SYNTHESIS AND REACTIVITY OF (DIENE)TRICARBONYLIRON(0) AND (VINYLKETENE)TRICARBONYLIRON(0) COMPLEXES

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University of Warwick
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To Pedro, my parents and my sisters

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DECLARATION

All the work described in this thesis, unless otherwise stated, was performed by the author in the Department of Chemistry, University of Warwick, between October 1987 and September 1990 and has not been previously submitted for a degree at any Institution.

Ana Cristina Reduto dos Reis

July 1991

SUMMARY

As a contribution to the study of η^4-$Fe(CO)_3$ complexes, a series of new (dienamide)tricarbonyliron(0) complexes ($R_2R_1C{=}CR_1CH{=}CHCONMe_2$)$Fe(CO)_3$ (120) (R_2=Me, R_1=R_3=H), (143) (R_1=R_2=R_3=H), (144) (R_1=R_2=Me, R_3=H), (145) (R_1=H, R_2=R_3=Me) and (146) (R_1=Me, R_2=R_3=H) were synthesised by the reaction of $Fe_2(CO)_9$ with the appropriate dienamides, obtained by standard methodology. Reaction of (120) with isobutyronitrile anion led to the isolation of 2-*N*,*N*-dimethylamide-3-isobutyronitrile-5-methyl-cyclopentanone (127) as a 3:1 mixture of the two stereoisomers 2α-3,5β and 2,5α-3β. Cyclopentanone formation also occurred on reaction of (143) under similar conditions, but reaction of (144) and (146) with isobutyronitrile anion gave the C-3 addition products $R_2R_1C{=}CR_1CH(C(CH_3)_2CN)CH_2CONMe_2$ (151) (R_1=R_2=Me, R_3=H) and (152) (R_1=Me, R_2=R_3=H). Addition of isobutyronitrile anion to the (methylester) tricarbonyliron(0) complexes ($R_2R_1C{=}CR_1CH{=}CHCO_2Me$)$Fe(CO)_3$ (131) (R_2=Me, R_1=R_3=H) and (148) (R_1=R_2=R_3=H) yielded new bis(isobutyronitrile) enones $R_2R_1C{=}CCH(C(CH_3)_2CN)CH_2C(C(CH_3)_2CN){=}O$ (133) (R_1=Me, R_2=R_3=H) and (150) (R_1=R_2=R_3=H).

The known (vinylketene)tricarbonyliron(0) complexes ($PhCH{=}CHCR_1{=}C{=}O$)$Fe(CO)_3$ (157) (R_1=Me,^{t}Bu) and the new (vinylketene) tricarbonyliron(0) complexes ($R_2CH{=}CHCR_1{=}C{=}O$)$Fe(CO)_3$ (290) (R_1 = -$(CH_2)_4CH{=}CH_2$-, R_2=Ph), (301) (R_1=^{t}Bu, R_2=-$C(CH)_4CNMe_2$) and (308) (R_1=Me, R_2= -$SO_2{}^t$Bu) were synthesised by addition of MeLi under an atmosphere of carbon monoxide to the corresponding (vinylketone)$Fe(CO)_3$ complexes, which were prepared from the reaction of $Fe_2(CO)_9$ with the appropriate vinylcarbonyl precursors. The reactivity of the vinylketene complexes towards inter- and intramolecular cycloaddition reactions was investigated.

ABBREVIATIONS

Me	Methyl
Et	Ethyl
Pr^i	Isomeric propyl
Bu^t	Tertiarybutyl
Ph	Phenyl
Ac	Acetyl
Cp	Cyclopentadienyl
In	Indenyl
Nu	Nucleophile
Diphos	1,2-Bis(diphenylphosphino)ethane
Ts	Tosyl
TBDMS	Tertiary butyldimethylsilyl
DMTS	Dimethylhexylsilyl
LDA	Lithium diisopropylamide
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
HMPA	Hexamethylphosphoric triamide
m-CPBA	*meta*-Chloroperbenzoic acid
THF	Tetrahydrofuran
NBA	*m*-Nitrobenzyl alcohol
r.t.	Room temperature
h	Hour
t.l.c	Thin layer chromatography
m.p.	Melting point
b.p.	Boiling point
i.r.	Infrared
n.m.r.	Nuclear magnetic resonance
MS	Mass spectroscopy

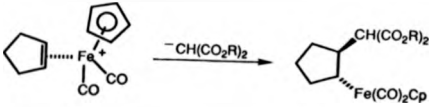
C.I.	Chemical ionisation
E.I.	Electron ionisation
FAB	Fast atom bombardment
s	Singlet
d	Doublet
t	Triplet
q	Quartet
m	Multiplet
dd	Doublet of doublets
dt	Doublet of triplets
dq	Doublet of quartets
td	Triplet of doublets
br	Broad
e.e.	Enantiomeric excess
HOMO	Highest occupied molecular orbital
LUMO	Lowest unoccupied molecular orbital

PART I - NUCLEOPHILIC ADDITION TO ORGANOTRANSITION METAL COMPLEXES CONTAINING UNSATURATED HYDROCARBON LIGANDS

I.1 INTRODUCTION

Transition metals are able to activate organic substrates and promote the formation of new carbon-carbon bonds with a high degree of regio- and stereoselectivity. In the case of organic fragments π-coordinated to transition metals, the metal ligand bonding generally results in a net withdrawal of electron density from the unsaturated hydrocarbon ligand to the adjacent metal centre thus promoting nucleophilic attack on the π-ligand.

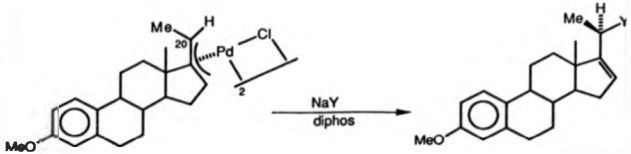
Nucleophilic attack in the main occurs onto the *exo*-face of the ligand, *i.e.*, onto the side of the ligand away from the metal. Thus, the stereochemistry of addition to olefins can be controlled by their coordination to metal centres, as illustrated by the addition of the malonate anion to (1) in which nucleophilic attack occurs specifically onto the *exo* face of the cyclopentene ring bound to the cationic iron centre to give the addition product (2).[1]



1 2

Nucleophilic addition to unsaturated hydrocarbons complexed to transition metals has been used to effect a wide range of regioselective and stereoselective transformations that would be difficult to achieve by other methods. Several representative examples are outlined below.

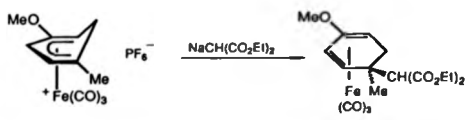
A major problem in steroid synthesis is the creation and control of stereochemistry at C-20. Using palladium as a template, excellent stereo- and regioselectivity has been achieved in the synthesis of (4) *via* the η^3-allyl complex (3).[1]



3 4

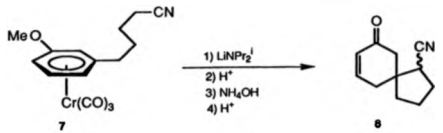
$^{-}Y = {}^{-}CH(CO_2Me)_2$ 81%; $^{-}CH(CO_2Me)(SO_2Ph)$ 82%

Quaternary carbon centres are difficult structural units to synthesise by classical organic reactions. Controlled formation of quaternary carbon centres has however been accomplished by regioselective nucleophilic attack on η^4-dienyl complexes. For example, the (η^4-hexadienyl) iron complex (5) reacts with diethyl sodiomalonate to give (6).[2]



5 6

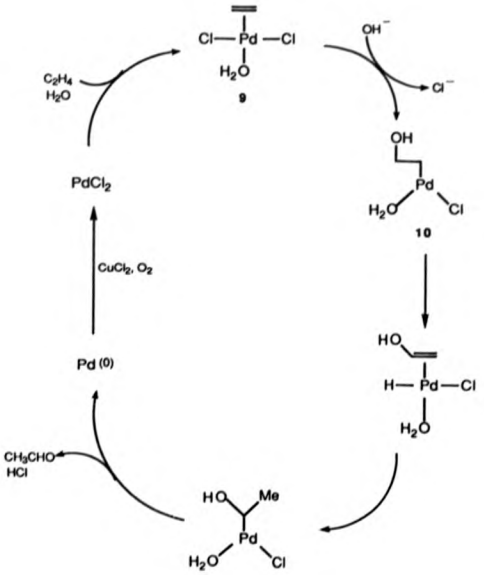
The synthesis of spiro-ring systems has attracted much attention because of their presence in a number of naturally occurring sesquiterpenes. Intramolecular nucleophilic attack on anisole-chromium complexes such as complex (7), provides a useful entry into spiro-compounds. A solution of (7) in THF was added to a solution of lithium diisopropylamide in THF. Addition of trifluoroacetic acid, washing the mixture with aqueous ammonium hydroxide, and treatment with concentrated hydrochloric acid afforded a mixture of diastereoisomeric spiro-cyclohexanones (8) in 96% yield.[4]



7 8

Transition metal catalysed nucleophilic addition may be preferable to the use of stoicheiometric amounts of transition metal, especially when the metal used is as expensive as palladium or rhodium.

J. Smidt[5] and his co-workers at Wacker-Chemie developed a catalytic process for conversion of ethylene into acetaldehyde using palladium(II) chloride. The mechanism is believed to involve the formation of a Pd(ethylene) complex (9) which undergoes nucleophilic attack by OH^- to give the alkyl complex (10). The reaction is rendered catalytic in palladium by the presence of $CuCl_2$ which reoxidises Pd(0) to Pd(II) and the Cu(I) thus produced is reoxidised to Cu(II) by molecular oxygen.


Cl—Pd—Cl
H2O
9
OH⁻
Cl⁻
OH
Pd
H2O
Cl
10
HO
H—Pd—Cl
H2O
HO
Me
Pd
H2O
Cl
CH3CHO
HCl
Pd (0)
CuCl2, O2
PdCl2
C2H4
H2O

The development of the Wacker process provided a unique oxidation method with broad application in organic synthesis.[4-13] Its successful commercialisation was a major step in the establishment of the importance of organometallic and homogeneous catalytic methods in industrial processes.

Whilst a lot of work has been done on nucleophilic addition to η^2-, η^3-, η^5-, and η^6-complexes, the study of η^4-complexes has been relatively neglected. The next three sections of this Introduction will review nucleophilic attack on the isoelectronic (η^4-diene) molybdenum and cobalt cationic complexes and (η^4-diene) iron neutral complexes. Section 1.1.4 analyses and compares the regiospecificity of nucleophilic attack on the three metal systems.

1.1.1 Nucleophilic attack on cationic molybdenum complexes of dienes

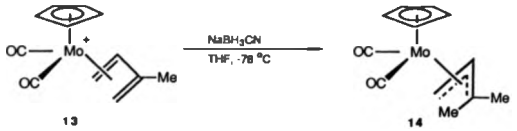
Cationic diene complexes of molybdenum react with a range of nucleophiles to give π-allyl complexes.

Early studies by Green[14,15] and co-workers showed that nucleophilic attack on $[(\eta^4\text{-diene})Mo(\pi\text{-}C_3H_5)(C_6H_6)]^+ \ BF_4^-$ (**11**) occurs regiospecifically at the diene terminus to give the substituted bis-π-allyl derivative (**12**).

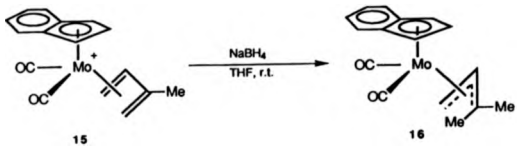
11 **12**

Nu= H, OMe, SMe, CN

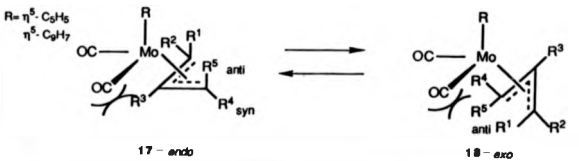
Later work by Faller[16] on substituted η^4-diene complexes showed unexpected specificity for attack at the more hindered diene terminus. For example, reduction of the cationic complex (**13**) gave the η^3-allyl complex (**14**).



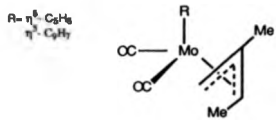
Similar results were obtained by Bottrill and Green[11] on η^5-indenyl complexes of the type $[Mo(diene)(CO)_2(\eta^5\text{-}C_9H_7)]^+$. For example, reaction of the 1,3-diene cation (15) with $NaBH_4$ resulted in regioselective formation of the 1-dimethyl η^3-allyl complex (16).



The regiospecificity of nucleophilic attack observed reflects the stability of the products. η^3-Allylic complexes can exist in two possible conformations, (17) and (18).[12]

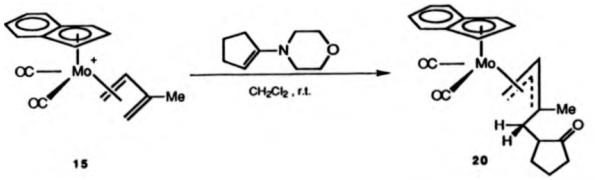


Two effects combine to disfavour nucleophilic attack at the less hindered terminus. Substituents (such as Me) on the central carbon of the allyl group destabilise the *endo* conformation (17)[16]. On the other hand, *anti*-methyl substituents destabilise the *exo* orientation (18). These effects disfavour the formation of (19) from nucleophilic attack on the less hindered terminal carbon.



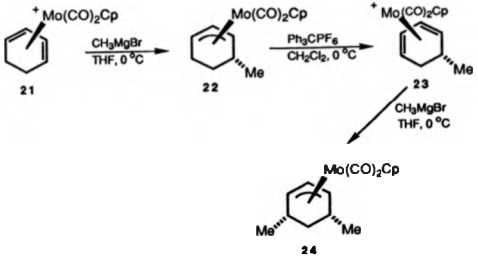
19

To investigate whether the formation of the *anti*-substituted allyl species was related to the size of the reacting nucleophile, the reaction of (15) with the bulky nucleophile 1-morpholinocyclopent-1-ene was examined.[17] Attack again occurred at the more hindered diene terminus and product (20) was obtained selectively in 66% yield.



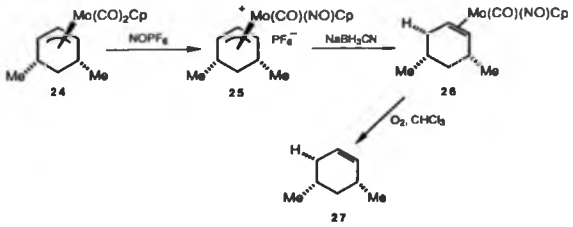
15 20

Stereocontrolled functionalisation of six- and seven-membered rings using organomolybdenum chemistry has been extensively studied.[1-9] Faller[4-8] and co-workers prepared substituted cyclohexene derivatives by sequential nucleophilic addition and hydride abstraction reactions on the (η^4-cyclohexa-1,3-diene) molybdenum cation (21). Addition of methylmagnesium bromide to (21) gave the methylated cyclohexenyl derivative (22), which was treated with triphenylcarbenium hexafluorophosphate to give the substituted η^4-cyclohexadiene cation (23). Addition of a second molecule of methylmagnesium bromide afforded the disubstituted allyl complex (24) in 98% yield.



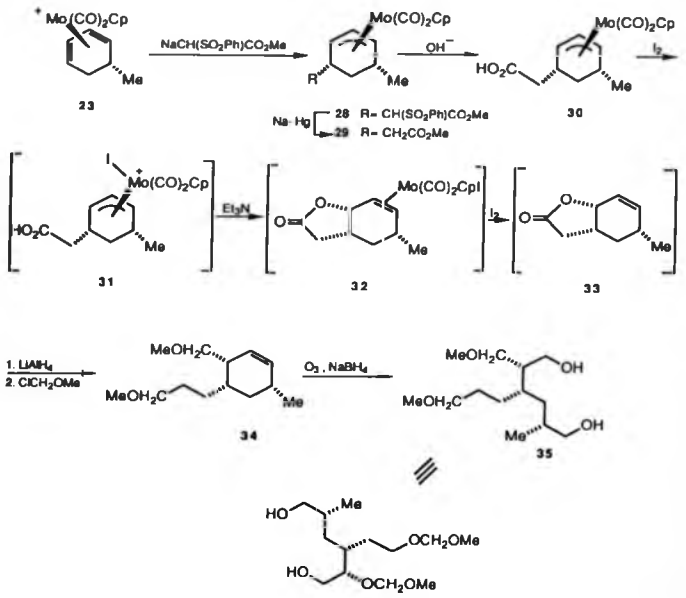
21 22 23 24

The manipulation of [(η^3-allyl)Mo(CO)$_2$(η^5-C$_5$H$_5$)] complexes such as (22) and (24) to give stable organic products is of major importance in the application of these systems to organic synthesis. Demetalation of (24) was accomplished in three steps, starting by treatment with nitrosonium hexafluorophosphate to give the cation (25).[2,8] This complex is reactive towards nucleophiles, and treatment with, for example, hydride reducing agents such as $NaBH_4$ or $NaBH_3CN$ gives the η^2-alkene complex (26). Complex (26) is readily oxidised by air to give the substituted cyclohexene (27).

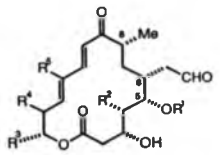


This procedure is acceptable for symmetric complexes like (24) but more than one product is expected for unsymmetrically-substituted derivatives.

Further studies by Pearson[11-13] and co-workers led to the development of methods for regioselective functionalization/demetalation of six-membered rings. For example, demetalation of the π-allyl molybdenum complex (30) is achieved by activation with iodine. The iodine is thought to form the cationic intermediate (31), which undergoes intramolecular nucleophilic attack to produce the lactone (33) with high regio- and stereocontrol.[13]



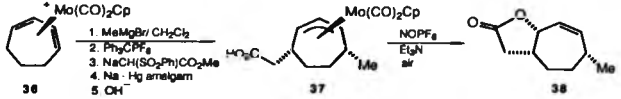
Reduction of the lactone (33) to its diol and protection as the bis-methoxymethyl ether (34) followed by ozonolysis gave, after reductive work up with $NaBH_4$, the acyclic derivative (35). This contains the relative stereochemistry at C-5, C-6 and C-8 present in compounds such as tylosin (I) and magnamycin B (II), both important macrolide antibiotics.



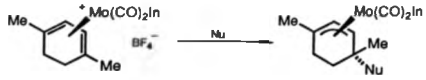
I R^1 = sugar residue; R^2 = Me; R^3 = Et; R^4 = CH_2 Omycinose; R^5 = Me

II R^1 = sugar; R^2 = OMe; R^3 = Me; R^4 = R^5 = H

An identical sequence of reactions has been performed on the cycloheptadiene-$Mo(CO)_3Cp$ system (36)[4,18,19]. Demetalation of (37), however, is more difficult than demetalation of (30), since iodine treatment gives the lactone (38) in poorer yield, and this is contaminated with an impurity, presumably the isomeric *trans* lactone. Much cleaner conversion of (37) to (38) (90% overall yield), was accomplished by treatment with $NOPF_6$ and triethylamine, followed by air oxidation.

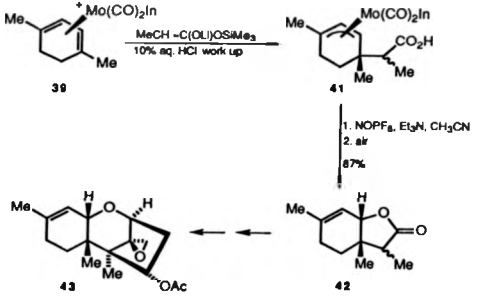


The preparation of quaternary carbon centres constitutes an important target in organic synthesis due to their presence in a broad range of natural products. Addition of carbon nucleophiles to the cationic molybdenum complex of 1,4-dimethyl-1,3-cyclohexadiene (39) has proved to be a successful method for the preparation of a series of (π-allyl) molybdenum complexes (40) containing quaternary carbon centres[4,18,19].



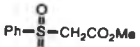
39 Nu- NaCN, $NaCH(CO_2Me)_2$, MeMgBr, $CH_2=CHCH_2MgBr$ 40

Reaction of (39) with the lithium enolate of trimethylsilyl propionate, followed by acidic workup, gave the carboxylic acid (41) in 93% yield. Treatment of this with $NOPF_6/Et_3N$, followed by exposure of the reaction mixture to air, afforded the lactone (42) which has been used as a intermediate in the total synthesis of the antibiotic trichodermin (43).[10]



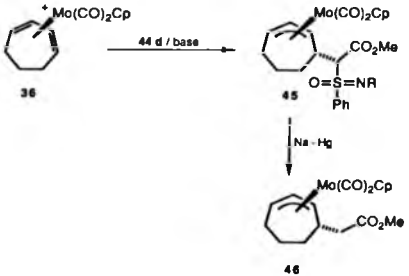
Nucleophilic addition to symmetrical complexes such as (39) yields racemic mixtures. Their resolution may not be worthwhile, unless both enantiomers are required, since at least 50% of the material will be wasted. An alternative approach to the preparation of optically pure addition products is to react the symmetrical metal complexes with optically active nucleophiles.

Asymmetric induction during nucleophilic addition has been observed when enolates derived from optically pure sulfoximinyl esters of type (44) were used as nucleophiles[8,9,10].



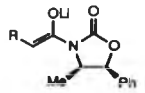
44 a R= Ts
b R= Me
c R=TBDMS
d R= DMTS

For example, reaction of the (-)-*N*-DMTS-substituted sulfoximinyl ester (**44 d**) with the (cycloheptadiene)$Mo(CO)_4$Cp cation (**36**) gave the addition product (**45**) as a mixture of diastereoisomers. Desulfonylation using sodium-mercury amalgam gave the ester (**46**) in 89% enantiomeric excess and 83% yield.[8,9]

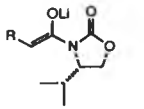


36 **45** **46**

Lower e.e. values were obtained, however, for addition of chiral sulfoximinyl esters (**44**) to the (cyclohexadiene)$Mo(CO)_2Cp$ cation (**21**) (generally less than 78%). For this complex better results were obtained using the chiral *N*-acyloxazolidinone enolates (**47**) and (**48**) developed by Evans and co-workers.[31-34]

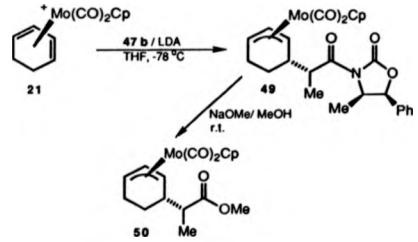


47a R= H
b R= Me



48a R=H
b R= Me
c R=SMe

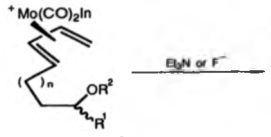
For example, reaction of the enolate (**47b**) with the cation (**21**) gave the addition product (**49**) in 85% e.e. (70% yield). The chiral auxiliary was removed (NaOMe, MeOH, room temperature) to yield the methyl ester (**50**).[34]



The use of the Evans' enolates (**47**) and (**48**) offers advantages over the sulfoximinyl esters (**44**) as the former possess a recoverable chiral auxiliary and they are obtained from commercially available and inexpensive aminoacid derivatives.

Finally in this section, some recent work reported by Lee[14] which has demonstrated the feasibility of extending nucleophilic attack on cationic η^4-diene complexes to intramolecular reactions is described.

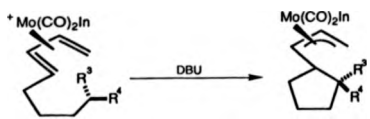
Diene cations (51) led to tetrahydrofuranyl or pyranyl systems (52) on treatment with triethylamine (for (51 a-e) or fluoride anion (for (51 f).



51 a R^1, R^2 = H; n= 1
b R^1 = Me; R^2 = H; n= 1
c R^1 = Pr^i; R^2 = H; n= 1
d R^1 = Ph; R^2 = H; n= 1
e R^1 = R^2 = H; n= 2
f R^1 = H; R^2 = $SiMe_2Bu^t$; n= 2

52 a R^1 = H; n= 1
b R^1 = Me; n= 1
c R^1 = Pr^i; n= 1
d R^1 = Ph; n= 1
e R^1 = H; n= 2

Cyclopentane derivatives (54) were obtained from cationic complexes (53) on reaction with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).



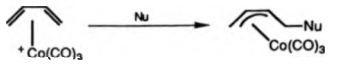
53 a R^3=R^4= CO_2 Me
b R^3= CO_2 Me, R^4=SO_2Ph
c R^3=R^4=SO_2Ph

54 a- c

This new method generates cyclic compounds linked to a molybdenum allyl complex which is capable of further elaboration[1,2,3], so enhancing the synthetic potential of the reaction.

1.1.2 Nucleophilic attack on cationic cobalt complexes of dienes

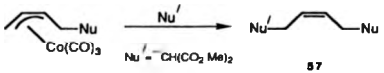
The reactivity of cobalt π-complexes of conjugated dienes has received surprisingly little study. Preliminary studies of nucleophilic additions to the parent compound [(η⁴-butadiene)Co(CO)$_3$]BF$_4$ (55) using a variety of carbon- and hetero-nucleophiles revealed that these gave the C-1 addition products (56 a-d) in moderate to good yields.[48]



55

56 a Nu= C_6H_5N
b Nu= $NaBH_3CN$
c Nu= PhMgBr
d Nu= PMe_3

The η³-allyl cobalt complexes (56) subsequently undergo nucleophilic addition at the other terminus to produce the alkenes (57).[48]



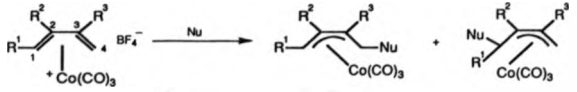
56 b Nu= H⁻
c Nu= ⁻CH(CO$_2$ Me)$_2$

57

Thus, sequential double nucleophilic addition to cation (55) constitutes a method for regioselective 1,4-functionalization of butadiene.

Studies on nucleophilic addition to 1-, 2- and 1,3-substituted [(η⁴-diene)Co(CO)$_3$]BF$_4$ complexes (58) showed preference for attack at C-4 (remote from the substituent) to give the η³-allyl complexes (59) as major or exclusive products.[48] By way of exception, the isoprene complex (58 b) shows a modest selectivity for C-1 attack (to produce (60)), with Nu=$NaBH_3CN$, PhMgBr and PMe_3.

In the case of the 1,3-dimethyl substituted complex (58 e), the general C-4 addition tendency is observed, except with Nu=pyridine, for which a 1:1 mixture of the two products (59) and (60) was obtained.

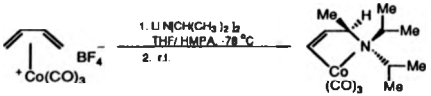


58 a R^1 = Me; R^2 = R^3 = H
b R^1 = R^3 = H; R^2 = Me
c R^1 = R^3 = H; R^2 = Ph
d R^1 = R^3 = H; R^2 = CH_2SiMe_3
e R^1 = R^3 = Me; R^2 = H

59 60

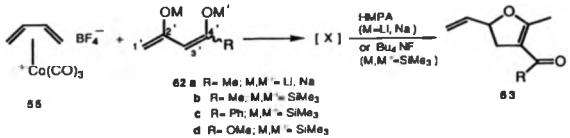
Nu= $NaBH_3CN$; PhMgBr; PMe_3 ; pyridine; $N(CH_2CH_3)_3$

A particularly surprising result was obtained on reaction of lithium diisopropylamide with (η^4-1,3-butadiene)$Co(CO)_3BF_4$ (55).[43] The formation of the metallacycle (61) indicates that nucleophilic attack by $N(Pr^i)_2$ occurs at C-2, which is the first such example involving a cationic diene complex.



