TITLE PREPARATION AND PROPERTIES OF HETERODIENE TRANSITION METAL COMPLEXES

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PREPARATION AND PROPERTIES OF HETERODIENE TRANSITION METAL COMPLEXES

by

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CONTENTS

Abbreviations

Me	Methyl
Et	Ethyl
n-Bu	Normal butyl
t-Bu	Tertiary butyl
Ph	Phenyl
Cp	Cyclopentadienyl
Cp*	1,2,3,4,5-Pentamethylcyclopentadienyl
COD	Cycloocta-1,5-diene
C_7H_8	Toluene
d.e.	Diastereomeric excess
dec	Decomposed
DIBAL	Diisobutylaluminium hydride
equ	Equivalent
Et_2O	Diethyl ether
LDA	Lithium diisopropylamide
THF	Tetrahydrofuran
m	Meta
p	Para
i.r.	Infra red
vs	Very strong
s	Strong
m	Medium
w	Weak

m.s.	Mass spectrometry
e.i.	Electron impact
c.i.	Chemical impact
n.m.r.	Nuclear magnetic resonance
s	Singlet
d	Doublet
t	Triplet
dd	Doublet of doublets
dt	Doublet of triplets
m	Multiplet
J	Coupling constant
n.O.e	Nuclear Overhauser enhancement
ppm	Parts per million
TMS	Tetramethylsilane

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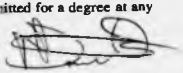
DECLARATION

All of the work described in this thesis unless otherwise stated was performed by the author in the department of chemistry at the University of Warwick between October 1986 and September 1989 and has not been previously submitted for a degree at any institution.



T.N. Danks

September 1989

PUBLICATIONS

Work related to this thesis has appeared in the literature as follows:-

1. Nucleophilic addition to tricarbonyliron complexes of α,ß-unsaturated ketones and the production of 1,4-diketones. T.N. Danks, D. Rakshit and S.E. Thomas, *J. Chem. Soc., Perkin Trans 1.*, 1988, 2091.

2. Pyrrole formation from a (1-azabutadiene)tricarbonyliron(0) complex. T.N. Danks and S.E. Thomas, *Tetrahedron Lett.*, 1988, 1425.

3. Fast atom bombardment mass spectra of $Fe(CO)_3R^1CH{=}CR^2COR^3$ compounds. R.D. Bowen, T.N. Danks, D. Mitchell, and S.E. Thomas, *Org. Mass Spectrom.*, 1988, **23**, 674.

4. Reactions of heterodiene metal carbonyl complexes. T.N. Danks, D. Rakshit and S.E. Thomas, *Phil. Trans. R. Soc. London A.*, 1988, **326**, 611.

5. Conversion of α,β-unsaturated carbonyl complexes into α,β-unsaturated ketene complexes. N.W. Alcock, T.N. Danks, C.J. Richards, and S.E. Thomas, *J. Chem. Soc., Chem. Commun.*, 1989, 21.

6. Nucleophilic addition to tricarbonyliron(0) complexes of 1-aza-1,3-dienes and the production of pyrroles. T.N. Danks and S.E. Thomas, *J. Chem. Soc., Perkin Trans 1.*, in press.

ABSTRACT

Part A of this thesis describes the reaction of nucleophiles with (1-heterodiene)tricarbonyliron(0) complexes.

Reaction of methyl-lithium with [($R^1CH{=}CHCR^2{=}NR^3$)$Fe(CO)_3$(0) (R^1=CH_3, R^2=H, R^3=$CH(CH_3)Ph$) ,(R^1=Ph, R^2=H, R^3=$CH(CH_3)Ph$), (R^1=Ph, R^2=CH_3, R^3=Ph), and (R^1=Ph, R^2=H, R^3=CH_2Ph)] leads to formation of 1, 2, 3- or 1, 2, 3, 5- substituted pyrroles.

Reaction of stabilised anions derived from $(CH_3)_2CHCN$ and $(CH_3)_2CHCO_2Et$ with [(PhCH=CHCOR), (R=CH_3 or $CH_2CH(CH_3)_2$)] and [PhCH=CHCH=NPh] has been shown not to be modified by coordination of the 1-heterodienes to the tricarbonyliron(0) moiety.

Coordination of [PhCH=CHCH=NR, (R=$CH(CH_3)$Ph or Ph)] to the tricarbonyliron(0) moiety protects the azadiene against reduction by $NaBH_4$. Reaction of [(PhCH=CHCOR)$Fe(CO)_3$, (R=CH_3 or H)] and [(PhCH=CHCH=NR)$Fe(CO)_3$ (R=$CH(CH_3)$Ph, Ph, or p-$C_4H_6OCH_3$] with $LiAlH_4$ yields a saturated alcohol or amine compared to the reaction of the free azadiene or oxadiene with $LiAlH_4$ which yields allylic amines or alcohols. Deuteration experiments indicate three hydrides (deuterides) are transferred to the coordinated azadiene.

Part B of this thesis describes approaches to cationic η^4-heterodiene complexes of CH_2=$CHCOCH_3$ and PhCH=CHCH=N-Ph *via* the η^2-complexes [$Cp^*Fe(CO)_2$ (η^2-$R^1CH{=}CHCR^2{=}X$)$^+BF_4^-$], [(R^1=Ph, R^2=H, X=NPh) or (R^1=H, R^2=CH_3, X=O)]. The literature synthesis of [$Cp^*Fe(CO)(\eta^4$-$CH_2{=}CHC(CH_3)CH_2)^+BF_4^-$] has been optimised.

INTRODUCTION.

A1 CHAPTER 1.

The chemistry described in chapters 2, 3 and 4 of this thesis is concerned with the reactivity of (1-azadiene)tricarbonyliron(0) complexes. As an introduction to this work the relatively extensive chemistry of (diene)tricarbonyliron(0) complexes is described and previous studies of (1-azadiene)tricarbonyliron(0) complexes are detailed.

A1.1 Chemistry of (1,3-Diene)tricarbonyliron(0) Complexes.

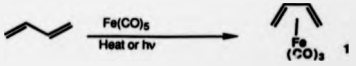
A1.1.1 Synthesis and Structure.

(1,3-Diene)tricarbonyliron(0) complexes have been known since 1930 when (buta-1,3-diene)tricarbonyliron(0) **1** was first synthesised.[1]

1

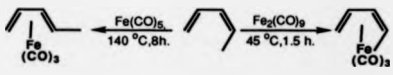
The crystal structure of **1**[2] has shown that the buta-1,3-diene ligand is planar and that the tricarbonyliron(0) moiety is coordinated to the cisoid form of buta-1,3-diene and is roughly equidistant from the four carbon atoms.

(1,3-Diene)tricarbonyliron(0) complexes are readily prepared by reaction of a 1,3-diene with ironpentacarbonyl, diironnonacarbonyl, or triirondodecacarbonyl in an inert solvent under thermal or photochemical conditions.[3] For example, reaction of buta-1,3-diene with iron pentacarbonyl under photochemical or thermal conditions leads to complex **1**.[1]



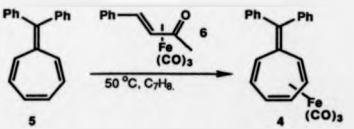
1

The high temperatures required for complexation when using iron pentacarbonyl often leads to diene isomerisation. This may be circumvented however, by use of diironnonacarbonyl which requires milder conditions. For example, in the synthesis of (*cis*-piperylene)tricarbonyliron(0) **2**,[4] the use of *cis*-piperylene and iron pentacarbonyl led to the formation of (*trans*-piperylene)tricarbonyliron(0) **3** whilst the use of diironnonacarbonyl and *cis*-piperylene under mild conditions led to the required *cis* product **2**.



3 **2**

It is also possible to prepare (1,3-diene)tricarbonyliron(0) complexes by transfer of the tricarbonyliron(0) moiety from a less stable complex.[5,6] This technique is particularly useful if the 1,3-diene used for the complexation is heat or light sensitive. For example, in the synthesis of (8,8-diphenylheptafulvene)tricarbonyliron(0) **4**, attempts to synthesise **4** from the free ligand and either ironpentacarbonyl or triirondodecacarbonyl under thermal or photochemical conditions led to decomposition of the 8,8-diphenylheptafulvene **5** and use of diironnonacarbonyl as a source of the tricarbonyliron(0) moiety under mild conditions led to formation of an uncharacterised and unstable diironhexacarbonyliron(0) complex of 8,8-diphenylheptafulvene.[5] (8,8-Diphenylheptafulvene)tricarbonyliron(0) **4** may be prepared, however, by reaction of **5** with (2-methyl-4-phenyl-1-oxabuta-1,3-diene)tricarbonyliron(0) **6** in toluene at 50 °C.[5]



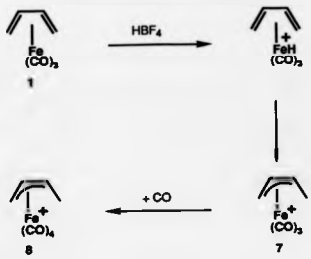
(2-Methyl-4-phenyl-1-oxabuta-1,3-diene)tricarbonyliron(0) **6** is slightly more unstable than many (1,3-diene)tricarbonyliron(0) complexes and readily releases its tricarbonyliron(0) moiety to form (8,8-diphenylheptafulvene)tricarbonyliron(0) **4**.

A1.1.2 Application of (1,3-Diene)tricarbonyliron(0) Complexes to Organic Synthesis.

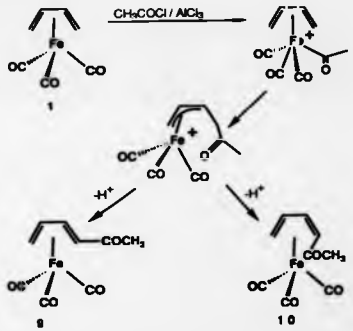
The use of (1,3-diene)tricarbonyliron(0) complexes in organic synthesis has received much attention.[7] Coordination of a 1,3-diene to the tricarbonyliron(0) moiety significantly alters the reactivity of the diene. The complexes, unlike the precursor 1,3-dienes, are inert to hydrogenation and bromination[8] and do not undergo Diels-Alder cycloadditions[8] or reactions with carbenes.[9] The complexes are known, however, to react with electrophiles[10] and nucleophiles[11] and to act as a protecting group for 1,3-dienes.[6,9,12]

A1.1.2.1 *Electrophilic Attack on (1,3-Diene)tricarbonyliron(0) Complexes.*

The simplest example of electrophilic attack on a (1,3-diene)tricarbonyliron(0) complex is protonation.[10] Protonation of **1** yields the η^3-allyl complex **7** which is coordinately unsaturated and disproportionates to yield the cationic tetracarbonyl complex **8**, inorganic iron, and unidentified organic products.

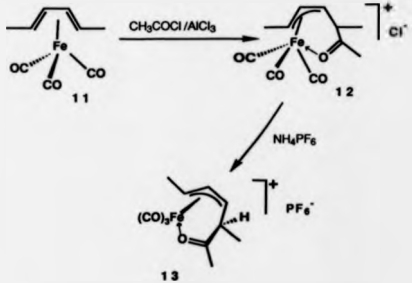


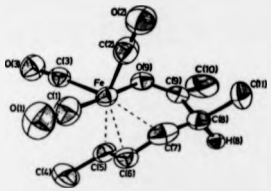
In the presence of acetyl chloride and aluminium trichloride, (buta-1,3-diene)tricarbonyliron(0) **1** undergoes a Friedel-Crafts type acylation[13] in a reaction which is controlled by the iron centre.



The relative proportion of isomers **9** and **10** in the product mixture depends on the work-up used.

Acylation of (hexa-2,4-diene)tricarbonyliron(0) **11** yields the intermediate η^3-allyl cation which was isolated by addition of ammonium hexafluorophosphate to yield **13**. The crystal structure of **13**[14] indicates that attack on the (1,3-diene)tricarbonyliron(0) complex **11** by the acyl cation occurs stereospecifically at the face *endo* to the tricarbonyliron(0) moiety.[14]



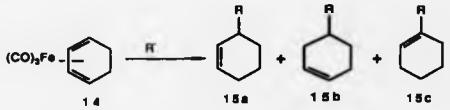


Similar results have also been obtained for (buta-1,3-diene)tricarbonyliron(0) **1**.[15]

A1.1.2.2 *Nucleophilic Attack on (1,3-Diene)tricarbonyliron(0) Complexes.*

The reaction of nucleophiles with (1,3-diene)tricarbonyliron(0) complexes has only been studied relatively recently.[11] It has been shown that the addition of stabilised

anions to (cyclohexa-1,3-diene)tricarbonyliron(0) **14** leads to the formation of the isomeric alkenes **15abc** after the addition of a proton source.

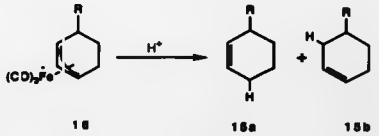


Typical results for the reaction are illustrated in Table 1.

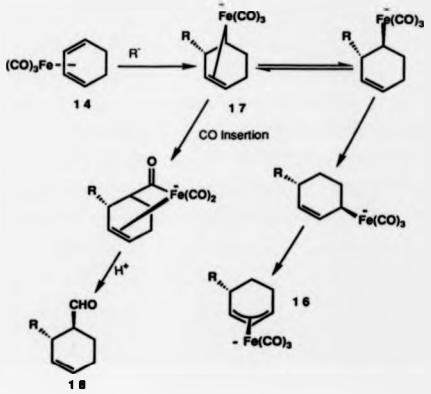
Table 1.

NUCLEOPHILE	ISOMER DISTRIBUTION %			YIELD %
	15a	15b	15c	
$LiC(CH_3)_2CN$	87	9	4	98
$LiCPh_3$	72	28	0	72
$LiC(CH_3)_2CO_2Et$	54	45	1	100

The formation of alkenes **15a** and **15b** may be explained by attack of the carbon nucleophile at the terminal position of the 1,3-diene leading to an anionic η^3-allyl iron complex **16**. Protonation of **16** at one end of the allylic system or the other leads to formation of alkenes **15a** or **15b**.



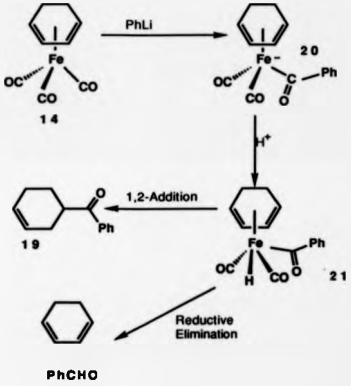
Formation of **15a** and **15b** may also be explained in terms of initial attack of the nucleophile at C_2 of the 1,3-diene leading to an anionic complex **17** which undergoes a series of hydrogen shifts giving the anionic η^3-allyliron complex **16.** Protonation of **16** leads to **15a** and **15b**.



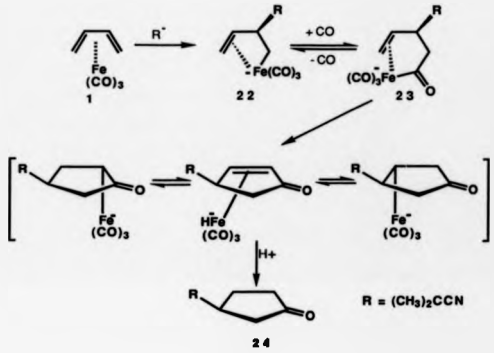
A small proportion of a γ,δ-unsaturated aldehyde **18** is also formed as a by-product. Formation of **18** may be explained in terms of carbonyl insertion into the iron-alkyl bond of **17** followed by protonation leading to **18** in low yield. Observation of the γ,δ-unsaturated aldehyde **18** in the product mixture provides evidence for the reaction proceeding by attack of the nucleophile at C_2. Attack by the nucleophile at C_1 leads directly to the η^3-allyl-anion **16** and does not involve formation of iron-alkyl bonds. Consequently, carbon monoxide insertion is not possible and as a result formation of a γ,δ-unsaturated aldehyde would not be observed. Formation of alkene **15c** is probably

a result of an acid-promoted isomerisation of **15a** or **15b** under the reaction or work-up conditions.

Grignard and organolithium reagents also react with (1,3-diene)tricarbonyliron(0) complexes.[11] For example, reaction of phenyl-lithium with (cyclohexa-1,3-diene)tricarbonyliron(0) **14** led to the formation of a γ,δ-unsaturated ketone **19** (26%), benzaldehyde (5%), and cyclohexa-1,3-diene (69 %). It is proposed that initial attack on **14** by phenyl-lithium occurs at a coordinated carbonyl leading to an anionic iron-acyl complex **20** which on protonation leads to an acyl hydride complex **21**. 1,2-Addition of the acyl group and the hydride to the diene leads to the γ,δ-unsaturated ketone **19** whilst a competing reaction, which involves reductive elimination of the acyl group and the hydride, leads to formation of benzaldehyde and the free diene.[11]



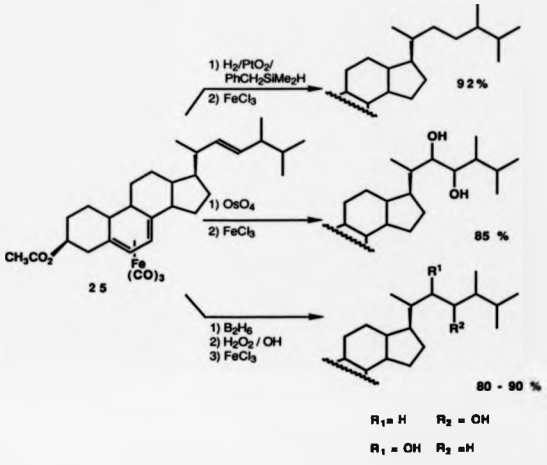
Addition of stabilised anions to (buta-1,3-diene)tricarbonyliron(0) **1** under an atmosphere of carbon monoxide leads to formation of cyclopentanones after addition of a proton source.[16] For example, attack of the stabilised anion derived from isobutyronitrile occurs at C_2 of the coordinated buta-1,3-diene leading to the anionic complex **22**. Insertion of carbon monoxide into the iron-alkyl bond of **22** leads to anion **23** which cyclises and on protonation gives a cyclopentanone **24** (85%).



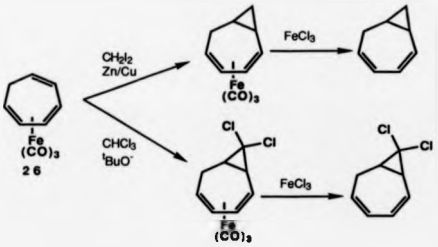
A1.1.2.3 *Tricarbonyliron(0) as a Protecting Group for 1,3-Dienes in Organic Synthesis.*

Coordination of conjugated dienes to the tricarbonyliron(0) moiety results in deactivation of the diene towards many common reagents. Since most (1,3-diene)tricarbonyliron(0) complexes are prepared under mild conditions, are relatively stable and are effectively decomposed by mild oxidising agents, the tricarbonyliron(0) moiety is suitable as a protecting group for 1,3-dienes in organic synthesis.

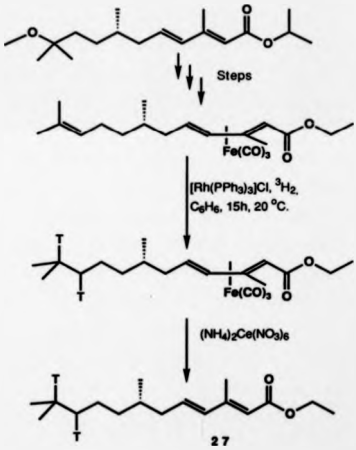
For example complexation has been used to protect the "B" ring diene of ergosteryl acetate as (ergosterylacetate)tricarbonyliron(0) **25** allowing selective chemical manipulation of the side chain.[6]



Carbenes are known to react with conjugated dienes in preference to isolated alkenes.[9] By coordination of a 1,3-diene to the tricarbonyliron(0) moiety, however, it is possible to reverse this preference. For example, treatment of (cyclohepta-1,3,5-triene)tricarbonyliron(0) **26** with carbene and dichlorocarbene results in reaction at the uncomplexed double bond.[9]



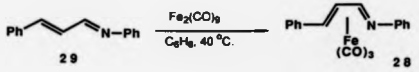
The tricarbonyliron(0) moiety has been used recently for the protection of a 1,3-diene allowing the selective homogeneous tritiation of an isolated alkene during the synthesis of the insect juvenile hormone 27.[12]



A1.2 Chemistry of (1-Azabuta-1,3-diene)tricarbonyliron(0) Complexes.

A1.2.1 Synthesis and Structure.

(1-Azabuta-1,3-diene)tricarbonyliron(0) complexes were first prepared twenty years ago by reaction of a 1-azabuta-1,3-diene with diironnonacarbonyl or triirondodecacarbonyl in an inert solvent.[17] For example (1,4-diphenyl-1-azabuta-1,3-diene)tricarbonyliron(0) **28** is formed on reaction of diironnonacarbonyl with 1,4-diphenyl-1-azabuta-1,3-diene **29** in benzene at 40 °C.

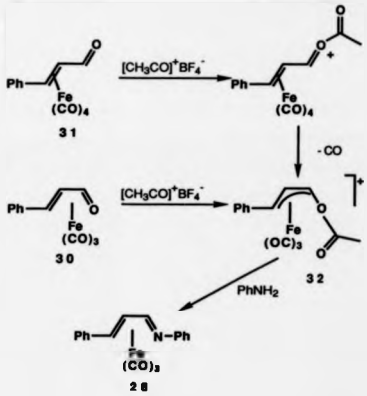


29 **28**

The crystal structure of **28**[18,19] shows that the azadiene adopts a planar cisoid geometry similar to its homodiene analogue. The nitrogen lone pair is not thought to play a significant role in the bonding of the azadiene to the tricarbonyliron(0) moiety.

(1-Azabuta-1,3-diene)tricarbonyliron(0) complexes may also be prepared from (1-oxadiene)tricarbonyliron(0) complexes. For example, (1,4-diphenyl-1-azabuta-1,3-diene)tricarbonyliron(0) **28** is formed on treatment of (4-phenyl-1-oxabuta-1,3-diene)tricarbonyliron(0) **30** or (4-phenyl-1-oxabuta-1,3-diene)tetracarbonyliron(0) **31** with $[CH_3CO]^+ BF_4^-$ followed by aniline.[20]

Attack on complexes **30** or **31** by the $[CH_3CO]^+$ cation occurs at oxygen and leads to a common η^3-allyl intermediate **32**. Nucleophilic attack of **32** by aniline leads to formation of (1,4-diphenyl-1-azabuta-1,3-diene)tricarbonyliron(0) **28**.[20]

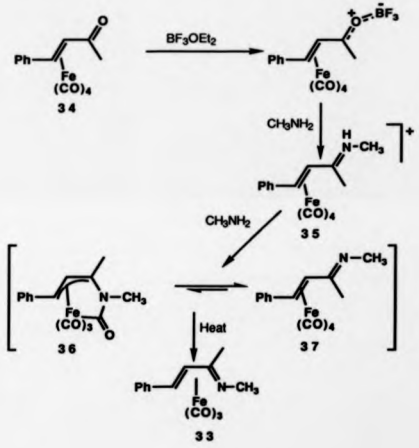


(1-Azabuta-1,3-diene)tricarbonyliron(0) complexes may also be formed by reaction of a primary amine with a (1-oxadiene)tetracarbonyliron(0) complex at 0 °C followed by heating.[17] For example, (1,4-diphenyl-1-azabuta-1,3-diene)tricarbonyliron(0) **28** is produced when aniline is added to (4-phenyl-1-oxabuta-1,3-diene)tetracarbonyliron(0) **31**.

(1-Azabuta-1,3-diene)tricarbonyliron(0) complexes may also be prepared by treatment of (1-oxabuta-1,3-diene)tetracarbonyliron(0) complexes with boron trifluoride etherate followed by two equivalents of a primary aliphatic amine.[21] Thus, (1,2-dimethyl-4-

phenyl-1-azabuta-1,3-diene)tricarbonyliron(0) **33** has been synthesised by reaction of (2-methyl-4-phenyl-1-oxabuta-1,3-diene)tetracarbonyliron(0) **34** with boron trifluoride etherate followed by the addition of two equivalents of methylamine.

The mechanism for the reaction is thought to involve activation of the carbonyl group by boron trifluoride followed by nucleophilic attack by one equivalent of methylamine leading to a cationic tetracarbonyliron(0) complex **35**. Treatment of **35** with a second equivalent of methylamine results in deprotonation and formation of a (η^3-allyl-*N*-carbamoyl)tricarbonyliron(0) complex **36** which exists in equilibrium with the (1-azabuta-1,3-diene)tetracarbonyliron(0) complex **37**. Heating the equilibrium mixture of **36** and **37** at 30 °C leads to loss of carbon monoxide and formation of (1,2-dimethyl-4-phenyl-1-azabuta-1,3-diene)tricarbonyliron(0) **33**.[22]

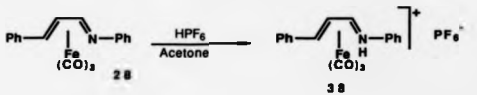


A1.2.2 Reactivity of (1-Azabuta-1,3-diene)tricarbonyliron(0) Complexes.

The reactivity of (1-azabuta-1,3-diene)tricarbonyliron(0) complexes has received very little attention and the results of the few studies undertaken on these complexes are described below.

A1.2.2.1 *Reactivity of (1-Azabuta-1,3-diene)tricarbonyliron(0) Complexes with Electrophiles.*

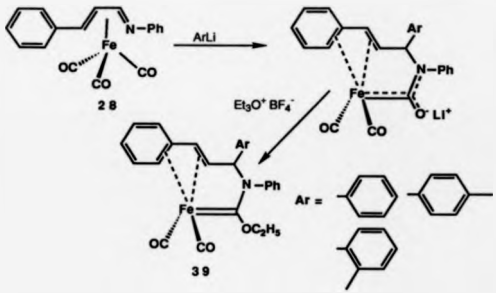
The only example of electrophilic attack on (1-azabuta-1,3-diene)tricarbonyliron(0) complexes is a protonation.[23] Treatment of (1,4-diphenyl-1-azabuta-1,3-diene)tricarbonyliron(0) **28** with hexafluorophosphoric acid leads to protonation at nitrogen and formation of the cationic complex **38**.[23]



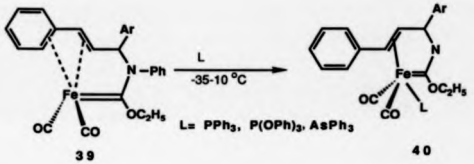
28 **38**

A1.2.2.2 *Reactivity of (1-Azabuta-1,3-diene)tricarbonyliron(0) Complexes with Nucleophiles.*

During the course of the work described in this thesis it was reported that treatment of (1,4-diphenyl-1-azabuta-1,3-diene)tricarbonyliron(0) **28** with aryl-lithium reagents followed by a triethyloxonium tetrafluoroborate quench leads to the formation of η^4-styrylcarbene complexes **39**.[24]

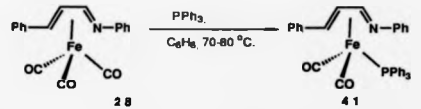


Treatment of **39** with triphenylphosphine, triphenylphosphite, or triphenylarsine leads to formation of η^2-carbene complexes **40**.



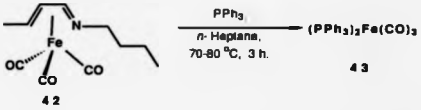
A1.2.2.3 ***Ligand Exchange Reactions.***

(1-Azabuta-1,3-diene)tricarbonyliron(0) complexes readily undergo ligand replacement reactions of the metal carbonyl or azadiene. Treatment of a solution of (1,4-diphenyl-1-azabuta-1,3-diene)tricarbonyliron(0) **28** with triphenylphosphine under thermal or photochemical conditions leads to formation of (1,4-diphenyl-1-azabuta-1,3-diene)triphenylphosphinedicarbonyliron(0) **41**.[17]



28 41

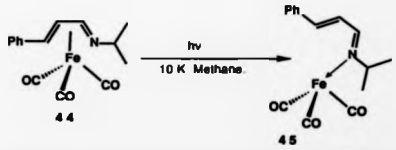
Treatment of (1-*n*-butyl-4-methyl-1-azabuta-1,3-diene)tricarbonyliron(0) **42** with triphenylphosphine however, results in displacement of the azadiene and formation of bis(triphenylphosphine)tricarbonyliron(0) **43**.[17]



42 43

Replacement of the azadiene of **42** by two triphenyphosphines presumably reflects the increased lability of the azadiene-metal bond in **42** relative to the azadiene-metal bond in **28**.[17]

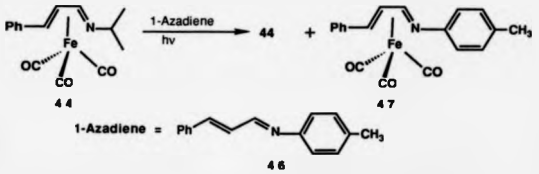
Irradiation of (1-isopropyl-4-phenyl-1-azabuta-1,3-diene)tricarbonyliron(0) **44** in a methane matrix at 10 K results in cleavage of the iron-olefin bond and formation of a sixteen-electron complex **45**.[25]



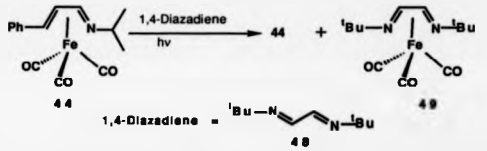
44 45

Complex **45** may only be observed at temperatures less than 10 K. Irradiation of **44** at room temperature results in no observed reaction. Formation and observation of **45** at 10 K is attributed to the inability of complex **45** to attain the activation energy for

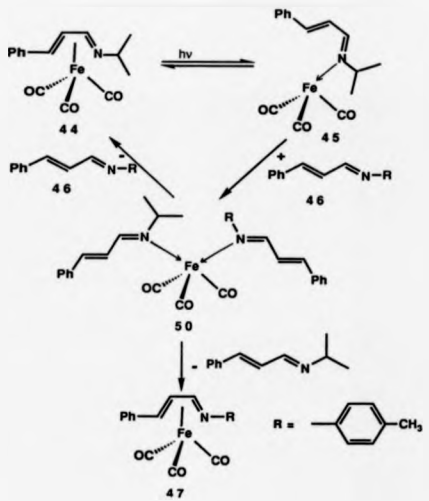
conversion to the original eighteen-electron complex **44**. Irradiation of a solution of (1-azabuta-1,3-diene)tricarbonyliron(0) complexes in the presence of other 1-azabuta-1,3-dienes or 1,4-diazabuta-1,3-dienes leads to substitution reactions. For example, irradiation of a solution of (1-isopropyl-4-phenyl-1-azabuta-1,3-diene)tricarbonyliron(0) **44** in the presence of 4-phenyl-1-(4-tolylphenyl)-1-azabuta-1,3-diene **46** results in formation of a mixture of the two complexes.



