6 Hz, $J_{1,2}$ 11.4 Hz, CHCHCH), 5.71 (1H, d, $J_{1,2}$ 11.5 Hz, $CH=C(CH_3)_2$), 4.44 (5H, d, J_{PH} 1.0 Hz, C_5H_5), 1.81 (3H, s, CH_3), 1.75 (3H, s, CH_3); $^{13}C-[^{1}H]$ n.m.r. δ 220.8 (d, J_{PC} 31.5 Hz, C≡O), 143.4 (s, $C(CH_3)_2$), 141.8 (d, J_{PC} 4.2 Hz, COCH), 136.5 (d, J_{PC} 42.6 Hz, PhC_{ipso}), 133.4 (d, J_{PC} 9.4 Hz, PhC_{ortho}), 129.6 (s, PhC_{para}), 127.9 (d, J_{PC} 10.2 Hz, PhC_{meta}), 124.3 (s, CH), 122.1 (s, CH), 85.4 (s, C_5H_5), 26.5 (s, CH_3), 18.6 (s, CH_3); $^{31}P-[^{1}H]$ n.m.r. δ73.5 ; m/z 520 (M^+).

Preparation of S(+)-$(C_5H_5)Fe(CO)(PPh_3)(COCH_2Si(CH_3)_3)$ 34.[29]

The complex S(+)-$(C_5H_5)Fe(CO)(PPh_3)(COCH_3)$ 22[33] (650mg, 1.43 mmol) was used in the synthesis of the product S(+)-34 (702mg, 93%) as described above (p.137); ^{1}H n.m.r. δ 7.6-7.3 (15H, m, Ph), 4.42 (5H, d, J_{PH} 1.2 Hz, C_5H_5), 2.75 and 1.74 (2H, AB system J_{AB} 11.4 Hz, CH_2), 0.01 (9H, s, $(CH_3)_3$); $[\alpha]_D^{20}$ + 187.7° (c 0.13, C_6H_6) [Lit.,[29] $[\alpha]_D^{23}$ + 188.8° (c 0.13, C_6H_6)].

Preparation of R(-)-$(C_5H_5)Fe(CO)(PPh_3)(COCH_2Si(CH_3)_3)$ 34.

The complex R(-)-$(C_5H_5)Fe(CO)(PPh_3)(COCH_3)$ 22[33] (630mg, 1.39 mmol) was used in the synthesis of the product R(-)-$(C_5H_5)Fe(CO)(PPh_3)(COCH_2Si(CH_3)_3)$ 34 (620mg, 85%) as described above (p.137); ^{1}H n.m.r. δ 7.6-7.3 (15H, m, Ph), 4.40 (5H, d, J_{PH} 1.2 Hz, C_5H_5), 2.74 and 1.74 (2H, AB system J_{AB} 11.4 Hz, CH_2), 0.02 (9H, s $(CH_3)_3$); $[\alpha]_D^{21}$ - 187.7° (c 0.13, C_6H_6).

Preparation of S(+)-Z- and E-$(C_5H_5)Fe(CO)(PPh_3)(COCH=CHCH_3)$ 37 and 36.[29]

The complex S(+)-$(C_5H_5)Fe(CO)(PPh_3)(COCH_2Si\ (CH_3)_3)$ 34 was used in the synthesis of a 2:1 mixture of S(+)-Z-37 and S(+)-E-

36 (80% overall yield) as described above (p.138):

S(+)-Z-(C_5H_5)Fe(CO)(PPh_3)($COCH{=}CHCH_3$) 37. ^{1}H n.m.r. δ 7.6-7.3 (15H, m, Ph), 6.56 (1H, dq, J_{cis} 11.2 Hz, $J_{1,3}$ 1.8Hz, COCH), 4.74 (1H, dq, J_{cis} 11.2 Hz, $J_{1,2}$ 7.2 Hz, C$\underline{H}$$CH_3$), 4.43 (5H, d, J_{PH} 1.2 Hz, C_5H_5), 1.33 (3H, dd, $J_{1,2}$ 7.2 Hz, $J_{1,3}$ 1.8 Hz, CH_3); $[\alpha]_D^{20}$ + 273.7° (c 0.12, C_6H_6) [Lit.,[29] $[\alpha]_D^{23}$ + 274.8° (c 0.12, C_6H_6)].

S(+)-E-(C_5H_5)Fe(CO)(PPh_3)($COCH{=}CHCH_3$) 36. ^{1}H n.m.r. δ 7.6-7.3 (15H, m, Ph), 6.52(1H, d, J_{trans} 15.2 Hz, COCH),5.49 (1H, dq, J_{trans} 15.2 Hz, $J_{1,2}$ 6.8 Hz, C$\underline{H}$$CH_3$), 4.41 (5H, d, J_{PH} 1.1 Hz, C_5H_5), 1.58 (3H, dd, $J_{1,2}$ 6.8 Hz, $J_{1,3}$ 1.4 Hz, CH_3); $[\alpha]_D^{20}$ + 174.3° (c 0.15, C_6H_6) [Lit.,[29] $[\alpha]_D^{23}$ + 175.3° (c 0.15, C_6H_6)] (see also p.196).

Preparation of R(-)-Z- and E-(C_5H_5)Fe(CO)(PPh_3) ($COCH{=}CHCH_3$) 37 and 36.

The complex R(-)-(C_5H_5)Fe(CO)(PPh_3)($COCH_2Si(CH_3)_3$) 34 was used in the synthesis of a 2:1 mixture of R(-)-Z-37 and R(-)-E-36 (71% overall yield) as described above (p.138):

R(-)-Z-(C_5H_5)Fe(CO)(PPh_3)($COCH{=}CHCH_3$) 37. ^{1}H n.m.r. δ 7.6-7.3 (15H, m, Ph), 6.56 (1H, dq, J_{cis} 11.2 Hz, $J_{1,3}$ 1.8 Hz, COCH), 4.72 (1H, dq, J_{cis} 11.2 Hz, $J_{1,2}$ 7.2 Hz, C$\underline{H}$$CH_3$), 4.42 (5H, d, J_{PH} 1.2 Hz, C_5H_5), 1.32 (3H, dd, $J_{1,2}$ 7.2 Hz, $J_{1,3}$ 1.8 Hz, CH_3); $[\alpha]_D^{20}$ - 272.9° (c 0.12, C_6H_6).

R(-)-E-(C_5H_5)Fe(CO)(PPh_3)($COCH{=}CHCH_3$) 36. ^{1}H n.m.r. δ 7.6-7.3 (15H, m, Ph), 6.51 (1H, J_{trans} 15.2 Hz, COCH), 5.49 (1H, dq, J_{trans} 15.1 Hz, $J_{1,2}$ 6.7 Hz, C$\underline{H}$$CH_3$), 4.42 (5H, d, J_{PH} 1.1 Hz, C_5H_5), 1.58 (3H, dd, $J_{1,2}$ 6.7 Hz, $J_{1,3}$ 1.1 Hz, CH_3); $[\alpha]_D^{20}$ -174.7° (c 0.15, C_6H_6) (see also p.196).

Preparation of $(C_5H_5)Fe(CO)(PPh_3)(COCH=CH_2)$ 52.[29]

Butyllithium (3.3ml, 5.29mmol) was added to a solution of the acetyl complex 22 (2.0g, 4.4mmol) in THF (15ml) at -78°C and the resulting red solution of enolate 23 stirred (-78°C; 45min). R-chloromenthyl ether[65] was added and after stirring (-78°C, 2h), the reaction mixture was allowed to warm to room temperature over 1h. Evaporation of the solvent, extraction with dichloromethane and filtration through alumina (grade I) with ethyl acetate gave an orange solution. After evaporation of the solvent and addition of dichloromethane (4ml), chromatography on alumina (grade I) gave two orange bands on elution with diethyl ether: dichloromethane (1:1) and ethyl acetate respectively. Removal of the solvent from the first fraction gave an orange crystalline solid identified, on the basis of the mass spectrum (m/z 622 (M^+)), as the β-menthoxy complex RR(SR)-53 (2.013g, 73.5%). Removal of the solvent from the second fraction gave an orange solid identified by ^1H n.m.r. spectroscopy as starting material 22 (307 mg, 15.4%). Complex 53 (2.0g, 3.22mmol) in THF (35ml) was added to sodium hydride (324mg, 13.5mmol) and stirred (20°C; 24h). After dropwise addition of methanol (10ml), evaporation of the solvent, extraction with dichloromethane and filtration through alumina (grade I) with ethyl acetate, an orange solution was obtained. Removal of solvent gave an orange solid, which was dissolved in dichloromethane and chromatographed on alumina (grade I), two orange bands being collected on elution with diethyl ether:dichloromethane (1:1) and ethyl acetate respectively. The first fraction dried to an orange crystalline solid and was identified as unreacted 53 (420mg, 21%). The second fraction dried to an orange solid and was identified as the acryloyl

complex 52 (903mg, 60%).[63] $\nu_{max.}$ 1910 vs (C≡O), 1605 s and 1570 s (C=O) cm^{-1}; ^1H n.m.r. δ 7.6-7.3 (15H, m, Ph), 6.60 (1H, dd, J_{trans} 17.0 Hz, J_{cis} 10.2 Hz, COCH), 4.93 (1H, dd, J_{trans} 17.0 Hz, J_{gem} 1.8 Hz, HCH), 4.53 (1H, dd, J_{cis} 10.2 Hz, J_{gem} 1.9 Hz, HCH), 4.45 (5H, d, J_{PH} 0.7 Hz, C_5H_5); m/z 466 (M^+) [Lit.,[63] ^1H n.m.r. δ 7.5-7.3 (15H, m, Ph), 6.60 (1H, dd, J_{trans} 17.0 Hz, J_{cis} 10.2 Hz, COCH), 4.93 (1H, dd, J_{trans} 17.0 Hz, J_{gem} 1.7 Hz, CH_2), 4.53 (1H, dd, J_{cis} 10.2 Hz, J_{gem} 1.7 Hz, CH_2), 4.45 (5H, d, J_{PH} 0.7 Hz, C_5H_5)].

Preparation of $(C_5H_5)Fe(CO)(PPh_3)(COCH=C(CH_3)_2)$ 54.[59]

Butyllithium (10.75ml, 17.2mmol) was added to a solution of the acetyl complex 22 (6g, 13.2mmol) in THF (30ml) at -78°C. The enolate 23 was stirred (-78°C;45mins) then acetone (1.95ml,26.6mmol-freshly distilled) in THF (10ml) was added dropwise and the orange/yellow solution stirred (-78°; 1h). Addition of methanol and removal of solvent gave an orange oil. Addition of dichloromethane (3ml) and chromatography on alumina (grade I) gave two orange bands on elution with dichloromethane:ethyl acetate (1:1) and ethyl acetate:methanol (19:1) respectively. Removal of solvent from the first fraction gave an orange solid, identified by ^1H n.m.r. spectroscopy as starting material 22 (1.382g, 23%). Removal of solvent from the second fraction gave an orange solid, identified by ^1H n.m.r. spectroscopy as the β-hydroxy complex 55 (4.665g, 69%); ^1H n.m.r. δ 7.6-7.3 (15H, m, Ph), 4.42 (5H, brs, C_5H_5), 4.05 (1H, s, OH), 3.19, 2.84 (2H, AB system, J_{AB} 17.8 Hz, $COCH_2$), 1.02 (3H, s, CH_3), 0.68 (3H, s, CH_3) [Lit.,[59] ^1H n.m.r. δ 7.5-7.3 (15H, m, Ph), 4.41 (5H, d, J_{PH} 1.2 Hz, C_5H_5), 4.06 (1H, s, OH), 3.17, 2.84 (2H, AB system, J_{AB} 18.0Hz, $COCH_2$),

1.02 (3H, s, CH_3), 0.69 (3H, s, CH_3)].

Complex 55 (4.55g, 8.89mmol) in THF (40ml) was added to sodium hydride (640mg, 26.7mmol) and stirred (20°C; 30mins). Methyl iodide (0.83ml, 13.34mmol) was added and after stirring (20°C; 12h) and dropwise addition of methanol, evaporation of the solvent gave a brown solid. Extraction with dichloromethane and filtration through alumina (grade I) with ethyl acetate gave an orange solution. Removal of the solvent gave an orange solid which was dissolved in dichloromethane and chromatographed on alumina (grade I), two orange bands being collected on elution with ethyl acetate and ethyl acetate:methanol (19:1) respectively. The first fraction dried to an orange solid and was identified as the β-methoxy complex 56 (3.97g, 85%) on the basis of the mass spectrum (m/z 526(M^+)). The second fraction dried to an orange solid, identified by ^1H n.m.r. spectroscopy as unreacted 55 (546mg, 12%).

Complex 56 (3.9g, 7.4mmol) in THF (30ml) was added to sodium hydride (642mg, 27mmol) and stirred (20°C; 64h). Addition of methanol, evaporation of the solvent, extraction with dichloromethane and filtration through alumina (grade I) with ethyl acetate gave an orange solution drying to an orange solid. Chromatography on alumina (grade I) gave two orange bands eluting with dichloromethane:diethyl ether (3:1) and ethyl acetate respectively. The second band dried to an orange solid and was identified as starting material 56(195mg, 5%) by ^1H n.m.r. spectroscopy. The first band dried to an orange solid and was identified as the complex 54 (2.8g, 79%). $\nu_{max.}$ 1915 vs (C≡O), 1580 s (C=O) cm^{-1}; ^1H n.m.r. δ 7.6-7.3 (15H, m, Ph), 6.56 (1H, s, COCH), 4.42 (5H, br s, C_5H_5), 1.59 (3H, s, CH_3), 1.55 (3H, s, CH_3); m/z 494 (M^+) [Lit.,[59] ^1H n.m.r. δ 7.5-7.3 (15H, m, Ph), 6.58 (1H, s, COCH), 4.42 (5H, d, J_{PH} 1.1 Hz, C_5H_5), 1.59 (3H, s, CH_3), 1.56 (3H, s, CH_3)].

Synthesis of $(C_5H_5)Fe(CO)(PPh_3)(COCH\text{—}CH_2)$ 70.

Method A

A zinc/copper couple was prepared by heating zinc (17mg, 0.26mmol) and cuprous chloride (3mg, 0.03mmol) at reflux in ether (30mins.).[78] Methylene iodide (0.11ml, 0.14mmol) and $(C_5H_5)Fe(CO)(PPh_3)(COCH=CH_2)$ 52 (50mg, 0.11mmol) were added and the mixture refluxed (3h). After solvent evaporation the resulting green solid was dissolved in dichloromethane and chromatographed on alumina (grade I), a green band eluting in dichloromethane (discarded), and an orange band eluting in diethyl ether:ethyl acetate (6:1). Removal of the solvent gave an orange solid which was identified by mass spectrometry and ^1H n.m.r. spectroscopy as 70 (15mg, 30%) (see below for spectroscopic details).

Method B

Diethylzinc (0.13ml, 0.33mmol) was added to a solution of $(C_5H_5)Fe(CO)(PPh_3)(COCH=CH_2)$ 52 (50mg, 0.11mmol) in toluene (2ml) at 0°C. After dropwise addition of methylene iodide (0.1ml, 1.24mmol) the solution was stirred (0°C; 20mins, 20°C; 40mins). After addition of methanol (0.5ml), removal of solvent and addition of dichloromethane, chromatography on alumina (grade I) gave two orange bands, eluting in diethyl ether:ethyl acetate (8:1) and ethyl acetate respectively, drying to orange solids. The product from the first band was identified by ^1H n.m.r. spectroscopy as 70 (32mg, 63%) (see below), and that from the second band as unreacted 52 (12mg, 24%).

Method C[80]

The iron dimer 24 (3.2g, 9.04mmol) in THF (30ml) was added to 2% sodium amalgam (40g) and stirred (20°C; 12h). The

resulting brown solution of $[(C_5H_5)Fe(CO)_2]^-Na^+$ 25 was decanted into a clean vessel and cooled (-78°C). Cyclopropanecarboxylic acid chloride (1.7ml, 18.75mmol) in THF (10ml) was added and the solution stirred (20°C; 72h). After filtration through celite with dichloromethane the solvent was evaporated and the red oil dissolved in dichloromethane and chromatographed on alumina (grade I), the product 71 eluting in diethyl ether:dichloromethane (1:1) and drying to a red oil (1.836g, 41%); Found:C, 53.82; H, 4.09: $C_{11}H_{10}FeO_3$ requires C, 53.70; H, 4.10%; $\nu_{max.}$ 2020 vs (C≡O), 1965 vs (C≡O) and 1630 s (C=O) cm^{-1}; ^1H n.m.r. δ 4.90 (5H, s, C_5H_5), 2.60 (1H, m, COCH),(0.99 (2H, m) and 0.65 (2H, m) (CH_2CH_2)); m/z 246 (M^+) [Lit.,[80] ^1H n.m.r. (CS_2) δ 4.72 (5H, C_5H_5), 2.38 (1H, COCH), 0.86 and 0.53 (4H, CH_2CH_2)]

Complex 71 (1.295g, 5.26mmol) and triphenylphosphine (1.791g, 6.84mmol) in benzene (30ml) were subjected to photolysis over four hours. Aliquots of the solution were removed at hourly intervals and the infrared spectrum recorded, the stretches assigned to 70 (vide infra) gradually replacing those of 71 (vide supra). Removal of the solvent gave a brown solid which, after addition of dichloromethane (4ml), was chromatographed on alumina (grade I), giving one band, eluting in petroleum ether, drying to a yellow oil, and a second band eluting in diethyl ether, and drying to an orange oil. The material from the first band was identified by ^1H n.m.r. spectroscopy as triphenylphosphine, the product from the second band as a 4:1 mixture of 70 and 71. Two crystallisations of the mixture from dichloromethane/hexane gave pure 70 as red crystals (1.103g, 40%); ν_{max} 1915 vs (C≡O), 1585 s (C=O) cm^{-1}; ^1H n.m.r. δ 7.6-7.3 (15H, m, Ph), 4.46 (5H, d, J_{PH} 1.1 Hz, C_5H_5), 2.85 (1H, m, COCH), 0.88-0.78 (1H, m, CH),(0.48-0.32 (2H, m) and 0.30-0.20 (1H, m) ($CHCH_2$); m/z 480 (M^+).

Synthesis of cis-$(C_5H_5)Fe(CO)(PPh_3)(COCH\!-\!\overset{CH_2}{}\!-\!CHCH_3)$ 72 and 73

A number of synthetic approaches to the diastereoisomeric complexes 72 and 73 were developed (see Chapter 3). In each case the reactions were monitored by TLC, the product spot being less polar than the starting material 37. The diastereoisomeric ratios were measured from the integral of the α-protons (COCH), 72 being assigned as the major diastereoisomer (see p. 46). Complexes 72 and 73 were chromatographically inseparable.

Method A

Diethylzinc (0.14ml, 0.36mmol) and methylene iodide (0.1ml, 1.24mmol) were added to Z-$(C_5H_5)Fe(CO)(PPh_3)(COCH{=}CHCH_3)$ 37 (50 mg, 0.104mmol) in toluene (1ml) and the solution was stirred (0°C; 10mins.). Addition of methanol (0.5ml) and removal of solvent gave an orange solid. Extraction with dichloromethane (2ml) and filtration through alumina (grade I) with diethyl ether gave an orange solution drying to an orange solid, identified as a 3:1 mixture of 72:73 (46mg, 89%) by ^1H n.m.r. spectroscopy and mass spectrometry (see below for spectroscopic details).

Method B

The reaction described for Method A was repeated under a variety of conditions which are summarised, together with the results, in table 3 (p. 47). Under optimum conditions, diethylzinc (0.06ml, 0.154mmol) and methylene iodide (0.033ml, 0.41mmol) were added to 37 (50mg, 0.104mmol) in toluene (1ml), and the solution stirred (20°C; 15mins.). After work up and chromatography (as for Method A) the product was isolated in 78% yield, 72:73= 4.5:1.

Method C

Typically, a Lewis acid was added to a solution of 37 (100mg, 0.208mmol) in toluene (2ml) and the solution stirred (20°C; 10mins.). After addition of diethylzinc and methylene iodide the solution was stirred. After addition of methanol (1ml), removal of solvent, extraction with dichloromethane and filtration through alumina (grade I) with dichloromethane:ethyl acetate (9:1), an orange solution drying to an orange solid was obtained. Addition of dichloromethane and chromatography on alumina (grade I) gave a band eluting in diethyl ether and drying to an orange solid, identified as the diastereoisomeric cyclopropyl complexes 72 and 73, by ^{1}H n.m.r. spectroscopy. The conditions and results are summarised in table 4 (p. 49). The optimum reaction conditions are outlined in method D.

Method D

Zinc dichloride (227mg, 1.67mmol) was added to a solution of Z-$(C_5H_5)Fe(CO)(PPh_3)(COCH{=}CHCH_3)$ 37 (200mg, 0.417mmol) in toluene (4ml) and stirred (20°C; 10mins), giving a fine, white suspension in solution. Diethylzinc (0.25ml, 0.623mmol) was added, followed by dropwise addition of methylene iodide (0.135ml, 1.67mmol). After stirring (20°C; 15mins.), addition of methanol (1ml), removal of solvent, addition of dichloromethane (2ml) and filtration through alumina (grade I) with diethyl ether:dichloromethane (1:1) an orange solution drying to an orange solid was obtained, identified by ^{1}H n.m.r. spectroscopy as the cyclopropyl complexes 72 and 73 (187mg, 91%), 72:73 = 9:1. (Repeating the reaction without addition of diethylzinc gave only 37). Crystallisation from dichloromethane/hexane gave orange crystals (72:73 = 12:1); Found: C, 70.43; H, 5.68, $C_{29}H_{27}FePO_2$ requires:

C, 70.46; H, 5.51%; $\nu_{max.}$ 1910 vs (C≡O), 1590 s (C=O) cm^{-1}; m/z 494 (M^+).

Major diastereoisomer RRS(SSR)-72. (The n.m.r. data was obtained from the product synthesised by Method D). ^1H n.m.r. δ 7.6-7.3 (15H, m, Ph), 4.41 (5H, d, J_{PH} 0.9 Hz, C_5H_5), 2.83 (1H, ddd, J_{cis} 7.8 Hz, J_{cis} 7.8 Hz, J_{trans} 5.4 Hz, COCH), 1.16-1.08 (1H, m, $C\underline{H}CH_3$), 1.04 (3H, d, $J_{1,2}$ 5.4 Hz, CH_3), 0.52-0.45 (1H, m, $\underline{H}CH$), 0.39-0.32 (1H, m, $HC\underline{H}$); ^{13}C-[^1H]n.m.r. δ 221.2 (d, J_{PC} 31.5Hz, C≡O), 136.6 (d, J_{PC} 42.1Hz, PhC_{ipso}), 133.4 (d, J_{PC} 9.8 Hz, PhC_{ortho}), 129.6 (s, PhC_{para}), 127.9 (d, J_{PC} 9.6 Hz, PhC_{meta}), 85.4 (s, C_5H_5), 45.5 (d, J_{PC} 5.9 Hz, $CO\underline{C}H$), 18.1 (s, CH), 15.7 (s, CH_2), 12.9 (s, CH_3); ^{31}P-[^1H]n.m.r. δ 73.3.

Minor diastereoisomer RSR(SRS)-73. (The n.m.r. data was obtained from the product synthesised by Method B (72:73 = 3:1)). ^1H n.m.r. δ 7.6-7.3 (15H, m, Ph), 4.44 (5H, d, J_{PH} 1.3 Hz, C_5H_5), 2.93 (1H, ddd, J_{cis} 8.1 Hz, J_{cis} 8.1 Hz, J_{trans} 5.4 Hz, COCH), 0.78-0.73 (1H, m, $\underline{H}CH$), 0.67-0.61 (1H, m, $HC\underline{H}$), 0.51 (3H, d, $J_{1,2}$ 6.1 Hz, CH_3) (remaining resonances obscured by those of 72).

Method E

Triethylaluminium (0.40ml, 0.40mmol) was added to a solution of Z-(C_5H_5)Fe(CO)(PPh_3)(COCH=$CHCH_3$) 37 (50mg, 0.104ml) and methylene iodide (0.033ml, 0.41mmol) in toluene (1ml) and the solution stirred (20°C; 15mins.). Addition of methanol (1ml) and removal of solvent gave a gelatinous orange product. Extraction with dichloromethane (3ml) and filtration through alumina (grade I) with diethyl ether gave, on removal of solvent, an orange solid identified by ^1H n.m.r. spectroscopy as an 8:1 mixture of 72 and 73 (45mg, 88%). Repeating the reaction but with prior addition of zinc dichloride(57mg, 0.42mmol), again gave an 8:1 mixture of 72 and 73 (38mg, 74%).

Method F

As for Method E, except that triethylaluminium was added to the toluene solution of 37 and methylene iodide at -40°C. After stirring (-40°C; 1h) the solution was allowed to warm to room temperature over two hours. Work up, as above, gave an orange solid, identified as a 16:1 mixture of 72 and 73 (38mg, 74%).

Synthesis of Cis-$(C_5H_5)Fe(CO)(PPh_3)(COCH\!\!-\!\!\overset{CH_2}{}\!\!-\!\!CHR$ 74 and 75.

The experiments outlined above in Methods B, D and F were repeated with other Z-α,β-unsaturated iron acyl complexes. The results are summarised in tables 5 (p.50) and 6 (p.52). In every case the diastereoisomeric cyclopropyl products were chromatographically inseparable. The diastereoisomeric ratios were obtained from the integrals of the α-protons (COCH) in the ^1H n.m.r. spectra, the major diastereoisomers being assigned by comparison with RRS(SSR)-72. The n.m.r. data for the major diastereoisomers were obtained from the product synthesised by Method D. In each case a single crystallisation of this product from dichloromethane/hexane gave orange crystals for which combustion analysis, infra-red and mass spectral data were obtained. The ^1H n.m.r. data for the minor diastereoisomer in each case was obtained, where possible, from the product synthesised by Method B.

Cis-$(C_5H_5)Fe(CO)(PPh_3)(COCH\!\!-\!\!\overset{CH_2}{}\!\!-\!\!CHCH_2CH_2CH_3)$ 76 and 77.

After crystallisation 76:77 = 18:1; Found: C, 71.24; H, 6.32, $C_{31}H_{31}FePO_2$ requires: C, 71.27, H, 5.98%; ν_{max} 1910 vs (C≡O), 1580 (C=O)cm^{-1}; m/z 522(M^+).

Major diastereoisomer RRS(SSR)-76. ^{1}H n.m.r. δ 7.6-7.3 (15H, m, Ph), 4.42 (5H, d, J_{PH} 1.0 Hz, C_5H_5), 2.80-2.73 (1H, m, COCH), 1.37-1.22 (4H, m, CH_2CH_2), 1.07-1.00 (1H, m, CH), 0.92-0.87 (3H, m, CH_3), 0.47-0.41 (1H, HCH), 0.33-0.27 (1H, m, HCH); ^{13}C-[^{1}H] n.m.r. δ 221.2 (d, J_{PC} 31.8 Hz, C≡O), 136.6 (d, J_{PC} 43.2 Hz, Ph-C_{ipso}), 133.4 (d, J_{PC} 9.7 Hz, PhC_{ortho}), 129.6 (s, PhC_{para}), 127.9 (d, J_{PC} 9.5 Hz, PhC_{meta}), 85.5 (s, C_5H_5), 45.2 (d, J_{PC} 5.9 Hz, COCH), 29.3 (s, CH_2CH_2), 24.4 (s, CH), 23.3 (s, CH_2CH_2), 14.3 (s, CH_2), 14.0 (s, CH_3); ^{31}P-[^{1}H] n.m.r. δ 73.0.

Minor diastereoisomer RSR(SRS)-77. ^{1}H n.m.r. δ 7.6-7.3 (15H, m, Ph), 4.44 (5H, d, J_{PH} 1.0 Hz, C_5H_5), 2.88-2.84 (1H, m, COCH), 0.75-0.70 (1H, m, HCH), 0.72 (3H, t, $J_{1,2}$ 7.3 Hz, CH_3), 0.68-0.61 (1H, m, HCH).

Cis-$(C_5H_5)Fe(CO)(PPh_3)$(COCHCH(CH$_2$)CHCH$_2$CH$_2$CH$_2$CH$_3$) 78 and 79.

After crystallisation, 78:79 = 16:1. Found: C, 71.80, H, 6.34, $C_{32}H_{33}FePO_2$ requires: C, 71.65, H, 6.20%; $\nu_{max.}$ 1912 vs (C≡O), 1595 s (C=O) cm^{-1}; m/z 536 (M^+).

Major diastereoisomer RRS(SSR)-78. ^{1}H n.m.r. δ 7.6-7.3 (15H, m, Ph), 4.43 (5H, d, J_{PH} 1.0 Hz, C_5H_5), 2.78 (1H, ddd, J_{cis} 8.0 Hz, J_{cis} 8.0 Hz, J_{trans} 5.6 Hz, COCH), 1.37-1.29 (6H, m, $CH_2CH_2CH_2$), 1.10-1.00 (1H, m, CH), 0.90 (3H, m, CH_3), 0.49-0.44 (1H, m, HCH), 0.33-0.27 (1H, m, HCH); ^{13}C-[^{1}H] n.m.r. δ 221.0 (d, J_{PC} 31.3 Hz, C≡O), 136.6 (d, J_{PC} 42.8 Hz, PhC_{ipso}), 133.4 (d, J_{PC} 9.4 Hz, Ph-C_{ortho}), 129.6 (s, PhC_{para}), 127.9 (d, J_{PC} 10.2 Hz, PhC_{meta}), 85.6 (s, C_5H_5), 45.3 (d, J_{PC} 6.1 Hz, COCH), 32.5 (s, $CH_2CH_2CH_2$), 27.0 (s, $CH_2CH_2CH_2$), 24.7 (s, CH), 22.6 (s, $CH_2CH_2CH_2$), 15.0 (s, CH_2), 14.3 (s, CH_3); ^{31}P-[^{1}H] n.m.r. δ 72.9.

Minor diastereoisomer RSR(SRS)-79. ^{1}H n.m.r. δ 7.6-7.3 (15H, m, Ph), 4.44 (5H, d, J_{PH} 1.2 Hz, C_5H_5), 2.93 (1H, ddd, J_{cis} 8.1 Hz, J_{cis} 8.1 Hz, J_{trans} 5.5 Hz, COCH), 0.81 (3H, t, $J_{1,2}$ 6.9 Hz, CH_3), 0.69-0.60 (1H, m, HCH).

Cis-(C_5H_5)Fe(CO)(PPh_3)(COCH$\overset{CH_2}{\diagup\!\!\diagdown}$CHCH($CH_3$)$_2$) 80 and 81.

After crystallisation 80:81 = 33:1; Found: C, 71.16, H, 5.63, $C_{31}H_{31}FePO_2$ requires: C, 71.27, H, 5.98%; $\nu_{max.}$ 1910 vs (C≡O), 1590 s (C=O) cm^{-1}; m/z 522 (M^+).

Major diastereoisomer RRR(SSS)-80. ^{1}H n.m.r. δ 7.6-7.3 (15H, m, Ph), 4.44 (5H, d, J_{PH} 0.8 Hz, C_5H_5), 2.70 (1H, ddd, J_{cis} 8.0 Hz, J_{cis} 8.0 Hz, J_{trans} 5.5 Hz, COCH), 1.67-1.54 (1H, m, CH(CH_3)$_2$), 0.92 (3H, d, $J_{1,2}$ 6.6 Hz, CH_3), 0.85 (3H, d, $J_{1,2}$ 6.6 Hz, CH_3), 0.79-0.70 (1H, m, COCHCH), 0.33-0.27 (1H, m, HCH), 0.22-0.15 (1H, m, HCH); ^{13}C-[^{1}H] n.m.r. δ 221.3 (d, J_{PC} 31.4 Hz, C≡O), 136.5 (d, J_{PC} 42.6 Hz, PhC_{ipso}), 133.4 (d, J_{PC} 9.5 Hz, PhC_{ortho}), 129.6 (s, PhC_{para}), 127.9 (d, J_{PC} 10.3 Hz, PhC_{meta}), 85.9 (s, C_5H_5), 45.6 (d, J_{PC} 7.3 Hz, COCH), 34.3 (s, COCHCH), 25.4 (s, CH(CH_3)$_2$), 23.5 (s, CH_3), 22.6 (s, CH_3), 15.0 (s, CH_2); ^{31}P-[^{1}H] n.m.r. δ 72.3.

Minor diastereoisomer RSS(SRR)-81. ^{1}H n.m.r. δ 7.6-7.3 (15H, m, Ph), 4.45 (5H, d, J_{PH} 1.1 Hz, C_5H_5), 2.87-2.81 (1H, m, COCH), 0.53 (3H, d, $J_{1,2}$ 6.5 Hz, CH_3).

Synthesis of (C_5H_5)Fe(CO)(PPh_3)(COCH$\overset{CH_2}{\diagup\!\!\diagdown}$C($CH_3$)$_2$) 82 and 83.

The experiments outlined above in Methods B, D and F were repeated with (C_5H_5)Fe(CO)(PPh_3)(COCH=C(CH_3)$_2$) 54 (see p.50 and p. 52). A single crystallisation gave 82:83 = 16:1 (Method B); Found: C, 70.93; H, 5.78, $C_{30}H_{29}FePO_2$ requires: C, 70,88; H, 5.75%;

ν_{max} 1915 vs (C≡O), 1605 s (C=O) cm^{-1}; m/z 508 (M^+), 480 (M^+-28).

Major diastereoisomer RR(SS)-82. ^1H n.m.r. δ 7.6-7.3 (15H, m, Ph), 4.39 (5H, d, J_{PH} 1.1 Hz, C_5H_5), 2.66 (1H, dd, J_{cis} 7.5 Hz, J_{trans} 5.5 Hz, COCH), 1.12 (3H, s, CH_3), 1.06 (3H, s, CH_3), 0.76 (1H, dd, J_{trans} 5.4 Hz, J_{gem} 3.6 Hz, CH), 0.24 (1H, dd, J_{cis} 7.6 Hz, J_{gem} 3.6 Hz, CH); ^{13}C-[^1H] n.m.r. δ 221.3 (d, J_{PC} 31.7 Hz, C≡O), 136.6 (d, J_{PC} 42.7 Hz, PhC_{ipso}), 133.4 (d, J_{PC} 9.3 Hz, PhC_{ortho}), 129.5 (s, PhC_{para}), 127.9 (d, J_{PC} 9.3 Hz, PhC_{meta}), 85.4 (s, C_5H_5), 54.8 (d, J_{PC} 6.8 Hz, CO<u>C</u>H), 27.7 (s, CH_3), 24.5 (s, <u>C</u>$(CH_3)_2$), 23.8 (s, CH_2), 19.4 (s, CH_3); ^{31}P-[^1H] n.m.r. δ 73.6.

Minor diastereoisomer RS(SR)-83. ^1H n.m.r. δ 7.6-7.3 (15H, m, Ph), 4.42 (5H, d, J_{PH} 1.0 Hz, C_5H_5), 2.77 (1H, dd, J_{cis} 7.6 Hz, J_{trans} 5.5 Hz, COCH), 1.04 (3H, s, CH_3), 0.49 (3H, s, CH_3).

Reaction of E-$(C_5H_5)Fe(CO)(PPh_3)(COCH{=}CHCH_3)$ 36 with diethylzinc and methylene iodide.

The diastereoisomeric ratios of 84:85 were calculated from the relative intensities of the resonances assigned to the methyl doublets in the ^1H n.m.r. spectra (toluene-d_8) for RRR(SSS)-84 (δ 0.95) and RSS(SRR) 85 (δ 1.00). The majority of the remaining resonances were coincidental. Subsequently, RSS(SRR)-85 was made highly stereoselectively allowing its complete characterisation and RRR(SSS)-84 to be further characterised. This data is given on page 199.