55 61

Divalent nucleophiles such as the β-dicarbonyl anion (62 a) and the related 1,3-bis(siloxy)dienes (62 b-d) react with the (η^4-diene)$Co(CO_3)^+$ complex (55) to give, after addition of HMPA, the 1,2 -addition products (63).[43]

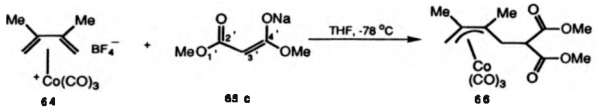


55

62 a R= Me; M,M'= Li, Na
b R= Me; M,M'= $SiMe_3$
c R= Ph; M,M'= $SiMe_3$
d R= OMe; M,M'= $SiMe_3$

63

Some information about the identity of the intermediate [X] has been obtained by reaction of the sodium enolate (65 c) with [(η^4-2,3-dimethyl-1,3-butadiene)Co $(CO)_3$]BF_4 (64).[44] Isolation and characterization of the stable adduct (66) demonstrates that the initial bond formation occurs between C-3' of the nucleophile and the diene terminal carbon.

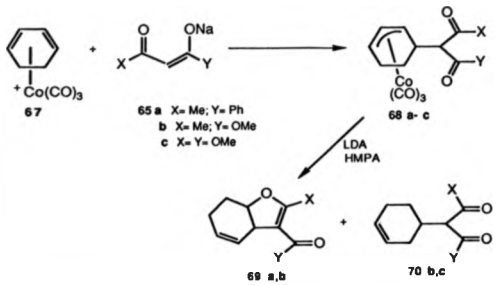


64

65 c

66

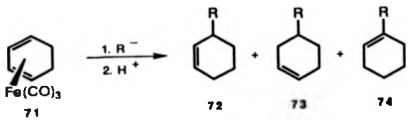
The cation [(η^4-1,3-cyclohexadiene)$Co(CO)_3$]$^+$ (67) likewise formed C-alkylated adducts (68 a-c) when treated with the sodium enolates from benzoylacetone, methyl acetoacetate or dimethyl malonate (65 a-c). Treatment of (68 a-c) with LDA/HMPA in THF gave the tetrahydrobenzofuran derivative (69 a) (80%), a mixture of (69 b) and the diene ketoester (70 b) (10:1, 65%) and the diene diester (70 c) (73%) respectively.



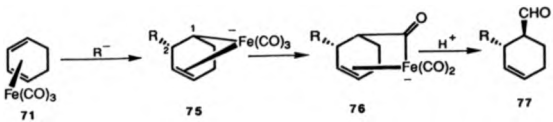
Nucleophilic addition of β dicarbonyl anions to $[(\eta^4\text{-diene})Co(CO)_3]^+$ complexes followed by protonation thus provides a new synthetic pathway to acyldihydrofurans and acyltetrahydrobenzofurans.

1.1.3 Nucleophilic attack on neutral iron complexes of dienes

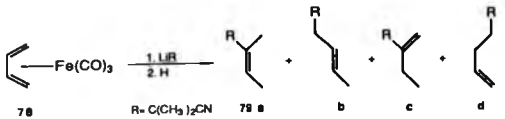
The first examples of nucleophilic addition to (η^4-diene)iron complexes involved attack on (1,3-cyclohexadiene)tricarbonyliron(0) (**71**) by a variety of carbon nucleophiles. Protonation of the intermediate with trifluoroacetic acid afforded a mixture of isomeric substituted alkenes (**72**)-(**74**).[4,5]



When R= $C(CH_3)_2CN$, a fourth cyclohexene derivative (77) was formed as a minor product. It was suggested to result from addition at C-2, which gives the intermediate (75), followed by migration of the alkyl ligand C-1 to a CO ligand to give (76). Protonation of the iron centre of (76) followed by a reductive elimination and decomplexation then gives product (77).

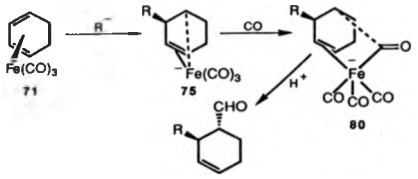


Further evidence for nucleophilic attack at the internal carbon C-2 of conjugated dienes coordinated to $Fe(CO)_3$ moieties was obtained when the parent acyclic complex (1,3-butadiene)$Fe(CO)_3$ (78) was reacted with 2-lithio-2-methylpropionitrile. This reaction gave a mixture of addition products (79 a-d) in a ratio of 89 : 6: 4 : 1.[45]

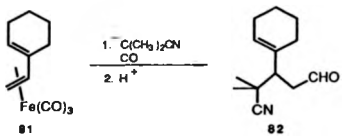


The nucleophilic addition reaction was also performed in the presence of external CO,[46] with the aim of investigating the CO incorporation process that led to the formation of (77). The anion $^-C(CH_3)_2CN$ was combined with the cyclohexadiene complex (71) under argon (-78 °C to +25 °C) and then exposed to CO at about 1.5 atm. Protonation and isolation of the organic products gave only the alkenes (72) and (73) (R=$C(CH_3)_2CN$), with no evidence for CO incorporation.

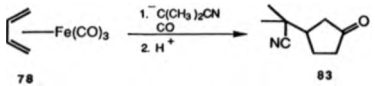
However, if CO was present at 1.4-1.5 atm during the mixing of anion and complex at -78 °C, protonation of the reaction mixture with trifluoroacetic acid afforded the product (77) in high yield (93%). The intermediate (80) was proposed as a precursor to (77).



Similarly, the reaction between (1-vinylcyclohexene)$Fe(CO)_3$ (81) and the anion derived from 2-methylpropionitrile under CO gave, after protonation, the carbonylation product (82) in 71% yield.[44]

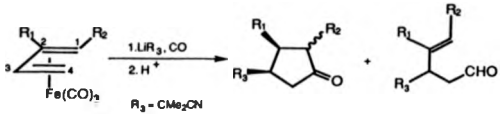


In the case of simple open-chain dienes, the formation of substituted cyclopentanones has been observed.[41] Addition of $LiC(CH_3)_2CN$ to $(\eta^4$-1,3-butadiene)$Fe(CO)_3$ (78) in the presence of 1.5 atm of carbon monoxide followed by protonation, yielded the cyclopentanone (83) with the unit derived from the anion in the C-3 position.



78 83

Studies on substituted diene complexes (84) afforded both cyclic and acyclic products (85) and (86), depending on the substituents and their relative positions on the diene.[42]



84 a R1 = Me; R2 = H
b R1 = H; R2 = Me
c R1 = OMe; R2 = H
d R1 = R2 = Me
e R1 = H; R2 = OMe
f R1 + R2 = $(CH_2)_4$

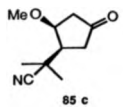
85 a (78%)
b (93%)*
c (70%)**

86 d (65%)
e (28%)
f (71%)

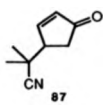
* sum of yields of 85 b and 88
** sum of yields of 85 c and 87

From the results obtained, the formation of a cyclopentanone product appears to be efficient only for monosubstituted diene complexes. With diene ligands bearing carbon substituents at both C-1 and C-2, (84 d) and (84 f), ring closure to form cyclopentanones is not observed and CO incorporation followed by protonation gives the aldehydes (86 d) and (86 f). Similarly, from (Z)-1-methoxy-1,3-butadiene complex (84 e), only the open-chain aldehyde (86)e was obtained.

The 2-methoxy-1,3-butadiene complex (**84 c**) does not give a cyclopentanone following the typical procedure (THF, -78 °C, 15 psi, CO) but, at higher CO pressures (50 psi), the cyclopentanone (**85 c**) is formed together with the cyclopentanone (**87**), resulting from loss of MeOH.

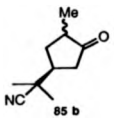


85 c

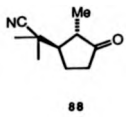


87

Steric effects seem to be limited for this type of reaction. For example, nucleophilic addition to complex (**84 b**) produces a 1:1 mixture of the cyclopentanones (**85 b**) (mixture of epimers) and (**88**), resulting from attack at C-3 and at C-2, respectively.

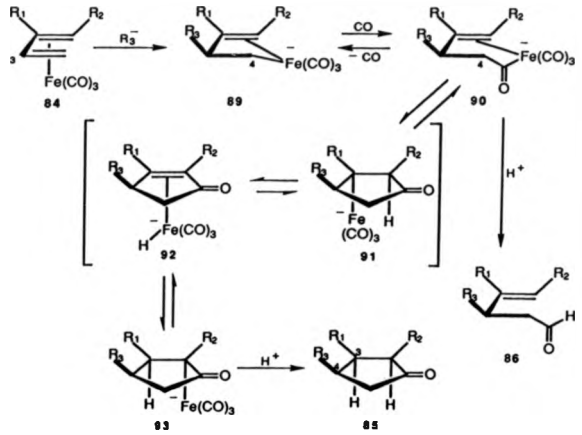


85 b



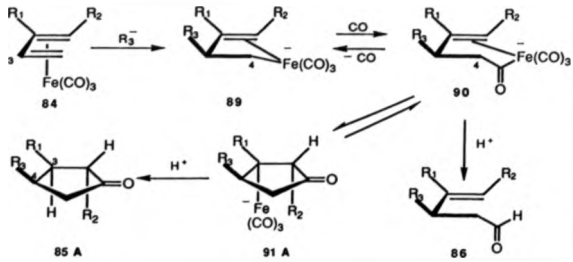
88

Semmelhack *et al*.[9] proposed the following mechanism for the formation of cyclopentanones (**85**) and γ,δ-unsaturated aldehydes (**86**).

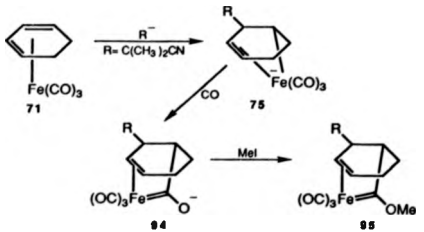


The formation of the less stable *cis*-3,4-disubstituted cyclopentanone (85) is consistent with kinetically controlled *anti*-addition of the nucleophile at C-3 of the diene ligand to give (89). This is followed by rapid migration of C-4 to a carbonyl ligand to give (90) and intramolecular alkene insertion to give (91).

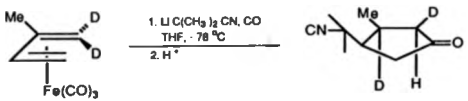
Although Semmelhack[41] proposes *anti* addition of the acyl group $^{-}Fe(CO)_4$ unit to the alkene ((90) → (91)), the possibility of *syn* addition cannot be ruled out on the basis of Semmelhack's results since the relative stereochemistry between C-2 and C-3 or C-2 and C-4 in the cyclopentanone product (85) is not established in any of the cases examined. The following alternative mechanism, in which *syn* addition of the acyl group and $^{-}Fe(CO)_4$ to the alkene occurs ((90) → (91 A)) provides a better rationalization of the results described in this thesis (see Results and Discussions - section I.2)



In the case of addition of $LiC(CH_3)_2CN$ to (1,3-cyclo-hexadiene)tricarbonyliron complex (71), the identity of the anionic intermediates corresponding (89) and (90) has been confirmed by ^1H n.m.r spectroscopy, and the acylferrate complex (94), equivalent to (90), has been successfully trapped with MeI to give the internally-bound (alkene) (methoxyalkylidene)tricarbonyliron species (95).[41]



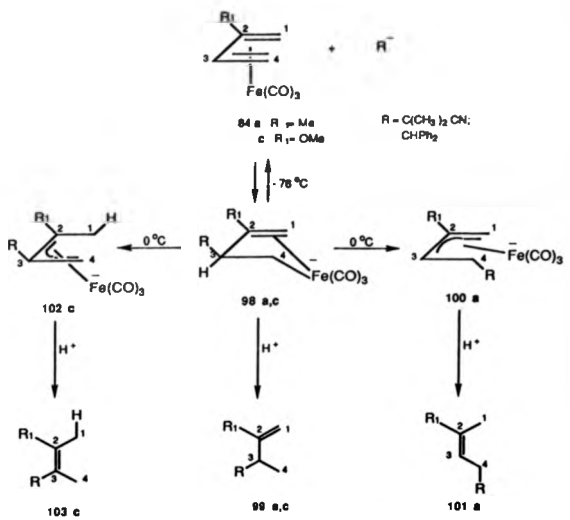
Deuterium labelling studies[47] supported the proposed β-hydride elimination/readdition from the postulated initial cyclopentanone intermediate (91) to the enolate-iron derivative (93). Starting from (η^4-1,1-dideuterio-2-methyl-1,3-butadiene)$(CO)_3Fe$ (96), reaction with $LiC(CH_3)_2CN$ following to the usual procedure gave the single dideuterio product (97), presumably *via* β-hydride elimination/readdition through the intermediate (92).



96 97

The hydrogen (deuterium) rearrangement is consistent with *cis*-β-hydride elimination and retention of configuration during protolytic cleavage of the final anionic iron intermediate (93).

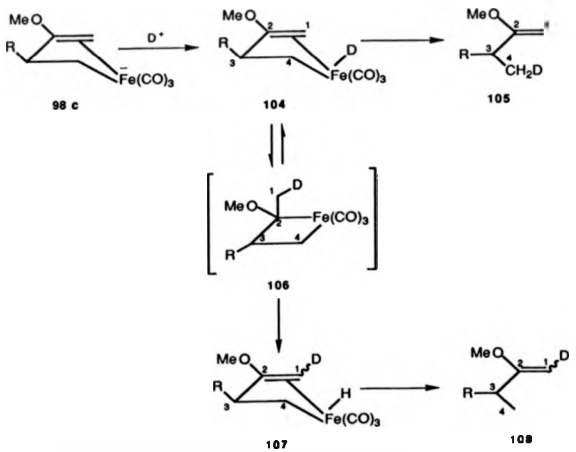
A further study of the addition of nucleophiles to (η^4-1,3-diene)tricarbonyliron complexes showed that the outcome of nucleophilic attack is temperature dependent.[48] Thus, addition of $LiC(CH_3)_2CN$ to (η^4-isoprene)tricarbonyliron (84 a) at - 78 °C occurs preferentially at the unsubstituted internal position (C-3) to give the anionic intermediate (98 a). Treatment with trifluoroacetic acid at this temperature followed by work-up gave the C-3 addition product (99 a) in 88% yield. When the reaction mixture was allowed to warm to 0 °C, rearrangement to the more stable η^3-allyl intermediate (100 a) occurred and, after 2 h at 25 °C, protonation with trifluoroacetic acid afforded the alkene (101 a) as a single product (70% yield).



The anionic intermediate from addition to (η^4-2-methoxy-1,3-butadiene) tricarbonyliron (**84 c**) equilibrates by a different mechanism. Reaction of $LiCHPh_1$ with (84c) at -78 °C for 0.5 h followed by additon of excess trifluoroacetic acid at -78 °C produces the substituted alkene (**99 c**) in 80% yield. Isomerization of the anionic intermediate (**98 c**) occurs upon warming, apparently *via* hydride transfer from C-3 to C-1, to give the allyl complex (**102 c**); after 2 h at 25 °C, quenching produces exclusively (**103 c**) (60% isolated).

Studies of the mechanisms of rearrangement of the anionic intermediates (**98a**) and (**98 c**) using deuterium labels have been reported.[1a] Reaction of tricarbonyl (η^4-2-methoxy-1,3-butadiene)iron (**84 c**) with diphenylmethyllithium initially at -78 °C

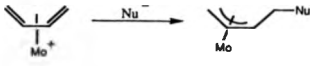
and then at 25 °C for 2 h, followed by cleavage with trifluoroacetic acid-*d* gave the substituted alkene (103) with deuterium exclusively at C-4 (66% yield), as expected. The same mixture held at -78 °C for 1 h and quenched in exactly the same way produced primarily the skeleton represented by (99 c) (71% yield), as expected, but only 20% of the product was D-labelled at C-4 (105). The remaining 80% D was located at the C-1 vinylic positions (108). Deuteration of the intermediate (98 c) has been suggested to produce the iron deuteride (104). Reductive elimination of (104) would give the minor product (105). Addition across the alkene ligand leads to the ferracyclobutane intermediate (106) which by selective β-hydride elimination produces (107). Reductive elimination of (107) accounts for the 1 : 1 mixture of the vinyldeuterium isomers isolated.



1.1.4 Regioselectivity of nucleophilic addition to (η^4-diene)MLn complexes where M= Mo, Co and Fe

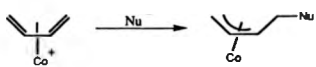
The regioselectivity of nucleophilic addition to dienes π-coordinated to transition metals has been found to depend on the nature of the metal.

The studies on nucleophilic attack on Mo^+-coordinated dienes reported to date show selectivity for attack at the diene terminus C-1 (see section 1.1.1). Schematically, the nucleophile adds to the η^4-diene complex (109) to give the η^3-allyl complex (110).



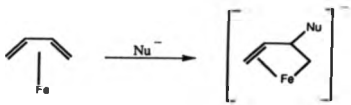
109 110

Nucleophilic attack on (η^4-diene)Co^+ complexes exhibits the same regio-preference, with one single exception having been reported so far (namely the nucleophilic addition of $^-N(Pr^i)_2$ to [(η^4-1,3-butadiene)$Co(CO)_4$]$^+$ - see section 1.1.2). In most cases, nucleophilic addition to diene-Co^+ complexes (111) affords the C-1 addition products (112).



111 112

In sharp contrast, however, nucleophilic addition to the closely related (η^4-diene)Fe complexes (113) occurs at the diene internal carbon C-2 at low temperatures to form the intermediate (114) (see section 1.1.3).



113 **114**

A number of theoretical attempts have been made to explain and predict the regioselectivity of nucleophilic attack on π-coordinated hydrocarbon moieties. Davies, Green and Mingos[11] produced an extensive analysis of nucleophilic addition to cationic complexes of dienes. After considering the transfer of electron density associated with the metal-ligand bonding, they concluded that nucleophilic addition to 18-electron cationic diene complexes is likely to be charge rather than orbital controlled, especially if the nucleophile is small and highly charged. Therefore the regioselectivity of such reactions is probably dominated by the positive charges on the diene carbon atoms.

Calculations based on perturbation theory arguments show that for *even* coordinated polyenes the positive charge on the terminal atoms is always larger than that on the internal carbon atoms, thus accounting for the regioselectivity observed for nucleophilic attack on cationic Mo and Co complexes of dienes. The exceptions found to this rule, and the inadequacy of its application to neutral compounds such as neutral (diene)Fe complexes, led to the development of more sophisticated m.o. calculations.

A perturbational analysis, based on extended Hückel calculations, of the reactions of nucleophiles with the complexes (η^4-butadiene)$Fe(CO)_3$ and -$Co(CO)_3^+$ has been recently reported.[12] This approach focuses on the shapes and energies of the molecular orbitals involved, namely the highest occupied molecular orbital (HOMO) of the nucleophile and the lowest unoccupied molecular orbital (LUMO) and the HOMO of the complex. The problem is thus reduced to the calculation of

the interaction energy ΔE arising from these three orbitals. This energy is a function of the overlap between the nucleophile orbital and the two orbitals of the complex as well as a function of the energy gaps separating the three orbitals.

It is possible to define the interaction energy ΔE as a function of the energy of the HOMO of the nucleophile, x.

The graph below is a plot of the difference between ΔE for terminal attack (ΔE_T) and ΔE for internal attack (ΔE_I) as a function of the $HOMO_{Nu}$ energy x, as calculated for nucleophilic addition to cobalt and iron (η^4-butadiene) complexes. When this function is positive, attack on the terminal carbon is preferred (zone T). $x_o(x_o')$ represents the value of the energy of the nucleophile HOMO where the preference in regioselectivity is changed for the iron (cobalt) complex.

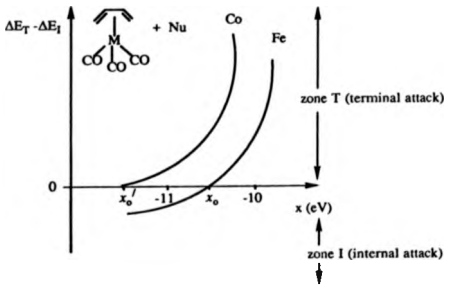


Diagram I.1.4-1. Interaction energy difference for nucleophilic addition to cobalt and iron complexes.

The curve for the cobalt remains above that for the iron, *i.e.*, there is a greater preference for terminal attack at a given x for the cobalt complex. The curve of the iron complex intersects the x axis at a higher energy value ($x_0 > x_0'$). Therefore a nucleophile that prefers the internal carbon in the case of iron may attack the terminal carbon in the case of cobalt.

The regioselectivity observed is determined by the balance between two types of interaction: (i) a two-electron attractive interaction between the $HOMO_{Nu}$ and $LUMO_{complex}$ and (ii) a four-electron destabilizing interaction between the $HOMO_{Nu}$ and the $HOMO_{complex}$. When M= Co^+, the $HOMO_{complex}$ contains a smaller butadiene character so that the incoming nucleophile suffers less electron repulsion from this orbital. In addition, the $LUMO_{complex}$ is more localized on the butadiene so that the two-electron stabilization between the $HOMO_{Nu}$ and the $LUMO_{complex}$ increases. Since the $LUMO_{complex}$ is mostly localized on the diene terminal carbons,[11] the attractive interaction between the nucleophile and the complex is larger for an approach to the terminal carbon, favouring the attack at the terminal centre C-1.

In the case of the (η^4-butadiene)$Fe(CO)_3$ complex, the destabilizing interaction between the $HOMO_{Nu}$ and the $HOMO_{complex}$ is larger, and since the $HOMO_{complex}$ is mostly localized on the diene terminal carbons,[11] attack at the internal centre C-2 is preferred.

For a particular metal complex, *i.e.*, at given energies of $(LUMO/HOMO)_{complex}$, the regioselectivity of nucleophilic addition to the diene ligand depends on the energy of the $HOMO_{Nu}$ (x).

Ab initio calculations of $HOMO_{Nu}$ energies for several anions[11] gave high x values for small, highly charged (hard) nucleophiles such as F^-, H^-, and OH^-, and low x values for larger, more polarizable (soft) nucleophiles, such as I^-, RS^-, and CN^-. Thus, according to diagram I.I.4-I, hard nucleophiles will favour C-1 attack while soft nucleophiles will favour C-2 attack.

The previous model, however, does not take specific account of nucleophile solvation, a factor known to be important in determining the relative reactivity and HOMO energies of nucleophiles.[41,60] It is apparent that hard nucleophiles have their x values greatly lowered by solvation whereas for soft nucleophiles, x is less affected.[61] Indeed, no satisfactory theoretical model exists which allows quantitatively reliable inclusion of this factor, and no systematic experimental studies of the influence of nucleophile hardness/softness and the effect of solvent on the regioselectivity of nucleophilic addition to (η^4-diene)MLn complexes have been reported so far.

I.2 RESULTS AND DISCUSSION

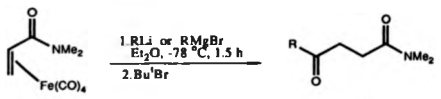
The enhancement of reactivity of unsaturated hydrocarbons resulting from their coordination to electron withdrawing transition metal centres opens a wide area of practical applications both in organic synthesis[4-6] and in industry.[4-6]

Studies on the reactivity of π-coordinated dienes have shown that nucleophilic additions to $(\eta^4\text{-diene})ML_n$ complexes with M=Mo, Co, Fe are characterised by a high degree of regio- and stereoselectivity (section I.1.1 to I.1.3). Of these three types of transition metal complexes, the Fe-coordinated dienes have received least attention to date.

This section reports and discusses the results of a series of experiments designed to investigate the reactivity of $(\eta^4\text{-diene})Fe(CO)_3$ complexes and their potential application to organic synthesis.

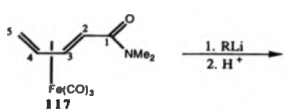
I.2.1 Nucleophilic addition to (2,4-hexadiene)$Fe(CO)_3$ complexes

It has previously been reported[4,5] that the iron tetracarbonyl complex of *N,N*-dimethylacrylamide (**115**) reacts with organo-lithium and Grignard reagents to give γ-ketoamides (**116**), *via* acyl transfer from the metal to the β carbon of the α,β unsaturated amide (**115**).



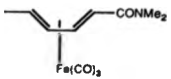
115 R= Me, Et, Bu, Ph **116**

This work suggested a study of the reactivity of (2,4-dienamide)tricarbonyliron(0) complexes (**117**). Addition of the acyl anion resulting from attack of the nucleophile at one of the iron carbonyl ligands, was predicted to occur at C-3 and/or C-5 to give, after protonation, the ketoamides (**118**) and (**119**) respectively.



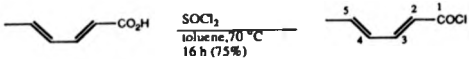
117 118 119

The first (2,4-dienamide) complex studied was the (*N,N*-dimethyl-2,4-hexadienamide)$Fe(CO)_3$ complex (120).



120

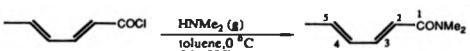
The amide ligand was prepared from commercially available 2,4-hexadienoic acid (121) by standard methodology. The acid was dissolved in toluene and heated at reflux with thionyl chloride, under nitrogen, for 18 h to yield the acid chloride (122). The product was distilled in the absence of moisture to prevent its hydrolysis.



121 122

The formation of the acid chloride (122) from the acid (121) was supported by a shift of the carbonyl stretch in the i.r. spectrum from 1 695 cm^{-1} in the acid to 1 740 cm^{-1} in the acid chloride. The ^1H n.m.r. spectrum of (122) showed a general downfield shift relative to the ^1H n.m.r. spectrum of (121). In the acid chloride spectrum, the C-5 methyl group appeared as a three proton doublet (J 6 Hz) at δ 1.93 (δ 1.88 for the acid), and the olefinic protons as a one-proton doublet (J 15 Hz) at δ 6.04 corresponding to H-2 (δ 5.83 for the acid), a two-proton multiplet at δ 6.20-6.55 due to H-4 and H-5 (δ 6.13-6.38 for the acid), and a one-proton doublet of doublets (J 10 and 15 Hz) at δ 7.47 attributable to H-3 (δ 7.40 for the acid).

The dimethylamide (123) was prepared in good yield by bubbling dimethylamine into a solution of the acid chloride (122) in toluene at 0 °C for 3 h. The solvent was then evaporated and the yellow residue obtained was redissolved in dichloromethane. Extraction with 10% $Na_2(CO)_3$ aqueous solution followed by washing of the aqueous phase with dichloromethane and evaporation of the solvent from the combined organic extracts afforded a yellow crystalline solid which was identified as *N,N*-dimethyl-2,4-hexadienamide (123) by comparison of its i.r. and ^1H n.m.r. spectra with literature data.[16]

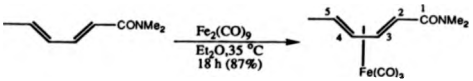


122 123

The i.r. spectrum of (123) contained an intense band at 1 658 cm^{-1} attributable to the carbonyl stretch of the amide group. An equally intense peak at 1 620 cm^{-1} and a less intense peak at 1 590 cm^{-1} account for the C=C bonds of the diene chain. The 220 MHz ^1H n.m.r. spectrum of (123) exhibited a three proton doublet (J 6 Hz) at δ 1.85, identified as the C-5 methyl group protons, and two three-proton

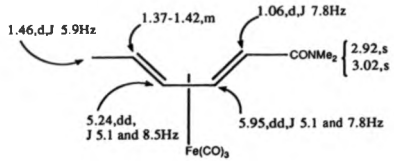
singlets at δ 3.03 and δ 3.10, corresponding to the two amide methyl groups. The olefinic protons appear as a two-proton multiplet at δ 6.10-6.35 (H-4 and H-5), containing a superimposed one-proton doublet (J 15 Hz) at δ 6.28 attributed to H-2, and a one-proton doublet of doublets (J 10 and 15 Hz) at δ 7.29, corresponding to H-3.