Similar results are obtained when complex **44** is irradiated in the presence of 1,4-di-*t*-butyl-1,4-diazabuta-1,3-diene **48**.



The azadiene substitution reaction is thought to proceed *via* an unstable sixteen-electron complex **45**. Formation of **45** occurs due to irradiation of **44**, and attack of **45** by the incoming azadiene results in formation of the eighteen-electron complex **50**. Complex **50** is unstable and decomposes by loss of an azadiene to generate the original complex **44** or the new complex **47**.



The relative proportion of **44** and **47** in the product mixture appears to depend on the basicity of the attacking ligand. Highly basic ligands appear to form more stable complexes and hence a greater proportion of these complexes appear in the product mixture.

Irradiation of a solution of (1-azabuta-1,3-diene)tricarbonyliron(0) complexes in the presence of tertiary phosphines leads to azadiene or metal carbonyl substitution and formation of three possible products. For example, irradiation of (1-*t*-butyl-4-phenyl-1-azabuta-1,3-diene)tricarbonyliron(0) **52** in the presence of triphenylphosphine leads to complexes **52, 43** and **53**.[25]

52

$Fe(CO)_3(PPh_3)_2$ 43

$Fe(CO)_4PPh_3$ 53

The relative amount of each complex formed depends on the ratio of complex to phosphine in the reaction mixture. A 1:1 mixture of complex and phosphine yields mainly **52**, whilst a 1:25 mixture yields mainly **43**.

A1.3 Aims.

The purpose of this work is to investigate the outcome of nucleophilic attack on (1-azabuta-1,3-diene)tricarbonyliron(0) complexes. It is intended that a range of known and new complexes should be synthesised and that their reactivity with several classes of nucleophiles be studied.

RESULTS AND DISCUSSION.

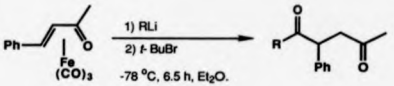
CHAPTER 2.

A2.1 Addition of Methyl-Lithium to (1-Azabuta-1,3-diene)-tricarbonyliron(0) Complexes and the Synthesis of Pyrroles.

Throughout this work diironnonacarbonyl was used as a source of the tricarbonyliron (0) moiety for synthesis of (1-heterobuta-1,3-diene)tricarbonyliron(0) complexes. Diironnonacarbonyl was synthesised by ultra-violet irradiation of a solution of ironpentacarbonyl in glacial acetic acid for 24 h under an atmosphere of nitrogen.[26] The orange plate-like crystals produced were washed with ethanol and diethyl ether and dried under reduced pressure. The product was identified as diironnonacarbonyl by comparison of its i.r. spectrum and melting point with literature values. The i.r. spectrum of diironnonacarbonyl contains peaks at 2 063 and 2 021 cm^{-1} which were assigned to the terminal carbonyl ligands and a peak at 1 828 cm^{-1} which was assigned to the bridging carbonyls.[27]

$$Fe(CO)_5 \xrightarrow[CH_3COOH]{h\nu} Fe_2(CO)_9 + CO \quad (50\ \%)$$

Recent interest in the reactivity of transition metal complexes containing 1-heterobuta-1,3-diene ligands led to an investigation of nucleophilic attack on tricarbonyliron(0) complexes of α,β-unsaturated ketones. Addition of a range of hard nucleophiles to (2-methyl-4-phenyl-1-oxabuta-1,3-diene)tricarbonyliron(0) **6** and related complexes led to the production of 1,4-diketones in good yield.[28, 29] For example, addition of methyl-lithium, ethyl magnesium bromide, or *n*-butyl-lithium to **6** led to the 1,4-diketones **54**, **55**, and **56** respectively.



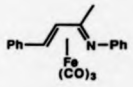
6

54 R = CH_3

55 R = C_2H_5

56 R = n-C_4H_9

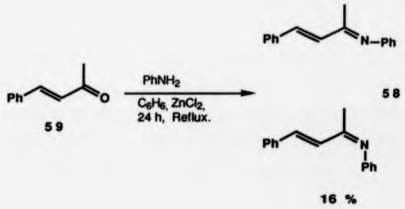
In order to investigate the effect on reactivity of replacing the oxygen atom in the ligand with a substituted nitrogen atom the complex (2-methyl-1,4-diphenyl-1-azabuta-1,3-diene)tricarbonyliron(0) **57** was synthesised.



57

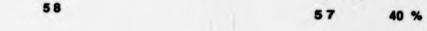
Complex **57** may be regarded as a nitrogen-containing analogue of complex **6**. The results of nucleophilic attack on complex **57** and other (1-azabuta-1,3-diene)tricarbonyliron(0) complexes are described in detail in this chapter.

2-Methyl-1,4-diphenyl-1-azabuta-1,3-diene **58** was synthesised using a literature procedure.[30] 1-oxadiene **59** and aniline were dissolved in dry benzene and heated at reflux in the presence of a catalytic quantity of zinc chloride until a stoichiometric quantity of water had been collected in a Dean and Stark trap. The solvent was removed under reduced pressure to yield a brown oil which was crystallised and recrystallised from ethanol to yield yellow crystals identified as a mixture of *E,E*- and *E,Z*- **58** on the basis of their ^1H n.m.r., i.r., and mass spectra and combustion analysis.

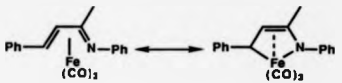


The ^1H n.m.r. spectrum of **58a** and **58b** contained two singlets at 2.06 and 2.45 ppm (ratio 3:1) which were assigned to the methyl group at C_2. The signals due to the protons at C_3 and C_4 could not be assigned since these peaks were obscured by the signals due to the phenyl protons. The i.r. spectrum contained diagnostic peaks at 1 633 and 1 603 cm^{-1} assigned to C=N- and C=C respectively. The mass spectrum of **58a** and **58b** gave a strong (62%) molecular ion at 221 and peaks at 220 (100%) and 206 (36%) resulting from loss of a proton and methyl group respectively.

Separation of **58a** and **58b** proved to be unnecessary since complexation to the tricarbonyliron(0) moiety occurred selectively. A mixture of azadienes **58a** and **58b** and diironnonacarbonyl was stirred in toluene at 40 °C for 2 h under an atmosphere of nitrogen to yield a red mixture. This mixture was filtered to remove the iron residues and the solvent was removed under reduced pressure to yield a dark red oil. This oil was crystallised and recrystallised from *n*-heptane to yield orange crystals identified as the new complex (2-methyl-1,4-diphenyl-1-azabuta-1,3-diene)tricarbonyliron(0) **57** on the basis of their ^1H n.m.r., ^{13}C n.m.r., i.r., and mass spectra and combustion analysis.



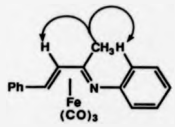
The ^{1}H n.m.r. spectrum of **57** contained a three-proton singlet at 2.42 ppm assigned to the methyl group at C_2 and two one-proton doublets at 3.20 (J = 10 Hz) and 5.60 ppm (J = 10 Hz) which were assigned to the protons at C_4 and C_3 respectively. The chemical shift of the proton at C_4 may be explained by assuming that structure **57b** makes a significant contribution to the overall bonding in the complex.



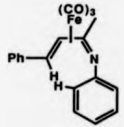
57a **57b**

Thus carbon C_4 of structure **57b** possesses significant sp^3 character and hence the proton attached to it should be observed at high field relative to the proton at C_3. The ^{13}C n.m.r. spectrum contained peaks at 16.5, 59.7, 71.3, and 124.1 ppm assigned to the methyl carbon, C_4, C_3, and C_2 respectively by comparison with ^{13}C n.m.r. spectra of related compounds synthesised later. The i.r. spectrum of **57** recorded as a solution in hexane contained peaks at 2 060, 1 995, and 1 983 cm^{-1} due to metal-carbonyl absorption. The mass spectrum was recorded using positive ion f.a.b. with *m*-nitrobenzylalcohol as the matrix (see Appendix 1).[31] The spectrum contained a protonated molecular ion peak at 362 (14%) and peaks at 333 (48%), 305 (50%), and 277 (100%) associated with the successive loss of carbonyl ligands.

The stereochemistry about the C=N bond of **57** was assigned as *E* on the basis of n.O.e. difference experiments. Irradiation of the signal due to the methyl group led to an enhancement of the signals due to the *ortho*-protons of the *N*-phenyl (9%) and the proton at C_3 (7%).



There was no evidence for the Z_{CN} isomer which is presumably unstable relative to the E_{CN} isomer owing to a strong steric interaction between the *ortho*-protons of the *N*-phenyl and the proton at C_4.

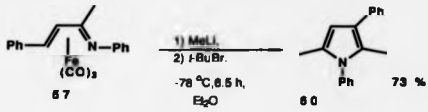


The ^{1}H n.m.r. spectrum of the supernatant liquid from the recrystallisation of **57** indicated the presence of complex **57** and a 3:1 mixture of azadienes **58** suggesting that isomerisation of **58** accompanies the selective complexation reaction.

Attempts to isolate pure E_{CN} isomer **58a** by decomplexation of **57** using alkaline hydrogen peroxide,[32] air oxidation, or ferric chloride,[6, 33] led in each case to the generation of a 3:1 mixture of azadienes **58**. Decomplexation using ceric ammonium nitrate[33] led to isolation of the hydrolysis product 2-methyl-4-phenyl-1-oxabuta-1,3-diene **59**.

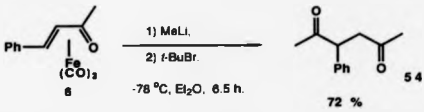
The reaction between complex **57** and methyl-lithium was studied. Methyl-lithium was added to a solution of **57** in diethyl ether and stirred at -78 °C for 6.5 h under an atmosphere of nitrogen to yield a dark mixture. The reaction was quenched using 2-bromo-2-methylpropane as a proton source and allowed to warm up to room temperature for 0.5 h. The black mixture produced was filtered through a plug of alumina to remove the iron residues and the solvent was removed under reduced

pressure to give an orange/brown oil. Chromatography of this oil on silica led to the isolation of a yellow oil. Examination of the ^1H n.m.r. and mass spectra of the oil led to speculation that the new pyrrole 2,5-dimethyl-1,3-diphenylpyrrole **60** had been generated.[34]

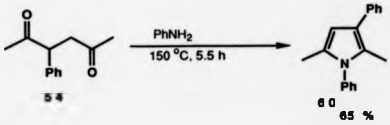


The ^1H n.m.r. spectrum of the yellow oil contained a pair of three-proton singlets at 2.08 and 2.16 ppm which were consistent with a 2,5-dimethylpyrrole. The one-proton singlet at 6.16 ppm was consistent with an isolated proton at C_4 of a pyrrole. The mass spectrum of **57** contained a molecular ion at 247 (100%).

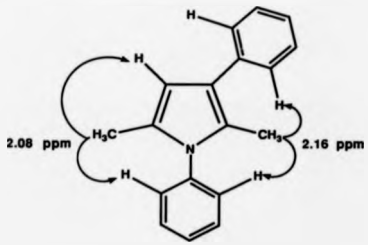
Confirmation of the formation of **60** from reaction of methyl-lithium with **57** was obtained by an independent synthesis of **60**. Authentic **60** was synthesised by a Paal-Knorr condensation.[35,35a] The 1,4-diketone required for the reaction was synthesised using a reaction developed in our laboratories.[28, 29] A solution of complex **6** in diethyl ether at -78 °C was treated with methyl-lithium and stirred at -78 °C for 6.5 h to yield a dark mixture. The reaction was quenched using 2-bromo-2-methylpropane as a proton source and allowed to warm up to room temperature for 0.5 h to yield a dark brown mixture. This mixture was filtered through a plug of alumina to remove the iron residues and the solvent removed under reduced pressure to yield a brown gum. Chromatography of this gum on silica led to isolation of a yellow oil identified as 3-phenylhexan-2,5-dione **54** by comparison of its ^1H n.m.r., i.r., and mass spectra with data quoted in the literature.[36]



An equimolar amount of aniline was mixed with **54** and the mixture was heated at 150 °C for 5.5 h to yield a dark brown oil. This oil was chromatographed on silica to yield a yellow oil identified as the novel 2,5-dimethyl-1,3-diphenyl pyrrole **60** on the basis of its ^{1}H n.m.r., ^{13}C n.m.r., and high resolution mass spectra.

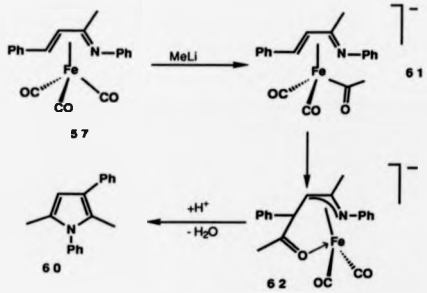


The two three-proton singlets at 2.08 and 2.16 ppm in the ^{1}H n.m.r. spectrum of **60** were assigned to the methyl groups at C_5 and C_2 respectively on the basis of n.O.e. difference spectroscopy. Irradiation of the methyl group at 2.08 ppm led to an enhancement of the signal due to the proton at C_4(6%) and the signal due to the *ortho*-protons of the *N*-phenyl (3%). Irradiation of the methyl group at 2.16 ppm led to an enhancement of signal due to the *ortho*-protons of the phenyl group at C_3 (5%) and the signal due to the *ortho*-protons of the *N*-phenyl (6%).



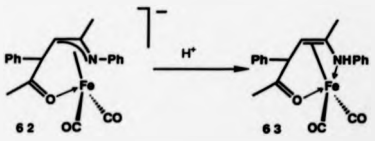
The ^{13}C n.m.r. spectrum of **60** contained peaks at 12.1 and 12.7 ppm which were assigned to the two methyl groups. Peaks at 106.5, 121.0, 125.0, and 128.5 ppm were assigned to carbons C_2, C_3, C_4, and C_5 respectively, by comparison with the ^{13}C n.m.r. spectra of related pyrroles discussed later in this thesis.

The mechanism for pyrrole formation from the reaction of methyl-lithium with (2-methyl-1,4-diphenyl-1-azabuta-1,3-diene)tricarbonyliron(0) **57** may be described in terms of attack by methyl-lithium at a metal carbonyl leading to the anionic iron-acyl complex **61**. Transfer of the acyl group to C_4 of the coordinated azadiene leads to formation of an anionic η^3-allyl complex **62**. It is envisaged that condensation of the azaallyl group of **62** and the ketone leads to formation of pyrrole **60** after protonation and loss of water.

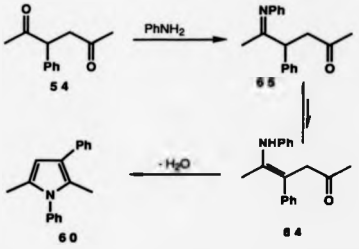


The low temperature required for conversion of complex **57** to pyrrole **60** contrasts strongly with that required for conversion of the 1,4-diketone **54** to the pyrrole **60** using classical Paal-Knorr conditions.[35, 35a, 37] Attempts to convert the 1,4-diketone **54** to **60** at temperatures less than 150 °C gave no evidence for pyrrole formation after 6.5 h. This suggests that the iron moiety is intimately involved in the ring closure step of pyrrole formation.

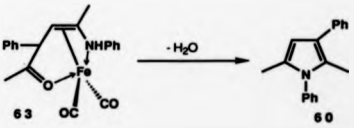
It is postulated that the iron moiety holds the nitrogen of the azaallyl group in proximity with C_5 in intermediate **62** thus, promoting ring closure upon addition of a proton source. Thus protonation at nitrogen may lead to an enamine complex **63** as an intermediate prior to the ring closure step.



This type of enamine has previously been hypothesised as a key intermediate in pyrrole formation.[37] Classical formation of pyrroles requires condensation of a primary amine with a 1,4-diketone leading to imine **65**. Tautomerism of **65** leads to the enamine **64** which cyclises forming a pyrrole after dehydration. Formation of **64** from **65** is not favoured and may be responsible for slow pyrrole formation under classical conditions.

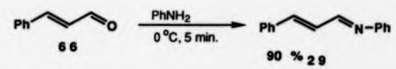


Pyrrole formation from complex **57** and methyl-lithium may proceed *via* the enamine complex **63** which is "trapped" in high concentration at low temperature by the iron carbonyl moiety. As a result, the rate of ring closure and hence pyrrole formation is increased.



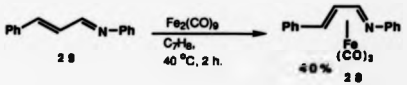
In order to define the scope of this unusual pyrrole formation reaction a range of (1-azabuta-1,3-diene)tricarbonyliron(0) complexes was synthesised and their reactivity with methyl-lithium assessed.

Initially, the reaction between methyl-lithium and the air-stable complex (1,4-diphenyl-1-azabuta-1,3-diene)tricarbonyliron(0) **28** was studied. 1,4-Diphenyl-1-azabuta-1,3-diene **29** was synthesised by condensation of aniline with cinnamaldehyde **66** at 0 °C. The yellow solid produced was dissolved in diethyl ether and the solution dried over magnesium sulphate. Removal of the solvent under reduced pressure led to isolation of yellow crystals which were recrystallised from ethanol and dried. Comparison of the ^1H n.m.r., i.r., and mass spectra and melting point of these crystals with literature values confirmed that they were 1-azabuta-1,3-diene **29**.[17]



66 **90 % 29**

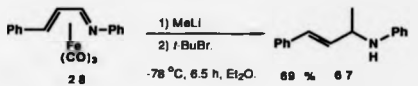
Imine **29** and diironnonacarbonyl were stirred in toluene at 40 °C for 2 h under an atmosphere of nitrogen to yield a red mixture. The work-up procedure described previously for complex **57** yielded a red oil which was crystallised and recrystallised from *n*-heptane to yield red/orange crystals identified as (1,4-diphenyl-1-azabuta-1,3-diene)tricarbonyliron(0) **28** by comparison of their ^1H n.m.r., i.r., and mass spectra and melting point with literature values.[17, 38]



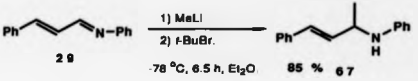
29 **40 % 28**

A solution of complex **28** in diethyl ether was stirred with methyl-lithium at -78 °C for 6.5 h under an atmosphere of nitrogen. The reaction was quenched using

2-bromo-2-methylpropane as a proton source to yield a dark brown mixture. A work-up as described for pyrrole **60** led to the isolation of the new amine 2-amino-*N*,4-diphenylbut-3-ene **67** which was identified by comparison of its ^1H n.m.r., i.r., and mass spectra with data from an authentic sample (see below).

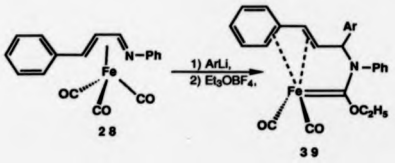


Authentic **67** was synthesised by reaction of methyl-lithium with 1,4-diphenyl-1-azabuta-1,3-diene **29** in diethyl ether at -78 °C for 6.5 h. The reaction was quenched using 2-bromo-2-methylpropane as a proton source and allowed to warm up to room temperature to yield a yellow mixture. Standard work-up led to the isolation of white crystals identified as 2-amino-*N*,4-diphenylbut-3-ene **67** on the basis of their ^1H n.m.r., ^{13}C n.m.r., i.r., and mass spectra and combustion analysis.



Formation of identical amines by reaction of methyl-lithium with complex **28** and 1-azadiene **29** suggests that decomplexation of **28** may occur prior to attack on the 1-azadiene **29** by methyl-lithium.

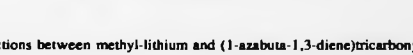
In a recent study, however, of the reaction of aryl-lithium with complex **28** followed by addition of triethyloxonium tetrafluoroborate, it was demonstrated that the reaction led to formation of a η^4-styrylcarbene complex **39**.[24]



28 39

This suggests that decomplexation may not necessarily occur prior to attack of methyl-lithium on **28** and that attack by methyl-lithium may occur directly on the face of the azadiene which is *exo* to the tricarbonyliron(0) moiety.

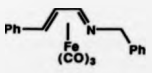
In an attempt to promote pyrrole formation from complex **28** its reaction with lithium dimethylcuprate was studied. It is known that cuprates promote 1,4-addition to α,β-unsaturated imines and carbonyl compounds[39] and it was postulated that addition of the cuprate to **28** may promote attack at C_4 or a coordinated carbonyl leading to a pyrrole. Methyl-lithium was added to a suspension of cuprous iodide in diethyl ether at -23 °C and stirred at this temperature for 0.5 h to yield a pale yellow solution. This solution was cooled to -78 °C and a solution of (1,4-diphenyl-1-azabuta-1,3-diene)tricarbonyliron(0) **28** in diethyl ether was added. The resulting solution was stirred at -78 °C for 6.5 h and then quenched using 2-bromo-2-methylpropane. A standard work-up led to isolation of white crystals identified as amine **67** by comparison of their ^{1}H n.m.r. and i.r. spectra with those of an authentic sample.



28 69 % 67

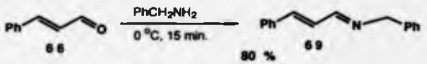
The reactions between methyl-lithium and (1-azabuta-1,3-diene)tricarbonyliron(0) complexes bearing substituents at nitrogen other than a phenyl group were studied

next. Initially the reaction between (1-benzyl-4-phenyl-1-azabuta-1,3-diene)tricarbonyliron(0) **68** and methyl-lithium was studied.



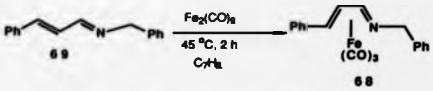
68

1-Benzyl-4-phenyl-1-azabuta-1,3-diene **69** was prepared by condensation of cinnamaldehyde **66** with benzylamine at 0 °C ; standard work-up led to a yellow oil which crystallised overnight at -20 °C. Recrystallisation from diethyl ether at -78 °C led to isolation of orange crystals identified as the 1-azadiene **69** on the basis of their ^1H n.m.r., ^{13}C n.m.r., i.r., and mass spectra and combustion analysis.



66 **80 %** **69**

Complexation of **69** to the tricarbonyliron(0) moiety by heating **69** with diironnonacarbonyl in toluene at 45 °C for 2 h led to formation of a red gum after filtration of the reaction mixture and removal of the solvent under reduced pressure. This gum was identified as the new complex **68** on the basis of its ^1H n.m.r. spectrum.



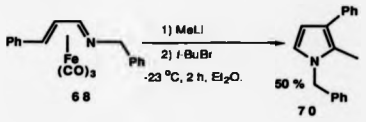
69 **68**

The ^1H n.m.r. spectrum of **68** contained a one-proton doublet at 3.09 ppm (J = 10 Hz) due to the proton at C_4. A pair of doublets at 3.47 and 3.87 ppm (J = 15 Hz) were assigned to the diastereotopic protons of the benzyl group. A one-proton

doublet of doublets at 5.55 ppm (J = 10 and 3 Hz) and a one-proton doublet at 6.70 ppm (J = 3 Hz) were assigned to the protons at C_3 and C_2 respectively.

Although complex **68** was stable in the form of a gum under an atmosphere of nitrogen, crystallisation proved impossible owing to the instability of the complex in solution. The crude complex was therefore used directly in the second stage of the reaction.

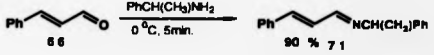
Methyl-lithium and crude **68** (90% **68**) in diethyl ether were stirred at -23 °C for 2 h under an atmosphere of nitrogen to yield a dark mixture. After quenching with 2-bromo-2-methylpropane, a standard work-up led to a yellow crystalline solid which was identified as 1-benzyl-2-methyl-3-phenylpyrrole **70** on the basis of its ^1H n.m.r., ^{13}C n.m.r., and high resolution mass spectra.



68 **70**

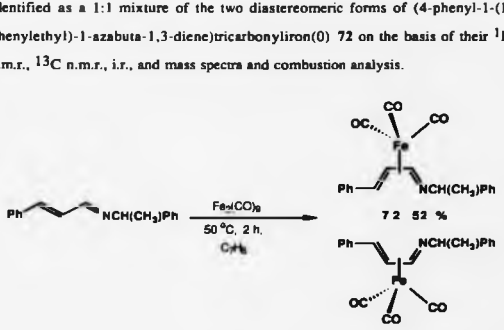
In contrast to complex **68**, the tricarbonyliron(0) complex of 4-phenyl-1-(1-phenylethyl)-1-azabuta-1,3-diene **71** proved to be crystalline and air-stable.

Cinnamaldehyde **66** and 1-phenylethylamine were condensed at 0 °C. A standard work-up gave a yellow oil which crystallised overnight at -20 °C. Recrystallisation from diethyl ether at -78 °C led to pale yellow crystals identified as 4-phenyl-1-(1-phenylethyl)-1-azabuta-1,3-diene **71** on the basis of their ^1H n.m.r., ^{13}C n.m.r., i.r., and mass spectra and combustion analysis.



66 90 % **71**

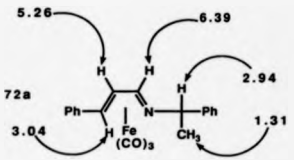
The 1-azadiene **71** was stirred with diironnonacarbonyl in toluene at 50 °C for 2 h to yield a deep red mixture. Normal work-up led to isolation of orange crystals identified as a 1:1 mixture of the two diastereomeric forms of (4-phenyl-1-(1-phenylethyl)-1-azabuta-1,3-diene)tricarbonyliron(0) **72** on the basis of their ^1H n.m.r., ^{13}C n.m.r., i.r., and mass spectra and combustion analysis.



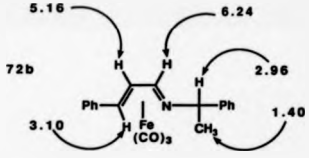
The ^1H n.m.r. spectrum of **72a** and **72b** recorded in $CDCl_3$ gave evidence for a 1:1 mixture of diastereomeric complexes since a pair of doublets (1:1) at 6.70 and 6.49 ppm (J = 3 Hz) due to the proton at C_2 for each complex was present. Also a pair of doublet of doublets at 5.80 and 5.53 ppm (J = 3 and 9 Hz) were assigned to the proton at C_3 by comparison with the ^1H n.m.r. spectra of related complexes. The assignment of other peaks in the spectrum was difficult owing to overlapping signals. Recrystallisation of **72** from *n*-heptane led to a slight enrichment of one diastereomer. Recording the ^1H n.m.r. spectrum of this mixture in $CDCl_3/C_6D_6$ (1:1) removed some of the ambiguities associated with overlapping signals and allowed peaks to be assigned to individual diastereomers on the basis of signal intensities.

The ^1H n.m.r. spectrum of the major isomer **72a** contained a three-proton doublet at 1.31 ppm (J = 6 Hz) which was assigned to the methyl protons of the 1-phenylethyl group. A one-proton quartet at 2.94 ppm (J = 6 Hz) and a one-proton doublet at 3.04 ppm (J = 9 Hz) were assigned to the methine proton of the 1-phenylethyl group

and the proton at C_4 respectively. A one-proton doublet of doublets at 5.26 ppm (J = 9 and 3 Hz) and a doublet at 6.39 ppm (J = 3 Hz) were assigned to the protons at C_3 and C_2 respectively.

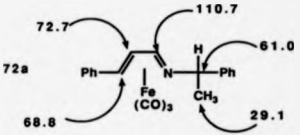


The minor diastereomer **72b** contained a three-proton doublet at 1.40 ppm (J = 6 Hz) and a one-proton quartet at 2.96 ppm (J = 6 Hz) which were assigned to the methyl and methine protons of the 1-phenylethyl group respectively. The one-proton doublets at 3.10 (J = 9 Hz) and 6.24 ppm (J = 3 Hz) were assigned to the protons at C_2 and C_4 respectively. The one-proton doublet of doublets at 5.16 ppm (J = 9 and 3 Hz) was assigned to the proton at C_3.

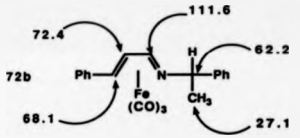


The ^{13}C n.m.r. spectrum of the mixture of diastereomers of **72** was difficult to assign due to complications associated with the proximity of resonances for each diastereomer. However a limited assignment of the ^{13}C n.m.r spectrum was possible from the $^{1}H/^{13}C$ heteronuclear shift correlation spectrum [40] of the enriched mixture of diastereomers.

The ^{13}C n.m.r. spectrum of the major isomer **72a** contained peaks at 29.1 and 61.0 ppm which were assigned to the methyl and methine carbons of the 1-phenylethyl group. Resonances at 68.8, 72.7, and 110.7 ppm were assigned to carbons C_4, C_3, and C_2 respectively by comparison with the ^{13}C n.m.r. spectra of related compounds.

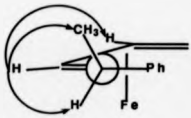


The ^{13}C n.m.r. spectrum of the minor isomer **72b** contained peaks at 27.1 and 62.2 ppm which were assigned to the methyl and methine carbons of the 1-phenylethyl group. Peaks at 68.1, 72.4, and 111.6 ppm were assigned to carbons C_4, C_3, and C_2 respectively by comparison with ^{13}C n.m.r. spectra of related compounds.

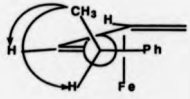


Examination of the enriched mixture of diastereomers of **72** by n.O.e. difference spectroscopy led to information about the conformation of the 1-phenylethyl group relative to the azadiene portion of the molecule for each diastereomer. Irradiation of the proton at C_2 of the major diastereomer **72a** led to an enhanced signal for the proton at C_3 (7%) and the methine (9%) and methyl (3%) protons of the 1-phenylethyl group. Irradiation of the methyl protons of the 1-phenylethyl group led to an enhanced signal for the protons at C_2 (3%) and the methine proton of the

1-phenylethyl group (4%). These results suggest that the 1-phenylethyl group adopts a conformation where the methyl and methine protons are close to the proton at C_2.



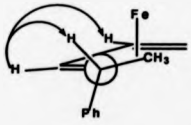
72a



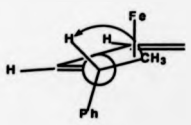
72a

Irradiation of the proton at C_2 of the minor diastereomer **72b** led to an enhancement of the signal due to the proton at C_3 (8%) and the methine proton (8%) of the 1-phenylethyl group. An enhancement of the signal due to the methyl protons of the 1-phenylethyl group was not observed. Irradiation of the methyl protons of the 1-phenylethyl group led to an enhanced signal due to the methine proton (12%). Enhancement of the signal due to the proton at C_2 was not observed.

These results suggest that the 1-phenylethyl group of the minor diastereomer adopts a conformation where only the methine proton is in the proximity of the proton at C_2 of the azadiene.