Method A

Zinc dichloride (57mg, 0.42mmol) was added to a solution of E-$(C_5H_5)Fe(CO)(PPh_3)(COCH{=}CHCH_3)$ 36 (50mg, 0.104mmol) in toluene (1ml) and stirred (20°C; 10mins.). Diethylzinc (0.06ml, 0.15mmol)

was added, followed by dropwise addition of methylene iodide (0.035 ml, 0.43mmol). After stirring (20°C; 1h), addition of methanol (0.5ml), removal of solvent, addition of dichloromethane and filtration through alumina (grade I) with ethyl acetate, removal of the solvent gave an orange solid. Addition of dichloromethane (1ml) and chromatography on alumina (grade I) gave two bands, eluting in diethyl ether:dichloromethane (1:1) and ethyl acetate respectively, each drying to an orange solid. The material from the second band was identified by ^{1}H n.m.r. spectrosoopy as starting material 36 (15mg, 30%). The product from the first band was identified by ^{1}H n.m.r. spectroscopy (see above) and mass spectrometry (m/z 494 (M^+)) as a 1.3:1 mixture of the diastereoisomeric cyclopropyl complexes 84 and 85 (62%), the diastereoisomers being chromatographically inseparable.

Method B

Triethylaluminium (0.40ml, 0.40mmol) was added to a solution of 36 (50mg, 0.104mmol) and methylene iodide (0.033ml, 0.41mmol) in toluene (1ml) at 20°C, and the solution stirred (20°C; 2h). Addition of methanol (1ml), and work up as for Method A, gave an orange solid which was dissolved in dichloromethane (2ml) and chromatographed on alumina (grade I) as above. The material from the second band was identified by ^{1}H n.m.r. spectroscopy as starting material 36 (32mg, 63%), and that from the first band as a 1:1 mixture (see above) of the diastereoisomeric cyclopropyl complexes 84 and 85 (6mg, 11%).

Reactions of E-(C_5H_5)Fe(CO)(PPh_3)(COCH=CHR) with diethylzinc and methylene iodide.

The reaction described above (Method A) was repeated on several other E-α,β-unsaturated iron acyl complexes and the results

are summarised in table 7 (p. 54). In each case the major diastereoisomer was 86, although the diastereoselectivity was low. Subsequently, the complexes 87 were synthesised highly diastereoselectively and fully characterised. The data for all complexes 87 and 86 is given on pages 200-203.

Synthesis of (±)-Cis-(EtO_2CCH—CH_2—$CHCH(CH_3)_2$) 100.

N-bromosuccinimide (265mg, 1.49mmol) in dichloromethane (9ml) was added dropwise to an orange solution of RRR(SSS)-80 and RSS(SRR)-81 (24:1) (703mg, 1.35mmol) in dichloromethane:ethanol (1:1, 18ml) at -40°C, the solution rapidly becoming green. After stirring (-40°C; 10mins., 20°C; 40mins.), the solution was washed with brine (4ml), and dried ($MgSO_4$). Removal of the solvent gave a green oil/solid which was chromatographed as a solution in dichloromethane on alumina (grade I). Elution with pentane gave a yellow band drying to a yellow oil identified as the ester 100 (126mg, 60%) (no other cyclopropyl products were detected on subsequent elution with pentane:diethyl ether (9:1)); $\nu_{max.}$ 1715 s (C=O) cm^{-1}; ^1H n.m.r. (C_7D_8) δ 4.04-3.90 (2H, m, $C\underline{H}_2CH_3$), 1.82-1.75 (1H, m, $C\underline{H}(CH_3)_2$), 1.54 (1H, ddd, J_{cis} 8.3 Hz, J_{cis} 8.3 Hz, J_{trans} 5.5 Hz, COCH), 1.01 (3H, d, $J_{1,2}$ 7.3 Hz, $CH_2C\underline{H}_3$), 0.99-0.93 (1H, m, CH), 0.96 (3H, d, $J_{1,2}$ 6.7 Hz, $CHC\underline{H}_3$), 0.90 (3H, d, $J_{1,2}$ 6.5 Hz, $CHC\underline{H}_3$), 0.69-0.59 (2H, m, $COCHC\underline{H}C\underline{H}$); ^1H n.m.r. ($CDCl_3$) δ 4.19-4.08 (2H, m, $C\underline{H}_2CH_3$), 1.73-1.64 (1H, m, COCH), 1.61-1.52 (1H, m, $C\underline{H}(CH_3)_2$), 1.26 (3H, t, $J_{1,2}$ 7.2 Hz, $CH_2C\underline{H}_3$), 1.03-0.82 (3H, m, CH_2CH), 1.02 (3H, d, $J_{1,2}$ 6.7 Hz, CH_3), 0.87 (3H, d, $J_{1,2}$ 6.6 Hz, CH_3); m/z (EI) 156 (M^+), 110, 100, 81, 72, 56, 55. [Lit.,[85] ^1H n.m.r. ($CDCl_3$) δ 4.14 (2H, q, $J_{1,2}$ 7.1 Hz, $C\underline{H}_2CH_3$), 1.68 (1H, ddd, J_{cis} 8.9 Hz, J_{cis} 7.7 Hz, J_{trans} 6.1 Hz, COCH), 1.26

(3H, t, $J_{1,2}$ 7.1 Hz, $CH_2\underline{CH}_3$), 1.30-0.70 (4H, m, $\underline{CH}(CH_3)_2$ and CH_2CH), 1.02 (3H, d, $J_{1,2}$ 6.5 Hz, CH_3), 0.88 (3H, d, $J_{1,2}$ 6.3 Hz, CH_3)].

Synthesis of (±)-Cis-(EtO_2CCH—CH_2—$CHCH_3$) 101

A 9:1 mixture of RRS(SSR)-72 and RSR(SRS)-73 (623mg, 1.30 mmol) in dichloromethane:ethanol (1:1) was treated with N-bromo-succinimide (249mg, 1.40mmol) as described above. After work up and chromatography, as above, a single product was isolated as a yellow oil, identified as 101 (104mg, 65%); ν_{max} 1715 s (C=O)cm^{-1}; ^1H n.m.r. (C_6D_6) δ 3.98 (2H, q, $J_{1,2}$ 7.0 Hz, $\underline{CH}_2CH_3$), 1.52 (1H, ddd, J_{cis} 8.2 Hz, J_{cis} 8.2 Hz, J_{trans} 5.5 Hz, COCH), 1.19 (3H, d, $J_{1,2}$ 6.0 Hz, $CH\underline{CH}_3$), 0.97 (3H, t, $J_{1,2}$ 7.0 Hz, $CH_2\underline{CH}_3$), 0.93-0.87 (1H, m, CH), 0.87-0.80 (1H, m, $\underline{CH}CH_3$), 0.65-0.59 (1H, m, CH); m/z (DCI/NH_3) 129 (M^++ 1), 100, 83, 55.

Chiral Shift experiment with (±)-Cis-(EtO_2CCH—CH_2—$CHCH_3$) 101.

A solution of R-(-)-2,2,2-trifluro-1-(9-anthryl)-ethanol[88] (17.25mg, 0.062mmol) in chloroform-d_1 (0.4ml) was added in 0.05ml aliquots to a solution of (±)-101 (1mg, 0.0078mmol) in chloroform-d_1 (0.5ml) and the ^1H n.m.r. spectrum taken after each addition. No resonance separations were observed.

Chiral Shift experiments with (±)- and (+)-2-phenylethylamine

A solution of R-(-)-2,2,2-trifluoro-1-(9-anthryl)-ethanol (18.2mg, 0.066mmol) in chloroform-d_1 (0.4ml) was added in 0.05ml aliquots to a solution of (±)-2-phenylethylamine (1mg, 0.0083mmol) in chloroform-d_1 (0.5ml). The ^1H n.m.r. spectrum after each

addition showed a gradual separation of the resonances of the α-protons ($C\underline{H}CH_3$). After all aliquots had been added, two sextets at δ 3.98 and 3.93, of equal intensity, were observed.

The reaction was repeated with R(+)-2-phenylethylamine. In this case a single sextet at δ 3.98 was observed confirming the enantiomeric purity of the amine.

Synthesis of Cis-(PhCH(CH_3)NHCOCH$\overset{CH_2}{\diagup\diagdown}CHCH_3$)RRS-102 and RSR-103.

The diastereoisomeric ratios of 102:103 were calculated from the integrals of the resonances in the ^1H n.m.r. spectra, assigned to the methyl groups substituted on the cyclopropane rings.

1) Synthesis of a 1:1 mixture of 102 and 103.

Bromine (0.05ml, 1.0mmol) was added dropwise to a solution of RRS(SSR)-72 and RSR(SRS)-73 (9:1) (400mg, 0.8mmol) in dichloromethane (15ml) at -40°C the solution immediately becoming green. After stirring (-40°C; 25mins.), R(+)-2-phenylethylamine (0.26ml, 2mmol) in dichloromethane (5ml) was added dropwise, and the solution stirred (-40°C; 5mins., 0°C; 40mins., 20°C; 20mins.). After addition of dil.HCl(3ml), the organic layer was removed and dried to give a green/brown solid. Trituration with ether (4 x 6 ml), removal of solvent and chromatography on alumina (grade I), of the material in dichloromethane, gave a green band eluting in diethyl ether and drying to a green solid. Flash chromatography on silica of the material in dichloromethane gave a green band, eluting with diethyl ether:ethyl acetate (9:1), drying to a green solid $(C_5H_5)Fe(CO)(PPh_3)(Br)$ 27. A second band eluted in diethyl ether:ethyl acetate (7:3), drying to a white solid identified as the diastereoisomeric amides 102 and 103 (1:1) (85

mg, 52%); m/z (DCI/NH_3) 204 (M^++1), 188, 120, 106, 100, 83. The ^1H n.m.r. spectroscopic details for RRS-102 and RSR-103 are given below. The resonances at δ 1.03 and 1.11 ($CH_2CHC\underline{H}_3$) were of equal intensity indicating 102:103 = 1:1.

The reaction was repeated with one-half equivalent of R(+)-2-phenylethylamine. The product was isolated in 18% yield, the ^1H n.m.r. spectrum again showing 102:103 = 1:1.

2) Synthesis of a 10:1 mixture of 102:103.

Addition of diethylzinc (0.91ml, 1mmol), and methylene iodide (0.28ml, 3.46mmol) to a solution of R(-)-Z-(C_5H_5)Fe(CO)(PPh_3)($COCH{=}CHCH_3$) 37 (400mg, 0.833mmol) in toluene (8ml) with zinc dichloride (440mg, 3.24mmol) gave, after work up and chromatography (see Method D, p.152), a 10:1 mixture of RRS-72:RSR-73 (323mg, 78%).

Decomplexation of the 10:1 mixture of 72:73 (200mg, 0.40mmol) as described above, gave the corresponding cyclopropyl amides RRS-102 and RSR-103 as a 10:1 mixture (50mg, 61%). Crystallisation from dichloromethane/hexane gave white needles (mpt. 85-86°C), 102:103 (10:1); Found: C, 76.50, H, 8.63, $C_{13}H_{17}NO$ requires: C, 76.80, H, 8.43%; $\nu_{max.}$ 1665 vs (C=O) cm^{-1}; (DCI/NH_3) 204 (M^++1), 188, 120, 106, 105, 100, 83.

RRS-102. ^1H n.m.r. ($CDCl_3$:C_6D_6=1:1) δ 7.13-7.02 (5H, m, Ph), 5.27 (1H, brs, NH), 5.11-5.02 (1H, qn, $J_{1,2}$ 7.1 Hz, C$\underline{H}$NH), 1.23 (3H, d, $J_{1,2}$ 6.9 Hz, NHCH$\underline{C}H_3$), 1.03 (3H, d, $J_{1,2}$ 5.6 Hz, $CH_2CHC\underline{H}_3$), 1.00-0.61 (4H, m, $CHCH_2CH$); ^{13}C-[^1H] n.m.r. ($CDCl_3$) δ 170.4 (s, C=O), 143.7 (s, PhC_{ipso}), 128.6, 127.2 and 126.2 (s, Ph), 48.8 (s, CHNH), 21.8 (s, NHCH$\underline{C}H_3$), 20.8 (s, CO$\underline{C}$H), 14.7 (s, $CH_2C\underline{H}CH_3$), 12.2 (s, $\underline{C}H_2CH\underline{C}H_3$).

3) Synthesis of a 10:1 mixture of 103:102.

Addition of diethylzinc (0.67ml, 0.74mmol) and methylene iodide (0.21ml, 2.6mmol) to a solution of S(+)-Z-(C_5H_5)Fe(CO)(PPh_3)($COCH=CHCH_3$) 37 (300mg, 0.625mmol) in toluene (8ml) with zinc dichloride (350mg, 2.58mmol) gave, after work up and chromatography (see Method D, p.152), a 10:1 mixture of S_{Fe}SR-72:S_{Fe}RS-73 (271mg, 88%).

Decomplexation of the 10:1 mixture of 72:73 (200mg, 0.40mmol) (see above) gave the corresponding cyclopropyl amides (63mg, 77%). Crystallisation from diethyl ether gave white needles (mpt. 96-97°C) 103:102 (10:1); Found: C, 76.95, H, 8.67, N, 6.69, $C_{13}H_{17}NO$ requires: C, 76.80, H, 8.43, N, 6.89%; $\nu_{max.}$ 1665 vs (C=O) cm^{-1}; m/z (DCI/NH_3) 204 (M^++1), 188, 120, 106, 105, 100, 83.

RSR-103. ^1H n.m.r. ($CDCl_3$:C_6D_6=1:1) δ 7.13-7.02 (5H, m, Ph), 5.26 (1H, brs, NH), 5.10-5.00 (1H, qn, $J_{1,2}$ 7.0 Hz, C$\underline{H}$NH), 1.22 (3H, d, $J_{1,2}$ 6.8 Hz, NHCH$\underline{CH_3}$), 1.11 (3H, d, $J_{1,2}$ 5.0 Hz, $CH_2CH\underline{CH_3}$), 1.00-0.60 (4H, m, $CHCH_2CH$); ^{13}C-[^1H] n.m.r. ($CDCl_3$) δ 170.4 (s, C=O), 143.6 (s, PhC_{ipso}), 128.6, 127.2, 126.2 (s, Ph), 48.8 (s, CHNH), 22.0 (s, NHCH$\underline{CH_3}$), 20.7 (s, CO$\underline{C}$H), 14.6 (s, $CH_2\underline{C}HCH_3$), 12.2 (s, CH_2), 12.1 (s, $CH_2CH\underline{CH_3}$).

Preparation of isopropylidene iodide.[90] (Aerobic conditions).

Acetone (8ml, 0.109mol) was added dropwise to hydrazine monohydrate (10ml, 0.206mol) at 0°C over half an hour, a slightly exothermic reaction occurring. After heating (100°C; 45mins.), the solution was extracted with dichloromethane (4 x 6ml) and dried ($MgSO_4$). After dilution with dichloromethane, and addition of triethylamine (24ml), iodine (34g, 0.134mol) was added over

half an hour, external cooling maintaining the reaction temperature at 20-30°C. The solution was washed with water (3 x 8ml), $Na_2S_2O_3$ aq. (3 x 10ml), 3M HCl (2 x 10ml) and brine (2 x 10ml). After drying ($MgSO_4$), removal of the solvent gave a purple oil which on distillation gave the desired product also as a purple oil (4.25g, 14%), bpt. 60°/17mmHg [Lit.,[90] 64°/20mmHg].

Reaction of $(C_5H_5)Fe(CO)(PPh_3)(COCH=CH_2)$ 52 with diethylzinc and isopropylidene iodide.

$(C_5H_5)Fe(CO)(PPh_3)(COCH=CH_2)$ 52 (100mg, 0.215mmol) and zinc dichloride (120mg, 0.88mmol) in toluene (2ml) were stirred (20°C; 10mins). Diethylzinc (0.45ml, 0.50mmol) and isopropylidene iodide (0.09ml, 0.814mmol) were added and the solution stirred (20°C; 20mins.). After addition of methanol (1ml), removal of the solvent gave an orange/white solid. Chromatography on alumina (grade I), gave two bands eluting in petroleum ether:diethyl ether (1:1) and diethyl ether:ethyl acetate (9:1) respectively, each drying to an orange solid. The material from the second band was identified as starting material 52 (40mg, 40%) by ^1H n.m.r. spectroscopy. Similarly the product from the first band was identified as a 3:2 mixture of the diastereoisomeric cyclopropyl complexes 82 and 83 (29.5mg, 27%).

Reaction of E-$(C_5H_5)Fe(CO)(PPh_3)(COCH=CHCH_3)$ 36 with diethylzinc and isopropylidene iodide.

E-$(C_5H_5)Fe(CO)(PPh_3)(COCH=CHCH_3)$ 36 (50mg, 0.104mmol) and zinc dichloride (60mg, 0.44mmol) in toluene (1ml) were stirred (20°C; 10mins.). Diethylzinc (0.06ml, 0.15mmol) and isopropylidene iodide (0.046ml, 0.42mmol) were added and the solution stirred (20°C; 2h). Addition of methanol (1ml), removal of solvent and chromatography on alumina (grade I) in dichloromethane gave two

bands eluting in diethyl ether:petroleum ether (1:1) and diethyl ether:ethyl acetate (1:1) respectively. Removal of solvent from the second band gave an orange solid identified by ^{1}H n.m.r. spectroscopy as starting material 36 (21mg, 42%). Removal of solvent from the first band gave an orange solid identified as a 1:1 mixture of the diastereoisomeric complexes 107 and 108 (9%) (m/z 522(M^+)). The diastereoisomeric ratio was determined from the relative intensities of the resonances in the ^{1}H n.m.r. spectrum assigned to the α-protons (COCH) at δ 2.45 and 2.34. Subsequently, both 107 and 108 were synthesised diastereoselectively, and the full spectroscopic data is given on pages 167 and 181 respectively.

Reaction of E-(C_5H_5)Fe(CO)(PPh_3)(COCH=CHR) with diethylzinc and isopropylidene iodide.

The reaction described above was repeated with other E-α,β-unsaturated iron acyl complexes. The results are summarised in table 8 (p. 72). Subsequently the major diastereoisomer 109 in each reaction, was synthesised diastereoselectively, allowing spectroscopic characterisation. The data for 109 and 110, are given in the following sections.

Reaction of Z-(C_5H_5)Fe(CO)(PPh_3)(COCH=$CHCH_3$) 37 with diethylzinc and isopropylidene iodide.

Z-(C_5H_5)Fe(CO)(PPh_3)(COCH=$CHCH_3$) 37 (200mg, 0.417mmol) and zinc dichloride (240mg, 1.76mmol) in toluene (4ml) were stirred (20°C; 10mins). Diethylzinc (0.60ml, 1.5mmol) was added followed by dropwise addition of isopropylidene iodide (0.192ml, 1.67mmol) over 15 minutes. After this time only trace amounts of starting material 37 were seen by TLC of a sample removed from the

reaction mixture. Addition of methanol (2ml), removal of solvent, filtration through alumina (grade I) with diethyl ether:ethyl acetate (9:1) and removal of solvent gave an orange solid. Chromatography on alumina (grade I), in dichloromethane, gave three bands eluting in diethyl ether:petroleum ether (1:1), diethyl ether:petroleum ether (3:1) and diethyl ether respectively. Removal of the solvent from the final band gave an orange solid identified by ^{1}H n.m.r. spectroscopy as the starting material 37 (12mg, 6%). Removal of the solvent from the first band gave an orange solid identified as a 9:1 mixture of the diastereoisomeric cyclopropyl complexes 115 and 116 (185mg, 85%). Crystallisation from dichloromethane/hexane gave red crystals (115:116 = 12:1); Found: C, 71.08, H, 6.15, $C_{31}H_{31}FePO_2$ requires: C, 71.27, H, 5.98%; ν_{max} 1905 vs (C≡O), 1605 s (C=O) cm^{-1}; m/z 522(M^+).

RSR(SRS)-(C_5H_5)Fe(CO)(PPh_3)(COCH-$CHCH_3$)-$C(CH_3)_2$ 115. ^{1}H n.m.r. δ 7.6-7.3 (15H, m, Ph), 4.37 (5H, d, J_{PH} 1.1 Hz, C_5H_5), 2.79 (1H, d, J_{cis} 8.0 Hz, COCH), 1.09-1.00 (4H, m, $CHCH_3$), 0.94 (3H, s, CH_3), 0.58 (3H, s, CH_3); ^{13}C-[^{1}H]n.m.r. δ 220.1 (d, J_{PC} 32.6 Hz, C≡O), 136.2 (d, J_{PC} 42.1 Hz, PhC_{ipso}), 133.3 (d, J_{PC} 10.0 Hz, PhC_{ortho}), 129.4 (s, PhC_{para}), 127.9 (d, J_{PC} 9.4 Hz, PhC_{meta}), 85.4 (s, C_5H_5), 56.8 (d, J_{PC} 6.2 Hz, COCH), 31.4 (s, $CHCH_3$), 29.3 (s, CCH_3), 28.7 (s, $C(CH_3)_2$), 13.9 (s, CCH_3), 9.1 (s, $CHCH_3$); ^{31}P-[^{1}H]n.m.r. δ 73.5.

RRS(SSR)-(C_5H_5)Fe(CO)(PPh_3)(COCH-$CHCH_3$)-$C(CH_3)_2$ 116. The spectroscopic data is given on page 181.

Removal of the solvent from the second band gave an orange solid identified as a diastereoisomeric mixture of 107 and 108 (6mg, 3%) , the ratio of 107:108 being >30:1; ν_{max} 1915

vs (C≡O), 1600 s (C=O) cm^{-1}; m/z 522 (M^+).

RSS(SRR)-(C_5H_5)Fe(CO)(PPh_3)(COCH-$C(CH_3)_2$-$CHCH_3$)107. ^1H n.m.r. δ 7.6-7.3 (15H, m, Ph), 4.40 (5H, d, J_{PH} 1.2 Hz, C_5H_5), 2.45 (1H, d, J_{trans} 5.3 Hz, COCH), 1.03 (3H, s, CH_3), 0.94 (3H, d, $J_{1,2}$ 6.3 Hz, $CHCH_3$), 0.93-0.87 (1H, m, $CHCH_3$), 0.56 (3H, s, CH_3).

RRR(SSS)-(C_5H_5)Fe(CO)(PPh_3)(COCH-$C(CH_3)_2$-$CHCH_3$) 108. The spectroscopic data is given on page 181.

Reaction of Z-(C_5H_5)Fe(CO)(PPh_3)(COCH=CHR) with diethylzinc and isopropylidene iodide.

The reaction described above was repeated with Z-(C_5H_5)Fe(CO)(PPh_3)(COCH=$CHCH_2CH_3$) 39, Z-(C_5H_5)Fe(CO)(PPh_3)(COCH=$CHCH_2CH_2CH_3$) 41 and Z-(C_5H_5)Fe(CO)(PPh_3)(COCH=$CHCH(CH_3)_2$) 45, no reaction occurring in the latter case. The results are summarised in table 10 (p. 76). Chromatography on alumina (grade I) allowed the separation, in each case, of the cis-substituted cyclopropyl complexes, 117 and 118, from the trans-isomers 109 and 110, the former eluting first. Each set of diastereoisomers were inseparable. The trans-isomers had previously been synthesised non-selectively (p. 164), and the ^1H n.m.r. data for the minor diastereoisomers 110 were taken from these spectra.

1. Reaction of Z-(C_5H_5)Fe(CO)(PPh_3)(COCH=$CHCH_2CH_3$) 39.

The cis-diastereoisomeric cyclopropyl products 119 and 120 eluted in diethyl ether:petroleum ether (2:3) drying to a red/orange solid (81.5%) (119:120 = 13:1). Crystallisation from dichloromethane/hexane gave red crystals (119:120 = 14:1); Found: C, 71.71, H, 6.34, $C_{32}H_{33}FePO_2$ requires: C, 71.65, H, 6.20%; ν_{max}.

1910 vs (C≡O), 1605 s (C=O) cm^{-1}; m/z 536(M^+).

RSR(SRS)-(C_5H_5)Fe(CO)(PPh_3)(COCH-$CHCH_2CH_3$) **119**. ^1H n.m.r. δ 7.6-7.3 (15H, m, Ph), 4.39 (5H, d, J_{PH} 1.1 Hz, C_5H_5), 2.80 (1H, d, J_{cis} 8.7 Hz, COCH), 1.62-1.33 (2H, m, CH_2), 0.95 (3H, s, CCH_3), 0.94-0.82 (4H, m, $CHCH_2CH_3$), 0.56 (3H, s, CCH_3); ^{13}C-[^1H]n.m.r. δ 221.3 (d, J_{PC} 32.4 Hz, C≡O), 137.3 (d, J_{PC} 42.4 Hz, PhC_{ipso}), 133.5 (d, J_{PC} 9.5 Hz, PhC_{ortho}), 129.5 (s, PhC_{para}), 128.0 (d, J_{PC} 9.3 Hz, PhC_{meta}), 85.5 (s, C_5H_5), 57.1 (d, J_{PC} 5.9 Hz, COCH), 39.8 (s, $CHCH_2$), 29.6 (s, CCH_3), 28.7 (s, $C(CH_3)_2$), 17.4 (s, CH_2), 14.3 (s, CH_2CH_3), 14.0 (s, CCH_3); ^{31}P-[^1H]n.m.r. δ 73.9.

RRS(SSR)-(C_5H_5)Fe(CO)(PPh_3)(COCH-$CHCH_2CH_3$) **120**. ^1H n.m.r. δ 7.6-7.3 (15H, m, Ph), 4.41 (5H, d, J_{PH} 0.9 Hz, C_5H_5), 1.12 (3H, s, CCH_3), 1.04 (3H, s, CCH_3).

The trans-diastereoisomeric cyclopropyl products **111** and **112** eluted in diethyl ether:petroleum ether (2:1) drying to a red solid (5.5%) (**111**:**112** = >30:1). Crystallisation from dichloromethane/hexane gave red crystals; ν_{max} 1910 vs (C≡O), 1600 s, (C=O) cm^{-1}; m/z 536(M^+).

RSS(SRR)-(C_5H_5)Fe(CO)(PPh_3)(COCH-$CHCH_2CH_3$) **111**. ^1H n.m.r. δ 7.6-7.3 (15H, m, Ph), 4.41 (5H, d, J_{PH} 0.9 Hz, C_5H_5), 2.53 (1H, d, J_{trans} 4.9 Hz, COCH), 1.43-1.15 (2H, m, CH_2) 1.04 (3H, s, CCH_3), 0.93-0.88 (4H, m, $CHCH_2CH_3$), 0.52 (3H, s, CCH_3).

RRR(SSS)-(C_5H_5)Fe(CO)(PPh_3)(COCH-$CHCH_2CH_3$) **112**. ^1H n.m.r. δ 7.6-7.3 (15H, m, Ph), 4.36 (5H, d, J_{PH} 1.2 Hz, C_5H_5), 2.46 (1H, d, J_{trans} 5.2 Hz, COCH), 1.14 (3H, s, CCH_3), 1.08 (3H, s, CCH_3), 0.80 (3H, t, $J_{1,2}$ 6.8 Hz, CH_2CH_3).

2. Reaction of Z-(C_5H_5)Fe(CO)(PPh_3)(COCH=$CHCH_2CH_2CH_3$) 41.

The cis-diastereoisomeric cyclopropyl products 121 and 122 eluted in diethyl ether:petroleum ether (1:1), drying to a red solid (82%) (121:122 = 14:1). Crystallisation from dichloromethane, hexane gave red crystals (121:122 = 22:1); Found: C, 72.21, H 6.61, $C_{33}H_{35}FePO_2$ requires: C, 72.00, H, 6.41%; ν_{max} 1910 vs (C≡O), 1600 s (C=O) cm^{-1}; m/z 550 (M^+), 522 (M^+-28).

RSR(SRS)-(C_5H_5)Fe(CO)(PPh_3)(COCH-$C(CH_3)_2CH_2CH_2CH_3$) 121. ^{1}H n.m.r. δ 7.6-7.3 (15H, m, Ph), 4.38 (5H, d, J_{PH} 1.0 Hz, C_5H_5), 2.80 (1H, d, J_{cis} 8.8 Hz, COCH), 1.57-1.20 (4H, m, CH_2CH_2), 0.95-0.85 (1H, m, $CHCH_2$), 0.94 (3H, s, CCH_3), 0.87 (3H, t, $J_{1,2}$ 7.3 Hz, CH_2CH_3), 0.56 (3H, s, CCH_3); ^{13}C-[^{1}H]n.m.r. δ 220,2 (d, J_{PC} 32.6 Hz, C≡O), 137.2 (d, J_{PC} 42.4 Hz, PhC_{ipso}), 133.4 (d, J_{PC} 9.5 Hz, PhC_{ortho}), 129.4 (s, PhC_{para}), 127.9 (d, J_{PC} 9.4 Hz, PhC_{meta}), 85.4 (s, C_5H_5), 57.1 (d, J_{PC} 5.6 Hz, COCH), 37.8 (s, $CHCH_2$), 29.5 (s, CCH_3), 28.6 (s, $C(CH_3)_2$), 26.3 (s, CH_2), 23.2 (s, CH_2), 14.3 (s, CCH_3), 14.0 (s, CH_2CH_3); ^{31}P-[^{1}H]n.m.r. δ 73.9.

RRS(SSR)-(C_5H_5)Fe(CO)(PPh_3)(COCH-$C(CH_3)_2CH_2CH_2CH_3$) 122. ^{1}H n.m.r. δ 7.6-7.3 (15H, m, Ph), 1.11 (3H, s, CCH_3), 1.02 (3H, s, CCH_3), 0.74 (3H, t, $J_{1,2}$ 6.8 Hz, CH_2CH_3).

The trans-diastereoisomeric cyclopropyl products 113 and 114 eluted in diethyl ether:petroleum ether (2:1) and dried to an orange/red solid (5.5%) (113:114 = >30:1); $\nu_{max.}$ 1910 vs (C≡O), 1600 s (C=O) cm^{-1}; m/z 550 (M^+).

RSS(SRR)-(C_5H_5)Fe(CO)(PPh_3)(COCH-$C(CH_3)_2CH_2CH_2CH_3$) 113. ^{1}H n.m.r. δ 7.6-7.3 (15H, m, Ph), 4.40 (5H, d, J_{PH} 1.0 Hz, C_5H_5), 2.53 (1H, d, J_{trans} 4.6 Hz, COCH), 1.32-1.20 (4H, m, CH_2CH_2), 1.03 (3H, s, CCH_3), 0.92-0.84 (4H, m, $CHCH_2CH_2CH_3$), 0.51 (3H, s, CCH_3).

RRR(SSS)-(C_5H_5)Fe(CO)(PPh_3)(COCH-$CHCH_2CH_2CH_3$) 114. ^{1}H n.m.r. δ 7.6-7.3 (15H, m, Ph), 4.36 (5H, d, J_{PH} 1.0 Hz, C_5H_5), 2.45 (1H, d, J_{trans} 4.5 Hz, COCH), 1.13 (3H, s, CCH_3), 1.07 (3H, s, CCH_3), 0.82 (3H, t, $J_{1,2}$ 7.3 Hz, CH_2CH_3).

Reaction of (C_5H_5)Fe(CO)(PPh_3)(COCH=$C(CH_3)_2$) 54 with diethylzinc and isopropylidene iodide.

The reaction described above (p.165) was repeated with (C_5H_5)Fe(CO)(PPh_3)(COCH=$C(CH_3)_2$) 54. The cyclopropyl product 123 eluted in diethyl ether:petroleum ether (1:1) on alumina (grade I), drying to an orange/red solid (89%). Crystallisation from dichloromethane/hexane gave orange needles of (C_5H_5)Fe(CO)(PPh_3)(COCH-$C(CH_3)_2$) 123; Found: C, 71.65, H, 6.37, $C_{32}H_{33}FePO_2$ requires: C, 71.65, H, 6.20%; $\nu_{max.}$ 1910 vs (C≡O), 1600 s(C=O) cm^{-1}; ^{1}H n.m.r. δ 7.6-7.3 (15H, m, Ph), 4.35 (5H, d, J_{PH} 1.0 Hz, C_5H_5), 2.61 (1H, s, COCH), 1.11 (3H, s, CH_3), 1.07 (3H, s, CH_3), 1.00 (3H, s, CH_3), 0.70 (3H, s, CH_3); ^{13}C-[^{1}H]n.m.r. δ 221.1 (d, J_{PC} 33.2 Hz, C≡O), 137.2 (d, J_{PC} 41.3 Hz, PhC_{ipso}), 133.4 (d, J_{PC} 9.5 Hz, PhC_{ortho}), 129.4 (s, PhC_{para}), 127.9 (d, J_{PC} 9.3 Hz, PhC_{meta}), 85.4 (s, C_5H_5), 65.0 (d, J_{PC} 5.3 Hz, CO<u>C</u>H), 34.1 (s, <u>C</u>$(CH_3)_2$), 33.2 (s, <u>C</u>$(CH_3)_2$), 24.1 (s, CH_3), 23.9 (s, CH_3), 17.4 (s, CH_3), 16.7 (s, CH_3); ^{31}P-[^{1}H]n.m.r. δ 74.4; m/z 536(M^+).

Synthesis of (±)-cis-(EtO_2CCH-$CHCH_3$)-124.

N-bromosuccinimide (180mg, 1.01mmol) in dichloromethane (6 ml) was added dropwise to a solution of the cyclopropyl complexes 115 and 116 (9:1)(479mg, 0.97mmol) in dichloromethane:ethanol (1:1)(12ml) at -40°, the solution rapidly becoming green. After stirring (-40°C; 10mins., 20°C; 40mins.), washing with brine (5ml),

removal of the organic layer and drying ($MgSO_4$), removal of solvent gave a green/brown solid/oil. Trituration with ether (6 x 4ml) and removal of solvent gave a green oil which was chromatographed on alumina (grade I) in dichloromethane, giving a yellow band, eluting in diethyl ether:petroleum ether (1:19) and drying to a yellow oil, and a green band, eluting in diethyl ether:petroleum ether (1:1) and tentatively assigned as $(C_5H_5)Fe(CO)(PPh_3)Br$ 27. The first band was the product 124 (70mg, 46%). $\nu_{max.}$ 1715 vs (C=O) cm^{-1}; ^1H n.m.r. ($CDCl_3$) δ 4.09 (2H, q, $J_{1,2}$ 7.1 Hz, $C\underline{H}_2CH_3$), 1.42-1.25 (2H, m, CHCH), 1.26 (3H, t, $J_{1,2}$ 7.1 Hz, $CH_2C\underline{H}_3$), 1.20 (3H, d, $J_{1,2}$ 6.4 Hz, $CHC\underline{H}_3$), 1.20 (3H, s, CCH_3), 1.15 (3H, s, CCH_3); ^1H n.m.r. (C_6D_6) δ 4.00 (2H, q, $J_{1,2}$ 7.1 Hz, $C\underline{H}_2CH_3$), 1.42 (1H, d, J_{cis} 8.8 Hz, COCH), 1.29 (3H, d, $J_{1,2}$ 6.5 Hz, $CHC\underline{H}_3$), 1.29 (3H, s, CCH_3), 0.99 (3H, t, $J_{1,2}$ 7.1 Hz, $CH_2C\underline{H}_3$), 0.90 (1H, m, $C\underline{H}CH_3$), 0.87 (3H, s, CCH_3); m/z (EI) 156(M^+), 140, 128, 110, 82, 55, 43. (N.B. It was concluded (see p. 79) that the literature data had been wrongly assigned [Lit.,[85] ^1H n.m.r. (C_6D_6) δ 4.01 (2H, q, $J_{1,2}$ 7.1 Hz, $C\underline{H}_2CH_3$), 1.28 (3H, s, CCH_3), 1.01 (3H, t, $J_{1,2}$ 7.1 Hz, $CH_2C\underline{H}_3$), 0.88 (3H, s, CCH_3), 0.84 (3H, d, $J_{1,2}$ 6.4 Hz, $CHC\underline{H}_3$)] (see p.186).

Reaction of Z-$(C_5H_5)Fe(CO)(PPh_3)(COCH=CHCH=CH_2)$ 49 with methylene iodide and diethylzinc.