The preparation of (*N,N*-dimethyl-2,4-hexadienamide)$Fe(CO)_3$ complex (120) from *N,N*-dimethyl-2,4-hexadienamide (123) was investigated using recently published complexation conditions.[49] The 2,4-dienamide (123) was heated with two equivalents of nonacarbonyldi-iron in dry diethyl ether at 35 °C for 18 h under a nitrogen atmosphere. The dark brown reaction mixture obtained was filtered through alumina, to remove iron residues, and the resulting yellow solution was concentrated under vacuum to give an orange solid. Column chromatography on silica gel yielded a yellow air-stable crystalline solid, m.p. 119-120°C, which was identified as the new (η^4-dienamide)tricarbonyliron(0) complex (120) on the basis of its i.r., ^{1}H n.m.r., ^{13}C n.m.r., MS and elemental analysis data.



123 **120**

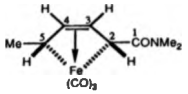
The i.r. spectrum of (120) in hexane showed three sharp peaks at 2 057, 1 996, and 1 980 cm^{-1} assignable to the three iron-carbonyl groups, and a less intense sharp peak at 1 650 cm^{-1} corresponding to the amide carbonyl group. The 400 MHz ^{1}H n.m.r. spectrum of (120) in $CDCl_3$ showed the chemical shift values and coupling constants indicated below.



120

The two three-proton singlets corresponding to the amide methyl groups are slightly shifted to lower δ values relative to the corresponding methyl groups in the uncomplexed amide (123) (from δ 3.03 and 3.10 in the amide to δ 2.92 and 3.02 in the amide complex (120)). A bigger downfield shift was observed for the three proton doublet corresponding to the C-5 methyl group (δ 1.85, J 6 Hz in the ligand to δ 1.46, J 5.9 Hz in the complex). The major changes in the spectrum, however, were observed for the olefinic protons H-2, H-3, H-4 and H-5. The one-proton doublet corresponding to H-2 was dramatically shifted from δ 6.28 in the amide (123) to δ 1.06 in the complex (120) and its coupling constant to H-3 lowered from 15 Hz in (123) to 7.8 Hz in (120). The change in δ value for the H-3 doublet of doublets was considerably smaller (δ 7.29 in (123) to δ 5.95 in (120)) but a similar reduction in its coupling constant to H-4 (10 Hz in (123) to 5.1 Hz in (120)) was observed. The H-4 signal, which appears as an unresolved multiplet at δ 6.10-6.25 in the dienamide 220 MHz ^{1}H n.m.r. spectrum, gives a one-proton doublet of doublets (J 5.1 and 8.5 Hz) at δ 5.24 in the 400 MHz ^{1}H n.m.r. spectrum of (120). The H-5 proton, second component of the multiplet at δ 6.10-6.35 in (123), undergoes a major shift to appear as a multiplet at δ 1.40 in the ^{1}H n.m.r. spectrum of (120).

The large upfield shift of the terminal diene protons H-2 and H-5, which are the nearest to and most directly affected by the bonding to the iron, suggests that the structure (124) plays an important role in the bonding of the (2,4-dienamide) tricarbonyliron(0) complex (120).[44]

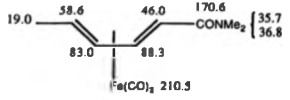


124

In structure (124) the terminal protons H-2 and H-5 are sp^3 hybridised and this is more consistent with their observed resonances. The central protons H-3 and H-4, however, are sp^2 hybridised and are expected to be found in the normal olefinic region as observed. The relatively small values of the H,H coupling constants obtained for vicinal olefinic protons in (120) (*trans* $J_{3,4}$=7.8 Hz, *trans* $J_{4,5}$=8.5 Hz, and *cis* $J_{3,4}$=5.1 Hz) have been attributed to the nonplanarity of the H and C atomsin the diene-iron carbonyl complex.[44] Similar conclusions were made from ^{13}C n.m.r. studies of methyl-substituted (diene)iron tricarbonyl complexes.[41] The comparison of ^{13}C shielding for dienetricarbonyliron complexes and uncomplexed dienes revealed that in complexed dienes there is a larger σ-bond character along the terminal bonds and a larger π-bond contribution along the central bond of the diene. These observations are consistent with available X-ray data for substituted (cyclohexadiene)$Fe(CO)_3$ complexes which show the diene 2,3-bond to be slightly shorter than the 1,2- and 3-4 bonds.[45]

The ^{13}C n.m.r. data for (120) also support the increased sp^2 character of C-2 and C-5 compared to C-3 and C-4 (see diagram below). The amide carbonyl group appeared as a weak peak at δ 170.6 and the iron-bonded C=O groups gave a very

weak broad signal at δ 210.5, which is attributed to free rotation of the $Fe(CO)_3$ moiety relative to the organic ligand.

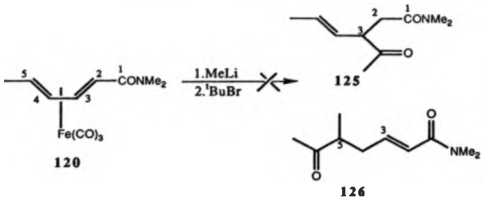


120

The FAB mass spectrum (NBA matrix) of (120) contained peaks at *m/z* 280, 252, 224, and 195, corresponding to the monoprotonated molecular ion $[MH]^+$ and successive loss of the three metal carbonyls.

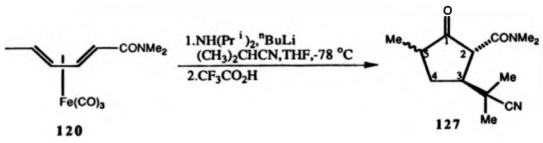
In order to compare the outcome of the addition of alkyl-lithium reagents to (2,4-dienamide) complexes, with the results obtained with the α,β-unsaturated amide complex (115), methyllithium was added to the iron tricarbonyl complex (120) under similar conditions.

Complex (120) was dissolved in dry diethyl ether and cooled to -78 °C. Methyllithium (1.5 equiv.) was added dropwise and the reaction mixture was stirred at -78 °C for 1.5 h. It was then quenched with *t*-butyl bromide, allowed to warm to room temperature, and filtered through a plug of alumina. Evaporation of the solvent gave an orange oil, which was shown to be a complicated mixture of products by ^1H n.m.r. spectroscopy. The 2,4-hexadienamide ligand (123) and the starting material (120) were identified as minor components of this mixture. The absence of a singlet at approximately δ 2.0 in the ^1H n.m.r. spectrum of the crude product mixture and of an absorption band at about 1 720 cm^{-1} in its i.r. spectrum revealed that acyl anion addition to give the ketoamides (125) or (126) had not occurred.



Nucleophilic addition to the complexed *N,N*-dimethyl-2,4-dienamide (**120**) was then investigated using a softer nucleophile.

The anion derived from isobutyronitrile was reacted with (2,4-dienamide) tricarbonyliron(0) (**120**) in THF, under nitrogen, (-78 °C to + 25 °C for 2 h). Protonation with trifluoroacetic acid followed by extraction of the reaction mixture with saturated sodium carbonate and diethyl ether afforded a clear, red organic phase. Filtration through a plug of alumina gave a yellow, clear solution which was dried ($MgSO_4$), filtered and the solvent evaporated to yield a yellow oil. Purification by preparative thin layer chromatography on silica gel afforded a colourless oil, the spectroscopic data of which support the formation of the cyclopentanone (**127**) as a 3:1 mixture of the two stereoisomers 2α-3,5β and 2,5α-3β, respectively.

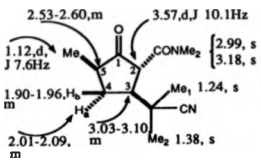


The i.r. spectrum of the product contains a C=O absorption band at 1 650 cm^{-1}, attributable to the amide carbonyl group, and a C=O stretching band at 1 748

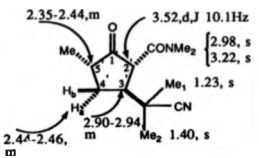
cm^{-1} within the range of carbonyl absorption frequencies observed for ketones in five-membered rings. The presence of a C≡N absorption band at 2 243 cm^{-1} agrees with addition of isobutyronitrile having occurred.

The EI mass spectrum of (127) (accurate mass) contains peaks at *m/z* 236 (9%) and 168 (100%) corresponding to the molecular ion M^+ and to M^+-$C(CH_3)_2CN$ respectively.

Evidence for the addition of isobutyronitrile is also given by the ^1H n.m.r. spectrum of the product (127). The diagram below shows the 400 MHz ^1H n.m.r. data for the 2α-3,5β- and 2,5α- 3β- isomers of (127) formed.



127 2 α-3,5β
major

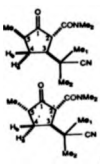


127 2,5α -3β
minor

The two isobutyronitrile methyl groups appear as three-proton singlets at δ 1.24 and δ 1.38 for the major isomer 2α-3,5β, and at δ 1.23 and δ 1.40 for the minor isomer 2,5α-3β. The 5-Me group gives the expected three-proton doublet at δ 1.12 (J 7.6 Hz) for the major isomer, but the corresponding doublet for the minor isomer is partially hidden by the former. The amide methyl peaks are visible as three-proton singlets at δ 2.99 and δ 3.18 for the major isomer and at δ 2.98 and δ 3.22 for the minor isomer in the 400 MHz ^1H n.m.r. spectrum of (127). Two one-proton doublets at δ 3.52 (J 10.0 Hz) and δ 3.57 (J 10.1 Hz) were assigned to 2-H in the minor and major isomers respectively. The 3-H proton appeared as a multiplet at δ 3.03-3.10 for the major isomer and at δ 2.90-2.94 for the minor

isomer. A one-proton multiplet at δ 2.53-2.60 was attributed to the 5-H proton in the major isomer, and the 5'-H proton (minor isomer) gave a one-proton multiplet at δ 2.35-2.44. The two 4-H protons give multiplets at higher field than the other ring protons. For the major isomer, 4-Ha and 4-Hb were identified as one-proton multiplets at δ 2.01-2.09 and δ 1.90-1.96, respectively. The 4-Ha proton in the minor isomer gave a broad, less shielded multiplet at δ 2.44-2.46. A ^{1}H-2D COSY-45 experiment identified 4-Hb in the minor isomer as being underneath the isobutyronitrile Me$_2$-peaks in the region δ 1.38-1.40 and allowed the complete assignment of the one-dimensional ^{1}H n.m.r. spectrum of the mixture of (127) isomers formed.

Further information about the stereochemistry of the two isomers formed was obtained from NOE difference spectra obtained by irradiation of 2-H, 5-Me, and the two isobutyronitrile methyl groups Me$_1$ and Me$_2$ of the major isomer. The % NOEs observed are indicated in the table below.



{ }	NOE observed (%)									
	2-H	NMe	3-H	3-Me$_1$	3-Me$_2$	4-Ha	4-Hb	5-H	5'-H	5-Me
2-H	-	+2.5/+1	+1	+1	+0.5	0	0	0	0	+0.5
3-Me$_1$	+2.5	+0.5	+3.5	-	+1	0	0	0	0	0
3-Me$_2$	0	0	+4	+1.5	-	+2	+3	0	0	0
5-Me	0	0	0	0	0	0	+2	+4	+3	-

Table 1.2.1- 1. NOE data from irradiation of (127) at δ 1.12, 1.24, 1.38 and 3.57 ppm.

Irradiation of 2-H (δ 3.57 ppm) produced large NOE differences for the two amide methyl groups, as expected. High NOE percentage values were also observed for the proton 3-H and for one of the isobutyronitrile methyl groups, 3-Me$_1$. A

smaller NOE was observed for the second isobutyronitrile methyl group 3-Me$_2$. Irradiation of 2-H also gave a small NOE difference for the 5-Me group, supporting the 2α-5β stereochemistry proposed for the major isomer.

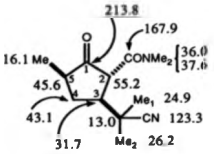
The isobutyronitrile methyl groups 3-Me$_1$ and 3-Me$_2$ were irradiated at δ 1.24 and 1.38 ppm, respectively. The proton 2-H presented a larger NOE from Me$_1$ irradiation (+ 2.5%) than the NOE observed for Me$_1$ when 2-H was irradiated (+ 1%). This effect can be explained in terms of different rates of relaxation to the equilibrium magnetization state of the 2-H and Me$_1$ protons following a perturbation.[47] In the case of 2-H, which is directly attached to the cyclopentanone framework, the rate of relaxation is higher than the relaxation rate for the more mobile Me$_1$ protons. Together with lower relaxation rates (higher relaxation times), the Me$_1$ protons present lower rates of NOE growth and require longer irradiation times to develop fully. The effect observed can thus be attributed to an incomplete development of the Me NOE signal during the time chosen for the 2-H irradiation experiment. The previous 2-H enhancement was not observed, however, upon irradiation of the more distant 3-Me$_2$ and 5-Me groups.

Besides a 2-H enhancement, irradiation of 3-Me$_1$ also gave a +0.5% NOE to the close amide methyl groups, +3.5% NOE to the 3-H proton, and +1% NOE to 3-Me$_2$. The enhancements produced from irradiation of 3-Me$_2$ showed a slightly closer proximity to 3-H (NOE +4%) and the +1.5% NOE observed for 3-Me$_1$ indicates a higher relaxation rate of this group compared with 3-Me$_2$, probably due to steric effects. The large NOE observed for the 4-H protons establishes the proximity of Me$_2$ to these protons.

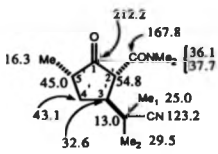
Finally, irradiation of 5-Me gave a +2% enhancement to the 4β proton Hb and a +4% NOE to 5-H. since the chemical shifts of 5-Me (δ 1.12, αββ isomer) and 5'-Me (δ 1.11, αβα isomer) are very close together, irradiation of the former was accomplished by irradiation of the latter and a +3% NOE was observed for 5'-H.

The ^{13}C n.m.r. data for the mixture of (127) isomers obtained is indicated below. The chemical shifts for the two isomers are very similar, the main

differences being observed for 3-Me$_a$ ($\Delta\delta$ = 3.3), C-1 ($\Delta\delta$ = 1.6), C-2 ($\Delta\delta$ = 0.4), and 5-Me ($\Delta\delta$ = 0.6).

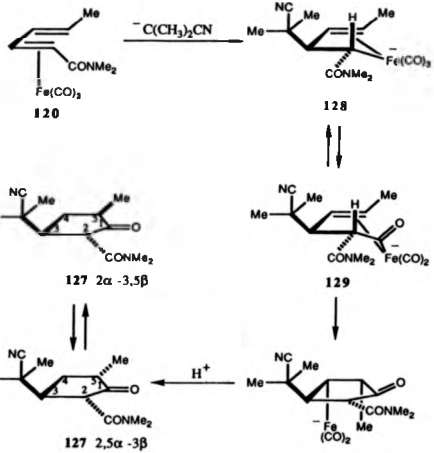


127 2α -3,5β



127 2,5α -3β

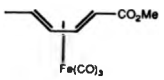
Thus, the data obtained suggest that nucleophilic addition of the isobutyronitrile anion to (*N,N*-dimethyl-2,4-hexadienamide)Fe(CO)$_3$ (**120**) occurs at the carbon atom β to the amide and subsequent acyl transfer from the metal followed by cyclisation produces the cyclopentanone derivative (**127**), with the substituent derived from the anion in the C-3 position. One possible mechanism for this reaction is indicated below.



Nucleophilic attack occurs on the side of the diene opposite to the iron moiety to give the anionic intermediate (128). Insertion of one of the CO Fe-ligands produces the acyliron complex (129) which then cyclizes to give the anionic iron intermediate (130). Protolytic cleavage of (130) affords the 2,5α-3β- substituted cyclopentanone (127) which isomerizes to give a 3:1 mixture of 5β : 5α isomers.

The work described can be related to investigations on nucleophilic addition to Me- and MeO- substituted (diene)tricarbonyliron(0) complexes reported by Semmelhack *et al* and reviewed in the introduction section 1.1.3. These authors found, however, that nucleophilic addition to 1-, 2- and 1,2- substituted (diene)$Fe(CO)_3$ complexes requires the presence of external carbon monoxide (1.5 atm) in order to achieve effective CO incorporation,[44] whereas the reaction reported above proceeded readily under a nitrogen atmosphere. Furthermore, the success of cyclopentanone formation in Semmelhack's systems had been found to depend critically on the structure of the diene and to be efficient only with monosubstituted dienes.[47]

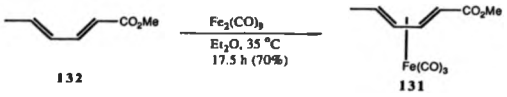
In order to obtain a further insight into the effect of different substituents on the outcome of this potentially very useful reaction, addition to the (2,4-hexadiene) methyl ester tricarbonyl iron complex (131) was investigated.



131

The complex (131) was prepared from 2,4-hexadiene methyl ester (132)[44] by heating with nonacarbonyldi-iron in dry diethyl ether at 35 °C under nitrogen, according to a standard procedure.[44] Filtration of the dark reaction mixture through alumina followed by evaporation of the solvent and column chromatography on silica gel using a 5% EtOAc-petroleum ether 40-60 °C mixture as solvent, afforded an

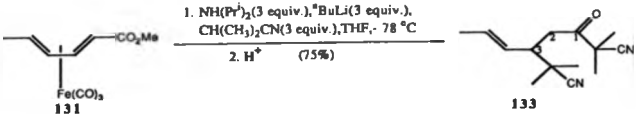
orange oil at room temperature which was identified as the stable tricarbonyliron(0) complex (131) on the basis of its i.r., 220 MHz ^{1}H n.m.r. and MS data, and by comparison with published data.[65,66]



132 131

Nucleophilic addition to the (2,4-hexadiene) methyl ester tricarbonyliron complex (131) was investigated by following the same procedure used for addition to the equivalent *N,N*-dimethylamide complex (120).[49]

The methyl ester complex (131) was reacted with the anion derived from isobutyronitrile (3 equiv.) in THF, under nitrogen, (-78 °C to 25 °C for 2 h). The orange reaction mixture was quenched with trifluoroacetic acid at -78 °C and allowed to warm to room temperature (1 h). The resulting red mixture was extracted with saturated aqueous sodium carbonate solution and diethyl ether, and the organic extracts were filtered through alumina to remove iron residues. Evaporation of the solvent and purification of the yellow oil obtained by thin layer chromatography on silica gel yielded a pale yellow oil which was identified as the new γ,δ-unsaturated ketone (133) on the basis of its i.r., ^{1}H n.m.r, ^{13}C n.m.r., and MS data.

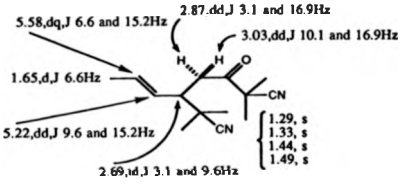


131 **133**

The EI mass spectrum of (133) contains peaks at *m/z* 233 (10%), 164 (100%), and 95 (13%) corresponding to the protonated molecular ion MH^+ and to successive loss of one and two isobutyronitrile groups, respectively. Intense peaks attributed to loss of the $-CH_2COCMe_2CN$ fragment (122, 88%) and to CMe_2CN (68, 69%) were also observed.

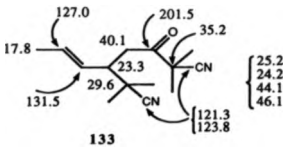
The i.r. spectrum of (133) in chloroform shows a sharp, intense band at 1 732 cm^{-1}, corresponding to the C=O group, and a weaker peak at 2 238 cm^{-1}, attributed to C≡N stretching.

The 400 MHz ^1H n.m.r. data for (133) in deuterated chloroform are indicated below.



133

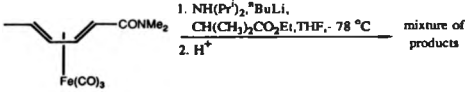
The full ^{13}C n.m.r. assignment for the bis-isobutyronitrile addition product (133) is shown in diagram 1.2.1- 5.



133

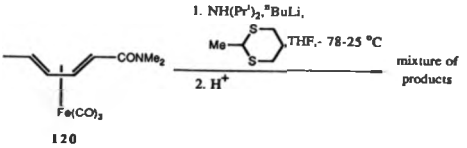
The role of the nucleophile in the reactivity of (*N,N*-dimethyl -2,4-hexadienamide)$Fe(CO)_3$ (120) has also been investigated.

Reaction of (120) with the anion derived from ethyl isobutyrate according to the usual procedure[61] afforded an orange oil which was analysed by i.r. and ^1H n.m.r. spectroscopy and shown to be a complex mixture of products.



120

The (*N,N*-dimethyl-2,4-hexadienamide)$Fe(CO)_3$ complex (120) was also reacted with 2-methyl-1,3-dithiane anion following the usual procedure (-78 °C to +25 °C for 2 h).[61] Quenching with trifluoroacetic acid followed by extraction with saturated aqueous sodium carbonate solution and diethyl ether, afforded an organic phase which was washed with brine, filtered through alumina, dried ($MgSO_4$), and the solvent evaporated under vacuum. The orange oil obtained was analysed by i.r. and ^1H n.m.r. spectroscopy and shown to be a complex mixture of products.

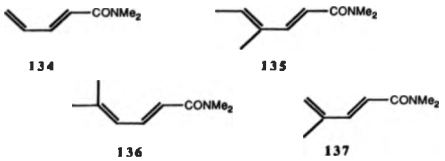


120

Thus, the results obtained on reaction of (*N,N,*-dimethyl-2,4-hexadienamide)Fe(CO)$_3$ (120) with ethyl isobutyrate and 2-methyl-1,3-dithiane anions in THF at -78 °C under N_2, followed by trifluoroacetic acid quenching, revealed that significant cyclopentanone formation had not occurred. These results contrast with the results obtained when isobutyronitrile anion was used under the same conditions.

1.2.2 Nucleophilic addition to (N,N-dimethyl-2,4-pentadienamide)$Fe(CO)_3$ complexes

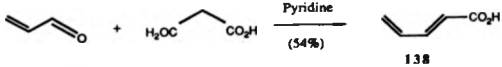
In order to investigate the scope and limitations of the [4+1] methodology for cyclopentanone formation described in section 1.2.1, a series of Me-substituted *N,N*-dimethyl-2,4-pentadienamides (134)-(137) were synthesised.



134 135 136 137

The 2,4-dienamides were prepared from the respective carboxylic acids.

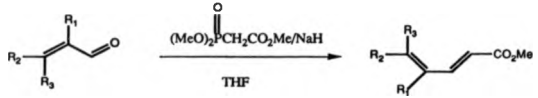
trans Vinylacrylic acid (138) was prepared in moderate yield (54%) from malonic acid and acrolein, according to a published modification to the Knoevenagel reaction.[48] Acrolein (1.2 equiv.) was added to a solution of malonic acid in dry pyridine at 0 °C and the reaction mixture was stirred at 40 °C for 5 h. Acidification of the resulting yellow solution followed by extraction with diethyl ether and evaporation of the ethereal phase, yielded a white crystalline solid which was identified as the 2,4-pentadienoic acid (138) on the basis of its m.p., i.r., and ^{1}H n.m.r. data, and by comparison with published data.[49,50]



138

The 4,5-, 5,5-, and 4-Me-substituted carboxylic acids used in the preparation of the dienamides (135)-(137) were synthesised from the correspondingly substituted aldehydes (139 a-c).[71]

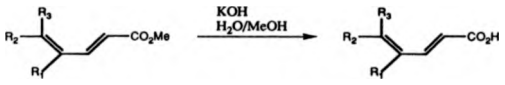
Reaction of the aldehydes (139 a-c) with trimethylphosphonoacetate in the presence of sodium hydride for 9 h at room temperature, yielded the substituted 2,4-pentadiene methyl esters (140 a-c) in good yields.



139 a R_1= R_2= Me; R_3= H
b R_1= H; R_2= R_3= Me
c R_1= Me; R_2= R_3=H

140 a (> 99%)
b (62%)
c (94%)

The 2,4-pentadienoic acids (141 a-c) were prepared by heating the corresponding methyl esters under nitrogen with potassium hydroxide in water and methanol for 12 h. Extraction with diethyl ether to remove neutral material, followed by careful acidification of the aqueous phase at 0 °C with dilute hydrochloric acid, precipitated the white crystalline 2,4-pentadienoic acids.



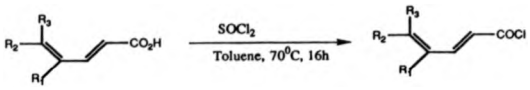
140 a-c

141 a 60%
b 70%
c 42%

The carboxylic acids (141 a-c) were characterized by i.r. and 220 MHz ^{1}H n.m.r. spectroscopy, and their melting points were measured. The data obtained showed good agreement with the data published for these compounds.[11-14]

The preparation of the 2,4-pentadienamides (134)-(137) from the respective carboxylic acids (138) and (141 a-c) was carried out following the standard methodology described for the preparation of 2,4-hexadienamide (123) (section 1.2.1).

The carboxylic acids (138) and (141 a-c) were converted into the corresponding acid chlorides (142 a-d) by heating with thionyl chloride (5 equiv.) in toluene, under nitrogen, for 16-18 h.

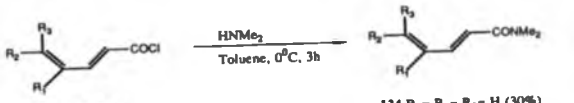


138, 141 a-c

142 a R_1= R_2= Me; R_3= H (75%)
b R_1= H; R_2= R_3= Me (54%)
c R_1= Me; R_2= R_3= H (99%)
d R_1= R_2= R_3= H (65%)

The acid chlorides (142 a-d) were obtained as mixtures with toluene, which were analysed by i.r. and ^{1}H n.m.r. and used in the preparation of the corresponding dienamides (134)-(137).

The solutions of (2,4-pentadiene) acid chlorides (142 a-d) in toluene, under nitrogen, were cooled to 0 °C and dimethylamine was bubbled into these solutions for *ca.* 3 h. The solvent was evaporated and the residue obtained was dissolved in dichloromethane. Extraction with 10% $Na_2(CO)_3$ aqueous solution, followed by washing of the aqueous phase with dichloromethane, and evaporation of the solvent from the combined organic extracts afforded the *N,N*-dimethyl-2,4-dienamides (134)-(137) as white/yellow crystalline solids, which were further purified by recrystallisation from hexane.



142 a-d

134 R_1= R_2= R_3= H (30%)
135 R_1= R_2= Me; R_3= H (86%)
136 R_1= H; R_2= R_3= Me (69%)
137 R_1= Me; R_2= R_3= H (51%)

The (*E*)-*N*,*N*-dimethyl-2,4-pentadienamide (134) was obtained as a stable yellow oil at room temperature, and its i.r. and 220 MHz ^{1}H n.m.r. data showed good agreement with published data.[84] The EI mass spectrum of (134) shows the molecular ion M^+ as a peak at *m/z* 125 (58%). The most intense peak in the spectrum (100%) was obtained at *m/z* 81 and was attributed to the loss of the $-NMe_2$ fragment. M^+-$CONMe_2$ gave a peak at *m/z* 53 (84%).

The novel *N*,*N*-dimethyl-2,4-pentadienamides (135)-(137) gave satisfactory i.r., ^{1}H n.m.r., ^{13}C n.m.r. and mass spectral data indicated in Tables I.2.2- 1-4 respectively. The melting point values measured for the three dienamides are also indicated in Table I.2.2- 1.

Table I.2.2- 1 Melting points and i.r. data for *N*,*N*-dimethyl-2,4-pentadienamides (135)-(137)

	m.p. (°C)[a]	i.r. (cm^{-1})[b]	
		$\nu_{C=O}$	$\nu_{C=C}$
R_1=R_2=R_3=H (136)	-	1 650	1 612, 1 595
R_1=R_2=Me; R_3=H (135)	50-52	1 645	1 626, 1 596
R_1=H; R_2=R_3=Me (136)	80-81	1 649	1 625, 1 590
R_1=Me; R_2=R_3=H (137)	45-47	1 643	-[c]

[a] Samples recrystallized from n-hexane. [b] All spectra measured in $CHCl_3$ solution.
[c] No distinguishable bands observed.