72b



72b

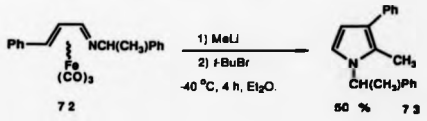
The most stable conformation for each diastereomer was calculated using the molecular modelling programme "CHEM-X". Calculations were performed on structures generated from the crystal structure of (1,4-diphenyl-1-azabuta-1,3-diene)tricarbonyliron(0) **28**,[18] [19] using the default parameters of the programme

which account for van der Waals forces only. The results obtained from these calculations are shown in Figure 1.

These structures represent the minimum energy conformation for each diastereomer. The minimisation was achieved by consideration of the interactions during rotation about the nitrogen bond to the 1-phenylethyl group, and by consideration of the interactions that occur from separate rotation of the phenyl group. After minimisation of energy for each rotation, a second combined rotation of the carbon nitrogen bond and phenyl group led to structures **72a** and **72b**. The structures generated by these calculations show good agreement with the observations from the n.O.e. experiments. Structure **72a** shows methyl and methine protons in the proximity of the proton at C_2 whereas structure **72b** only has a methine proton in the proximity of C_2.

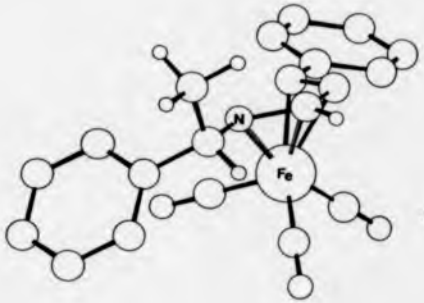
Due to the difficulty encountered separating the diastereomers of **72**, the reaction with methyl-lithium was performed using a 1:1 mixture of diastereomers.

Methyl-lithium was stirred with a solution of **72** in diethyl ether at -40 °C for 4 h under an atmosphere of nitrogen. The reaction was quenched with a proton source, standard work-up led to the isolation of an orange oil identified as 2-methyl-3-phenyl-1-(1-phenylethyl)pyrrole **73** on the basis of its ^1H n.m.r., ^{13}C n.m.r., i.r., and high resolution mass spectra.

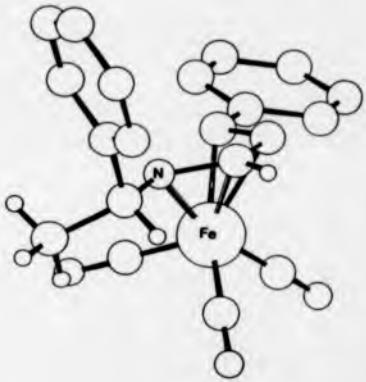


72 **50 %** **73**

The conformation of the 1-phenylethyl group of pyrrole **73** with respect to the substituents at C_2 and C_5 was studied by molecular modelling and n.O.e. difference spectroscopy. The result of this molecular modelling calculation is shown in Figure 2. This structure suggests that in the minimum energy conformation the



72a



72b

Figure 1. Calculated Lowest Energy Comformations for Diastereomers of 4-Phenyl-1-(1-phenylethyl)-1-azabuta-1,3-diene)tricarbonyliron(0) **72a** and **72b**

methyl group is in the proximity of the proton at C_5 of the pyrrole and the methine proton is in the proximity of the methyl group at C_2 of the pyrrole.

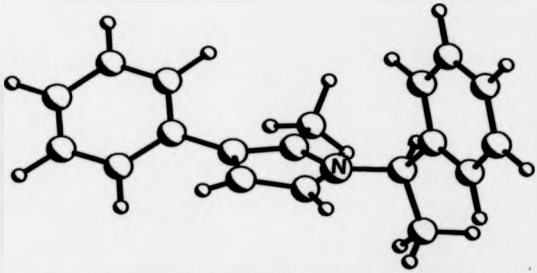
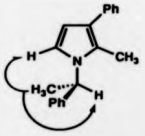


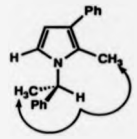
Figure 2. Lowest Energy Conformation for 1-(1-phenylethyl)-2-methyl-3-phenylpyrrole **73**

This result was confirmed by n.O.e. difference spectroscopy.

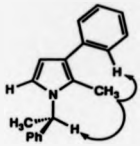
Irradiation of the methyl group of the 1-phenylethyl group led to an enhancement of the signals due to the proton at C_5 (9%) and the methine proton of the 1-phenylethyl group (9%). Enhancement of the signal due to the methyl protons at C_2 was not observed.



Irradiation of the methine proton of the 1-phenylethyl group led to an enhancement of the signal due to the methyl group at C_2 (8%) and the methyl group of the 1-phenylethyl fragment (7%). Enhancement of the signal due to the proton at C_4 was not observed.



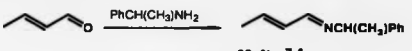
Irradiation of the signal due to the methyl group at C_2 led to an enhancement of the signals due to the methine proton (9%) and the *ortho*-protons of the phenyl group at C_3. An enhancement of the signal due to the methyl protons of the 1-phenylethyl group was not observed.



These results indicate that the 1-phenylethyl group adopts a conformation in which the methine proton is in the proximity of the methyl protons at C_2 and the methyl protons of the 1-phenylethyl group are in the proximity of the proton at C_5. These observations agree with the outcome of the molecular modelling calculations.

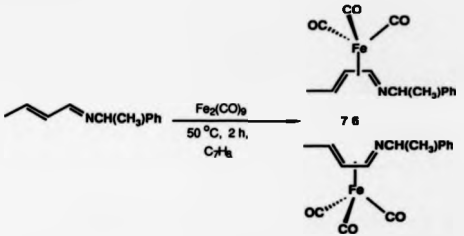
The effect on complexation and pyrrole formation of replacing the phenyl group at C_4 of the 1-azadiene by an alkyl group was studied next. 4-Methyl-1-(1-phenylethyl)-1-azabuta-1,3-diene **74** was synthesised by condensation of crotonaldehyde **75** with 1-

phenylethylamine at 0 °C. The orange oil produced was dissolved in diethyl ether and the solution was dried over magnesium sulphate. Removal of the solvent under reduced pressure and drying the resultant oil under high vacuum for 24 h gave a yellow oil identified as the 1-azadiene **74** on the basis of its ^{1}H n.m.r., ^{13}C n.m.r., i.r., and high resolution mass spectra.



75 **90 % 74**

Azadiene **74** was stirred with diironnonacarbonyl in toluene at 50 °C for 2 h under an atmosphere of nitrogen to yield a dark brown mixture. Standard work-up of this mixture led to a brown oil identified as a 1:1 mixture of diastereomers of (4-methyl-1-(1-phenylethyl)-1-azabuta-1,3-diene)tricarbonyliron(0) **76** on the basis of its ^{1}H n.m.r. spectrum.



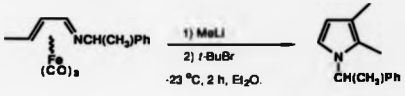
The ^{1}H n.m.r. spectrum of **76** contained overlapping multiplets at 1.20-1.50 ppm which were assigned to four sets of methyl protons. A pair of one-proton multiplets at 1.53 and 1.88 ppm were assigned to the proton at C_4 for each diastereomer. A two-proton multiplet at 2.95 ppm was attributed to the overlapping quartets of the methine protons. A pair of one-proton doublet of doublets at 4.83 and 4.93 ppm (J =

10 and 3 Hz) and a pair of one-proton doublets at 6.33 and 6.55 ppm (J = 3 Hz) were assigned to the protons at C_3 and C_2 for each diastereomer respectively.

Complexes **76a** and **76b** were extremely air-sensitive and hence it was not possible to isolate them by chromatography or crystallisation. Thus it was impossible, unfortunately, to derive information relating to the conformation of the 1-phenylethyl group relative to the azadiene fragment of the molecule for each diastereomer using n.O.e. difference spectroscopy.

Due to the air sensitivity of complexes **76a** and **76b** and difficulty encountered in purification, the complexes were reacted in a crude form with methyl-lithium.

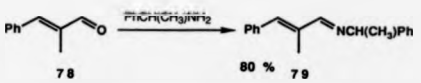
Crude **76** (80% **76**) was dissolved in diethyl ether and cooled to -23 °C and stirred with methyl-lithium at this temperature for 2 h, to yield a brown mixture. After quenching with 2-bromo-2-methylpropane standard work-up led to isolation of white crystals identified as 2,3-dimethyl-1-(1-phenylethyl)-pyrrole **77** on the basis of their ^1H n.m.r., ^{13}C n.m.r., and high resolution mass spectra.



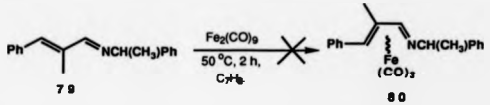
76 **25 %** **77**

The low yield of pyrrole **77** from this reaction is almost certainly a reflection of the highly air sensitive nature of the starting complex.

Finally the effect of placing a substituent at C_3 of the 1-azadiene on complexation and pyrrole formation was studied. α-Methylcinnamaldehyde **78** was condensed with 1-phenylethylamine at 0 °C to yield a yellow oil which after a normal work-up gave pale yellow crystals identified as 3-methyl-4-phenyl-1-(1-phenylethyl)-1-azabuta-1,3-diene **79** on the basis of their ^1H n.m.r., ^{13}C n.m.r., i.r., and high resolution mass spectra and combustion analysis.



Azadiene **79** was stirred with diironnonacarbonyl in toluene at 50 °C for 2 h under an atmosphere of nitrogen to yield a black mixture. Filtration of this mixture and removal of the solvent under reduced pressure led to a black oil. All attempts to isolate (3-methyl-4-phenyl-1-(1-phenylethyl)-1-azabuta-1,3-diene)tricarbonyliron(0) **80** from this oil by crystallisation or chromatography led to decomposition and generation of the starting 1-azadiene **79**.



The formation of pyrroles **70**, **73**, and **77** from complexes **68**, **72**, and **76** must be assumed to proceed *via* a mechanism involving attack on a coordinated carbonyl leading to an iron-acyl complex as described earlier. The failure of complex **28** to form a pyrrole is difficult to explain. If attack by methyl-lithium at a metal carbonyl is controlled solely by steric factors at C_2 then formation of a pyrrole from complex **68** which contains a hydrogen at C_2 and a benzyl group at nitrogen seems anomalous. Control by electronic factors therefore seems most likely but analysis of ^{1}H and ^{13}C n.m.r. data of the complexes failed to reveal any uniform or convincing trends.

A2.2 Conclusions to Chapter 2

The chemistry discussed in this chapter has shown that methyl-lithium reacts with (1-azadiene)tricarbonyliron(0) complexes leading to formation of pyrroles.

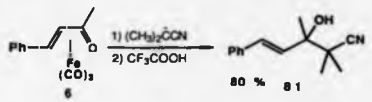
The low temperatures required for these pyrrole formations contrast with those required for the classical synthesis of pyrroles and indicate that the iron carbonyl moiety is intimately involved in the ring closure step of the reaction.

CHAPTER 3.

A3.1 Addition of Stabilised Anions to (1-Heterobuta-1,3-diene) tricarbonyliron(0) Complexes.

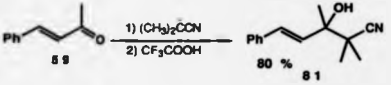
In order to assess the reactivity of (1-heterodiene)tricarbonyliron(0) complexes with a different class of nucleophiles, their reactivity with stabilised anions was studied. Recent studies of the reaction of stabilised anions with (buta-1,3-diene)tricarbonyliron(0) **1** have shown attack to occur at the diene leading to a range of substituted alkenes,[11] (see section A1.1.2.2). In this chapter reactions of stabilised anions with (1-heterodiene)tricarbonyliron(0) complexes are discussed.

Initially the reaction of the stabilised anion derived from isobutyronitrile with (2-methyl-4-phenyl-1-oxabuta-1,3-diene)tricarbonyliron(0) **6** was studied. Butyl-lithium was stirred with a solution of diisopropylamine in THF at -78 °C for 20 min under an atmosphere of nitrogen. Isobutyronitrile was added and the resulting pale yellow solution was stirred for a further 20 min at -78 °C. A solution of **6** in THF was added at -78 °C and the resulting mixture was allowed to warm up to 20 °C and stirred at this temperature for 3 h to yield a dark mixture. The mixture was cooled to -78 °C and the reaction was quenched using trifluoroacetic acid and stirred at 20 °C for 1 h to yield a dark mixture. This mixture was poured onto saturated sodium carbonate solution and extracted using diethyl ether. After washing the organic extracts with water and drying over magnesium sulphate, the solvent was removed under reduced pressure to yield a dark oil. Chromatography of this oil on silica led to isolation of a colourless oil which crystallised overnight at -20 °C. Recrystallisation from a mixture of hexane and ethanol led to white crystals identified as 3-hydroxy-2,2,3-trimethyl-5-phenylpent-4-enonitrile **81** by comparison of their ^{1}H n.m.r., i.r., and mass spectra and melting point with data from an authentic sample.



6

Authentic **81** was prepared by reaction of the stabilised anion from isobutyronitrile with 2-methyl-4-phenyl-1-oxabuta-1,3-diene **59** in THF under identical conditions to those used for complex **6** to yield a colourless oil which crystallised overnight at -20 °C. Recrystallisation of this oil led to white crystals identified as **81** on the basis of their ^{1}H n.m.r., ^{13}C n.m.r., i.r., and mass spectra and combustion analysis.

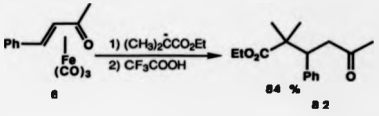


59

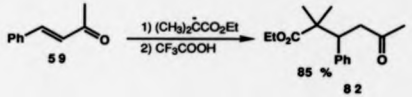
The ^{1}H n.m.r. spectrum of **81** contained two three-proton singlets at 1.40 and 1.42 ppm which were assigned to the diastereotopic methyl groups at C_2. A third three-proton singlet at 1.58 ppm was assigned to the methyl group at C_3. A sharp one-proton singlet at 1.90 ppm which disappeared after a D_2O shake was assigned to the hydroxyl proton and a pair of one-proton doublets at 6.41 and 6.81 ppm (J = 17 Hz) were assigned to the protons at C_4 and C_5 respectively. The ^{13}C n.m.r. spectrum of **81** contained peaks at 21.3 and 22.3 ppm which were assigned to the diastereotopic methyl carbons at C_2. A peak at 24.4 ppm was assigned to the methyl carbon at C_3. Peaks at 41.7 and 74.9 ppm were assigned to carbons C_2 and C_3 respectively and the signal at 124.2 ppm was assigned to the carbon of the nitrile group. The signals due to carbons C_4 and C_5 were difficult to assign with certainty since these peaks were obscured by the signals due to the phenyl carbons. The i.r. spectrum contained diagnostic peaks at 3 610(broad) and 2 235w cm^{-1} which were assigned to the hydroxyl and nitrile groups respectively. The mass spectrum of **81** contained a weak

molecular ion peak at 215 (5.2%) and a base peak at 147 which was due to loss of the isobutyronitrile group from C_3.

The stabilised anion derived from ethyl isobutyrate was next added to (2-methyl-4-phenyl-1-oxabuta-1,3-diene)tricarbonyliron(0) **6**. Ethyl isobutyrate was added to a solution of lithium diisopropylamide (LDA) in THF at -78 °C and stirred for 20 min under an atmosphere of nitrogen to yield a pale yellow solution. A solution of **6** in THF was added at -78 °C and the reaction was allowed to warm up to 20 °C and stirred at this temperature for 3 h to yield a dark mixture. The reaction was cooled to -78 °C and quenched using trifluoroacetic acid and stirred at 20 °C for 1 h to yield a dark mixture. Standard work-up led to isolation of white crystals which were recrystallised from hexane to yield white crystals identified as ethyl 2,2-dimethyl-5-keto-3-phenylhexanoate **82** by comparison of their ^1H n.m.r., i.r., and mass spectra with data from an authentic sample.



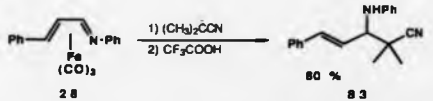
Authentic **82** was synthesised by addition of 2-methyl-4-phenyl-1-oxabuta-1,3-diene **59** in THF to a solution of the anion derived from ethyl isobutyrate in THF at -78 °C under an atmosphere of nitrogen. After a normal reaction and standard work-up, off-white crystals were collected and recrystallised from hexane to yield white crystals identified as ethyl 2,2-dimethyl-5-keto-3-phenylhexanoate **82** on the basis of their ^1H n.m.r., ^{13}C.n.m.r., i.r., and mass spectra and combustion analysis.



The ^1H n.m.r. spectrum of **82** contained three-proton singlets at 1.09, 1.14, and 2.00 ppm which were assigned to the diastereotopic methyl groups at C_2 and the methyl group at C_5 respectively. The three-proton triplet at 1.24 ppm (J = 7 Hz) and the two-proton quartet at 4.15 ppm (J = 7 Hz) were assigned to the ethyl group of the ester. The pair of one-proton doublet of doublets at 2.70 (J = 17 and 4 Hz) and 3.05 ppm (J = 17 and 11 Hz) were assigned to the diastereotopic hydrogens at C_4. The one-proton doublet of doublets at 3.60 ppm (J = 11 and 4 Hz) was assigned to the proton at C_3.

The ^{13}C n.m.r. spectrum of **82** contained peaks at 14.0, 21.3, 24.4, and 30.2 ppm which were assigned to the methyl of the ethyl ester, the diastereotopic methyl groups at C_2, and the methyl group at C_5 respectively. Peaks at 45.0, 45.8, 47.8, and 60.5 ppm were assigned to carbons C_4, C_2, the methylene fragment of the ethyl group and the carbon at C_3 respectively. The peaks at 177.0 and 206.9 ppm were assigned to the carbons of the ester and ketone carbonyl groups respectively. The i.r. spectrum of **82** contained diagnostic peaks at 1 735s and 1 720s cm^{-1} which were assigned to the carbonyl groups of an ester and ketone respectively. The mass spectrum of **82** contained a molecular ion at 262 (4.9 %) and a fragment ion at 147 (100 %) which was due to loss of the ethyl isobutyrate group.

The reaction of the stabilised anion derived from isobutyronitrile with (1,4-diphenyl-1-azabuta-1,3-diene)tricarbonyliron(0) **28** under standard conditions was studied next. Normal work-up yielded a brown oil which was chromatographed on silica to give a colourless oil identified as 2,2-dimethyl-5-phenyl-3-phenylaminopent-4-enonitrile **83** on the basis of its ^1H n.m.r., ^{13}C n.m.r., i.r., and high resolution mass spectra.

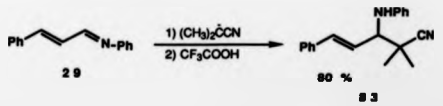


28 — 80 % — 83

The ^{1}H.n.m.r. spectrum of **83** contained a pair of three-proton singlets at 1.45 and 1.53 ppm which were assigned to the diastereotopic methyl groups at C_2. A broad two-proton signal at 3.82 ppm was assigned to the amino proton and the methine proton at C_3. After a D_2O shake this signal collapsed to a one-proton doublet (J = 8 Hz). The one-proton doublet of doublets at 6.23 ppm (J = 8 and 3 Hz) was assigned to the proton at C_4. The signal due to the proton at C_5 could not be assigned since it was obscured by the signals due to the phenyl protons.

The ^{13}C n.m.r. spectrum of **83** contained a peak at 24.4 ppm which was assigned to the methyl groups at C_2. The signals at 38.2 and 62.9 ppm were assigned to carbons C_2 and C_3 respectively. The signal at 123.5 ppm was assigned to the carbon of the nitrile group. The signals due to carbons C_4 and C_5 could not be assigned since these peaks were obscured by the signals due to the phenyl carbons. The i.r. spectrum contained characteristic peaks at 3 370m and 2 238s cm^{-1} which were assigned to NH and CN respectively. The mass spectrum of **83** contained a molecular ion at 276 (3.0%) and a base peak at 208 which was associated with loss of the isobutyronitrile fragment from C_3.

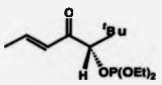
Addition of a solution of 1,4-diphenyl-1-azabuta-1,3-diene **29** to the stabilised anion derived from isobutyronitrile under standard conditions followed by a standard work-up led to a colourless oil identified as **83** by comparison of its ^{1}H n.m.r., i.r., and mass spectra to those of an authentic sample of **83** synthesised previously.



29 — 80 % — 83

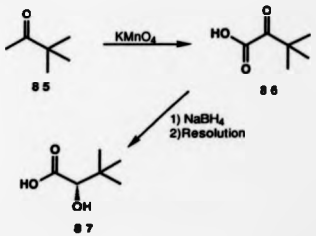
Since the same products were obtained on reaction of stabilised anions with either a (1-heterodiene)tricarbonyliron(0) complex or the corresponding free 1-heterodiene, it appears that coordination of a 1-heterodiene to the tricarbonyliron(0) moiety does not modify its reactivity with respect to stabilised carbanions. In view of these facts, it was decided not to pursue this area any further at this stage.

During the course of this work however, the reaction of the stabilised anion derived from isobutyronitrile and the ironcarbonyl(0) complex of ligand **84** was reported by Helquist and his co-workers.[41]



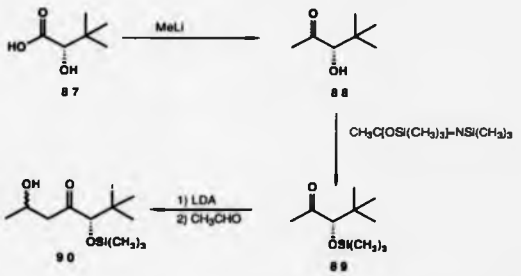
84

The ligand **84** was synthesised in an enantiomerically pure form from pinacolone **85**. Oxidation of **85** using potassium permanganate led to the α-keto acid **86** which was selectively reduced using sodium borohydride leading to the racemic α-hydroxy acid. This α-hydroxy acid was readily resolved using (*S*)-1-phenylethylamine to yield **87**.

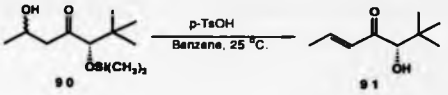


85 **86** **87**

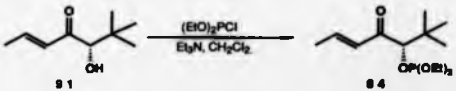
Attack of (*S*)-**87** by methyl-lithium led to the (*S*)-hydroxy ketone **88** after addition of a proton source. Protection of the hydroxy group as its trimethylsilyl ether **89** was followed by aldol condensation to yield alcohol **90** as a diastereomeric mixture (1:1).



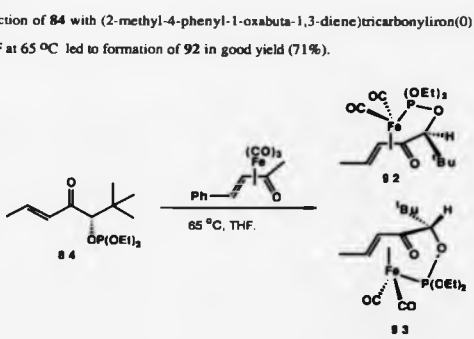
Acid promoted dehydration of the keto alcohol **90** led to enone **91** and simultaneous removal of the silyl protecting group.



The final step of the synthesis involved formation of the phosphite **84** by reaction of **91** with diethylchlorophosphite under base catalysis.

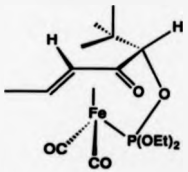


Reaction of **84** with (2-methyl-4-phenyl-1-oxabuta-1,3-diene)tricarbonyliron(0) **6** in THF at 65 °C led to formation of **92** in good yield (71%).



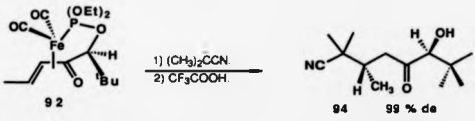
84

Recrystallisation of the product mixture led to pure **92**. The high diastereofacial selectivity for this complexation reaction is almost certainly a result of steric factors. Failure of the reaction to yield significant quantities of **93** is attributed to a strong steric interaction between the *t*-butyl group and the proton at C_3.



93

Addition of the stabilised anion derived from isobutyronitrile to **92** in THF occurred exclusively at C_4 of the coordinated enone leading to **94** after addition of a proton source.

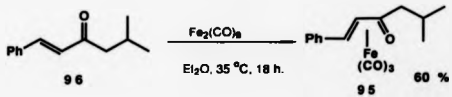


92 94 99 % de

The high d.e. for this reaction suggests decomplexation does not occur prior to addition of the nucleophile, which is directed to the face of the ligand *exo* to the iron carbonyl moiety yielding **94**.

Since attack at C_4 of **92** by the anion derived from isobutyronitrile conflicted with our results using **6**, where attack occurred at C_2, it was decided to investigate whether attack at C_4 as observed by Helquist and his co-workers[41] was a result of steric hindrance at C_2 or whether other factors were involved.

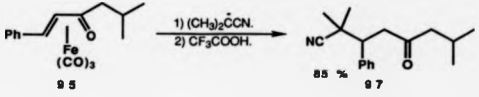
In order to assess the effect of increasing bulk at C_2 and the effect that this may have on the addition of stabilised anions, the anion derived from isobutyronitrile was added to (2-isobutyl-4-phenyl-1-oxabuta-1,3-diene)tricarbonyliron(0) **95**. Complex **95** was synthesised by reaction of 2-isobutyl-4-phenyl-1-oxabuta-1,3-diene **96** with diironnonacarbonyl in diethyl ether at 35 °C for 18 h under an atmosphere of nitrogen. A standard work-up led to isolation of red crystals identified as (2-isobutyl-4-phenyl-1-oxabuta-1,3-diene)tricarbonyliron(0) **95** by comparison of their melting point, ^1H n.m.r., and i.r. spectra with literature values.[29]



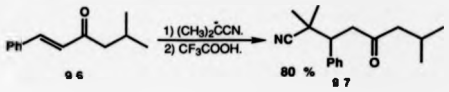
96 95 60 %

The anion derived from isobutyronitrile was synthesised using the previously described procedure. After addition of a solution of complex **95** and a normal reaction procedure the reaction was quenched using trifluoroacetic acid. A standard work-up

led to isolation of a colourless oil identified as 2,2,7-trimethyl-5-keto-3-phenyloctanitrile **97** by comparison of its ^1H n.m.r., i.r., and mass spectra with data from an authentic sample.



Authentic **97** was synthesised by reaction of the stabilised anion derived from isobutyronitrile with 2-isobutyl-4-phenyl-1-oxabuta-1,3-diene **96** under identical conditions. After a standard work-up the yellow oil produced was kugelrohr distilled to yield a colourless oil identified as 2,2,7-trimethyl-5-keto-3-phenyloctanitrile **97** on the basis of its ^1H n.m.r., ^{13}C n.m.r., i.r., and high resolution mass spectra.



The ^1H n.m.r. spectrum of **97** contained a pair of three-proton doublets at 0.74 and 0.77 ppm (J = 7 Hz) which were assigned to the diastereotopic methyl groups at C_7. The three-proton singlets at 1.14 and 1.42 ppm were assigned to the diastereotopic methyl groups at C_2. The multiplets at 2.02 and 2.20 ppm were assigned to the methine proton at C_7 and the protons at C_6, and the multiplet at 2.80-3.20 ppm was assigned to the proton at C_3 and the diastereotopic protons at C_4. The ^{13}C n.m.r. spectrum of **97** contained peaks at 22.1, 22.3, and 24.2, and 25.3 ppm which were assigned to the diastereotopic methyl groups at C_2 and C_7. The peaks at 26.7, 36.2, 45.5, 48.4, and 52.5 ppm were assigned to carbons C_7, C_2, C_6, C_4, and C_3 respectively. The peak at 124.2 ppm was assigned to the nitrile carbon and the peak at 207.6 ppm was assigned to the carbonyl carbon. The i.r. spectrum of **97** contained

diagnostic peaks at 2 238w and 1 723s cm^{-1} which were assigned to CN and C=O respectively. The mass spectrum contained a molecular ion at 257 (2.3%) and significant peaks at 200 (7.1%), 85 (100%) and 57 (96%) which were due to loss of the isobutyl fragment, cleavage of the bond between C_4 and C_5, and the isobutyl fragment respectively.

The results from this work suggest that coordination of a heterodiene to the tricarbonyliron(0) moiety does not modify the reactivity of the heterodiene towards stabilised anions. The position of attack by the anion derived from isobutyronitrile appears to be determined by steric factors at C_2, since increasing the bulk of the group at C_2 from methyl to isobutyl leads to attack at C_4 rather than at C_2. Attack on complex **84** at C_4 as observed by Helquist and his co-workers[41] therefore probably reflects the bulk at C_2 rather than other factors.

A3.2 Conclusions to Chapter 3.

The chemistry discussed in this chapter indicates that coordination of a 1-heterodiene to the tricarbonyliron(0) does not modify the properties of the 1-heterodiene with respect to its reactions with stabilised anions. It appears that the position of attack by the carbanion is determined solely by steric factors at C_2 of the heterodiene. The results obtained by Helquist and co-workers have indicated that addition of the anion derived from isobutyronitrile to 1-oxadiene complex **92** occurs stereospecifically at the face of the diene which is *exo* to the ironcarbonyl(0) moiety. This work however did not report the nature of the product which arises from addition of the anion derived from isobutyronitrile to the free oxadiene **84**, and it is therefore not possible to determine with certainty, whether the high d.e. for the addition reaction results from coordination of the oxadiene to the ironcarbonyl moiety or is a result of the chirality of the oxadiene ligand itself.

CHAPTER 4

A4.1 Addition of Hydride Transfer Reducing Agents to (1-Heterodiene)tricarbonyliron(0) Complexes.

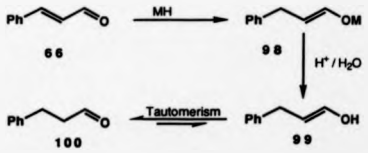
The chemistry discussed in this chapter describes the reactions of (1-heterodiene)tricarbonyliron(0) complexes and 1-heterodienes with hydride transfer reducing agents. As an introduction to this work previous methods used for the selective reduction of 1-heterodienes are discussed.

Many specialised reagents have been developed for the selective reduction of oxadienes and numerous reports have appeared in the literature describing procedures for selective reduction of the C=C and C=O bonds. In contrast the number of reports concerning the reduction of oxadienes to saturated alcohols is relatively few.

A4.1.1 Selective Reduction of 1-Oxadienes.