Method A

Z-$(C_5H_5)Fe(CO)(PPh_3)(COCH=CHCH=CH_2)$ 49 (100mg, 0.203mmol) and zinc dichloride (109mg, 0.8mmol) were stirred (20°C; 10mins.) in toluene (2ml). Diethylzinc (0.1ml, 0.25mmol) and methylene iodide (0.016ml, 0.2mmol) were added and the reaction stirred (20°C; 30mins.). Addition of methanol (1ml), removal of solvent

and chromatography on alumina (grade I) in dichloromethane gave two bands eluting in diethyl ether:petroleum ether (7:3) and diethyl ether:ethyl acetate (9:1) respectively. Removal of the solvent from the first band gave an orange solid (30mg), identified as a 2:1 mixture of the products 130:127 (see below for spectroscopic details). Removal of the solvent from the second band gave an orange solid (62mg) identified as a 2:1 mixture of the starting material 49: the product 129 (see p.174 for spectroscopic details).

Method B

The reaction described above was repeated but with a four-fold excess of methylene iodide and a three-fold excess of diethylzinc. On work up, 130 was isolated as the only product (82%), no trace of the minor diastereoisomer 131 being seen. Crystallisation from dichloromethane/hexane gave orange crystals.

RRR(SSS)-$(C_5H_5)Fe(CO)(PPh_3)(COCH\text{-}CHCH\text{-}CH_2)$ 130. Found: C, 71.45, H, 5.58, $C_{31}H_{29}FePO_2$ requires: C, 71.55, H, 5.62%; $\nu_{max.}$ 1910 vs (C≡O), 1595 s (C=O) cm^{-1}; ^1H n.m.r. δ 7.6-7.3 (15H, m, Ph), 4.48 (5H, d, J_{PH} 1.3 Hz, C_5H_5), 2.89 (1H, ddd, J_{cis} 8.0 Hz, J_{cis} 8.0 Hz, J_{trans} 5.7 Hz, COCH), (0.85-0.81 (1H, m,), 0.75-0.70 (1H, m), 0.50-0.38 (4H, m) & 0.19-0.15 (2H, m)) ($CH_2CHCHCH_2CH_2$); $^{13}C\text{-}[^1H]$ n.m.r. δ 221.3 (d, J_{PC} 32.4 Hz, C≡O), 136.4 (d, J_{PC} 41.8 Hz, PhC_{ipso}), 133.4 (d, J_{PC} 10.0 Hz, PhC_{ortho}), 129.6 (s, PhC_{para}), 127.9 (d, J_{PC} 9.7 Hz, PhC_{meta}), 85.4 (s, C_5H_5), 45.5 (d, J_{PC} 6.7 Hz, COCH), 28.7 (s, CH), 14.6 (s, CH_2), 9.3 (s, CH), 5.1 (s, CH_2), 4.9 (s, CH_2); $^{31}P\text{-}[^1H]$n.m.r. δ 73.5; m/z 520(M^+), 492 (M^+-28).

RRR(SSS)-(C_5H_5)Fe(CO)(PPh_3)(COCH(-CH_2-)CHCH=CH_2) 127. (The data for 127 is taken from the mixture with 130 (Method A). No trace of a second diastereoisomer 128 could be detected). ^{1}H n.m.r. δ 7.6-7.3 (15H, m, Ph), 5.81-5.70 (1H, m, C<u>H</u>=CH_2), 5.09 (1H, dd, J_{trans} 17.3 Hz, J_{gem} 2.0 Hz, CH=C<u>H</u>(H)), 4.89 (1H, dd, J_{cis} 10.2 Hz, J_{gem} 2.1 Hz, CH=CH(<u>H</u>)), 4.41 (5H, d, J_{PH} 1.0 Hz, C_5H_5), 3.16-3.09 (1H, m, COCH), 1.81-1.71 (1H, m, C<u>H</u>CH=CH_2), 0.67-0.60 (1H, m, HC<u>H</u>). (Resonance due to remaining proton cannot be identified).

Preparation of cyclopropanecarboxaldehyde.[92]

Dimethyl sulphoxide (2.15ml, 30.39mmol) in dichloromethane (5ml) was added, over three mintues, to a solution of oxalyl chloride (1.22ml, 13.93mmol) in dichloromethane (25ml) at -78°C. After stirring (-78°C; 10mins), cyclopropanecarbinol (1ml, 12.67 mmol) in dichloromethane (10ml) was added dropwise over eight minutes, the solution rapidly becoming more viscous and a white precipitate forming. After stirring (-78°C; 15mins.), water (40ml) was added and the stirring continued (20°C; 10mins.). The organic layer was removed and the aqueous layer extracted with dichloromethane (2 x 7ml). The extracts were combined with the organic layer and washed with dil. HCl_{aq}(15ml), water (15ml), dil. K_2CO_{3aq} (15ml) and water (15ml) and then dried ($MgSO_4$). Removal of the solvent gave a pale yellow oil identified as the product (407mg, 46%); $\nu_{max.}$ 1715 vs (C=O) cm^{-1}; ^{1}H n.m.r. δ 8.87 (1H, d, $J_{1,2}$ 5.8 Hz, CHO), 1.84-1.79 (1H, m, C<u>H</u>CH_2), 1.07-1.03 (4H, m, CH_2CH_2).

Synthesis of Z- and E-$(C_5H_5)Fe(CO)(PPh_3)(COCH{=}CHC\overset{CH_2}{\overset{/\backslash}{H}}-CH_2)$ 129 and 132.

n-Butyllithium (1.42ml, 2.27mmol) was added to a solution of $(C_5H_5)Fe(CO)(PPh_3)(COCH_2Si(CH_3)_3)$ 34 (1g, 1.90mmol) in THF (15ml) at -78°C and stirred (-78°C; 45mins.). The cyclopropanecarboxaldehyde (300mg) obtained previously was added, the red solution becoming brown/orange. After stirring, removal of the solvent, addition of dichloromethane and filtration through alumina (grade I) with ethyl acetate, removal of the solvent gave an orange oil which was chromatographed on alumina (grade I) in dichloromethane. Two bands were eluted, in diethyl ether:petroleum ether (3:2) and diethyl ether:petroleum ether (2:1) respectively. The first band gave an orange solid identified as Z-129 (146mg, 15%) (see p.172), and removal of the solvent from the second band gave a red/orange oil identified as E-132 (584mg, 61%).

Z-$(C_5H_5)Fe(CO)(PPh_3)(COCH{=}CHC\overset{CH_2}{\overset{/\backslash}{H}}-CH_2)$ 129. Found: C, 70.93, H, 5.39, $C_{30}H_{27}FePO_2$ requires: C, 71.16, H, 5.37%; $\nu_{max.}$ 1915 vs (C≡O), 1605 s and 1560 s (C=O) cm^{-1}; ^1H n.m.r. δ 7.6-7.3 (15H, m, Ph), 6.62 (1H, d, J_{cis} 11.1 Hz, COCH), 4.45 (5H, d, J_{PH} 1.1 Hz, C_5H_5), 3.93 (1H, dd, J_{cis} 10.7 Hz, $J_{1,2}$ 10.7 Hz, COCHCH), 1.74-1.66 (1H, m, $CHCH_2$), (0.66-0.58 (1H, m), 0.55-0.46 (1H, m), and 0.28-0.10 (2H, m))(CH_2CH_2); ^{13}C-[^1H]n.m.r. δ 220.6 (d, J_{PC} 31.5 Hz, C≡O), 142.0 (d, J_{PC} 4.3 Hz, COCH), 136.6 (d, J_{PC} 43.1 Hz, PhC_{ipso}), 133.4 (d, J_{PC} 9.7 Hz, PhC_{ortho}), 130.4 (s, COCHCH), 129.6 (s, $Ph\text{-}C_{para}$), 127.9 (d, J_{PC} 9.6 Hz, PhC_{meta}), 85.4 (s, C_5H_5), 11.2 (s, CH CH_2), 8.3 (s, CH_2), 7.6 (s, CH_2); ^{31}P-[^1H]n.m.r. δ 73.6; m/z 506(M^+).

E-(C_5H_5)Fe(CO)(PPh_3)(COCH=CHCH(-CH_2-)CH_2) 132. Found: C, 71.18, H, 5.44, $C_{30}H_{27}FePO_2$ requires: C, 71.16, H, 5.37%; $\nu_{max.}$ 1910 vs (C≡O), 1610 s and 1560 s (C=O) cm^{-1}; ^1H n.m.r. δ 7.6-7.3 (15H, m, Ph), 6.68 (1H, d, J_{trans} 15.0 Hz, COCH), 4.97 (1H, dd, J_{trans} 14.9 Hz, $J_{1,2}$ 9.8 Hz, COCHC<u>H</u>), 1.26-1.20 (1H, m, C<u>H</u>CH_2), (0.77-0.73 (2H, m) and 0.40-0.37 (2H,m))(CH_2CH_2); m/z 506(M^+).

Reaction of Z-(C_5H_5)Fe(CO)(PPh_3)(COCH=CHCH(-CH_2-)CH_2) 129 with diethylzinc and methylene iodide.

Zinc dichloride (55mg, 0.4mmol) and 129 (52mg, 0.102mmol) in toluene (1ml) were stirred (20°C; 10mins.), and then diethylzinc (0.15ml, 0.165mmol) and methylene iodide (0.032ml, 0.40mmol) were added. After stirring (20°C; 15mins.), addition of methanol (1ml), removal of solvent, addition of dichloromethane and filtration through alumina (grade I) with diethyl ether:ethyl acetate (9:1), removal of solvent gave an orange solid identified by ^1H n.m.r. spectroscopy as RRR(SSS)-130 (44mg, 86%) (see p.172).

Reaction of Z-(C_5H_5)Fe(CO)(PPh_3)(COCH=CHCH=C(CH_3)$_2$) 51 with diethylzinc and isopropylidene iodide.

Method A

Zinc dichloride (120mg, 0.90mmol) and 51 (105mg, 0.202mmol) in toluene (2ml) were stirred, and diethylzinc (0.6ml, 0.66mmol) was added followed by isopropylidene iodide (0.022ml, 0.19mmol) added over five minutes. After stirring (20°C; 15mins.), addition of methanol (1ml), removal of solvent and addition of dichloromethane, chromatography on silica gave four bands eluting in petroleum ether:diethyl ether (19:1), petroleum ether:diethyl ether (9:1), petroleum ether:diethyl ether (1:1) and diethyl

ether:ethyl acetate (9:1) respectively. Removal of solvent from the bands gave an orange solid from band one identified as 135 (12mg, 10%), an orange/brown oil from band two, identified as 126 (8mg, 7%), a red solid from band three, identified as 134 (60mg, 53%), and an orange solid from the final band, identified as starting material 51 (24mg, 23%). Spectroscopic data is given below (see also table 11, p. 85).

Method B

The reaction described above was repeated with a fourfold excess of isopropylidene iodide. After work up a single product was isolated, identified as the complex 135 (77%). No trace of the minor diastereoisomer 136 was detected.

RSR(SRS)-(C_5H_5)Fe(CO)(PPh_3)(COCH-CH-CH-$C(CH_3)_2$-$C(CH_3)_2$ 135

Crystallisation from dichloromethane/hexane gave orange/red crystals. Found: C, 73.83, H, 7.04, $C_{37}H_{41}FePO_2$ requires: C, 73.51, H, 6.84%; $\nu_{max.}$ 1910 vs (C≡O), 1600 s (C=O) cm^{-1}; ^1H n.m.r. δ 7.6-7.3 (15H, m, Ph), 4.40 (5H, d, J_{PH} 1.2 Hz, C_5H_5), 2.89 (1H, d, J_{cis} 9.0 Hz, COCH), 1.10 (3H, s, CH_3), 1.04 (6H, s, CH_3CH_3), 0.91 (3H, s, CH_3), 0.85 (3H, s, CH_3), 0.75 (1H, dd, $J_{1,2}$ 9.3 Hz, $J_{1,2'}$ 9.2 Hz, CHCHCH), 0.70 (3H, s, CH_3), 0.56 (1H, d, $J_{1,2}$ 9.4 Hz, COCHCHCH); ^{13}C-[^1H]n.m.r. δ 221.3 (d, J_{PC} 33.3 Hz, C≡O), 136.2 (d, J_{PC} 42.3 Hz, PhC_{ipso}), 133.4 (d, J_{PC} 9.5 Hz, PhC_{ortho}), 129.4 (s, PhC_{para}), 128.0 (d, J_{PC} 9.4 Hz, PhC_{meta}), 85.3 (s, C_5H_5), 57.9 (d, J_{PC} 5.6 Hz, COCH), 34.2 (s, CH), 29.2 (s, CH_3), 28.8 (s, $C(CH_3)_2$), 28.1 (s, CH), 24.2 (s, CH_3), 23.4 (s, CH_3), 21.7 (s, $C(CH_3)_2$), 21.4 (s, $C(CH_3)_2$), 17.7 (s, CH_3), 17.4 (s, CH_3), 15.6 (s, CH_3); ^{31}P-[^1H]n.m.r. δ 74.4; m/z 604 (M^+).

RSR(SRS)-(C_5H_5)Fe(CO)(PPh_3)(COCH-CHCH=$C(CH_3)_2$) 126. Isolated as a brown/orange oil together with unidentified contaminants The diastereoisomer 133 could not be detected. $\nu_{max.}$ 1910 vs (C≡O), 1600 s (C=O) cm^{-1}; ^1H n.m.r. δ 7.6-7.3 (15H, m, Ph), 5.28 (1H, d, $J_{1,2}$ 9.1 Hz, C<u>H</u>=$C(CH_3)_2$), 4.35 (5H, d, J_{PH} 0.8 Hz, C_5H_5), 2.98 (1H, d, J_{cis} 8.9 Hz, COCH), 1.74 (3H, s, CH_3), 1.67 (3H, s, CH_3), 0.96 (3H, s, CH_3), 0.69 (3H, s, CH_3); m/z 562(M^+).

Z-(C_5H_5)Fe(CO)(PPh_3)(COCH=CHCH-$C(CH_3)_2$) 134. Crystallisation from dichloromethane/hexane gave red crystals. Found: C, 72.39, H, 6.35, $C_{34}H_{35}FePO_2$ requires: C, 72.60, H, 6.27%; $\nu_{max.}$ 1910 vs (C≡O), 1600 s (C=O) cm^{-1}; ^1H n.m.r. δ 7.6-7.3 (15H, m, Ph), 6.58 (1H, d, J_{cis} 11.3 Hz, COCH), 4.43 (5H, d, J_{PH} 1.2 Hz, C_5H_5), 4.39 (1H, dd, J_{cis} 11.2 Hz, $J_{1,2}$ 11.2 Hz, COCHC<u>H</u>), 1.45 (1H, d, $J_{1,2}$ 10.3 Hz, C<u>H</u>$C(CH_3)_2$), 1.05 (3H, s, CH_3), 0.98 (3H, s, CH_3), 0.97 (3H, s, CH_3), 0.96 (3H, s, CH_3); m/z 562(M^+).

Synthesis of Z-(C_5H_5)Fe(CO)(PPh_3)(COCH=CHCH-$C(CH_3)_2$) 137 and 138.

Method A

Zinc dichloride (120mg, 0.88mmol) and Z-(C_5H_5)Fe(CO)(PPh_3)(COCH=CHCH=$C(CH_3)_2$) 51 (105mg, 0.20mmol) were stirred (20°C; 10mins.) in toluene (2ml), and then diethylzinc (0.3ml, 0.33mmol) and methylene iodide (0.017ml, 0.20mmol) were added. After stirring (20°C; 15mins.), addition of methanol (1ml), removal of solvent and chromatography on alumina (grade I), two bands eluting in petroleum ether:diethyl ether (3:1) and diethyl ether respectively were collected. Removal of the solvent from the second band gave an orange solid identified by ^1H n.m.r. spectroscopy

as the starting material 51 (67mg, 64%). Removal of the solvent from the first band gave a 5:1 mixture of the diastereoisomeric products 137:138 (32mg, 30%) (See below for spectroscopic details).

Method B

Zinc dichloride (120mg, 0.88mmol) and Z-(C_5H_5)Fe(CO)(PPh_3)(COCH=CHCH=CH_2) 49 (102mg, 0.20mmol) were stirred (20°C; 10mins.), in toluene (2ml), and then diethylzinc (0.6ml, 0.66mmol) was added followed by isopropylidene iodide (0.022ml, 0.19mmol) over five minutes. After stirring (20°C; 15mins.), addition of methanol, removal of solvent and chromatography on alumina (grade I) in dichloromethane, two bands eluting in petroleum ether: diethyl ether (4:1) were discarded whilst a third band eluting in petroleum ether:diethyl ether (3:1) was collected. Removal of solvent gave an orange solid identified as a 5:1 mixture of the diastereoisomeric products 138:137 (16mg, 15%). Starting material 49 (42mg, 41%) was also recovered.

The stereochemistries of 137 and 138 were assigned arbitarily. The spectroscopic data given below was obtained from the 5:1 mixtures of 137:138 (Method A) and 138:137 (Method B) respectively.

Z-(C_5H_5)Fe(CO)(PPh_3)(COCH=CHCH-$C(CH_3)_2$) 137. Accurate mass: Found 534.1414, $C_{32}H_{31}FePO_2$ requires: 534.1411; $\nu_{max.}$ 1910 vs (C≡O), 1600 s (C=O) cm^{-1}; ^1H n.m.r. δ 7.6-7.3 (15H, m, Ph), 6.63 (1H, d, J_{cis} 11.2 Hz, COCH), 4.45 (5H, d, J_{PH} 0.9 Hz, C_5H_5), 4.33 (1H, dd, J_{cis} 11.1Hz, $J_{1,2}$ 11.2 Hz, COCHCH), 1.89-1.75 (1H, m, CHCH$_2$), 1.05 (3H, s, CH_3), 0.92 (3H, s, CH_3), 0.65 (1H, dd, J_{cis} 8.6 Hz, J_{gem} 4.0 Hz, HCH), 0.24 (1H, dd, J_{trans} 4.7 Hz, J_{gem} 4.4 Hz, HCH).

Z-$(C_5H_5)Fe(CO)(PPh_3)(COCH{=}CHCH(CH_2)C(CH_3)_2)$ 138. $\nu_{max.}$ 1915 vs (C≡O), 1605 s (C=O) cm^{-1}; ^1H n.m.r. δ 7.6-7.3 (15H, m, Ph), 6.58 (1H, d, J_{cis} 11.2 Hz, COCH), 4.43 (5H, d, J_{PH} 1.0 Hz, C_5H_5), 4.24 (1H, dd, J_{cis} 11.1 Hz, $J_{1,2}$ 10.9 Hz, COCHCH), 1.85-1.71 (1H, m, $CHCH_2$), 1.04 (3H, s, CH_3), 0.97 (3H, s, CH_3), 0.54 (1H, dd, J_{cis} 8.3 Hz, J_{gem} 4.1 Hz, HCH), 0.21 (1H, dd, J_{trans} 4.6 Hz, J_{gem} 4.4 Hz, HCH); m/z 534(M^+).

Preparation of ethylidene iodide.[93] (Aerobic conditions)

Acetaldehyde (6ml, 0.107mol) was added dropwise (over 30mins.) to stirring hydrazine monohydrate (10ml, 0.206mol) at 0°C. After stirring (0°C; 15mins.) the reaction was extracted with dichloromethane (6 x 4ml), the combined extracts dried ($MgSO_4$) and then diluted by addition of dichloromethane (100ml). After addition of triethylamine (24ml), iodine (29g, 0.114mol) was added over thirty minutes, the solution temperature being maintained between 20-30°C by external cooling. After washing with water (5 x 10ml), 5% $Na_2S_2O_{3aq}$ (5 x 10ml), 3M HCl_{aq} (2 x 10ml) and sat. $NaCl_{aq}$ (2 x 10ml) and drying ($MgSO_4$), removal of solvent gave a brown oil which was distilled to give a pale yellow oil (Bpt. 63-65°/15mm) [Lit.,[93] Bpt. 50-51°/7.2mm] as the product (9.35g, 31%); ^1H n.m.r. δ 5.23 (1H, q, $J_{1,2}$ 6.7 Hz, CH), 2.93 (3H, d, $J_{1,2}$ 6.7 Hz, CH_3).

Reaction of $(C_5H_5)Fe(CO)(PPh_3)(COCH{=}CH_2)$ 52 with diethylzinc and ethylidene iodide.

Zinc dichloride (113mg, 0.84mmol) and 52 (100mg, 0.21mmol) were stirred (20°C; 10mins.), in toluene (2ml). After addition of diethylzinc (0.12ml, 0.3mmol) and ethylidene iodide (0.085ml,

0.84mmol) the reaction was stirred (20°C; 2h). Addition of methanol, removal of solvent and chromatography on alumina (grade I) in dichloromethane gave three bands eluting in diethyl ether: petroleum ether (1:1), diethyl ether:petroleum ether (5:1) and diethyl ether:ethyl acetate (19:1) respectively. Removal of the solvent from the final band gave starting material 52 (23mg, 23%). Removal of the solvent from the first band gave an orange solid identified by ^{1}H n.m.r. spectroscopy as a 3:1 mixture of the cis-substituted cyclopropyl complexes 72:73 (7mg, 7%), and the second band dried to an orange solid identified by ^{1}H n.m.r. spectroscopy as a 2:1 mixture of the trans-isomers 84:85 (66mg, 64%). The spectroscopic data for the cis- and trans-products is given on pages 153 and 199 respectively.

Reaction of $(C_5H_5)Fe(CO)(PPh_3)(COCH=C(CH_3)_2)$ 54 with diethylzinc and ethylidene iodide.

Zinc dichloride (220mg, 1.61mmol) and 54 (200mg, 0.408mmol) were stirred (20°C; 10mins.) in toluene (4ml) and then diethylzinc (0.24ml, 0.6mmol) and ethylidene iodide (0.17ml, 1.68mmol) were added. After stirring (20°C; 15mins.), addition of methanol (2ml), removal of solvent and chromatography on alumina (grade I), in dichloromethane gave two bands eluting in diethyl ether: petroleum ether (1:1) and diethyl ether respectively. Removal of the solvent from the first band gave an orange solid identified as an 8:1 mixture of the cis-substituted cyclopropyl complexes 116:115 (15mg, 7%), the synthesis of which had been reported previously (p.165); $\nu_{max.}$ 1910 vs (C≡O), 1600 s (C=O) cm^{-1}; m/z 522(M^+), 494(M^+-28).

RRS(SSR)-(C_5H_5)Fe(CO)(PPh_3)(COCH-C(CH_3)$_2$) 116. ^{1}H n.m.r. δ 7.6-7.3 (15H, m, Ph), 4.36 (5H, d, J_{PH} 1.3 Hz, C_5H_5), 2.80 (1H, d, J_{cis} 8.3 Hz, COCH), 1.08 (3H, s, CH_3), 1.03 (3H, s, CH_3), 0.63 (3H, d, $J_{1,2}$ 6.4 Hz, $CHCH_3$).

RSR(SRS)-(C_5H_5)Fe(CO)(PPh_3)(COCH-C(CH_3)$_2$) 115. Spectrosoopic data is given on page 166.

Removal of the solvent from the second band gave an orange solid identified as an 8:1 mixture of the trans-substituted cyclopropyl complexes 108:107 (170mg, 80%) which had been synthesised previously (p.164). Crystallisation from dichloromethane/hexane gave orange crystals (108:107 = 12:1); Found: C, 71.54, H, 6.11, $C_{31}H_{31}FePO_2$ requires: C, 71.27, H, 5.98%; $\nu_{max.}$ 1915 vs (C≡O), 1600 s (C=O) cm^{-1}; m/z 522(M^+).

RRR(SSS)-(C_5H_5)Fe(CO)(PPh_3)(COCH-C(CH_3)$_2$) 108. ^{1}H n.m.r. δ 7.6-7.3 (15H, m, Ph), 4.37 (5H, d, J_{PH} 1.1 Hz, C_5H_5), 2.34 (1H, d, J_{trans} 5.4 Hz, COCH), 1.11 (3H, s, CH_3), 1.05 (3H, s, CH_3), 1.09-1.03 (1H, m, $CHCH_3$), 0.79 (3H, d, $J_{1,2}$ 6.3 Hz, $CHCH_3$); ^{13}C-[^{1}H] n.m.r. δ 220.1 (d, J_{PC} 31.5 Hz, C≡O), 136.9 (d, J_{PC} 42.6 Hz, PhC_{ipso}), 133.4 (d, J_{PC} 9.5 Hz, PhC_{ortho}), 129.5 (s, PhC_{para}), 127.9 (d, J_{PC} 9.3 Hz, PhC_{meta}), 85.4 (s, C_5H_5), 63.4 (s, COCH), 29.4 (s, $C(CH_3)_2$), 28.3 (s, CH), 21.7 (s, CCH_3), 21.2 (s, CCH_3), 13.1 (s, $CHCH_3$); ^{31}P-[^{1}H]n.m.r. δ 73.7.

Spectroscopic data for RSS(SRR)-107 is given on page 167

Reaction of Z-(C_5H_5)Fe(CO)(PPh_3)(COCH=CHR) with diethylzinc and ethylidene iodide.

The reaction described above for (C_5H_5)Fe(CO)(PPh_3)(COCH=C(CH_3)$_2$) 54 was repeated with several Z-α,β-unsaturated iron acyl complexes. The results are summarised in table 14 (p. 94). In

each case the cis-diastereoisomers (methyl to iron) 143 and 144 eluted first in diethyl ether:petroleum ether (1:1). The trans-diastereoisomers 145 and 146 were eluted in diethyl ether. The spectroscopic data are given below.

1. Reaction of Z-(C_5H_5)Fe(CO)(PPh_3)(COCH=$CHCH_3$) 37.

A single cis-diastereoisomer 140 (5%) was collected.

RSR(SRS)-(C_5H_5)Fe(CO)(PPh_3)(COCH(-$CHCH_3$)-CH_3) 140. $\nu_{max.}$ 1910 vs (C≡O), 1605 s (C=O) cm^{-1}; ^1H n.m.r. δ 7.6-7.3 (15H, m, Ph), 4.39 (5H, d, J_{PH} 1.4 Hz, C_5H_5), 2.96 (1H, dd, J_{cis} 8.5 Hz, J_{cis} 8.5 Hz, COCH), 1.09-0.97 (2H, m, CHCH), 1.01 (3H, $J_{1,2}$ 6.4 Hz, CH_3), 0.56 (3H, d, $J_{1,2}$ 6.4 Hz, CH_3); m/z 508 (M^+).

A 9:1 mixture of the trans-diastereoisomers 141:142 (90%) was collected. Crystallisation from dichloromethane/hexane gave red crystals (141:142 = 16:1); Found: C, 70.58, H, 5.77, $C_{30}H_{29}FePO_2$ requires C, 70.88, H, 5.75%; $\nu_{max.}$ 1910 vs (C≡O), 1595 s (C=O) cm^{-1}; m/z 508 (M^+).

RSS(SRR)-(C_5H_5)Fe(CO)(PPh_3)(COCH(-$CHCH_3$)-CH_3) 141. ^1H n.m.r. δ 7.6-7.3 (15H, m, Ph), 4.39 (5H, d, J_{PH} 1.3 Hz, C_5H_5), 2.62 (1H, dd, J_{cis} 8.4 Hz, J_{trans} 4.3 Hz, COCH), 1.05 (3H, d, $J_{1,2}$ 5.8 Hz, CH_3), 1.00-0.80 (5H, m, $CHCHCH_3$); ^{13}C-[^1H]n.m.r. δ 221.2 (d, J_{PC} 33.1 Hz, C≡O), 136.9 (d, J_{PC} 42.6 Hz, PhC_{ipso}), 133.4 (d, J_{PC} 9.5 Hz, PhC_{ortho}), 129.6 (s, PhC_{para}), 128.0 (d, J_{PC} 9.4 Hz, PhC_{meta}), 85.4 (s, C_5H_5), 55.3 (d, J_{PC} 6.5 Hz, CO$\underline{C}$H), 27.5 (s, $\underline{C}HCH_3$), 23.8 (s, $\underline{C}HCH_3$), 18.3 (s, CH_3), 12.7 (s, CH_3); ^{31}P-[^1H]n.m.r. δ 73.6.

RRR(SSS)-(C_5H_5)Fe(CO)(PPh_3)(COCH-$CHCH_3$) 142. ^{1}H n.m.r. δ 7.6-7.3 (15H, m, Ph), 4.42 (5H, br s, C_5H_5), 2.68 (1H, dd, J_{cis} 8.5 Hz, J_{trans} 4.6 Hz, COCH), 0.95 (3H, d, $J_{1,2}$ 5.9 Hz, CH_3), 0.56 (3H, d, $J_{1,2}$ 6.2 Hz, CH_3). Remaining resonances obscured by those of 141.

2. Reaction of Z-(C_5H_5)Fe(CO)(PPh_3)(COCH=$CHCH_2CH_2CH_3$) 41.

A 10:1 mixture of the cis-diastereoisomers 147:148 (3%) was isolated. $\nu_{max.}$ 1910 vs (C≡O), 1600 s (C=O) cm^{-1}; m/z 536(M^+).

RRSR(SSRS)-(C_5H_5)Fe(CO)(PPh_3)(COCH-$CHCH_2CH_2CH_3$) 147. ^{1}H n.m.r. δ 7.6-7.3 (15H, m, Ph), 4.40 (5H, d, J_{PH} 1.3 Hz, C_5H_5), 2.94 (1H, dd, J_{cis} 8.5 Hz, J_{cis} 8.5 Hz, COCH), 1.53-0.71 (9H, m, $CHCHCH_2CH_2CH_3$), 0.53 (3H, d, $J_{1,2}$ 6.3 Hz, $CHCH_3$).

RSRS(SRSR)-(C_5H_5)Fe(CO)(PPh_3)(COCH-$CHCH_2CH_2CH_3$) 148. ^{1}H n.m.r. δ 2.93 (dd, J_{cis} 8.4 Hz, J_{cis} 8.4 Hz, COCH). No other resonances could be assigned to 148.

A 12:1 mixture of the trans-diastereoisomers 149:150 (84%) was isolated. Crystallisation from dichloromethane/hexane gave orange needles (149:150 = 14:1); Found: C, 71.67, H. 6.31, $C_{32}H_{33}FePO_2$ requires: C, 71.65, H, 6.20%; $\nu_{max.}$ 1915 vs (C≡O), 1590 s (C=O) cm^{-1}; m/z 536(M^+).

RRSS(SSRR)-(C_5H_5)Fe(CO)(PPh_3)(COCH-$CHCH_2CH_2CH_3$) 149. ^{1}H n.m.r. δ 7.6-7.3 (15H, m, Ph), 4.39 (5H, d, J_{PH} 1.4 Hz, C_5H_5), 2.61 (1H, dd, J_{cis} 7.6 Hz, J_{trans} 5.5 Hz, COCH), 1.36-1.27 (4H, m, CH_2CH_2), 0.97-0.73 (8H, m, $CHCHCH_3$ and CH_2CH_3); ^{13}C-[^{1}H]n.m.r. δ 221.2 (d, J_{PC} 32.7 Hz, C≡O), 136.8 (d, J_{PC} 42.6 Hz, PhC_{ipso}), 133.4 (d, J_{PC} 9.4 Hz, PhC_{ortho}), 129.5 (s, PhC_{para}), 127.9 (d, J_{PC} 9.4 Hz,

PhC_{meta}), 85.4 (s, C_5H_5), 55.1 (d, J_{PC} 6.7 Hz, COCH), 33.7 (s, $\underline{C}HCH_2$), 29.2 (s, $CH\underline{C}H_2$), 23.2 (s, $\underline{C}H_2CH_3$ and $\underline{C}HCH_3$), 18.5 (s, $CH\underline{C}H_3$), 13.9 (s, $CH_2\underline{C}H_3$); ^{31}P-[^1H]n.m.r. δ 73.5.

RSRR(SRSS)-(C_5H_5)Fe(CO)(PPh_3)(COCH(CHCH$_3$)-$CHCH_2CH_2CH_3$) 150. ^1H n.m.r. δ 7.6-7.3 (15H, m, Ph), 4.42 (5H, d, J_{PH} 1.0 Hz, C_5H_5), 2.66 (1H, m, COCH), 0.96 (3H, d, $J_{1,2}$ 6.1 Hz, $CHCH_3$), 0.73 (3H, t, $J_{1,2}$ 6.8 Hz, CH_2CH_3). (The remaining resonances were obscured by those of 149).

3. Reaction of Z-(C_5H_5)Fe(CO)(PPh_3)($COCH{=}CHCH_2CH_2CH_2CH_3$) 43.

A mixture of the diastereoisomers 151 and 152 (4%) was isolated, the diastereoisomeric ratio being tentatively assigned as 10:1 (see below); $\nu_{max.}$ 1915 vs (C≡O), 1605 s (C=O), cm^{-1}; m/z 550(M^+).

RRSR(SSRS)-(C_5H_5)Fe(CO)(PPh_3)(COCH(CHCH$_3$)-$CHCH_2CH_2CH_2CH_3$) 151. ^1H n.m.r. δ 7.6-7.3 (15H, m, Ph), 4.40 (5H, d, J_{PH} 1.3 Hz, C_5H_5), 2.93 (1H, dd, J_{cis} 8.5 Hz, J_{cis} 8.5 Hz, COCH), 1.59-0.84 (8H, m, $CHCHCH_2CH_2CH_2$), 0.89 (3H, t, $J_{1,2}$ 7.2 CH_2CH_3), 0.54 (3H, d, $J_{1,2}$ 6.4 Hz, $CHCH_3$).

RSRS(SRSR)-(C_5H_5)Fe(CO)(PPh_3)(COCH(CHCH$_3$)-$CHCH_2CH_2CH_2CH_3$) 152. ^1H n.m.r. δ 4.39 (d, J_{PH} 1.0 Hz, C_5H_5) (No other resonances for 152 could be seen).

A 15:1 mixture of the diastereoisomers 153 and 154 (82%) was isolated. Crystallisation from dichloromethane/hexane gave orange crystals (153:154 = 20:1); Found: C, 71.77, H, 6.48, $C_{33}H_{35}FePO_2$ requires: C, 72.00, H, 6.41%; $\nu_{max.}$ 1915 vs (C≡O), 1600 s (C=O) cm^{-1}; m/z 550(M^+).

RRSS(SSRR)-(C_5H_5)Fe(CO)(PPh_3)(COCH-$CHCH_3$-$CHCH_2CH_2CH_2CH_3$) 153. ^{1}H n.m.r. δ 7.6-7.3 (15H, m, Ph), 4.39 (5H, d, J_{PH} 1.1 Hz, C_5H_5), 2.60 (1H, dd, J_{cis} 7.9 Hz, J_{trans} 5.1 Hz, COCH), 1.37-1.22 (6H, m, $CH_2CH_2CH_2$), 0.90-0.78 (8H, m, $CHCH_3$, CH and CH_2CH_3); ^{13}C-[^{1}H]n.m.r. δ 221.3 (d, J_{PC} 31.6 Hz, C≡O), 136.9 (d, J_{PC} 42.7 Hz, PhC_{ipso}), 133.4 (d, J_{PC} 9.5 Hz, PhC_{ortho}), 129.6 (s, PhC_{para}), 127.9 (d, J_{PC} 9.5 Hz, PhC_{meta}), 85.5 (s, C_5H_5), 55.2 (d, J_{PC} 7.0 Hz, COCH), 34.0 (s, CH), 32.5 (s, CH_2), 26.9 (s, CH_2), 23.1 (s, CH), 22.5 (s, CH_2), 18.6 (s, $CHCH_3$), 14.3 (s, CH_2CH_3); ^{31}P-[^{1}H]n.m.r. δ 73.4.

RSRR(SRSS)-(C_5H_5)Fe(CO)(PPh_3)(COCH-$CHCH_3$-$CHCH_2CH_2CH_2CH_3$) 154. ^{1}H n.m.r. δ 7.6-7.3 (15H, m, Ph), 4.42 (5H, d, J_{PH} 1.0 Hz, C_5H_5), 2.65 (1H, m, COCH), 0.96 (3H, d, $J_{1,2}$ 6.3 Hz, $CHCH_3$). (The remaining resonances were obscured by those of 153).