Table 12.2- 2. ^{1}H n.m.r. data for *N,N*-dimethyl-2,4-pentadienamides (135)-(137)

	^{1}H n.m.r. (δ)[a]						
	4-Me	5-Me	NMe$_2$	5-H	4-H	2-H	3-H
R_1=R_2=R_3=H (134)	-	-	3.06,s 3.14,s	5.49,d (J 10) 5.62,d (J 17)	6.57,dt (J 10,11 and 17)	6.48,d (J 15)	7.35,dd (J 11 and 15)
R_1=R_2=Me; R_3=H (135)	1.74,s	1.75,d (J 8.2[b])	2.97,s 3.06,s	5.88-5.91,m	-	6.14,d (J 15.1)	7.25,d (J 15.1)
R_1=H; R_2=R_3=Me (136)	-	1.87,s 1.90,s	3.04,s 3.09,s	-	6.04,brd (J 11)	6.26,d (J 15)	7.62,dd (J 11 and 15)
R_1=Me; R_2=R_3=H (137)	1.92,s	-	3.06,s 3.14,s	5.31,s 5.36,s	-	6.33,d (J 15)	7.38,d (J 15)

[a] All spectra in $CDCl_3$. [b] J given in Hz.

Table 12.2- 3. ^{13}C n.m.r. data for *N,N*-dimethyl-2,4-pentadienamides (135) and (136)

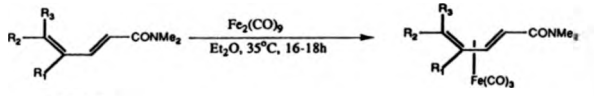
	^{13}C n.m.r. (δ)[a]							
	4-Me	5-Me	NMe$_2$	C-2	C-5	C-4	C-3	C=O
R_1=R_2=Me; R_3=H (135)	11.8	14.2	35.6 37.2	114.0	133.6	134.4	147.0	167.2
R_1=H; R_2=R_3=Me (136)	-	18.7 (*cis*) 26.3 (*trans*)	35.6 37.1	117.7	123.9	138.8	144.1	167.8

[a] All spectra in $CDCl_3$, proton decoupled.

Table 1.2.3 - 4 EI MS data for *N,N*-dimethyl-2,4-pentadienamides (135)-(137)

	m/z	% int	Assignment of ion
R_1=R_2=R_3=Me: R_4=H (135)	153	11	M^+
	72	100	$CONMe_2$
	44	59	NMe_2
R_1=H: R_2=R_3=Me R_4=H (136)	153	95	M^+
	138	43	M^+-Me
	109	87	M^+-NMe_2
	81	100	M^+-$CONMe_2$
	72	25	$CONMe_2$
R_2=Me: R_1=R_3=H (137)	141	52	M^+
	98	100	M^+-NMe_2+H
	72	69	$CONMe_2$
	44	73	NMe_2

Preparation of irontricarbonyl complexes of the *N,N*-dimethyl-2,4-pentadienamides (134)-(137) was investigated by heating the dienamides with two equivalents of nonacarbonyldi-iron in dry diethyl ether, according to the procedure described for the preparation of (*N,N*-dimethyl-2,4-hexadienamide)$Fe(CO)_3$ (120) (section I.2.1 - page 37).[69] The reaction conditions and yield of $Fe(CO)_3$ complexes obtained are indicated below.



134-137

143 R_1= R_2= R_3= H (75%)
144 R_1= R_2= Me; R_3= H (69%)
145 R_1= H; R_2= R_3= Me (52%)
146 R_1= Me, R_2= R_3= H (64%)

The novel (2,4-pentadienamide)$Fe(CO)_3$ complexes (143)-(146) were obtained as stable yellow/orange crystalline solids except for the (5,5-dimethyl-2,4-pentadienamide)$Fe(CO)_3$ complex (145) which was obtained as a yellow oil, unstable at room temperature under a nitrogen atmosphere.

The stable tricarbonyliron(0) complexes (143), (144), and (146) gave satisfactory i.r., ^1H n.m.r., ^{13}C n.m.r., MS and micro-analytical spectral data, indicated in tables 1.2.2- 5-9. The i.r. and FAB mass spectral data obtained for (145) are also included in these tables. Melting points for the stable complexes are included in table 1.2.2- 5.

Table 1.2.2- 5. Melting points and i.r. data for (*N,N*-dimethyl-2,4-pentadienamide)$Fe(CO)_3$ complexes (143)-(146)

	m.p. (°C)[a]	i.r. (cm^{-1})[b]	
		ν_{CO}	$\nu_{C=O}$
(143)	94-95	2 063, 2 001, 1 987	1 649
(144)	103-104	2 055, 1 993, 1 976	1 649
(145)	-	2 055, 1 991, 1 975	1 651
(146)	71-72	2 060, 1 998, 1 983	1 649

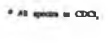
[a] Samples recrystallized from *n*-hexane. [b] All spectra measured in *n*-hexane solution.

Table 1.2.2- 6 ^{1}H n.m.r. data for (*N,N*-dimethyl-2,4-pentadienamide)Fe(CO)$_3$ complexes (143), (144) and (146)

		^{1}H n.m.r. (δ)[a]						
		2-H	5-H	5-Me	4-Me	NMe	4-H	5-H
R_1=R_2=R_3=H	(143)	1.08,d (*J* 7.7[b])	0.54, dd (*J* 2.7 and 9.4 *cis*) 1.95,dd (*J* 2.7 and 7.0 *trans*)	-	-	2.94,s 3.04,s	5.43,m	6.12,dd (*J* 5.0 and 7.7)
R_1=R_2=Me; R_3=H	(144)	0.91,d (*J* 7.5)	1.26,br q (*J* 6.4)	1.47,d (*J* 6.4)	2.18,s	2.93,s 3.02,s	-	5.88,d (*J* 7.5)
R_1=Me; R_2=R_3=H	(146)	0.87,d (*J* 7.4)	0.58,dd (*J* 1.0 and 2.6) 1.96, dd (*J* 1.8 and 2.5)	-	2.21,s	2.93,s 3.02,s	-	5.98,br d (*J* 7.4)

[a] All spectra in $CDCl_3$. [b] *J* given in Hz.

Table 1.2.2- 7. ^{13}C n.m.r. data for (*N,N*-dimethyl-2,4-pentadienamide)Fe(CO)$_3$ complexes (143), (144) and (146)



		^{13}C n.m.r. (δ)[a]							
		4-Me	5-Me	NMe	C-2	C-5	C-4	C-3	C=O	C=O
R_1=R_2=R_3=H	(143)	-	-	35.7 36.8	40.5	46.8	84.5	87.6	170.5	209.9 br
R_1=R_2=Me; R_3=H	(144)	15.7	17.8	35.7 36.8	43.2	58.9	83.8	102.7	171.7	210.7 br
R_1=Me; R_2=R_3=H	(146)	22.6	-	35.8 36.8	43.6	44.8	84.8	102.3	170.9	210.0 br

[a] All spectra in $CDCl_3$.

Table 1.3.2- 8. FAB MS data for (*N,N*-dimethyl 2,4-pentadienamide)$Fe(CO)_3$ complexes (143)-(146)

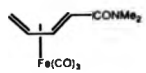
	m/z	% int	Assignment of ion
R_1=R_2=R_3=H (143)	266	100	MH^+
	238	18	MH^+-CO
	209	53	MH^+-2CO
	181	49	MH^+-3CO
R_1=R_2=Me; R_3=H (144)	294	100	MH^+
	265	22	M^+-CO
	237	52	M^+-2CO
	209	53	M^+-3CO
R_1=H, R_2=R_3=Me (145)	294	64	MH^+
	265	29	M^+-CO
	237	89	M^+-2CO
	208	100	M^+-3CO-H
R_1=Me; R_2=R_3=H (146)	280	100	MH^+
	251	23	M^+-CO
	223	49	M^+-2CO
	195	70	M^+-3CO

Table 1.3.2- 9 Microanalysis data for (*N,N*-dimethyl 2,4-pentadienamide)$Fe(CO)_3$ complexes (143),(144), and (146)[a]

	C	H	N
R_1=R_2=R_3=H (143)	45.43(45.12)	4.19(4.18)	5.28(5.28)
R_1=R_2=Me; R_3=H (144)	48.90(49.17)	5.18(5.16)	4.73(4.78)
R_1=Me; R_2=R_3=H (146)	47.41(47.34)	4.73(4.70)	4.98(5.02)

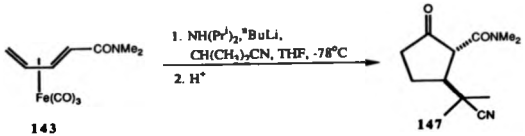
[a]Calculated figures in parenthesis.

The first (2,4-pentadienamide) complex studied with respect to nucleophilic addition was the (*N,N*-dimethyl-2,4-pentadienamide)$Fe(CO)_3$ complex (**143**).



143

The isobutyronitrile anion was reacted with (2,4-pentadienamide)tricarbonyliron(0) (143) in THF, according to the general method described for nucleophilic addition of the same anion to the (2,4-dienamide)$Fe(CO)_3$ complex (120). The dark orange reaction mixture was quenched with trifluoroacetic acid at -78 °C and the red coloured reaction mixture obtained at room temperature was filtered through alumina. The light yellow filtrate was evaporated and thin layer chromatography of the residue afforded a colourless oil which was identified as the cyclopentanone (147) on the basis of its i.r., ^1H n.m.r. and high resolution mass spectral data.

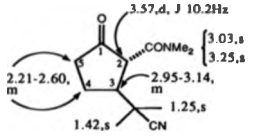


143 **147**

The i.r. spectrum of (147) shows a sharp, medium size band at 1 741 cm^{-1}, which was attributed to the cyclopentanone C=O stretching, and a sharp, more intense band at 1 643 cm^{-1}, assigned to the amide C=O group. Evidence for addition of isobutyronitrile is given by the presence of a sharp, weak absorption band at 2 230 cm^{-1}, attributed to C≡N stretching.

The EI mass spectrum of (147) contains a weak peak at *m/z* 222 (8%) attributed to its molecular ion M^+, and two intense peaks at *m/z* 154 (54%) and 72 (100%) corresponding to M^+-$C(CH_3)_2CN$ and $CONMe_2$, respectively.

Evidence for addition of isobutyronitrile is also present in the 400 MHz ^1H n.m.r. spectrum of (147). The data obtained are indicated in the diagram below.

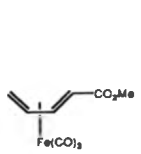


147

Diagram 1.2.2-1 ^{1}H n.m.r. chemical shifts of (147).

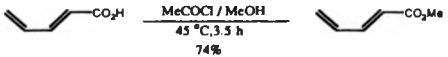
As was observed for 2-dimethylamide-3-isobutyronitrile-5-methylcyclopentanone (127) obtained from addition of the isobutyronitrile anion to the (2,4-hexadienamide)Fe(CO)$_3$ complex (120) (section 1.2.1) the isobutyronitrile group at C-3 has a fixed spacial orientation and its methyl groups Me$_1$ and Me$_2$ give individual three proton singlets (δ 1.25 and δ 1.42, respectively) in the ^{1}H n.m.r. spectrum of (147). The 2-amide methyl groups appear as two three-proton singlets at δ 3.03 and δ 3.25, slightly shifted downfield relative to the corresponding methyl groups in the 2,3,5-substituted cyclopentanone (127). The 2-H proton gave a one-proton doublet at δ 3.57 (*J* 10.2 Hz) attributed to *trans*-coupling to the proton 3-H, which appears as a one-proton multiplet at 2.95-3.14, partially hidden by one of the amide methyl peaks. The unresolved four-proton multiplet at δ 2.21-2.60 was assigned to the two 4-H and the two 5-H protons.

In order to investigate the effect of replacing the amide group with an ester group on the outcome of nucleophilic addition of the anion derived from isobutyronitrile, the ((2,4-pentadiene) methyl ester)$Fe(CO)_3$ complex (**148**) was synthesized.



148

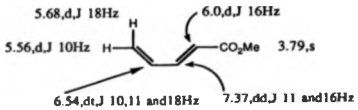
The methyl ester ligand (**149**) was prepared from the corresponding 2,4-pentadienoic acid (**138**) by heating with acetyl chloride and methanol at 45 °C for 3.5 h.[44] The resulting yellow reaction mixture was cooled to room temperature and the excess acetyl chloride was hydrolysed by pouring the reaction mixture into ice. Extraction with diethyl ether followed by washing of the organic extracts with water, drying ($MgSO_4$) and evaporation of the solvent, yielded an orange oil which was identified as the (2,4-pentadiene) methyl ester (**149**) on the basis of its i.r. and ^1H n.m.r. spectral data.



138 **149**

The i.r. spectrum of (149) showed an intense band at 1 706 cm^{-1}, attributable to the ester C=O absorption. Two less intense bands at 1 644 and 1 598 cm^{-1} were assigned to the diene C=C stretching.

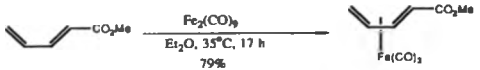
The 220 MHz ^1H n.m.r. data obtained for (149) are indicated in the diagram below.



149

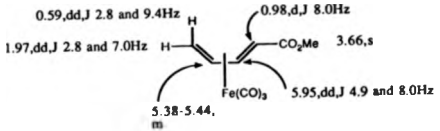
Diagram 1.2.2-2 ^1H n.m.r. chemical shifts of (149)

The preparation of the [((*E*)-2,4-pentadiene)methyl ester]$Fe(CO)_4$ complex (148) from (2,4-pentadiene) methyl ester (149) was attempted using the general procedure described for the preparation of all the tricarbonyliron(0) complexes reported in this thesis.[11] The (2,4-diene) methyl ester (149) was heated with two equivalents of nonacarbonyldi-iron in dry diethyl ether at 35 °C for 17 h under a nitrogen atmosphere. The dark brown reaction mixture obtained was filtered through alumina to remove iron residues, and the resulting yellow solution was concentrated under vacuum. Column chromatography on silica gel yielded an orange air-stable oil which was identified as the novel (η^4-diene)tricarbonyliron(0) complex (148) on the basis of its i.r., ^1H n.m.r., ^{13}C n.m.r. and MS spectral data.



149 **148**

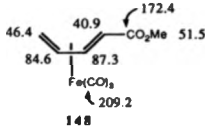
The i.r. spectrum of (148) in hexane showed three sharp peaks at 2 068, 2 008 and 1 995 cm^{-1} attributed to the three iron-carbonyl groups, and a less intense sharp peak at 1 726 cm^{-1} assignable to the ester carbonyl group. The 400 MHz ^1H n.m.r. spectrum of (148) in $CDCl_3$ showed the chemical shift values and coupling constants indicated below.



148

Diagram I.2.2-3 ^1H n.m.r. chemical shifts of (148)

The large upfield shift of the terminal diene protons H-2 and H-5 relative to H-3 and H-4 agrees with a considerably higher sp^2 character being associated with the C-2 and C-5 orbitals compared with the C-3 and C-4 orbitals. Similar conclusions can be inferred from the ^{13}C n.m.r. data obtained for the complex (148) and indicated in the diagram below.

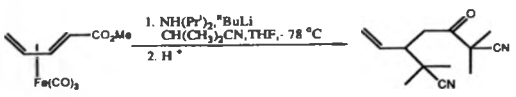


148

Diagram 1.2.2-4 ^{13}C n.m.r. chemical shifts of (148)

The EI mass spectrum of (148) contains peaks at *m/z* 252 (9%), 196 (42%) and 168 (57%), attributable to the molecular ion M^+ and to loss of two and three carbonyl groups, respectively.

The methyl ester complex (148) was reacted with the anion derived from isobutyronitrile (3 equiv.) in THF, under nitrogen (-78 °C to +25 °C for 2 h). The dark reaction mixture obtained was quenched with trifluoroacetic acid at -78 °C and allowed to warm to room temperature (1 h). The resulting dark mixture was extracted with saturated aqueous sodium carbonate solution and diethyl ether, and the organic extracts were filtered through alumina. Evaporation of the solvent and purification of the yellow oil obtained by thin layer chromatography on silica gel yielded the new (*E*)-1,3-diisobutyronitrile-4-ene-pentanone (150) which was identified on the basis of its i.r., ^1H n.m.r., ^{13}C n.m.r., and MS data.

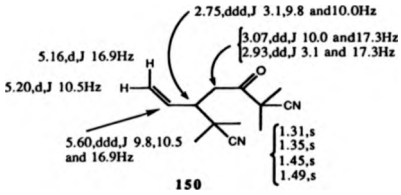


148 **150**

The EI mass spectrum of (150) contains peaks at *m/z* 219 (12%), 150 (100%), and 81 (26%) corresponding to the molecular ion MH^+ and to successive loss of the two isobutyronitrile groups. Medium size peaks attributed to loss of the -C(O)CMe$_2$CN fragment (122, 46%) and to CMe$_2$CN (68, 43%) were also detected.

The i.r. spectrum of (150) in chloroform shows a sharp, intense band at 1 733 cm^{-1}, attributed to the C=O group, and a weaker peak at 2 240 cm^{-1}, corresponding to C≡N stretching.

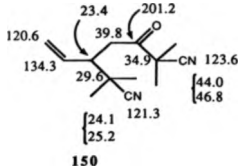
The 400 MHz ^{1}H n.m.r. data for (150) are indicated in the diagram below.



150

Diagram 1.2.2-5. ^{1}H n.m.r. chemical shifts for (150)

The ^{13}C n.m.r. data obtained for the bis-isobutyronitrile addition product (150) are indicated in the diagram below.

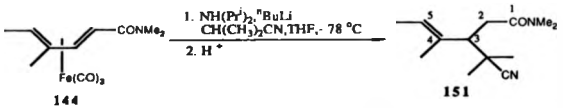


150

Diagram I.2.2-6 ^{13}C n.m.r. chemical shifts for (150)

The reactivity towards nucleophilic addition of the 4,5-, 5,5- and 4-methyl substituted (2,4-pentadienamide)$Fe(CO)_3$ complexes (144), (145), and (146) was also investigated.

The anion derived from isobutyronitrile was reacted with (*N,N*-dimethyl -4-methylhexadienamide)$Fe(CO)_3$ (144), according to the usual procedure (-78 °C to +25 °C for 2 h).[47] Quenching with trifluoroacetic acid, followed by work-up in the presence of air and filtration through alumina yielded a pale yellow oil, which was identified as the *N,N*-dimethyl-3-isobutyronitrile-4-methyl-4-hexenamide (151) on the basis of its i.r., ^1H n.m.r., and mass spectral data.

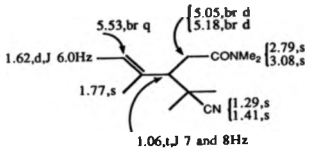


144 **151**

The CI mass spectrum of (151) contained peaks at *m/z* 223 (100%) and 154 (40%), corresponding to the protonated molecular ion MH^+ and to MH^+-$CONMe_2$+3 H, respectively. A weaker peak at *m/z* 72 (25%) was attributed to the $CONMe_2$ fragment.

The i.r. spectrum of (151) showed a C≡N weak absorption band at 2 230 cm^{-1} and an intense absorption band at 1 640 cm^{-1}, attributed to the amide C=O stretching.

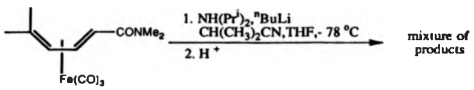
Evidence for addition of isobutyronitrile is also given by the 220 MHz ^1H n.m.r. data obtained for (151) and indicated in the diagram below.



151

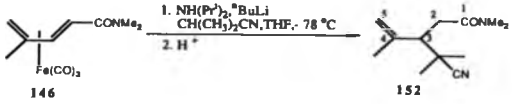
Diagram 1.2.2-7 ^1H n.m.r. chemical shifts for (151)

Starting from the relatively unstable complex (*N,N*-dimethyl-5-methyl -2,4-hexadienamide)$Fe(CO)_3$ (145), reaction with isobutyronitrile anion following the usual procedure[47] gave a yellow liquid which was analysed by i.r. and ^1H n.m.r. spectroscopy, and shown to be a complicated mixture of addition products.



145

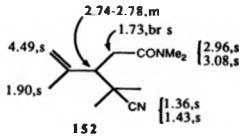
Nucleophilic addition of the isobutyronitrile anion to the 4-Me substituted (2,4-pentadienamide)$Fe(CO)_3$ complex (146) following the usual method,[41] yielded an air-stable yellow oil which was identified as the *N,N*-dimethyl -3-isobutyronitrile-4-methyl-4-pentenamide (152) on the basis of its i.r. and ^1H n.m.r. spectral data.



146 152

The i.r. spectrum of (152) shows a weak peak at 2 240 cm^{-1}, attributed to C≡N stretching, and a strong band at 1 641 cm^{-1}, due to the amide C=O absorption.

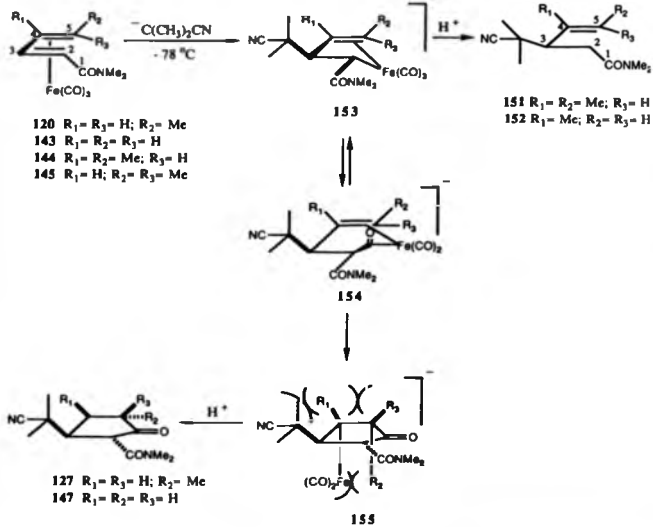
The 220 MHz ^1H n.m.r. data obtained for (152) are indicated in the diagram below.



152

Diagram 1.2.2-8. ^1H n.m.r. chemical shifts of (152)

It has thus been observed that nucleophilic addition of the isobutyronitrile anion to 4,5-, 5,5- and 4-methyl-substituted (*N,N*-dimethyl-2,4-pentadienamide)$Fe(CO)_3$ complexes (144)-(146) at -78 °C, under N_2, followed by trifluoroacetic acid quenching, does not lead to CO insertion and cyclopentanone formation, in contrast to the results obtained for the 5-methyl and unsubstituted (*N,N*-dimethyl -2,4-pentadienamide)$Fe(CO)_3$ complexes (120) and (143). A possible rationalisation of these results can be obtained from a closer analysis of the structure of the intermediates in the mechanism proposed for cyclopentanone formation, indicated below.



120 $R_1 = R_3 = H$; $R_2 = Me$
143 $R_1 = R_2 = R_3 = H$
144 $R_1 = R_2 = Me$; $R_3 = H$
145 $R_1 = H$; $R_2 = R_3 = Me$

153

151 $R_1 = R_2 = Me$; $R_3 = H$
152 $R_1 = Me$; $R_2 = R_3 = H$

154

155

127 $R_1 = R_3 = H$; $R_2 = Me$
147 $R_1 = R_2 = R_3 = H$

Spectroscopic evidence for nucleophilic attack at the C-3 position was obtained for the (5-methyl-pentadienamide)-, (pentadienamide)-, (4,5-dimethyl-pentadienamide)-, and (4-methyl-pentadienamide)$Fe(CO)_3$ complexes (120), (143), (144), and (146) (section I.2.1 page 41, and section I.2.2 pages 60, 67 and 69, respectively). Addition of the isobutyronitrile anion occurs *trans* to the metal unit to give the intermediate (153). Acyl transfer from the metal to the carbon α to the amide group (C-2) leads to the acyliron intermediate (154). Intramolecular alkene insertion to give the anionic intermediate (155), followed by protonation, affords the cyclopentanone products (127) and (147) for $R_1=R_2=H$, $R_3=Me$ and $R_1=R_2=R_3=H$, respectively.

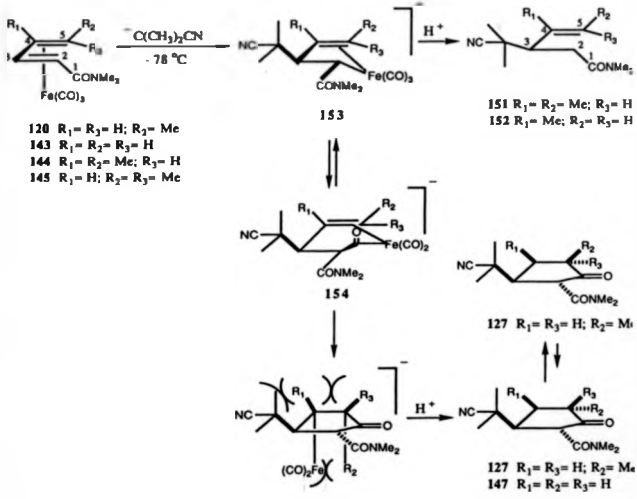
When $R_1=Me$ (complexes (144) and (146), high steric hinderance is expected between the 4-Me and the isobutyronitrile group at C-3, disfavouring the formation of the intermediate (155). For these complexes C=O incorporation does not occur and quenching with trifluoroacetic acid leads to the 3-isobutyronitrile-4-pentenamide addition products (151) and (152).

These results agree with a series of 1-, 2-, and 1,2- substituted diene complexes, for which cyclopentanone formation has proved to be efficient only with monosubstituted dienes.[41]

In the case of the (5,5-dimethyl-pentadienamide)$Fe(CO)_3$ complex (145), an additional destabilization of (155) is expected as a result of the proximity between the R_2 Me group at C-5 and the $Fe(CO)_3$ moiety at C-4. The i.r. data obtained for the mixture of products resulting from the reaction of (145) with the isobutyronitrile anion (following the usual procedure) agree with no cyclopentanone product(s) having been formed.

1.3 CONCLUSIONS

Nucleophilic addition of the anion derived from isobutyronitrile to (*N,N*-dimethyl-2,4-pentadienamide)$Fe(CO)_3$ complexes has proved to be a potentially useful reaction for the preparation of substituted cyclopentanone rings. This reaction is believed to involve attack of the anion at the carbon β to the amide group and on the face of the diene opposite to the metal moiety. Subsequent acyl transfer from the metal to the carbon α to the amide group followed by cyclisation produces the cyclopentanone ring, as shown in the proposed mechanism indicated below.



120 R_1= R_3= H; R_2= Me
143 R_1= R_2= R_3= H
144 R_1= R_2= Me; R_3= H
145 R_1= H; R_2= R_3= Me

153

151 R_1= R_2= Me; R_3= H
152 R_1= Me; R_2= R_3= H

154

127 R_1= R_3= H; R_2= M

155

127 R_1= R_3= H; R_2= Me
147 R_1= R_2= R_3= H

The success of cyclopentanone formation seems to depend on the substitution pattern of the dienamide ligand. Dienamides containing a substituent at C-4 ($R_1 \neq H$) disfavour cyclization due to steric hinderance between R_1 and the adjacent isobutyronitrile group. Multiple substitution at C-5 ($R_2 = R_3 = Me$) also failed to give the cyclopentanone product.

I.4 EXPERIMENTAL

All reactions were performed using standard vacuum line techniques,[74] under an atmosphere of nitrogen unless otherwise stated.