A4.1.1.1 *The Selective Reduction of the C=C Bond of a 1-Oxadiene.*

Reduction of the carbon-carbon double bond of **66** may be achieved by conjugate addition of hydride leading to enolate **98**. Protonation of **98** yields the enol **99** which tautomerises to the saturated aldehyde **100**.[42]

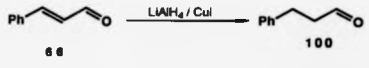


Conjugate addition of hydride to **66** may be promoted by use of lithium aluminium hydride at 35 °C.[43] The selectivity of this reduction, however, is poor and a high proportion of saturated and allylic alcohols are observed in the product mixture.

Formation of a large proportion of the saturated alcohol may be avoided by very careful control of the reaction stoichiometry.[43]

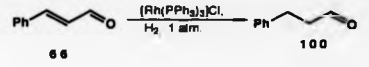
66 100

Conjugate addition of hydride to 1-oxadienes has also been promoted using a reagent based on cuprous iodide and lithium aluminium hydride.[42]



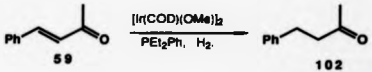
66 100

Direct selective reduction of the C=C double bond may also be achieved by homogeneous catalysis.[44] Thus, use of Wilkinson's catalyst under mild conditions leads to reduction of oxadiene **66** and formation of aldehyde **100**. The selectivity for this reaction is very high, and over-reduction to alcohols is not observed.[44]



66 100

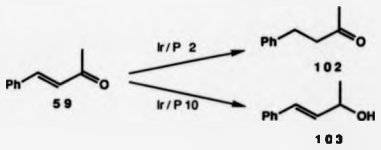
Recently a catalyst based on iridium **101** has been used to convert 1-oxadiene **59** into ketone **102** in high yield.[45]



59 102

Formation of allyl alcohol **103** is also observed. The proportion of **102** and **103** in the product mixture appears to depend on the iridium/phosphine ratio in the catalyst. A

small ratio (approx. 2) leads to predominantly C=C reduction whereas a large ratio (approx. 10) results in formation of mainly allylic alcohol **103**.[45]



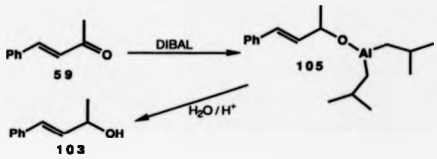
Hydrogen in the presence of a range of heterogeneous catalysts is also known to selectively reduce the C=C double bond of a 1-oxadiene. For example, reaction of 4-phenyl-1-oxabuta-1,3-diene **66** with H_2/PtO_2[46], H_2/Ni[47], or $H_2/Pd/C$[47] under mild conditions gives 3-phenylpropanal **100** in high yield.

A4.1.1.2 *The Selective Reduction of the Carbonyl Group of a 1-Oxadiene.*

Selective reduction of the carbonyl group of a 1-oxadiene has been studied extensively. The use of sodium borohydride or lithium aluminium hydride at low temperatures (0 °C) yields the required allylic alcohol. A small proportion of over-reduction, however, is also observed. For example, reaction of oxadiene **59** with lithium aluminium hydride at 0 °C yields allylic alcohol **103** and the saturated alcohol **104** (10:1).[43]

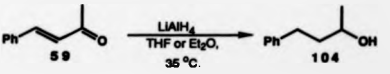
Exclusive reduction of the carbonyl group may also be achieved by use of aluminium hydride,[48] diisobutylaluminium hydride,[49] lithium *n*-butylborohydride,[50] 9-borobicyclo[3,3,1]nonane (9-BBN)[43] or sodium borohydride/lanthanoid chloride, [51] as the source of hydride.

The mechanism for the reduction involves attack by hydride at C_2 of the oxadiene leading to intermediate **105**. Addition of a proton source leads to formation of the required allylic alcohol **103**.

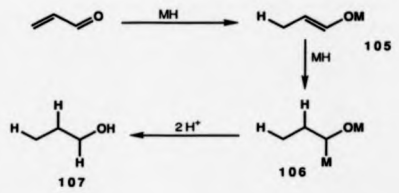


A4.1.1.3 ***The Total Reduction of a 1-Oxadiene.***

Reduction of a 1-oxadiene to a saturated alcohol may be effected by use of hydride transfer reagents or hydrogen and heterogeneous catalysts. Reaction of the oxadiene **59** with an excess of lithium aluminium hydride at 35 °C results in formation of 4-phenylbutan-2-ol **104** as the major product.[43]

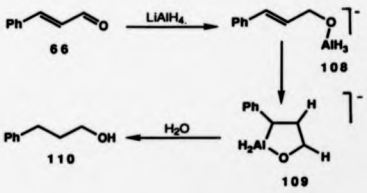


The reaction has been explained in terms of initial attack by hydride at C_4[43] or C_2[52]. The proposed mechanism for attack at C_4 is shown below.[43]



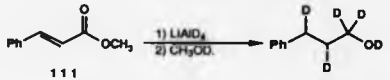
Initial hydride attack gives enolate **105** which on addition of a second hydride at C_3 results in formation of the dimetallic species **106**. This yields the saturated alcohol **107** on addition of a proton source. To date there appears to be very little evidence in support of this mechanism.

Formation of saturated alcohols from reaction of lithium aluminium hydride with a 1-oxadiene has also been suggested to occur by initial attack on oxadiene **66** by hydride at C_2 leading to intermediate **108**.[52] Intramolecular transfer of a second hydride to C_3 leads to formation of the five membered cyclic intermediate **109** and finally addition of a proton source to **109** gives the saturated alcohol **110.**



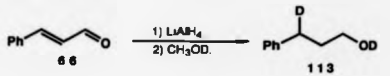
Evidence to support this mechanism has been obtained from the following experiments.

i) Reduction of methyl cinnamate **111** with lithium aluminium deuteride led to formation of the pentadeuteroalcohol **112** after addition of a deuterium source.[53]



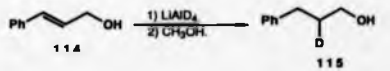
111 **112**

ii) Reduction of cinnamaldehyde **66** using lithium aluminium hydride followed by addition of a deuterium source led to alcohol **113**.[52]



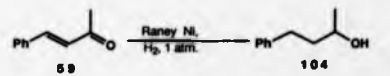
66 **113**

iii) Reduction of cinnamyl alcohol **114** with lithium aluminium deuteride followed by addition of a proton source gave alcohol **115**. [52]



114 **115**

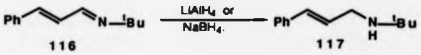
1-oxadienes may also be converted to saturated alcohols by use of hydrogen and a heterogeneous catalyst. For example, reduction of oxadiene **59** using hydrogen at one atmosphere and Raney nickel leads to formation of 4-phenylbutan-2-ol **104**.[54]



59 **104**

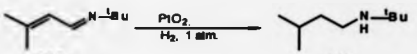
4.1.2 The Selective Reduction of 1-Azadienes.

Selective reduction of 1-azadienes has not been extensively studied. A recent report[53] has shown that reduction of 1-azadienes using hydride transfer reagents leads to formation of only the corresponding allylamine; over reduction is not observed. For example, reduction of 1-*t*-butyl-4-phenyl-1-azabuta-1,3-diene **116** using lithium aluminium hydride or sodium borohydride at 0 °C leads directly to *N*-*t*-butyl-*N*-3-phenylprop-2-ene amine **117**.[55]



116 117

Total reduction of 1-azadienes has also been reported. Reaction of 1-*t*-butyl-4,4-dimethyl-1-azabuta-1,3-diene **118** using hydrogen at one atmosphere in the presence of a PtO_2 catalyst leads directly to *N*-*t*-butyl-*N*-isopentylamine **119**.[56]



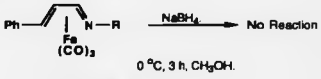
118 119

A4.2 Reaction of Lithium Aluminium Hydride and Sodium Borohydride with (1-Heterodiene)tricarbonyliron(0) Complexes.

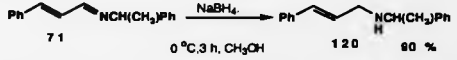
The first reaction to be studied was the addition of (4-phenyl-1-(1-phenylethyl)-1-azabuta-1,3-diene)tricarbonyliron(0) **72** to sodium borohydride. A solution of **72** in methanol was added to sodium borohydride at 0 °C and the resulting mixture was stirred at 0 °C for 3 h under an atmosphere of nitrogen to yield an orange mixture. This mixture was poured onto saturated sodium chloride solution and extracted using diethyl ether. The combined organic extracts were washed with water and dried over magnesium sulphate. Removal of the solvent under reduced pressure led to an orange

oil. The ^1H n.m.r. spectrum of this oil indicated the presence of only the starting complex **72**.

In order to confirm the lack of reactivity between sodium borohydride and (1-azadiene)tricarbonyliron(0) complexes, the reduction of a second complex was attempted. (1,4-Diphenyl-1-azabuta-1,3-diene)tricarbonyliron(0) **28** was dissolved in methanol and added to sodium borohydride under conditions described for complex **72**. Standard work-up led to an orange oil which was identified as complex **28** on the basis of its ^1H n.m.r. spectrum.



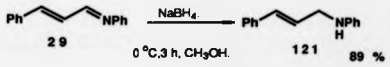
Sodium borohydride was reacted with the free azadiene **71** under identical conditions to those used above. After work-up and chromatography, a colourless oil was isolated which was identified as the new allyl amine *N*-(1-phenylethyl)-*N*-3-phenylprop-2-ene amine **120** on the basis of its ^1H n.m.r., ^{13}C n.m.r., i.r., and mass spectra and combustion analysis.



The ^1H n.m.r. spectrum of **120** contained a three-proton doublet at 1.46 ppm (J = 8 Hz) and a one-proton quartet at 3.96 ppm (J = 8 Hz) which were assigned to the 1-phenylethyl group. The two-proton doublet at 3.32 ppm (J = 6 Hz) and the one-proton doublet of triplets at 6.35 ppm (J = 16 and 6 Hz) were assigned to the protons at C_1 and C_2 respectively. The signal due to the proton at C_3 was obscured by the signals due to the phenyl protons. A broad one-proton signal at 3.52 ppm was assigned to the

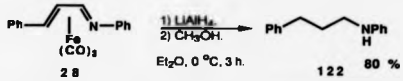
proton at nitrogen. The ^{13}C n.m.r. spectrum contained peaks at 24.0 and 57.3 ppm which were assigned to the 1-phenylethyl group. The peak at 49.4 ppm was assigned to the carbon C_1. The peaks due to carbons C_2 and C_3 were difficult to assign since they were obscured by the signals due to the phenyl carbons. The i.r. spectrum of **120** contained a diagnostic peak at 3 338 cm^{-1}(broad) which was assigned to NH. The mass spectrum contained a molecular ion at 237 (22.0%) and a fragmentation peak at 222 (23.6%) which was due to the loss of a methyl group. The peak at 117 (100%) was assigned to $PhHC{=}CHCH_2^+$.

Reduction of azadiene **29** with sodium borohydride under conditions identical to those used for reduction of **71**, followed by standard work-up and chromatography led to a colourless oil which was identified as 1-*N*-phenyl-*N*-3-phenylprop-2-ene amine **121** on the basis of its ^1H n.m.r., ^{13}C n.m.r., i.r., and high resolution mass spectra.



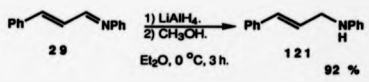
These results indicate that a 1-azadiene may be protected against reduction by sodium borohydride by coordination to the tricarbonyliron(0) moiety. In order to determine the degree of deactivation resulting from coordination to the tricarbonyliron(0) moiety, lithium aluminium hydride was reacted with complex **28**.

A solution of complex **28** in diethyl ether was added to a suspension of lithium aluminium hydride in diethyl ether at 0 °C and the resulting mixture was stirred at this temperature for 3 h under an atmosphere of nitrogen. The reaction was quenched using methanol and allowed to warm up to room temperature for 1 h to yield a dark mixture. This mixture was filtered through a plug of alumina to remove the solid residues and the solvent was removed under reduced pressure to yield an orange oil. Chromatography of this oil on silica led to isolation of a colourless oil identified as *N*-phenyl-*N*-3-phenylpropylamine **122** on the basis of its ^1H n.m.r., ^{13}C n.m.r., i.r., and high resolution mass spectra.



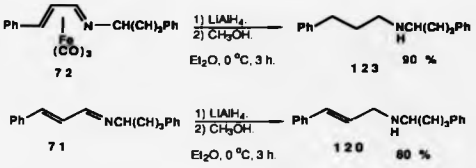
The ^{1}H n.m.r. spectrum of **122** contained a two-proton quintet at 1.91 ppm (J = 9 Hz) which was assigned to the protons at C_2. A pair of two-proton triplets at 2.21 (J = 9 Hz) and 3.12 ppm (J = 9 Hz) were assigned to methylene protons at C_3 and C_1 respectively. A broad one-proton signal at 3.40 ppm which disappeared after a D_2O shake was assigned to the amino proton. The ^{13}C n.m.r. spectrum contained significant peaks at 30.8, 33.2, and 43.1 ppm which were assigned to carbons C_2, C_3 and C_1 respectively by comparison to ^{13}C n.m.r. spectra of related compounds discussed in this thesis. The i.r. spectrum of **122** contained a diagnostic peak at 3 410 cm^{-1} (broad) which was assigned to NH. The mass spectrum of **122** contained a molecular iron at 211 (27.0%) and a peak at of 106 (100%) which was assigned to the fragment which arises from cleavage of the carbon-carbon bond α to nitrogen.

1,4-Diphenyl-1-azabuta-1,3-diene **29** was reduced using lithium aluminium hydride under identical conditions to those used for complex **28**; standard work-up and chromatography led to a colourless oil identified as 1-*N*-phenyl-*N*-3-phenylprop-2-ene amine **121** by comparison of its ^{1}H n.m.r. and i.r., spectra with an authentic sample of **121** synthesised earlier.



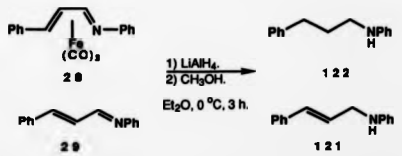
Complex **72** and azadiene **71** were also reduced using lithium aluminium hydride under identical conditions to those described for complex **28**; standard work-up and chromatography led to isolation of *N*-(1-phenylethyl)-*N*-3-phenylpropylamine **123**

and *N*-(1-phenylethyl)-*N*-3-phenylprop-2-ene amine **120** identified on the basis of their ^{1}H n.m.r., ^{13}C n.m.r., i.r., and mass spectra and combustion analysis.



The results obtained from these reductions indicate that coordination of a 1-azadiene to the tricarbonyliron(0) moiety activates the azadiene to attack by lithium aluminium hydride, yet deactivates it toward attack by sodium borohydride. For the purpose of demonstrating the need for the azadiene to be coordinated to the tricarbonyliron(0) moiety, rather than simply being present in the reaction mixture, in order to effect complete reduction of the azadiene, a "mixed" reduction was performed.

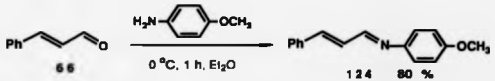
A 1:1 mixture of complex **28** and azadiene **29** was reduced using lithium aluminium hydride under normal conditions. Standard work-up led to an orange oil which was identified as a mixture of amines **122** and **121** (1:1) on the basis of its ^{1}H n.m.r. spectrum.



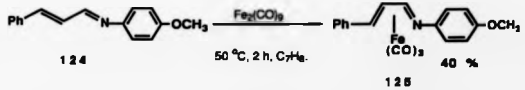
Thus it appears that the tricarbonyliron(0) moiety must be present in a stoichiometric quantity in the reaction mixture and is intimately involved in the reduction process.

1-(4-Methoxyphenyl)-4-phenyl-1-azabuta-1,3-diene **124** and its tricarbonyliron(0) complex **125** were reduced next.

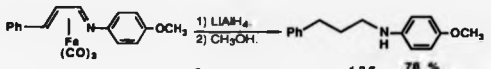
The 1-azadiene **124** was prepared by stirring a solution of 4-methoxyaniline in diethyl ether with a solution of cinnamaldehyde **66** in diethyl ether at 0 °C for 1 h under an atmosphere of nitrogen. The yellow solid produced was washed with cold diethyl ether and recrystallised from ethanol to yield yellow plate-like crystals identified as 1-(4-methoxyphenyl)-4-phenyl-1-azabuta-1,3-diene **124** on the basis of their ^{1}H n.m.r., ^{13}C n.m.r., i.r., and high resolution mass spectra.



Complex **125** was prepared by heating azadiene **124** with diironnonacarbonyl in toluene at 50 °C for 2 h under an atmosphere of nitrogen. Standard work-up followed by chromatography led to isolation of dark red crystals identified as complex **125** by comparison of their ^{1}H n.m.r. and i.r. spectra and melting point with literature values.[35]

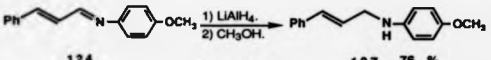


Complex **125** was reduced using lithium aluminium hydride under normal conditions. Standard work-up followed by chromatography led to isolation of white crystals identified as *N*-(4-methoxyphenyl)-*N*-3-phenylpropylamine **126** on the basis of their ^{1}H n.m.r., ^{13}C n.m.r., i.r., and mass spectra and combustion analysis.



125 0 °C, 3 h, Et_2O. 126 78 %

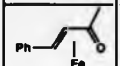
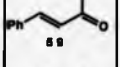
Reduction of 1-azadiene **124** using sodium borohydride or lithium aluminium hydride under normal conditions followed by standard work-up led to white crystals identified as *N*-(4-methoxyphenyl)-*N*-3-phenylprop-2-ene amine **127** on the basis of their ^1H n.m.r., ^{13}C n.m.r., i.r., and high resolution mass spectra.



124 0 °C, 3 h, Et_2O. 127 76 %

The reduction of 1-oxadienes and (1-oxadiene)tricarbonyliron(0) complexes using lithium aluminium hydride was also studied. Results obtained using standard conditions are shown in Table 2.

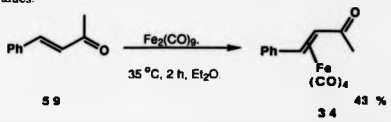
Table 2

Compound	1,2-Addition %	1,4-Addition %	Yield %
 6	0	100	80
 30	0	100	90
 59	90	10	87
 66	90	10	79

These results indicate that the tricarbonyliron(0) moiety also activates the 1-oxadienes in a similar way to the 1-azadienes. The observation of slight over-reduction (approx. 10%) of the free 1-oxadiene using lithium aluminium hydride is consistent with reports in the literature and indicates the increased activity of the 1-oxadiene ligands.[43]

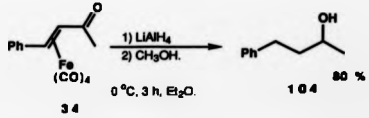
In order to investigate the activating effect of the tricarbonyliron(0) moiety on carbons C_3 and C_4 of the oxadienes, reduction of (2-methyl-4-phenyl-1-oxabuta-1,3-diene)tetracarbonyliron(0) **34** with lithium aluminium hydride was attempted.

Complex **34** was synthesised by stirring 2-methyl-4-phenyl-1-oxabuta-1,3-diene **54** with diironnonacarbonyl in diethyl ether at 35 °C for 2 h under an atmosphere of nitrogen. Standard work-up and chromatography led to yellow crystals identified as complex **34** by comparison of their ^1H n.m.r. and i.r. spectra and melting point with literature values.[58]



59 **34** 43 %

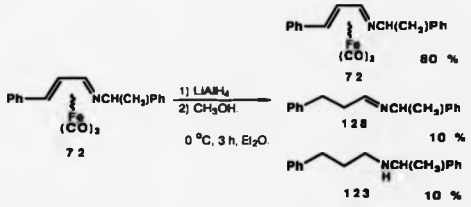
A solution of complex **34** in diethyl ether was added to a suspension of lithium aluminium hydride in diethyl ether at 0 °C. After a normal reaction and standard work-up: chromatography led to isolation of a colourless oil identified as 4-phenylbutan-2-ol **104** by comparison of its ^1H n.m.r. spectrum with data from an authentic sample.



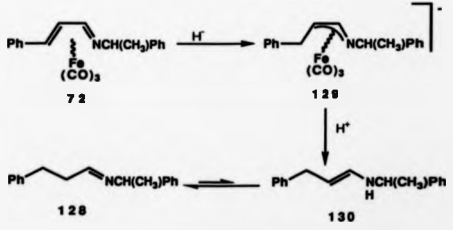
34 **104** 80 %

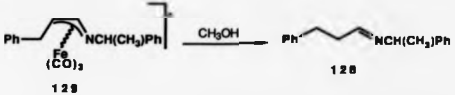
Trapping and deuteration experiments gave some insight into the course of these reductions.

Initially, (4-phenyl-1-(1-phenylethyl)-1-azabuta-1,3-diene)tricarbonyliron(0) was reacted with less than a stoichiometric quantity of hydride ion (<1/4 equivalent of lithium aluminium hydride) under standard conditions; normal work-up led to an orange oil which was identified as complex **72** (80%), amine **123** (10%), and 4-phenyl-1-(1-phenylethyl)-1-azabut-1-ene **128** (10%) on the basis of its ^{1}H n.m.r spectrum.



Observation of **128** in the product mixture suggests that initial attack by hydride occurs at C_4 leading to an azaallyl intermediate **129**. Quenching **129** with a proton source would then lead to enamine **130**, if the proton is delivered to the nitrogen. This enamine readily tautomerises to imine **128**.

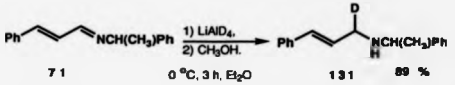




129 128

In order to investigate further the position of attack by hydride on azadiene **71** and complex **72**, deuteration experiments were performed.

Initially a solution of azadiene **71** was added to a suspension of lithium aluminium deuteride at 0 °C. After a normal reaction, standard work-up and chromatography, a colourless oil was isolated which was identified as *N*-(1-phenylethyl)-*N*-1-deutero-3-phenylprop-2-ene amine **131** on the basis of its ^{1}H n.m.r., ^{2}H n.m.r., and mass spectra.

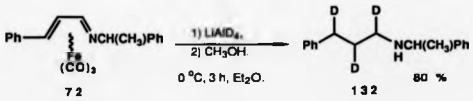


71 131 89 %

The ^{1}H n.m.r. spectrum of **131** contained the expected signals from the 1-phenylethyl group. A broad one-proton signal at 3.25 ppm was assigned to the proton at C_1. A one-proton doublet of doublets at 6.30 ppm (J = 17 and 7 Hz) was assigned to the proton at C_2. The ^{2}H n.m.r. spectrum of **131** contained a single peak at 3.33 ppm which was assigned to the deuterium at C_1. The mass spectrum of **131** contained a molecular ion at 238 (17.0%) and a base peak at 118 which was assigned to loss of the 1-phenylethyl amino group. These results are consistent with the incorporation of a single deuterium at C_1.

Complex **72** was next reduced using lithium aluminium deuteride under normal conditions. Standard work-up and chromatography led to isolation of a colourless oil

tentatively identified as *N*-(1-phenylethyl)-*N*-1,2,3-trideutero-3-phenylpropylamine **132** on the basis of its ^1H n.m.r., ^2H n.m.r., and mass spectra.

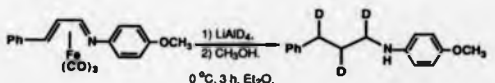


The ^1H n.m.r. spectrum of **132** contained the expected three-proton doublet and one-proton quartet associated with the 1-phenylethyl group. In addition the spectrum contained a pair of broad two-proton signals at 1.75 and 2.55 ppm which were assigned to the overlapping signals due to NH and the proton at C_2 and the overlapping signals from the protons at C_1 and C_3 respectively. The ^2H n.m.r. spectrum contained two broad signals at 1.77 and 2.51 ppm (ratio 1:2) which were assigned to the deuteria at C_2, and C_1 and C_3 respectively. The mass spectrum of **132** contained a molecular ion at 242 (8.2%) and a base peak at 105 associated with the 1-phenylethyl fragment.

These results suggest that equal amounts of deuterium has been incorporated at C_1, C_2, and C_3 of amine **132**. However, since the signals due to the protons at C_1 and C_3 overlapped, independent confirmation of the site of deuterium incorporation was sought.

The amine produced from reduction of complex **125** using lithium aluminium hydride gives an ^1H n.m.r. spectrum which does not contain overlapping signals for the protons at C_1, C_2, and C_3. Therefore reduction of **125** using lithium aluminium deuteride should give more precise information about the position of attack by hydride (deuteride). Complex **125** was reduced using lithium aluminium deuteride under normal conditions; standard work-up and chromatography led to isolation of a colourless oil identified as *N*-1-(4-methoxyphenyl)-*N*-1,2,3-trideutero-3-

phenylpropylamine **133** on the basis of its ^{1}H n.m.r., ^{2}H n.m.r., and ^{13}C n.m.r. spectra.



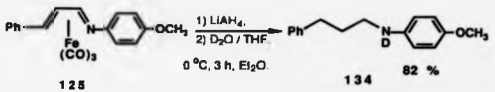
125 **133** **76 %**

The ^{1}H n.m.r. spectrum of **133** contained two broad one-proton doublets at 2.70 (J = 6 Hz) and 3.00 ppm (J = 7 Hz) which were assigned to the protons at C_3 and C_2 respectively. A broad one-proton multiplet at 1.90 ppm was assigned to the proton at C_2. The broad peak centred at 3.40 ppm.was assigned to the NH proton

The ^{2}H n.m.r. spectrum of **133** contained three broad, equal intensity signals at 1.89, 2.68, and 3.07 ppm which were assigned to the deuteria at carbons C_2, C_3, and C_1 respectively.

The ^{13}C n.m.r. spectrum of **133** contained triplets at 30.5 (J_{CD}= 18 Hz), 32.9 (J_{CD} = 20 Hz), and 43.9 ppm (J_{CD} = 20 Hz) which were assigned to carbons C_2, C_3, and C_1 by comparison of the spectrum with those of related compounds. The mass spectrum of **133** contained an expected molecular ion at 244 (40%). These results clearly indicate that reduction of complex **125** using lithium aluminium deuteride yields amine **133** which contains deuteria at carbons C_1, C_2, and C_3.

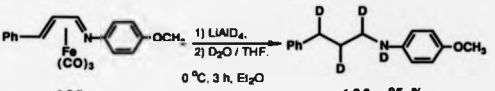
In order to confirm the position of the proton(s) derived from methanol, a deuterium quench was performed. Complex **125** was reduced using lithium aluminium hydride under standard conditions and the reaction was quenched using a solution of D_2O in THF. Care was taken to prevent water entering the work-up and all filtrations were performed using alumina deactivated with D_2O. Removal of the solvent under reduced pressure led to isolation of a brown oil identified as amine **134** on the basis of its ^{1}H n.m.r. spectrum.



125 134 82 %

The ^1H n.m.r. spectrum of **134** contained the characteristic two-proton signals at 1.96, 2.75, and 3.12 ppm associated with the protons at C_2, C_3, and C_1 respectively. The broad signal at 3.40 ppm due to NH integrated to significantly less than one proton (1/3 H) which suggested deuterium had been incorporated at this point.

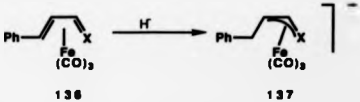
Complex **125** was also reduced using lithium aluminium deuteride under normal conditions and quenched with D_2O. Filtration of the reaction mixture through a plug of D_2O deactivated alumina and removal of the solvent under reduced pressure led to a dark oil identified as amine **135** on the basis of its ^1H n.m.r. spectrum.



125 135 85 %

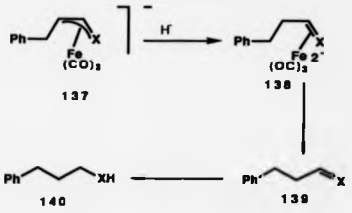
The ^1H n.m.r. spectrum of **135** contained the expected signals for the protons on carbons C_1, C_2, and C_3. A signal due to the proton at NH was not observed which suggests deuterium incorporation at this position had occured.

Reduction of (1-heterodiene)tricarbonyliron(0) **136** complexes appears to involve initial attack by hydride at C_4 of the coordinated diene, leading to an η^3-heteroallyl intermediate **137**.



136 137

It is postulated that attack of intermediate **137** by a second hydride occurs at C_3 to give intermediate **138**. Intermediate **138** is unstable and decomposes to yield the saturated imine or carbonyl compound **139**. Reduction of **139** to the alcohol or amine may now follow the normal mechanism for addition of hydride to an imine or carbonyl compound to yield **140**.



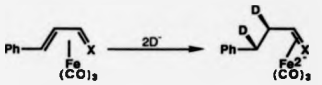
The exact position of aluminium in intermediates **137** and **138** is open to speculation but it is likely that bonding to the hetero atom is involved.

A4.5 Conclusions to Chapter 4.

The chemistry discussed in this chapter has shown that the tricarbonyliron(0) moiety may be used as an effective protecting group for 1-azadienes against attack by hydride derived from sodium borohydride. The use of lithium aluminium hydride however, results in reduction of a coordinated 1-heterodiene to its corresponding saturated alcohol or amine.

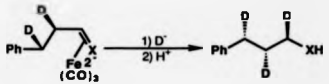
The mechanism for this reduction has been shown to proceed by initial attack on the 1-heterodiene by hydride at C_4. Deuteration experiments have indicated that three hydrogens derived from the reducing agent are transferred to the heterodiene and that protonation occurs at the hetero atom.

The stereochemistry of this reduction, however, is uncertain although it is likely that attack on the (heterodiene)tricabonyliron(0) complex **136** by the first two hydride (deuterides) occurs on the face of the diene which is *exo* to the tricarbonyl(0) moiety leading to intermediate **141**.



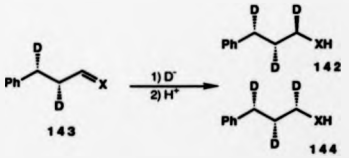
136 **141**

It is possible that attack of **141** by a third hydride (deuteride) may occur on the face of the ligand which is *exo* to iron, before the complex decomposes, thus leading to a stereospecifically deuterated three carbon fragment **142**.



141 **142**

Decomplexation before attack by the third hydride (deuteride), however, would lead to a mixture of products **142** and **144**.



143

CHAPTER 5.

Experimental.

All reactions performed under nitrogen were carried out using standard Schlenk line techniques.[58] *Diethyl ether* was dried over sodium wire; *THF* was dried over sodium benzophenone ketyl and was distilled; *acetonitrile* was dried over calcium hydride and distilled; *toluene* was dried over P_2O_5 and distilled. *Light petroleum* refers to the fraction boiling between 30-40 °C. *Methyl-lithium* (Aldrich) was used as a 1.4 M solution in diethyl ether and *butyl-lithium* (Aldrich) was used as a 2.5 M solution in hexanes.