4. Reaction of Z-(C_5H_5)Fe(CO)(PPh_3)(COCH=CHCH(CH_3)$_2$) 45.

Only the trans-substituted diastereoisomers 155 and 156 were isolated (95%, 155:156 = 28:1). Crystallisation from dichloromethane/hexane gave red crystals of 155. Subsequently an X-ray crystal structure analysis of 155 was undertaken (see p.95 and Appendix 1).

RRSS(SSRR)-(C_5H_5)Fe(CO)(PPh_3)(COCH-$CHCH_3$-$CHCH(CH_3)_2$) 155. Found: C, 71.46, H, 6.40 $C_{32}H_{33}FePO_2$ requires: C, 71.65, H, 6.20%; $\nu_{max.}$ 1915 vs (C≡O), 1585 s (C=O) cm^{-1}; ^{1}H n.m.r. δ 7.6-7.3 (15H, m, Ph), 4.42 (5H, d, J_{PH} 1.2 Hz, C_5H_5), 2.60 (1H, dd, J_{cis} 8.3 Hz, J_{trans} 2.9 Hz, COCH), 1.71-1.61 (1H, m, $CH(CH_3)_2$), 0.91 (3H, d, $J_{1,2}$ 6.5 Hz, H_3CCHCH_3), 0.85 (3H, d, $J_{1,2}$ 6.7 Hz, H_3CCHCH_3), 0.78-0.74 (4H, m, $CHCH_3$), 0.64-0.60 (1H, m, CH); ^{13}C-[^{1}H]n.m.r. δ 221.3 (d, J_{PC} 32.7 Hz, C≡O), 136.9 (d, J_{PC} 42.5 Hz, PhC_{ipso}),

133.4 (d, J_{PC} 9.7 Hz, PhC_{ortho}), 129.6 (s, PhC_{para}), 127.9 (d, J_{PC} 9.5 Hz, PhC_{meta}), 85.6 (s, C_5H_5), 55.6 (d, J_{PC} 6.7 Hz, CO$\underline{C}$H), 43.6 (s, $\underline{C}HCH(CH_3)_2$), 25.5 (s, $\underline{C}H(CH_3)_2$), 23.4 (s, CH_3), 23.3 (s, $\underline{C}HCH_3$), 22.7 (s, CH_3), 18.9 (s, $CH\underline{C}H_3$); $^{31}P-[^1H]$n.m.r. δ 73.1; m/z 536(M^+), 508(M^+-28).

RSRR(SRSS)-$(C_5H_5)Fe(CO)(PPh_3)(COCH(CHCH_3)CH(CH_3)_2)$ 156. ^1H n.m.r. δ 7.6-7.3 (15H, m, Ph), 0.98 (3H, d, $J_{1,2}$ 6.7 Hz, $CHC\underline{H}_3$). (The remaining resonances were obscured by those of 155).

Synthesis of (±)-trans-$(EtO_2CCH(CHCH_3)C(CH_3)_2)$ 157.

N-bromosuccinimide (141mg, 0.81mmol) in dichloromethane (5ml) was added dropwise to an orange solution of RRR(SSS)-108 and RSS(SRR)-107 (8:1)(376mg, 0.72mmol), in dichloromethane: ethanol (1:1, 10ml) at -40°C, the solution becoming green. After stirring (-40°C; 10mins., 20°C; 40mins.), the solution was washed with brine (4ml) and dried ($MgSO_4$). Removal of the solvent gave a green oil/solid, and chromatography on alumina (grade I) in dichloromethane gave a yellow band, eluting in petroleum ether: diethyl ether (19:1), and a green band eluting in diethyl ether. Removal of the solvent from the second band gave a green solid, the iron bromide 27. Removal of the solvent from the first band gave the product 157 as a yellow oil (43mg, 39%); $\nu_{max.}$ 1715 vs (C=O) cm^{-1}; ^1H n.m.r. (C_6D_6) δ 4.07-4.00 (2H, m, $C\underline{H}_2CH_3$), 1.50 (1H, m, $C\underline{H}CH_3$), 1.30 (3H, s, CCH_3), 1.16 (1H, d, J_{trans} 5.4 Hz, COCH), 1.01 (3H, t, $J_{1,2}$ 7.1 Hz, $CH_2C\underline{H}_3$), 0.88 (3H, s, CCH_3), 0.84 (3H, d, $J_{1,2}$ 6.3 Hz, $CHC\underline{H}_3$); m/z (EI) 156(M^+), 140, 110, 82, 65, 55, 43. It was concluded that the literature data[85] for 157 was wrong (see p. 98 and p.170). [Lit.,[85] ^1H n.m.r. (C_6D_6) δ

4.00 (2H, q, $J_{1,2}$ 7.1 Hz, $C\underline{H}_2CH_3$), 1.4-0.8 (2H, m, CHCH), 1.28 (3H, d, $J_{1,2}$ 5.9 Hz, $CHC\underline{H}_3$), 1.28 (3H, s, CCH_3), 1.00 (3H, t, $J_{1,2}$ 7.1 Hz, $CH_2C\underline{H}_3$), 0.88 (s, CCH_3)].

Synthesis of (±)-($EtO_2CCH(CHCH_3)CHCH_3$)-158.

Addition of N-bromosuccinimide (265mg, 1.52mmol) to a 9:1 mixture of RSS(SRR)-141 and RRR(SSS)-142 (686mg, 1.35mmol), gave, after work up and chromatography as described above, the product 158 as a yellow oil (86mg, 45%); $\nu_{max.}$ 1715 vs (C=O) cm^{-1}; ^1H n.m.r. (C_6H_6) δ 4.02 (2H, q, $J_{1,2}$ 7.1 Hz, $C\underline{H}_2CH_3$), 1.34 (1H, dd, J_{cis} 8.8 Hz, J_{trans} 4.8 Hz, COCH), 1.33-1.29 (1H, m, $C\underline{H}CH_3$), 1.24 (3H, d, $J_{1,2}$ 6.2 Hz, $CHC\underline{H}_3$), 0.99 (3H, t, $J_{1,2}$ 7.1 Hz, $CH_2C\underline{H}_3$), 0.78 (3H, d, $J_{1,2}$ 5.9 Hz, $CHC\underline{H}_3$), 0.76-0.71 (1H, m, $C\underline{H}CH_3$); m/z (CI/NH_3) 143(M^++1), 127, 97, 69. [Lit.,[96] ^1H n.m.r. (CCl_4) δ 4.02 (2H, q, CH_2), 1.23 (3H, t, $CH_2C\underline{H}_3$) and 1.10 (1H, dd, J_{cis} 8.0 Hz, J_{trans} 6.0 Hz, COCH) superimposed on broad multiplet, total of 12H].

Reactions of E-(C_5H_5)Fe(CO)(PPh_3)($COCH{=}CHCH_3$) 36 with sulphur and phosphorus ylids.

t-Butyllithium (0.12ml, 0.283mmol) was added to a solution/suspension of diphenylmethylsulphonium tetrafluoroborate 181[106] (84mg, 0.29mmol) in THF (3ml) at -78°C and the solution stirred (-78°C; 45mins.).[105] A solution of 36 (130mg, 0.27mmol) in THF (4ml) at -78°C was added and the solution stirred (-78°C; 2h, 20°C; 1h). Addition of methanol (2ml) removal of solvent, addition of dichloromethane and filtration through alumina (grade I) with ethyl acetate gave, on removal of solvent, recovered starting

material 36 (118mg, 91%).

Butyllithium (0.13ml, 0.21mmol) was added dropwise to a suspension of methyltriphenylphosphonium iodide (85mg, 0.21mmol) in THF (3ml) at 0°C, a red solution of the methylide being formed. After stirring (0°C; 10mins., 20°C; 40mins.) the solution was cooled (-78°C) and a solution of 36 (100mg, 0.208mmol) in THF (3ml) at -78°C was added. After stirring (-40°C; 1h, 20°C; 1h) work up, as described above, gave only recovered starting material 36 (98mg, 98%).

Reactions of E-(C_5H_5)Fe(CO)(PPh_3)($COCH=CHCH_3$) 36 with the α-lithiosulphide derived from thioanisole.

Method A

Butyllithium (3.2ml, 5.12mmol) was added dropwise to a solution of thioanisole (774mg, 6.24mmol) in THF (15ml) at 0°C, and the solution stirred (0°C; 2h) and then cooled (-78°C). A solution of 36 (600mg, 1.25mmol) in THF at -78°C was added, the solution rapidly becoming red indicating enolate formation. After stirring (-40°C; 2h), addition of methanol, removal of solvent and chromatography on alumina (grade I), a single band was collected eluting in diethyl ether:petroleum ether (1:1). Removal of solvent gave an orange solid, identified as a 19:1 mixture of the sulphenyl complexes 182:183 (82%). Crystallisation from dichloromethane/hexane gave orange crystals of 182 (see p.191 for spectroscopic data).

Method B

The reaction described above was repeated, but after stirring the reaction (-40°C;2h) was allowed to warm rapidly to room temp-

erature and stirred (20°C; 20mins.). Work up and chromatography, as above, gave a single product band identified as a 20:1 mixture of the diastereoisomeric cyclopropyl complex 85:84 (42%). The spectroscopic data for 85 and 84 are given on page 199.

Non-stereoselective synthesis of $(C_5H_5)Fe(CO)(PPh_3)(COCH_2CH(CH_3)CH_2SPh)$ 182 and 183.[109,110]

Thiophenol (5.6g, 50.9mmol) was added dropwise to methacrolein (3.6g, 51.4mmol) at 0°C, followed by addition of five drops of triethylamine. After stirring (0°C; 15mins., 20°C; 1h), the reaction mixture was poured into ether (40ml), washed with $1MHCl_{aq}$ (3 x 5ml) and dried ($MgSO_4$). Removal of solvent gave a cloudy oil which was distilled to give the β-sulphenylated aldehyde 184 as a clear liquid. (7.308g, 79%; b.pt. 108-110°/2mmHg); $\nu_{max.}$ 1710 vs (C=O); ^{1}H n.m.r. δ9.68 (1H, d, $J_{1,2}$ 1.1 Hz, CHO), 7.39-7.22 (5H, m, Ph), 3.31, 2.93 (2H, ABX system, J_{AB} 13.4 Hz, J_{AX} 6.6 Hz, J_{BX} 7.0 Hz, $C\underline{H}_2SPh$), 2.66-2.61 (1H, m, $C\underline{H}CH_3$), 1.24 (3H, d, $J_{1,2}$ 7.3 Hz, CH_3). [Lit.,[109] ^{1}H n.m.r. (CCl_4) δ 9.6 (1H, s), 7.4-7.1 (5H, m), 3.2 (1H, dd, J = 12 and 6 Hz), 2.8 (1H, dd, J = 12 and 7 Hz), 2.5 (1H, ddq, J = 6,7 and 7 Hz), 1.15 (3H, d, J = 7 Hz)].

Sodium borohydride (480mg, 12.63mmol) was added, over forty minutes, to a solution of 184 (7.308g, 40.6mmol) in ethanol (38ml) at 20°C. The solution was poured into a stirring mixture of ether (100ml) and $1MHCl_{aq}$ (50ml), and then the organic layer was removed and the aqueous layer extracted with diethyl ether (3 x 20ml). The organic layer was combined with the extracts, washed with sat. Na_2CO_{3aq} (15ml) and dried ($MgSO_4$). Removal of solvent and distillation gave a clear liquid identified as the alcohol 185 (5.299g, 72%; b.pt 128-129°/2mmHg); ^{1}H n.m.r. δ 7.37-7.24 (5H, m, Ph), 3.61-3.58 (2H, m, $C\underline{H}_2OH$), 3.07, 2.83 (2H, ABX system,

J_{AB} 12.9 Hz, J_{AX} 6.4 Hz, J_{BX} 6.9 Hz, C$\underline{H}_2$SPh), 1.97-1.91 (2H, m, C$\underline{H}$CH$_3$ and OH), 1.04 (3H, d, $J_{1,2}$ 7.0 Hz, CH$_3$). [Lit.,[109] ^{1}H n.m.r. (CCl_4) δ 7.19 (5H, m), 3.8 (1H,s), 3.42 (2H, d, J = 3Hz), 2.8 (2H, m), 1.8 (1H, m), 0.9 (3H, d, J = 4 Hz)].

The alcohol 185 (5.299g, 29.1mmol) in carbon tetrachloride (3ml) was added dropwise to a solution of phosphorus tribromide[110] (1.6ml, 16.9mmol) in carbon tetrachloride (16ml) under nitrogen. After refluxing (1h), the mixture was poured into ice-water, the organic layer removed and the aqueous layer extracted with carbon tetrachloride (2 x 10ml). The combined organic extracts were dried ($MgSO_4$), the solvent removed, and the resulting oil distilled to give the bromide 186 as a clear liquid (1.81g, 26% ; b.pt 110^o/ 2mmHg); ^{1}H n.m.r. δ 7.4-7.18 (5H, m, Ph), 3.59, 3.49 (2H, ABX system, J_{AB} 10.0 Hz, J_{AX} 5.1 Hz, J_{BX} 5.0 Hz, CH_2Br), 3.07, 2.90 (2H, ABX system, J_{AB} 13.3 Hz, J_{AX} 7.0 Hz, J_{BX} 6.5 Hz, C$\underline{H}_2$SPh), 2.13-2.05 (1H, m, C$\underline{H}$CH$_3$), 1.16 (3H, d, $J_{1,2}$ 6.7 Hz, CH_3).

$[(C_5H_5)Fe(CO)_2]_2$ 24 (1.7g, 4.80mmol) was added to 2% sodium amalgam (4g) in THF (30ml) and stirred (20^{o}C; 12h). After cooling (-78^{o}C) the bromide 186 (760mg, 3.22mmol) in THF (5ml) was added and the solution stirred (20^{o}C; 12h). Removal of solvent, addition of dichloromethane (5ml), filtration through alumina (grade I) with diethyl ether and removal of solvent gave crude 187 as a red oil. Acetonitrile (40ml) and triphenylphosphine (1.2g, 4.58mmol) were added to crude 187 and the solution heated at reflux (4h). Removal of solvent and chromatography on alumina (grade I) gave a band eluting in diethyl ether:ethyl acetate (9:1), drying to an orange solid identified as a 1:1 mixture of the sulphenyl complexes 182:183 (603mg, 31%).

The data for RR(SS)-182 was obtained from the complex synthesised previously (p.188). The data for RS(SR)-183 was

obtained from the 1:1 mixture of 182:183, the synthesis of which was described above.

RR(SS)-$(C_5H_5)Fe(CO)(PPh_3)(COCH_2CH(CH_3)CH_2SPh)$ 182. Found: C, 69.71, H, 5.56, $C_{35}H_{33}FePO_2S$ requires: C, 69.54, H, 5.50%; $\nu_{max.}$ 1910 vs (C≡O), 1600 s (C=O) cm^{-1}; ^1H n.m.r. δ 7.5-7.1 (20H, m, Ph), 4.38 (5H, d, J_{PH} 1.4 Hz, C_5H_5), 3.15, 2.49 (2H, ABX system, J_{AB} 17.1 Hz, J_{AX} 5.0 Hz, J_{BX} 7.3 Hz, $COCH_2$), 2.76, 2.67 (2H, ABX system, J_{AB} 12.4 Hz, J_{AX} 6.3 Hz, J_{BX} 6.9 Hz, $C\underline{H}_2SPh$), 1.95 (1H, m, $C\underline{H}CH_3$), 0.57 (3H, d, $J_{1,2}$ 6.7 Hz, CH_3); ^{13}C-[^1H] n.m.r. δ 220.6 (d, J_{PC} 31.2 Hz, C≡O), 137.7, 128.7 and 125.3 (s, SPh), 136.5 (d, J_{PC} 43.0 Hz, $PPhC_{ipso}$), 133.3 (d, J_{PC} 9.9 Hz, $PPhC_{ortho}$), 129.7 (s, $PPhC_{para}$), 128.0 (d, J_{PC} 10.0 Hz, $PPhC_{meta}$), 85.3 (s, C_5H_5), 71.9 (s, $CO\underline{C}H_2$), 40.5 (s, $\underline{C}H_2SPh$), 29.5 (s, CH), 19.5 (s, CH_3); ^{31}P-[^1H]n.m.r. δ 72.3; m/z 604 (M^+), 576 (M^+-28).

RS(SR)-$(C_5H_5)Fe(CO)(PPh_3)(COCH_2CH(CH_3)CH_2SPh)$ 183. ^1H n.m.r. δ 7.5-7.1 (20H, m, Ph), 4.36 (5H, d, J_{PH} 1.1 Hz, C_5H_5), 2.96, 2.72, 2.51 and 2.24 (4H, 2ABX systems-overlapping those of 182), 1.99-1.89 (1H, m, $C\underline{H}CH_3$), 0.84 (3H, d, $J_{1,2}$ 6.7 Hz, CH_3).

Reactions of E-$(C_5H_5)Fe(CO)(PPh_3)(COCH{=}CHCH_3)$ 36 with the α-lithiosulphoxide derived from phenyl methyl sulphoxide.

Method A.

Methyllithium (1.13ml, 1.81mmol) was added dropwise to a solution of phenyl methyl sulphoxide (294mg, 2.1mmol) in THF (4ml) at -78°C,[112] and the solution stirred (-78°C; 30mins.). A solution of 36 (200mg, 0.417mmol) in THF (4ml) at -78°C was added, and the reaction stirred (-78°C; 30mins., -40°C; 6h), the solution becoming red indicating enolate formation. Addition of methanol, removal of solvent, addition of dichloromethane (3ml) and chroma-

tography on alumina (grade V) gave two bands eluting in diethyl ether:petroleum ether (1:1) and diethyl ether respectively, and a third band eluting just behind the second band. Removal of solvent from the final band gave a pale yellow oil, identified by ^{1}H n.m.r. spectroscopy as phenyl methyl sulphoxide (102mg). Removal of solvent from the first band gave an orange solid identified by ^{1}H n.m.r. spectroscopy as a 3:1 mixture of the diastereoisomeric cyclopropyl complexes 85:84 (76mg, 37%) (see p.199 for spectroscopic details). Removal of solvent from the second band gave a 20:1 mixture of the sulphinyl complexes 189:192 (153mg, 59%). Crystallisation from dichloromethane/hexane gave 189 as red crystals, on one of which a X-ray crystal structure analysis was performed (see p.111).

RRR(SSS)-(C_5H_5)Fe(CO)(PPh_3)($COCH_2CH(CH_3)CH_2S(O)Ph$) 189. Found: C, 67.75, H, 5.49, $C_{35}H_{33}FePO_3S$ requires: C, 67.75, H, 5.36%; $\nu_{max.}$ 1915 vs (C≡O), 1595 s (C=O) cm^{-1}; ^{1}H n.m.r. δ 7.6-7.3 (20H, m, Ph), 4.41 (5H, d, J_{PH} 1.0 Hz, C_5H_5), 3.20 (1H, one part of ABX system, J_{AB} 17.3 Hz, J_{AX} 4.7 Hz, $COCH(H)$), 2.66-2.51 (3H, m, $COCH(H)$ and CH_2S), 2.14-2.08 (1H, m, $CHCH_3$), 0.67 (3H, d, $J_{1,2}$ 6.8 Hz, CH_3); ^{13}C-[^{1}H]n.m.r. δ 220.6 (d, J_{PC} 31.2 Hz, C≡O), 136.5 (d, J_{PC} 43.3 Hz, $PPhC_{ipso}$), 133.4 (d, J_{PC} 9.7 Hz, $PPhC_{ortho}$), 129.8 (s, $PPhC_{para}$), 128.1 (d, J_{PC} 9.5 Hz, $PPhC_{meta}$), 130.7, 129.1 124.2 (s, SPh), 85.4 (s, C_5H_5), 71.1 (s, $COCH_2$), 65.4 (s, CH_2S), 26.6 (s, CH), 20.0 (s, CH_3); ^{31}P-[^{1}H]n.m.r. δ 72.0; m/z 620 (M^+).

RSS(SRR)-(C_5H_5)Fe(CO)(PPh_3)($COCH_2CH(CH_3)CH_2S(O)Ph$) 192. ^{1}H n.m.r. δ 0.91 (3H, d, $J_{1,2}$ 7.4 Hz, CH_3). No other resonances could be assigned to 192.

Repeating the reaction either with a smaller excess of the sulphoxide, or over a shorter time period, gave lower yields of the products.

Method B.

The experiment described above was repeated but after stirring (-78°C; 30mins., -40°C; 6h) was allowed to warm rapidly to room temperature. After stirring (20°C; 15mins.) the reaction was worked up as described above. A single product band was collected and identified as an 8:1 mixture of the cyclopropyl complexes 85:84 (90%) (see p.199 for spectrosoopic data).

Oxidation of $(C_5H_5)Fe(CO)(PPh_3)(COCH_2CH(CH_3)CH_2SPh)$ 182 and 183.[113]

Method A.

m-Chloroperbenzoic acid (25mg, 0.144mmol) in chloroform (3ml) was added dropwise, over ten minutes, to a solution of RR(SS)-$(C_5H_5)Fe(CO)(PPh_3)(COCH_2CH(CH_3)CH_2SPh)$ 182 (75mg, 0.124 mmol) in chloroform (5ml) and $NaHCO_{3aq}$ (5ml) at 0°C. After stirring (0°C; 30mins.), removal of the organic layer and extraction of the aqueous layer with chloroform (3 x 4ml), the combined organic fractions were dried (K_2CO_3) and the solvent removed. Chromatography of the resulting orange solid on alumina (grade V) in dichloromethane gave a single product eluting in diethyl ether. Removal of solvent gave an orange solid identified by ^1H n.m.r. spectroscopy as a 1:1 mixture of the sulphinyl complexes 189 and 190 (63mg, 82%). The spectroscopic data for RRR(SSS)-189 is given on page 192. The ^1H n.m.r. data for RRS(SSR)-190, from the 1:1 mixture with 189, is given below.

RRS(SSR)-$(C_5H_5)Fe(CO)(PPh_3)(COCH_2CH(CH_3)CH_2S(O)Ph)$ 190. ^1H n.m.r. δ 7.6-7.3 (15H, m, Ph), 4.40 (5H, d, J_{PH} 1.2 Hz, C_5H_5), 3.12 (1H, one part of ABX system, J_{AB} 17.5 Hz, J_{AX} 4.6 Hz, $COC\underline{H}(H)$), 2.66-2.38 (3H, m, $COCH(\underline{H})$ and CH_2S), 2.18-2.05 (1H, m, $C\underline{H}CH_3$), 0.76 (3H, d, $J_{1,2}$ 6.6 Hz, CH_3).

Method B.

The reaction described above was repeated on a 1:1 mixture of 182:183. On work up and chromatography a 1:1:1:1 mixture of the sulphinyl complexes 189-192 (78%) was isolated. Data for 189, 190 and 192 has been given previously.

RSR(SRS)-$(C_5H_5)Fe(CO)(PPh_3)(COCH_2CH(CH_3)CH_2S(O)Ph)$ 191. ^1H n.m.r. δ 0.94 (3H, d, $J_{1,2}$ 6.1 Hz, CH_3). No other resonances could be assigned to 191.

Reaction of $(C_5H_5)Fe(CO)(PPh_3)(COCH_2CH(CH_3)CH_2S(O)Ph)$ 189 and 190 with methyllithium.

Methyllithium (1ml, 1.6mmol) was added dropwise to a solution of 189 and 190 (1:1) (100mg, 0.161mmol) in THF (3ml) at -40°C, the solution remaining orange. After stirring (-40°C; 2h) the reaction was allowed to warm rapidly to room temperature and stirred (20°C; 1h). Addition of methanol, removal of solvent, addition of dichloromethane and filtration through alumina (grade V) with diethyl ether gave, on removal of solvent, only recovered starting material (97mg).

Reaction of E-$(C_5H_5)Fe(CO)(PPh_3)(COCH{=}CHCH_3)$ 36 with the α-lithiosulphoxide derived from p-tolyl methyl sulphoxide.

Methyllithium (1.1ml, 1.8mmol) was added dropwise to a solution of p-tolyl methyl sulphoxide (327mg, 2.12mmol) in THF (4ml) at -78°C. After stirring (-78°C; 30mins.), a solution of 36 (200mg, 0.417mmol) in THF (4ml) at -78°C was added and the solution stirred (-78°C; 30mins., -40°C; 6h), rapidly becoming red. Addition of methanol, removal of solvent, addition of dichloromethane and chromatography on alumina (grade V) gave two

bands, eluting in diethyl ether:petroleum ether (1:1) and diethyl ether respectively, and a third band also eluting in diethyl ether. Removal of solvent from the final band gave p-tolyl methyl sulphoxide (161mg). Removal of solvent from the first band gave an orange solid, identified by ^{1}H n.m.r. spectroscopy as a 4:1 mixture of the cyclopropyl complexes 85:84 (82mg, 40%). (see p.199 for spectroscopic data). Removal of the solvent from the second band gave an orange solid, identified by ^{1}H n.m.r. spectroscopy as an 18:1 mixture of the sulphinyl complexes 193:194 (142mg, 54%). Crystallisation from dichloromethane/hexane gave 193 as orange needles.

RRR(SSS)-(C_5H_5)Fe(CO)(PPh_3)($COCH_2CH(CH_3)CH_2S(O)$p-tolyl) 193.

Found: C, 67.92, H, 5.84, $C_{36}H_{35}FePO_3S$ requires: C, 68.14, H, 5.52%; $\nu_{max.}$ 1915 vs (C≡O), 1605 s (C=O) cm^{-1}; ^{1}H n.m.r. δ 7.6-7.3 (19H, m, Ph), 4.40 (5H, brs, C_5H_5), 3.18 (1H, one part of ABX system, J_{AB} 17.3 Hz, J_{AX} 4.7 Hz, $COCH(H)$), 2.65-2.49 (3H, m, $COCH(H)$ and CH_2S), 2.41 (3H, s, $C_6H_4CH_3$), 2.11-2.05 (1H, m, $CHCH_3$), 0.64 (3H, d, $J_{1,2}$ 6.7 Hz, $CHCH_3$); ^{13}C-[^{1}H]n.m.r. δ 220.5 (d, J_{PC} 31.3 Hz, C≡O), 141.0, 124.2 (s, SC_6H_4), 136.5 (d, J_{PC} 43.2 Hz, $PPhC_{ipso}$), 133.3 (d, J_{PC} 9.5 Hz, $PPhC_{ortho}$), 129.7 (s, $PPhC_{para}$), 128.1 (d, J_{PC} 10.4 Hz, PhC_{meta}), 85.4 (s, C_5H_5), 71.2 (s, $COCH_2$), 65.3 (s, CH_2S), 26.6 (s, CH), 21.4 (s, $C_6H_4CH_3$), 20.0 (s, $CHCH_3$); ^{31}P-[^{1}H]n.m.r. δ 72.1; m/z 634(M^+). Spectroscopic data for SRR-194 is given on page 197.

Preparation of R(+)-p-tolyl methyl sulphoxide.[115]

Methyl iodide (1.6ml, 25.7mmol) in diethyl ether (15ml) was added dropwise onto magnesium turnings (500mg) in diethyl ether (3ml). After 2ml of solution had been added, heating was used to initiate reaction which was maintained at reflux by further addi-

tion of methyl iodide solution. After stirring (20°C; 20mins) the solution was added dropwise, over thirty minutes, to a solution of 1R, 2S,5R-(-)-menthyl S-p-toluenesulphinate (2.5g, 8.49mmol) in THF (5ml) at 0°C, a white precipitate forming rapidly. After stirring (20°C; 2h), addition of sat. NH_4Cl_{aq} (8ml), removal of the organic layer, extraction of the aqueous layer with diethyl ether (2 x 4ml) and drying the combined organic layers (Na_2SO_4, $MgSO_4$), removal of the solvent gave a pale yellow oil. Chromatography on silica gave two bands eluting in diethyl ether and diethyl ether:ethyl acetate (3:2) respectively. The product from the first band was identified as menthol, and that from the second as R(+)-p-tolyl methyl sulphoxide (630mg, 48%). ^1H n.m.r. δ 7.6-7.3 (4H, m, Ph), 2.72 (3H, s, SCH_3), 2.43 (3H , s, $C_6H_4CH_3$); $[\alpha]_D^{20}$ + 189.2° (c1.2, $CHCl_3$). [Lit.,[115] $[\alpha]_D$ + 192° (c1.2, $CHCl_3$)].

Chiral shift experiments with E-$(C_5H_5)Fe(CO)(PPh_3)(COCH=CHCH_3)$ 36.

On addition of R(-)-2,2,2-trifluoro-1-(9-anthryl)ethanol (7mg, 0.025mmol) in chloroform-d_1 (0.3ml) to a solution of E-(±)-36 (2mg, 0.0042mmol) in chloroform-d_1 (0.5ml), the resonance in the ^1H n.m.r. spectrum at δ 1.58 ($CHCH_3$) split into two doublets at δ 1.52 (d, $J_{1,2}$ 6.8 Hz) and δ 1.47 (d, $J_{1,2}$ 6.7 Hz), Repeating the experiment with R(-)-36 (p.145), gave a single doublet at δ 1.52, and with S(+)-36 (p.145) a single doublet at δ 1.47 confirming the enantiomeric purity of both samples.

Reaction of S(+)-E-$(C_5H_5)Fe(CO)(PPh_3)(COCH=CHCH_3)$ 36 with the α-lithiosulphoxide derived from R(+)-p-tolyl methyl sulphoxide.

The reaction described previously (see p.194) was repeated between the anion formed on deprotonation of R(+)-p-tolyl sulphoxide (167mg, 1.08mmol) with methyllithium (0.55ml, 0.88mmol), and S(+)-36 (200mg, 0.417mmol). After work up and

chromatography a 25:1 mixture of the diastereoisomeric cyclopropyl complexes SRR-85:SSS-84 (146mg, 71%) was isolated as a red oil which would not crystallise (see page 199 for spectroscopic details). A 9:1 mixture of the sulphinyl complexes SRR-194: SSR-195 (48mg, 18%) was also obtained. R(+)-p-tolyl methyl sulphoxide (62mg) was also collected, $[\alpha]_D^{20}$ + 191.5° (c 1.2, $CHCl_3$).

SRR-(C_5H_5)Fe (CO)(PPh_3)($COCH_2CH(CH_3)CH_2S(O)$p-tolyl) 194. ^{1}H n.m.r. δ 7.6-7.3 (19H, m, Ar), 4.40 (5H, brs, C_5H_5), 3.03, 2.58 (2H, ABX system, J_{AB} 17.6 Hz, J_{AX} 5.5 Hz, J_{BX} 6.1 Hz, $COCH_2$), 2.44 (3H, s, $C_6H_4CH_3$) 2.26-2.07 (3H, m, $CHCH_2S$), 0.90 (3H, d, $J_{1,2}$ 6.5 Hz, $CHCH_3$).

SSR-(C_5H_5)Fe(CO)(PPh_3)($COCH_2CH(CH_3)CH_2S(O)$p-tolyl) 195. ^{1}H n.m.r. δ 0.72 (d, $J_{1,2}$ 6.6 Hz, $CHCH_3$). No other resonances could be identified.

Reaction of R(-)-E-(C_5H_5)Fe(CO)(PPh_3)($COCH=CHCH_3$) 36 with the α-lithiosulphoxide derived from R(+)-p-tolyl methyl sulphoxide.

The reaction described above was repeated with R(-)-36. A 1:1 mixture of the diastereoisomeric cyclopropyl complexes RSS-85: RRR-84 (27mg, 13%) was isolated, and a 26:1 mixture of the diastereoisomeric sulphinyl complexes RRR-193:RSR-198 (190mg, 72%). The spectroscopic data for RRR(SSS)-193 is given on page 195.

RSR-(C_5H_5)Fe(CO)(PPh_3)($COCH_2CH(CH_3)CH_2S(O)$p-tolyl) 198. ^{1}H n.m.r. δ 0.94 (d, $J_{1,2}$ 6.6 Hz, $CHCH_3$). No other resonances for 198 could be identified.

Reaction of (±)-E-(C_5H_5)Fe(CO)(PPh_3)($COCH=CHCH_3$) 36 with the α-lithiosulphoxide derived from R(+)-p-tolyl methyl sulphoxide.

The reaction described previously (see p.194) was repeated between the anion generated on treatment of R(+)-p-tolyl

methyl sulphoxide (160mg, 1.04mmol) with methyllithium (0.6ml, 1mmol) and (±)-36 (500mg, 1.04mmol). On work up and chromatography on alumina (grade V), three bands were eluted.

Band 1: Eluting in diethyl ether:petroleum ether (1:3) and drying to an orange oil. The ^{1}H n.m.r. identified the oil as a 16:1 mixture of the cyclopropyl complexes 85:84 (21%). By the use of a chiral shift reagent (see p.206) the major diastereoisomer 85 was shown to be predominantly the SRR enantiomer, SRR:RSS = 4:1. The absolute stereochemistry of the minor diastereoisomer 84 could not be determined.

Band 2: Eluting in diethyl ether:petroleum ether (1:1) and drying to an orange solid. By the use of a chiral shift reagent (see p.196) identified as a 3:2 mixture of S(+):R(-)-36 (210mg, 42%).

Band 3: Eluting in diethyl ether and drying to an orange solid, identified by ^{1}H n.m.r. spectroscopy as a 45:9:2:1 mixture of the sulphinyl complexes RRR-193:SRR-194:RSR-198:SSR-195 (184mg, 28%).

Synthesis of Trans-$(C_5H_5)Fe(CO)(PPh_3)(COCH\text{-}CH_2CHCH_3)$ 85 and 84.

Method A

Methyllithium (0.23ml, 0.375mmol) was added dropwise to a solution of E-$(C_5H_5)Fe(CO)(PPh_3)(COCH{=}CHCH_3)$ 36 (100mg, 0.208mmol) and methylene iodide (0.037ml, 0.46mmol) in THF (5ml) at -78°C. After stirring (-78°C; 2h), addition of methanol, removal of solvent and chromatography on alumina (grade I) gave two bands eluting in diethyl ether:petroleum ether (4:1) and diethyl ether: ethyl acetate (9:1) respectively. Removal of solvent from the first band gave a mixture of the diastereoisomeric cyclopropyl complexes 85 and 84 (>50:1) (10mg, 10%). Spectroscopic data is given below. Removal of solvent from the second band gave recovered starting

material 36 (73mg, 73%). Repeating the reaction but quenching immediately after methyllithium addition, or with larger excesses of reagents, gave essentially the same results.

Method B

Methyllithium (0.2ml, 0.32mmol) was added dropwise to a solution of E-$(C_5H_5)Fe(CO)(PPh_3)(COCH{=}CHCH_3)$ 36 (400mg, 0.83mmol) and methylene iodide (0.03ml, 0.37mmol) in THF (20ml) at -78°C. Methylene iodide (0.03ml, 0.37mmol) was added, followed by methyllithium (0.2ml, 0.32mmol), and these two additions were repeated a further twenty-eight times until a total of 11.1mmol of methylene iodide and 9.6mmol of methyllithium had been added over one hour. Over this time a white precipitate was formed and the solution became viscous. Addition of methanol (3ml) and removal of solvent gave an orange oil. Filtration of the oil in dichloromethane through alumina (grade I) with diethyl ether gave, on removal of solvent, an orange solid identified by ^{1}H n.m.r. spectroscopy as the diastereoisomeric cyclopropyl complexes 85 and 84 (85:84 = >50:1) (349mg, 85%). Crystallisation from dichloromethane/hexane gave 85 as orange crystals, on one of which an X-ray crystal structure analysis was undertaken (p.122). (The ^{1}H n.m.r. data for the minor diastereoisomer is taken from a previous experiment (p.157) in which a 1.3:1 mixture of 84:85 had been synthesised).