Tetrahydrofuran was distilled under nitrogen from sodium benzophenone ketyl and *pyridine* was distilled from potassium hydroxide. *Diethyl ether* and *toluene* were dried over sodium wire. *Methyllithium* (1.4 M in diethyl ether) and *n-butyllithium* (2.5 M in hexanes) were purchased from Aldrich and their concentrations checked before each utilization by titration against diphenylacetic acid.[75] *Malonic acid* was used as supplied by Sigma. *Sorbic acid* (> 98.5%) and *acrolein* (stabilized with quinol, 98%) were purchased from BDH. *Trimethylphosphonoacetate* (> 98%), and *trans-2-methyl-2-butenal* (97%) were supplied by Lancaster Synthesis. *Sodium hydride* was used as an 80% dispersion in mineral oil obtained from Aldrich. *Dimethylamine hydrochloride* (97%), *3-methyl-2-butenal* (97%), *methacrolein* (95%) and *isobutyronitrile* (99%) were also supplied by Aldrich. *Thionyl chloride* was purchased from Fisons. *Diisopropylamine* was distilled from calcium hydride and stored over molecular sieves. *Nonacarbonyldi-iron* was prepared by a published procedure.[76] *Methyl sorbate* was prepared from sorbic acid using an ethanoyl chloride-methanol mixture at 50 ^{o}C.[44]

Column chromatography was performed on SiO_2 (Merck, Art. 9385, 40-63 μm)[77] and thin layer chromatography (tlc) was performed on glass based SiO_2 plates (20 cm x 20 cm x 1 mm; Merck, Art. 7747, 60 PF_{254}). The Al_2O_3 used for filtrations was deactivated with H_2O (Brockmann grade 4, Al_2O_3 : H_2O = 10 : 1 w/w).

Melting points were determined on a Gallenkamp MF B 595 010M melting point apparatus and are uncorrected. The melting points of complexes were measured in nitrogen filled capillaries, and subsequent examination by tlc was used to establish whether decomposition had taken place.

Elemental analysis were performed by MEDAC Ltd.

I.r. spectra were recorded on Perkin Elmer 580B and 1720X instruments.

^{1}H n.m.r. spectra were recorded on Perkin Elmer R34 (220 MHz) and Bruker WH400 (400 MHz) spectrometers. ^{13}C n.m.r. spectra were recorded on a Bruker WH400 instrument operating at 100.6 MHz. All chemical shifts are quoted in ppm relative to a TMS standard.

Mass spectra were recorded on a Kratos MS 80 instrument using FAB (*m*-nitrobenzyl alcohol as matrix[48]), CI (NH_3 as reactant gas) and EI (70 eV) techniques.

I.4.1 Synthesis of unsaturated acids (138) and (141 a-c)

Trans-Vinylacrylic acid (138).[88]

To a solution of malonic acid (9.0 g, 86.2 mmol) in dry pyridine (20.4 ml) which was cooled in a freezing mixture, acrolein (7.02 ml, 104 mmol) was added gradually. A yellow, viscous mixture was formed which was allowed to warm to r.t. It was stirred at 40 °C for 5 h and the clear, yellow solution obtained was acidified with hydrochloric acid and extracted with diethyl ether (3 x 150 ml). The organic phase was dried ($MgSO_4$), filtered and the solvent evaporated to yield (138) as a white solid (4.56 g, 54%), m.p. 68-69 °C (lit.[88] m.p. 72 °C); ν_{max} ($CHCl_3$) 1 690 (C=O), 1 637 and 1 600 cm^{-1} (C=C); δ_H (220 MHz; CCl_4) 5.49 (1 H, d, J 10 Hz, -CH=C*H*$_2$ *trans*), 5.62 (1 H, d, J 17 Hz, -CH=C*H*$_2$ *cis*), 5.87 (1 H, d, J 15 Hz -CH=C*H*CO_2H), 6.46 (1 H, ddd, J 10, 11 and 17 Hz, -C*H*=CH_2), and 7.31 (1 H, dd, J 11 and 15 Hz, -C*H*=$CHCO_2$H) (lit.[89] δ_H (100 MHz; CCl_4) 5.46 (1 H, d, J 10 Hz, -CH=C*H*$_2$ *trans*), 5.60 (1 H, d, J 16 Hz, -CH=C*H*$_2$ *cis*), 5.86 (1 H, d, J 16 Hz, -CH=C*H*CO_2H), 6.44 (1 H, dt, J 10, 11 and 16 Hz, -C*H*=CH_2), and 7.31 (1 H, dd, J 11 and 16 Hz, -C*H*=$CHCO_2$H).

(E,E)-4-Methyl-2,4-hexadienoic acid (141 a).[91]

Trimethylphosphonoacetate (10 ml, 60.3 mmol) was added dropwise, under nitrogen, to a stirred suspension of sodium hydride (2.16 g, 72.1 mmol, 80% in oil) in tetrahydrofuran (440 ml). When evolution of hydrogen ceased, (*E*)-2-methyl-2-butenal (5.0 g, 57.7 mmol) was added dropwise with ice cooling and the reaction mixture was then stirred for 9 h at room temperature. The tetrahydrofuran was evaporated, water (300 ml) was added, and the product extracted with diethyl ether (3 x 300 ml). Evaporation of the ether gave the crude methyl ester of the required acid as a yellow oil (8.0 g, 100%): ν_{max} ($CHCl_3$) 1 750 (C=O), 1 632 and 1 623 cm^{-1} (C=C); δ_H (220 MHz; $CDCl_3$) 1.77 (3 H, s, -C*Me*=CHMe), 1.82 (3 H, d, J 7 Hz, -CMe=CH*Me*), 3.76 (3 H, s, CO_2*Me*), 5.83 (1 H, d, J 16 Hz, -CH=C*H*CO_2Me), 6.03 (1 H, q, J 7 Hz, -CMe=C*H*Me), and 7.37 (1 H, d, J 16 Hz, -C*H*=$CHCO_2$Me).

To the ester (0.50 g, 3.57 mmol) water (3.6 ml) and methanol (1.4 ml) were added under nitrogen. To the resulting two phase system, potassium hydroxide (0.37 g, 5.57 mmol) was added and the reaction mixture was stirred for 17 h at 30 °C. Water (15 ml) was added, and neutral material was removed by extraction with ether (3 x 30 ml). Acidification of the aqueous solution at 0 °C with 2M hydrochloric acid precipitated the title acid (**141 a**) as a white solid which was separated by filtration and dried (0.27 g, 60%), m.p. 91-92 °C (lit.[11] m.p. 94-95 °C); $\nu_{max.}$ ($CHCl_3$) 1 684 (C=O), 1 630 and 1 618 cm^{-1} (C=C); δ_H (220 MHz; $CDCl_3$) 1.80 (3 H, s, -C*Me*=CHMe), 1.84 (3 H, d, J 7 Hz, -CMe=CH*Me*), 5.83 (1 H, d, J 16 Hz, -CH=C*H*CO_2H), 6.09 (1 H, q, J 7 Hz, -CMe=C*H*Me), and 7.44 (1 H, d, J 16 Hz, -C*H*=CHCO_2H) (lit.[11] δ_H (60 MHz; $CDCl_3$) 1.79 (3 H, s, -C*Me*=CHMe), 1.84 (3 H, partly obscured d, J *c.* 6 Hz, -CMe=CH*Me*), 5.83 (1 H, d, J 16.0 Hz, -CH=C*H*CO_2H), 6.0 (1 H, m, -CMe=C*H*Me), 7.50 (1 H, d, J 16.0 Hz, -C*H*=CHCO_2H), and 12.64 (1 H, br, s, CO_2H)); *m/z* (EI) 126 (M^+, 42%), 111 (M^+-Me, 100), and 81 (M^+-CO_2H, 88).

(E)-5-Methyl-2,4-hexadienoic acid (**141 b**).

According to the procedure previously described for the preparation of the acid (**141 a**), trimethylphosphonoacetate (7.6 ml, 46 mmol) was added dropwise, under nitrogen, to a stirred mixture of sodium hydride (1.65 g, 55 mmol, 80% in oil) and dry THF (340 ml). When evolution of hydrogen ceased, 3-methyl-2-butenal (2.6l ml, 44.0 mmol) was added dropwise with ice cooling and the reaction mixture was stirred for 8.5 h at room temperature. The solvent was then evaporated, water was added (250 ml) and the product extracted with ether (3 x 200 ml). Evaporation of the ether afforded the methyl ester of the title acid as a pale yellow oil (3.82 g, 62%); $\nu_{max.}$ ($CHCl_3$) 1 705 (C=O), 1 637 and 1 612 cm^{-1} (C=C); δ_H (220 MHz; $CDCl_3$) 1.89 (3 H, s, -CH=CMe_a), 1.91 (3 H, s, -CH=CMe_a), 3.77 (3 H, s, CO_2Me), 5.84 (1 H, d, J 16 Hz, -CH=C*H*CO_2Me), 6.06 (1 H, br d, J 12 Hz, -C*H*=CMe_a), and 7.64 (1 H, dd, J 12 and 16 Hz, -C*H*=CHCO$_2$Me) (lit.[11] δ_H

(60 MHz; $CDCl_3$) 1.90 (6 H, br s, -CH=C*Me*$_2$), 3.73 (3 H, s, CO_2*Me*), 5.73 (1 H, d, J 15 Hz, -CH=C*H*CO_2Me), 5.97 (1 H, d, J 10.5 Hz, -C*H*=CMe$_2$), and 7.56 (1 H, dd, J 10.5 and 15 Hz, -C*H*=CHCO$_2$Me).

The ester (3.8 g, 27 mmol) was hydrolysed by heating under nitrogen with potassium hydroxide (2.8 g, 42 mmol) in water (27 ml) and methanol (11 ml) for 12 h at 35 °C. Water (100 ml) was added, and neutral material was removed by extraction with ether. Careful acidification of the aqueous solution at 0 °C with 2 M hydrochloric acid precipitated the title acid (14l b) as a white, crystalline solid (2.37 g, 70% overall), m.p. 99-100 °C (lit.[13] m.p. 104-105 °C); $\nu_{max.}$ ($CHCl_3$) 1 690 (C=O), 1 635 and 1 620 cm^{-1} (C=C); δ_H (220 MHz; $CDCl_3$) 1.93 (3 H, s, -CH=C*Me*$_2$), 1.94 (3 H, s, -CH=C*Me*$_2$), 5.82 (1 H, d, J 16 Hz, -CH=C*H*CO_2H), 6.08 (1 H, d, J 12 Hz, -C*H*=CMe$_2$), and 7.73 (1 H, dd, J 12 and 16 Hz, -C*H*=CHCO$_2$H).

(E)-4-Methyl-2,4-pentadienoic acid (14l c).

Method as for preparation of acid (14l a). To a suspension of sodium hydride (1.74 g, 58.1 mmol, 80% in oil) in dry tetrahydrofuran (280 ml), under N_2, trimethylphosphonoacetate (8.0 ml, 48.4 mmol) was added dropwise. When evolution of hydrogen ceased, the reaction mixture was cooled to 0 °C and a solution of methacrolein (3.9 ml, 46.2 mmol) in dry THF (50 ml) was added dropwise. The mixture was stirred at room temperature for 11 h, and the tetrahydrofuran was evaporated. The solid residue obtained was dissolved in water (200 ml) and the solution extracted with ether (3 x 200 ml). The combined organic extracts were dried ($MgSO_4$), filtered and the solvent evaporated to yield the methyl ester of the title acid as a pale-yellow liquid (5.49 g, 94%); $\nu_{max.}$ 1 712 (C=O), 1 630 and 1 607 cm^{-1} (C=C); δ_H (220 MHz; $CDCl_3$) 1.90 (3 H, s, -C*Me*=CH$_2$), 3.79 (3H, s, CO_2*Me*), 5.39 (2 H, br, s, -CMe=C*H*$_2$), 5.94 (1 H, d, J 16 Hz, -CH=C*H*CO_2Me), and 7.43 (1 H, d, J 16 Hz, -C*H*=CHCO$_2$Me).

The ester (5.35 g, 42 mmol) was hydrolysed by heating under nitrogen with potassium hydroxide (4.4 g, 66 mmol) in water (42 ml) and methanol (17 ml) at

35 °C for 9 h. Water (150 ml) was added to the reaction mixture and the neutral material was removed by extraction with ether (3 x 150 ml). The aqueous phase was cooled (0 °C) and careful acidification with 2 M hydrochloric acid precipitated the title acid (141 e) as a white solid (1.99 g, 40% overall), m.p. 70-72 °C (lit.[14] m.p. 64-65 °C); ν_{max} ($CHCl_3$) 1 673 cm^{-1} (C=O); δ_H (220 MHz; $CDCl_3$) 1.92 (3 H, s, -C*Me*=CH_a), 5.44 (2 H, br s, -CMe=CH_a), 5.93 (1 H, d, J 16 Hz, -CH=C*H*CO_2H), and 7.50 (1 H, d, J 16 Hz, -C*H*=CHCO$_2$H (lit.[8] δ_H (100 MHz; $CDCl_3$) 1.90 (3 H, t, J 2.2 Hz, Me), 5.40 (2 H, m, -CMe=CH_a), 5.89 (1 H, d, J 15.8 Hz, -CH=C*H*CO_2H), and 7.45 (1 H, d, J 15.8 Hz, -CH=C*H*CO_2H).

1.4.2 **Synthesis of acid chlorides (122 and (142 a-d)**

General method

The 2,4-dienoic acid was dissolved in the minimum amount of toluene at r.t. and thionyl chloride (5 equiv.) was added dropwise. The reaction mixture was refluxed under nitrogen for 16-18 h. The resulting solution was rotary evaporated to remove the excess of thionyl chloride and the remaining mixture of acid chloride and toluene was analysed by i.r. and n.m.r. and used for the preparation of the corresponding 2,4-dienamide. The (2,4-hexadiene) acid chloride (122) was distilled under reduced pressure.

((E,E)-2,4-Hexadiene) acid chloride (122).

2,4-Hexadienoic acid (121) (10 g, 89.2 mmol), $SOCl_2$ (32.4 ml, 446 mmol), toluene (30 ml). Reaction Time: 18 h. Reaction mixture distilled to yield (122) as a light yellow liquid (8.78 g, 75%), b.p. 58-61 °C/70 mm Hg; ν_{max} ($CHCl_3$) 1 745 (C=O), 1 635 and 1 590 cm^{-1} (C=C); δ_H (220 MHz; $CDCl_3$) 1.93 (3 H, d, J 6 Hz, Me), 6.04 (1 H, d, J 15 Hz, -CH=C*H*COCl), 6.20-6.55 (2 H, m, -C*H*=C*H*Me), and 7.47 (1 H, dd, J 10 and 15 Hz, -C*H*=CHCOCl).

((E)-2,4-Pentadiene) acid chloride (142 d).

2,4-Pentadienoic acid (138) (4.29 g, 43.7 mmol), $SOCl_2$ (15.9 ml, 218 mmol), toluene (5 ml). Reaction mixture heated at 40 °C for 24 h. Evaporation of excess thionyl chloride gave a 37% solution of (142 d) in toluene (by ^{1}H n.m.r.) (2.7 g, 54%); δ_H (220 MHz ; $CDCl_3$) 5.79 (1 H, d, J 10 Hz, -CH=CH_a *cis*), 5.87 (1 H, d, J 17 Hz, -CH=CH_a *trans*), 6.21 (1 H, d, J 15 Hz, -CH=C*H*COCl), 6.48-6.67 (1 H, m, -C*H*=CH_a), 7.55 (1 H, dd, J 10 and 15 Hz, -C*H*=CHCOCl).

((E,E)-4-Methyl-2,4-hexadiene) acid chloride (142 a).

4-Methyl-2,4-hexadienoic acid (141 a) (3.57 g, 28.3 mmol) in toluene (20 ml). $SOCl_2$ (10.3 ml, 142 mmol) added dropwise and reaction mixture refluxed for 18 h. Evaporation of excess thionyl chloride afforded a 9:2 mixture of toluene and acid chloride (142 a) (3.94 g, 96%); $\nu_{max.}$ ($CHCl_3$) 1 735 (C=O), 1 620 and 1 587 cm^{-1} (C=C); δ_H (220 MHz; $CDCl_3$) 1.77 (3 H, s, -CH*Me*=CHMe), 1.85 (3 H, d, J 7 Hz, -CHMe=CH*Me*), 6.01 (1 H, d, J 15 Hz, -CH=C*H*COCl), 6.15-6.30 (1 H, m, -CHMe=C*H*Me), and 7.48 (1 H, d, J 15 Hz, -C*H*=CHCOCl).

((E)-5-Methyl-2,4-hexadiene) acid chloride (142 b).

5-Methyl-2,4-hexadienoic acid (141 b) (2.0 g, 16 mmol) in toluene (10 ml), $SOCl_2$ (5.75 ml, 80 mmol). Reaction mixture heated at 40 °C for 24 h. Evaporation of excess thionyl chloride afforded the acid chloride (142 b) as a 2:5 mixture with toluene (2.27 g, 99%); $\nu_{max.}$ ($CHCl_3$) 1 740 (C=O) 1 626 and 1 585 cm^{-1} (C=C); δ_H (220 MHz; $CDCl_3$) 1.96 (6 H, s, -CH=CMe_a), 6.02 (1 H d, J 15 Hz, -CH=C*H*COCl), 6.11 (1 H, d, J 12 Hz, -C*H*=CMe_a), and 7.80 (1 H, dd, J 12 and 15 Hz, -C*H*=CHCOCl).

((E)-4-Methyl-2,4-pentadiene) acid chloride (142 c).

4-Methyl-2,4-pentadienoic acid (141 c) (1.80 g, 16.1 mmol) dissolved in toluene (5.5 ml), $SOCl_2$ (5.82 ml, 80.5 mmol). Reaction mixture heated at 40 °C for 10 h.

Excess $SOCl_2$ evaporated to yield 9:1 mixture of toluene and acid chloride (142 c) (1.37 g, 65%); ν_{max} ($CHCl_3$) 1 734 (C=O), 1 622 and 1 583 cm^{-1} (C=C); δ_H (220 MHz; $CDCl_3$) 1.92 (3 H, s, -CH*Me*=CH_2), 5.58 (2 H, s, -CHMe=CH_2), 6.12 (1 H, d, J 15 Hz, -CH=C*H*COCl), and 7.54 (1 H, d, J 15 Hz, -*CH*=CHCOCl).

1.4.3 Synthesis of *N,N*-dimethylamides (123) and (134)-(137)

General Method

A solution of the (2,4-diene) acid chloride in toluene under nitrogen was cooled to 0 °C. In a separate container, under N_2, dimethylamine was generated by adding a 10% w/v NaOH aqueous solution onto dimethylamine hydrochloride (5 equiv.) dropwise with stirring. This container was connected to the reaction mixture vessel containing the cold acid chloride solution and dimethylamine was bubbled into this solution until all dimethylamine has been released (*ca.* 3 h). The solvent was evaporated and the residue obtained was dissolved in dichloromethane. This solution was extracted with 10% Na_2CO_3 aqueous solution and the aqueous phase washed with dichloromethane. The combined organic extracts were evaporated to yield the dimethylamide as a solid. The 2,4-dienamides prepared were further purified by recrystallisation from hexane.

(E,E)-N,N-Dimethyl-2,4-hexadienamide (123).

(2,4-Hexadiene) acid chloride (122) (2.3 g, 17.6 mmol), toluene (5 ml). Dimethylamine (4.4 equiv.) bubbled into the reaction mixture at 0 °C for 3.5 h. Extraction of dichloromethane solution with 10% $Na_2CO_{3(aq)}$ and evaporation of solvent afforded the dienamide (123) as a yellow crystalline solid (2.38 g, 97%); ν_{max} ($CHCl_3$) 1 658 (C=O), 1 629 and 1 599 cm^{-1} (C=C) (lit.[44] ν_{max} ($CHCl_3$) 1 650 (C=O), 1 620 and 1 590 cm^{-1} (C=C); δ_H (220 MHz ; $CDCl_3$) 1.85 (3 H, d, J 6 Hz, -CH=CH*Me*), 3.03 (3 H, s, -CON*Me*$_2$), 3.10 (3 H, s, -CON*Me*$_2$), 6.10-6.35

(2 H, m, -*CH*=*CH*Me), 6.28 (1 H, d, J 15 Hz, -CH=*CH*CONMe$_2$), and 7.29 (1 H, dd, J 10 and 15 Hz, -*CH*=CHCONMe$_2$) (lit.[88] δ_H (60 MHz; $CDCl_3$) 1.88 (3 H, d, J 6 Hz, -CH_3=CH_3*Me*), 3.06 (6 H, s, CON*Me*$_2$), 5.84-6.50 (3 H, m, -*CH*=CH-*CH*=*CH*Me), and 7.28-7.90 (1 H, m, -*CH*=CHCONMe$_2$)).

(E)-N,N-Dimethyl-2,4-pentadienamide (134).

(2,4-Pentadiene) acid chloride (142 a) (3.29 g, 28.2 mmol), toluene (6 ml), dimethylamine (5 equiv.). Reaction time : 2.5 h. Chromatography on SiO_2, diethyl ether, gave (134) as a yellow oil (0.90 g, 30%); $\nu_{max.}$ ($CHCl_3$) 1 650 (C=O), 1 612 and 1 595 cm^{-1} (C=C) (lit.[88] $\nu_{max.}$ ($CHCl_3$) 1 653 (C=O) and 1 616 cm^{-1} (C=C)); δ_H (220 MHz; $CDCl_3$) 3.06 (3 H, s, -CON*Me*$_2$), 3.14 (3 H, s, -CON*Me*$_2$), 5.49 (1 H, d, J 10 Hz, -CH=C*H*$_2$ *cis*), 5.62 (1 H, d, J 17 Hz, -CH=C*H*$_2$ *trans*), 6.48 (1 H, d, J 15 Hz, -CH=*CH*CONMe$_2$), 6.57 (1 H, dt, J 10, 11 and 17 Hz, -*CH*=CH$_2$), and 7.35 (1 H, dd, J 11 and 15 Hz, -*CH*=CHCONMe$_2$)(lit.[88] δ_H (60 MHz; $CDCl_3$) 3.07 (6 H, s, -CON*Me*$_2$), 5.27-5.77 (2 H, m, -CH=C*H*$_2$), 6.17-7.53 (3 H, m, -*CH*=*CH*-*CH*=CH$_2$)); *m/z* (EI) 125 (M^+, 58%), 81 (M^+-NMe$_2$, 100), 72 (CONMe$_2$, 24), and 53 (M^+-CONMe$_2$, 84).

(E,E)-N,N-Dimethyl-4-methyl-2,4-hexadienamide (135).

(4-Methyl-2,4-hexadiene) acid chloride (142 a) (3.90 g, 27.0 mmol) obtained as a 2:9 mixture with toluene, dimethylamine (5 equiv.). Reaction time: 3 h. Recrystallisation from hexane afforded the dienamide (135) as a pale-yelow crystalline solid (3.54 g, 86%), m.p. 50-52 °C; $\nu_{max.}$ ($CHCl_3$) 1 645 (C=O), 1 626 and 1 596 cm^{-1} (C=C); δ_H (400 MHz; $CDCl_3$) 1.74 (3 H, s, -C*Me*=CHMe), 1.75 (3 H, d, J 8.2 Hz, -CMe=CH*Me*), 2.97 (3 H, s, -CON*Me*$_2$), 3.06 (3 H, s, -CON*Me*$_2$), 5.88-5.91 (1 H, m, -CMe=*CH*Me), 6.14 (1 H, d, J 15.1 Hz, -CH=*CH*CONMe$_2$), and 7.25 (1 H, d, J 15.1 Hz, -*CH*=CHCONMe$_2$); δ_C [^{1}H] (100.6 MHz; $CDCl_3$) 11.8 (-*C*Me=CHMe), 14.2 (-CMe=CH*Me*), 35.6 (NMe), 37.2 (NMe), 114.0 (-CH=*CH*CONMe$_2$), 133.6

(-CMe=*C*HMe), 134.4 (-*C*Me=CHMe), 147.0 (-*C*H=CHCONMe$_2$), and 167.2 (*C*ONMe$_2$); *m/z* (EI) 153 (M†, 11%), 72 (CONMe$_2$, 100), and 44 (NMe$_2$, 59).

(E)-N,N-Dimethyl-5-methyl-2,4-hexadienamide (136).

(5-Methyl-2,4-hexadiene) acid chloride (142 b) (2.20 g, 15.2 mmol) obtained as a 2:5 mixture with toluene, dimethylamine (5 equiv.). Reaction time: 2.5 h. Recrystallisation from hexane yielded yellow-straw needle crystals of hexadienamide (136) (1.6 g, 69%), m.p. 80-81 °C; ν_{max} ($CHCl_3$) 1 649 (C=O), 1 625 and 1 590 cm^{-1} (C=C); δ_H (220 MHz; $CDCl_3$) 1.87 (3 H, s, -CH=C*Me*$_2$), 1.90 (3 H, s, -CH=C*Me*$_2$), 3.04 (3 H, s, -CON*Me*$_2$), 3.09 (3 H, s, -CON*Me*$_2$) 6.04 (1 H, br d, J 11 Hz, -C*H*=CMe$_2$), 6.26 (1 H, d, J 15 Hz, -CH=C*H*CONMe$_2$), and 7.62 (1 H, dd, J 11 and 15 Hz, -C*H*=CHCONMe$_2$); δ_C (^{1}H) (100.6 MHz; $CDCl_3$) 18.7 (-CH=C*Me*$_2$ *cis*), 26.3 (-CH=CH*Me*$_2$ *trans*), 35.6 (NMe), 37.1 (NMe), 117.7 (-CH=*C*HCONMe$_2$), 123.9 (-CH=*C*Me$_2$), 138.8 (-*C*H=CMe$_2$), 144.1 (-*C*H=CHCON*Me*$_2$), and 167.8 (-CONMe$_2$); *m/z* (EI) 153 (M†, 100%), 138 (M†-Me, 45), 109 (M†-NMe$_2$, 92), and 72 (-CONMe$_2$, 26).

(E)-N,N-Dimethyl-4methyl-2,4-pentadienamide (137).

(4-Methyl-2,4-pentadiene) acid chloride (142 c) (1.37 g, 10.5 mmol) obtained as a 1:9 mixture with toluene, dimethylamine (5 equiv.). Reaction time: 3 h. Recrystallisation from hexane gave the dienamide (137) as a white crystalline solid (0.74 g, 51%), m.p. 45-47 °C; ν_{max} ($CHCl_3$) 1 643 cm^{-1} (C=O); δ_H (220 MHz; $CDCl_3$) 1.92 (3 H, s, -C*Me*=CH$_2$), 3.06 (3 H, s, CON*Me*$_2$), 3.14 (3 H, s, CON*Me*$_2$), 5.31 (1 H, s, -CMe=C*H*$_2$), 5.36 (1 H, s, -CMe=C*H*$_2$), 6.33 (1 H, d, J 15 Hz, -CH=C*H*CONMe$_2$), and 7.38 (1 H, d, J 15 Hz, -C*H*=CHCONMe$_2$); *m/z* (EI) 141 (MH†, 71%), 72 (CONMe$_2$, 94), and 44 (NMe$_2$, 100).

1.4.4 Synthesis of $Fe(CO)_3$ complexes (120) and (143) - (146)

General method[9]

The dienamide was heated with nonacarbonyldi-iron(0) (2 equiv.) in dry diethyl ether (5 ml/g $Fe_2(CO)_9$) at 35 °C, under N_2, for 16-18 h. The reaction mixture was cooled to room temperature and filtered through alumina to remove iron residues. The solvent was evaporated under vacuum and the dark orange oil/solid obtained was purified by column chromatography to yield the (dienamide)$Fe(CO)_3$ complexes as yellow/orange crystalline solids.

((E,E)-N,N-Dimethyl-2,4-hexadienamide)tricarbonyliron(0) (120).