Diisopropylamine was dried over calcium hydride and distilled and was stored over molecular sieves.

Chromatography was performed on silica (Merck 40-60 μm) and filtrations were performed on deactivated basic alumina (Brockmann grade 4).

Melting points were determined using a Gallenkamp capillary melting point apparatus and are uncorrected.

Elemental analyses were performed by Butterworth Laboratories and City University Chemistry Department.

I.r. spectra were recorded using a Perkin Elmer 580B instrument and are calibrated against a polystyrene standard at 1 603 cm^{-1}.

^1H n.m.r. spectra were recorded using a Perkin Elmer R34 and Bruker WH400 instruments operating at 220 and 400 MHz respectively.

^{13}C n.m.r. spectra were recorded using a Bruker WH400 instrument operating at 100.62 MHz.

All chemical shifts are quoted in ppm relative to a TMS standard.

^2H n.m.r. spectra were recorded using a Bruker WH400 instrument operating at 62.42 MHz. All chemical shifts are quoted in ppm relative to an HOD standard.

E.i. mass spectra were recorded using a Kratos MS 80 instrument operating at 70 eV.

F.a.b. mass spectra were recorded using a Kratos MS 80 instrument with *m*-nitrobenzylalcohol as a matrix.

Preparation of 2-methyl-1,4-diphenyl-1-azabuta-1,3-diene **58.**

1-Oxadiene **59** (7.30 g, 0.05 mol) was dissolved in benzene (25 ml) and stirred with a catalytic quantity of dry zinc chloride (1 g, 7.33 mmol). Aniline (4.65 g, 0.05 mol) was added slowly and the resulting mixture was heated under reflux until a stoichiometric quantity of water had been collected in a Dean and Stark trap. The solvent was removed under reduced pressure to yield an orange/brown oil. This oil was crystallised and recrystallised from aqueous ethanol to yield 1-azadiene **58** as yellow crystals (1.74 g, 16 %), (Found: C, 86.81; H, 7.02; N, 6.18. $C_{16}H_{15}N$ requires C, 86.83; H, 6.83; N, 6.32 %); $\nu_{max.}$ (nujol) 1 603w (C=C) and 1 590m cm^{-1} (C=N); δ_H (220 MHz; $CDCl_3$) 2.08-2.46 (3H, m, C*H*$_3$), and 6.70-7.70 (12 H, m, Aryl-*H* and PhC*H*=C*H*); *m/z* (e.i.) 221 (M^+, 61 %) 220 (100 M-H).

Preparation of (2-methyl-1,4-diphenyl-1-azabuta-1,3-diene)tricarbonyliron(0) **57.**

Diironnonacarbonyl (1.30 g, 3.57 mmol) and 2-methyl-1,4-diphenyl-1-azabuta-1,3-diene **58** (0.79 g, 3.57 mmol) were added to toluene (25 ml) and the resulting mixture stirred at 40 °C for 3.0 h under an atmosphere of nitrogen. The red mixture produced was filtered and the solvent removed from the filtrate under reduced pressure to yield a dark red oil which was crystallised from *n*-heptane. A solution of the product in diethyl ether was filtered through a plug of alumina and the solvent removed from the filtrate under reduced pressure to yield fine orange/red crystals of complex **57** (0.51 g, 40 %), m.p. 129-130 °C (Found: C, 62.98; H, 4.16; N, 3.79. $C_{19}H_{15}FeNO_3$ requires C, 63.18; H, 4.18; N, 3.87 %); $\nu_{max.}$ (hexane) 2 060vs (C≡O), 1 995vs (C≡O), and 1 983vs cm^{-1} (C≡O); δ_H (220 MHz; $CDCl_3$) 2.42 (3H, s, C*H*$_3$), 3.20 (1H, d, J = 10 Hz, PhC*H*=CH), 5.60 (1H, d, J = 10 Hz, PhCH=C*H*), and 6.70-7.50 (10H, m, 2xAryl-*H*); δ_C (100.62 MHz; $CDCl_3$) 16.5 (*C*H$_3$), 59.7 (C_4), 71.3 (C_3), 124.1 (C_2), 121.4, 123.0, 126.5, 126.6, 128.5, 128.6, 139.3, and 149.8 (Aromatics); *m/z* (f.a.b.) 362 (M^++1, 14 %), 333 (48, M-CO), 305 (50, M-2CO), and 277 (100, M-3CO).

Reaction of methyl-lithium with (2-methyl-1,4-diphenyl-1-azabuta-1,3-diene)tricarbonyliron(0) **57.**

Methyl-lithium (0.71 ml, 1.00 mmol) was added to a solution of (2-methyl-1,4-diphenyl-1-azabuta-1,3-diene)tricarbonyliron(0) **57** (0.18 g, 0.50 mmol) in diethyl ether (10 ml) at -78 °C. After stirring the solution at -78 °C for 6.5 h under an atmosphere of nitrogen the resulting orange/brown solution was quenched with 2-bromo-2-methylpropane (1.37 g, 10.00 mmol) and allowed to warm to room temperature over 0.5 h. The dark brown mixture was filtered through a plug of alumina to remove the iron residues and the solvent was removed under reduced pressure to yield an orange/brown oil. This oil was chromatographed on silica using light petroleum/diethyl ether (4:1) as the eluent to yield a straw coloured liquid which was identified as 2,5-dimethyl-1,3-diphenylpyrrole **60** by comparison of its ^{1}H n.m.r. and mass spectra with those of an authentic sample (0.09 g, 73 %), δ_H (220 MHz; $CDCl_3$) 2.08 (3H, s, C*H*$_3$), 2.16 (3H, s, C*H*$_3$), 6.16 (1H, s, H-4), and 7.20-7.50 (10H, m, 2xAryl-*H*); *m/z* (e.i.) 247 (M^+, 100 %).

Preparation of (2-methyl-4-phenyl-1-oxabuta-1,3-diene)tricarbonyliron(0) **6.**

Diironnonacarbonyl (2.60 g, 7.14 mmol) and 2-methyl-4-phenyl-1-oxabuta-1,3-diene **59** (0.52 g, 3.57 mmol) were dissolved in diethyl ether and heated at 34 °C for 18.0 h under an atmosphere of nitrogen. The dark mixture produced was filtered through a plug of alumina to remove the iron residues and the solvent removed under reduced pressure. The dark red oil produced was chromatographed on silica using light petroleum/ethyl acetate (15:1) as the eluent to yield complex **6** as deep red crystals (0.79 g, 77 %), m.p. 87-89 °C, (Lit.,[23] 88-89 °C) ν_{max} (cyclohexane) 2 076s (C≡O), 2 013s (C≡O), and 1 990s cm^{-1} (C≡O), [Lit.,[23] (cyclohexane) 2 060s (C≡O), 2 005s (C≡O), and 1 985s cm^{-1} (C≡O)]; δ_H (220 MHz; $CDCl_3$) 2.55 (3H, s, C*H*$_3$), 3.12 (1H, d, J = 9 Hz, PhC*H*=CH), 6.06 (1H, d, J = 9 Hz, PhCH=C*H*), and 7.15-7.40 (5H, m, Aryl-*H*), [Lit.,[23] ($CDCl_3$) 2.05 (3H, s, C*H*$_3$), 3.30 (1H, d, J = 9 Hz, PhC*H*=CH), 6.02 (1H, d, J = 9 Hz, PhCH=C*H*), and 7.27 (5H, m, Aryl-*H*)].

The synthesis of 3-phenylhexane-2,5-dione **54.**

To a solution of **6** (0.14 g, 0.49 mmol) in diethyl ether (20 ml) at -78 °C was added methyl-lithium (0.52 ml, 0.73 mmol) and the resulting solution was stirred at -78 °C for 6.5 h under an atmosphere of nitrogen. The reaction was quenched using 2-bromo-2-methylpropane (1.00 g, 7.30 mmol) as a proton source and allowed to warm up to room temperature for 0.5 h to give a dark mixture. This mixture was filtered through a plug of alumina to remove the iron residues and the solvent was removed under reduced pressure to yield a brown oil. This oil was chromatographed on silica using light petroleum/diethyl ether (2:1) as the eluent to yield **54** as a straw coloured liquid. (0.07 g, 75 %), $\nu_{max.}$ ($CHCl_3$) 3 060, 3 025, 2 930, 1 715 (C=O)s, 1 604, 1 497, 1 456, 1 420, 1 400, 1 360, 1 236, 1 226, 1 160, 1 030, 748, and 702 cm^{-1} [Lit., [36](neat) 3 060, 3 030, 2 910, 1 715 (C=O)s, 1 700, 1 601, 1 493, 1 455, 1 416, 1 396, 1 364, 1 230, 1 214, 1 154, 1 028, 750, and 698 cm^{-1}]; δ_H (220 MHz; $CDCl_3$) 2.13 (3H, s, CH_3), 2.17 (3H, s, CH_3), 2.57 (1H, dd, J = 18 and 4 Hz, one H of CH_2CO), 3.45 (1H, dd, J = 18 and 10 Hz, one H of CH_2CO), 4.25 (1H, dd, J = 10 and 4 Hz, PhC*H*), and 7.20-7.40 (5H, m, Aryl-*H*), [Lit., [36] δ_H ($CDCl_3$) 2.12 (3H, s, CH_3), 2.16 (3H, s, CH_3), 2.57 (1H, dd, J = 18 and 4 Hz, one H of CH_2CO), 3.44 (1H, dd, J = 18 and 10 Hz, one H of CH_2CO), 4.22 (1H, dd, J = 10 and 4 Hz, PhC*H*), and 7.20-7.40 (5H, m, Aryl-*H*)].

Reaction of 3-phenylhexane-2,5-dione **54** *with aniline.*

3-Phenylhexane-2,5-dione **54** (0.050 g, 0.263 mmol) was added to aniline (0.024 g, 0.260 mmol) and the mixture heated at 150 °C for 5.5 h to yield a dark brown oil. The oil was chromatographed on silica using light petroleum/diethyl ether (4:1) as the eluent to yield 2,5-dimethyl-1,3-diphenylpyrrole **60** as a straw coloured liquid (0.042 g, 65 %), b.p. 232-235 °C @ 763 mmHg (Found: *m/z* 247.1352. $C_{18}H_{17}N$ requires 247.1361); δ_H (220 MHz; $CDCl_3$) 2.08 (3H, s, CH_3), 2.16 (3H, s, CH_3), 6.16 (1H, s, H-4), and 7.20-7.50 (10H, m, 2xAryl-*H*); δ_C (100.62 MHz; $CDCl_3$)

12.1, 12.7 (2xCH_3), 106.5 (C_4), 121.0 (C_3), 125.0 (C_2), 128.5 (C_5), 124.9, 127.6, 127.7, 128.1, 128.3, 129.0, 137.3, and 138.8 (2xPh); *m/z* (e.i.) 247 (M^+, 100 %).

Synthesis of 1,4-diphenyl-1-azabuta-1,3-diene **29.**

Aniline (4.65 g, 0.05 mol) was added to 1-oxadiene **66** (6.60 g, 0.05 mol) at 0 °C and the resulting mixture stirred for 5 min. The yellow solid produced was dissolved in diethyl ether (20 ml) and the solution was dried over magnesium sulphate. The solvent was removed under reduced pressure to yield a yellow solid which was recrystallised from ethanol to give azadiene **29** as pale yellow crystals (9.30 g, 90 %), m.p. 108-109 °C $\nu_{max.}$ (nujol) 1 626m (C=C) and 1 578m cm^{-1} (C=N), [Lit.,[17] 1 621 (C=C) and 1 571m cm^{-1} (C=N)]; δ_H (220 MHz; $CDCl_3$) 7.10-7.60 (12H, m, Aryl-*H* and PhC*H*=C*H*), and 8.28 (1H, m, *H*C=N-), [Lit.,[17] 7.00-7.45 (12H, m, Aryl-*H* and Ph*H*C=C*H*), and 8.12 (1H, q, *H*C=N-)].

Synthesis of (1,4-diphenyl-1-azabuta-1,3-diene)tricarbonyliron(0) **28.**

Diironnonacarbonyl (1.30 g, 3.57 mmol) and 1,4-diphenyl-1-azabuta-1,3-diene (0.74 g, 3.57 mmol) were stirred in toluene (20 ml) and heated at 50 °C for 2.0 h under an atmosphere of nitrogen to yield a dark red mixture. This mixture was filtered to remove the iron residues and the solvent removed under reduced pressure to yield dark red gum. This gum was chromatographed on silica using light petroleum/diethyl ether (7:3) as the eluent to yield complex **28** as a dark red crystalline solid (0.50 g, 40 %), m.p. 108-109 °C, (Lit.,[17] 108.5-109.5 °C) $\nu_{max.}$ (cyclohexane) 2 060s (C≡O), 2 001s (C≡O) and 1 991s cm^{-1}(C≡O), [Lit.,[38] 2 063 (C≡O), 2 003 (C≡O), and 1 991 cm^{-1} (C≡O)]; δ_H (220 MHz; $CDCl_3$), 3.44 (1H, d, J = 10 Hz, PhC*H*=CH), 5.58 (1H, dd, J = 10 and 3 Hz, PhCH=C*H*CH), and 6.90-7.80 (11H, m, 2xAryl-H and N=C*H*), [Lit.,[17] (100 MHz; $CDCl_3$) 3.35 (1H, broad, PhC*H*=CH), and 5.65 (1H, broad, PhCH=C*H*CH)]; *m/z* (f.a.b.) 348 (M^++1, 22%), 319 (13, M-CO), 291 (19, M-2CO), and 263 (100, M-3CO).

Reaction of methyl-lithium with (1,4-diphenyl-1-azabuta-1,3-diene)tricarbonyliron (0) **28**.

Methyl-lithium (0.74 ml, 1.00 mmol) was added to a solution of (1,4-diphenyl-1-azabuta-1,3-diene)tricarbonyliron(0) **28** (0.18 g, 0.52 mmol) in diethyl ether (15 ml) at -78 °C and the resulting orange solution stirred at -78 °C for 6.5 h under an atmosphere of nitrogen. The reaction was quenched with 2-bromo-2-methylpropane (0.69 g, 5.0 mmol) and allowed to warm to room temperature over 0.5 h. The resulting dark-brown mixture was filtered through a plug of alumina to remove the iron residues and the solvent removed under reduced pressure to yield a dark brown oil. The oil was chromatographed on silica using light petroleum/diethyl ether (9:1) as the eluent to yield a white crystalline solid which was identified as amine **67** by comparison of its ^{1}H n.m.r., i.r., and mass.spectra with those of an authentic sample (0.08 g, 69 %), m.p 48-50 °C $\nu_{max.}$(hexane) 3 424w (NH) and 1 605m cm^{-1} (C=C); δ_H (220 MHz; $CDCl_3$) 1.37 (3H, d, *J* = 7 Hz, C*H*$_3$), 3.67 (1H, broad,s, N*H*), 4.15 (1H, m, C*H*CH$_3$), 6.23 (1H, dd, *J* = 7 and 11 Hz, C*H*=CHPh), and 6.50-7.50 (11H, m, PhC*H*=CH and 2xAryl-*H*).

Reaction of methyl-lithium with 1,4-diphenyl-1-azabuta-1,3-diene **29**.

Methyl-lithium (2.14 ml, 3.00 mmol) was added to a solution of 1,4-diphenyl-1-azabuta-1,3-diene **29** (0.30 g, 1.45 mmol) in diethyl ether (30 ml) at -78 °C and the resulting solution stirred at -78 °C for 6.5 h under a nitrogen atmosphere. The reaction was quenched with 2-bromo-2-methylpropane (2.00 g, 14.5 mmol) and allowed to warm to room temperature over 0.5 h. The reaction mixture was filtered through a plug of alumina and the solvent removed under reduced pressure to yield a yellow oil. The oil was chromatographed on silica using diethyl ether/light petroleum (9:1) as the eluent to yield amine **67** as white crystals (0.28 g, 87 %), m.p. 49-50 °C (Found: C, 85.80; H, 7.82; N, 6.05. $C_{16}H_{17}N$ requires C, 86.05; H, 7.68; N, 6.27 %); $\nu_{max.}$(hexane) 3 420w (NH) and 1 605m cm^{-1} (C=C); δ_H (220 MHz; $CDCl_3$)

1.38 (3H, d, J = 7 Hz, C*H*$_3$), 3.68 (1H, broad s, N*H*), 4.15 (1H, m, C*H*CH$_3$), 6.23 (1H, dd, J = 7 and 11 = Hz, PhCH=C*H*CH), and 6.50-7.50 (11H, m, PhC*H*=CH and Aryl-*H*); δ_C (100.62 MHz; $CDCl_3$) 21.9 (*C*H$_3$), 50.7 (*C*HCH$_3$), 113.3, 117.2, 126.2, 127.2, 128.4, 129.0, 129.1, 133.1, 136.8, and 147.3 (Aromatics and PhC*H*=*C*H); *m/z* (e.i.) 223 (M^+, 30 %), 208 (18, M-CH$_3$), and 131 (100, M-NHPh).

***Addition of dimethyl-lithium cuprate to (1,4-diphenyl-1-azabuta-1,3-diene)tricarbonyliron(0)* 28.**

To a suspension of cuprous iodide (0.07 g, 0.37 mmol) in diethyl ether (5 ml) at -23 °C was added methyl-lithium (0.54 ml, 0.74 mmol) to yield a bright yellow suspension which faded to a pale yellow solution on final addition of methyl-lithium. This solution was stirred for 0.5 h under an atmosphere of nitrogen and then cooled to -78 °C.

To the cuprate was added a solution of complex **28** (0.090 g, 0.26 mmol) in diethyl ether (10 ml) and the resulting solution was stirred at -78 °C for 6.5 h under an atmosphere of nitrogen. The reaction was quenched using 2-bromo-2-methylpropane (0.46 g, 3.80 mmol) as a proton source and allowed to warm up to room temperature for 0.5 h to yield a dark mixture. This mixture was filtered through a plug of alumina to remove the solid residues and the solvent was removed under reduced pressure to give an orange/brown oil. Chromatography of this oil on silica using light petroleum/diethyl ether (9:1) as the eluent led to isolation of white crystals identified as amine **67** by comparison of their ^{1}H n.m.r. and i.r. spectra with data from an authentic sample (0.04 g, 69 %), m.p. 48-50 °C ν_{max}.(hexane) 3 418w (NH) and 1 605m cm^{-1} (C=C); δ_H (220 MHz; $CDCl_3$) 1.38 (3H, d, J = 7 Hz, C*H*$_3$), 3.68 (1H, broad s, N*H*), 4.15 (1H, m, C*H*CH$_3$), 6.25 (1H, dd, J = 7 and 11 Hz, C*H*=CHPh), and 6.50-7.50 (11H, m, CH=C*H*Ph and Aryl-H).

Preparation of 1-benzyl-4-phenyl-1-azabuta-1,3-diene **69.**

Benzylamine (1.07 g, 10.00 mmol) was added to 1-oxadiene **66** (1.32 g, 10.00 mmol) at 0 °C and the resulting mixture stirred for 15 min. The yellow oil produced was dissolved in diethyl ether (20 ml) and dried over magnesium sulphate. The solvent was removed under reduced pressure to yield a yellow oil which crystallised on standing at -20 °C for 12 h. Recrystallisation from diethyl ether at -78 °C yielded azadiene **69** as pale yellow crystals (1.77 g, 80 %), m.p. 27-28 °C (Found: C, 86.80; H, 6.94; N, 6.58. $C_{16}H_{15}N$ requires C, 86.83; H, 6.84; N, 6.33 %); $\nu_{max.}$ (hexane) 1 635s (C=N) and 1 620w cm^{-1} (C=C); δ_H (220 MHz; $CDCl_3$) 4.70 (2H, s, CH_2), 6.90-7.60 (12H, m, PhC*H*=C*H* and Aryl-*H*), and 8.17 (1H, m, *H*C=N-); δ_C (100.62 MHz; $CDCl_3$) 65.1 (CH_2), 126.8, 127.0, 127.9, 128.0, 128.4, 128.6, 129.0, 135.5, 139.0, (Aromatics and C_3), 141.8 (C_4), and 163.2 (C_2); *m/z* (e.i.) 221 (M^+, 41 %) and 91 (100, C_7H_7).

Preparation of (1-benzyl-4-phenyl-1-azabuta-1,3-diene)tricarbonyliron(0) **68.**

Diironnonacarbonyl (1.30 g, 3.57 mmol) and 1-benzyl-4-phenyl-1-azabuta-1,3-diene **69** (0.79 g, 3.57 mmol) were added to toluene (20 ml) and heated at 45 °C for 2.0 h under an atmosphere of nitrogen to yield a deep red mixture. The mixture was filtered through a plug of alumina to remove the iron residues and the solvent removed under reduced pressure to give a deep red gum. The gum was identified as (1-benzyl-4-phenyl-1-azabuta-1,3-diene)tricarbonyliron(0) **68** on the basis of its ^1H n.m.r. spectrum, δ_H (220 MHz; $CDCl_3$) 3.09 (1H, d, J = 10 Hz, PhC*H*=CH), 3.47 (1H, d, J = 15 Hz, 1H of PhCH_2N=), 3.87 (1H, d, J = 15 Hz, 1H of PhCH_2N=), 5.55 (1H, dd, J = 3 and 10 Hz, PhCH=C*H*), 6.70 (1H, d, J = 3 Hz, *H*C=N-), and 7.00-7.50 (10H, m, Aryl-*H*).

Reaction of methyl-lithium with (1-benzyl-4-phenyl-1-azabuta-1,3-diene)tricarbonyliron(0) **68.**

A solution the crude **68** was used in the second stage of the reaction without further purification. Methyl-lithium (5.1 ml, 7.14 mmol) was added to a solution of crude **68** in diethyl ether (30 ml) at -23 °C and the resulting solution stirred at -23 °C for 2.0 h under an atmosphere of nitrogen to yield a brown mixture. After quenching with 2-bromo-2-methylpropane (9.78 g, 71.4 mmol), the mixture was allowed to warm up to room temperature and filtered through a plug of alumina and the solvent removed under reduced pressure to leave a brown gum. The gum was chromatographed on silica using light petroleum/diethyl ether (4:1) as the eluent to yield 1-benzyl-2-methyl-3-phenylpyrrole **70** as pale yellow crystals (0.44 g, 50 %), m.p. 53.5-54.5 °C (Found: *m/z* 247.1356. $C_{18}H_{17}N$ requires 247.1361); δ_H (220 MHz; $CDCl_3$) 2.37 (3H, s, CH_3), 5.11 (2H, s, CH_2), 6.37 (1H, d, J = 3 Hz, H-4), 6.73 (1H, d, J = 3 Hz, H-5), and 7.00-7.60 (10H, m, Aryl-*H*); δ_C (100.62 MHz; $CDCl_3$) 10.7 (CH_3), 50.6 (CH_2), 107.6 (C_4), 120.4 (C_5), 122.5 (C_3), 125.1 (C_2), 125.0, 126.3, 127.3, 127.8, 128.2, 128.6, 137.4, and 138.0 (2xPh); *m/z* (e.i.) 247 (M^+, 49 %) and 91 (100, C_7H_7).

Preparation of 4-phenyl-1-(1-phenylethyl)-1-azabuta-1,3-diene **71.**

1-Phenylethylamine (2.42 g, 20.00 mmol) was added to 1-oxadiene **66** (2.64 g, 20.00 mmol) at 0 °C and the resulting mixture stirred at 0 °C for 5 min to yield a yellow solid. The solid was dissolved in diethyl ether and the resulting solution dried over magnesium sulphate and the solvent was removed under reduced pressure. The resulting yellow oil was crystallised and recrystallised from diethyl ether and then dried *in vacuo* for 24 h to yield the azadiene **71** as pale yellow crystals (4.23 g, 90 %), m.p. 40-41 °C (Found: C, 86.96; H, 7.38; N, 6.12. $C_{17}H_{17}N$ requires C, 86.76; H, 7.28; N, 5.95 %); $\nu_{max.}$ (Nujol) 1 640s (C=N) and 1 620m cm^{-1} (C=C); δ_H (220 MHz; $CDCl_3$) 1.57 (3H, d, J = 7 Hz, CH_3), 4.43 (1H, q, J = 7 Hz, $CHCH_3Ph$), 6.80-7.60 (12H, m, Aryl-H and $PhCH{=}CH$), and 8.12 (1H, d, J = 9

Hz, *H*C=N-); δ_C (100.62 MHz; $CDCl_3$) 24.4 (CH*C*H$_3$Ph), 69.6 (*C*HCH$_3$Ph), 126.5, 126.8, 127.1, 128.2, 128.4, 128.7, 128.9, 135.6, 144.7 (Aromatics and C_3), 141.6 (C_4), and 161.2 (C_2); *m/z* (e.i.) 235 (M^+, 40 %), 220 (33, M-CH_3), and 105 (100, CHCH$_3$Ph).

Preparation of (4-phenyl-1-(1-phenylethyl)-1-azabuta-1,3-diene)tricarbonyliron(0) **72.**

Diironnonacarbonyl (1.30 g, 3.57 mmol) and 4-phenyl-1-(1-phenylethyl)-1-azabuta-1,3-diene **71** (0.84 g, 3.57 mmol) were added to toluene (20 ml) and stirred at 50 ^oC for 2.0 h under an atmosphere of nitrogen to yield a deep red mixture. The mixture was filtered and the solvent removed under reduced pressure to give a dark red oil which was chromatographed on silica using light petroleum/ethyl acetate (20:1) as the eluent to yield orange crystals of a 1:1 mixture of the two diastereoisomeric forms of complex **72** (0.70 g, 52 %), (Found: C, 64.18; H, 4.60; N, 3.82. $C_{20}H_{15}FeNO_3$ requires C, 64.02; H, 4.57; N, 3.73 %); $\nu_{max.}$ (hexane) 2 080vs (C≡O), 2 017vs (C≡O), and 1 985vs cm^{-1} (C=O); δ_H [diastereoisomer **72a**] (400 MHz; C_6D_6:$CDCl_3$, 1:1) 1.31 (3H, d, J = 6 Hz, CHC*H*$_3$Ph), 2.94 (1H, q, J = 6 Hz, C*H*CH$_3$Ph), 3.04 (1H, d, J = 9 Hz, PhC*H*=CH), 5.26 (1H, dd, J = 3 and 9 Hz, PhCH=C*H*), 6.39 (1H, d, J = 3 Hz, *H*C=N), and 7.00-7.30 (10H, m, Aryl-*H*), [diastereoisomer **72b**] (400 MHz; C_6D_6:$CDCl_3$, 1:1) 1.40 (3H, d, J = 6 Hz, CHC*H*$_3$Ph), 2.96 (1H, q, J = 6 Hz, C*H*CH$_3$Ph), 3.10 (1H, d, J = 9 Hz, PhC*H*=CH), 5.16 (1H, dd, J = 3 and 9 Hz, PhCH=C*H*), 6.24 (1H, d, J = 3 Hz, *H*C=N), and 7.00-7.30 (10H, m, Aryl-*H*); δ_C [diastereoisomer **72a**] (100.62MHz; C_6D_6:$CDCl_3$, 1:1) 29.1 (CH*C*H$_3$Ph), 61.0 (*C*HCH$_3$Ph), 68.8 (C_4), 72.7 (C_3), and 110.7 (C_2) (Aromatics not assigned), [diastereoisomer **72b**] (100.62 MHz; C_6D_6:$CDCl_3$, 1:1) 27.1 (CH*C*H$_3$Ph), 62.2 (*C*HCH$_3$Ph), 68.1 (C_4), 72.4 (C_3), and 111.6 (C_2) (Aromatics not assigned); *m/z* (f.a.b.) 376 (M^++1, 78 %), 347 (10, M-CO), 319 (51, M-2CO), and 291 (73, M-3CO).

Reaction of methyl-lithium with (4-phenyl-1-(1-phenylethyl)-1-azabuta-1,3-diene)tricarbonyliron(0) **72**.

Methyl-lithium (1.22 ml, 1.71 mmol) was added to a solution of complex **72** (0.32 g, 0.85 mmol) in diethyl ether (20 ml) and the resulting solution stirred at -40 °C for 4.0 h under an atmosphere of nitrogen to yield a dark orange mixture. The reaction was quenched with 2-bromo-2-methylpropane (2.34 g, 17.10 mmol) and allowed to warm to room temperature over 0.5 h. The mixture was filtered through a plug of alumina to remove the iron residues and the solvent removed under reduced pressure to yield a dark oil. The oil was chromatographed on silica using light petroleum/diethyl ether (4:1) as the eluent to yield the pyrrole **73** as an orange liquid (0.11 g, 50 %), b.p.195-200 °C @ 763 mmHg (Found: *m/z* 261.1513. $C_{19}H_{19}N$ requires 261.1517); δ_H (220 MHz; $CDCl_3$) 1.86 (3H, d, J = 9 Hz, CH(C*H*$_3$)Ph), 2.23 (3H, s, CC*H*$_3$), 5.40 (1H, q, J = 9 Hz, C*H*(CH$_3$)Ph), 6.43 (1H, d, J = 4 Hz, H-4), 6.95 (1H, d, J = 4 Hz, H-5), and 7.00-7.60 (10H, m, Aryl-H); δ_C (100.62 MHz; $CDCl_3$) 10.8 (C-*C*H$_3$), 22.3 (CH(*C*H$_3$)Ph), 55.1 (*C*H(CH$_3$)Ph), 107.4 (C_4), 116.6 (C_5), 122.4 (C_3), 125.2 (C_2), 124.9, 125.6, 127.0, 128.0, 128.1, 128.6, 137.4, and 143.5 (2xPh); *m/z* (e.i.) 261 (M^+, 15 %), 157 (25, M+1-CHCH$_3$Ph), and 105 (100, CHCH$_3$Ph).

Preparation of 4-methyl-1-(1-phenylethyl)-1-azabuta-1,3-diene **74**.