RSS(SRR)-$(C_5H_5)Fe(CO)(PPh_3)(COCH\text{-}CHCH_3)$ 85. Found: C, 70.59, H, 5.76, $C_{29}H_{27}FePO_2$ requires: C, 70.46, H, 5.51%; ν_{max} 1910 vs (C≡O), 1595s(C=O) cm^{-1}; ^{1}H n.m.r. ($CDCl_3$) δ 7.6-7.3 (15H, m, Ph), 4.44 (5H, d, J_{PH} 0.9 Hz, C_5H_5), 2.66 (1H, ddd, J_{cis} 7.7 Hz, J_{trans} 4.0 Hz, J_{trans} 4.0 Hz, COCH), 1.09-1.05 (1H, m, HCH), 0.96 (3H, d, $J_{1,2}$ 6.0 Hz, CH_3), 0.60-0.52 (1H, m, $CHCH_3$), 0.29-0.23 (1H, m,

HCH); ^{1}H n.m.r. (C_7D_8) δ 7.8-7.6, 7.2-7.0 (15H, m, Ph), 4.28 (5H, d, J_{PH} 0.9 Hz, C_5H_5), 2.75 (1H, ddd, J_{cis} 7.7 Hz, J_{trans} 3.9 Hz, J_{trans} 3.9 Hz, COCH), 1.41-1.35 (1H, m, HCH), 1.00 (3H, d, $J_{1,2}$ 6.0 Hz, CH_3), 0.81-0.75 (1H, m, $CHCH_3$), 0.29-0.24 (1H, m, HCH); ^{13}C-[^{1}H]n.m.r. ($CDCl_3$) δ 220.8 (d, J_{PC} 31.6 Hz, C≡O), 136.9 (d, J_{PC} 42.7 Hz, PhC_{ipso}), 133.4 (d, J_{PC} 10.3 Hz, PhC_{ortho}), 129.5 (s, PhC_{para}), 127.9 (d, J_{PC} 9.5 Hz, PhC_{meta}), 84.9 (s, C_5H_5), 49.0 (br s, COCH), 18.8 (s, $CHCH_3$), 18.2 (s, CH_3), 18.1 (s, CH_2); ^{31}P-[^{1}H]n.m.r. δ 74.2; m/z 494 (M^+).

RRR(SSS)-(C_5H_5)Fe(CO)(PPh_3)(COCH-CH_2-$CHCH_3$) 84. ^{1}H n.m.r. ($CDCl_3$) δ 0.98 (d, $J_{1,2}$ 6.2 Hz, CH_3) (All other resonances overlapped or coincided with those of 85); ^{1}H n.m.r. (C_7D_8) δ 4.30 (5H, d, J_{PH} 1.0 Hz, C_5H_5), 0.95 (3H, d, $J_{1,2}$ 6.1 Hz).

Synthesis of Trans-(C_5H_5)Fe(CO)(PPh_3)(COCH-CH_2-CHR) 87 and 86.

The reaction described above (Method B) was repeated on other E-α,β-unsaturated iron acyl complexes and the results are summarised in table 16 (p.124). In each case a single crystallisation gave the diastereomerically pure complexes 87. The spectroscopic data for the minor diastereoisomers 86 was obtained, where possible, from the ^{1}H n.m.r. spectra of the samples synthesised previously (p.158) with reverse diastereoselectivity (see table 7, p.54). Resonances not given for diastereoisomers 86 were obscured by those of diastereoisomers 87.

RSS(SRR)-(C_5H_5)Fe(CO)(PPh_3)(COCH-CH_2-$CHCH_2CH_2CH_3$) 89 (89%). Found: C, 71.15, H, 6.11, $C_{31}H_{31}FePO_2$ requires: C, 71.27, H, 5.98%; $\nu_{max.}$ 1910 vs (C≡O), 1600 s (C=O) cm^{-1}; ^1H n.m.r. δ 7.6-7.3 (15H, m, Ph), 4.44 (5H, d, J_{PH} 0.9 Hz, C_5H_5), 2.71 (1H, ddd, J_{cis} 7.8 Hz, J_{trans} 4.0 Hz, J_{trans} 4.0 Hz, COCH), 1.38-1.31 (3H, m, CH and CH_2CH_2), 1.09-1.04 (2H, m, CH_2CH_2), 0.87 (3H, t, $J_{1,2}$ 7.1 Hz, CH_3), 0.74-0.70 (1H, m, CH), 0.33-0.27 (1H, m, CH); ^{13}C-[^1H]n.m.r. δ 221.8 (d, J_{PC} 31.7 Hz, C≡O), 137.0 (d, J_{PC} 42.6 Hz, PhC_{ipso}), 133.5 (d, J_{PC} 9.4 Hz, PhC_{ortho}), 129.5 (s, PhC_{para}), 127.9 (d, J_{PC} 9.4 Hz, PhC_{meta}), 84.9 (s, C_5H_5), 47.6 (d, J_{PC} 5.7 Hz, COCH), 35.9 (s, CH_2CH_2), 24.5 (s, CH), 22.1 (s, CH_2CH_2), 17.2 (s, CH_2), 14.1 (s, CH_3); ^{31}P-[^1H]n.m.r. δ 74.8; m/z 522 (M^+).

RRR(SSS)-(C_5H_5)Fe(CO)(PPh_3)(COCH-CH_2-$CHCH_2CH_2CH_3$) 88. ^1H n.m.r. δ 7.6-7.3 (15H, m, Ph) 4.45 (5H, d, J_{PH} 1.0 Hz, C_5H_5) 2.70-2.64 (1H, m, COCH), 0.91 (3H, t, $J_{1,2}$ 6.9 Hz, CH_3), 0.57-0.51 (1H, m, CH), 0.28-0.22 (1H, m, CH).

RSS(SRR)-(C_5H_5)Fe(CO)(PPh_3)(COCH-CH_2-$CHCH_2CH_2CH_2CH_3$) 91 (82%). Found: C, 71.43, H, 6.35, $C_{32}H_{33}FePO_2$ requires: C, 71.65, H, 6.20%; ν_{max} 1910 vs (C≡O), 1590 s (C=O) cm^{-1}; ^1H n.m.r. δ 7.6-7.3 (15H, m, Ph), 4.44 (5H, d, J_{PH} 1.0 Hz, C_5H_5), 2.73 (1H, ddd, J_{cis} 7.7 Hz, J_{trans} 3.9 Hz, J_{trans} 3.9 Hz, COCH), 1.35-1.24 (5H, m, CH and CH_2CH_2) 1.13-1.06 (2H, m, CH_2CH_2), 0.90 (3H, t, $J_{1,2}$ 6.9 Hz, CH_3), 0.74-0.70 (1H, m, CH), 0.34-0.29 (1H, m, CH); ^{13}C-[^1H]n.m.r. δ 220.9 (d, J_{PC} 32.6 Hz, C≡O), 137.0 (d, J_{PC} 42.6 Hz, PhC_{ipso}), 133.5 (d, J_{PC} 9.5 Hz, PhC_{ortho}), 129.5 (s, PhC_{para}), 127.9 (d, J_{PC} 9.4 Hz, PhC_{meta}), 84.9 (s, C_5H_5), 47.7 (d, J_{PC} 5.7 Hz, COCH), 33.4 (s, CH_2CH_2), 31.3 (s, CH_2CH_2), 24.7 (s, CH), 22.5 (s, CH_2CH_2),

17.2 (s, CH_2), 14.1 (s, CH_3); ^{31}P-[^1H]n.m.r. δ 74.8; m/z 536(M^+).

RRR(SSS)-(C_5H_5)Fe(CO)(PPh_3)(COCH-CH_2-$CHCH_2CH_2CH_2CH_3$) 90. ^1H n.m.r. δ 7.6-7.3 (15H, m, Ph), 4.45 (5H, d, J_{PH} 1.0 Hz, C_5H_5), 2.69-2.64 (1H, m, COCH), 0.57-0.51 (1H, m, CH), 0.27-0.22 (1H, m, CH).

RSR(SRS)-(C_5H_5)Fe(CO)(PPh_3)(COCH-CH_2-$CHCH(CH_3)_2$) 93 (82%). Found: C, 71.43, H, 6.29, $C_{31}H_{31}FePO_2$ requires: C, 71.27, H, 5.98%; ν_{max}. 1910 vs (C≡O), 1600 s (C=O) cm^{-1}; ^1H n.m.r. δ 7.6-7.3 (15H, m, Ph), 4.45 (5H, brs, C_5H_5), 2.79 (1H, ddd, J_{cis} 7.9 Hz, J_{trans} 4.0 Hz, J_{trans} 4.0 Hz, COCH), 1.07-1.00 (5H, m, CH, CH and CH_3), 0.88-0.76 (4H, m, CH and CH_3), 0.39-0.33 (1H, m, CH); ^{13}C-[^1H] n.m.r. δ 220.9 (d, J_{PC} 31.7 Hz, C≡O), 137.0 (d, J_{PC} 42.5 Hz, PhC_{ipso}), 133.5 (d, J_{PC} 10.3 Hz, PhC_{ortho}), 129.5 (s, PhC_{para}), 127.9 (d, J_{PC} 10.0 Hz, PhC_{meta}), 84.8 (s, C_5H_5), 46.9 (s, CO<u>C</u>H), 32.5 (s, CH), 32.3 (s, CH), 22.2 (s, CH_3), 21.4 (s, CH_3), 16.2 (s, CH_2); ^{31}P-[^1H]n.m.r. δ 75.5; m/z 522(M^+).

RRS(SSR)-(C_5H_5)Fe(CO)(PPh_3)(COCH-CH_2-$CHCH(CH_3)_2$) 92. ^1H n.m.r. δ 7.6-7.3 (15H, m, Ph), 4.46 (5H, d, J_{PH} 1.1 Hz, C_5H_5), 2.78-2.71 (1H, m, COCH), 0.59-0.53 (1H, m, CH), 0.34-0.28 (1H, m, CH).

RSS(SRR)-(C_5H_5)Fe(CO)(PPh_3)(COCH-CH_2-$CHC(CH_3)_3$) 95 (22%). Found: C, 71.39, H, 6.27, $C_{32}H_{33}FePO_2$ requires: C, 71.65, H, 6.20%; ν_{max}. 1910 vs (C≡O), 1590 s (C=O) cm^{-1}; ^1H n.m.r. δ 7.6-7.3 (15H, m, Ph), 4.44 (5H, d, J_{PH} 1.1 Hz, C_5H_5), 2.83 (1H, ddd, J_{cis} 8.2 Hz, J_{trans} 4.2 Hz, J_{trans} 4.2 Hz, COCH), 1.05-0.85 (2H, m, CH and CH), 0.84 (9H, s, $C(CH_3)_3$), 0.49-0.43 (1H, m, CH); ^{13}C-[^1H] n.m.r. δ 220.8 (d, J_{PC} 31.2 Hz, C≡O), 137.1 (d, J_{PC} 42.4 Hz, PhC_{ipso}),

133.5 (d, J_{PC} 9.6 Hz, PhC_{ortho}), 129.5 (s, PhC_{para}), 127.9 (d, J_{PC} 10.0 Hz, PhC_{meta}), 84.8 (s, C_5H_5), 43.9 (d, J_{PC} 5.3 Hz, CO<u>C</u>H), 35.5 (s, CH), 29.9 (s, <u>C</u>$(CH_3)_3$), 28.4 (s, C(<u>C</u>$H_3)_3$), 13.5 (s, CH_2); $^{31}P-[^1H]$n.m.r. δ 75.6; <u>m/z</u> 536(M^+).

<u>RRR(SSS)-(C_5H_5)Fe(CO)(PPh_3)(COCH-CHC$(CH_3)_3$)$_3$ 94</u>. ^1H n.m.r. δ 7.6-7.3 (15H, m, Ph), 4.45 (5H, d, J_{PH} 1.1 Hz, C_5H_5), 2.82-2.77 (1H, m, COCH), 1.20-1.15 (1H, m, CH), 0.84 (9H, s, $C(CH_3)_3$), 0.50-0.35 (2H, m, CH and CH).

<u>Synthesis of (±)-Trans-(EtO_2CCH-CHCH$(CH_3)_2$) 201</u>.

N-Bromosuccinimide (227mg, 1.28mmol) in dichloromethane (9ml) was added dropwise to a solution of RSR(SRS)-<u>93</u> and RRS(SSR)-<u>92</u> (>50:1) (600mg, 1.15mmol) in dichloromethane:ethanol (1:1, 18ml) at -40°C, the solution rapidly becoming green. After stirring (-40°C; 10mins., 20°C; 40mins.), the solution was washed with brine (4ml) and then dried ($MgSO_4$). Removal of the solvent gave a green/oil solid which was dissolved in dichloromethane and chromatographed on alumina (grade I). The product eluted in pentane and dried to a yellow oil (108mg, 60%); $\nu_{max.}$ 1710 s (C=O) cm^{-1}; ^1H n.m.r. δ 4.15-4.08 (2H, m, C<u>H</u>$_2$$CH_3$), 1.40 (1H, ddd, J_{cis} 8.4 Hz, J_{trans} 4.3 Hz, J_{trans} 4.3 Hz, COCH), 1.28-1.19 (1H, m, CH), 1.26 (3H, t, $J_{1,2}$ 7.1 Hz, CH_2C<u>H</u>$_3$) 1.13-0.96 (8H, m, CH, CH and CH(C<u>H</u>$_3)_2$), 0.76-0.70 (1H, m, CH); <u>m/z</u> (EI) 156 (M^+), 110, 110, 81, 72, 56, 55. [Lit.,[85] ^1H n.m.r. δ 4.10 (2H, q, $J_{1,2}$ 7.1 Hz, C<u>H</u>$_2$$CH_3$), 1.50-0.90 (3H, m, CH, CH and CH), 1.25 (3H, t, $J_{1,2}$ 7.1 Hz, CH_2C<u>H</u>$_3$), 0.98 6H, d, $J_{1,2}$ 1.2 Hz, CH(C<u>H</u>$_3)_2$), 0.85-0.60 (1H, m, CH)].

Synthesis of (±)-Trans-($EtO_2CCH(CH_2)$-$CHCH_3$) 202.

A mixture of RSS(SRR)-85 and RRR(SSS)-84 (85:84 = >50:1) (600mg, 1.21mmol) was decomplexed as described above. The product 202 was isolated as a yellow oil 77mg(50%); $\nu_{max.}$ 1710 vs (C=O) cm^{-1}; ^1H n.m.r. δ 4.10 (2H, q, $J_{1,2}$ 7.3 Hz, $C\underline{H}_2CH_3$), 1.40-1.23 (2H, m, $C\underline{H}CH_3$ and COCH), 1.25 (3H, t, $J_{1,2}$ 7.2 Hz, $CH_2C\underline{H}_3$), 1.19-1.12 (1H, m, CH), 1.10 (3H, d, $J_{1,2}$ 5.9 Hz, $CHC\underline{H}_3$), 0.68-0.62 (1H, m, CH); ^1H n.m.r. (C_6D_6) δ 3.98 (2H, q, $J_{1,2}$ 6.9 Hz, $C\underline{H}_2CH_3$), 1.41-1.35 (1H, m, $C\underline{H}CH_3$), 1.23 (1H, ddd, J_{trans} 4.5Hz, J_{trans} 4.5Hz, J_{cis} 8.0Hz, COCH), 1.19-1.12 (1H, m, CH), 0.97 (3H, t, $J_{1,2}$ 7.2 Hz, $CH_2C\underline{H}_3$), 0.74 (3H, d, $J_{1,2}$ 5.9 Hz, $CHC\underline{H}_3$), 0.35-0.29 (1H, m, CH); m/z (DCI/NH_3) 129 (M^++1) 100, 83, 55.

Synthesis of Trans-($PhCH(CH_3)NHCOCH(CH_2)$-$CHCH_3$) RSS-203 and RRR-204.

The diastereoisomeric ratios of 203:204 were calculated from the integrals of the resonances in the ^1H n.m.r. spectra assigned to the methyl groups substituted on the cyclopropane rings (δ 0.89 and 0.85).

1) Synthesis of a 1:1 mixture of 203 and 204.

Bromine (0.05ml, 1.0mmol) was added dropwise to a solution of RSS(SRR)-85 and RRR(SSS)-84 (>50:1) (400mg, 0.83mmol) in dichloromethane (15ml) at -40°C, the solution immediately becoming green. After stirring (-40°C; 25mins.), R(+)-2-phenylethylamine (0.26ml, 2mmol) in dichloromethane (5ml) was added dropwise, and the solution stirred (-40°C; 5mins., 0°C; 40mins., 20°C; 20mins.). After addition of dil. HCl(3ml), the organic layer was removed and dried to give a green/brown solid. Trituration with diethyl ether (2 x 6ml) and dichloromethane (2 x 6ml), removal of solvent and chromatography on alumina (grade I) gave a green band, eluting in diethyl ether, and drying to a green solid. Chromatography of the material in dichloromethane on silica gave a green band, eluting with diethyl ether:ethyl acetate (9:1), drying to a green

solid $(C_5H_5)Fe(CO)(PPh_3)(Br)$ 27. A second band eluted in diethyl ether:ethyl acetate (7:3), drying to a white solid identified as the diastereoisomeric amides 203 and 204 (118mg, 70%). The data for 203 and 204 is given below. The resonances in the ^1H n.m.r. spectrum ($CDCl_3$:C_6D_6 = 3:1) at δ 0.89 and 0.85 ($CH_2CHC\underline{H}_3$) were of equal intensity indicating that 203:204 = 1:1 .

On repeating the reaction with one-half equivalent of amine, a 1:1 mixture of 203:204 was again isolated (12%).

2) Synthesis of RSS-203.

R(-)-E-$(C_5H_5)Fe(CO)(PPh_3)(COCH{=}CHCH_3)$ 36 (385mg, 0.80mmol) in THF (20ml) at -78°C was treated with methylene iodide (0.9ml, 11.1mmol) and methyllithium (6ml, 9.6mmol) over thirty consecutive additions as described previously (Method B, p.199). After work up, a mixture of RSS-85 and RRR-84 (85:84 = >50:1) (343mg, 87%) was isolated as an orange oil.

Decomplexation, as described above, on the >50:1 mixture (200mg, 0.40mmol) gave, after work up, the corresponding amides RSS-203 and RRR-204 (>50:1) (56mg, 69%). Crystallisation from dichloromethane/hexane gave white needles (mpt. 111-112°C); Found: C, 77.05, H, 8.67, N, 6.80, $C_{13}H_{17}NO$ requires: C, 76.80, H, 8.43, N, 6.89%; $\nu_{max.}$ 1665 vs (C=O) cm^{-1}; ^1H n.m.r. ($CDCl_3$:C_6D_6 = 3:1) δ 7.13-7.02 (5H, m, Ph), 5.33 (1H, brs, NH), 5.02-4.93 (1H, qn, $J_{1,2}$ 7.1 Hz, C$\underline{H}$NH), 1.26 (3H, d, $J_{1,2}$ 6.9 Hz, NHCH$\underline{CH}_3$), 1.24-1.19 (1H, m, C$\underline{H}$CH$_3$), 1.04-0.97 (1H, m, COCH), 0.89 (3H, d, $J_{1,2}$ 6.0 Hz, CH$\underline{CH}_3$), 0.68-0.63 (1H, m, $\underline{H}$CH), 0.32-0.26 (1H, m, HC$\underline{H}$); ^{13}C-{^1H}n.m.r. ($CDCl_3$) δ 172.2 (s, C=O), 143.6 (s, PhC_{ipso}), 128.6, 127.2 (s, Ph), 48.9 (s, CHNH), 23.7 (s, CO$\underline{C}$H), 21.9 (s, NHCH$\underline{CH}_3$), 17.9 (s, CH$\underline{CH}_3$), 15.4 (s, $\underline{CH}_2\underline{C}HCH_3$); m/z (DCI/$NH_3$) 204 ($M^+$+1), 188, 120, 106, 105, 100, 83.

3) Synthesis of RRR-204.

S(+)-E-(C_5H_5)Fe(CO)(PPh_3)(COCH=CHCH$_3$) 36 (300mg, 0.625mmol) in THF (18ml) at -78°C was treated with methylene iodide (0.675ml, 8.33mmol) and methyllithium (4.5ml, 7.2mmol) over thirty consecutive additions (see Method B, p.199). Work up gave a mixture of SRR-85 and SSS-84 (85:84 = >50:1) (250mg, 81%) as an orange oil.

Decomplexation, as described above, on the >50:1 mixture (200mg, 0.40mmol) gave the corresponding amides RRR-204 and RSS-203 (>50:1) (64mg, 79%). Crystallisation from dichloromethane/hexane gave white crystals (mpt. 127-128°C); Found: C, 76.85, H, 8.62, N, 6.81, $C_{13}H_{17}NO$ requires: C, 76.80, H, 8.43, N, 6.89%; $\nu_{max.}$ 1665 vs (C=O) cm^{-1}; ^1H n.m.r. ($CDCl_3$:C_6D_6 = 3:1) δ 7.13-7.02 (5H, m, Ph), 5.34 (1H, brs, NH), 5.02-4.93 (1H, qn, $J_{1,2}$ 7.1 Hz, C<u>H</u>NH), 1.25 (3H, d, $J_{1,2}$ 6.9 Hz, NHCHC<u>H</u>$_3$), 1.23-1.17 (1H, m, C<u>H</u>CH$_3$), 1.06-1.00 (1H, m, COCH), 0.85 (3H, d, $J_{1,2}$ 6.0 Hz, CHC<u>H</u>$_3$), 0.68-0.63 (1H, m, <u>H</u>CH), 0.36-0.30 (1H, m, HC<u>H</u>); ^{13}C-[^1H]n.m.r. ($CDCl_3$) δ 172.2 (s, C=O), 143.5 (s, PhC_{ipso}), 128.6, 127.2, 126.2 (s, Ph), 48.8 (s, CHNH), 23.6 (s, CO<u>C</u>H), 21.8 (s, NHCH<u>C</u>H$_3$), 17.9 (s, CH<u>C</u>H$_3$), 15.5 (s, <u>C</u>H$_2$<u>C</u>HCH$_3$); <u>m/z</u> (DCI/NH_3) 204 (M^++1), 188, 120, 106, 105, 100, 83.

Chiral shift experiments with (C_5H_5)Fe(CO)(PPh_3)(COCH-CH_2-$CHCH_3$) 85.

On addition of a solution of R(-)-2,2,2-trifluoro-1-(9-anthryl)ethanol (5mg, 0.018mmol) in toluene-d_8 (0.114ml) to a solution of (±)-85 (1mg, 0.002mmol) in toluene-d_8 (0.5ml), the resonance in the ^1H n.m.r. spectrum at δ 1.00 (CH_3) split into two doublets at δ 0.97 and δ 0.94. Repeating the experiment with R(-)-85 gave a single doublet at δ 0.97, and with S(+)-85 a single

doublet at δ 0.94.

Reaction E-(C_5H_5)Fe(CO)(PPh_3)(COCH=$CHCH_3$) 36 with ethylidene iodide and methyllithium.

Ethylidene iodide (0.038ml, 0.38mmol) and methyllithium (0.2ml, 0.32mmol) were added to a solution of 36 (400mg, 0.83 mmol) in THF (20ml) at -78°C. The additions were repeated until a total of thirty consecutive additions had been made over one hour. Addition of methanol and removal of solvent gave an orange oil. After filtration through alumina (grade I) with diethyl ether:ethyl acetate (9:1), removal of solvent gave an orange solid which was dissolved in dichloromethane and chromatographed on alumina (grade I). Three bands, eluting in diethyl ether:petroleum ether (1:1), diethyl ether and diethyl ether:ethyl acetate (9:1) respectively were collected, each drying to an orange solid. The material from the final band was recovered 36 (84mg, 21%), and that from the first band was identified as the diastereoisomeric cyclopropyl complexes RSS(SRR)-141 and RRR(SSS)-142 (193mg, 47%) (141:142 = >50:1), the spectroscopic data for which is given on page 182. The product from the second band was identified as RRS(SRR)-209 (90mg, 22%).

RRS(SRR)-(C_5H_5)Fe(CO)(PPh_3)(COCH-$\overset{CHCH_3}{\diagup\diagdown}$-$CHCH_3$) 209. Found; C, 70.68, H 5.84, $C_{30}H_{29}FePO_2$ requires: C, 70.88, H, 5.75%; $\nu_{max.}$ 1915 vs (C≡O), 1595 s (C=O) cm^{-1}; ^1H n.m.r. δ 7.6-7.3 (15H, m, Ph), 4.43 (5H, d, J_{PH} 0.8 Hz, C_5H_5), 2.37 (1H, dd, J_{trans} 4.2 Hz, J_{trans} 4.2 Hz, COCH), 1.41-1.27 (1H, m, CH), 0.99 (3H, d, $J_{1,2}$ 6.3 Hz, CH_3), 0.97 (3H, d, $J_{1,2}$ 6.2 Hz, CH_3), 0.89-0.80 (1H, m, CH); ^{13}C-[^1H]n.m.r. δ 220.9 (d, J_{PC} 31.5 Hz, C≡O), 136.9 (d, J_{PC} 42.6 Hz,

PhC_{ipso}), 133.4 (d, J_{PC} 10.1 Hz, PhC_{ortho}), 129.5 (s, PhC_{para}), 127.9 (d, J_{PC} 9.4 Hz, PhC_{meta}), 84.9 (s, C_5H_5), 58.0 (d, J_{PC} 5.7 Hz, CO<u>C</u>H), 24.2 (s, CH), 22.8 (s, CH), 12.1 (s, CH_3) 11.9 (s, CH_3); $^{31}P-[^1H]$n.m.r. δ 74.5 <u>m/z</u> 508 (M^+).

<u>Reaction of E-$(C_5H_5)Fe(CO)(PPh_3)(COCH=CHR)$ with ethylidene iodide and methyllithium</u>.

The reaction described above was repeated with other E-α,β-unsaturated iron acyl complexes and the results are summarised in table 17 (p.132). The <u>cis</u>- and <u>trans</u>- (methyl to iron) isomers were separable chromatographically, the <u>cis</u>- ones eluting first in each case. Crystallisation from dichloromethane/hexane gave orange crystals of the major diastereoisomers. Where a second diastereoisomer could be detected the diastereoisomeric ratios, measured from the ^1H n.m.r. or ^{31}P n.m.r. spectra, were all >50:1.

<u>1) Reaction of E-$(C_5H_5)Fe(CO)(PPh_3)(COCH=CHCH_2CH_2CH_3)$ 40</u>.

<u>RSSS(SRRR)-$(C_5H_5)Fe(CO)(PPh_3)(COCH(CHCH_3)-CHCH_2CH_2CH_3)$ 216 (59%)</u>. Found: C, 71.36, H, 6.25, $C_{32}H_{33}FePO_2$ requires: C, 71.65, H, 6.20%; $\nu_{max.}$ 1915 vs (C≡O), 1595 s (C=O) cm^{-1}; ^1H n.m.r. δ 7.6-7.3 (15H, m, Ph), 4.43 (5H, d, J_{PH} 0.8 Hz, C_5H_5), 2.71 (1H, dd, J_{cis} 8.1 Hz, J_{trans} 4.7 Hz, COCH), 1.27-0.8 (6H, m, $CHCHCH_2CH_2$), 1.07 (3H, d, $J_{1,2}$ 5.4 Hz, $CHCH_3$), 0.82 (3H, t, $J_{1,2}$ 6.7 Hz, CH_2CH_3); $^{13}C-[^1H]$ n.m.r. δ 221.2 (d, J_{PC} 32.9 Hz, C≡O), 137.0 (d, J_{PC} 42.4 Hz, PhC_{ipso}) 133.4 (d, J_{PC} 10.4 Hz, PhC_{ortho}), 129.5 (s, PhC_{para}), 127.9 (d, J_{PC} 9.3 Hz, PhC_{meta}), 85.3 (s, C_5H_5), 54.0 (d, J_{PC} 5.9 Hz, CO<u>C</u>H), 35.9 (s, CH_2), 29.6 (s, CH), 26.4 (s, CH), 22.1 (s, CH_2), 14.0 (s, CH_3), 12.8 (s, CH_3); $^{31}P-[^1H]$n.m.r. δ 74.2; <u>m/z</u> 536 (M^+).

RRRR(SSSS)-(C_5H_5)Fe(CO)(PPh_3)(COCH(CHCH$_3$)-$CHCH_2CH_2CH_3$) 217. ^{1}H n.m.r. δ 0.53 (d, $J_{1,2}$ 6.9 Hz, $CHCH_3$). No other resonances could be assigned to 217.

RSSR(SRRS)-(C_5H_5)Fe(CO)(PPh_3)(COCH(CHCH$_3$)-$CHCH_2CH_2CH_3$) 211 (19%). Found: C, 71.75, H, 6.17, $C_{32}H_{33}FePO_2$ requires: C, 71.65, H, 6.20%; $\nu_{max.}$ 1915 vs (C≡O), 1600 s (C=O) cm^{-1}: ^{1}H n.m.r. δ 7.6-7.3 (15H, m, Ph), 4.42 (5H, d, J_{PH} 0.8 Hz, C_5H_5), 2.42 (1H, dd, J_{trans} 4.3 Hz, J_{trans} 4.3 Hz, COCH), 1.42-1.19 (5H, m, CH and CH_2CH_2), 1.00 (3H, d, $J_{1,2}$ 6.4 Hz, $CHCH_3$), 1.00-0.88 (1H, m, CH), 0.89 (3H, t, $J_{1,2}$ 7.1 Hz, CH_2CH_3); ^{13}C-[^{1}H]n.m.r. δ 220.9 (d, J_{PC} 32.3 Hz, C≡O), 137.0 (d, J_{PC} 42.6 Hz, PhC_{ipso}), 133.5 (d, J_{PC} 9.5 Hz, PhC_{ortho}), 129.5 (s, PhC_{para}), 127.9 (d, J_{PC} 9.4 Hz, PhC_{meta}), 84.9 (s, C_5H_5), 56.9 (d, J_{PC} 5.6 Hz, COCH), 30.2 (s, CH), 29.8 (s, CH_2), 23.2 (s, CH), 22.7 (s, CH_2), 14.1 (s, CH_3), 12.5 (s, CH_3); ^{31}P-[^{1}H]n.m.r. δ 75.1; m/z 536(M^+), 508 (M^+-28).

RRRS(SSSR)-(C_5H_5)Fe(CO)(PPh_3)(COCH(CHCH$_3$)-$CHCH_2CH_2CH_3$) 210. ^{31}P-[^{1}H] n.m.r. δ 74.5. (see page 211 for further spectroscopic data).

2) Reaction of E-(C_5H_5)Fe(CO)(PPh_3)(COCH=CHCH(CH_3)$_2$) 44.

RSSS(SRRR)-(C_5H_5)Fe(CO)(PPh_3)(COCH(CHCH$_3$)-CHCH(CH_3)$_2$) 218 (54%). Found: C, 71.70, H, 6.30, $C_{32}H_{33}FePO_2$ requires: C, 71.65, H, 6.20%; $\nu_{max.}$ 1910 vs (C≡O), 1590 s (C=O) cm^{-1}; ^{1}H n.m.r. δ 7.6-7.3 (15H, m, Ph), 4.37 (5H, brs, C_5H_5), 2.85 (1H, dd, J_{cis} 8.2 Hz, J_{trans} 4.7 Hz, COCH), 1.09-0.81 (3H, m, CHCHCH), 1.08 (3H, d, $J_{1,2}$ 5.4 Hz, $CHCH_3$), 0.86 (3H, d, $J_{1,2}$ 6.3 Hz, $CHCH_3$), 0.82 (3H, d, $J_{1,2}$ 6.3 Hz,

$CHC\underline{H}_3$); ^{13}C-[^1H]n.m.r. δ 221.2 (d, J_{PC} 33.1 Hz, C≡O), 137.1 (d, J_{PC} 42.5 Hz, PhC_{ipso}), 133.4 (d, J_{PC} 9.9 Hz, PhC_{ortho}), 129.5 (s, PhC_{para}), 127.9 (d, J_{PC} 9.9 Hz, PhC_{meta}), 85.1 (s, C_5H_5), 53.0 (d, J_{PC} 5.6 Hz, $CO\underline{C}H$), 37.7 (s, CH), 32.5 (s, CH), 25.2 (s, CH), 22.0 (s, CH_3), 21.3 (s, CH_3), 12.8 (s, CH_3); ^{31}P-[^1H] n.m.r. δ 75.0; m/z 536(M^+).

(No trace of the minor diastereoisomer 219 was detected).

RSSR(SRRS)-$(C_5H_5)Fe(CO)(PPh_3)(COCH(CHCH_3)CHCH(CH_3)_2)$ 220 (6%). Found: C, 71.64, H, 6.29, $C_{32}H_{33}FePO_2$ requires: C, 71.65, H, 6.20%; $\nu_{max.}$ 1915 vs (C≡O), 1590 s (C=O) cm^{-1}; ^1H n.m.r. δ 7.6-7.3 (15H, m, Ph), 4.42 (5H, d, J_{PH} 0.7 Hz, C_5H_5), 2.50 (1H, dd, J_{trans} 4.3 Hz, J_{trans} 4.3 Hz, COCH), 1.43-1.25 and 1.10-0.81 (12H, m, $CHCH_3$ and $CHCH(CH_3)_2$); ^{31}P-[^1H] n.m.r. δ 75.9; m/z 536 (M^+).

(No trace of the minor diastereoisomer 221 was detected)

Preparation of butylidene iodide

Butylidene iodide was prepared from butanal by the same method as that outlined previously for the preparation of ethylidene iodide (p.179), and was isolated as a yellow oil (44%) (bpt. 49°C/2mmHg); ^1H n.m.r. δ 5.13 (1H, t, $J_{1,2}$ 6.6 Hz, CHI_2), 2.38-2.31 (2H, m, $C\underline{H}_2CHI_2$), 1.52-1.39 (2H, m, $C\underline{H}_2CH_3$), 0.97 (3H, t, $J_{1,2}$ 7.4 Hz, $CH_2C\underline{H}_3$).

Reaction of E-$(C_5H_5)Fe(CO)(PPh_3)(COCH=CHCH_3)$ 36 with butylidene iodide and methyllithium.

Butylidene iodide (0.05ml, 0.38mmol) and methyllithium (0.2ml, 0.32mmol) were added to a solution of 36 (400mg, 0.83mmol) in THF (20ml) at -78°C. The additions were repeated a

further twenty-nine times over one hour, and the reaction was worked up as described previously (p.207). Chromatography on alumina (grade I) in dichloromethane gave two bands eluting in diethyl ether:petroleum ether (4:1) and diethyl ether respectively. Removal of solvent from the first band gave an orange solid identified as the previously synthesised diastereoisomeric cyclopropyl complexes RRSS(SSRR)-149 and RSRR(SRSS)-150 (302mg, 68%), the spectroscopic data for which is given on page 183. Removal of solvent from the second band gave a mixture of 210 and 211 (111mg, 25%) (210:211 = >50:1).

RRRS(SSSR)-$(C_5H_5)Fe(CO)(PPh_3)(COCH(CHCH_2CH_2CH_3)CHCH_3)$ 210 (25%). Found C, 71.81, H, 6.50, $C_{32}H_{33}FePO_2$ requires: C, 71.65, H, 6.20%; $\nu_{max.}$ 1910 vs (C≡O), 1595 s (C=O) cm^{-1}; ^1H n.m.r. δ 7.6-7.3 (15H, m, Ph), 4.42 (5H, d, J_{PH} 0.9 Hz, C_5H_5), 2.42 (1H, dd, J_{trans} 4.0 Hz, J_{trans} 4.0 Hz, COCH), 1.42-1.18 (5H, m, CH and CH_2CH_2), 0.97 (3H, d, $J_{1,2}$ 6.1 Hz, $CHCH_3$), 0.92 (3H, t, $J_{1,2}$ 7.0 Hz, CH_2CH_3), 0.98-0.84 (1H, m, CH); ^{13}C-[^1H]n.m.r. δ 221.0 (d, J_{PC} 31.4 Hz, C≡O), 137.0 (d, J_{PC} 42.6 Hz, PhC_{ipso}), 133.4 (d, J_{PC} 9.5 Hz, PhC_{ortho}), 129.5 (s, PhC_{para}), 127.9 (d, J_{PC} 9.4Hz, PhC_{meta}), 84.9 (s, C_5H_5), 56.9 (d, J_{PC} 6.1 Hz, COCH), 29.6 (s, CH_2), 29.2 (s, CH), 24.2 (s, CH), 23.0 (s, CH_2), 14.0 (s, CH_3), 12.4 (s, CH_3); ^{31}P-[^1H]n.m.r. δ 74.5; m/z 536(M^+).