N,N-Dimethyl-2,4-hexadienamide (123) (0.50 g, 3.59 mmol), $Fe_2(CO)_9$ (2.61 g, 7.18 mmol), Et_2O (13 ml). Reaction time: 18 h. Chromatography on SiO_2, 10% Et_2O-petroleum ether 40-60 °C gave (120) as a yellow crystalline solid (0.87 g, 87%), m.p. 119-120 °C (hexane) (Found: C, 47.60; H, 4.76; N, 4.96. $C_{11}H_{11}FeNO_4$ requires C, 47.34; H, 4.70; N, 5.02%); ν_{max} (hexane) 2 057, 1 996, and 1 980 (C≡O), 1 650 cm^{-1} (C=O); δ_H (400 MHz; $CDCl_3$) 1.06 (1 H, d, J 7.8 Hz, -CH=C*H*CONMe$_2$), 1.40 (1 H, m, -CH=C*H*Me), 1.46 (3 H, d, J 5.9 Hz, -CH=CH*Me*), 2.92 (3 H, s, NMe), 3.02 (3 H, s, NMe), 5.24 (1 H, dd, J 5.1 and 8.5 Hz, -C*H*=CHMe), and 5.95 (1 H, dd, J 5.1 and 7.8 Hz -C*H*=CHCONMe$_2$); δ_C {^{1}H} (100.6 MHz; $CDCl_3$) 19.0 (-CH=CH*Me*), 35.7 (NMe), 36.8 (NMe), 46.0 (-CH=*C*HCONMe$_2$), 58.6 (-CH=*C*HMe), 83.0 (-*C*H=CHMe), 88.3 (-*C*H=CHCONMe$_2$), 170.6 (C=O), and 210.5 br (C≡O); *m/z* (FAB) 280 (MH^+, 100%), 252 (MH^+-CO, 17), 224 (MH^+-2CO, 46), and 195 (MH^+-3CO, 47).

((E)-N,N-Dimethyl-2,4-pentadienamide)tricarbonyliron(0) (143).

N,N-Dimethyl-2,4-pentadienamide (134) (0.22 g, 1.76 mmol), $Fe_2(CO)_9$ (1.28g, 3.52 mmol), Et_2O (6.5 ml). Reaction time: 17 h. Chromatography on SiO_2, 5% Et_2O -petroleum ether 40-60 °C gave (143) as an orange crystalline solid (0.35 g,

75%), m.p. 94-95 °C (hexane) (Found: C, 45.43; H, 4.19; N, 5.28. $C_{12}H_{11}FeNO_4$ requires C, 45.32; H, 4.18; N, 5.28%); ν_{max} (hexane) 2 063, 2 008, and 1 987 (C≡O), 1 649 cm^{-1} (C=O); δ_H (400 MHz; $CDCl_3$) 0.54 (1 H, dd, J 2.7 and 9.4 Hz, -CH=C*H*$_a$ *cis*), 1.08 (1 H, d, J 7.7 Hz, -CH=C*H*CONMe$_a$), 1.95 (1 H, dd, J 2.7 and 7.0 Hz, -CH=C*H*$_a$ *trans*), 2.94 (3 H, s, NMe), 3.04 (3 H, s, NMe), 5.43 (1 H, m, -C*H*=CH$_a$), and 6.12 (1 H, dd, J 5.0 and 7.7 Hz, -C*H*=CHCONMe$_a$); δ_C {^{1}H} (100.6 MHz; $CDCl_3$) 35.7 (NMe), 36.8 (NMe), 40.5 (-CH=*C*HCONMe$_a$), 46.8 (-CH=*C*H$_a$), 84.5 (-*C*H=CH$_a$), 87.6 (-*C*H=CHCONMe$_a$), 170.5 (C=O), and 209.9 br (C≡O); *m/z* (FAB) 266 (MH^+, 100%), 238 (MH^+-CO, 18), 209 (MH^+-2CO, 53), and 181 (MH^+-3CO, 49).

((E,E)-N,N-Dimethyl-4-methyl-2,4-hexadienamide)tricarbonyliron(0) (144).

N,N-Dimethyl-4-methyl-2,4-hexadienamide (135) (1.0 g, 6.53 mmol), $Fe_2(CO)_9$ (4.75 g, 13.1 mmol), Et_2O (24 ml). Reaction time: 16 h. Chromatography on SiO_2, 10% Et_2O-petroleum ether 40-60 °C gave (144) as a yellow crystalline solid (1.31 g, 69%), m.p. 103-104 °C (hexane) (Found: C, 48.90; H, 5.18; N, 4.73. $C_{12}H_{13}FeNO_4$ requires C, 49.17; H, 5.16; N, 4.78%); ν_{max} (hexane) 2 055, 1 993 and 1 976 (C≡O), 1 649 cm^{-1} (C=O); δ_H (400 MHz; $CDCl_3$) 0.91 (1 H, d, J 7.5 Hz, -CH=C*H*CONMe$_a$), 1.26 (1 H, br q, J 6.4 Hz, -CMe=C*H*Me), 1.47 (3 H, d, J 6.4 Hz, -CMe=CH*Me*), 2.18 (3 H, s, -C*Me*=CHMe), 2.93 (3 H, s, NMe), 3.02 (3 H, s, NMe), and 5.88 (1 H, d, J 7.5 Hz, -C*H*=CHCONMe$_a$); δ_C {^{1}H} (100.6 MHz; $CDCl_3$) 15.7 (-*C*Me=CHMe), 17.8 (-CMe=CH*Me*), 35.7 (NMe), 36.8 (NMe), 43.2 (-CH=*C*HCONMe$_a$), 58.9 (-*C*Me=CHMe), 83.8 (-*C*Me=CHMe), 102.7 (-*C*H=CHCONMe$_a$), 171.7 (C=O), and 210.7 br (C≡O); *m/z* (FAB) 294 (MH^+, 100%), 265 (M^+-CO, 22), 237 (M^+-2CO, 52), and 209 (M^+-3CO, 53).

((E)-N,N-Dimethyl-5-methyl-2,4-hexadienamide)tricarbonyliron(0) (145).

N,N-Dimethyl-5-methyl-2,4-hexadienamide (136) (0.41 g, 2.68 mmol), $Fe_2(CO)_9$ (1.95 g, 5.35 mmol), Et_2O (10 ml). Reaction time: 16 h. Reaction mixture filtered through

alumina to yield (145) as a yellow oil unstable at room temperature under nitrogen (0.41 g, 52%); $\nu_{max.}$ (hexane) 2 052, 1 991, and 1 975 (C≡O), 1 651 cm^{-1} (C=O); *m/z* (FAB) 294 (MH^+, 64%), 265 (M^+-CO, 29), 237 (M^+-2CO, 89), and 208 (M^+-H-3CO, 100).

((E)-N,N-Dimethyl-4-methyl-2,4-pentadienamide)tricarbonyliron (0) (146).

N,N-Dimethyl-4-methyl-2,4-pentadienamide (137) (0.40 g, 2.87 mmol), $Fe_2(CO)_9$ (2.09 g, 5.74 mmol), Et_2O (10.5 ml). Reaction time: 16 h. Chromatography on SiO_2, 10% Et_2O-petroleum ether 40-60 °C gave (146) as an orange crystalline solid (0.51 g, 64%), m.p. 71-72 °C (hexane) (Found: C, 47.41; H, 4.73; N, 4.96. $C_{11}H_{11}FeNO_4$ requires C, 47.34; H, 4.70; N, 5.02%); $\nu_{max.}$ (hexane) 2 060, 1 998, and 1 983 (C≡O), 1 649 cm^{-1} (C=O); δ_H (400 MHz; $CDCl_3$) 0.58 (1 H, dd, J 1.0 and 2.6 Hz, -CMe=C*H*$_a$ *cis*), 0.87 (1 H, d, J 7.4 Hz, -CH=C*H*CONMe$_2$), 1.96 (1 H, dd, J 1.8 and 2.5 Hz -CMe=C*H*$_a$ *trans*), 2.21 (3 H, s, -C*Me*=CH$_2$), 2.93 (3 H, s, NMe), 3.02 (3 H, s, NMe), and 5.98 (1 H, br d, J 7.4 Hz, -C*H*=CHCONMe$_2$); δ_C (^{1}H) (100.6 MHz; $CDCl_3$) 22.6 (-C*Me*=CH$_2$), 35.8 (NMe), 36.8 (NMe), 43.6 (-CH=C*H*CONMe$_2$), 44.8 (-CMe=C*H*$_2$), 86.8 (-C*Me*=CH$_2$), 102.3 (-C*H*=CHCONMe$_2$), 170.9 (C=O), and 210.0 br (C≡O); *m/z* (FAB) 280 (MH^+, 100%), 251 (M^+-CO, 23), 223 (M^+-2CO, 49) and 195 (M^+-3CO, 70).

1.4.5 Synthesis of ((E)-2,4-pentadiene) methyl ester (149).[44]

(E)-2,4-Pentadienoic acid (138) (1.0 g, 10.2 mmol) was dissolved in dry methanol (3 ml) and the light yellow solution obtained was cooled to 0 °C. Acetyl chloride (0.77 ml, 10.6 mmol) was added dropwise and the cooling bath was removed. The dark red reaction mixture obtained was stirred at 45 °C for 3.5 h. It was then poured into ice (40 ml) and extracted with diethyl ether (3 x 40 ml). The orange organic phase was washed with water (80 ml), dried ($MgSO_4$) and filtered. The solvent was removed under reduced pressure to yield (149) as an orange oil (0.85g, 74%); $\nu_{max.}$($CHCl_3$) 1 706 (C=O), 1 644 and 1 598 cm^{-1} (C=C); δ_H (220 MHz;

$CDCl_3$) 3.79 (3 H, s, Me), 5.56 (1 H, d, J 10 Hz, -CH=C*H*$_2$ *trans*), 5.68 (1 H, d, J 18 Hz, -CH=C*H*$_2$ *cis*), 6.0 (1 H, d, J 16 Hz, -CH=C*H*CO_2Me), 6.54 (1 H, dt, J 10, 11 and 18 Hz, -C*H*=CH_2) 7.37 (1 H, dd, J 11 and 16 Hz, -C*H*=$CHCO_2$Me).

1.4.6 Synthesis of ((2,4-diene) methyl ester)Fe(CO)$_3$ complexes (131) and (148)

General method[69]

These were prepared using the method described for the preparation of (2,4-dienamide)Fe(CO)$_3$ complexes in section 1.4.4.

[(E,E)-(2,4-Hexadiene)methyl ester]tricarbonyliron(0) **(131)**.

(2,4-Hexadiene) methyl ester (132) (0.52 g, 4.12 mmol), $Fe_2(CO)_9$ (3.0 g, 8.2 mmol), diethyl ether (15 ml). Reaction time: 17.5 h. Chromatography on SiO_2, 5% EtOAc-petroleum ether 40-60 °C gave (131) as an orange oil (0.77 g, 70%); $\nu_{max.}$ ($CHCl_3$) 2 060 and 1 997 br (C≡O), 1 710 cm^{-1} (C=O) (lit.[68] $\nu_{max.}$ ($CHCl_3$) 2 100 and 2 050 (C≡O), 1 725 cm^{-1} (C=O); δ_H (220 MHz; $CDCl_3$) 0.98 (1 H, d, J 9 Hz, -CH=C*H*CO_2Me), 1.47 (4 H, m, -CH=C*HMe*), 3.68 (3 H, s -CH=CO_2*Me*), 5.26 (1 H, m, -C*H*=CHMe), and 5.83 (1 H, dd, J 6 and 9 Hz, -C*H*=CHCO$_2$Me) (lit.[68] δ_H (220 MHz; $CDCl_3$) 1.0 (1 H, d, J 9 Hz, -CH=C*H*CO_2Me), 1.45 (4 H, m, -CH=C*HMe*), 3.65 (3 H, s, -CH=CHCO$_2$*Me*), 5.25 (1 H, m, -C*H*=CHMe), and 5.80 (1 H, dd, J 7 and 9 Hz, -C*H*=CHCO$_2$Me)); *m/z* (EI) 266 (M^+, 6%), and 238 (M^+-CO, 24) (lit.[68] *m/z* (EI) 266 (M^+, 9%), 238 (M^+-CO, 32), 210 (M^+-2CO, 59), and 182 (M^+-3CO, 51)).

[(E)-(2,4-Pentadiene) methyl ester)]tricarbonyliron(0) **(148)**.

(2,4-Pentadiene) methyl ester (149) (0.29 g, 2.60 mmol), $Fe_2(CO)_9$ (1.89 g, 5.2 mmol), diethyl ether (10 ml). Reaction time: 17 h. Chromatography on SiO_2, 5% EtOAc-petroleum ether 40-60 °C gave (148) as an orange oil (0.52 g, 79%); $\nu_{max.}$ (*hexane*) 2 068, 2 008 and 1 995 (C≡O), 1 726 cm^{-1} (C=O); δ_H (400 MHz;

$CDCl_3$) 0.59 (1 H, dd, J 2.8 and 9.4 Hz, -CH=CH_a *cis*), 0.98 (1 H, d, J 8.0 Hz, -CH=CH_b), 1.97 (1 H, dd, J 2.8 and 7.0 Hz, -CH=CH_a *trans*) 3.66 (3 H, s, CO_2Me), 5.38-5.44 (1 H, m, -C*H*=CH_2), and 5.95 (1 H, dd, J 4.9 and 8.0 Hz -C*H*=$CHCO_2$Me); δ_C [^{1}H] (100.6 MHz; $CDCl_3$) 40.9 (-CH=*C*HCO_2Me), 46.4 (-CH=CH_2), 51.5 (Me), 84.6 (-*C*H=CH_2), 87.3 (-*C*H=$CHCO_2$Me), 172.4 (C=O), and 209.2 br (C=O); *m/z* (EI) 252 (M$^+$, 9%), 196 (M$^+$-2CO, 42), and 168 (M$^+$-3CO, 57).

I.4.7 Reaction of (2,4-dienamide)Fe(CO)$_3$ complexes (120, (143), (144) and (146) with isobutyronitrile anion

General method[61]

To a solution of diisopropylamine (3 equiv.) in dry THF at -78 °C under nitrogen, was added *n*-butyllithium (3 equiv.). The mixture was stirred for 20 min and isobutyronitrile (3 equiv.) was added. After stirring at -78 °C for 20 min a solution of the complex in dry THF was added rapidly. The cooling bath was removed and the reaction mixture was stirred at 25 °C for 2 h. The mixture was recooled to -78 °C, trifluoroacetic acid (20 equiv.) was added dropwise, and the mixture was stirred at 25 °C for 1 h. The mixture was poured into saturated aqueous sodium carbonate solution, and the aqueous layer was extracted twice with diethyl ether. The combined organic layers were washed with saturated aqueous sodium chloride and filtered through a plug of alumina to remove iron residues. The filtrate was dried ($MgSO_4$), filtered and concentrated under vacuum. The residue was purified by thin layer chromatography (tlc) on silica gel.

Reaction of ((E,E)-N,N-dimethyl-2,4-hexadienamide)Fe(CO)$_3$ (120).

Diisopropylamine (0.26 ml, 1.86 mmol) in THF (5 ml), n-butyllithium (0.74 ml, 1.85 mmol), isobutyronitrile (0.18 ml, 1.98 mmol). (*N,N*-Dimethyl-2,4-hexadienamide) Fe(CO)$_3$ (120) (0.175 g, 0.627 mmol) in THF (3 ml). Orange reaction mixture

quenched with trifluoroacetic acid (0.97 ml, 12.5 mmol) at -78 °C. Red reaction mixture at room temperature. Work up in the presence of air and filtration of iron residues with alumina plug gave light yellow solution. Tlc on SiO_2, Et_2O, yielded 2-*N,N*-dimethylamide-3-isobutyronitrile-5-methyl-cyclopentanone (127) (3:1 mixture of 2α-3,5β and 2,5α-3β isomers) as a colourless oil (0.080 g, 54%); ν_{max} ($CHCl_3$) 2243 (C≡N), 1748 (cyclopentanone C=O), and 1650 cm^{-1} (amide C=O); δ_H (400 MHz; $CDCl_3$) 1.11 (3 H, partially obscured d, J 7 Hz, -CH_3C*H*M*e*-, minor isomer), 1.12 (3 H, d, J 7.6 Hz, -CH_3C*H*M*e*-, major isomer), 1.23 (3 H, s, -CMe_2CN, minor isomer), 1.24 (3 H, s, -CMe_2CN, major isomer), 1.38 (3 H, s, -CMe_2CN, major isomer), 1.40 (3 H, s, -CMe_2CN, minor isomer), 1.90-1.96 (1 H, m, -C*H*$_3$CHMe-, major isomer), 2.01-2.09 (1 H, m, -C*H*$_3$CHMe-, major isomer), 2.35-2.44 (1 H, m, -CH_3C*H*Me-, minor isomer), 2.44-2.46 (1 H, m, -C*H*$_3$CHMe-, minor isomer), 2.53-2.60 (1 H, m, -CH_3C*H*Me-, major isomer), 2.90-2.94 (1 H, m, -CH_3C*H*CMe_2CN-, minor isomer), 2.98 (3 H, s, NMe, minor isomer), 2.99 (3 H, s, NMe, major isomer), 3.03-3.10 (1 H, m, -CH_3C*H*CMe_2CN-, major isomer), 3.18 (3 H, s, NMe, major isomer), 3.22 (3 H, s, NMe, minor isomer), 3.52 (1 H, d, J 10.1 Hz, -C*H*$CONMe_2$-, minor isomer), and 3.57 (1 H, d, J 10.0 Hz, -C*H*$CONMe_2$-, major isomer); δ_C (100.6 MHz; $CDCl_3$) 13.0 (-CMe_2CN), 16.1 (-CH_3CH*Me*-, major isomer), 16.3 (-CH_3CH*Me*-, minor isomer), 24.9 (-*Me*$_2$CN, major isomer), 25.0 (-*Me*$_2$CN, minor isomer), 26.2 (-*Me*$_2$CN, major isomer), 29.5 (-*Me*$_2$CN, minor isomer), 31.7 (-CH_3C*H*CMe_2CN-, major isomer), 32.6 (-CH_3C*H*CMe_2CN-, minor isomer), 36.0 (NMe, major isomer), 36.1 (NMe, minor isomer), 37.6 (NMe, major isomer), 37.7 (NMe, minor isomer), 43.1 (-C*H*$_2$CHMe-, major and minor isomers), 45.0 (-CH_3C*H*Me-, minor isomer), 45.6 (-CH_3C*H*Me-, major isomer), 54.8 (-C*H*$CONMe_2$-, minor isomer), 55.2 (-C*H*$CONMe_2$-, major isomer), 123.2 (C≡N, minor isomer), 123.3 (C≡N, major isomer), 167.8 (C=O amide, minor isomer), 167.9 (C=O amide, major isomer), 212.2 (C=O cyclopentanone, minor isomer), and 213.8 (C=O cyclopentanone, major isomer); *m/z* (EI) 236 (M^+, 9%), and 168 (M^+ -CMe_2CN, 100).

Reaction of ((E)-N,N-dimethyl-2,4-pentadienamide)Fe(CO)$_3$ (143).

Diisopropylamine (0.48 ml, 3.39 mmol) in THF (8 ml), n-butyllithium (1.36 ml, 3.39 mmol), isobutyronitrile (0.31 ml, 3.39 mmol). (*N,N*-Dimethyl- 2,4-pentadienamide) $Fe(CO)_3$ (**143**) (0.300 g, 1.13 mmol) in THF (5 ml). Dark orange reaction mixture quenched with trifluoroacetic acid (1.74 ml, 22.6 mmol) at -78 ^oC. Red coloured reaction mixture at room temperature. Work up and filtration through alumina gave light yellow solution. Tlc on SiO_2, Et_2O, afforded 2α-*N,N*-dimethylamide-3β-isobutyronitrile-cyclopentanone (**147**) as a colourless oil (0.170 g, 68%); $\nu_{max.}$ ($CHCl_3$) 2 230 (C≡N), 1 741 (cyclopentanone C=O), and 1 643 cm^{-1} (amide C=O); δ_H (400 MHz; $CDCl_3$) 1.28 (3 H, s -CMe_2CN), 1.44 (3 H, s, -CMe_2CN), 2.95-3.14 (1 H, m, -*CH*CMe_2CN-), 2.21-2.60 (4 H, m, -CH_2CH_2-), 3.03 (3 H, s, NMe), 3.25 (3 H, s, NMe), 3.57 (1 H, d, J 10.2 Hz, -*CH*$CONMe_2$-); *m/z* (EI) 222 (M^+, 8%), 154 (M^+-CMe_2CN, 54), 72 ($CONMe_2$, 100).

Reaction of ((E,E)-N,N-dimethyl-4-methyl-2,4-hexadienamide)Fe(CO)$_3$ (144).

Diisopropylamine (0.72 ml, 5.13 mmol) in THF (10 ml), *n*-butyllithium (2.2 ml, 5.13 mmol), isobutyronitrile (0.47 ml, 5.13 mmol). (*N,N*-Dimethyl-4-methyl-2,4 -hexadienamide)$Fe(CO)_3$ (**144**) (0.500 g, 1.71 mmol) in THF (9 ml). Dark orange reaction mixture quenched with trifluoroacetic acid (2.63 ml, 34.1 mmol) at -78 ^oC. Dark red reaction mixture at room temperature. Work up in the presence of air and filtration through alumina gave a light yellow solution. TLC on SiO_2, Et_2O, afforded *N,N*-dimethyl-3-isobutyronitrile-4-methyl-4-hexenamide (**151**) as a pale yellow oil (0.28 g, 74%); $\nu_{max.}$ ($CHCl_3$) 2 230 (C≡N), and 1 640 cm^{-1} (C=O); δ_H (220 MHz; $CDCl_3$) 1.06 (1 H, t, J 7 and 8 Hz, -*CH*CMe_2CN-), 1.29 (3 H, s, -CMe_2CN), 1.41 (3 H, s, -CMe_2CN), 1.62 (3 H, d, J 6 Hz, -CMe=CH*Me*), 1.77 (3 H, s, -*CMe*=CHMe), 2.97 (3 H, s, NMe), 3.08 (3 H, s, NMe), 5.05 (1 H, br s, -CH_2CONMe_2), 5.18 (1 H, br s, -CH_2CONMe_2), and 5.53 (1 H, br q, -CMe=*CH*Me); *m/z* (CI) 223 (MH^+, 100%), 154 (MH^+-$CONMe_2$+3H, 40), and 72 ($CONMe_2$, 25).

Reaction of ((E)-N,N-dimethyl-4-methyl-2,4-pentadienamide)Fe(CO)$_3$ (146).

Diisopropylamine (0.36 ml, 2.58 mmol) in THF (6 ml), *n*-butyllithium (1.03 ml, 2.58 mmol), isobutyronitrile (0.24 ml, 2.58 mmol). (*N,N*-Dimethyl-4-methyl-2,4-pentadienamide)Fe(CO)$_3$ (146) (0.240 g, 0.860 mmol) in THF (3 ml). Dark orange reaction mixture quenched with trifluoroacetic acid (1.32 ml, 17.2 mmol) at -78 ^{o}C. Red reaction mixture at room temperature. Work up and filtration through alumina gave a yellow solution. Evaporation of the solvent under *vacuum* afforded *N,N*-dimethyl-3-isobutyronitrile-4-methyl-4-pentenamide (152) as a yellow oil (0.17 g, 95%); $\nu_{max.}$ ($CHCl_3$) 2 240 (C≡N), and 1 642 cm^{-1} (C=O); δ_H (220 MHz; $CDCl_3$) 1.36 (3 H, s, CMe_2CN), 1.43 (3 H, s, CMe_2CN), 1.73 (2 H, br s, $-CH_2CONMe_2$), 1.90 (3 H, s, $-CMe=CH_2$), 2.76 (1 H, m, $-CHCMe_2CN-$), 2.96 (3 H, s, NMe), 3.08 (3 H, s, NMe), and 4.49 (2 H, s, $-CMe=CH_2$).

1.4.8 Reaction of ((2,4-diene)methyl ester)Fe(CO)$_3$ complexes (131) and (148) with isobutyronitrile anion

General Method[41]

As described for reaction of (2,4-dienamide) Fe(CO)$_3$ complexes with isobutyronitrile, section 1.4.7.

Reaction of [((E,E)-2,4-hexadiene)methyl ester]Fe(CO)$_3$ (131).

Diisopropylamine (0.24 ml, 1.69 mmol) in dry THF (5 ml), n-butyllithium (0.68 ml, 1.69 mmol), isobutyronitrile (0.15 ml, 1.69 mmol). [((*E,E*)-2,4-hexadiene)methyl ester]$FeCO_3$ (131) (0.150 g, 0.564 mmol) dissolved in dry THF (2 ml). Dark orange/ brown reaction mixture quenched with trifluoroacetic acid (0.87 ml, 11.3 mmol) at -78 ^{o}C. Dark red/ brown reaction mixture at room temperature. Work up followed by filtration through alumina gave a light yellow solution. Thin layer chromatography on SiO_2 yielded (*E*)-1,3-diisobutyronitrile-4-ene-hexanone (133) as a

pale-yellow oil (0.098 g, 75%); $\nu_{max.}$ ($CHCl_3$) 2 238 (C≡N), and 1 732 (C=O); δ_H (400 MHz; $CDCl_3$) 1.29 (3 H, s, -CHC*Me*$_2$CN-), 1.33 (3 H, s, -CHC*Me*$_2$CN), 1.44 (3 H, s, -CHC*Me*$_2$CN-), 1.49 (3 H, s,-COC*Me*$_2$CN), 1.65 (3 H, d, J 6.5 Hz, -CH=CH*Me*), 2.69 (1 H, td, J 3.1 and 9.7 Hz, -C*H*CMe$_2$CNCH=CHMe), 2.87 (1 H, dd, J 3.1 and 16.9 Hz, -C*H*$_2$COCMe$_2$CN), 3.03 (1 H, dd, J 10.1 and 16.9 Hz, -C*H*$_2$COCMe$_2$CN), 5.22 (1 H, dd, J 9.5 and 15.1 Hz -C*H*=CHMe), and 5.58 (1 H, dq, J 6.7 and 15.3 Hz, -CH=C*H*Me); δ_C (100.6 MHz; $CDCl_3$) 17.8 (-CH=CH*Me*), 23.3 (-*C*HCMe$_2$CN-), 24.2 (-CHC*Me*$_2$CN-), 25.2 (-CHC*Me*$_2$CN-), 29.6 (-CHC*Me*$_2$CN-), 35.2 (-COCMe$_2$CN), 40.1 (-*C*H$_2$COCMe$_2$CN), 44.1 (-COC*Me*$_2$CN), 46.1 (-COC*Me*$_2$CN), 121.3 (-CHCMe$_2$*C*N-), 123.8 (-COCMe$_2$*C*N), 127.0 (-CH=*C*HMe) 131.5 (-*C*H=CHMe), and 201.5 (C=O); *m/z* (EI) 233 (MH^+, 10%), 164 (M^+-CMe_2CN, 100), 122 (M^+-CH_2COCMe_2CN, 88), 95 (M^+-$2CMe_2CN$-H, 13) and 68 (CMe_2CN, 69).

Reaction of [((E)-2,4-pentadiene)methyl ester]Fe(CO)$_3$ (148).