1-Phenylethylamine (2.42 g, 20.00 mmol) was added to 1-oxadiene **75** (1.40 g, 20.00 mmol) at 0 °C and stirred for 15 min to yield a yellow oil. The oil was dissolved in diethyl ether (10 ml) and the resulting solution dried over magnesium sulphate and the solvent was removed under reduced pressure to yield a yellow oil which was dried *in vacuo* for 24 h to give azadiene **74** as a pale yellow liquid (3.11 g, 90 %), b.p. 220-225 °C @ 14 mmHg (dec); (Found: *m/z* 173.1202. $C_{12}H_{15}N$ requires 173.1204); $\nu_{max.}$ (thin film) 1 660s (C=N) and 1 627m cm^{-1} (C=C); δ_H (220 MHz; $CDCl_3$) 1.53 (3H, d, J = 9 Hz, CHC*H*$_3$Ph), 1.87 (3H, d, J = 6 Hz, C*H*$_3$C=CH), 4.36 (1H, q, J = 6 Hz, C*H*CH$_3$Ph), 6.10-6.50 (2H, m, CH$_3$C*H*=C*H*),

7.20-7.60 (5H, m, Aryl-*H*), and 8.00 (1H, d, J = 10 Hz, *H*C=N-); δ_C (100.62 MHz; $CDCl_3$) 18.0 (C_4-CH_3), 24.3, ($CHCH_3Ph$), 69.2 ($CHCH_3Ph$), 126.3, 126.5, 128.1, 144.8 (Aromatics), 131.9 (C_3), 140.2 (C_4), and 161.0 (C_2); *m/z* (e.i.) 173 (M^+, 23 %), 158 (30, M-CH_3), and 105 (100, $CHCH_3Ph$).

Preparation of (4-methyl-1-(1-phenylethyl)-1-azabuta-1,3-diene)tricarbonyliron(0) **76.**

Diironnonacarbonyl (1.30 g, 3.57 mmol) and azadiene **74** (0.62 g, 3.57 mmol) were added to toluene (20 ml) and heated at 50 °C for 2.0 h under an atmosphere of nitrogen to yield a dark brown mixture. The mixture was filtered to remove the iron residues and the solvent removed under reduced pressure to give a dark oil identified as a 1:1 diastereoisomeric mixture of the unstable complex (4-methyl-1-(1-phenylethyl)-1-azabuta-1,3-diene)tricarbonyliron(0) **76** by its ^1H n.m.r. spectrum, δ_H (220 MHz; $CDCl_3$) 1.20-1.50 (12H, m, 4xCH_3), 1.53 (1H, m, CH_3CH=CH), 1.88 (1H, m, CH_3CH=CH), 2.95 (2H, m, $CH(CH_3)Ph$), 4.83 (1H, dd, J = 3 and 10 Hz, CH_3CH=C*H*), 4.93 (1H, dd, J = 3 and 10 Hz, CH_3CH=C*H*), 6.33 (1H, d, J = 3 Hz, *H*C=N-), 6.55 (1H, d, J = 3 Hz, *H*C=N-), and 7.10-7.60 (10H, m, Aryl-*H*).

Reaction of methyl-lithium with (4-methyl-1-(1-phenylethyl)-1-azabuta-1,3-diene)tricarbonyliron(0) **76.**

Crude **76** was dissolved in diethyl ether (20 ml), cooled to -23 °C and methyl-lithium (5.1 ml, 7.14 mmol) was added to the solution which was stirred at -23 °C for 2.0 h. After quenching with 2-bromo-2-methylpropane (9.78 g, 71.4 mmol) the resulting dark brown mixture was filtered through a plug of alumina to remove the iron residues and the solvent removed under reduced pressure to yield a dark brown oil which was chromatographed on silica using light petroleum/diethyl ether (7:2) as the eluent to give pyrrole **77** as white crystals (0.18 g, 25 %), m.p. 68-69 °C (Found: *m/z* 199.1362. $C_{14}H_{17}N$ requires 199.1361); δ_H (220 MHz; $CDCl_3$) 1.79 (3H, d, J =

8 Hz, $CHCH_3Ph$), 1.99 (3H, s, C_3CH_3), 2.04 (3H, s, C_2CH_3), 5.26 (1H, q, J = 8 Hz, $CHCH_3Ph$), 6.08 (1H, d, J = 3 Hz, H-4), 6.88 (1H, d, J = 3 Hz, H-5), and 7.20-7.50 (5H, m, Aryl-*H*); δ_C 100.62 MHz; $CDCl_3$) 9.6, 11.2 (2xCCH_3), 22.3 ($CHCH_3Ph$), 54.9 ($CHCH_3Ph$), 108.2 (C_4), 114.9 (C_3), 115.4 (C_5), 124.5 (C_2), 125.6, 126.9, 128.5, and 143.9 (Ph); *m/z* (e.i.) 199 (M^+, 58 %), 105 (100, $CHCH_3Ph$), and 95 (M+1-$CHCH_3Ph$).

Preparation of 3-methyl-4-phenyl-1-(1-phenylethyl)-1-azabuta-1,3-diene **79.**

1-Phenylethylamine (2.42 g, 20.00 mmol) was added to 1-oxadiene **78** (2.92 g, 20.00 mmol) and the resultant mixture stirred at 0 °C for 10 min to yield a yellow oil. The oil was dissolved in diethyl ether and the resulting solution dried over magnesium sulphate and the the solvent was removed under reduced pressure to yield a yellow oil which crystallised on standing. The crystals were recrystallised from diethyl ether to yield 1-azadiene **79** as pale yellow crystals (3.98 g, 80 %), m.p. 45-46 °C (Found: C, 86.45; H, 7.78; N, 5.44. $C_{18}H_{19}N$ requires C, 86.70; H, 7.68; N, 5.62 %); $\nu_{max.}$ (Nujol) 1 630s (C=N) and (C=C) cm^{-1}; δ_H (220 MHz; $CDCl_3$) 1.57 (3H, d, J = 5 Hz, $CHCH_3Ph$), 2.23 (3H, s, $CH{=}CCH_3$), 4.53 (1H, q, J = 5 Hz, $CHCH_3Ph$), 6.87 (1H, s, PhC*H*=C), 7.20-7.70 (10H, m, Aryl-*H*), and 8.18 (1H, s, *H*C=N-); δ_C (100.62 MHz; $CDCl_3$) 13.1 (C_3-CH_3), 24.9 ($CHCH_3Ph$), 69.0 ($CHCH_3Ph$), 126.3, 126.4, 127.2, 127.9, 128.0, 128.9, 136.4, 145.3 (aromatics), 136.9 (C_3), 138.3 (C_4), and 163.7 (C_2); *m/z* (e.i.) 249 (M^+, 69 %), 234 (18, M-CH_3), 144 (69, M-$PhCHCH_3$), and 105 (100, $PhCHCH_3$).

Addition of the stabilised anion derived from isobutyronitrile to 2-methyl-4-phenyl-1-oxabuta-1,3-diene)tricarbonyliron(0) **6.**

To a solution of diisopropylamine (0.303 g, 3.00 mmol) in THF (20 ml) at -78 °C was added butyl-lithium (1.20 ml, 3.00 mmol) and the resulting solution was stirred at -78 °C for 20 min under an atmosphere of nitrogen. Isobutyronitrile (0.207 g, 3.00

mmol) was added and the solution was stirred a further 20 min. To the pale yellow solution produced was added a solution of complex **6** (0.286 g, 1.00 mmol) in THF (20 ml) and the resulting orange solution was allowed to warm up to 20 °C and stirred at this temperature for 3.0 h to yield a brown solution. This solution was cooled to -78 °C and the reaction was quenched using trifluoroacetic acid (2.28 g, 20.00 mmol) and stirred at 20 °C for 1 h. The dark red mixture produced was poured onto saturated sodium carbonate solution (30 ml) and extracted using diethyl ether (3x20 ml). The combined organic layers were washed with saturated sodium chloride solution (30 ml) and dried over magnesium sulphate. The solvent was removed under reduced pressure to yield a dark red oil. This oil was chromatographed on silica using light petroleum/diethyl ether (2:1) as the eluent to yield a colourless oil which crystallised overnight at -20 °C. The grey crystals produced were recrystallised from a mixture of hexane and ethanol (20:1) to yield white crystals identified as hydroxynitrile **81** by comparison of their ^{1}H n.m.r., i.r., and mass spectra with data from an authentic sample (0.172 g, 80 %), m.p. 74-75 °C ν_{max} 3 618broad (OH) and 2 236w cm^{-1} (C≡N); δ_H (220 MHz; $CDCl_3$) 1.39 (3H, s, one CH_3 of $(CH_3)_2CCN$), 1.42 (1H, s, one CH_3 of $(CH_3)_2CCN$), 1.57 (3H, s, CH_3CO), 1.92 (1H, s, O*H*), 6.40 (1H, d, J = 17 Hz, PhCH=C*H*), 6.81 (1H, d, J = 17 Hz, PhC*H*=CH), and 7.30-7.60 (6H, m, Aryl-*H*); *m/z* 215 (M^+, 5.2 %) and 147 (100 , M-$(CH_3)_2CCN$).

Addition of the stabilised anion derived from isobutyronitrile to 2-methyl-4-phenyl-1-oxabuta-1,3-diene **59**.

To a solution of diisopropylamine (1.02 g, 10.08 mmol) in THF (50 ml) at -78 °C under an atmosphere of nitrogen was added butyl-lithium (4.03 ml, 10.08 mmol) and the resulting solution was stirred at -78 °C for 20 min. Isobutyronitrile (0.69 g, 10.08 mmol) was added and the solution stirred for a further 20 min. A solution of oxadiene **59** (0.49 g, 3.36 mmol) in THF (20 ml) was added and the resulting yellow solution was allowed to warm up to 20 °C and stirred at this temperature for 3.0 h. The yellow solution produced was cooled to -78 °C and the reaction was quenched using

trifluoroacetic acid (7.66 g, 67.20 mmol) and stirred at 20 °C for 1.0 h. The solution produced was poured onto saturated sodium carbonate solution (100 ml) and extracted using diethyl ether (3x40 ml). The combined organic extracts were washed with saturated sodium chloride solution (100 ml) and dried over magnesium sulphate. The solvent was removed under reduced pressure to yield a yellow oil. This oil was chromatographed on silica using light petroleum/diethyl ether (2:1) as the eluent to yield a colourless oil which crystallised overnight at -20 °C. These crystals were recrystallised from a mixture of hexane and ethanol (20:1) to yield the hydroxynitrile **81** (0.58 g, 80 %), m.p. 74-75 °C (Found: C, 78.12; H, 7.94; N, 6.17. $C_{14}H_{17}NO$ requires C, 78.10; H, 7.96; N, 6.51 %); $\nu_{max.}$ (CCl_4) 3 615broad (OH), and 2 238w cm^{-1} (C≡N); δ_H (220 MHz; $CDCl_3$) 1.40 (3H, s, one CH_3 of $(CH_3)_2CCN$), 1.42 (3H, s, one CH_3 of $(CH_3)_2CCN$), 1.58 (3H, s, CH_3CO), 1.90 (1H, s, O*H*), 6.40 (1H, d, J = 17 Hz, PhCH=C*H*), 6.81 (1H, d, J = 17 Hz, PhC*H*=CH), and 7.30-7.60 (5H, m, Aryl-*H*); δ_C (100.6 MHz; $CDCl_3$) 21.8 (CH_3), 22.3 (CH_3), 24.4 (CH_3C_3), 41.7 (C_2), 75.0 (C_3), 124.2 (C≡N), 126.5, 127.8, 128.5, 136.0 (Aromatics), 130.5 (C_4), and 130.6 (C_5); *m/z* (e.i.) 215 (M^+, 1 %) and 147 (100, M-$(CH_3)_2CCN$).

Addition of the stabilised anion derived from ethyl isobutyrate to (2-methyl-4-phenyl-1-oxabuta-1,3-diene)tricarbonyliron(0) **6**.

To a solution of diisopropylamine (0.303 g, 3.00 mmol) in THF (20 ml) at -78 °C was added butyl-lithium (1.20 ml, 3.00 mmol) and the resulting solution was stirred at -78 °C for 20 min under an atmosphere of nitrogen. Ethyl isobutyrate (0.348 g, 3.00 mmol) was added and the solution was stirred for a further 20 min at -78 °C. To pale yellow solution produced, a solution of complex **6** (0.286 g, 1.00 mmol) in THF (20 ml) was added and the reaction was allowed to warm up to 20 °C and stirred at this temperature for 3.0 h to yield a dark mixture. The reaction was cooled to -78 °C and was quenched using trifluoroacetic acid (2.28 g, 20.00 mmol) and allowed to warm up to 20 °C and was stirred at this temperature for 1.0 h. The resulting brown

mixture was poured onto saturated sodium carbonate solution (30 ml) and extracted using diethyl ether (3x30 ml). The combined organic extracts were washed with saturated sodium chloride solution (30 ml) and dried over magnesium sulphate. The solvent was removed under reduced pressure to yield a brown oil which was chromatographed on silica using light petroleum/diethyl ether (3:1) as the eluent to give off-white crystals which were recrystallised from hexane to yield white crystals identified as keto-ester **82** by comparison of their i.r. and ^1H n.m.r. spectra and melting point with data from an authentic sample (0.22 g, 84 %), m.p. 64-65 °C $\nu_{max.}$ (CCl_4) 1 740s (ester C=O), and 1 720s cm^{-1} (ketone C=O); δ_H (220 MHz; $CDCl_3$) 1.09 (3H, s, CH_3C), 1.14 (3H, s, CH_3C), 1.25 (3H, t, J = 7 Hz, CH_3CH_2), 2.00 (3H, s, CH_3CO), 2.71 (1H, dd, J = 17 and 4 Hz, one H of $CHCH_2$), 3.05 (1H, dd, J = 11 and 17 Hz, one H of $CHCH_2$), 3.61 (1H, dd, J = 11 and 4 Hz, $PhCHCH_2$), 4.14 (2H, t, J = 7 Hz, CH_2CH_3), and 7.10-7.50 (5H, m, Aryl -*H*).

Addition of the stabilised anion derived from ethyl isobutyrate to 2-methyl-4-phenyl-1-oxabuta-1,3-diene **59**.

To a solution of diisopropylamine (1.012 g, 10.0 mmol) in THF (25 ml) at -78 °C was added butyl-lithium (4.00 ml, 10.0 mmol) and the resulting solution was stirred at -78 °C for 20 min under an atmosphere of nitrogen, ethyl isobutyrate (1.16 g, 10.0 mmol) was added and the solution was stirred for a further 20 min at -78 °C. A solution of oxadiene **59** (0.49 g, 3.36 mmol) in THF (25 ml) was added and the resulting solution was allowed to warm up to 20 °C and was stirred at this temperature for 3.0 h. The reaction mixture was cooled to -78 °C and the reaction was quenched using trifluoroacetic acid (7.65 g, 67.11 mmol) and stirred at 20 °C for 1.0 h. The yellow solution produced was poured onto saturated sodium carbonate solution (100 ml) and extracted using diethyl ether (3x50 ml). The combined organic extracts were washed with saturated sodium chloride solution (50 ml) and dried over magnesium sulphate and the solvent removed under reduced pressure to yield a colourless oil which crystallised overnight at -20 °C. The off-white crystals produced

were recrystallised twice from hexane to yield the keto-ester **82** as white crystals (0.75 g, 85 %), m.p. 64-65 °C (found: C, 73.17; H, 8.46. $C_{16}H_{22}O_3$ requires C, 73.26; H, 8.46 %); $\nu_{max.}$ (CCl_4) 1 735s (Ester C=O), and 1 720s cm^{-1} (Ketone C=O); δ_H (220 MHz; $CDCl_3$) 1.09 (3H, s, CH_3C), 1.14 (3H, s, CH_3C), 1.24 (3H, t, J = 7 Hz, CH_3CH_2), 2.00 (3H, s, CH_3CO), 2.70 (1H, dd, J = 17 and 4 Hz, one H of $CHCH_2$), 3.05 (1H, dd, J =11 and 17 Hz, one H of $CHCH_2$), 3.60 (1H, dd, J = 11 and 4 Hz, $PhCHCH_2$), 4.15 (2H, q, J =7 Hz, CH_3CH_2), and 7.10-7.40 (5H, m, Aryl-*H*); δ_C (100.62 MHz; $CDCl_3$) 14.0 (CH_3CH_2), 21.3 (CCH_3), 24.4 (CCH_3), 30.2 (C_5), 45.0 (C_4), 45.8 (C_2), 47.2 (CH_2CH_3), 60.5 (C_3), 177.0 (C=O ester), and 206.9 (C=O ketone); *m/z* (e.i.) 262 (M^+, 4.9 %), and 147 (100, M-$(CH_3)_2CCO_2Et$).

Addition of the stabilised anion derived from isobutyronitrile to (1,4-diphenyl-1-azabuta-1,3-diene)tricarbonyliron(0) **28**.

To solution of diisopropylamine (0.303 g, 3.00 mmol) in THF (20 ml) at -78 °C was added butyl-lithium (1.20 ml, 3.00 mmol) and the resultant solution was stirred at -78 °C for 20 min. Isobutyronitrile (0.207 g, 3.00 mmol) was added and the solution stirred at -78 °C for further 20 min to yield a pale yellow solution. To this solution at -78 °C was added a solution of **28** (0.347 g, 1.00 mmol) in THF (20 ml) and the resulting solution was allowed to warm up to 20 °C and stirred at this temperature for 3.0 h. The reaction mixture was cooled to -78 °C and the reaction was quenched using trifluoracetic acid (2.28 g, 20.00 mmol) as a proton source to yield a dark orange mixture which was allowed to warm up to 20 °C and stirred at this temperature for 1.0 h. The dark mixture produced was poured onto saturated sodium carbonate solution (30 ml) and extracted using diethyl ether (3x30 ml). The combined extracts were washed with saturated sodium chloride solution (30 ml) and dried over magnesium sulphate. The solvent was removed under reduced pressure to yield a yellow oil. This oil was chromatographed on silica using light petroleum and diethyl ether (2:1) as the eluent to yield amine **83** as a colourless oil (0.22 g, 80 %), b.p.

160-163 °C @ 1 mmHg (Found: *m/z* 276.1630. $C_{19}H_{20}N_2$ requires 276.1626); $\nu_{max.}$ (liquid film) 3 380m (NH), and 2 238w cm^{-1} (C≡N); δ_H (220 MHz; $CDCl_3$) 1.45 (3H, s, one CH_3 of $(CH_3)_2CCN$), 1.52 (3H, s, one CH_3 of $(CH_3)_2CCN$), 3.92 (2H, broad, =CHC*H*NH), 3.92 (D_2O, 1H, d, J = 7 Hz, =CHC*H*NH), 6.22 (1H, dd, J = 14 and 7 Hz, CH=C*H*CH), and 6.50-7.60 (11H, m, 2xAryl-*H* and PhC*H*=CH); δ_C (100.62 MHz; $CDCl_3$) 24.4 ($2CH_3$), 38.2 (C_2), 62.9 (C_3), 114.0, 123.5 (C≡N), 118.5, 125.5, 126.5, 128.0, 128.5, 129.3, 134.0, 135.8, and 146.5 (Aromatics and PhCH=CH); *m/z* (e.i.) 276 (M^+, 3.0 %) and 208 (100, M-$(CH_3)_2CCN$).

Addition of the stabilised anion derived from isobutyronitrile to 1,4-diphenyl-1-azabuta-1,3-diene **29.**

To a solution of diisopropylamine (1.02 g, 10.08 mmol) in THF (50 ml) of -78 °C was added butyl-lithium (4.03 ml, 10.05 mmol) and the resulting solution was stirred at -78 °C for 20 min. Isobutyronitrile (0.69 g, 10.00 mmol) was added and the solution stirred at -78 °C for a further 20 min. To the pale yellow solution produced was added a solution of **29** (0.70 g, 3.38 mmol) in THF (20 ml) and the reaction mixture was allowed to warm up to 20 °C and was stirred at this temperature for 3.0 h under an atmosphere of nitrogen. The reaction was cooled to -78 °C and quenched using trifluoroacetic acid (7.71 g, 67.63 mmol) as a proton source and allowed to warm up to 20 °C and was stirred at this temperature for 1.0 h. The resulting yellow mixture was poured onto saturated sodium carbonate solution (100 ml) and extracted using diethyl ether (3x40 ml). The combined organic extracts were washed with saturated sodium chloride solution (100 ml) and dried over magnesium sulphate and the solvent was removed under reduced pressure to yield a yellow oil. Chromatography of this oil on silica using light petroleum/diethyl ether (2:1) as the eluent led to isolation of a colourless oil identified as amine **83** by comparison of its ^1H n.m.r., ir., and mass spectra with data from an authentic sample (0.75 g, 80 %), b.p. 160-164 °C @ 1 mmHg $\nu_{max.}$ (liquid film) 3 378m (NH) and 2 238w cm^{-1}

(C≡N); δ_H (220 MHz; $CDCl_3$) 1.45 (3H, s, one CH_3 of $(CH_3)_2CCN$), 1.52 (3H, s, one CH_3 of $(CH_3)_2CCN$), 3.92 (2H, broad, =CHC*H*NH), 3.92 (D_2O, 1H, d, J = 7 Hz, =CHC*H*NH), 6.23 (1H, dd, J = 14 and 7 Hz, CH=C*H*CH), and 6.50-7.60 (11H, m, 2xAryl-*H* and PhC*H*=CH); *m/z* 276 (M^+, 1 %) and 208 (100, M-$(CH_3)_2CCN$).

Preparation of (2-isobutyl-4-phenyl-1-oxabuta-1,3-diene)tricarbonyliron(0) **95.**

Diironnonacarbonyl (2.60 g, 7.14 mmol) and 2-isobutyl-4-phenyl-1-oxabuta-1,3-diene **96** (0.67 g, 3.57 mmol) were stirred in diethyl ether at 34 °C for 18.0 h under an atmosphere of nitrogen. The dark mixture produced was filtered through a plug of alumina to remove the iron residues and the solvent removed under reduced pressure. The dark red oil produced was chromatographed on silica using light petroleum/ethyl acetate (10:1) as the eluent to yield complex **95** as deep red crystals (0.70 g, 60 %), m.p. 87-88 °C (dec), (Lit., [29] 88 °C); $\nu_{max.}$ (cyclohexane) 2 073s (C≡O), 2 015s (C≡O), and 1 987s cm^{-1} (C≡O), [Lit., [29] 2 080 (C≡O), 2 020 (C≡O), and 1 990 cm^{-1} (C≡O)]; δ_H (220 MHz; $CDCl_3$) 1.05 (3H, d, J = 6 Hz, CHC*H*$_3$), 1.09 (3H, d, J = 6 Hz, CHC*H*$_3$), 2.10 (1H, m, C*H*$(CH_3)_2$), 2.45 (1H, dd, J = 15 and 6 Hz, one H of C*H*$_2$CH), 3.00 (1H, dd, J = 15 and 6 Hz, 1H of C*H*$_2$CH), 3.15 (1H, d, J = 10 Hz, PhC*H*=CH), 6.06 (1H, d, J = 10Hz, PhCH=C*H*CO), and 7.10-7.50 (5H, m, Aryl-*H*), [Lit.,[29] ($CDCl_3$) 1.05 (3H, d, J = 6 Hz, CHC*H*$_3$), 1.10 (3H, d, J = 6 Hz, CHC*H*$_3$), 2.00-2.15 (1H, m, C*H*$(CH_3)_2$), 2.45 (1H, dd, J = 14 and 6 Hz, 1H of C*H*$_2$CO), 3.00 (1H, dd, J = 14 and 6 Hz, 1H of C*H*$_2$CO), 3.10 (1H, d, J = 9 Hz, PhC*H*=CH), 6.05 (1H, d, J = 9 Hz, PhCH=C*H*-CO) and 7.20-7.40 (5H, m, Aryl-*H*)].

Addition of the stabilised anion derived from isobutyronitrile to (2-isobutyl-4-phenyl-1-oxabuta-1,3-diene)tricarbonyliron(0) **95.**

To a solution of diisopropylamine (0.303 g, 3.00 mmol) in THF (20 ml) at -78 °C was added butyl-lithium (1.20 ml, 3.00 mmol) and the resulting solution was stirred

at -78 °C for 20 min under an atmopshere of nitrogen. Isobutyronitrile (0.207g, 3.00 mmol) was added and the solution stirred for a further 20 min at -78 °C. A solution of complex **95** (0.328 g, 1.00 mmol) in THF (20 ml) was added and the reaction was allowed to warm up to 20 °C and stirred at this temperature for 3.0 h to yield a red solution. The reaction was cooled to -78 °C and was quenched using trifluoroacetic acid (2.28 g, 20.00 mmol) as a proton source and allowed to warm up to 20 °C and was stirred at this temperature for 1.0 h to produce a dark mixture. This mixture was poured onto saturated sodium carbonate solution (20 ml) and was extracted with diethyl ether (3x30 ml). The combined organic layers were washed with saturated sodium chloride solution (50 ml) and dried over magnesium sulphate. Removal of the solvent under reduced pressure led to a brown oil which was chromatographed on silica using light petroleum/diethyl ether (2:1) as the eluent to yield a colourless oil identified as keto-nitrile **97** by comparison of its ^1H n.m.r. and i.r. spectra with those of an authentic sample (0.216 g, 84 %), b.p. 160-165 °C @ 1 mmHg $\nu_{max.}$ (Hexane) 2 238w (C≡N) and 1 720s cm^{-1} (C=O); δ_H (220 MHz; $CDCl_3$) 0.74 (3H, d, J = 7 Hz, $CHCH_3$), 0.77 (3H, d, J = 7 Hz, $CHCH_3$), 2.05 (1H, m, $CH(CH_3)_2$), 2.20 (2H, m, CH_2CO), 2.80-3.40 (3H, m, $CHCH_2CO$), and 7.20-7.50 (5H, m, Aryl-*H*).

Addition of the stabilised anion derived from isobutyronitrile to 2-isobutyl-4-phenyl-1-oxabuta-1,3-diene **96**.

To a solution of diisopropylamine (1.02 g, 10.08 mmol) in THF (50 ml) at -78 °C was added butyl-lithium (4.03 ml, 10.08 mmol) and the resulting solution was stirred at this temperature for 20 min under an atmosphere of nitrogen. Isobutyronitrile (0.69 g, 10.00 mmol) was added and the solution produced was stirred at -78 °C for a further 20 min. A solution of oxadiene **96** (0.63 g, 3.35 mmol) in THF (20 ml) was added and the resulting solution was allowed to warm up to 20 °C and was stirred at this temperature for 3.0 h. The resulting yellow solution was cooled to -78 °C and the reaction was quenched using trifluoroacetic acid as a proton source (7.64 g, 67.20

mmol) and allowed to stir at 20 °C for 1.0 h and was then poured onto saturated sodium carbonate solution (100 ml) and extracted using diethyl ether (3x50 ml). The combined organic extracts were washed with saturated sodium chloride solution (100 ml) and dried over magnesium sulphate and the solvent was removed under reduced pressure to give a yellow oil. This oil was kugelrohr distilled to yield the keto-nitrile **97** as a colourless oil (0.69 g, 80 %), b.p. 160-165 °C @ 1 mmHg (Found: *m/z* 257.1731. $C_{17}H_{23}NO$ requires 257.1780); ν_{max} (Hexane) 2 238w (C≡N), and 1 723s cm^{-1} (C=O); δ_H (220 MHz; $CDCl_3$) 0.74 (3H, d, *J* = 7 Hz, C*H*$_3$CH), 0.77 (3H, d, *J* = 7 Hz, C*H*$_3$CH), 1.14 (3H, s, one CH_3 of (C*H*$_3$)$_2$CCN), 1.42 (3H, s, one CH_3 of (C*H*$_3$)$_2$CCN), 2.02 (1H, m, C*H*(CH$_3$)$_2$), 2.20 (2H, m, C*H*$_2$CO), 2.80-3.20 (3H, m, CHC*H*$_2$CO), and 7.20-7.50 (5H, m, Aryl-*H*); δ_C (100.62 MHz; $CDCl_3$) 22.1 (*C*H$_3$CH), 22.2 (*C*H$_3$CH), 24.1 (*C*H$_3$C), 25.2 (*C*H$_3$C), 26.7 (C_7), 36.2 (C_2), 45.5 (C_6), 48.4 (C_4), 52.5 (C_3), 124.1 (C≡N), 127.4, 128.3, 128.6, 139.2 (Aromatics), and 207.5 (C=O); *m/z* (e.i.) 257 (M^+, 2.3 %), 200 (M-57), 85 (100, M-172), and 57 (96, M-200).

Reaction of sodium borohydride with (4-phenyl-1-(1-phenylethyl)-1-azabuta-1,3-diene)tricarbonyliron(0) **72**.

To sodium borohydride (0.10 g, 2.70 mmol) at 0 °C was added a solution of complex **72** (0.20 g, 0.53 mmol) in methanol (30 ml) and the resulting mixture was stirred at 0 °C for 3.0 h under an atmosphere of nitrogen to yield an orange mixture. This mixture was poured onto saturated sodium chloride solution (30 ml) and extracted using diethyl ether (3x20 ml). The combined organic extracts were washed with water and dried over magnesium sulphate. Removal of the solvent under reduced pressure led to isolation of an orange oil which was identified as the original complex **72** on the basis of its ^1H n.m.r. spectrum.

Reaction of sodium borohydride with (1,4-diphenyl-1-azabuta-1,3-diene)tricarbonyliron(0) **28.**

To sodium borohydride (0.15 g, 3.95 mmol) at 0 °C was added a solution of complex **28** (0.28 g, 0.80 mmol) in methanol (20 ml) and the resulting mixture was stirred at 0 °C for 3.0 h under an atmosphere of nitrogen. The resulting orange mixture was poured onto saturated sodium chloride solution (30 ml) and extracted using diethyl ether (3x30 ml). The combined organic extracts were washed with water (30 ml) and dried over magnesium sulphate and the solvent was removed under reduced pressure to yield an orange oil which was identified as the original complex **28** on the basis of its ^{1}H n.m.r. spectrum.

Reaction of sodium borohydride with 4-phenyl-1-(1-phenylethyl)-1-azabuta-1,3-diene **71.**

To sodium borohydride (0.58 g, 15.26 mmol) at 0 °C was added a solution of azadiene **71** (0.72 g, 3.06 mmol) in methanol (30 ml) and the resulting mixture was stirred at 0 °C for 3.0 h under an atmosphere of nitrogen to yield a yellow mixture. This mixture was poured onto saturated sodium chloride solution (50 ml) and extracted using diethyl ether (3x30 ml). The combined organic extracts were washed with water (50 ml) and dried over magnesium sulphate. The solvent was removed under reduced pressure to give a yellow oil. This oil was kugelrohr distilled and yielded amine **120** as a colourless oil (0.65 g, 90 %), b.p. 146-150 °C @ 1 mmHg (Found: C, 74.50; H, 7.32; N, 5.36. $C_{17}H_{20}NCl$ requires C, 74.57; H, 7.36; N, 5.12 %); $\nu_{max.}$ (liquid film) 3 338w (NH) and 1 603m cm^{-1} (C=C); δ_H (220 MHz; $CDCl_3$) 1.46 (3H, d, J = 8 Hz, $CHCH_3$), 3.32 (2H, m, CH_2CH=), 3.50 (1H, broad, N*H*), 3.95 (1H, q, J = 8 Hz, $CHCH_3$), 6.36 (1H, dt, J = 16 and 6 Hz, CH_2CH=CH), 6.52 (1H, d, J = 16 Hz, PhC*H*=CH), and 7.10-7.60 (10H, m, 2xAryl-*H*); δ_C (100.62 MHz; $CDCl_3$), 24.0 (CH_3CH), 49.3, (C_1), 57.3 ($HNCHCH_3$), 126.0, 126.4, 120.7, 127.0, 128.2, 128.3, 130.8, 136.9, and

145.2 (aromatics, C_2, and C_3); *m/z* 237 (M^+, 22 %), 222 (23.6, M-CH_3), 117 (100, M-122), and 105 (72.7, M-CH(CH_3)Ph).