RSSR(SRRS)-$(C_5H_5)Fe(CO)(PPh_3)(COCH(CHCH_2CH_2CH_3)CHCH_3)$ 211. ^{31}P-[^1H]n.m.r. δ 75.1. (see page 209 for further spectroscopic data).

Reaction of E-$(C_5H_5)Fe(CO)(PPh_3)(COCH=CHR)$ with butylidene iodide and methyllithium

The reaction described above was repeated with other E-α,β-

unsaturated iron acyl complexes and the results are summarised in table 17 (p.132). The cis- and trans-(n-propyl to iron) isomers were separated by chromatography, the cis-isomers eluting first in each case. Crystallisation from dichloromethane/hexane gave orange crystals of the major diastereoisomers. Where a second diastereoisomer could be detected the diastereoisomeric ratios, measured from the ^{1}H n.m.r. spectra, were all >50:1.

1) Reaction of E-$(C_5H_5)Fe(CO)(PPh_3)(COCH{=}CHCH_2CH_2CH_3)$ 40.

RSS(SRR)-$(C_5H_5)Fe(CO)(PPh_3)(COCH(CHCH_2CH_2CH_3)\text{-}CHCH_2CH_2CH_3)$ 222 (67%). Found: C, 72.61, H. 6.76, $C_{34}H_{37}FePO_2$ requires: C, 72.34, H, 6.61%; $\nu_{max.}$ 1915 vs (C≡O), 1600 s (C=O) cm^{-1}; ^{1}H n.m.r. δ 7.6-7.3 (15H, m, Ph), 4.39 (5H, d, J_{PH} 1.0 Hz, C_5H_5), 2.73 (1H, dd, J_{cis} 8.3 Hz, J_{trans} 5.1 Hz, COCH),(1.36-1.20 (7H, m) and 0.95-0.81 (9H, m))($CHCH_2CH_2CH_3$ and $CHCH_2CH_2CH_3$); $^{13}C\text{-}[^{1}H]$n.m.r. δ 220.2 (d, J_{PC} 33.0 Hz, C≡O), 137.0 (d, J_{PC} 43:1 Hz, PhC_{ipso}), 133.5 (d, J_{PC} 10.1 Hz, PhC_{ortho}), 129.5 (s, PhC_{para}), 127.9 (d, J_{PC} 9.9 Hz, PhC_{meta}), 85.3 (s, C_5H_5), 54.0 (d, J_{PC} 5.8 Hz, COCH), 36.2 (s, CH_2), 32.7 (s, CH), 29.3 (s, CH_2), 29.0 (s, CH), 23.2 (s, CH_2), 22.1 (s, CH_2), 14.0 (s, $2CH_3$); $^{31}P\text{-}[^{1}H]$ n.m.r. δ 74.0; m/z 564(M^+), 536 (M^+-28).

RRR(SSS)-$(C_5H_5)Fe(CO)(PPh_3)(COCH(CHCH_2CH_2CH_3)\text{-}CHCH_2CH_2CH_3)$ 223. ^{1}H n.m.r. δ 4.42 (5H, d, J_{PH} 1.0 Hz, C_5H_5), 0.72 (3H, t, $J_{1,2}$ 7.2 Hz, CH_3). No other resonances could be assigned to 223.

RRS(SSR)-$(C_5H_5)Fe(CO)(PPh_3)(COCH(CHCH_2CH_2CH_3)\text{-}CHCH_2CH_2CH_3)$ 224 (16%). Found: C, 72.51, H, 6.87, $C_{34}H_{37}FePO_2$ requires: C, 72.34, H, 6.61%; $\nu_{max.}$ 1915 vs (C≡O), 1595 s (C=O) cm^{-1}; ^{1}H n.m.r. δ 7.6-7.3 (15H, m, Ph), 4.43 (5H, d, J_{PH} 1.0 Hz, C_5H_5), 2.49 (1H, dd, J_{trans} 4.1 Hz, J_{trans} 4.1 Hz, COCH), 1.43-1.14 (9H

m, $CHCH_2CH_2$ and CH_2CH_2), 0.96-0.86 (1H, m, CH), 0.93 (3H, t, $J_{1,2}$ 7.5 Hz, CH_3), 0.88 (3H, t, $J_{1,2}$ 7.2 Hz, CH_3); ^{13}C-[^1H]n.m.r. δ 221.2 (d, J_{PC} 32.3 Hz, C≡O), 137.1 (d, J_{PC} 42.3 Hz, PhC_{ipso}), 133.5 (d, J_{PC} 10.9 Hz, PhC_{ortho}), 129.5 (s, PhC_{para}), 127.9 (d, J_{PC} 10.9 Hz, PhC_{ortho}), 84.9 (s, C_5H_5), 55.8 (d, J_{PC} 6.4 Hz, COCH), 30.3 (s, CH), 30.2 (s, CH_2), 30.0 (s, CH), 29.5 (s, CH_2), 23.1 (s, CH_2), 22.8 (s, CH_2), 14.2 (s, CH_3), 14.1 (s, CH_3); ^{31}P-[^1H]n.m.r. δ 75.0; m/z 564(M^+), 536(M^+-28).

2) Reaction of E-$(C_5H_5)Fe(CO)(PPh_3)(COCH{=}CHCH(CH_3)_2)$ 44.

RSSS(SRRR)-$(C_5H_5)Fe(CO)(PPh_3)(COCH(CHCH_2CH_2CH_3)\text{-}CHCH(CH_3)_2)$ 225 (58%).

Found: C, 72.65, H, 6.71, $C_{34}H_{37}FePO_2$ requires: C, 72.34, H, 6.61%; $\nu_{max.}$ 1915 vs (C≡O), 1600 s (C=O) cm^{-1}; ^1H n.m.r. δ 7.6-7.3 (15H, m, Ph), 4.39 (5H, d, J_{PH} 1.3 Hz, C_5H_5), 2.90 (1H, dd, J_{cis} 8.8 Hz, J_{trans} 4.8 Hz, COCH), (1.45-1.25 (4H, m) and 1.03-0.80 (12H, m) ($CHCH_2CH_2CH_3$ and $CHCH(CH_3)_2$); ^{13}C-[^1H]n.m.r. δ 220.2 (d, J_{PC} 32.0 Hz, C≡O), 137.1 (d, J_{PC} 42.1 Hz, PhC_{ipso}), 133.4 (d, J_{PC} 9.6 Hz, PhC_{ortho}), 129.4 (s, PhC_{para}), 127.9 (d, J_{PC} 9.3 Hz, PhC_{meta}), 85.1 (s, C_5H_5), 53.1 (d, J_{PC} 5.4 Hz, COCH), 37.0 (s, CH), 32.4 (s, CH), 31.5 (s, CH), 29.1 (s, CH_2), 23.2 (s, CH_2), 22.1 (s, CH_3), 21.3 (s, CH_3), 14.0 (s, CH_3); ^{31}P-[^1H]n.m.r. δ 74.9; m/z 564 (M^+).

(No trace of the minor diastereoisomer 226 was detected).

RSSR(SRRS)-$(C_5H_5)Fe(CO)(PPh_3)(COCH(CHCH_2CH_2CH_3)\text{-}CHCH(CH_3)_2)$ 227 (5%). Found: C, 72.55, H, 6.67, $C_{34}H_{37}FePO_2$ requires: C, 72.34, H, 6.61%; $\nu_{max.}$ 1915 vs (C≡O), 1595 s (C=O) cm^{-1}; ^1H n.m.r. δ 7.6-7.3 (15H,

m, Ph), 4.43 (5H, d, J_{PH} 1.2 Hz, C_5H_5), 2.56 (1H, dd, J_{trans} 4.2 Hz, J_{trans} 4.2 Hz, COCH), 1.62-0.83 (10H, m, $CHCH_2CH_2$ and $CHCHCH_3$), 1.08 (3H, d, $J_{1,2}$ 6.5 Hz, $CHCH_3$), 0.94 (3H, t, $J_{1,2}$ 7.1 Hz, CH_2CH_3); m/z 564(M^+).

(No trace of the minor diastereoisomer 228 was detected).

REFERENCES

REFERENCES

1. E.J. Ariëns, Trends In Pharmacol Sci., 1986, 200.
2. P.F White, J. Ham, W.L. Way and A.J. Trevor, Anesthesiology, 1980, 52, 231.
3. D. Hartley and D. Middlemass, J.Med.Chem., 1971, 14 895.
4. D.W. Graham, W.T. Ashton, L. Barash, J.E. Brown, R.D. Brown, L.F. Canning, A. Chen, J.P. Springer and E.F. Rogers, J.Med. Chem., 1987, 30, 1074.
5. P.E. Burt, M. Elliott, A.W. Farnham, N.F. Janes, P.H. Needham, and D.A. Pulman, Pesticide Sci., 1974, 5, 791.
6. For examples see:
   a) R. Pellicciari, B. Natalini, S. Cecchetti, B. Porter, A. Roda, B. Grigolo and R. Balducci, J.Med.Chem., 1988, 31, 730.
   b) M. Elliott and N.F. Janes, Chem.Soc.Rev., 1978, 7, 473.
   c) D. Arlt, M. Jautelat and R. Lantzsch, Angew.Chem.Int.Ed. Engl., 1981, 20, 703.
7. For examples see
   a) J. Salaun and B. Karkour, Tetrahedron Lett., 1988, 29, 1537.
   b) E.A. Mash and J.A. Fryling, J.Org.Chem., 1987, 52, 3000.
   c) J.E. Baldwin, J. Löliger, N. Neuss, L.L. Huckstep and N. De La Higuera, J.Am.Chem.Soc., 1973, 95, 3796.
8. J.W. Scott and J.D. Morrison (Eds.), "Asymmetric Synthesis", Vol. 4, p.1, Academic Press, New York, 1984.
9. R.B. Mitra, G.H. Kulkarni and P.N. Khanna, Synth.Commun., 1987, 17, 1089.
10. S. Hanessian, "Total Synthesis of Natural Products:The 'Chiron' Approach", Pergamon Press, Oxford, 1983.

11. G.M. Coppola and H.F. Schuster, "Asymmetric Synthesis, Construction of Chiral Molecules Using Amino Acids", John Wiley and Sons, New York, 1987.

12. J. Jacques, A. Collet and S.H. Wilen, "Enantiomers, Racemates and Resolutions", John Wiley and Sons, New York, 1981.

13. T. Schotten, W. Boland and L. Jaenicke, Tetrahedron Lett., 1986, 27, 2349.

14. H.B. Kagan and J.C. Fiaud, Top. Stereochem., 1988, 18, 249.

15. S. Miyano, L. D.-L. Lu, S.M. Viti and K.B. Sharpless, J.Org. Chem., 1985, 50, 4350.

16. J.M. Brown and A.P. James, J.Chem.Soc.,Chem.Commun., 1987, 181.

17. W.H. Pirkle and D.W. House, J.Org.Chem., 1979, 44, 1957.

18. J.D. Morrison (Ed.), "Asymmetric Synthesis", Vols. 1-5, Academic Press, New York, 1983-1985.

19. For reviews see:

    a) J.D. Morrison (Ed.), "Asymmetric Synthesis", Vol. 5, Academic Press, New York, 1985.

    b) H. Brunner, Top. Stereochem., 1988, 18, 129.

20. G.M. Whitesides and C-H Wong, Angew.Chem.Int.Ed.Engl., 1985, 24, 617.

21. Y. Gao, R.M. Hanson, J.M. Klunder, S.Y. Ko, H. Masamune and K.B. Sharpless, J.Am.Chem.Soc., 1987, 109, 5765.

22. For examples see:

    a) A. Nakamura, A. Konishi, Y. Tatsuno and S. Otsuka, J.Am. Chem.Soc., 1978, 100, 3443.

    b) A. Nakamura, A. Konishi, R. Tsujitani, M. Kudo and S. Otsuka, J.Am.Chem.Soc., 1978, 100, 3449.

    c) T. Aratani, Pure Appl.Chem., 1985, 57, 1845.

23. H. Fritschi, U. Leutenegger and A. Pfalz, Angew.Chem.Int. Ed. Engl., 1986, 25, 1005.

24. For examples see:

a) M.D. Cooke and E.O. Fischer, J.Organomet.Chem., 1973, 56, 279.

b) A. Davison, W.C. Krusell and R.C. Michaelson, J.Organomet. Chem., 1974, 72, C7.

c) T.C. Flood, F.J. DiSanti and D.L. Miles, Inorg.Chem., 1976, 15, 1910.

25. M. Brookhart, D. Timmers, J.R. Tucker, G.D. Williams, G.R. Husk, H. Brunner and B. Hammer, J.Am.Chem.Soc., 1983, 105, 6721.

26. D.A. Evans, Aldrichimica Acta, 1982, 15, 23.

27. W.A. Kleschick, M.W. Reed and J. Bordner, J.Org.Chem., 1987, 52, 3168.

28. S.G. Davies, "Organotransition Metal Chemistry:Applications to Organic Synthesis", Pergamon Press, Oxford, 1982.

29. S.G. Davies, I.M. Dordor-Hedgecock, R.J.C. Easton, S.C. Preston, K.H. Sutton, and J.C. Walker, Bull.Soc.Chim.Fr., 1987, 608.

30. L.S. Liebeskind, M.E. Welker and R.W. Fengl, J.Am.Chem.Soc., 1986, 108, 6328.

31. For examples see:

a) G. Bashiardes and S.G. Davies, Tetrahedron Lett., 1987, 28, 5563.

b) R.P. Beckett and S.G. Davies, J.Chem.Soc.,Chem.Commun., 1988, 160.

32. S.G. Davies and J.I. Seeman, Tetrahedron Lett., 1984, 25, 1845.

33. The iron acyl complex $(C_5H_5)Fe(CO)(PPh_3)(COCH_3)$ is available either as a racemate or in enantiomerically pure S(+) and R(-) forms from B.P. Chemicals Ltd., New Specialities

Business, Belgrave House, 76 Buckingham Palace Rd., London, SW1W 0SU.

34. K. Stanley and M.C. Baird, J.Am.Chem.Soc., 1975, 97, 6598.

35. H. Brunner and E. Schmidt, J.Organomet.Chem., 1972, 36, C18.

36. N. Aktogu, H. Felkin, G.J. Baird, S.G. Davies and O. Watts, J.Organomet.Chem., 1984, 262, 49.

37. K. Yamamoto, S. Shigeaki and J. Tsuji, Chem.Letts., 1978, 649.

38. R.B. King and F.G.A. Stone, Inorg.Synth., 1963, 7, 110.

39. T.S. Piper and G. Wilkinson, J.Inorg.Nucl.Chem., 1956, 3, 104.

40. a) J.P. Bibler and A. Wojcicki, Inorg.Chem., 1966, 5, 889.
b) M. Green and D.J. Westlake, J.Chem.Soc.A, 1971, 367.

41. P. Warner, Part II thesis, University of Oxford, 1983.

42. a) H. Brunner, personnal communication.
b) S.G. Davies, unpublished results.

43. a) J.P. Collman, Acc.Chem.Res., 1975, 8, 342.
b) R.W. Johnson and R.G. Pearson, J.Chem.Soc., Chem.Commun., 1970, 986.

44. K.S. Holland, personnal communication.

45. J.I. Seeman and S.G. Davies, J.Am.Chem.Soc., 1985, 107, 6522.

46. S.G. Davies, I.M. Dordor-Hedgecock, K.H. Sutton and M.J. Whittaker, J.Am.Chem.Soc., 1987, 109, 5711.

47. B.K. Blackburn, S.G. Davies and M.J. Whittaker in "Stereochemistry of Organometallic and Inorganic Compounds", Vol.3, Elsevier, Amsterdam, 1988. In press.

48. S.G. Davies, J.I. Seeman and I.H. Williams, Tetrahedron Lett., 1986, 27, 619.

49. I. Bernal, H. Brunner and M. Muschiol, Inorg.Chim.Acta., 1988, 142, 235.

50. S.L. Brown, S.G. Davies, D.F. Foster, J.I. Seeman and P. Warner, Tetrahedron Lett., 1986, 27, 623.

51. G.J. Baird, J.A. Bandy, S.G. Davies and K. Prout, J.Chem. Soc.,Chem.Commun., 1983, 1202.

52. S.G. Davies, I.M. Dordor, J.C. Walker and P. Warner, Tetrahedron Lett., 1984, 25, 2709.

53. P.W. Ambler and S.G. Davies, Tetrahedron Lett., 1985, 26, 2129.

54. P.W. Ambler, Part II thesis, University of Oxford, 1985.

55. S.G. Davies, I.M. Dordor-Hedgecock, P. Warner, R.H. Jones and K. Prout, J.Organomet.Chem., 1985, 285, 213.

56. S.G. Davies, I.M. Dordor-Hedgecock and P. Warner, Tetrahedron Lett., 1985, 25, 2125.

57. For examples see:

a) S.G. Davies and J.C. Walker, J.Chem.Soc.,Chem.Commun., 1985, 209.

b) Idem, ibid, 1986, 495.

c) S.G. Davies, I.M. Dordor-Hedgecock, K.H. Sutton, J.C. Walker, R.H. Jones and K. Prout, Tetrahedron, 1986, 42, 5123.

d) S.G. Davies, I.M. Dordor-Hedgecock, K.H. Sutton and J.C. Walker, Tetrahedron Lett., 1986, 27, 3787.

58. S.G. Davies and J.C. Walker, J.Chem.Soc.,Chem.Commun., 1986, 609.

59. S.G. Davies, R.J.C. Easton, A. Gonzalez, S.C. Preston, K.H. Sutton and J.C. Walker, Tetrahedron, 1986, 42, 3987.

60. For a review see H.E. Simmons, T.L. Cairns, S.A. Vladuchick, and C.M. Hoiness, Org.React., 1973, 20, 1.

61. For reviews see:

a) M. Brookhart and W.B. Studabaker, Chem.Rev., 1987, 87, 411.

b) W. Kirmse, "Carbene Chemistry", (2nd ed.), Academic Press, New York, 1971.

62. For reviews see:

a) B.M. Trost and L.S. Melvin, "Sulphur Ylides, Emerging Synthetic Intermediates", Academic Press, New York, 1975.

b) Y.G. Gololobov, A.N. Nesmeyanov, V.P. Lysenko and I.E. Boldeskul, Tetrahedron, 1987, 43, 2609,

63. S.G. Davies, R.J.C. Easton, J.C. Walker and P. Warner, Tetrahedron, 1986, 42, 175.

64. For a review see D.J. Ager, Synthesis, 1984, 384.

65. A gift from M. Wills.

66. Chem-X, developed and designed by Chemical Design Ltd., Oxford, England.

67. S.G. Davies, R.J.C. Easton, K.H. Sutton and J.C. Walker, J.Chem.Soc.,Perkin Trans. I, 1987, 489.

68. H. Abdallah, R. Grée and R. Carrié, Tetrahedron Lett., 1982, 23, 503.

69. J. Furukawa and N. Kawabata, Adv.Organomet.Chem., 1974, 12, 83.

70. a) J. Furukawa, N. Kawabata and J. Nishimura, Tetrahedron, 1968, 24, 53.

b) Idem, ibid, 1969, 25, 2647.

c) J. Nishimura, J. Furukawa, N. Kawabata and M. Kitayama, ibid, 1971, 27, 1799.

d) J. Nishimura, J. Furukawa, N. Kawabata and H. Koyama, Bull.Chem.Soc.Jpn., 1971, 44, 1127.

71. a) D.B. Miller, Tetrahedron Lett., 1964, 989.

b) K. Maruoka, Y. Fukutani and H. Yamamoto, J.Org.Chem., 1985, 50, 4412.

72. J. H.-H. Chan and B. Rickborn, J.Am.Chem.Soc., 1968, 90, 6406.

73. S. Sawada, J. Oda and Y. Inouye, J.Org.Chem., 1968, 33, 2141.

74. S. Sawada, K. Takehana and Y. Inouye, J.Org.Chem., 1968, 33, 1767.

75. C.R. Johnson and M.R. Barbachyn, J.Am.Chem.Soc., 1982, 104, 4290.

76. For examples see:

a) E.A. Mash and K.A. Nelson, J.Am.Chem.Soc., 1985, 107, 8256.

b) Idem, Tetrahedron, 1987, 43, 679.

c) E.A. Mash, K.A. Nelson and P.C. Heidt, Tetrahedron Lett., 1987, 28, 1865.

77. a) I. Arai, A. Mori and H. Yamamoto, J.Am.Chem.Soc., 1985, 107, 8254.

b) Idem, Tetrahedron, 1986, 42, 6447.

78. R.J. Rawson and I.T. Harrison, J.Org.Chem., 1970, 35, 2057.

79. D. Cremer and J. Gauss, J.Am.Chem.Soc., 1986, 108, 7467.

80. M.I. Bruce, M.Z. Iqbal and F.G.A. Stone, J.Organomet.Chem., 1969, 20, 161.

81. L.M. Jackman and S. Sternhall, "Applications of Nuclear Magnetic Resonance Spectroscopy", Pergamon Press, Oxford, 1969, (p. 286).

82. K.R. Hanson, J.Am.Chem.Soc., 1966, 88, 2731.

83. M.E.C. Polywka, personnal communication.

84. J.P. Dinnocenzo and M. Schmittel, J.Am.Chem.Soc., 1987, 109, 1561

85. M.P. Doyle, R.L. Dorow, W.E. Buhro, J.H. Griffin, W.H. Tamblyn and M.L. Trudell, Organometallics, 1984, 3, 44.

86. a) Y. Kusuyama, Bull.Chem.Soc.Jpn., 1979, 52, 1944.

b) Y. Kusuyama, S. Inoshita, G. Okada, M. Yanagi, K. Tokami, H. Fuchu, Y. Tsuno and M. Mishima, Org.Magn.Reson., 1982, 20, 159.

87. For examples see:

a) H. J. Callot, F. Metz and C. Piechocki, Tetrahedron, 1982, 38, 2365.

b) M. Julia and C. Descoins, Bull.Soc.Chim.Fr., 1970, 1805.

88. W.H. Pirkle, D.L. Sikkenga and M.S. Pavlin, J.Org.Chem., 1977, 42, 384.

89. T. Sugiyama, A. Kobayashi and K. Yamashita, Agr.Biol.Chem., 1975, 39, 1483.

90. A. Pross and S. Sternhall, Aust.J.Chem., 1970, 23, 989.

91. M.P. Doyle, K-L. Loh, L.I. Nishioka and M.B. McVickar, Tetrahedron Lett., 1986, 27, 4395.

92. a) K. Omura and D. Swern, Tetrahedron, 1978, 34, 1651.

b) A.J. Mancuso, D.S. Brownfain and D. Swern, J.Org.Chem., 1979, 44, 4148.

93. E.C. Friedrich, S.N. Falling and D.E. Lyons, Synth.Commun., 1975, 5, 33.

94. K.S. Sutton, personnal communication.

95. P.S. Wharton and T.I. Bair, J.Org.Chem., 1965, 30, 1681.

96. J.J. Gajewski, R.J. Weber, R. Braun, M.L. Manion and B. Hymen, J.Am.Chem.Soc., 1977, 99, 816.

97. P.A. Grieco and R.S. Finkelhor, Tetrahedron Lett., 1972, 3781.

98. R.B. Mitra, Z. Muljiani and G.B. Reddy, Synth.Commun., 1986, 16, 1099.

99. For examples see:

a) T. Cohen and M. Myers, J.Org.Chem., 1988, 53, 457.

b) J.J. Tufariello, A.G. Milowsky, M. Al-Nuri and S. Goldstein, Tetrahedron Lett., 1987,28,267

c) J.M. Mélot, F. Texier-Boullet and A. Foucaud, Synthesis, 1987, 364

100. C.R. Johnson, R.A. Kirchhoff, R.J. Reischer and G.F. Katekar, J.Am.Chem.Soc., 1973, 95, 4287.

101. C.R. Johnson and C.W. Schroeck, J.Am.Chem.Soc., 1973, 95, 7418.

102. T. Mukaiyama, K. Fujimoto and T. Takeda, Chem.Letts., 1979, 1207.

103. M.J. De Vos and A. Krief, Tetrahedron Lett., 1983, 24, 103.

104. A. Krief, W. Dumont and P. Pasau, Tetrahedron Lett., 1988, 29, 1079.

105. G.A. Russell, J.R. Dodd, T.Ku, C. Tanger and C.S.C. Chung, J.Am.Chem.Soc., 1974, 96, 7255.

106. A gift from J.C. Walker.

107. E.J. Corey and D. Seebach, J.Org.Chem., 1966, 31, 4097.

108. a) E. Schaumann, C. Friese and C. Spanka, Synthesis, 1986, 1035.

b) K. Tanaka, K. Minami and A. Kaji, Chem.Letts., 1987, 809.

109. B.M. Trost, D.E. Keeley, H.C. Arndt, J.H. Rigby and M. J. Bogdanowicz, J.Am.Chem.Soc., 1977, 99, 3080.

110. M. Watanabe, S. Nakamori, H. Hasegawa, K. Shirai and T. Kumamoto, Bull.Chem.Soc.Jpn., 1981, 54, 817.

111. S.G. Davies, unpublished results.

112. T. Durst, M.J. LeBelle, R. Van der Elzen and K.-C.-Tin, Can.J.Chem., 1974, 52, 761.

113. F.A. Davis, A.J. Friedman and U.K. Nadir, J.Am.Chem.Soc., 1978, 100, 2844.

114. J. Jacobus and K. Mislow, J.Am.Chem.Soc., 1967, 89, 5228.

115. G. Solladié, J. Hutt and A. Girardin, Synthesis, 1987, 173.

116. S. Masamune, W. Choy, J.S. Peterson and L.R. Sita, Angew. Chem.Int.Ed.Engl., 1985, 24, 1.

117. For examples see:

a) M.R. Binns, R.K. Haynes, A.A. Katsifis, P.A. Schober and S.C. Vonwiller, Tetrahedron Lett., 1985, 26, 1565.

b) M.R. Binns, O.L. Chai, R.K. Haynes, A.A. Katsifis, P.A. Schober and S.C. Vonwiller, ibid., 1985, 26, 1569.

c) D.H. Hua, M.J. Coulter and G. Sinai-Zingde, J.Org.Chem., 1987, 52, 719.

118. a) G. Chassaing and A. Marquet, Tetrahedron, 1978, 34, 1399.

b) S. Wolfe, L.A. LaJohn and D.F. Weaver, Tetrahedron Lett., 1984, 25, 2863.

119. For examples see:

a) G. Köbrich and R.H. Fischer, Tetrahedron, 1968, 24, 4343.

b) G. Cainelli, A. U. Ronchi, F.Bertini, P. Grasselli and G. Zubiani, Tetrahedron, 1971, 27, 6109.

c) R. Tarhouni, B. Kirschleger, M. Rambaud and J. Villieras, Tetrahedron Lett., 1984, 25, 835.

120. K.M. Sadhu and D.S. Matteson, Tetrahedron Lett., 1986, 27, 795.

121. M. Wills, personnal communication.

122. D.F. Schriver, "The Manipulation of Air-Sensitive Compounds", McGraw-Hill Book Company, New York, 1962.

123. W.C. Still, M. Kahn and A. Mitra, J.Org.Chem., 1978, 43, 2923.

X-Ray Crystal Structure Analyses

General

Crystal data for the X-ray crystal structure analyses contained in this thesis, which were measured using Enraf-Nonius CAD-4 diffractometers, are presented below. Graphite monochromated Molybdenum or Copper X-radiation (as specified below) and the $\omega/2\theta$ scan technique were used to measure reflection intensities out to a Bragg angle θ, also given below. The space group was, in each case, determined unambiguously as a result of the structure analysis but initially indicated by systematic absences of appropriate reflections. The cell parameters were determined, in each case, by least square refinement; the setting angles of 25 accurately centred reflections being used. The data were corrected for Lorentz, polarisation and absorption effects[1] and equivalent reflections were merged. Reflections with $I>3\sigma(I)$ were considered to be observed and were used in the structure analyses. The structures were solved by direct methods and electron density Fourier Synthesis.

Final full-matrix least squares refinement included, in each case, parameters for atomic positions, temperature factors, an overall scale factor and an extinction parameter.[2] All hydrogen atoms were included in calculated positions, being allowed to "ride" on their respective carbon atoms. Final difference Fourier syntheses showed no significant residual electron density and detailed analyses failed to reveal any systematic errors in the structure solutions. All calculations were performed with the CRYSTALS package on the Chemical Crystallography Laboratory VAX 11/750 computer.

References

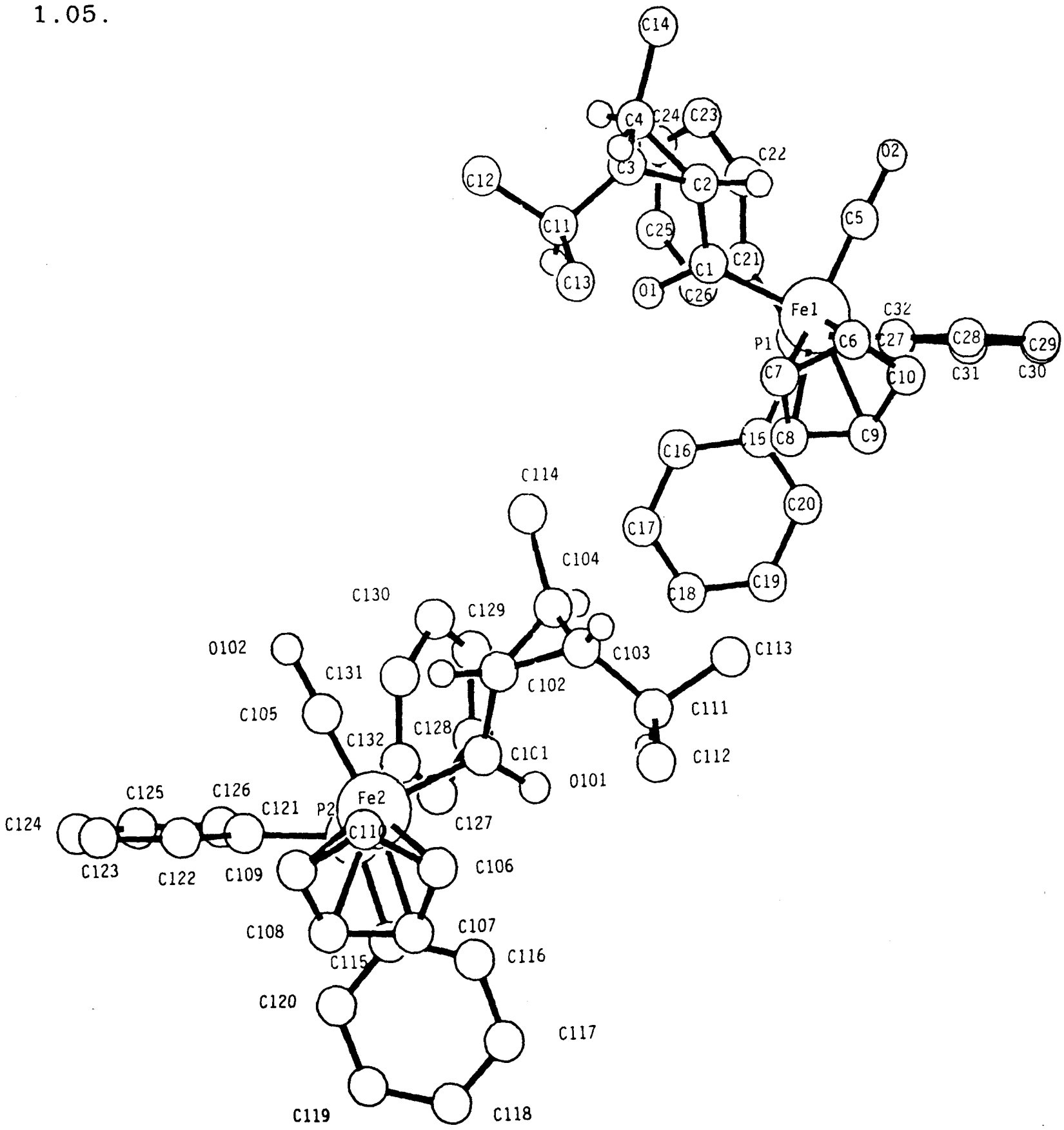
1) A.C.T. North, D.C. Philips and F.S. Mathews, Acta Crystallogr. Sect. A, 1968, 24, 351.

2) A.C. Larson, "Crystallographic Computing", Ed. F.R. Ahmed, Munttsguard, 1970, p.170.

Appendix 1

Crystal Data for RRSS(SSRR)-(C_5H_5)Fe(CO)(PPh_3)(COCH(CHCH$_3$)$_2$) 155

$C_{32}H_{33}FeO_2P$, M=536.434, triclinic, a=9.834(3), b=15.422(2), c=18.549(3) A, α=92.15(1)°, β=96.35(2)°, γ=90.09(2)°, U=2793.7 A^3, Z=4, D_{calc}=1.28 Mgm^{-3}, u(Cu-K_α)= 50.83cm^{-1}, θ_{max}=65°, space group P1, relative transmission factors 1.00-3.16, crystal dimensions 0.75 by 0.51 by 0.19 mm, number of reflections [I>3σ(I)] 4778, R=0.058, R_w=0.073, GOF= 1.05.