Diisopropylamine (0.27 ml, 1.90 mmol) in dry THF (5 ml), n-butyllithium (0.76 ml, 1.90 mmol), isobutyronitrile (0.18 ml, 1.90 mmol). [((*E*)-2,4-pentadiene)methyl ester]Fe(CO)$_3$ (148) (0.160 g, 0.635 mmol) dissolved in dry THF (2 ml). Dark reaction mixture quenched with trifluoroacetic acid (0.98 ml, 12.7 mmol) at -78 °C. No noticeable change of the reaction mixture colour at room temperature. Work up followed by filtration through alumina gave an orange solution. Thin layer chromatography on SiO_2 yielded (*E*)-1,3-diisobutyronitrile-4-ene-pentanone (150) as a yellow oil (0.090 g, 56%); $\nu_{max.}$ ($CHCl_3$) 2 240 (C≡N), and 1 733 (C=O); δ_H (400 MHz; $CDCl_3$) 1.31 (3 H, s, -CHC*Me*$_2$CN-), 1.35 (3 H, s, -COCMe$_2$CN), 1.45 (3 H, s, -CHC*Me*$_2$CN-), 1.49 (3 H, s, -COCMe$_2$CN), 2.75 (1 H, td, J 3.0 and 9.7 Hz, -CHCMe$_2$CN-), 2.93 (1 H, dd, J 3.1 and 17.3 Hz, -C*H*$_2$COCMe$_2$CN), 3.07 (1 H, dd, J 10.0 and 17.3 Hz, -C*H*$_2$COCMe$_2$CN), 5.16 (1 H, d, J 17.3 Hz, -CH=C*H*$_2$ *cis*, 5.20 (1 H, d, J 10.5 Hz, -CH=C*H*$_2$ *trans*), and 5.60 (1 H, dt, J 9.9 and 16.9 Hz -C*H*=CH$_2$); δ_C (100.6 MHz; $CDCl_3$) 23.4 (-CHCMe$_2$CN-), 24.1 (-CHC*Me*$_2$CN-), 25.2

(-CHC*Me*$_2$CN-), 29.6 (-CHC*Me*$_2$CN-), 34.9 (-CO*C*Me$_2$CN), 39.8 (-*C*H$_2$COCMe$_2$CN), 44.0 (-COC*Me*$_2$CN), 46.8 (-COC*Me*$_2$CN), 120.6 (-CH=*C*H$_2$), 121.3 (-CHCMe$_2$*C*N-), 123.6 (-COCMe$_2$*C*N), 134.3 (-*C*H=CH$_2$), and 201.2 (C=O); *m/z* (EI) 219 (MH†, 12%), 150 (M†-CMe$_2$CN, 100), and 68 (CMe$_2$CN, 43).

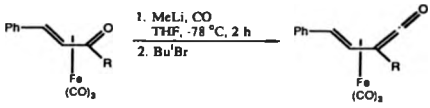
PART II - CYCLOADDITIONS AND ANNULATIONS OF TRANSITION METAL COMPLEXES

II.1 INTRODUCTION

Background - Reactivity of (vinylketene)tricarbonyliron(0) complexes

The study of the reactivity of (η^4-vinylketene)tricarbonyliron(0) complexes has been relatively neglected until recently, mainly due to the difficulty of preparing these species as stable complexes in high yields.

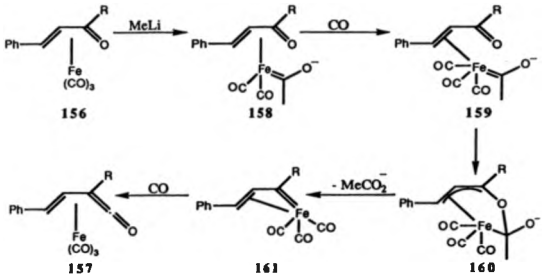
A facile and efficient route for the preparation of 2,4-substituted (η^4-vinylketene)Fe(CO)$_3$ complexes (157) from the corresponding (and readily available) (η^4-vinylketone)Fe(CO)$_3$ complexes (156) has, however, recently been reported by Thomas and co-workers.[43]



156 R= Me, ^{n}Bu, ^{t}Bu, Ph 157

The reaction is thought to involve attack of methyllithium on a metal carbonyl ligand of (156) to form the metal acyl/carbene anion (158). Carbonylation of (158) gives the anionic complex (159) which undergoes a metathesis-type reaction between its iron-carbon and carbon-oxygen double bonds to generate the (vinylcarbene)tricarbonyliron intermediate (161) and a carboxylate ion.[44] Insertion of

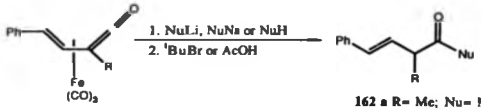
carbon monoxide into the metal carbene bond gives the (η^4-vinylketene)$Fe(CO)_3$ complexes (157).



This new route to (vinylketene)$Fe(CO)_3$ complexes means that for the first time a systematic investigation of the reactivity of these species is feasible.

Some aspects of the reactivity of (vinylketene)tricarbonyliron(0) complexes (157) have already been investigated within the research group at Warwick[41] and these are outlined below.

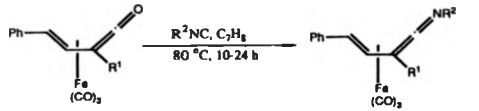
I) A range of sulphur, carbon, oxygen and nitrogen nucleophiles attack at C-1 to yield the β,γ-unsaturated carbonyl products (162 a-e).[42]



157 a R= Me
b R= ^{t}Bu

162 a R= Me; Nu= Me
b R= Me; Nu= CMe_2CO_2
c R= ^{t}Bu, Nu= $NHCH_2Ph$
d R= ^{t}Bu; Nu= OMe
e R= ^{t}Bu; Nu= S^{t}Bu

2) Heating (vinylketene)tricarbonyliron(0) complexes with isonitriles at 80 °C yields (vinylketenimine)tricarbonyliron(0) complexes (163).[82]

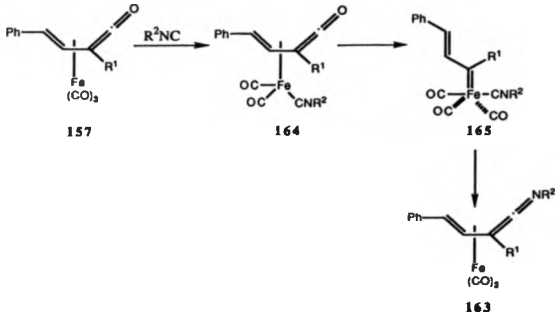


157 R^1= ^{t}Bu, Me
R^2= ^{t}Bu, cyclohexyl, 2,6-dimethylphenyl, CH(Me)Ph, CH(Me)^{t}Bu

163

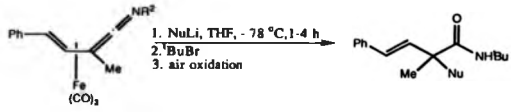
The reaction is believed to proceed *via* a (vinylketene)dicarbonylisonitrileiron(0) complex (164) (isolated for R^1=Me, R^2=^{t}Bu R^1=Me, R^2=cyclohexyl and R^1=R^2=^{t}Bu) which rearranges into a carbene tricarbonylisonitrile complex (165) under

the reaction conditions. Insertion of the isonitrile ligand into the metal carbene bond leads to the vinylketenimine product (163).



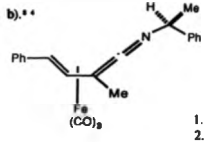
157 164 165 163

Nucleophilic attack of alkylithium reagents on the (vinylketenemine)tricarbonyliron(0) complex (163 a) occurs at C-2 and leads, after oxidative work up, to β,γ-unsaturated amides containing an α quaternary centre.[8,9]



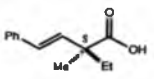
163 a Nu= Me, Et, nBu, tBu 166

This reaction has been used in the preparation of homochiral β,γ-unsaturated carboxylic acids (**168 a, b**) from homochiral (vinylketenimine)$Fe(CO)_3$ complexes (**167 a, b**).[4,6]

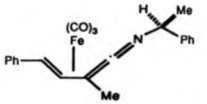


167 a

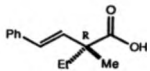
1. EtLi, - 78 °C, 1 h
2. TFA, - 78 °C-r.t., 16 h
3. Jones' reagent



168 a e.e.= 92%

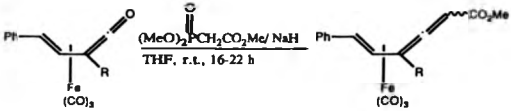


167 b



168 b e.e.= 96%

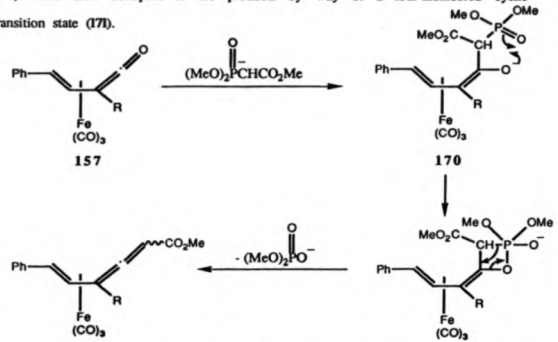
3) Reaction of (vinylketene)tricarbonyliron(0) complexes (**157 a, b**) with trimethylphosphonoacetate in the presence of sodium hydride leads to the (vinylallene)$Fe(CO)_3$ complexes (**169 a, b**) in good yields.[4,6]



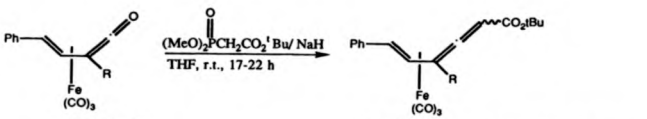
157 a R= Me
b R= ^{t}Bu

169 a R= Me (72%; diastereoisomeric ratio 70:30)
b R= ^{t}Bu (67%; diastereoisomeric ratio 76:24)

A possible mechanism for the Wittig-type reaction involved is initiated by nucleophilic attack of the phosphonate anion at C-1 to form the betaine complex (170). This then collapses to the products by way of a four-membered cyclic transition state (171).



Better stereoselectivity is obtained when the (vinylketene)$Fe(CO)_3$ complexes (**157 a, b**) react with *t*-butyl diethylphosphonoacetate under similar conditions. This gives the allenes (**172 a, b**) with diastereoisomeric ratios of 98:2 and 86:14, respectively.



157 a R= Me
b R= ^{t}Bu

172 a R= Me (70%; diastereoisomeric ratio 98:2
b R= ^{t}Bu (40%; diastereoisomeric ratio 86:14

Aims

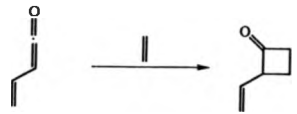
The reactivity of (vinylketene)tricarbonyliron(0) complexes towards unsaturated functional groups such as C=C, C=N, C≡C, and C≡N has not yet been investigated. The research described in this part of the thesis is directed towards determining whether or not (vinylketene)tricarbonyliron(0) complexes will react with unsaturated linkages. The investigations are stimulated by two important areas of chemistry which are described in the remaining part of this Introduction. These are a) the reported reactions of "free" (*i.e.* uncomplexed) vinylketenes with alkenes, dienes and alkynes and b) transition-metal mediated reactions which are postulated to occur *via* transition-metal complexes of vinylketenes.

II.1.1 **Reactivity of "free" vinylketenes towards alkenes, dienes, and alkynes**

"Free" vinyl ketenes are highly unstable organic molecules which are generated *in situ* by either HCl elimination from unsaturated acid chlorides or electrocyclic opening of cyclobutenones.

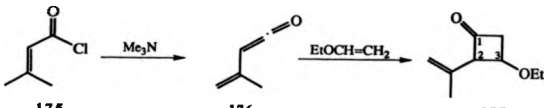
Reactions of vinylketenes with alkenes

Alkenes and vinylketenes react together *via* a [2+2] cycloaddition process to give 2-vinylcyclobutanones (**174**). These are valuable intermediates in the synthesis of five-, six-, and eight-membered mono- as well as bi- and polycyclic systems.[44-98]



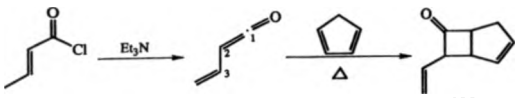
173 **174**

For example, reaction of 3,3-dimethylacryloyl chloride (**175**) with trimethylamine in the presence of ethyl vinyl ether has been reported to give 3-ethoxy-2-isopropenyl-cyclobutanone (**177**), presumably *via* cycloaddition to the ketene intermediate (**176**).[81]



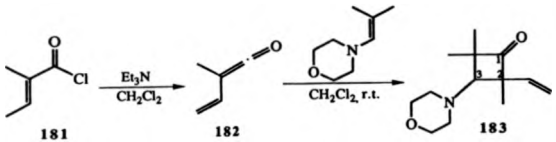
175 **176** **177**

Similarly, bicyclo[3.2.0]heptane systems have been prepared from reaction of vinylketenes with cyclopentadiene, as exemplified by the synthesis of the ethylidenecyclobutanone (180) from *trans*-2-butenoyl chloride (178) and triethylamine.[8]



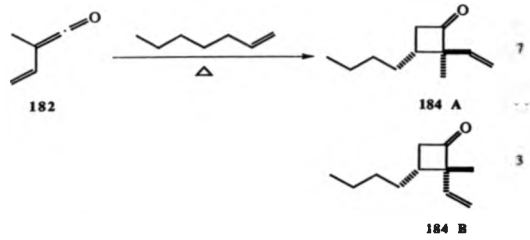
178 179 180

Addition of vinylketenes to enamines provides a method for the preparation of 3-amino-2-vinylcyclobutanones.[8] For example, reaction of 2,3-dimethylacryloyl chloride (181) with 2-methyl-1-morpholinopropene in the presence of triethylamine gives the cyclobutanone (183).



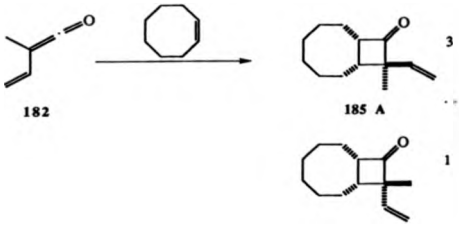
181 182 183

Studies on [2+2] cycloaddition reactions of vinylketenes to simple, non-activated olefins showed good regioselectivity but rather poor stereoselectivity.[8] For example, reaction of methylvinylketene (182), generated *in situ* from the acid chloride (181), with 1-heptene gives the [2+2] cycloadducts (184 A) and (184 B) in a 7:3 ratio (40% yield).



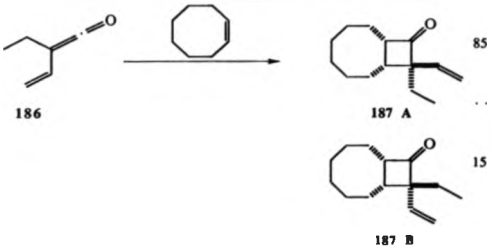
182 184 A 184 B

Similarly, addition of methylvinylketene (182) to (*Z*)-cyclooctene afforded a 3:1 mixture of *cis*-fused cycloadducts (185 A) and (185 B) (60%).



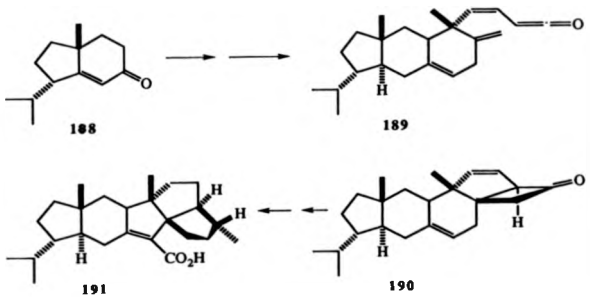
182 185 A 185 B

When (*Z*)-cyclooctene is reacted with ethylvinylketene (186) a 85:15 ratio of isomers (187 A) and (187 B) is obtained (52%), which has been attributed to the slightly larger effective bulk of the ethyl group in (186) than of the methyl group in (182).



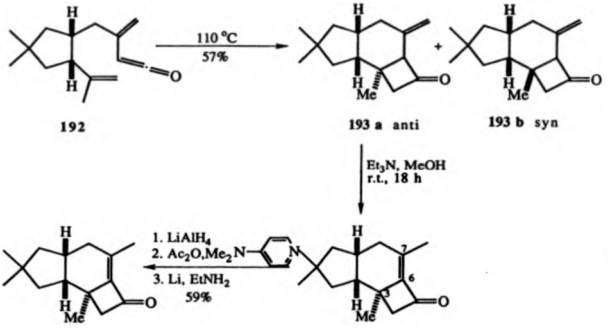
186 187 A 187 B

Intramolecular vinylketene/alkene cycloadditions have been used in major synthetic endeavours. For example ,the conversion of (189) to (190) constitutes the key step in the synthesis of (±)-retigeranic acid (191) from hydrindenone (188).[5,6]



188 189 190 191

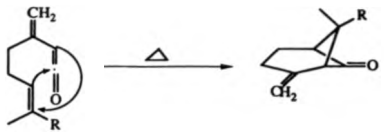
Moderate diastereoselectivity was observed in the intramolecular vinylketene/alkene addition which transforms vinylketene (192) into vinylcyclobutanone (193). This was a crucial step in a preparation of the sesquiterpene (±)-6-protoilludene (195).[64] The 1:3 mixture of isomers (193 a) and (193 b) obtained from the cycloaddition was treated with excess NEt_3 in methanol and the desired 3α-isomer (194a) was separated by flash chromatography. Reduction with $LiAlH_4$ followed by acetylation of the resulting allylic alcohol and hydrogenolysis gave (±)-6-protoilludene (195).



192 193 a anti 193 b syn

195 194 a

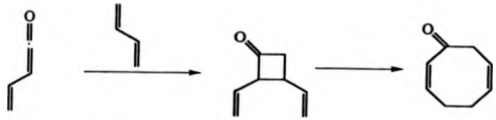
The regiochemistry of the intramolecular cycloaddition has been found to depend on the substitution pattern of the alkene.[67] When the terminal carbon of the alkene is highly substituted, bond formation occurs exclusively between the carbonyl carbon and the internal end of the double bond. This regiospecificity has been used in the preparation of the bicyclo[3.1.1]heptan-6-ones (197) from the vinylketenes (196), providing a valuable method for the synthesis of a selection of terpenes.[68]



196 R= Me, $(CH_2)_2CH{=}CMe_2$ 197

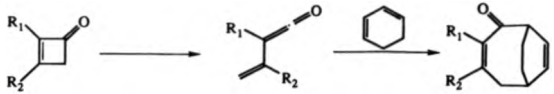
Reactions of vinylketenes with dienes

Reaction of vinylketenes with conjugated dienes results in an overall [4+4] annulation reaction and constitutes an interesting approach to eight-membered carbocycles. The reaction proceeds *via* a [2+2] cycloaddition to give a 2,3-divinylcyclobutanone (198) which then undergoes a [3,3] sigmatropic rearrangement to give (199).



173 198 199

For example, a series of substituted vinylketenes (201), generated by electrocyclic opening of the corresponding cyclobutenones (200), has been reacted with 1,3-cyclohexadiene.[11] The [4+4] cycloadducts (202) obtained are potentially useful intermediates in the synthesis of functionalized cyclooctanes.



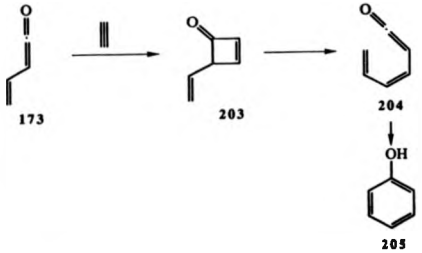
200 a R_1= H; R_2= Me
b R_1= H; R_2= ^tBu
c R_1= R_2= Me

201

202

Reactions of vinylketenes with alkynes

Vinylketenes react with alkynes to give phenols. The process is thought to involve a [2+2] cycloaddition to give the cyclobutenone intermediate (203) which then undergoes a 4-electron electrocyclic cleavage to give the dienylketene (204). Electrocyclic closure of (204) followed by tautomerization affords the phenol ring (205).



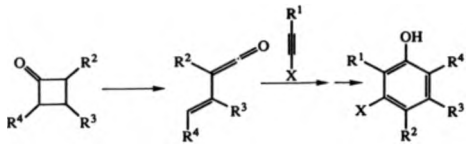
173

203

204

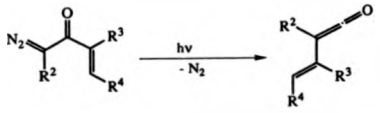
205

The reaction described has been used in the preparation of a series of substituted phenols starting from the cyclobutenones (206). Electrocyclic opening of (206) presumably yielded the vinylketenes (207), which were intercepted with heterosubstituted acetylenes, affording the highly substituted phenols (208) with good regiocontrol.[100]



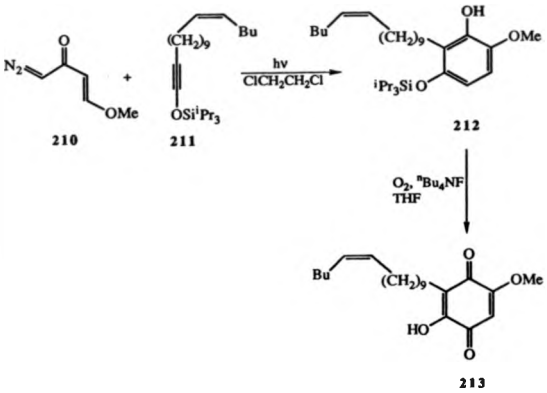
206 207 208

A "second-generation" version of this annulation strategy involves the preparation of the vinylketene intermediates (207) *via* the photochemical Wolff rearrangement of unsaturated α-diazoketones (209).[101]



209 207

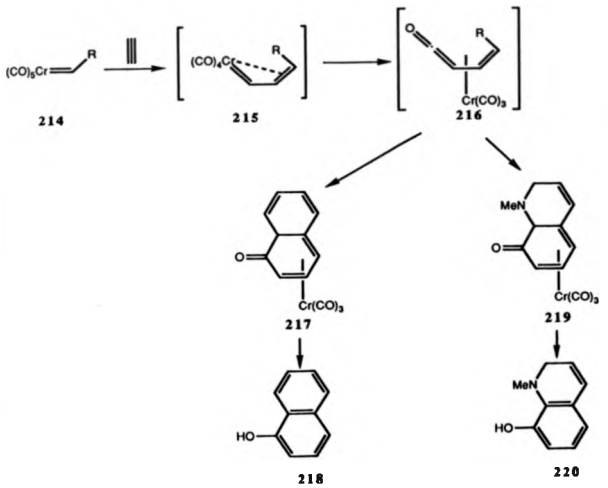
A wide range of readily available aryl and heteroaryl diazoketones have been found to undergo aromatic annulation, providing an efficient route to substituted naphthalenes, benzofurans, benzothiophenes, indoles and carbazoles.[102] Among the acetylene derivatives tested, siloxyacetylenes have proven to be particularly effective ketenophile components for annulation. For example, irradiation of the diazoketone (210) in the presence of the siloxyacetylene (211) gives the phenol (212) and this has been used as a pivotal step in the total synthesis of maesanin (213), a host defense stimulant.[103]



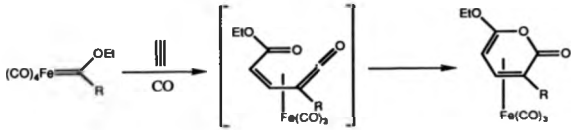
210 211 212 213

II.1.2 Reactions in which vinylketene complexes are postulated as reaction intermediates

Transition-metal vinylketene complexes have been proposed as intermediates in reactions leading to a variety of organic products.[104-106] For example, the formation of naphthols[107-109] and indole derivatives[110] from the reaction of chromium pentacarbonyl carbene complexes (214) with alkynes has been accounted for by the mechanism shown below which invokes vinylketene complexes (216) as intermediates.



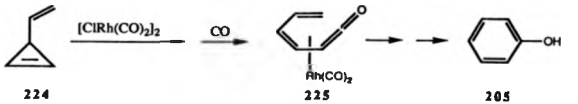
Readily available (ethoxyalkylidene)tetracarbonyliron(0) complexes (221) were reacted with alkynes under an atmosphere of carbon monoxide to afford 6-ethoxy-α-pyrones.[111] The reaction mechanism is believed to involve a (vinylketene)Fe(CO)$_3$ complex (222), which cyclizes to give the pyrone complexes (223).



221 222 223

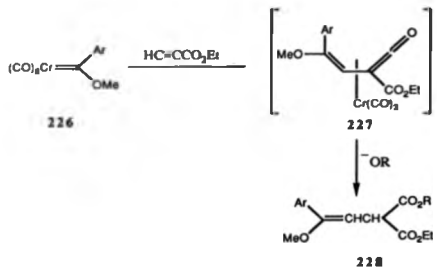
R= Ph, ^{n}Bu, ^{t}Bu

Vinylketene complexes of the type (225) have been postulated as key intermediates in metal-catalyzed carbonylation of vinylcyclopropenes (224) to give phenols.[112]



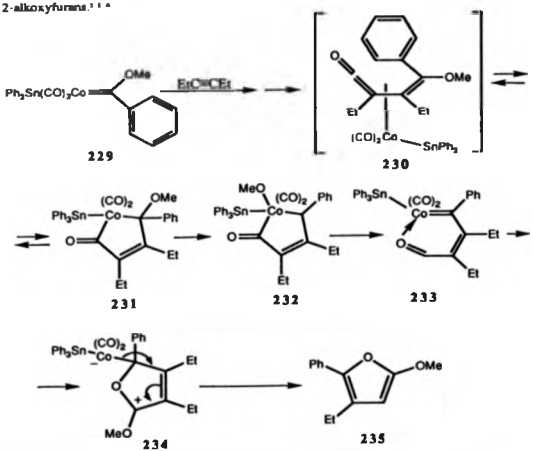
224 225 205

Indirect evidence for the participation of vinylketene complexes in some reactions can be obtained by trapping with alcohols or alkoxides. This principle has been used in the preparation of aryl vinyl ethers (228) by reaction of arylmethoxychromium-carbene complexes (226) with ethyl propiolate followed by nucleophilic attack by alkoxide at the ketene carbon of the intermediate (227).[113]



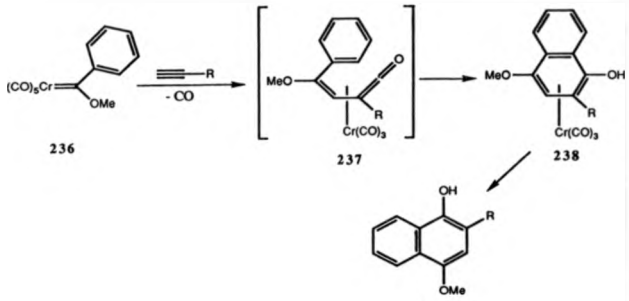
226 227 228

In one type of reaction a coordinated vinylketene intermediate has been isolated. Thus it proved possible to isolate the vinylketene complex (230) from reaction of the (methoxyalkylidene)(triphenylstannyl)tricarbonylcobalt complex (229) with diethylacetylene. The overall process constitutes an efficient route to the preparation of 2-alkoxyfurans.[114]

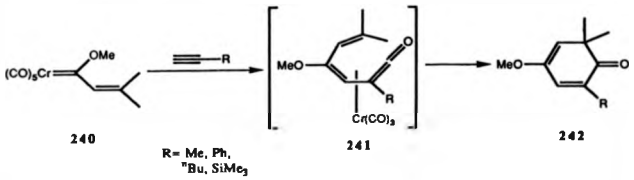


229 230 231 232 233 234 235

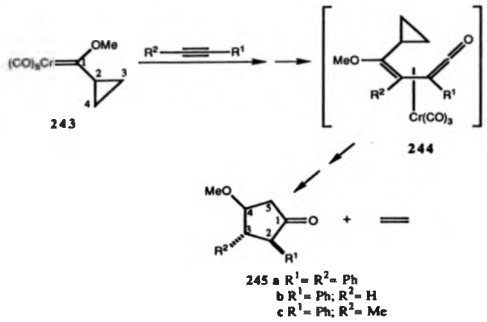
The question of the regioselectivity obtained with unsymmetrical acetylenes is of fundamental concern for synthetic utility. The reaction of (methoxyphenylcarbene) pentacarbonyl chromium (236) with aliphatic terminal alkynes has been reported to yield regiospecifically 2-alkylnaphthol compounds (239).[116]



Similarly, reaction of α,β-unsaturated carbene complexes such as (240) with terminal alkynes results in regioselective cyclohexadienone formation. The alkyl substituent becomes adjacent to the carbonyl group derived from carbon monoxide to give the 2-substituted product (242).[116]



The same regioselectivity is observed when the cyclopropylcarbenechromium complex (243) is reacted with alkynes to give cyclopentanones (245).[117] Carbons 4 and 5 in (245) come from the carbene complex (C-1 and C-2 in (243)) and the alkyne is incorporated into the 2,3-positions. The carbonyl carbon arises from a CO ligand of the carbene complex (243), which implies that C-3 and C-4 of (243) are lost as a two carbon fragment. Thus, this reaction provides a direct, regio- and stereoselective approach to five-membered ring systems.