Reaction of sodium borohydride with 1,4-diphenyl-1-azabuta-1,3-diene **29.**

To sodium borohydride (0.38 g, 10.00 mmol) at 0 °C was added a solution of azadiene **28** (0.41 g, 1.98 mmol) in methanol (40 ml) and the resulting solution was stirred at 0 °C for 3.0 h under an atmosphere of nitrogen to yield a yellow mixture. This mixture was poured onto saturated sodium chloride solution (50 ml) and was extracted using diethyl ether (3x40 ml). The combined organic extracts were washed with water and dried over magnesium sulphate and the solvent was removed under reduced pressure to yield a yellow oil which was kugelrohr distilled to give a colourless oil identified as amine **121** by comparison of its boiling point ^1H n.m.r. and i.r. spectra with data from an authentic sample (0.37 g, 89 %), b.p. 140-145 °C @ 1 mmHg ν_{max} (liquid film) 3 410broad (NH) and 1 603w cm^{-1} (C=C); δ_H (220 MHz; $CDCl_3$) 3.80 (1H, broad, N*H*), 3.95 (2H, d, J = 7, Hz, CH_2CH=), 6.35 (1H, dt, J = 18 and 7 Hz, CH=C*H*CH_2), and 6.60-7.60 (11H, m, 2xAryl-*H* and CH=C*H*Ph).

Reaction of lithium aluminium hydride with (1,4-diphenyl-1-azabuta-1,3-diene)tricarbonyliron (0) **28.**

To a suspension of lithium aluminium hydride (0.110 g, 2.89 mmol) in diethyl ether (5 ml) at 0 °C was added a solution of complex **28** (0.200 g, 0.58 mmol) in diethyl ether (20 ml) and the resulting mixture stirred at 0 °C for 3.0 h under an atmosphere of nitrogen. The reaction was quenched with methanol (0.92 g, 28.75 mmol) and allowed to warm up to room temperature for 1.0 h. The resulting solution was filtered through a plug of alumina to remove the solid residues and the solvent removed under reduced presure to yield a yellow oil. This oil was chromatographed on silica using light petroleum/diethyl ether (2:1) as the eluent to yield amine **122** as a colourless liquid (0.097 g, 80 %) b.p. 150-152 °C @ 1 mmHg (Found: 211.1360.

$C_{15}H_{17}N$ requires 211.1361); $\nu_{max.}$ (liquid film) 3 410broad (NH) and 1 604w cm^{-1}(C=C); δ_H (220 MHz; $CDCl_3$) 1.91 (2H, quintet, J = 9 Hz, $CH_2CH_2CH_2$), 2.21 (2H, t, J = 9 Hz, $PhCH_2CH_2$), 3.12 (2H, t, J = 9 Hz, $HNCH_2CH_2$), 3.40 (1H, broad, N*H*), and 6.50-7.50 (10H, m, 2xAryl-*H*); δ_C (100.62 MHz; $CDCl_3$) 30.8 (C_2), 33.1 (C_3), 43.1 (C_1), 112.51, 116.93, 125.70, 128.17, 128.98, 141.45, and 148.13 (Aromatics); *m/z* 211 (M^+, 27 %), 106 (100, M^+-$PhCH_2CH_2$), and 91 (20, M-120, C_7H_7).

Reaction of lithium aluminium hydride with 1,4-diphenyl-1-azabuta-1,3-diene **29.**

To a suspension of lithium aluminium hydride (0.38 g, 10.00 mmol) in diethyl ether (20 ml) at 0 °C was added a solution of **29** (0.41 g, 1.98 mmol) in diethyl ether (30 ml) and the resulting mixture was stirred at 0 °C for 3.0 h under an atmosphere of nitrogen. The reaction was quenched using methanol (3.20 g, 100.00 mmol) as a proton source and allowed to warm up to room temperature for 1.0 h. The dark mixture produced was filtered through a plug of alumina to remove the solid residues and the solvent removed under reduced pressure to yield a yellow oil. This oil was Kugelrohr distilled to yield amine **121** as a colourless liquid (0.38 g, 92 %), b.p. 140-142 °C @ 1 mmHg (Found: *m/z* 209.1207. $C_{15}H_{15}N$ requires 209.1204); $\nu_{max.}$ (liquid film) 3 415m (NH) and 1 604m cm^{-1} (C=C); δ_H (220 MHz; $CDCl_3$) 3.80 (1H, broad, N*H*), 3.95 (2H, d, J = 7 Hz, $=CHCH_2N$), 6.35 (1H, dt, J = 18 and 7 Hz, $CH=CHCH_2$), and 6.50-7.50 (11H, m, 2xAryl-*H* and $PhCH=CH$); δ_C (100.62 MHz; $CDCl_3$) 46.1 (C_1), 112.9, 117.5, 126.2, 126.9, 127.4, 128.4, 129.1, 131.4, 136.7, and 147.9 (C_2, C_3, and aromatics); *m/z* (e.i.) 209 (M^+, 40 %) and 117 (100, M-NHPh).

Reaction of lithium aluminium hydride with (4-phenyl-1-(1-phenylethyl)-1-azabuta-1,3-diene)tricarbonyliron(0) **72.**

To a suspension of lithium aluminium hydride (0.100 g, 2.63 mmol) in diethyl ether (15 ml) at 0 °C was added a solution of complex **72** (0.200 g, 0.53 mmol) in diethyl

ether (10 ml) and the resulting mixture was stirred at 0 °C for 3.0 h under an atmosphere of nitrogen. The reaction was quenched using methanol (0.84 g, 26.30 mmol) as a proton source and allowed to warm up to room temperature for 1.0 h. The resulting brown mixture was filtered through a plug of alumina to remove the solid residues and the solvent was removed under reduced pressure to yield a yellow oil. This oil was chromatographed on silica using light petroleum/diethyl ether (2:1) as the eluent to yield **123** as a colourless liquid (0.113 g, 89 %), b.p. 150-152 °C @ 1 mmHg (Found: C, 85.33; H, 8.70; N, 6.00. $C_{17}H_{21}N$ requires C, 85.31; H, 8.84; N, 5.85 %); $\nu_{max.}$ (liquid film) 3 320m cm^{-1} (NH); δ_H (220 MHz; $CDCl_3$) 1.37 (3H, d, J = 7 Hz, CH_3CH), 1.58 (1H, broad, *NH*), 1.81 (2H, quintet, J = 8 Hz, $CH_2CH_2CH_2$), 2.60 (4H, m, $PhCH_2CH_2CH_2$), 3.78 (1H, q, J = 7 Hz, $CHCH_3$), and 7.10-7.50 (10H, m, 2xAryl-*H*); δ_C (100.62 MHz; $CDCl_3$) 24.16 (CH_3CH), 31.76 (C_2), 33.53 (C_3), 47.22 (C_1), 58.19 ($CHCH_3$), 125.57, 126.43, 126.70, 128.15, 128.21, 128.26, 142.08, and 145.67 (Aromatics); *m/z* 239 (M^+, 12.6 %), 224 (62, M-CH_3), and 105 (100, M-$CH(CH_3)Ph$).

Reaction of lithium aluminium hydride with 4-phenyl-1-(1-phenylethyl)-1-azabuta-1,3-diene **71**.

To a suspension of lithium aluminium hydride (0.33 g, 8.68 mmol) in diethyl ether (20 ml) at 0 °C was added a solution of azadiene **71** (0.41 g, 1.74 mmol) in diethyl ether (20 ml) at 0 °C and the resulting mixture was stirred at this temperature for 3.0 h under an atmosphere of nitrogen. The reaction was quenched using methanol (2.79 g, 86.80 mmol) as a proton source and allowed to warm up to room temperature for 1.0 h. The resulting mixture was filtered through a plug of alumina to remove the solid residues and the solvent was removed under reduced pressure a yellow oil. Kugelrohr distillation of this oil led to isolation of a colourless oil identified as amine **120** by comparison of its ^1H n.m.r., i.r., and mass spectra with data from an authentic sample of **120** (0.33 g, 80 %), b.p. 147-150 °C @ 1 mmHg $\nu_{max.}$ (liquid film) 3 339broad (NH) and 1 605m cm^{-1} (C=C); δ_H (220 MHz; $CDCl_3$), 1.46 (3H,

d, J = 8 Hz, $CHCH_3$), 3.32 (2H, m, $=CHCH_2NH$), 3.52 (1H, broad, N*H*), 3.96 (1H, q, J = 8 Hz, $CHCH_3$), 6.35 (1H, dt, J = 16 and 6 Hz, $CH=CHCH_2$), 6.52 (1H, d, J = 16 Hz, Ph*CH*=CH), and 7.10-7.60 (10H, m, 2xAryl-*H*); *m/z* (e.i.) 237 (M^+, 20 %), and 117 (100, M-NHCH(CH_3)Ph).

Reaction of lithium aluminium hydride with a mixture of 1,4-diphenyl-1-azabuta-1,3-diene **29** *and (1,4-diphenyl-1-azabuta-1,3-diene)tricarbonyliron(0)* **28.**

To a suspension of lithium aluminium hydride (0.11 g, 2.89 mmol) in diethyl ether (10 ml) at 0 °C was added a solution of azadiene **29** (0.06 g, 0.29 mmol) and complex **28** (0.10 g, 0.29 mmol) in diethyl ether (10 ml) and the resulting mixture was stirred at 0 °C for 3.0 h under an atmosphere of nitrogen to yield a dark mixture. The reaction was quenched using methanol (0.92 g, 28.75 mmol) as a proton source and allowed to warm up to room temperature for 1.0 h. The dark mixture produced was filtered through a plug of alumina to remove the solid residues and the solvent was removed under reduced pressure to give a dark oil. The ^1H n.m.r. spectrum of this oil indicated the presence of a mixture of amines **121** and **122** (1:1) by comparison to the ^1H n.m.r. spectra with those of authentic samples.

Synthesis of 1-(4-methoxyphenyl)-4-phenyl-1-azabuta-1,3-diene **124.**

To a solution of oxadiene **66** (1.32 g, 0.01 mol) in diethyl ether (10 ml) at 0 °C was added a solution of 4-methoxyaniline (1.23 g, 0.01 mol) in diethyl ether (20 ml) and the resulting solution was stirred at 0 °C for 1.0 h to yield a yellow suspension. The solid was collected and washed with cold diethyl ether recrystallised from ethanol and dried under reduced pressure to yield yellow plate like crystals of azadiene **124** (1.90 g, 80 %), m.p.124-125 °C (Found: *m/z* 237.1147. $C_{16}H_{15}NO$ requires 237.1153); $\nu_{max.}$ (nujol) 1 630m (C=N) and 1 608m cm^{-1} (C=C); δ_H (220 MHz; $CDCl_3$) 3.84 (3H, s, OCH_3), 6.90-7.70 (11H, m, 2xAryl-*H* and Ph*CH*=C*H*), and 8.34 (1H, m, *H*C=N); δ_C (100.62 MHz; $CDCl_3$) 55.3 (OCH_3), 114.3, 122.0, 127.2, 128.6,

129.1, 135.6, 142.7, 144.5, 158.3 (Aromatics, C_3, and C_4), and 159.2 (*C*=N); *m/z* (e.i.) 237 (M^+, 24%) and 236 (100, M-H).

Synthesis of (1-(4-methoxyphenyl)-4-phenyl-1-azabuta-1,3-diene)tricarbonyliron(0) **125.**

To a suspension of diironnonacarbonyl (1.30 g, 3.57 mmol) in toluene (20 ml) was added azadiene **124** (0.85 g, 3.57 mmol) and the resulting mixture was heated at 50 °C for 2.0 h under an atmosphere of nitrogen to yield a dark red mixture. This mixture was filtered through a plug of alumina to remove the iron residues and the solvent removed under reduced pressure to yield a dark red oil. This oil was chromatographed on silica using light petroleum/diethyl ether (2:1) as the eluent to yield complex **125** as a deep red crystalline solid (0.54 g, 40 %), m.p. 220 °C (dec) (Lit.,[38] >215 °C) $\nu_{max.}$ (Pentane) 2 057s (C≡O), 1 996s (C≡O), and 1 985s cm^{-1} (C≡O), [Lit., [38] 2 059s (C≡O), 1 998s (C≡O), and 1 987s cm^{-1} (C≡O)]; δ_H (220 MHz; $CDCl_3$) 3.40 (1H, d, J = 10 Hz, PhC*H*=CH), 3.78 (3H, s, OCH_3), 5.74 (1H, dd, J = 9 and 3 Hz, PhCH=C*H*), 6.70-7.00 (4H, m, *p*-$CH_3OC_6H_4$), 7.06 (1H, d, J = 3 Hz, *H*C=N-) and 7.20-7.50 (5H, m, Aryl-*H*), [Lit.,[38] (60 MHz; CCl_4) 3.32 (1H, d, J = 9 Hz, PhC*H*=CH), 3.70 (3H, s, OCH_3), and 5.58 (1H, PhCH=C*H*)]; *m/z* (f.a.b.) 378 (M^++1, 4 %), 349 (3, M-CO), 321 (15, M-2CO), and (100, M-3CO).

Reaction of lithium aluminium hydride with 1-(4-methoxyphenyl)-4-phenyl-1-azabuta-1,3-diene)tricarbonyliron(0) **126.**

To a suspension of lithium aluminium hydride (0.18 g, 4.74 mmol) in diethyl ether (20 ml) at 0 °C was added a solution of complex **125** (0.36 g, 0.95 mmol) in diethyl ether (20 ml) and the resulting mixture stirred at 0 °C for 3.0 h under an atmosphere of nitrogen to yield a brown suspension. The reaction was quenched using methanol (1.52 g, 47.50 mmol) and allowed to warm up to room temperature over 1.0 h. The reaction mixture was filtered through a plug of alumina to remove the solid residues

and the solvent removed under reduced pressure to yield a yellow oil. This oil was chromatographed on silica using light petroleum/diethyl ether (2:1) as the eluent to yield amine **126** as white crystals (0.18 g, 78 %), m.p. 45-46 °C (Found: C, 79.54; H, 7.99; N, 5.72. $C_{16}H_{16}NO$ requires C, 79.63; H, 70.94; N, 5.80 %); $\nu_{max.}$ ($CHCl_3$) 3 410m cm^{-1} (NH); δ_H (400 MHz; $CDCl_3$) 1.96 (2H, dt, J = 7 and 7.5 Hz, $CH_2CH_2CH_2$), 2.75 (2H, d, J = 7.5 Hz, CH_2CH_2Ph), 3.12 (2H, d, J = 7 Hz, CH_2CH_2NH), 3.35 (1H, broad, N*H*), 3.76 (3H, s, OCH_3), and 6.50-7.40 (9H, m, 2xAryl-*H*); δ_C (100.62 MHz; $CDCl_3$) 31.06 (C_2), 33.31 (C_3), 44.31 (C_1), 55.69 (OCH_3), 113.94, 114.77, 123.78, 128.27, 141.61, 142.5, and 151.90 (aromatics); *m/z* 241 (M^+, 45 %) and 136 (100, M-$PhCH_2CH_2$).

Addition of lithium aluminium hydride to 1-(4-methoxyphenyl)-4-phenyl-1-azabuta-1,3-diene **124**.

To a suspension of lithium aluminium hydride (0.42 g, 11.05 mmol) in diethyl ether (10 ml) at 0 °C was added slowly a solution of azadiene **124** (0.52 g, 2.19 mmol) in diethyl ether (10 ml) and the resulting mixture was stirred at 0 °C for 3.0 h. The reaction was quenched using methanol (3.54 g, 110.50 mmol) and allowed to warm up to room temperature for 1.0 h. The suspension produced was filtered through a plug of alumina to remove the solid residues and the solvent removed under reduced pressure to yield white crystals. These crystals were recrystallised from pentane/diethyl ether (20:1) to yield allyl amine **127** as white crystals (0.40 g, 76 %), m.p. 71-72 °C (Found: *m/z* 239.1285. $C_{16}H_{17}NO$ requires 239.1288); $\nu_{max.}$ (Nujol) 3 380 cm^{-1} (NH); δ_H (220 MHz; $CDCl_3$) 3.62 (1H, broad, N*H*), 3.77 (3H, s, OCH_3), 3.92 (2H, d, J = 7 Hz, $=CHCH_2$), 6.40 (1H, dt, J = 17 and 7 Hz, $CH_2CH=CH$), and 6.50-7.50 (11H, m, 2xAryl-*H* and =C*H*Ph); δ_C (100.62 MHz; $CDCl_3$) 47.11 (OCH_3), 55.69, ($=CHCH_2NH$), 114.31, 114.82, 126.19, 127.27, 127.37, 128.44, 131.33, 136.81, 142.16, and 152.21 (Aromatics and PhC*H*=C*H*); *m/z* (e.i.) 239 (M^+, 70 %) and 117 (100, M-122).

Reaction of lithium aluminium hydride with (2-methyl-4-phenyl-1-oxabuta-1,3-diene)tricarbonyliron(0) **6.**

To a suspension of lithium aluminium hydride (0.140 g, 3.68 mmol) in diethyl ether (10 ml) at 0 °C was added a solution of complex **6** (0.210 g, 0.73 mmol) in diethyl ether (20 ml) and the resulting mixture was stirred at 0 °C for 3.0 h under an atmosphere of nitrogen. The reaction was quenched using methanol (1.18 g, 36.88 mmol) and allowed to warm up to room temperature for 1.0 h to yield a dark mixture. This mixture was filtered to remove the solid residues and the solvent was removed under reduced pressure to yield a brown oil. Chromatography of this oil on silica using light petroleum/diethyl ether (2:1) as the eluent led to isolation of a colourless oil identified as 4-phenylbutan-2-ol **104** (0.099 g, 90 %) by comparison of its ^1H n.m.r. spectrum to that of an authentic sample.

Reaction of lithium aluminium hydride with (4-phenyl-1-oxabuta-1,3-diene)tricarbonyliron(0) **30.**

To a suspension of lithium aluminium hydride (0.140 g, 3.68 mmol) in diethyl ether (10 ml) at 0 °C was added a solution of complex **30** (0.20 g, 0.74 mmol) in diethyl ether (10 ml) and the resulting mixture was stirred at 0 °C for 3.0 h under an atmosphere of nitrogen to yield a brown mixture. The reaction was quenched using methanol (1.16 g, 36.72 mmol) and allowed to warm up to room temperature for 1.0 h. The resulting mixture was filtered through a plug of alumina to remove the solid residues and the solvent removed under reduced pressure to yield a colourless oil. Chromatography of this oil on silica using light petroleum/diethyl ether (2:1) as the eluent led to isolation of a colourless oil identified as alcohol **110** (0.09 g, 90 %) by comparison of its ^1H n.m.r. spectrum to that of an authentic sample.

Addition of lithium aluminium hydride to 2-methyl-4-phenyl-1-oxabuta-1,3-diene **59**.

To a suspension of lithium aluminium hydride (0.44 g, 11.6 mmol) in diethyl ether (10 ml) at 0 °C was added a solution of oxadiene **59** (0.34 g, 2.33 mmol) in diethyl ether (20 ml) and stirred at 0 °C for 3.0 h under an atmosphere of nitrogen. The reaction was quenched using methanol (1.87 g, 58.30 mmol) and allowed to warm up to room temperature for 1.0 h. The resulting mixture was filtered through a plug of alumina to remove the solid residues and the solvent was removed under reduced pressure to yield a yellow oil. Chromatography of this oil on silica using light petroleum/diethyl ether (2:1) as the eluent led to isolation of a colourless liquid identified as 4-phenylbutan-3-ene-2-ol **103** (0.30 g, 87 %) by comparison of its ^1H n.m.r. spectrum with that of an authentic sample.

Reaction of lithium aluminium hydride with 4-phenyl-1-oxabuta-1,3-diene **66**.

To a suspension of lithium aluminium hydride (0.29 g, 7.63 mmol) in diethyl ether (10 ml) at 0 °C was added a solution of oxadiene **66** (0.20 g, 1.52 mmol) in diethyl ether (20 ml) and the resulting mixture was stirred at 0 °C for 3.0 h under an atmosphere of nitrogen. The reaction was quenched using methanol (2.44 g, 76.30 mmol) and allowed to warm up to room temperature for 1.0 h to yield a yellow mixture. This mixture was filtered through a plug of alumina to remove the solid residues and the solvent was removed under reduced pressure to give a yellow oil. Chromatography of this oil on silica using light petroleum/diethyl ether (2:1) as the eluent led to isolation of pale yellow crystals identified as cinnamyl alcohol **114** (0.16 g, 79 %) by comparison of their ^1H n.m.r. spectrum with that of an authentic sample.

Preparation of (2-methyl-4-phenyl-1-oxabuta-1,3-diene)tetracarbonyliron(0) **34**.

Diironnonacarbonyl (1.30 g, 3.57 mmol) and oxadiene **59** (0.52 g, 3.57 mmol) were stirred in diethyl ether (15 ml) at 37 °C for 2.0 h under an atmosphere of nitrogen. The red mixture produced was filtered through a plug of alumina to remove the iron

residues and the solvent was removed under reduced pressure to yield a red oil. This oil was chromatographed on silica using light petroleum/diethyl ether (4:1) as the eluent to yield complex **34** as yellow crystals (0.48 g, 43 %), m.p. 53-55 °C, (Lit.,[58] 53-54 °C); $\nu_{max.}$ (*n*-hexane) 2 098s (C≡O), 2 033s (C≡O), 2 020s (C≡O), 1 992s (C≡O), and 1 685m cm^{-1}(C=O); [Lit.,[58] (*n*-hexane) 2 095 (C≡O), 2 032 (C≡O), 2 020 (C≡O), 1 993 (C≡O), and 1 684 cm^{-1} (C=O)]; δ_H (220 MHz; CCl_4) 2.60 (3H, s, C*H*$_3$), 4.45 (1H, d, J = 12 Hz, PhC*H*=CH), 5.16 (1H, d, J = 12 Hz, PhCH=C*H*), and 7.10-7.60 (5H, m, Aryl-*H*), [Lit.,[58] (CCl_4) 2.77 (3H, s, C*H*$_3$), 4.43 (1H, d, J = 11 Hz, PhC*H*=CH), 5.17 (1H, d, J = 11 Hz, PhCH=C*H*), and 7.65 (5H, m, Aryl-*H*].

Reaction of lithium aluminium hydride with (2-methyl-4-phenyl-1-oxabuta-1,3-diene)tetracarbonyliron(0) **34.**

To a suspension of lithium aluminium hydride (0.120 g, 3.16 mmol) in diethyl ether (10 ml) at 0 °C was added a solution of complex **34** (0.198 g, 0.63 mmol) in diethyl ether (10 ml) and the resulting mixture was stirred at 0 °C for 3.0 h under an atmosphere of nitrogen. The reaction was quenched using methanol (1.01 g, 31.56 mmol) and allowed to warm up to room temperature for 1.0 h. the dark mixture produced was filtered through a plug of alumina to remove the solid residues and the solvent was removed under reduced pressure to give a dark oil. Chromatography of this oil on silica using light petroleum/diethyl ether (2:1) as the eluent led to isolation of a colourless oil identified as 4-phenylbutan-2-ol **104** (0.076 g, 80 %) by comparison of its ^1H n.m.r. spectrum with that of an authentic sample of **104**.

Trapping experiment.

To a stirring suspension of lithium aluminium hydride (0.020 g, 0.53 mmol) in diethyl ether (10 ml) at 0 °C was added a solution of complex **72** (1.00 g, 2.67 mmol) in diethyl ether (40 ml) and the resulting mixture was stirred at 0 °C for 3.0 h under an atmosphere of nitrogen to give a dark mixture. The reaction was quenched

using methanol (0.17 g, 5.26 mmol) and allowed to warm up to room temperature for 1.0 h. The dark mixture produced was filtered through a plug of alumina to remove the solid residues and the solvent was removed under reduced pressure to yield an orange oil.The ^{1}H n.m.r. spectrum of this oil indicated the presence of complex **72** (80 %), amine **123** (10 %), and imine **128** (10 %) by comparison of the ^{1}H n.m.r. spectra with those of authentic samples.

Reaction of lithium aluminium deuteride with 4-phenyl-1-(1-phenylethyl)-1-azabuta-1,3-diene **71.**

To a suspension of lithium aluminium deuteride (0.240 g, 5.71 mmol) in diethyl ether (10 ml) at 0 °C was added a solution of azadiene **71** (0.268 g, 1.14 mmol) in diethyl ether (10 ml) and the resulting suspension was stirred at 0 °C for 3.0 h under an atmosphere of nitrogen. The reaction was quenched with methanol (1.65 g, 51.56. mmol) as a proton source and allowed to warm up to room temperature for 1.0 h. The reaction mixture was filtered through a plug of alumina to remove the solid residues and the solvent removed under reduced pressure to yield a yellow oil. This yellow oil was chromatographed on silica using light petroleum/diethyl ether (2:1) as the eluent to yield amine **131** (0.243 g, 90 %), (Found: *m/z* 238.1595. $C_{17}H_{18}ND$ requires 238.1580); δ_H (400 MHz; $CDCl_3$) 1.41 (3H, d, J = 7 Hz, CHC*H*$_3$), 3.26 (1H, m, =CHC*H*DN), 3.87 (1H, q, J = 7 Hz, CHCH$_3$), 6.29 (1H, dd, J = 16 and 7 Hz, CH=C*H*CHD), 6.47 (1H, d, J = 16 Hz, PhC*H*=CH), and 7.10-7.50 (10H, m, 2xAryl-*H*); δ^2_H (61.4 MHz; $CHCl_3$) 3.33 (1D, broad, =CHCH*D*NH); *m/z* (e.i.) 238 (M^+, 17.3 %), 223 (16.7, M-CH$_3$), 118 (100, M-NHCH(CH$_3$)Ph), and 105 (72.7, M-CH(CH$_3$)Ph).

Reaction of lithium aluminium deuteride with (4-phenyl-1-(1-phenylethyl-1-azabuta-1,3-diene)tricarbonyliron(0) **72.**

To a suspension of lithium aluminium deuteride (0.120 g, 2.86 mmol) in diethyl ether (5 ml) at 0 °C was added a solution of complex **72** (0.214 g, 0.57 mmol) in diethyl

ether (20 ml) and the resulting suspension was stirred at 0 °C for 3.0 h under an atmosphere of nitrogen. The reaction was quenched using methanol (0.92 g, 28.60 mmol) and allowed to warm up to room temperature for 1.0 h. The resultant suspension was filtered through a plug of alumina to remove the iron residues and the solvent removed under reduced pressure to yield a brown oil. Chromatography of this oil on silica using pentane/diethyl ether (2:1) as the eluent lead to isolation of amine **132** as a colourless liquid (0.11 g, 80 %), (Found: 242.1857. $C_{17}H_{18}D_3N$ requires 242.1862); δ_H (400 MHz; $CDCl_3$) 1.38, (3H, d, J = 7 Hz, CH_3CH), 1.82 (1H, m, CHDC*H*DCHD), 2.60 (2H, m, C*H*DCHC*H*D), 3.75, (1H, q, J = 7 Hz, $CHCH_3$), and 7.10-7.40 (10H, m, Aryl-*H*); δ^2_H (61.41 MHz; $CHCl_3$), 1.77 (1D, broad, CHDCH*D*CHD) and 3.51 (2D, Broad, C*H*DCHDCH*D*); *m/z* 242 (M^+, 8.2 %), 227 (M-CH_3) and 105 (100, M-137).

Reaction of lithium aluminium deuteride with (1-(4-methoxyphenyl)-4-phenyl-1-azabuta-1,3-diene)tricarbonyliron(0) **125** *followed by a proton quench.*

To a suspension of lithium aluminium deuteride (0.140 g, 3.33 mmol) in diethyl ether (5 ml) at 0 °C was added a solution of complex **125** (0.252 g, 0.67 mmol) in diethyl ether (20 ml) and the resulting mixture was stirred at 0 °C for 3.0 h under an atmosphere of nitrogen. The reaction was quenched using methanol (1.06 g, 32.12 mmol) as a proton source and allowed to warm up to room temperature for 1.0 h to yield a dark mixture. This mixture was filtered to remove the solid residues and the solvent was removed under reduced pressure to give a dark oil. This oil was chromatographed on silica using light petroleum/diethyl ether (2:1) as the eluent to yield a colourless oil identified as amine **133** (0.124 g, 76 %), δ_H (400 MHz; $CDCl_3$) 1.90 (1H, m, CHDC*H*DCHD), 2.71 (1H, m, PhC*H*D), 3.09 (1H, m, NHC*H*D), 3.40 (1H, broad, NH), 3.74 (3H, s, OCH_3), and 6.30-7.40 (9H, m, 2xAryl-*H*); δ^2_H (61.42 MHz; $CHCl_3$), 1.90 (1D, broad, CHDCH*D*CHD), 2.69 (1D, broad, CH*D*Ph), and 3.07 (1D, broad, CH*D*N); *m/z* (e.i.) 244 (M^+, 45 %) and 107 (100, M-PhCHDCHD).

Reaction of lithium aluminium hydride with (1-(4-methoxyphenyl)-4-phenyl-1-azabuta-1,3-diene)tricarbonyliron(0) **125** *followed by a deuterium quench.*

To a suspension of lithium aluminium hydride (0.170 g, 4.47 mmol) in diethyl ether (10 ml) at 0 °C was added a solution of complex **125** (0.338 g, 0.90 mmol) in diethyl ether (20 ml) and the resulting mixture was stirred at 0 °C for 3.0 h under an atmosphere of nitrogen. The reaction was quenched with a solution of D_2O (0.89 g, 44.50 mmol) in THF (10 ml) and allowed to warm up to room temperature for 1.0 h to yield a dark mixture. This mixture was filtered through a plug of alumina (deactivated with D_2O) to remove the solid residues and the solvent was removed under reduced pressure to yield a dark oil. The ^1H n.m.r. spectrum of this oil indicated the presence of amine **134** by comparison to the spectra of related compounds.(0.178 g, 82 %), δ_H (400 MHz; $CDCl_3$) 1.95 (2H, dt, J = 7 and 7.5 Hz, $CH_2CH_2CH_2$), 2.75 (2H, t, J = 7.5 Hz, $PhCH_2CH_2$), 3.12 (2H, t, J = 7 Hz, $NHCH_2CH_2$), 3.76 (3H, s, OCH_3), and 6.50-7.50 (9H, m, 2xAryl-*H*).