Final Atomic Positional Coordinates
with
Estimated Standard Deviations
in Parentheses

Atom	x/a	y/b	z/c	U(iso)
FE(1)	0.0916(1)	0.58891(6)	0.82186(5)	0.0384
P(1)	0.0711(2)	0.56728(9)	0.70379(8)	0.0387
O(1)	-0.1923(5)	0.6134(3)	0.7838(2)	0.0559
O(2)	0.2313(5)	0.7527(3)	0.8152(3)	0.0749
C(1)	-0.0889(6)	0.6431(4)	0.8188(3)	0.0436
C(2)	-0.1021(7)	0.7256(4)	0.8648(4)	0.0519
C(3)	-0.2249(7)	0.7449(4)	0.9059(4)	0.0553
C(4)	-0.2091(7)	0.7915(4)	0.8389(4)	0.0614
C(5)	0.1727(6)	0.6873(4)	0.8173(3)	0.0473
C(6)	0.156(1)	0.5636(6)	0.9298(4)	0.0752
C(7)	0.029(1)	0.5261(8)	0.9111(6)	0.0790
C(8)	0.043(1)	0.4641(5)	0.8536(5)	0.0669
C(9)	0.1790(9)	0.4658(5)	0.8417(4)	0.0636
C(10)	0.2495(8)	0.5262(5)	0.8879(4)	0.0662
C(11)	-0.3442(7)	0.6831(5)	0.9101(4)	0.0601
C(12)	-0.4741(8)	0.7342(6)	0.9170(5)	0.0899
C(13)	-0.317(1)	0.6253(7)	0.9736(6)	0.1063
C(14)	-0.168(1)	0.8872(5)	0.8436(6)	0.0961
C(15)	-0.0073(7)	0.4632(4)	0.6727(3)	0.0460
C(16)	-0.1477(7)	0.4523(5)	0.6790(4)	0.0610
C(17)	-0.2105(9)	0.3728(6)	0.6599(5)	0.0794
C(18)	-0.137(1)	0.3051(5)	0.6333(5)	0.0789
C(19)	-0.000(1)	0.3151(5)	0.6285(6)	0.0831
C(20)	0.0638(8)	0.3940(5)	0.6479(5)	0.0703
C(21)	-0.0284(6)	0.6450(4)	0.6471(3)	0.0401
C(22)	-0.0260(7)	0.7324(5)	0.6679(4)	0.0556
C(23)	-0.0962(8)	0.7931(5)	0.6242(5)	0.0667
C(24)	-0.1722(8)	0.7653(7)	0.5604(5)	0.0704
C(25)	-0.1780(9)	0.6784(7)	0.5391(4)	0.0780
C(26)	-0.1067(8)	0.6197(5)	0.5824(4)	0.0681
C(27)	0.2329(7)	0.5644(4)	0.6621(4)	0.0456
C(28)	0.3547(6)	0.5646(4)	0.7067(4)	0.0517
C(29)	0.2337(7)	0.5620(4)	0.5855(4)	0.0578
C(30)	0.357(1)	0.5576(5)	0.5568(5)	0.0718
C(31)	0.479(1)	0.5569(5)	0.6020(6)	0.0684
C(32)	0.4815(7)	0.5603(5)	0.6752(5)	0.0636
H(1)	-0.0011(7)	0.7250(4)	0.8793(4)	0.127(6)
H(2)	-0.2360(7)	0.7625(4)	0.9574(4)	0.127(6)
H(3)	-0.2700(7)	0.7974(4)	0.7925(4)	0.127(6)
H(4)	0.177(1)	0.6101(6)	0.9684(4)	0.127(6)
H(5)	-0.057(1)	0.5407(8)	0.9325(6)	0.127(6)
H(6)	-0.030(1)	0.4261(5)	0.8274(5)	0.127(6)
H(7)	0.2206(9)	0.4288(5)	0.8047(4)	0.127(6)
H(8)	0.3492(8)	0.5404(5)	0.8910(4)	0.127(6)
H(9)	-0.3545(7)	0.6455(5)	0.8647(4)	0.127(6)
H(10)	-0.5530(8)	0.6937(6)	0.9188(5)	0.127(6)
H(11)	-0.4605(8)	0.7707(6)	0.9630(5)	0.127(6)
H(12)	-0.4934(8)	0.7725(6)	0.8748(5)	0.127(6)
H(13)	-0.232(1)	0.5907(7)	0.9685(6)	0.127(6)
H(14)	-0.303(1)	0.6627(7)	1.0191(6)	0.127(6)
H(15)	-0.396(1)	0.5850(7)	0.9760(6)	0.127(6)
H(16)	-0.246(1)	0.9238(5)	0.8242(6)	0.127(6)
H(17)	-0.141(1)	0.9036(5)	0.8960(6)	0.127(6)
H(18)	-0.088(1)	0.8967(5)	0.8155(6)	0.127(6)
H(19)	-0.2011(7)	0.5018(5)	0.6977(4)	0.127(6)
H(20)	-0.3094(9)	0.3645(6)	0.6660(5)	0.127(6)
H(21)	-0.185(1)	0.2490(5)	0.6175(5)	0.127(6)
H(22)	0.053(1)	0.2652(5)	0.6103(6)	0.127(6)
H(23)	0.1638(8)	0.4011(5)	0.6438(5)	0.127(6)
H(24)	0.0262(7)	0.7520(5)	0.7150(4)	0.127(6)
H(25)	-0.0918(8)	0.8563(5)	0.6387(5)	0.127(6)
H(26)	-0.2232(8)	0.8086(7)	0.5292(5)	0.127(6)
H(27)	-0.2346(9)	0.6590(7)	0.4932(4)	0.127(6)
H(28)	-0.1103(8)	0.5569(5)	0.5669(4)	0.127(6)
H(29)	0.4268(6)	0.5652(4)	0.7492(4)	0.127(6)
H(30)	0.1353(7)	0.5636(4)	0.5651(4)	0.127(6)
H(31)	0.359(1)	0.5548(5)	0.5031(5)	0.127(6)
H(32)	0.568(1)	0.5538(5)	0.5805(6)	0.127(6)
H(33)	0.5539(7)	0.5609(5)	0.7175(5)	0.127(6)

Final Atomic Positional Coordinates
with
Estimated Standard Deviations
in Parentheses

Atom	x/a	y/b	z/c	U(iso)
FE(2)	-0.6715(1)	0.08852(6)	0.82503(5)	0.0387
P(2)	-0.7058(2)	0.06304(9)	0.70766(8)	0.0390
O(101)	-0.4043(5)	0.1088(3)	0.7845(3)	0.0596
O(102)	-0.8103(6)	0.2527(3)	0.8144(3)	0.0767
C(101)	-0.4909(6)	0.1422(4)	0.8187(3)	0.0454
C(102)	-0.4605(7)	0.2267(4)	0.8599(3)	0.0525
C(103)	-0.3191(7)	0.2497(4)	0.9004(4)	0.0545
C(104)	-0.3660(7)	0.2910(4)	0.8319(4)	0.0606
C(105)	-0.7544(7)	0.1865(4)	0.8179(4)	0.0510
C(106)	-0.569(1)	0.0295(7)	0.9154(5)	0.0761
C(107)	-0.610(1)	-0.0352(5)	0.8604(4)	0.0658
C(108)	-0.750(1)	-0.0342(4)	0.8501(4)	0.0605
C(109)	-0.8004(9)	0.0286(5)	0.8945(5)	0.0659
C(110)	-0.688(1)	0.0690(5)	0.9346(4)	0.0710
C(111)	-0.1993(7)	0.1869(5)	0.9065(4)	0.0619
C(112)	-0.197(1)	0.1327(8)	0.9738(6)	0.1074
C(113)	-0.0667(8)	0.2389(6)	0.9134(5)	0.0900
C(114)	-0.406(1)	0.3871(5)	0.8323(6)	0.0971
C(115)	-0.6503(7)	-0.0441(4)	0.6774(3)	0.0448
C(116)	-0.5108(8)	-0.0627(5)	0.6894(4)	0.0584
C(117)	-0.465(1)	-0.1442(6)	0.6705(4)	0.0694
C(118)	-0.553(1)	-0.2064(5)	0.6404(5)	0.0724
C(119)	-0.691(1)	-0.1898(5)	0.6282(5)	0.0740
C(120)	-0.7394(8)	-0.1082(4)	0.6474(4)	0.0611
C(121)	-0.8866(6)	0.0667(4)	0.6691(4)	0.0424
C(122)	-0.9899(7)	0.0625(5)	0.7142(4)	0.0612
C(123)	-1.1250(8)	0.0626(5)	0.6875(5)	0.0712
C(124)	-1.1608(8)	0.0665(5)	0.6134(6)	0.0716
C(125)	-1.0609(9)	0.0724(5)	0.5677(5)	0.0712
C(126)	-0.9241(8)	0.0731(5)	0.5952(4)	0.0602
C(127)	-0.6266(6)	0.1358(4)	0.6484(3)	0.0406
C(128)	-0.5666(7)	0.1036(5)	0.5876(4)	0.0542
C(129)	-0.5060(8)	0.1597(6)	0.5429(4)	0.0670
C(130)	-0.5050(8)	0.2482(6)	0.5593(5)	0.0679
C(131)	-0.5653(8)	0.2809(5)	0.6180(4)	0.0613
C(132)	-0.6248(7)	0.2235(4)	0.6624(4)	0.0544
H(101)	-0.5557(7)	0.2255(4)	0.8740(3)	0.116(6)
H(102)	-0.2850(7)	0.2710(4)	0.9507(4)	0.116(6)
H(103)	-0.3258(7)	0.2953(4)	0.7850(4)	0.116(6)
H(104)	-0.473(1)	0.0455(7)	0.9361(5)	0.116(6)
H(105)	-0.547(1)	-0.0740(5)	0.8355(4)	0.116(6)
H(106)	-0.807(1)	-0.0737(4)	0.8148(4)	0.116(6)
H(107)	-0.8988(9)	0.0431(5)	0.8972(5)	0.116(6)
H(108)	-0.693(1)	0.1173(5)	0.9718(4)	0.116(6)
H(109)	-0.2101(7)	0.1474(5)	0.8622(4)	0.116(6)
H(110)	-0.119(1)	0.0912(8)	0.9762(6)	0.116(6)
H(111)	-0.187(1)	0.1729(8)	1.0177(6)	0.116(6)
H(112)	-0.285(1)	0.0996(8)	0.9724(6)	0.116(6)
H(113)	-0.0650(8)	0.2740(6)	0.8693(5)	0.116(6)
H(114)	-0.0615(8)	0.2786(6)	0.9575(5)	0.116(6)
H(115)	0.0132(8)	0.1987(6)	0.9174(5)	0.116(6)
H(116)	-0.336(1)	0.4222(5)	0.8112(6)	0.116(6)
H(117)	-0.411(1)	0.4070(5)	0.8838(6)	0.116(6)
H(118)	-0.497(1)	0.3948(5)	0.8036(6)	0.116(6)
H(119)	-0.4451(8)	-0.0171(5)	0.7115(4)	0.116(6)
H(120)	-0.365(1)	-0.1578(6)	0.6790(4)	0.116(6)
H(121)	-0.518(1)	-0.2650(5)	0.6270(5)	0.116(6)
H(122)	-0.756(1)	-0.2356(5)	0.6056(5)	0.116(6)
H(123)	-0.8396(8)	-0.0956(4)	0.6399(4)	0.116(6)
H(124)	-0.9643(7)	0.0601(5)	0.7678(4)	0.116(6)
H(125)	-1.1979(8)	0.0597(5)	0.7208(5)	0.116(6)
H(126)	-1.2593(8)	0.0653(5)	0.5932(6)	0.116(6)
H(127)	-1.0872(9)	0.0757(5)	0.5142(5)	0.116(6)
H(128)	-0.8516(8)	0.0788(5)	0.5620(4)	0.116(6)
H(129)	-0.5678(7)	0.0396(5)	0.5764(4)	0.116(6)
H(130)	-0.4641(8)	0.1367(6)	0.4993(4)	0.116(6)
H(131)	-0.4596(8)	0.2887(6)	0.5284(5)	0.116(6)
H(132)	-0.5665(8)	0.3450(5)	0.6282(4)	0.116(6)
H(133)	-0.6666(7)	0.2474(4)	0.7057(4)	0.116(6)

Bond Lengths
with
Estimated Standard Deviations
in Parentheses

FE(1)	P(1)	2.190(2)
FE(1)	C(1)	1.960(6)
FE(1)	C(5)	1.722(7)
FE(1)	C(6)	2.083(8)
FE(1)	C(7)	2. 97(8)
FE(1)	C(8)	2.103(7)
FE(1)	C(9)	2.113(7)
FE(1)	C(10)	2..25(7)
P(1)	C(15)	1.826(6)
P(1)	C(21)	1.837(6)
P(1)	C(27)	1.844(6)
O(1)	C(1)	1.222(7)
O(2)	C(5)	1.165(7)
C(1)	C(2)	1.518(9)
C(2)	C(3)	1.521(9)
C(2)	C(4)	1.516(9)
C(3)	C(4)	1.48(1)
C(3)	C(11)	1.52(1)
C(4)	C(14)	1.53(1)
C(6)	C(7)	1.37(1)
C(6)	C(10)	1.38(1)
C(7)	C(8)	1.42(1)
C(8)	C(9)	1.38(1)
C(9)	C(10)	1.37(1)
C(11)	C(12)	1.52(1)
C(11)	C(13)	1.50(1)
C(15)	C(16)	1.409(9)
C(15)	C(20)	1.370(9)
C(16)	C(17)	1.39(1)
C(17)	C(18)	1.38(1)
C(18)	C(19)	1.37(1)
C(19)	C(20)	1.39(1)
C(21)	C(22)	1.387(9)
C(21)	C(26)	1.394(9)
C(22)	C(23)	1.394(9)
C(23)	C(24)	1.38(1)
C(24)	C(25)	1.38(1)
C(25)	C(26)	1.37(1)
C(27)	C(28)	1.379(9)
C(27)	C(29)	1.420(9)
C(28)	C(32)	1.434(9)
C(29)	C(30)	1.38(1)
C(30)	C(31)	1.39(1)
C(31)	C(32)	1.35(1)

Bond Angles
with
Estimated Standard Deviations
in Parentheses

C(14)	C(4)	C(3)	120.1(7)
O(2)	C(5)	FE(1)	177.9(6)
C(7)	C(6)	FE(1)	71.4(5)
C(10)	C(6)	FE(1)	72.4(4)
C(10)	C(6)	C(7)	109.7(8)
C(6)	C(7)	FE(1)	70.3(5)
C(8)	C(7)	FE(1)	70.4(4)
C(8)	C(7)	C(6)	107.0(8)
C(7)	C(8)	FE(1)	70.0(5)
C(9)	C(8)	FE(1)	71.3(4)
C(9)	C(8)	C(7)	106.3(8)
C(8)	C(9)	FE(1)	70.6(4)
C(10)	C(9)	FE(1)	71.6(4)
C(10)	C(9)	C(8)	110.3(8)
C(6)	C(10)	FE(1)	69.2(4)
C(9)	C(10)	FE(1)	70.6(4)
C(9)	C(10)	C(6)	106.7(8)
C(12)	C(11)	C(3)	109.9(6)
C(13)	C(11)	C(3)	111.0(7)
C(13)	C(11)	C(12)	109.7(7)
C(16)	C(15)	P(1)	117.5(5)
C(20)	C(15)	P(1)	123.9(5)
C(20)	C(15)	C(16)	118.5(6)
C(17)	C(16)	C(15)	119.8(7)
C(18)	C(17)	C(16)	120.5(8)
C(19)	C(18)	C(17)	119.8(7)
C(20)	C(19)	C(18)	120.3(8)
C(19)	C(20)	C(15)	121.1(8)
C(22)	C(21)	P(1)	119.9(5)
C(26)	C(21)	P(1)	122.3(5)
C(26)	C(21)	C(22)	117.9(6)
C(23)	C(22)	C(21)	120.9(7)
C(24)	C(23)	C(22)	119.4(8)
C(25)	C(24)	C(23)	120.8(7)
C(26)	C(25)	C(24)	119.0(8)
C(25)	C(26)	C(21)	122.1(8)
C(28)	C(27)	P(1)	118.8(5)
C(29)	C(27)	P(1)	121.3(5)
C(29)	C(27)	C(28)	119.9(6)
C(32)	C(28)	C(27)	119.6(7)
C(30)	C(29)	C(27)	119.2(7)
C(31)	C(30)	C(29)	120.6(8)
C(32)	C(31)	C(30)	121.4(7)
C(31)	C(32)	C(28)	119.3(8)
C(1)	FE(1)	P(1)	92.1(2)
C(5)	FE(1)	P(1)	92.5(2)
C(5)	FE(1)	C(1)	92.5(3)
C(6)	FE(1)	P(1)	156.8(3)
C(6)	FE(1)	C(1)	107.5(4)
C(6)	FE(1)	C(5)	98.8(4)
C(7)	FE(1)	P(1)	136.8(4)
C(7)	FE(1)	C(1)	83.7(3)
C(7)	FE(1)	C(5)	130.5(5)
C(7)	FE(1)	C(6)	38.4(4)
C(8)	FE(1)	P(1)	100.1(3)
C(8)	FE(1)	C(1)	100.0(3)
C(8)	FE(1)	C(5)	161.9(3)
C(8)	FE(1)	C(6)	65.0(3)
C(8)	FE(1)	C(7)	39.6(4)
C(9)	FE(1)	P(1)	93.5(2)
C(9)	FE(1)	C(1)	138.0(3)
C(9)	FE(1)	C(5)	128.8(3)
C(9)	FE(1)	C(6)	63.6(3)
C(9)	FE(1)	C(7)	64.3(3)
C(9)	FE(1)	C(8)	38.1(3)
C(10)	FE(1)	P(1)	120.1(3)
C(10)	FE(1)	C(1)	145.4(3)
C(10)	FE(1)	C(5)	97.9(3)
C(10)	FE(1)	C(6)	38.4(3)
C(10)	FE(1)	C(7)	64.6(4)
C(10)	FE(1)	C(8)	64.5(3)
C(10)	FE(1)	C(9)	37.8(3)
C(15)	P(1)	FE(1)	113.8(2)
C(21)	P(1)	FE(1)	118.6(2)
C(21)	P(1)	C(15)	103.0(3)
C(27)	P(1)	FE(1)	115.6(2)
C(27)	P(1)	C(15)	102.3(3)
C(27)	P(1)	C(21)	101.3(3)
O(1)	C(1)	FE(1)	124.1(5)
C(2)	C(1)	FE(1)	117.9(4)
C(2)	C(1)	O(1)	117.9(6)
C(3)	C(2)	C(1)	123.3(6)
C(4)	C(2)	C(1)	118.7(6)
C(4)	C(2)	C(3)	58.4(4)
C(4)	C(3)	C(2)	60.6(5)
C(11)	C(3)	C(2)	125.0(6)
C(11)	C(3)	C(4)	121.4(6)
C(3)	C(4)	C(2)	61.0(4)
C(14)	C(4)	C(2)	118.0(7)

Anisotropic Temperature Factors

Atom	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
FE(1)	0.0473(6)	0.0367(5)	0.0329(5)	0.0046(4)	0.0035(4)	0.0023(4
P(1)	0.0413(9)	0.0372(9)	0.0388(9)	0.0023(7)	0.0077(7)	0.0011(7
O(1)	0.050(3)	0.080(3)	0.052(3)	-0.026(2)	-0.003(2)	0.003(2)
O(2)	0.083(4)	0.055(3)	0.099(4)	0.006(3)	-0.011(3)	-0.018(3)
C(1)	0.049(4)	0.064(4)	0.026(3)	-0.001(3)	0.001(3)	0.000(3)
C(2)	0.049(4)	0.055(4)	0.056(4)	-0.012(3)	0.003(3)	0.007(3)
C(3)	0.059(4)	0.066(5)	0.048(4)	-0.012(3)	0.006(3)	0.013(4)
C(4)	0.063(5)	0.054(4)	0.080(5)	0.020(4)	0.021(4)	0.009(4)
C(5)	0.050(4)	0.046(4)	0.048(4)	0.004(3)	-0.004(3)	0.007(3)
C(6)	0.141(9)	0.072(6)	0.044(5)	0.004(4)	-0.002(5)	0.020(6)
C(7)	0.112(8)	0.128(9)	0.086(7)	0.072(7)	0.049(6)	0.035(7)
C(8)	0.089(7)	0.068(5)	0.068(6)	0.031(4)	-0.008(5)	-0.023(5)
C(9)	0.101(7)	0.049(4)	0.060(5)	0.017(4)	0.005(5)	0.013(4)
C(10)	0.074(5)	0.072(5)	0.067(5)	0.027(4)	-0.011(4)	0.007(4)
C(11)	0.071(5)	0.063(5)	0.053(4)	0.004(4)	0.020(4)	0.001(4)
C(12)	0.065(6)	0.089(6)	0.125(8)	0.005(6)	0.008(5)	0.005(5)
C(13)	0.104(8)	0.17(1)	0.14(1)	0.096(9)	0.059(7)	0.044(7)
C(14)	0.106(7)	0.051(5)	0.17(1)	0.004(6)	0.038(7)	0.002(5)
C(15)	0.058(4)	0.045(4)	0.041(4)	-0.001(3)	0.011(3)	-0.009(3)
C(16)	0.059(5)	0.068(5)	0.073(5)	-0.021(4)	0.017(4)	-0.022(4)
C(17)	0.079(6)	0.085(6)	0.090(6)	-0.022(5)	0.014(5)	-0.029(5)
C(18)	0.102(7)	0.054(5)	0.107(7)	-0.013(5)	0.014(6)	-0.029(5)
C(19)	0.096(7)	0.046(5)	0.142(9)	-0.021(5)	0.019(6)	0.002(5)
C(20)	0.075(5)	0.048(5)	0.101(6)	-0.015(4)	0.008(5)	0.002(4)
C(21)	0.040(4)	0.045(4)	0.039(4)	0.010(3)	0.007(3)	0.006(3)
C(22)	0.048(4)	0.063(5)	0.062(5)	0.019(4)	0.006(3)	0.006(3)
C(23)	0.063(5)	0.067(5)	0.089(6)	0.033(5)	0.010(4)	0.012(4)
C(24)	0.066(5)	0.109(8)	0.076(6)	0.049(6)	0.002(5)	0.026(5)
C(25)	0.085(6)	0.126(8)	0.055(5)	0.025(5)	-0.014(4)	0.020(6)
C(26)	0.073(5)	0.088(6)	0.050(4)	0.002(4)	-0.003(4)	0.016(4)
C(27)	0.059(4)	0.032(3)	0.058(4)	0.001(3)	0.021(4)	0.003(3)
C(28)	0.038(4)	0.058(4)	0.071(5)	0.021(4)	0.008(3)	0.007(3)
C(29)	0.064(5)	0.066(5)	0.058(5)	-0.006(4)	0.027(4)	-0.008(4)
C(30)	0.094(7)	0.073(5)	0.076(6)	-0.017(4)	0.043(5)	-0.016(5)
C(31)	0.082(7)	0.061(5)	0.111(8)	-0.005(5)	0.063(6)	-0.001(4)
C(32)	0.047(4)	0.059(5)	0.115(7)	0.012(5)	0.030(5)	0.010(3)

Bond Lengths
with
Estimated Standard Deviations
in Parentheses

FE(2)	P(2)	2.187(2)
FE(2)	C(101)	1.976(6)
FE(2)	C(105)	1.721(7)
FE(2)	C(106)	2.098(8)
FE(2)	C(107)	2.109(7)
FE(2)	C(108)	2.130(7)
FE(2)	C(109)	2.138(7)
FE(2)	C(110)	2.091(7)
P(2)	C(115)	1.829(6)
P(2)	C(121)	1.843(6)
P(2)	C(127)	1.832(6)
O(101)	C(101)	1.220(7)
O(102)	C(105)	1.161(7)
C(101)	C(102)	1.499(9)
C(102)	C(103)	1.539(9)
C(102)	C(104)	1.503(9)
C(103)	C(104)	1.470(9)
C(103)	C(111)	1.52(1)
C(104)	C(114)	1.54(1)
C(106)	C(107)	1.42(1)
C(106)	C(110)	1.40(1)
C(107)	C(108)	1.37(1)
C(108)	C(109)	1.38(1)
C(109)	C(110)	1.39(1)
C(111)	C(112)	1.53(1)
C(111)	C(113)	1.52(1)
C(115)	C(116)	1.397(9)
C(115)	C(120)	1.379(9)
C(116)	C(117)	1.38(1)
C(117)	C(118)	1.36(1)
C(118)	C(119)	1.37(1)
C(119)	C(120)	1.39(1)
C(121)	C(122)	1.389(9)
C(121)	C(126)	1.386(9)
C(122)	C(123)	1.37(1)
C(123)	C(124)	1.38(1)
C(124)	C(125)	1.37(1)
C(125)	C(126)	1.39(1)
C(127)	C(128)	1.404(9)
C(127)	C(132)	1.367(9)
C(128)	C(129)	1.40(1)
C(129)	C(130)	1.39(1)
C(130)	C(131)	1.38(1)
C(131)	C(132)	1.400(9)

Bond Angles
with
Estimated Standard Deviations
in Parentheses

C(101)	FE(2)	P(2)	92.4(2)
C(105)	FE(2)	P(2)	91.7(2)
C(105)	FE(2)	C(101)	92.7(3)
C(106)	FE(2)	P(2)	137.4(3)
C(106)	FE(2)	C(101)	83.4(3)
C(106)	FE(2)	C(105)	130.8(4)
C(107)	FE(2)	P(2)	100.7(2)
C(107)	FE(2)	C(101)	99.9(3)
C(107)	FE(2)	C(105)	161.8(3)
C(107)	FE(2)	C(106)	39.6(3)
C(108)	FE(2)	P(2)	94.0(2)
C(108)	FE(2)	C(101)	137.7(3)
C(108)	FE(2)	C(105)	128.8(3)
C(108)	FE(2)	C(106)	64.2(3)
C(108)	FE(2)	C(107)	37.8(3)
C(109)	FE(2)	P(2)	119.9(3)
C(109)	FE(2)	C(101)	145.4(3)
C(109)	FE(2)	C(105)	98.0(3)
C(109)	FE(2)	C(106)	64.8(3)
C(109)	FE(2)	C(107)	64.3(3)
C(109)	FE(2)	C(108)	37.6(3)
C(110)	FE(2)	P(2)	157.1(3)
C(110)	FE(2)	C(101)	107.6(3)
C(110)	FE(2)	C(105)	98.4(4)
C(110)	FE(2)	C(106)	39.1(3)
C(110)	FE(2)	C(107)	65.4(3)
C(110)	FE(2)	C(108)	63.7(3)
C(110)	FE(2)	C(109)	38.4(3)
C(115)	P(2)	FE(2)	114.4(2)
C(121)	P(2)	FE(2)	114.5(2)
C(121)	P(2)	C(115)	103.3(3)
C(127)	P(2)	FE(2)	118.5(2)
C(127)	P(2)	C(115)	102.8(3)
C(127)	P(2)	C(121)	101.2(3)
O(101)	C(101)	FE(2)	123.0(5)
C(102)	C(101)	FE(2)	117.1(4)
C(102)	C(101)	O(101)	119.8(6)
C(103)	C(102)	C(101)	123.1(6)
C(104)	C(102)	C(101)	119.4(6)
C(104)	C(102)	C(103)	57.8(4)
C(104)	C(103)	C(102)	59.9(4)
C(111)	C(103)	C(102)	123.4(6)
C(111)	C(103)	C(104)	121.9(6)
C(103)	C(104)	C(102)	62.4(4)
C(114)	C(104)	C(102)	118.6(6)
C(114)	C(104)	C(103)	120.2(7)
O(102)	C(105)	FE(2)	178.8(6)
C(107)	C(106)	FE(2)	70.6(4)
C(110)	C(106)	FE(2)	70.2(5)
C(110)	C(106)	C(107)	106.8(8)
C(106)	C(107)	FE(2)	69.8(4)
C(108)	C(107)	FE(2)	71.9(4)
C(108)	C(107)	C(106)	106.8(7)
C(107)	C(108)	FE(2)	70.3(4)
C(109)	C(108)	FE(2)	71.5(4)
C(109)	C(108)	C(107)	110.6(8)
C(108)	C(109)	FE(2)	70.9(4)
C(110)	C(109)	FE(2)	69.0(4)
C(110)	C(109)	C(108)	107.2(8)
C(106)	C(110)	FE(2)	70.7(4)
C(109)	C(110)	FE(2)	72.6(4)
C(109)	C(110)	C(106)	108.6(8)
C(112)	C(111)	C(103)	111.8(7)
C(113)	C(111)	C(103)	108.7(6)
C(113)	C(111)	C(112)	107.3(7)
C(116)	C(115)	P(2)	117.5(5)
C(120)	C(115)	P(2)	123.4(6)
C(120)	C(115)	C(116)	118.9(6)
C(117)	C(116)	C(115)	119.7(8)
C(118)	C(117)	C(116)	120.7(8)
C(119)	C(118)	C(117)	120.7(8)
C(120)	C(119)	C(118)	119.3(8)
C(119)	C(120)	C(115)	120.6(8)
C(122)	C(121)	P(2)	120.1(5)
C(126)	C(121)	P(2)	121.9(5)
C(126)	C(121)	C(122)	118.0(6)
C(123)	C(122)	C(121)	121.8(7)
C(124)	C(123)	C(122)	119.5(8)
C(125)	C(124)	C(123)	120.0(7)
C(126)	C(125)	C(124)	120.2(8)
C(125)	C(126)	C(121)	120.5(7)
C(128)	C(127)	P(2)	121.3(5)
C(132)	C(127)	P(2)	120.4(5)
C(132)	C(127)	C(128)	118.3(6)
C(129)	C(128)	C(127)	120.8(7)
C(130)	C(129)	C(128)	119.2(8)
C(131)	C(130)	C(129)	120.6(7)
C(132)	C(131)	C(130)	119.3(8)
C(131)	C(132)	C(127)	121.8(7)

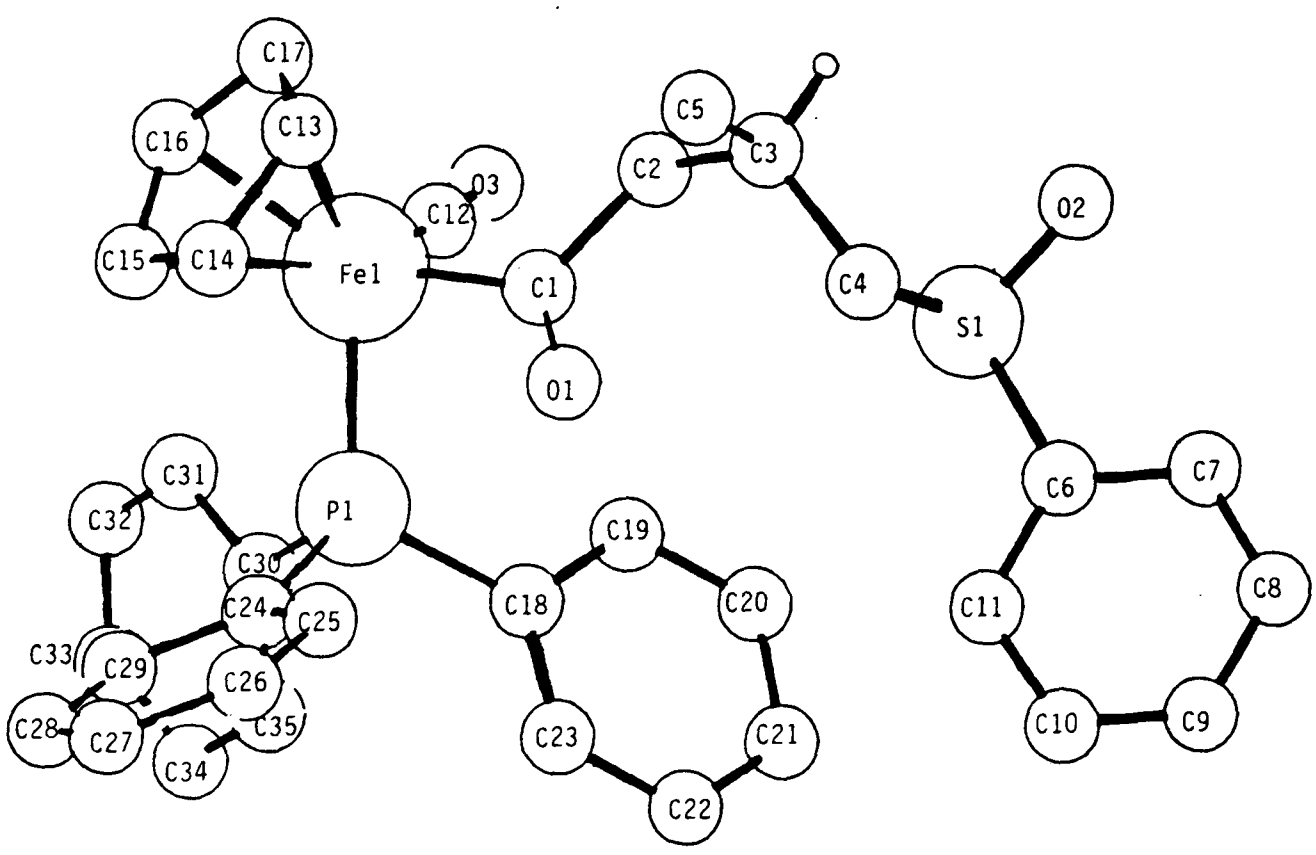
Anisotropic Temperature Factors

Atom	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
FE(2)	0.0522(6)	0.0347(5)	0.0352(5)	0.0026(4)	0.0133(4)	-0.0012(4)
P(2)	0.0417(9)	0.0359(8)	0.0407(9)	0.0044(7)	0.0068(7)	0.0004(7)
O(101)	0.052(3)	0.079(3)	0.059(3)	-0.020(3)	0.011(2)	0.003(2)
O(102)	0.091(4)	0.054(3)	0.118(5)	0.002(3)	0.041(3)	0.018(3)
C(101)	0.045(4)	0.062(4)	0.034(3)	0.001(3)	0.003(3)	0.002(3)
C(102)	0.057(4)	0.055(4)	0.051(4)	-0.009(3)	0.015(3)	-0.010(3)
C(103)	0.051(4)	0.065(4)	0.053(4)	-0.007(4)	0.007(3)	-0.015(3)
C(104)	0.064(5)	0.053(4)	0.070(5)	0.011(4)	0.013(4)	-0.003(3)
C(105)	0.062(5)	0.041(4)	0.065(5)	0.003(3)	0.029(4)	0.000(3)
C(106)	0.094(7)	0.120(8)	0.061(6)	0.051(6)	-0.010(5)	-0.019(6)
C(107)	0.100(7)	0.062(5)	0.066(5)	0.027(4)	0.031(5)	0.025(5)
C(108)	0.107(7)	0.041(4)	0.058(5)	0.014(4)	0.011(5)	-0.012(4)
C(109)	0.094(6)	0.069(5)	0.076(6)	0.031(5)	0.042(5)	0.003(5)
C(110)	0.151(9)	0.062(5)	0.044(5)	-0.006(4)	0.022(5)	-0.027(6)
C(111)	0.060(5)	0.066(5)	0.060(5)	0.006(4)	-0.001(4)	-0.008(4)
C(112)	0.090(7)	0.18(1)	0.14(1)	0.098(9)	-0.014(6)	-0.029(7)
C(113)	0.066(6)	0.096(7)	0.124(8)	0.020(6)	0.021(5)	-0.003(5)
C(114)	0.098(7)	0.060(5)	0.16(1)	0.012(6)	0.008(6)	-0.001(5)
C(115)	0.075(5)	0.043(4)	0.031(3)	0.004(3)	0.015(3)	0.001(3)
C(116)	0.072(5)	0.068(5)	0.045(4)	-0.005(3)	0.004(4)	0.022(4)
C(117)	0.110(7)	0.076(6)	0.051(5)	-0.002(4)	0.013(5)	0.041(5)
C(118)	0.17(1)	0.048(5)	0.062(6)	0.008(4)	0.041(6)	0.031(6)
C(119)	0.126(8)	0.045(5)	0.086(6)	-0.008(4)	0.043(6)	-0.011(5)
C(120)	0.082(5)	0.047(4)	0.069(5)	-0.003(4)	0.028(4)	-0.010(4)
C(121)	0.032(3)	0.037(3)	0.068(5)	-0.000(3)	0.008(3)	-0.005(3)
C(122)	0.050(5)	0.070(5)	0.070(5)	0.015(4)	0.010(4)	0.001(4)
C(123)	0.046(5)	0.076(6)	0.105(7)	0.008(5)	0.006(5)	0.004(4)
C(124)	0.039(5)	0.081(6)	0.121(8)	-0.015(5)	-0.009(5)	0.005(4)
C(125)	0.068(6)	0.079(6)	0.081(6)	-0.010(5)	-0.030(5)	0.012(4)
C(126)	0.066(5)	0.066(5)	0.053(4)	-0.009(4)	-0.011(4)	0.001(4)
C(127)	0.033(3)	0.049(4)	0.044(4)	0.005(3)	-0.006(3)	0.001(3)
C(128)	0.054(4)	0.075(5)	0.046(4)	0.021(4)	0.011(3)	0.006(4)
C(129)	0.065(5)	0.106(7)	0.056(5)	0.036(5)	0.007(4)	0.003(5)
C(130)	0.056(5)	0.106(7)	0.083(6)	0.053(6)	-0.004(4)	-0.019(5)
C(131)	0.065(5)	0.077(5)	0.066(5)	0.035(4)	-0.015(4)	-0.019(4)
C(132)	0.052(4)	0.064(5)	0.053(4)	0.013(4)	-0.007(3)	-0.008(3)

Appendix 2

Crystal Data for RRR(SSS)-$(C_5H_5)Fe(CO)(PPh_3)(COCH_2CH(CH_3)CH_2S(O)Ph)$ 189.

$C_{35}H_{33}FeO_3PS$, M=620.526, monoclinic, a=9.510(2), b=10.146(3), c=15.857(3) A, β=96.44(2)°, U=1520.40 A^3, Z=2, D_{calc}=1.36 Mgm^{-3}, u(Mo-K_α)=6.45cm^{-1} θ_{max}=27°, space group $P2_1$, relative transmission factors 1.00-1.06, crystal dimensions 0.58 by 0.35 by 0.21 mm, number of reflections [I>3σ(I)] 2939, R=0.030, R_w=0.035, GOF=1.05.



Final Atomic Positional Coordinates
with
Estimated Standard Deviations
in Parentheses

Atom	x/a	y/b	z/c	U(iso)
FE(1)	0.40779(4)	-0.8571(1)	0.33741(3)	0.0299
P(1)	0.62387(8)	-0.9336(1)	0.33300(5)	0.0289
S(1)	0.2095(1)	-1.3485(2)	0.18288(6)	0.0558
O(1)	0.3917(3)	-0.9920(3)	0.1807(2)	0.0490
O(2)	0.0671(4)	-1.4079(4)	0.1830(3)	0.0744
O(3)	0.3357(3)	-1.0291(3)	0.4716(2)	0.0587
C(1)	0.3354(3)	-0.9755(3)	0.2445(2)	0.0332
C(2)	0.1935(4)	-1.0458(5)	0.2497(3)	0.0472
C(3)	0.1119(4)	-1.0914(5)	0.1654(3)	0.0529
C(4)	0.1855(5)	-1.1993(4)	0.1200(3)	0.0505
C(5)	0.0751(6)	-0.9778(6)	0.1063(4)	0.0791
C(6)	0.2978(4)	-1.4403(4)	0.1085(2)	0.0479
C(7)	0.2294(5)	-1.5456(5)	0.0669(3)	0.0593
C(8)	0.2986(7)	-1.6163(6)	0.0095(4)	0.0771
C(9)	0.4323(8)	-1.5825(7)	-0.0036(5)	0.0847
C(10)	0.4998(6)	-1.4834(7)	0.0377(5)	0.0786
C(11)	0.4347(5)	-1.4094(5)	0.0962(3)	0.0627
C(12)	0.3660(4)	-0.9650(4)	0.4163(2)	0.0381
C(13)	0.2785(4)	-0.7171(4)	0.2692(3)	0.0446
C(14)	0.4219(5)	-0.6819(4)	0.2697(3)	0.0442
C(15)	0.4790(5)	-0.6623(4)	0.3554(3)	0.0440
C(16)	0.3719(5)	-0.6852(4)	0.4062(3)	0.0489
C(17)	0.2473(5)	-0.7208(4)	0.3528(3)	0.0511
C(18)	0.6445(3)	-1.1065(3)	0.3030(2)	0.0320
C(19)	0.5647(4)	-1.1997(4)	0.3410(3)	0.0419
C(20)	0.5837(5)	-1.3335(4)	0.3276(3)	0.0491
C(21)	0.6838(4)	-1.3740(4)	0.2760(3)	0.0525
C(22)	0.7607(5)	-1.2836(4)	0.2376(3)	0.0518
C(23)	0.7410(4)	-1.1495(4)	0.2505(3)	0.0464
C(24)	0.7236(3)	-0.8388(3)	0.2611(2)	0.0317
C(25)	0.6825(3)	-0.8455(5)	0.1745(2)	0.0425
C(26)	0.7445(4)	-0.7639(5)	0.1192(3)	0.0514
C(27)	0.8465(4)	-0.6745(4)	0.1500(3)	0.0477
C(28)	0.8892(4)	-0.6682(4)	0.2355(3)	0.0448
C(29)	0.8284(4)	-0.7495(3)	0.2913(2)	0.0393
C(30)	0.7430(3)	-0.9304(4)	0.4326(2)	0.0374
C(31)	0.7032(4)	-0.8661(5)	0.5026(2)	0.0481
C(32)	0.7942(5)	-0.8602(7)	0.5770(3)	0.0662
C(33)	0.9245(6)	-0.9163(6)	0.5815(3)	0.0684
C(34)	0.9663(5)	-0.9806(6)	0.5128(3)	0.0669
C(35)	0.8748(4)	-0.9902(5)	0.4389(3)	0.0588
H(1)	0.2143(4)	-1.1269(5)	0.2847(3)	0.077(3)
H(2)	0.1317(4)	-0.9855(5)	0.2791(3)	0.077(3)
H(3)	0.0212(4)	-1.1280(5)	0.1817(3)	0.077(3)
H(4)	0.1267(5)	-1.2206(4)	0.0654(3)	0.077(3)
H(5)	0.2801(5)	-1.1660(4)	0.1078(3)	0.077(3)
H(6)	0.0216(6)	-1.0105(6)	0.0525(4)	0.077(3)
H(7)	0.1660(6)	-0.9369(6)	0.0936(4)	0.077(3)
H(8)	0.0170(6)	-0.9106(6)	0.1329(4)	0.077(3)
H(9)	0.1319(5)	-1.5701(5)	0.0790(3)	0.077(3)
H(10)	0.2499(7)	-1.6911(6)	-0.0228(4)	0.077(3)
H(11)	0.4814(8)	-1.6327(7)	-0.0461(5)	0.077(3)
H(12)	0.5989(6)	-1.4623(7)	0.0269(5)	0.077(3)
H(13)	0.4859(5)	-1.3366(5)	0.1292(3)	0.077(3)
H(14)	0.2107(4)	-0.7360(4)	0.2178(3)	0.077(3)
H(15)	0.4738(5)	-0.6722(4)	0.2186(3)	0.077(3)
H(16)	0.5787(5)	-0.6372(4)	0.3757(3)	0.077(3)
H(17)	0.3800(5)	-0.6778(4)	0.4694(3)	0.077(3)
H(18)	0.1540(5)	-0.7446(4)	0.3720(3)	0.077(3)
H(19)	0.4941(4)	-1.1694(4)	0.3790(3)	0.077(3)
H(20)	0.5259(5)	-1.4003(4)	0.3547(3)	0.077(3)
H(21)	0.6992(4)	-1.4701(4)	0.2664(3)	0.077(3)
H(22)	0.8325(5)	-1.3130(4)	0.2001(3)	0.077(3)
H(23)	0.7972(4)	-1.0832(4)	0.2218(3)	0.077(3)
H(24)	0.6089(3)	-0.9108(5)	0.1519(2)	0.077(3)
H(25)	0.7149(4)	-0.7682(5)	0.0567(3)	0.077(3)
H(26)	0.8898(4)	-0.6137(4)	0.1105(3)	0.077(3)
H(27)	0.9644(4)	-0.6039(4)	0.2571(3)	0.077(3)
H(28)	0.8601(4)	-0.7442(3)	0.3535(2)	0.077(3)
H(29)	0.6082(4)	-0.8230(5)	0.4994(2)	0.077(3)
H(30)	0.7637(5)	-0.8159(7)	0.6282(3)	0.077(3)
H(31)	0.9907(6)	-0.9111(6)	0.6350(3)	0.077(3)
H(32)	1.0632(5)	-1.0199(6)	0.5155(3)	0.077(3)
H(33)	0.9036(4)	-1.0404(5)	0.3893(3)	0.077(3)

Bond Lengths
with
Estimated Standard Deviations
in Parentheses

FE(1)	P(1)	2.2050(9)
FE(1)	C(1)	1.964(3)
FE(1)	C(12)	1.742(4)
FE(1)	C(13)	2.097(4)
FE(1)	C(14)	2.088(4)
FE(1)	C(15)	2.098(4)
FE(1)	C(16)	2.105(4)
FE(1)	C(17)	2.093(4)
P(1)	C(18)	1.834(3)
P(1)	C(24)	1.835(3)
P(1)	C(30)	1.837(3)
S(1)	O(2)	1.482(4)
S(1)	C(4)	1.812(5)
S(1)	C(6)	1.786(4)
O(1)	C(1)	1.207(4)
O(3)	C(12)	1.154(4)
C(1)	C(2)	1.537(5)
C(2)	C(3)	1.539(6)
C(3)	C(4)	1.523(6)
C(3)	C(5)	1.502(9)
C(6)	C(7)	1.380(6)
C(6)	C(11)	1.373(6)
C(7)	C(8)	1.381(7)
C(8)	C(9)	1.355(9)
C(9)	C(10)	1.33(1)
C(10)	C(11)	1.392(8)
C(13)	C(14)	1.409(6)
C(13)	C(17)	1.390(6)
C(14)	C(15)	1.419(6)
C(15)	C(16)	1.387(6)
C(16)	C(17)	1.423(6)
C(18)	C(19)	1.392(5)
C(18)	C(23)	1.377(5)
C(19)	C(20)	1.389(5)
C(20)	C(21)	1.385(6)
C(21)	C(22)	1.359(6)
C(22)	C(23)	1.391(6)
C(24)	C(25)	1.387(5)
C(24)	C(29)	1.392(5)
C(25)	C(26)	1.384(5)
C(26)	C(27)	1.377(6)
C(27)	C(28)	1.371(6)
C(28)	C(29)	1.384(5)
C(30)	C(31)	1.378(5)
C(30)	C(35)	1.386(5)
C(31)	C(32)	1.384(5)
C(32)	C(33)	1.358(7)
C(33)	C(34)	1.367(8)
C(34)	C(35)	1.382(6)

Bond Angles
with
Estimated Standard Deviations
in Parentheses

C(1)	FE(1)	P(1)	90.6(1)
C(12)	FE(1)	P(1)	95.2(1)
C(12)	FE(1)	C(1)	93.7(2)
C(13)	FE(1)	P(1)	135.8(1)
C(13)	FE(1)	C(1)	83.8(1)
C(13)	FE(1)	C(12)	128.9(2)
C(14)	FE(1)	P(1)	99.7(1)
C(14)	FE(1)	C(1)	99.9(2)
C(14)	FE(1)	C(12)	159.6(2)
C(14)	FE(1)	C(13)	39.3(2)
C(15)	FE(1)	P(1)	92.8(1)
C(15)	FE(1)	C(1)	139.3(2)
C(15)	FE(1)	C(12)	126.2(2)
C(15)	FE(1)	C(13)	66.0(2)
C(15)	FE(1)	C(14)	39.6(2)
C(16)	FE(1)	P(1)	120.9(1)
C(16)	FE(1)	C(1)	146.3(2)
C(16)	FE(1)	C(12)	94.9(2)
C(16)	FE(1)	C(13)	65.6(2)
C(16)	FE(1)	C(14)	65.5(2)
C(16)	FE(1)	C(15)	38.5(2)
C(17)	FE(1)	P(1)	158.5(1)
C(17)	FE(1)	C(1)	107.0(2)
C(17)	FE(1)	C(12)	95.9(2)
C(17)	FE(1)	C(13)	38.7(2)
C(17)	FE(1)	C(14)	65.6(2)
C(17)	FE(1)	C(15)	65.8(2)
C(17)	FE(1)	C(16)	39.6(2)
C(18)	P(1)	FE(1)	118.2(1)
C(24)	P(1)	FE(1)	112.6(1)
C(24)	P(1)	C(18)	105.2(1)
C(30)	P(1)	FE(1)	117.0(1)
C(30)	P(1)	C(18)	99.6(2)
C(30)	P(1)	C(24)	102.3(1)
C(4)	S(1)	O(2)	106.4(2)
C(6)	S(1)	O(2)	106.6(2)
C(6)	S(1)	C(4)	96.4(2)
O(1)	C(1)	FE(1)	124.2(3)
C(2)	C(1)	FE(1)	118.7(2)
C(2)	C(1)	O(1)	117.0(3)
C(3)	C(2)	C(1)	117.0(3)
C(4)	C(3)	C(2)	114.4(4)
C(5)	C(3)	C(2)	111.7(4)
C(5)	C(3)	C(4)	110.1(4)
C(3)	C(4)	S(1)	112.1(3)
C(7)	C(6)	S(1)	119.2(3)
C(11)	C(6)	S(1)	119.9(4)
C(11)	C(6)	C(7)	120.8(4)
C(8)	C(7)	C(6)	118.9(5)
C(9)	C(8)	C(7)	119.6(6)
C(10)	C(9)	C(8)	121.7(6)
C(11)	C(10)	C(9)	120.8(6)
C(10)	C(11)	C(6)	118.1(6)
O(3)	C(12)	FE(1)	175.4(3)
C(14)	C(13)	FE(1)	70.0(2)
C(17)	C(13)	FE(1)	70.5(2)
C(17)	C(13)	C(14)	108.1(4)
C(13)	C(14)	FE(1)	70.7(2)
C(15)	C(14)	FE(1)	70.6(2)
C(15)	C(14)	C(13)	107.9(4)
C(14)	C(15)	FE(1)	69.8(2)
C(16)	C(15)	FE(1)	71.0(2)
C(16)	C(15)	C(14)	107.8(4)
C(15)	C(16)	FE(1)	70.5(2)
C(17)	C(16)	FE(1)	69.8(2)
C(17)	C(16)	C(15)	108.3(4)
C(13)	C(17)	FE(1)	70.8(2)
C(16)	C(17)	FE(1)	70.6(2)
C(16)	C(17)	C(13)	107.9(4)
C(19)	C(18)	P(1)	117.3(2)
C(23)	C(18)	P(1)	123.9(3)
C(23)	C(18)	C(19)	118.6(3)
C(20)	C(19)	C(18)	120.8(4)
C(21)	C(20)	C(19)	119.3(4)
C(22)	C(21)	C(20)	120.3(4)
C(23)	C(22)	C(21)	120.4(4)
C(22)	C(23)	C(18)	120.6(4)
C(25)	C(24)	P(1)	118.8(3)
C(29)	C(24)	P(1)	121.8(3)
C(29)	C(24)	C(25)	119.0(3)
C(26)	C(25)	C(24)	120.3(4)
C(27)	C(26)	C(25)	120.2(4)
C(28)	C(27)	C(26)	120.0(4)
C(29)	C(28)	C(27)	120.4(4)
C(28)	C(29)	C(24)	120.2(4)
C(31)	C(30)	P(1)	120.1(3)
C(35)	C(30)	P(1)	121.3(3)
C(35)	C(30)	C(31)	118.5(3)
C(32)	C(31)	C(30)	120.3(4)
C(33)	C(32)	C(31)	120.4(5)
C(34)	C(33)	C(32)	120.2(4)
C(35)	C(34)	C(33)	119.8(4)
C(34)	C(35)	C(30)	120.6(5)

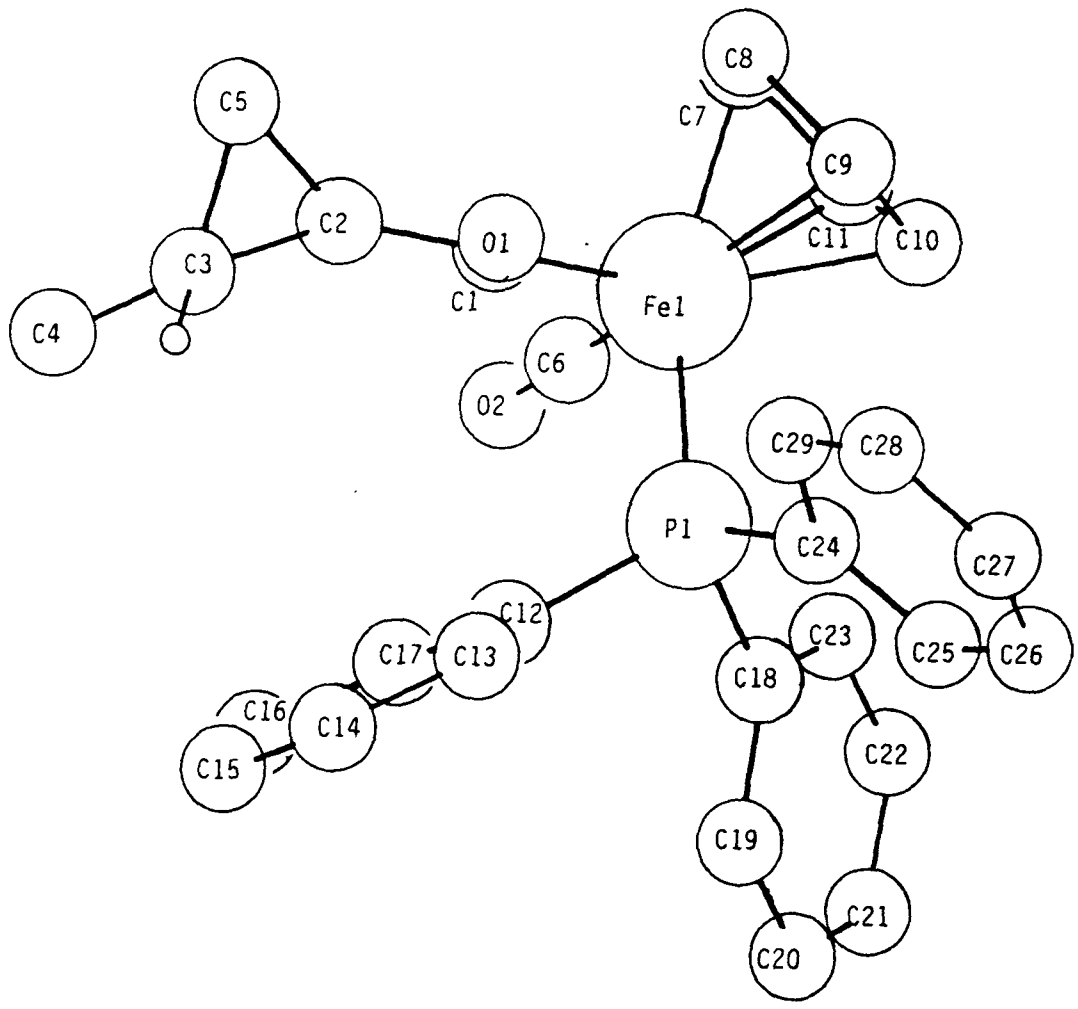
Anisotropic Temperature Factors

Atom	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
FE(1)	0.0339(2)	0.0217(2)	0.0366(2)	-0.0001(2)	0.0040(2)	0.0031(2
P(1)	0.0315(4)	0.0230(4)	0.0334(4)	0.0003(3)	0.0043(3)	-0.0009(3
S(1)	0.0698(6)	0.0617(6)	0.0491(5)	-0.0050(6)	0.0231(4)	-0.0135(7
O(1)	0.047(1)	0.072(2)	0.046(2)	-0.017(1)	0.014(1)	-0.021(1)
O(2)	0.082(2)	0.068(2)	0.133(3)	-0.007(2)	0.066(2)	-0.019(2)
O(3)	0.077(2)	0.055(2)	0.060(2)	0.019(2)	0.023(2)	0.003(2)
C(1)	0.032(2)	0.029(2)	0.040(2)	-0.001(1)	0.004(1)	-0.000(1)
C(2)	0.046(2)	0.055(2)	0.063(3)	-0.025(2)	0.023(2)	-0.015(2)
C(3)	0.029(2)	0.073(3)	0.089(3)	-0.036(3)	0.007(2)	-0.009(2)
C(4)	0.053(2)	0.050(2)	0.056(2)	-0.015(2)	0.009(2)	-0.013(2)
C(5)	0.077(4)	0.101(5)	0.125(5)	-0.052(4)	-0.052(3)	0.043(3)
C(6)	0.052(2)	0.053(2)	0.042(2)	0.008(2)	0.006(2)	0.006(2)
C(7)	0.063(3)	0.056(3)	0.060(3)	-0.001(2)	0.004(2)	0.007(2)
C(8)	0.112(5)	0.061(3)	0.074(4)	-0.006(3)	0.011(3)	0.022(3)
C(9)	0.124(6)	0.075(4)	0.109(5)	0.011(4)	0.054(5)	0.046(4)
C(10)	0.070(3)	0.089(4)	0.131(6)	0.042(4)	0.049(4)	0.031(3)
C(11)	0.053(2)	0.064(3)	0.080(3)	0.019(2)	0.012(2)	0.006(2)
C(12)	0.042(2)	0.033(2)	0.042(2)	-0.002(2)	0.009(1)	0.007(2)
C(13)	0.050(2)	0.032(2)	0.063(3)	0.004(2)	-0.006(2)	0.012(2)
C(14)	0.066(3)	0.024(2)	0.061(3)	0.011(2)	0.006(2)	0.008(2)
C(15)	0.058(2)	0.019(2)	0.077(3)	-0.004(2)	-0.004(2)	0.002(2)
C(16)	0.073(3)	0.035(2)	0.056(3)	-0.010(2)	0.006(2)	0.018(2)
C(17)	0.054(2)	0.039(2)	0.078(3)	-0.002(2)	0.012(2)	0.018(2)
C(18)	0.030(2)	0.026(2)	0.043(2)	-0.000(1)	0.005(1)	0.001(1)
C(19)	0.055(2)	0.028(2)	0.054(2)	-0.000(2)	0.019(2)	0.005(2)
C(20)	0.069(2)	0.025(2)	0.079(3)	0.006(2)	0.025(2)	0.002(2)
C(21)	0.061(2)	0.030(2)	0.089(3)	-0.006(2)	0.012(2)	0.011(2)
C(22)	0.051(2)	0.040(2)	0.095(3)	-0.013(2)	0.029(2)	0.009(2)
C(23)	0.045(2)	0.035(2)	0.079(3)	-0.005(2)	0.026(2)	0.001(2)
C(24)	0.032(1)	0.025(2)	0.041(2)	0.003(1)	0.006(1)	-0.001(1)
C(25)	0.043(2)	0.047(2)	0.042(2)	0.002(2)	0.010(1)	-0.010(2)
C(26)	0.053(2)	0.063(3)	0.047(2)	0.010(2)	0.013(2)	-0.007(2)
C(27)	0.051(2)	0.043(2)	0.068(3)	0.016(2)	0.026(2)	-0.001(2)
C(28)	0.041(2)	0.032(2)	0.079(3)	0.001(2)	0.015(2)	-0.009(2)
C(29)	0.037(2)	0.032(2)	0.051(2)	-0.002(2)	0.004(1)	-0.004(1)
C(30)	0.039(2)	0.035(2)	0.039(2)	0.004(2)	-0.002(1)	-0.003(1)
C(31)	0.066(2)	0.041(2)	0.042(2)	-0.001(2)	-0.009(2)	0.005(2)
C(32)	0.095(3)	0.062(3)	0.051(2)	-0.004(3)	-0.014(2)	0.007(4)
C(33)	0.086(3)	0.079(3)	0.057(3)	0.007(3)	-0.026(2)	-0.016(3)
C(34)	0.043(2)	0.104(4)	0.076(3)	0.016(3)	-0.015(2)	0.009(3
C(35)	0.046(2)	0.082(3)	0.056(3)	0.004(2)	-0.002(2)	0.013(2

Appendix 3

Crystal Data for $(C_5H_5)Fe(CO)(PPh_3)(COCH\text{-}CHCH_3)$ 85

$C_{29}H_{27}FeO_2P$, M=494.34, monoclinic, a=15.78(5), b=19.25(1), c=7.99(9) A, α=90.00°, β=94.07°, γ=90.00°, U=2424.6 A^3, Z=4, D_{calc}=1.35Mgm^{-3}, μ(Cu-K_α)= 57.79 cm^{-1}, θ_{max}=60°, space group P21$_c$ relative transmission factors 1.00-1.49, crystal dimensions 0.30 by 0.30 by 0.60 mm, number of reflections [I>3σ(I)] 3581, R=0.0552 R_w=0.0615.



Final Atomic Positional Coordinates
with
Estimated Standard Deviations
in Parentheses

Atom	x/a	y/b	z/c	U(iso)
FE(1)	1865.3(3)	3501.8(3)	1340.8(7)	333
P(1)	3086.3(6)	3602.0(4)	2812(1)	332
O(1)	2272(2)	4866(2)	438(4)	580
O(2)	923(2)	3372(2)	4275(4)	645
C(1)	1791(2)	4518(2)	1209(4)	370
C(2)	1080(3)	4891(2)	1955(6)	522
C(3)	1245(4)	5622(3)	2576(7)	716
C(4)	828(7)	5858(5)	4127(10)	1136
C(5)	712(3)	5508(2)	1052(7)	675
C(6)	1308(2)	3444(2)	3110(5)	399
C(7)	1431(3)	3524(2)	-1240(5)	478
C(8)	896(3)	3101(2)	-346(6)	505
C(9)	1390(3)	2542(2)	359(6)	538
C(10)	2224(3)	2629(2)	-68(6)	540
C(11)	2260(3)	3244(2)	-1060(5)	511
C(12)	3234(2)	4389(2)	4111(5)	363
C(13)	3824(3)	4892(2)	3849(7)	602
C(14)	3887(4)	5476(3)	4876(9)	728
C(15)	3384(4)	5549(3)	6173(6)	636
C(16)	2798(3)	5053(2)	6451(6)	561
C(17)	2717(3)	4473(2)	5432(5)	530
C(18)	3301(2)	2926(2)	4404(5)	392
C(19)	3924(3)	3013(2)	5718(5)	481
C(20)	4071(3)	2506(2)	6922(5)	527
C(21)	3610(3)	1908(2)	6827(6)	557
C(22)	2978(3)	1805(2)	5557(6)	572
C(23)	2831(3)	2322(2)	4352(5)	495
C(24)	4033(2)	3593(2)	1613(5)	384
C(25)	4696(2)	3128(2)	1929(5)	452
C(26)	5408(3)	3159(3)	972(6)	549
C(27)	5454(3)	3644(3)	-246(6)	581
C(28)	4792(3)	4099(2)	-606(6)	558
C(29)	4079(3)	4073(2)	305(5)	465
H(1)	850(3)	4456(2)	2438(6)	923(35)
H(2)	1772(4)	5903(3)	2812(7)	923(35)
H(3)	989(7)	6350(5)	4387(10)	923(35)
H(4)	197(7)	5822(5)	3931(10)	923(35)
H(5)	1025(7)	5554(5)	5092(10)	923(35)
H(6)	918(3)	5641(2)	-57(7)	923(35)
H(7)	88(3)	5600(2)	1048(7)	923(35)
H(8)	275(3)	3177(2)	-236(6)	923(35)
H(9)	1176(3)	2152(2)	1040(6)	923(35)
H(10)	2712(3)	2315(2)	262(6)	923(35)
H(11)	2777(3)	3443(2)	-1535(5)	923(35)
H(12)	1257(3)	3952(2)	-1883(5)	923(35)
H(13)	4209(3)	4840(2)	2917(7)	923(35)
H(14)	4312(4)	5844(3)	4662(9)	923(35)
H(15)	3443(4)	5967(3)	6918(6)	923(35)
H(16)	2422(3)	5108(2)	7399(6)	923(35)
H(17)	2281(3)	4112(2)	5644(5)	923(35)
H(18)	4265(3)	3451(2)	5791(5)	923(35)
H(19)	4517(3)	2575(2)	7859(5)	923(35)
H(20)	3728(3)	1536(2)	7686(6)	923(35)
H(21)	2632(3)	1369(2)	5512(6)	923(35)
H(22)	2376(3)	2252(2)	3432(5)	923(35)
H(23)	4666(2)	2772(2)	2833(5)	923(35)
H(24)	5884(3)	2823(3)	1202(6)	923(35)
H(25)	5969(3)	3668(3)	-903(6)	923(35)
H(26)	4830(3)	4452(2)	-1515(6)	923(35)
H(27)	3596(3)	4399(2)	30(5)	923(35)

Bond Lengths
with
Estimated Standard Deviations
in Parentheses

FE(1)	P(1)	2.194(1)
FE(1)	C(1)	1.961(4)
FE(1)	C(6)	1.722(4)
FE(1)	C(7)	2.129(4)
FE(1)	C(8)	2.113(4)
FE(1)	C(9)	2.123(4)
FE(1)	C(10)	2.123(4)
FE(1)	C(11)	2.119(4)
P(1)	C(12)	1.842(4)
P(1)	C(18)	1.835(4)
P(1)	C(24)	1.832(4)
O(1)	C(1)	1.214(4)
O(2)	C(6)	1.157(5)
C(1)	C(2)	1.493(5)
C(2)	C(3)	1.509(7)
C(2)	C(5)	1.487(6)
C(3)	C(4)	1.514(9)
C(3)	C(5)	1.448(7)
C(7)	C(8)	1.405(6)
C(7)	C(11)	1.413(6)
C(8)	C(9)	1.422(6)
C(9)	C(10)	1.393(7)
C(10)	C(11)	1.429(7)
C(12)	C(13)	1.370(6)
C(12)	C(17)	1.390(6)
C(13)	C(14)	1.391(7)
C(14)	C(15)	1.358(8)
C(15)	C(16)	1.361(7)
C(16)	C(17)	1.383(6)
C(18)	C(19)	1.397(6)
C(18)	C(23)	1.380(6)
C(19)	C(20)	1.380(6)
C(20)	C(21)	1.362(7)
C(21)	C(22)	1.387(7)
C(22)	C(23)	1.393(6)
C(24)	C(25)	1.388(5)
C(24)	C(29)	1.401(5)
C(25)	C(26)	1.405(6)
C(26)	C(27)	1.354(7)
C(27)	C(28)	1.378(7)
C(28)	C(29)	1.385(6)

Bond Angles
with
Estimated Standard Deviations
in Parentheses

C(1)	FE(1)	P(1)	89.3(1)
C(6)	FE(1)	P(1)	92.6(1)
C(6)	FE(1)	C(1)	94.4(2)
C(7)	FE(1)	P(1)	136.7(1)
C(7)	FE(1)	C(1)	85.1(2)
C(7)	FE(1)	C(6)	130.5(2)
C(8)	FE(1)	P(1)	160.6(1)
C(8)	FE(1)	C(1)	107.0(2)
C(8)	FE(1)	C(6)	96.4(2)
C(8)	FE(1)	C(7)	38.7(2)
C(9)	FE(1)	P(1)	123.3(1)
C(9)	FE(1)	C(1)	146.0(2)
C(9)	FE(1)	C(6)	93.4(2)
C(9)	FE(1)	C(7)	65.0(2)
C(9)	FE(1)	C(8)	39.2(2)
C(10)	FE(1)	P(1)	95.6(1)
C(10)	FE(1)	C(1)	141.1(2)
C(10)	FE(1)	C(6)	123.8(2)
C(10)	FE(1)	C(7)	65.2(2)
C(10)	FE(1)	C(8)	65.2(2)
C(10)	FE(1)	C(9)	38.3(2)
C(11)	FE(1)	P(1)	101.7(1)
C(11)	FE(1)	C(1)	101.8(2)
C(11)	FE(1)	C(6)	158.4(2)
C(11)	FE(1)	C(7)	38.9(2)
C(11)	FE(1)	C(8)	65.3(2)
C(11)	FE(1)	C(9)	65.2(2)
C(11)	FE(1)	C(10)	39.4(2)
C(12)	P(1)	FE(1)	116.5(1)
C(18)	P(1)	FE(1)	114.9(1)
C(18)	P(1)	C(12)	100.5(2)
C(24)	P(1)	FE(1)	115.9(1)
C(24)	P(1)	C(12)	103.2(2)
C(24)	P(1)	C(18)	103.9(2)
O(1)	C(1)	FE(1)	122.8(3)
C(2)	C(1)	FE(1)	120.1(3)
C(2)	C(1)	O(1)	116.9(3)
C(3)	C(2)	C(1)	117.6(4)
C(5)	C(2)	C(1)	118.0(4)
C(5)	C(2)	C(3)	57.8(3)
C(4)	C(3)	C(2)	118.3(6)
C(5)	C(3)	C(2)	60.3(3)
C(5)	C(3)	C(4)	118.4(6)
C(3)	C(5)	C(2)	61.9(3)
O(2)	C(6)	FE(1)	176.6(3)
C(8)	C(7)	FE(1)	70.1(2)
C(11)	C(7)	FE(1)	70.2(2)
C(11)	C(7)	C(8)	108.3(4)
C(7)	C(8)	FE(1)	71.2(2)
C(9)	C(8)	FE(1)	70.8(2)
C(9)	C(8)	C(7)	107.9(4)
C(8)	C(9)	FE(1)	70.0(2)
C(10)	C(9)	FE(1)	70.8(2)
C(10)	C(9)	C(8)	108.3(4)
C(9)	C(10)	FE(1)	70.9(2)
C(11)	C(10)	FE(1)	70.2(2)
C(11)	C(10)	C(9)	108.1(4)
C(9)	C(11)	FE(1)	70.9(2)
C(10)	C(11)	FE(1)	70.4(2)
C(10)	C(11)	C(7)	107.4(4)
C(13)	C(12)	P(1)	123.8(3)
C(17)	C(12)	P(1)	117.8(3)
C(17)	C(12)	C(13)	118.4(4)
C(14)	C(13)	C(12)	120.1(4)
C(15)	C(14)	C(13)	121.0(5)
C(16)	C(15)	C(14)	119.5(4)
C(17)	C(16)	C(15)	120.4(4)
C(16)	C(17)	C(12)	120.5(4)
C(19)	C(18)	P(1)	121.5(3)
C(23)	C(18)	P(1)	120.3(3)
C(23)	C(18)	C(19)	118.1(4)
C(20)	C(19)	C(18)	121.0(4)
C(21)	C(20)	C(19)	119.7(4)
C(22)	C(21)	C(20)	121.1(4)
C(23)	C(22)	C(21)	118.7(4)
C(22)	C(23)	C(18)	121.3(4)
C(25)	C(24)	P(1)	122.9(3)
C(29)	C(24)	P(1)	118.2(3)
C(29)	C(24)	C(25)	118.9(3)
C(26)	C(25)	C(24)	119.7(4)
C(27)	C(26)	C(25)	120.5(4)
C(28)	C(27)	C(26)	120.7(4)
C(29)	C(28)	C(27)	119.9(4)
C(28)	C(29)	C(24)	120.3(4)

Anisotropic Temperature Factors

Atom	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
FE(1)	369(3)	342(3)	295(3)	-25(2)	7(2)	19(2)
P(1)	364(5)	319(5)	316(5)	17(4)	21(4)	6(4)
O(1)	690(20)	464(16)	653(21)	97(15)	136(16)	39(14)
O(2)	760(21)	705(21)	607(22)	66(16)	274(18)	-23(17)
C(1)	454(21)	382(19)	296(19)	31(15)	-26(16)	14(16)
C(2)	674(28)	379(21)	640(28)	31(19)	104(22)	169(20)
C(3)	962(39)	633(32)	803(39)	-317(28)	-212(31)	239(29)
C(4)	2132(96)	1581(75)	1047(60)	-650(57)	-160(61)	1143(72)
C(5)	754(32)	551(27)	817(38)	-36(25)	-92(28)	185(24)
C(6)	413(20)	413(21)	386(22)	-8(16)	73(17)	-33(16)
C(7)	525(24)	602(25)	354(22)	-71(19)	-39(18)	5(19)
C(8)	477(23)	575(26)	515(26)	-108(20)	-68(19)	-87(20)
C(9)	783(33)	429(23)	523(26)	-128(19)	-55(23)	-104(21)
C(10)	764(33)	531(26)	514(27)	-191(21)	-131(23)	227(23)
C(11)	558(26)	729(28)	348(23)	-107(20)	24(19)	68(21)
C(12)	384(19)	346(18)	363(21)	8(15)	-37(15)	-11(15)
C(13)	706(30)	547(26)	706(31)	-142(23)	247(24)	-171(23)
C(14)	870(38)	604(31)	1076(47)	-290(30)	189(34)	-340(28)
C(15)	966(38)	575(28)	564(31)	-235(23)	-41(27)	-62(27)
C(16)	852(35)	654(29)	362(24)	-175(21)	11(23)	-19(25)
C(17)	638(26)	545(24)	468(26)	-40(20)	137(21)	-100(21)
C(18)	428(19)	400(20)	358(21)	22(16)	22(16)	52(16)
C(19)	500(23)	518(23)	441(24)	26(18)	-39(19)	70(19)
C(20)	701(29)	704(30)	335(23)	49(21)	-18(19)	225(24)
C(21)	877(34)	548(27)	459(27)	167(21)	91(25)	241(25)
C(22)	811(32)	454(23)	584(29)	187(21)	38(25)	20(22)
C(23)	572(24)	441(23)	493(25)	79(18)	-3(20)	16(19)
C(24)	404(20)	389(19)	364(20)	-38(15)	29(15)	-8(15)
C(25)	483(22)	506(23)	398(23)	-75(17)	24(17)	71(18)
C(26)	458(24)	708(29)	585(30)	-182(24)	35(21)	117(21)
C(27)	496(26)	855(34)	577(30)	-219(26)	179(22)	-80(24)
C(28)	611(27)	621(27)	533(28)	-26(21)	203(22)	-93(22)
C(29)	517(23)	480(22)	432(23)	47(18)	118(18)	1(18)