Reaction of lithium aluminium deuteride with 1-(4-methoxyphenyl)-4-phenyl-1-azabuta-1,3-diene)tricarbonyliron(0) **125** *followed by a deuterium quench.*

To a supension of lithium aluminium deuteride (0.200 g, 4.76mmol) diethyl ether (5 ml) at 0 °C was added a solution of complex **72** (0.361 g, 0.96 mmol) in diethyl ether (10 ml) and the resulting mixture was stirred at 0 °C for 3.0 h under an atmosphere of nitrogen. The reaction was quenched with a solution of D_2O (0.96 g, 48.00 mmol) in THF (10 ml) and stirred at room temperature for 1.0 h to yield a dark mixture. This mixture was filtered through a plug of alumina (deactivated with D_2O) to remove the solid residues and the solvent was removed under reduced pressure to yield a yellow oil. The ^1H n.m.r. spectrum of this oil indicated the presence of amine **135** by comparison to the spectra of related compounds (0.200 g, 85 %), δ_H (400 MHz; $CDCl_3$), 1.91 (1H, m, CHDC*H*DCHD), 2.70 (1H, m, PhC*H*DCHD), 3.08 (1H, m, C*H*DNH), 3.75 (3H, s, OCH_3), and 6.40-7.50 (9H, m, 2xAryl-*H*).

Synthesis of diironnonacarbonyl.

Iron pentacarbonyl (112.00 g, 0.57 mol) was dissolved in glacial acid (300 ml) and the resulting solution was irradiated with ultra-violet light for 24 h under an atmosphere of nitrogen. The orange crystals produced were collected by filtration and washed with ethanol (150 ml) and diethyl ether (75 ml) and dried under reduced pressure to yield diironnonacarbonyl as orange plate-like crystals (52 g, 50 %), m.p.110 °C (dec) (Lit., [27] 110-120 °C) $\nu_{max.}$ (nujol) 2 063 (C≡O), 2 021 (C≡O), and 1 828 cm^{-1} (C=O), [Lit.,[27] 2 080 (C≡O), 2 034 (C≡O), and 1 828 cm^{-1} (C=O)].

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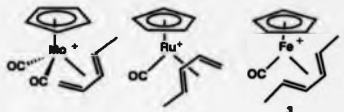
B1 INTRODUCTION.

The formation of cationic η^4-diene transition metal complexes is well known and many compounds of this type e.g. ***1***, ***2***, and ***3*** have been synthesised.[1, 2, 3]

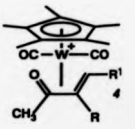


1 ***2*** ***3***

By comparison, the number of reports of cationic η^4-heterodiene transition metal complexes is relatively small.

The chemistry discussed in this chapter describes experiments designed to synthesise cationic transition metal complexes bearing a 1-heterodiene ligand. As an introduction to this work the synthesis and chemistry of known η^4-1-heterodiene cationic complexes is described.

The first acyclic cationic complex of a 1-oxadiene ***4*** was synthesised two years ago.[4, 5] The complex is based on tungsten and was synthesised *via* the multistage route discussed below.

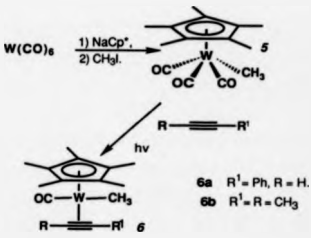


4

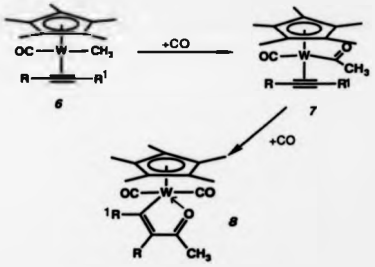
4a R^1 = Ph, R = H
4b R^1 = R = CH_3

Reaction of tungsten hexacarbonyl with the sodium salt of 1,2,3,4,5-pentamethylcyclopentadiene followed by addition of methyl iodide led to the tungsten-alkyl complex *5*. Treatment of *5* with an alkyne followed by irradiation with ultra-

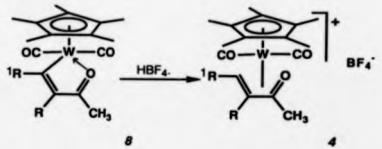
violet light resulted in displacement of two metal carbonyl ligands and formation of the tungsten alkyne complex *6*.



Stirring a solution of complex *6* in dichloromethane under an atmosphere of carbon monoxide led to carbonyl insertion into the tungsten-methyl bond and formation of the acyl complex *7*. Attack of *7* by a second carbon monoxide resulted in intramolecular coupling of the acyl group and alkyne to give complex *8*.

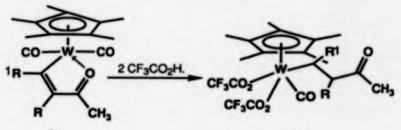


Finally, addition of tetrafluoroboric acid to complex *8* led to protonation at the β-carbon of the oxadiene and formation of the η^4-1-oxadiene complex *4*.



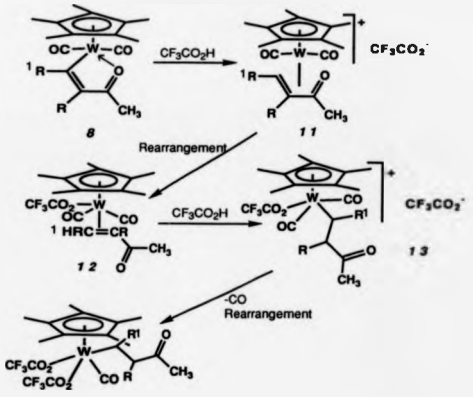
8 *4*

Treatment of complex *8* with trifluoroacetic acid, however, leads to complex *10*. Complex *10* forms as a result of the increased coordinating ability of the trifluoroacetate anion compared to the tetrafluoroborate anion.[5]



8 *10*

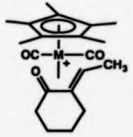
The mechanism of this reaction is thought to involve initial formation of the 1-oxadiene complex *11*. In the presence of the trifluoroacetate anion however, complex *11* is unstable and rearranges to the η^2-complex *12*. Protonation of *12* on the oxadiene leads to complex *13* which readily loses carbon monoxide and rearranges to form complex *10*.



8 11 12 13 10

Similar results have also been obtained for Cp derivatives of complex **4**.

Cyclic 1-oxadiene cationic complexes have also been synthesised. For example, complex ***14*** was synthesised by a related intramolecular route to that described for complex ***4***.[6]



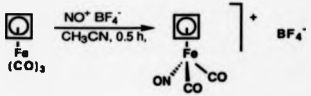
14a M = W
14b M = Mo

B2 RESULTS AND DISCUSSION.

B2.1 Approaches to the Synthesis of Cationic 1-Heterodiene Complexes of Iron.

The multistep route required for the synthesis of cation *4* prompted an investigation into the possibility of developing a simpler route to η^4-heterodiene cationic complexes of the less expensive element iron.

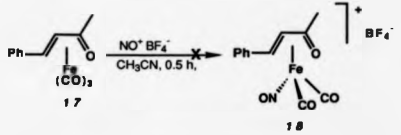
Initially it was decided to attempt to replace a carbonyl ligand of an iron(0) species with a nitrosyl ligand thus generating a cationic complex. This type of ligand substitution is well known for related iron complexes. For example, treatment of (cyclobutadiene)tricarbonyliron(0) *15* with nitrosyl tetrafluoroborate leads to the cationic complex *16*.[7]



15 *16*

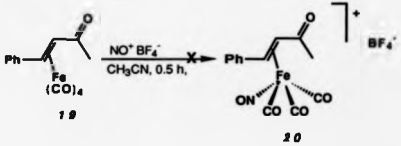
In the first instance the reaction between (2-methyl-4-phenyl-1-oxabuta-1,3-diene)tricarbonyliron(0) *17* and nitrosyl tetrafluoroborate was examined.

A solution of nitrosyl tetrafluoroborate in acetonitrile was added to a solution of complex *17* in acetonitrile and stirred at 0 °C. The reaction was followed by i.r. spectroscopy. No change in the i.r. spectrum was observed however, even after 4 h of stirring. Removal of the solvent under reduced pressure led to a red oil which was identified as the original complex *17* on the basis of its ^{1}H n.m.r. and i.r. spectra. There was no evidence for formation of complex *18*.



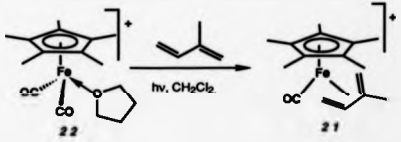
17 18

Formation of a cationic complex from a (1-oxadiene)tetracarbonyliron(0) complex was examined next. A solution of nitrosyl tetrafluoroborate in acetonitrile was added to a solution of complex ***19*** in acetonitrile. After stirring for 4 h standard work-up led to a red oil which was identified as complex ***19*** on the basis of its ^1H n.m.r. and i.r. spectra.



19 20

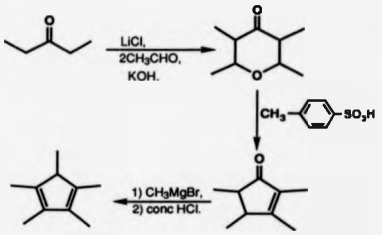
In view of these results this approach to cationic complexes was pursued no further. A recent communication[8] has described the direct synthesis of a diene cation complex of iron ***21*** from readily accessible and well known organoiron complexes.



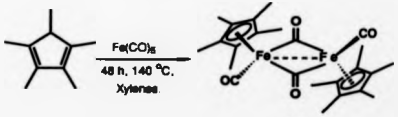
22 21

Thus it was decided to adapt the synthesis of ***21*** to give a heterodiene complex.

1,2,3,4,5-Pentamethylcyclopentadiene was synthesised by a literature route outlined below[9] and then converted into the THF cation ***22*** by further literature procedures.[10, 11]



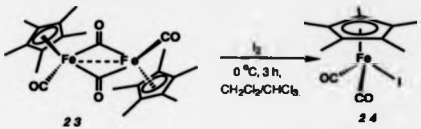
Ironpentacarbonyl and Cp*H were dissolved in xylenes and heated under reflux for 48 h. Additional ironpentacarbonyl was added to the reaction after 24 h. The reaction mixture was filtered and the residues were extracted with dichloromethane.[11] The solvent was removed under reduced pressure to yield dark red crystals identified as $Cp^*_2Fe_2(CO)_4$ ***23*** by comparison of their ^1H n.m.r., i.r., and mass spectra with literature values.[12]



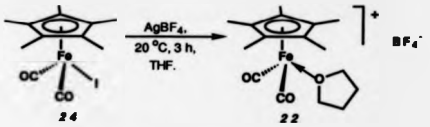
23

Dimer ***23*** was dissolved in dichloromethane and cooled to 0 °C and to this solution a solution of iodine in dichloromethane/chloroform was added. The resulting solution was stirred at 0 °C for 3 h. The reaction mixture was washed with saturated sodium

thiosulphate solution and water and dried over magnesium sulphate. Removal of the solvent under reduced pressure led to isolation of red crystals identified as $Cp^*Fe(CO)_2I$ ***24*** on the basis of their ^1H n.m.r., i.r., and mass spectra.



Conversion of iodide ***24*** to the THF cation ***22*** was accomplished by stirring ***24*** with silver tetrafluoroborate in THF at 20 °C for 3 h under an atmosphere of nitrogen. The reaction mixture was filtered through celite to remove the solid residues and the solvent was removed under reduced pressure to yield a red oil. Crystallisation and recrystallisation of this oil from THF/diethyl ether yielded red crystals identified as cation ***22*** by comparison of their ^1H n.m.r., i.r., and mass spectra with literature values.[11]

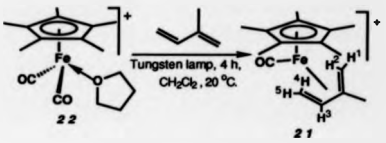


Initially the synthesis of complex ***21*** was repeated in order to optimise conditions for the reaction, as very little detail relating to reaction conditions appeared in the communication.[8] In addition, the product ***21*** was only characterised on the basis of its infra red spectrum; ^1H n.m.r. and mass spectra were not reported.

Complex ***22*** and isoprene were dissolved in dichloromethane and irradiated for 3 h with 250 nm light under an atmosphere of nitrogen. The solvent and excess diene

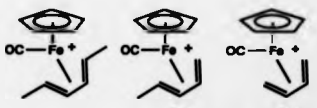
were removed under reduced pressure to yield a red oil. The ^1H n.m.r. and i.r. spectra of this oil gave no evidence for the presence of iron carbonyl or organic fragments and suggested that complex ***22*** had been destroyed. Repeated attempts to generate complex ***21*** using 250 nm light over varying time periods only resulted in destruction of the complex.

In view of these observations a solution of complex ***22*** and isoprene was irradiated using light from a tungsten lamp and the reaction was followed by i.r. spectroscopy. During the course of the reaction the carbonyl peaks at 2 085 and 2 005 cm^{-1} due to the THF cation ***22*** gradually disappeared and a peak at 2 020 cm^{-1} appeared. The reaction was complete after 4 h. The solvent was removed under reduced pressure and the pale orange oil produced was crystallised and recrystallised from a mixture of dichloromethane/diethyl ether to yield pale yellow crystals identified as complex ***21*** by comparison of their i.r. and ^1H n.m.r. spectra with data quoted in the literature.[3, 8,13]



22 ***21***

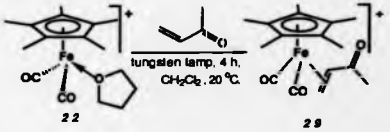
The assignment of the ^1H n.m.r. spectrum of complex ***21*** was made by comparison of its spectrum to the spectra of related complexes ***25***, ***26***, and ***27*** reported in the literature.[3,13]



25 ***26*** ***27***

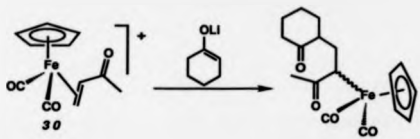
The ^{1}H n.m.r. spectrum of ***21*** contained a pair of one-proton doublets at 0.48 (J = 3 Hz) and 2.86 ppm (J = 3 Hz) which were assigned to protons H^2 and H^1 respectively. A pair of one-proton doublet of doublets at 0.75 (J = 10 and 3 Hz) and 2.78 ppm (J = 7 and 3 Hz) were assigned to protons H^4 and H^5 respectively. A one-proton multiplet at 5.80 ppm was assigned to proton H^3. A fifteen-proton singlet at 1.80 ppm and a three-proton singlet at 2.55 ppm were assigned to the methyl groups of Cp* and isoprene respectively. The i.r. spectrum of ***22*** contained an expected metal carbonyl peak at 2 020 cm^{-1}.[8]

Synthesis of a 1-heterodiene complex was examined next. A solution of the THF cation ***22*** and 2-methyl-1-oxabuta-1,3-diene ***28*** in dichloromethane was irradiated with a tungsten lamp using conditions described for the synthesis of complex ***21***; standard work-up led to a dark oil. The i.r. spectrum of this oil contained a pair of intense peaks at 2 045 and 1 995 cm^{-1} which were assigned to metal carbonyls. An additional peak at 1 705 cm^{-1} revealed that an organic carbonyl group was also present. Attempts to obtain a satisfactory ^{1}H n.m.r. spectrum failed and only a broad spectrum was obtained. The results from this experiment suggested that the η^2-alkene complex ***29*** had formed.



22 ***29***

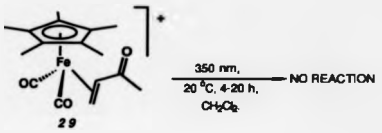
This type of complex ***29*** is known and has been reported in the literature.[13] For example complex ***30*** has been synthesised and used in Michael-type condensation reactions.[14]



30 **31**

In an attempt to generate the η^4-complex from ***29*** a solution of the THF cation ***21*** and 1-oxadiene ***28*** in dichloromethane was irradiated with a tungsten lamp for up to 20 h; standard work-up led to a red oil which was tentatively identified as complex ***29*** on the basis of its i.r. spectrum.

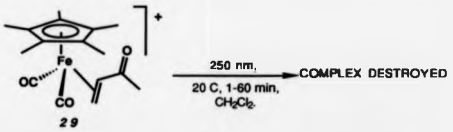
Irradiation of complex ***29*** with a more energetic light source was attempted next. A solution of complex ***29*** in dichloromethane was irradiated for up to 20 h using 350 nm light; standard work-up led to a dark oil which was identified as the η^2-complex ***29***.



29

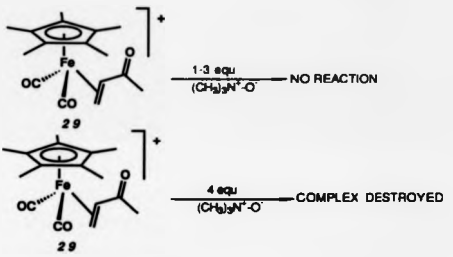
Since it appeared impossible to remove a metal carbonyl ligand from ***29*** and hence promote formation of the η^4-complex under mild conditions, more forcing conditions were employed.

Irradiation of a solution of ***29*** in dichloromethane using 250 nm light led to a dark oil after standard work-up. The i.r. spectrum of this oil indicated that complex ***29*** had been destroyed.



29

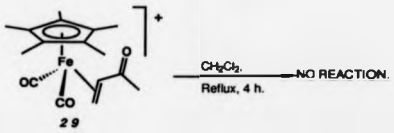
Removal of a metal carbonyl ligand from complex ***29*** using chemical means was attempted next. A solution of complex ***29*** in acetone was stirred with one equivalent of trimethylamine-*N*-oxide for 4 h.[15] After removal of the solvent under reduced pressure a dark oil was isolated. The i.r. spectrum of this oil indicated that a reaction had not occured. Similar results were obtained after reaction of complex ***29*** with two and three equivalents of trimethylamine-*N*-oxide. Use of four equivalents of trimethylamine-*N*-oxide however, resulted in destruction of complex ***29***.



29

29

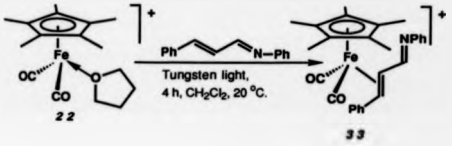
Finally a solution of complex ***29*** in dichloromethane was heated at reflux for 4 h under an atmosphere of nitrogen. The resulting orange solution was filtered to remove the iron residues and the solvent was removed under reduced pressure to yield a dark oil. The i.r. spectrum of this oil suggested that it was the original η^2-complex ***29***.



29

Since it does not appear possible to generate a cationic η^4-complex based on an oxadiene, formation of a complex based on an azadiene was examined. Initially a solution of complex ***22*** in dichloromethane was stirred with 1,4-diphenyl-1-azabuta-1,3-diene ***32*** whilst being irradiated with light from a tungsten lamp for 4 h under an atmosphere of nitrogen.

The solvent was removed under reduced pressure and the yellow solid produced was washed with diethyl ether to remove the excess azadiene to yield a dark oil which was tentatively identified as the η^2-complex ***33*** on the basis of its i.r. spectrum.

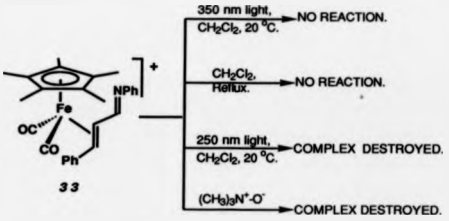


22 *33*

The i.r. spectrum of ***33*** contained a pair of intense signals at 2 038 and 1 990 cm^{-1} which were assigned to the dicarbonyliron(0) moiety. In addition a peak at 1 590 cm^{-1} was assigned to C=N-. All attempts to obtain a satisfactory ^1H n.m.r. spectrum of complex ***33*** failed.

Attempts to convert the η^2-complex ***33*** to its η^4-counterpart using conditions previously described for complex ***29*** failed and either resulted in destruction of complex ***33*** or regeneration of the original η^2-complex ***33***. These results are outlined in Scheme 1 below.

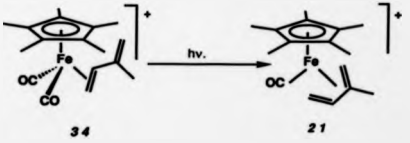
Scheme 1



B2.2 Conclusions

The results obtained from Section B of this thesis indicate that it may not be possible to synthesise cationic η^4-heterodiene complexes by direct reaction of a 1-heterodiene with the cationic organoiron precursor $[Cp^*Fe(CO)_2THF]^+ BF_4^-$ ***22*** as observed for homodiene analogues, and only cationic η^2-1-heterodiene iron complexes are observed.

These results indicate that the mechanism for the formation of the η^4-homodiene complex may involve initial formation of an η^2-complex ***34*** which converts to the η^4-complex ***21*** upon prolonged irradiation of ***34*** with light from a tungsten lamp.



B3 EXPERIMENTAL

Synthesis of [Cp$_2$Fe$_2$(CO)$_4$] 23.*

Iron pentacarbonyl (10.00 g, 51.00 mmol) and 1,2,3,4,5-pentamethylcyclopentadiene (2.02 g, 15.00 mmol) were dissolved in xylenes (75 ml) and heated under reflux at 150 °C for 48 h. Additional iron pentacarbonyl (3.00 g, 15.00 mmol) was added to the mixture after 24 h. The dark solution produced was filtered and the residues extracted with dichloromethane (3 x 25 ml). The solvent was removed under reduced pressure to yield deep red needle-like crystals identified as dimer *23* on the basis of their ^{1}H n.m.r., i.r., and mass spectra (2.21 g, 60 %), $\nu_{max.}$ (cyclohexane) 1 930 (C≡O) and 1 763 cm^{-1} (C=O), [Lit.,[12] (cyclohexane) 1 932 (C≡O) and 1 764 cm^{-1}(C=O)]; δ_H (220 MHz; CS_2) 1.61 (s, $(CH_3)_5C_5$), [Lit.,[12] (CS_2) 1.62 (s, $(CH_3)_5C_5$)]; *m/z* (e.i.) 494 (M^+, 18%) and 247 (100, M^+-Cp*Fe(CO)$_2$).

*Synthesis of [Cp*Fe(CO)$_2$I] 24.*

Dimer *23* (0.20 g, 0.40 mmol) was dissolved in dichloromethane (10 ml) and chloroform (20 ml) and cooled to 0 °C. To this solution was added slowly a solution of iodine (0.12 g, 0.47 mmol) in chloroform (10 ml). The resulting solution was stirred at 20 °C for 3.0 h. The solution produced was washed with saturated sodium thiosulphate solution (20 ml) and water (2x20 ml) and dried over magnesium sulphate. The solvent was removed under reduced pressure to yield red crystals identified as complex *24* on the basis of their ^{1}H n.m.r., i.r., and mass spectra (0.26 g, 86 %), m.p. 139-140 °C, (Lit.,[16] 139 °C) $\nu_{max.}$ (cyclohexane) 2 019s (C≡O) and 1 976s cm^{-1} (C≡O), [Lit.,[16] (cyclohexane) 2 017vs (C≡O) and 1 980vs cm^{-1} (C≡O)]; δ_H (220 MHz; C_6D_6) 2.00 (s, C(CH$_3$)5), [Lit.,[16] (C_6D_6) 1.57 (s, C5(CH$_3$)5)]; *m/z* (e.i.) 374 (M^+ ,32 %) and 318 (100 , M-2CO).

*Synthesis of [Cp*Fe(CO)$_2$THF]$^+$BF$_4^-$ 22.*

To a solution of iodide ***24*** (0.41 g, 1.10 mmol) in THF (5 ml) at 20 °C was added silver tetrafluoroborate (0.22 g, 1.13 mmol) and the resulting solution was stirred at 20 °C for 3.0 h under an atmosphere of nitrogen. The solvent was removed under reduced pressure and the residues were extracted using dichloromethane (3 x 5ml). The combined extracts were filtered through a celite plug to remove the solid residues and the solvent was removed under reduced pressure to give red crystals. These crystals were recrystallised from THF/diethyl ether, and dried to yield dark red crystals identified as the THF salt ***22*** on the basis of their ^{1}H n.m.r., i.r., and mass spectra (0.40 g, 90 %), $\nu_{max.}$ (CH_2Cl_2) 2 060s (C≡O) and 1 998s cm^{-1} (C≡O), [Lit.,[11] 2 085s (C≡O) and 2 003s cm^{-1} (C≡O)]; δH (220 MHz; ($CD_3)_2CO$) 1.80 (15H, s, $(CH_3)_3C_5$), 2.18 (4H, broad, $(CH_2)_2$), 3.68 (4H, broad, $(CH_2)_2O$), [Lit.,[11] 1.84 (15H, s, ($CH_3)_5C_5$), 2.17 (4H, s, $2CH_2$), 3.70 (4H, m, $(CH_2)_2O$)]; *m/z* (e.i.) 319 (2 %, M$^+$-BF_4), 247 (10, Cp*Fe(CO)$_2$), 219 (16, Cp*Fe(CO)), and 191 (32, Cp*Fe).

*Synthesis of [Cp*Fe(CO).η-^{4}(CH$_2$=C(CH$_3$)CH=CH$_2$)] $^+$BF$_4^-$ 21.*

Isoprene (0.23 g, 3.40 mmol) and the THF cation ***22*** (0.07 g, 0.17 mmol) were stirred in dichloromethane (10 ml) and irradiated with a tungsten lamp at 20 °C under an atmosphere of nitrogen until all the bands in the i.r. due to the starting material had disappeared. The reaction was complete after 4.0 h. The reaction mixture was filtered to remove the solid residues and the solvent and excess isoprene were removed under reduced pressure to yield a red oil. This oil was crystallised and recrystallised from dichloromethane and diethyl ether to give yellow crystals identified as complex ***21*** on the basis of their ^{1}H n.m.r., i.r., and mass spectra (0.041 g, 64 %), $\nu_{max.}$ (CH_2Cl_2) 2 020 cm^{-1}s (C≡O), [Lit.,[8] 2 023 (C≡O)]; δH (220 MHz; ($CD_3)_2CO$) 0.48 (1H, d, J = 4 Hz, H-2), 0.75 (1H, dd, J = 10 and 3 Hz, H-4), 1.80 (15H, s, $(CH_3)_5C_5$), 2.55 (3H, s, =CC*H*$_3$), 2.78 (1H, dd, J = 7 and 3 Hz, H-5), 2.86 (1H, d, J = 3 Hz, H-1) and 5.80 (1H, m, H-3); *m/z* (e.i.) 259 (20, M-CO-BF_4).

*Synthesis of [Cp*Fe(CO)$_2$ (η^2-CH$_2$=CH-CO-CH$_3$)]$^+$BF$_4^-$ **28**.*

A solution of oxadiene ***28*** (0.35 g, 4.93 mmol) and THF cation ***22*** (0.10 g, 0.25 mmol) were stirred in dichloromethane (10 ml) at 20 °C and irradiated with a tungsten lamp for 3-20 h under an atmosphere of nitrogen. The reaction mixture was filtered to remove the iron residues and the solvent removed under reduced pressure to give a dark oil which was identified as complex ***29*** on the basis of its i.r. spectrum $\nu_{max.}$ (CH_2Cl_2) 2 045s (C=O), 1 995s (C=O), and 1 705m cm^{-1}(C=O).

*Reaction of trimethylamine-N-oxide with complex **29**.*

To a solution of complex ***28*** (0.10 g, 0.25 mmol) in acetone (10 ml) was added trimethylamine-*N*-oxide (0.02 g, 0.27 mmol) and the resulting mixture was stirred at 20 °C for 3 h under an atmosphere of nitrogen. The reaction mixture was filtered to remove the iron residues and the solvent was removed under reduced pressure to give a dark oil. The i.r. spectrum of this oil indicated that the original complex ***29*** had been regenerated.

*Synthesis of [η-^{5}-Cp*Fe(CO)$_2$(PhCH=CH-CH=NPh)]$^+$ BF$_4^-$ **33**.*

A solution of 1-azadiene ***32*** (0.455 g, 2.20 mmol) and the THF cation ***22*** (0.044 g, 0.11 mmol) in dichloromethane was stirred and irradiated with a tungsten lamp at 20 °C for 3-20 h under an atmosphere of nitrogen. The reaction mixture was filtered to remove the iron residues and the solvent was removed under reduced pressure to give a yellow solid. The excess azadiene was removed by washing this solid with dimethyl ether and the resulting oil was dried in vacuo. The i.r. spectrum of this oil suggested complex ***33*** had formed.

$\nu_{max.}$ (CH_2Cl_2) 2 038s (C=O), 1 990s (C=O), and 1 590m cm^{-1}(C=N-).

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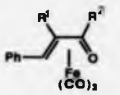
Appendix 1

Fast atom bombardment mass spectra of (1-oxadiene)tricarbonyliron(0) complexes

Due to the difficulty encountered in our laboratory obtaining satisfactory e.i. and c.i. mass spectra of (1-oxadiene)tricarbonyliron(0) complexes containing a molecular ion and peaks arising from the loss of carbonyl ligands it was decided to develop a procedure to obtain these spectra using fast atom bombardment techniques. The (1-oxadiene)tricarbonyliron(0) complexes listed below were used in this study.

	R^1 =	R^2 =
I	H	H
II	H	CH_3
III	D	CD_3
Iv	H	$(CH_2)_2CH_3$
v	H	$CH_2CH(CH_3)_2$
vi	H	$C(CH_3)_2$



An initial survey of f.a.b. matrices indicated that *m*-nitrobenzylalcohol was most suitable for this study.

In general the positive ion mass spectra contained a protonated molecular ion and significant peaks associated with $[MH\text{-}CO]^+$, $[MH\text{-}2CO]^+$ and $[MH\text{-}3CO]^+$. The base peak was due to $[M\text{-}3CO]^+$. An interesting peak at $[M+69]^+$ was observed for each complex. Deuteration experiments indicated that the peak at $[M+69]^+$ contained only one oxadiene fragment. The mass spectrum of the tetradeutero complex III contained an $[M+69]^+$ peak which appeared at 359 compared to 355 for the undeuterated compound II.

The negative ion mass spectra of complexes I-vi contained strong $[M]^-$ peaks. The base peaks were assigned to $[M\text{-}CO]^-$. In addition significant peaks at $[M\text{-}2CO]^-$ and $[M\text{-}3CO]^-$ were also observed.

Results obtained from the f.a.b. mass spectra of (1-azadiene)tricarbonyliron(0) complexes indicate that this procedure is also suitable for analysis of these systems.

Appendix 2.

Reprints of publications arising from this work.