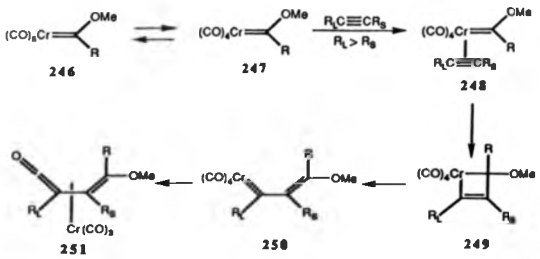


243

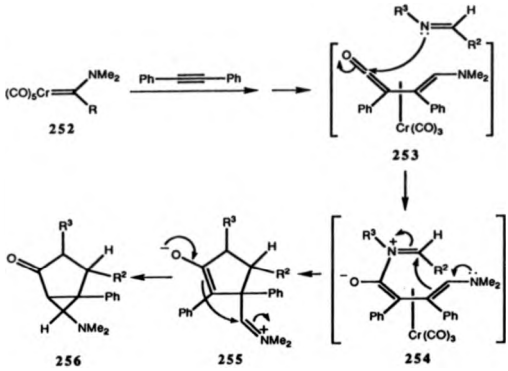
244

245 a $R^1 = R^2 = Ph$
b $R^1 = Ph$; $R^2 = H$
c $R^1 = Ph$; $R^2 = Me$

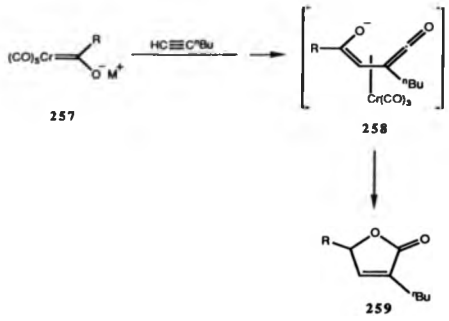
The observed regioselectivity has been explained in terms of the preferred conformation of the acetylene complex (248) which yields the chromacyclobutene (249) and the vinylcarbene complex intermediate (250).[118]



Chromium aminocarbene complexes such as (252) are also thought to form unstable ketene complexes when reacted with non-terminal alkynes. Reaction of the enaminoketene intermediate (253) with imines is postulated to involve regioselective attack of the nucleophilic nitrogen at the electrophilic ketene carbonyl carbon and provides a useful entry to bicyclo[3.1.0]lactams (256).[110]



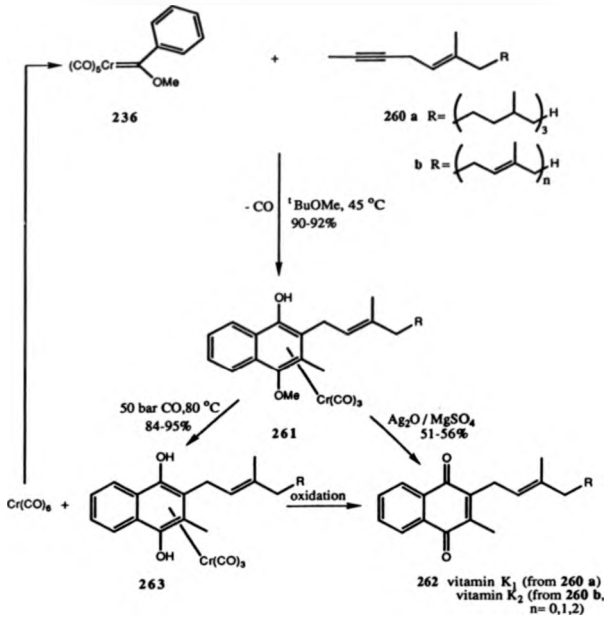
Anionic (1-oxidoalkylidene)pentacarbonylchromium complexes (257) also react regioselectively with hexyne.[110] The vinylketene complex (258) is proposed as an intermediate *en route* to the isolated 2-furanone product (259).



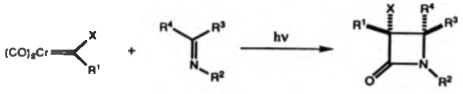
257 258 259

Vinylketene complexes have been postulated and/or isolated as intermediates in a series of reactions used in natural product synthesis. Most examples use readily available transition metal carbene complexes as starting materials. Reaction of these complexes with alkynes gives vinylketene intermediates which can undergo cycloaddition to form the hydroquinone skeleton. Alternatively vinylketene complexes are reacted with imines to give β-lactams.[211]

The remarkable selectivity observed in the reaction of carbene complexes with alkynes was first applied in the preparation of the hydroquinone ring present in vitamins of the K1 and K2 series.[210] The synthesis starts with the methoxy(phenyl)carbene complex (236) and the readily-obtainable enynes (260). Heating at 45 °C in ^{t}butylmethylether gives the tricarbonyl(dihydrovitamin K)chromium complexes (261). Direct oxidation with silver oxide or, in a more efficient process, decomplexation under CO followed by oxidation, gives vitamin K (262) (biologically active *E* isomer only) in good yields.



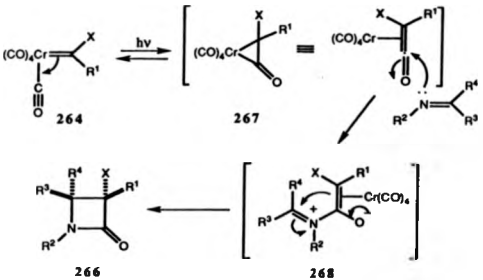
An important reaction involving ketene complexes is the photolysis of alkoxy- and aminocarbene complexes of chromium in the presence of imines to produce β-lactams.[1 2 3]



264 265 266

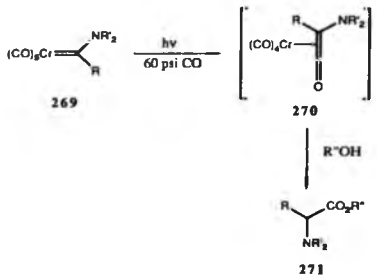
R^1, R^2, R^3, R^4 = Me, Ph; X = OMe, NR_2

The reaction is believed to involve nucleophilic attack of the imine nitrogen onto a photolytically generated, metal-coordinated ketene (267) to give a tetracarbonylchromium intermediate (268) which undergoes cyclization to yield the β-lactams (266).[1,2,4]



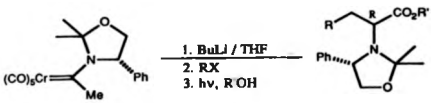
264 267 266 268

Photolysis of chromium aminocarbene complexes (269) in methanol or ^{t}butyl alcohol solvent produces α-aminoesters (271) in good to excellent yields via nucleophilic attack on the photogenerated ketene complex (270).[144]



269 270 271

This efficient approach to α-amino acid synthesis has given encouraging results starting from the optically active (S)-aminocarbene complex (272). Base-assisted alkylation of the methyl group followed by photolysis in methanol produced the alanine derivatives (273 a, b) with high diastereoselectivity.



272

273 a R= $PhCH_2$, R^1= ^{t}Bu
42% yield, > 93% d.e.
b R=$^t BuO_2CCH_2$, R^1= Me
52% yield, > 93% d.e.

The above summary of this rapidly growing and complex area of transition-metal chemistry illustrates that vinylketene complexes are frequently postulated as important intermediates, mostly on the basis of indirect evidence. The mechanisms advanced include steps in which (a) isolated double bonds, (b) double bonds present in aromatic substituents such as aryl or pyrrole groups, and (c) carbon-oxygen double bonds each undergo intramolecular cyclisation reactions with postulated intermediate vinylketene complexes. Furthermore it has been suggested that an intermediate ketene complex reacts with amines to give β-lactams.

II.2 RESULTS AND DISCUSSION

Although the organic chemistry of ketenes is fairly well documented,[1 0 6, 1 0 7] the chemistry of their organometallic complexes has only recently started to be systematically investigated.[1 0 8]

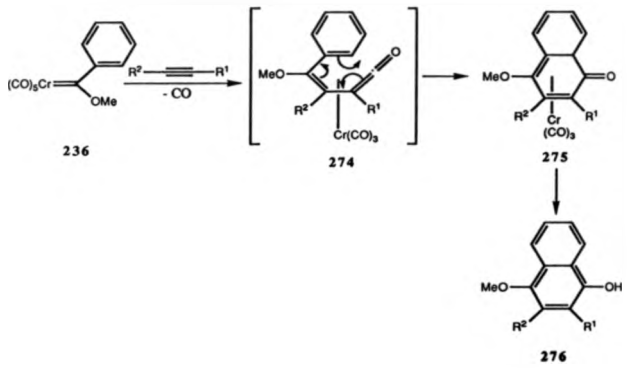
Vinylketenes and vinylketene complexes have been proposed as intermediates in several reactions of synthetic interest (sections II.1.1 and II.1.2). Thus, the synthesis of stable vinylketene complexes and studies of their reactivity should facilitate the establishment of the role of vinylketene complexes in many transition-metal centred reactions.

Stable tricarbonyliron(0) vinylketene complexes have been recently prepared from readily-available (vinylketone)tricarbonyliron(0) complexes.[2 0] This section describes the application of this general preparative method to the synthesis of new vinylketene complexes designed to undergo intra- and intermolecular cycloaddition reactions with C, C and C, N multiple bonds, and the results of these reactions.

II.2.1 Intramolecular cyclisation reactions of (vinylketene)$Fe(CO)_3$ complexes

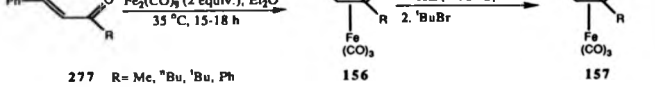
Cycloaddition to aromatic C=C bonds

One of the most important applications of transition-metals in organic synthesis is the preparation of naphthols (276) from chromium carbene complexes (236). This is proposed to proceed *via* a metal-coordinated vinylketene intermediate (274) which undergoes electrocyclic 1,6 ring-closure involving the phenyl substituent to give the cyclohexadienone complex (275).[1 0 4]



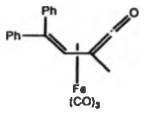
236 274 275 276

Stable (vinylketene)tricarbonyliron(0) complexes (157), analogous to the postulated intermediate (274) can be conveniently prepared by heating the vinylketones (277) with nonacarbonyldi-iron to give the tricarbonyliron(0) complexes (156), followed by treatment of complexes (156) with methyllithium under an atmosphere of carbon monoxide.[*]



277 R= Me, ^{n}Bu, ^{t}Bu, Ph 156 157

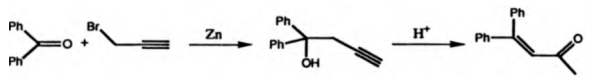
The similarity between complexes (157) and (274) suggested that it would be interesting to probe the reactivity of (4-phenylvinylketene)$Fe(CO)_3$ complexes towards electrocyclic 1,6-ring closure to form naphthols. Thus, the 4,4-diphenylvinylketene complex (278) was chosen as the first target molecule.



278

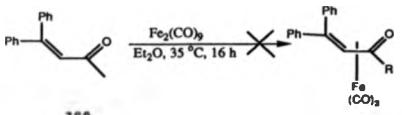
The preparation of this molecule was attempted starting from the α,β-unsaturated ketone (280) according to the methodology described for the synthesis of (157).

The 4,4-diphenyl-3-buten-2-one (280) was prepared by acidification of 1,1-diphenyl-but-3-yn-1-ol (279), obtained from reaction of benzophenone with propargyl bromide in the presence of zinc (49% overall yield).[188] The i.r. and ^{1}H n.m.r. spectral data for both intermediate (279) and final product (280) showed good agreement with literature data.[188]



279 280

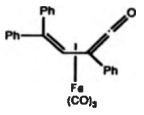
Reaction of the vinylketone (280) with two equivalents of nonacarbonyldi-iron, according to the procedure published for the preparation of complexes (156),[69] led to a complicated mixture of products containing unreacted ketone (280) as the main component. None of the expected vinylketone tricarbonyliron(0) complex (281) was isolable from this mixture, making the preparation of the vinylketene complex (278) impracticable by this route.



280 **281**

One of the minor products isolated from heating 1-methyl-4,4-diphenylvinylketone (280) with nonacarbonyldi-iron suggested that the methyl group carbon on C-1 had been attacked (the three-proton singlet at δ 1.70 in (280) is replaced by two doublets at δ 2.18 and δ 2.27 (J 7 Hz) in the minor product). In order to prevent the formation of this type of product, a substituent lacking α-hydrogen atoms (e.g. Ph) may be required at C-1.

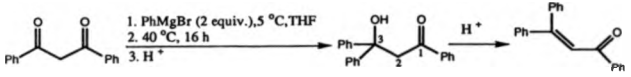
The preparation of (2,4,4-triphenylvinylketene)$Fe(CO)_4$ (282) was therefore attempted from the triphenyl-substituted vinylketone (284).



282

Dibenzoylmethane was reacted with 2 equivalents of phenylmagnesium bromide in THF for 16 h (5-60 °C). The yellow reaction mixture obtained was poured into ice water and acidified with acetic acid (20% w/v). The mixture was extracted with diethyl ether, dried ($MgSO_4$) and the solvent evaporated to yield the 1,1,3-triphenyl-1-hydroxy-propan-3-one (283), identified on the basis of its ^1H n.m.r. spectrum. (The spectrum contained a two-proton singlet at δ 3.97 assigned to the

2-H protons, a one-proton singlet at δ 5.50 attributed to OH, and a fifteen-proton multiplet at δ 7.70-8.10 corresponding to the three phenyl groups). Dehydration by treatment with conc. sulphuric acid gave the 1,3,3-triphenyl vinylketone (284) in good yield (91% overall)

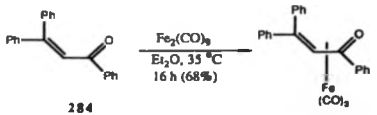


283 284

The 220 MHz ^{1}H n.m.r. spectrum of (284) showed a one-proton singlet at δ 5.62, attributed to the C-2 vinylic proton and a fifteen-proton multiplet at δ 7.18-8.05, due to the protons of the three phenyl groups. The i.r. spectrum of (284) in chloroform showed an intense band at 1 668 cm^{-1} attributed to the ketone carbonyl stretching mode.

The synthesis of the (1,3,3-triphenvinylketone)$Fe(CO)_4$ complex (285) was attempted following the general procedure reported for the preparation of the (α,β-unsaturated ketone)tricarbonyliron(0) complexes (156).[88]

The vinylketone (284) was heated with nonacarbonyldi-iron (2 equiv.) in dry diethyl ether at 35 °C, under nitrogen, for 16h. The dark-brown reaction mixture was cooled to room temperature and filtered through alumina to remove iron residues. The orange filtrate was evaporated under vacuum and the orange residue obtained was purified by column chromatography on silica gel to yield a rather unstable orange oil identified as the new (vinylketone)tricarbonyliron(0) complex (285) on the basis of i.r., ^{1}H n.m.r. and mass spectroscopy.

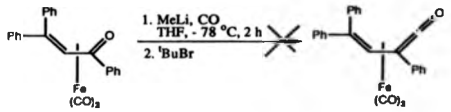


284 **285**

The i.r. spectrum of (**285**) in hexane showed three sharp peaks at 2 067, 2 010 and 1 994 cm^{-1} assignable to the three iron-bound carbonyl groups. The 220 MHz ^1H n.m.r. spectrum of (**285**) in $CDCl_3$ showed a sixteen-proton multiplet at δ 7.13-8.16, including the C-2 proton as well as the fifteen phenyl protons.

The FAB mass spectrum (NBA matrix) of (**285**) showed peaks at *m/z* 340 (34%), 285 (100%) and 263 (73%) attributed to the ionic species M^+-3CO, MH^+-$Fe(CO)_3$ and M^+-3CO-Ph, respectively.

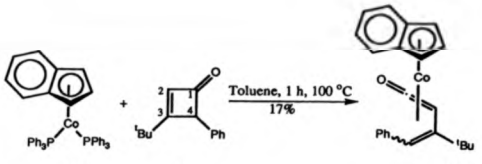
Preparation of the vinylketene complex (**282**) was attempted by treatment of the vinylketone (**285**) with methyllithium under an atmosphere of carbon monoxide, according to the procedure used for the preparation of complexes (**157**).[69] This method proved to be unsuccessful and the only identified product of the reaction was the decomplexed vinylketone (**284**). Failure to convert the vinylketone complex (**285**) to the vinylketene complex (**282**) is almost certainly a reflection of the instability of (**285**).



285 **282**

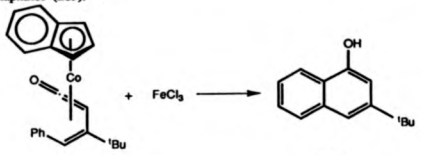
Thus, disappointingly, it was not possible to prepare the (vinylketene)$Fe(CO)_3$ complexes (**278**) and (**282**) from the corresponding enones (**280**) and (**284**) *via* the

synthetic method described,[188] and so the study of their reactivity towards intramolecular cycloaddition could not be undertaken. However, after completion of this research, preparation of the (*E*-2-^{t}butyl-3-phenylvinylketene)(η^5-indenyl)cobalt (I) complex (288) by reaction of (bistriphenylphosphine)(η^4-indenyl)Co (286) with 3-^{t}butyl-4-phenylcyclobutenone (287) was reported.[189]



286 287 288 E /Z > 98:2

As anticipated by the reactivity studies proposed for the (vinylketene)Fe(CO)$_4$ complexes (278) and (282), it was shown that oxidation of the (vinylketene)Co(η^5-C_9H_7) complex (288) in the presence of $FeCl_3$ gave the ^{t}butyl substituted naphthol (289).[189]

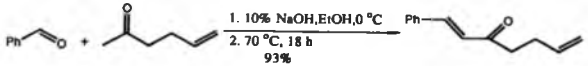


288 289

Cycloaddition to aliphatic C=C bonds

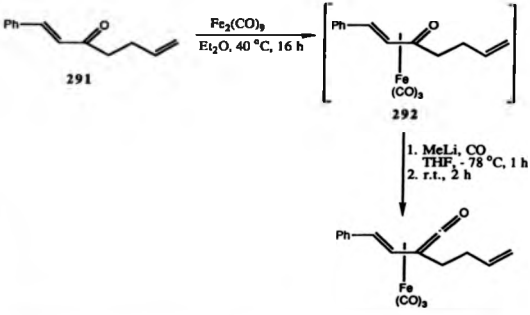
The preparation of (1-phenyl-1,6-heptadien-3-ketene)tricarbonyliron(0) (290) was undertaken with the aim of studying the reactivity of vinylketene complexes towards intramolecular cycloaddition to aliphatic C=C bonds.

The 1-phenyl-1,6-heptadiene-3-one (291) was prepared from a mixture of 5-hexen-2-one and benzaldehyde in a 3:1 solution of ethanol:water. A 10% w/v aqueous sodium hydroxide solution was added to this mixture at low temperature (0 °C and the reaction mixture was then heated at 70 °C for 18 h. Extraction of the resulting mixture with dichloromethane led to the isolation of product (291) as a yellow oil. The i.r., ^{1}H n.m.r. and mass spectra of this yellow oil were found to be in good agreement with the literature data available for compound (291).[118]



291

Reaction of the enone (291) with nonacarbonyldi-iron in diethyl ether under nitrogen[119] led to the isolation, in low yield, of an unstable tricarbonyliron(0) complex, assumed to have structure (292) (i.r. data only), and starting material (291). In order to avoid isolation of complex (292), the crude product obtained from the reaction of vinylketone (291) with $Fe_2(CO)_9$ was dissolved in dry tetrahydrofuran and reacted with 1.1 equivalents of methyllithium at -78 °C under a carbon monoxide atmosphere.[119] The new (vinylketene)tricarbonyliron(0) complex (290) was isolated as a stable orange solid (m.p. 64-66 °C), and identified by i.r., ^{1}H n.m.r., ^{13}C n.m.r. and mass spectroscopy.



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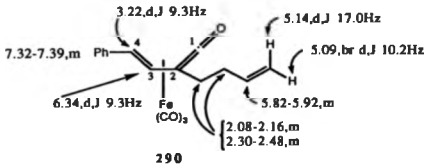
290

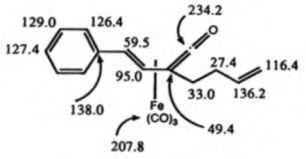
The i.r. spectrum of (290) in hexane showed intense bands at 2 061, 2 003 and 1 995 cm^{-1}, attributed to iron-bound C≡O group stretching, and a less intense band at 1 786 cm^{-1} attributed to the ketene C=O stretching. The 400 MHz ^1H n.m.r. spectrum of (290) showed the chemical shift values and coupling constants indicated below.



290

The alkyl protons of the C-2 side chain appear as one-proton and three-proton multiplets at δ 2.08-2.16 and δ 2.30-2.48, respectively. The C-3 and C-4 vinylic protons give one-proton doublets (*J* 9.3 Hz) at δ 6.34 and δ 3.22, whilst the side-chain vinylic protons appear as two one-proton doublets at δ 5.09 (*J* 10.2 Hz, *trans*) and δ 5.14 (*J* 17.0 Hz, *cis*) (terminal protons) and a one-proton multiplet at δ 5.82-5.92 (internal vinylic proton).

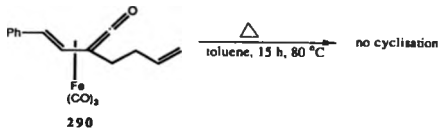
The ^{13}C n.m.r. assignment for the vinylketene complex (290) is indicated in the diagram below. The chemical shifts of the (4-phenylvinylketene)-frame correspond closely with those found in the (η^4-vinylketene)iron(0) complexes (157).[44]



290

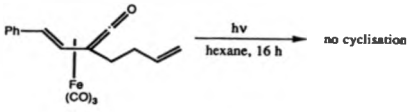
The FAB mass spectrum of (290) shows peaks at *m/z* 339 (8%), attributed to the protonated molecular ion MH^+, and at 283 (11%) due to loss of the C-2 side chain from the molecular ion M^+. The most intense peak, at *m/z* 226 (100%), corresponds to M^+-$(CH_2)_2CH{=}CH_2$-2CO-H, and loss of two more CO groups gives a peak at *m/z* 191 (7%).

The reactivity of (1-phenyl-1,6-heptadien-3-ketene)tricarbonyliron(0) (290) towards intramolecular cycloaddition was investigated under several reaction conditions. The complex was dissolved in toluene, heated under nitrogen and the reaction was monitored by i.r. spectroscopy. After 15 h at 80 °C the reaction mixture was evaporated and analysed. Its ^1H n.m.r. spectrum showed that unreacted vinylketene complex (290) was present as the major component of a complex mixture of products.



290

In a second attempt at cyclisation, (1-phenyl-1,6-heptadien-3-ketene)$Fe(CO)_3$ (290) was dissolved in hexane and irradiated with a 100 watt lamp for 16h. Once again, starting vinylketene was recovered, together with some unidentifiable decomposition products.



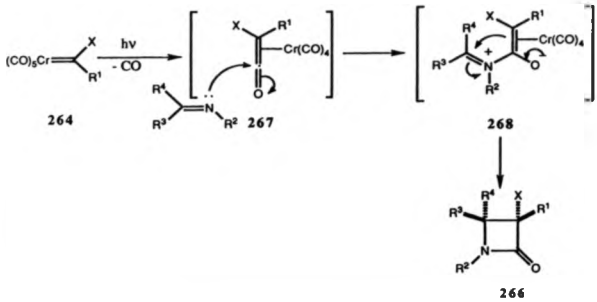
290

Finally, the reaction was attempted by heating a chloroform solution of (290) in the presence of trimethylamine N-oxide. In this case no starting material was recovered but spectroscopic analysis of the oil obtained showed it to be a complicated mixture of products.

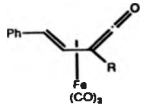
In conclusion, cycloaddition between the alkene and ketene units in complex (290) could not be achieved cleanly.

II.2.2 Intermolecular cyclisation reactions of (vinylketene)$Fe(CO)_3$ complexes

A most synthetically interesting reaction postulated to involve a metal-stabilized ketene (267) is the formation of β-lactams (266) by photolysis of chromium carbene complexes (264) in the presence of imines.[121] The reaction is believed to occur *via* nucleophilic attack of the imine onto the ketene carbonyl carbon atom to give the intermediate (268) which undergoes ring-closure to produce the β-lactams (266).[122]

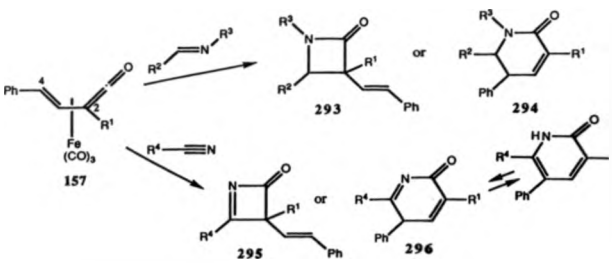


The postulated reactivity of chromium ketene complexes towards imines outlined above suggests the study of the reactivity of other metal-stabilised ketene species with imines. Thus, the (vinylketene)tricarbonyliron(0) complexes (157 a, b) were synthesised in order to investigate their reactivity towards nucleophilic attack/cyclisation in the presence of C=N and C≡N bonds.

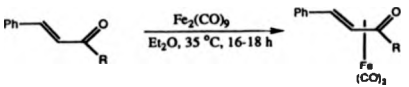


157 a R= Me
b R= ^{t}Bu

Reaction of the vinylketene complexes (157) with imines or nitriles may lead to either 4- or 6-membered rings depending on whether ring-closure occurs at C-2 or C-4 of the vinylketene complex. Thus, at least in principle, a range of nitrogen-containing cyclic products (293)-(296) is available *via* this route.



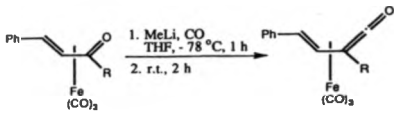
(Vinylketene)tricarbonyliron(0) complexes (**157** a, b) were prepared from the corresponding vinylketones (**277** a, b) in two steps, according to a literature procedure.[4,8] Thus the vinylketones (**277** a) and (**277** b) were reacted with 2 equiv. of nonacarbonyldi-iron(0) in dry diethyl ether at 35 °C for 18 h and 16 h, respectively. Filtering the reaction mixture through alumina followed by column chromatography purification yielded the (vinylketone)$Fe(CO)_3$ complexes (**156** a, b) in good yields.



277 a R= Me
b R= ^{t}Bu

156 a R= Me (73%)
b R= ^{t}Bu (75%)

The vinylketone complexes (**156** a, b) were converted into the vinylketene complexes (**157** a, b) by adding 1.1 equiv. of methyllithium to a solution of (**156**) in THF, at -78 °C, under carbon monoxide. The reaction mixture was then allowed to warm up to room temperature and was stirred for 2 h. Filtering through alumina followed by purification by column chromatography on silica gel yielded the (vinylketene)$Fe(CO)_3$ complexes (**157** a, b) as yellow crystalline solids.



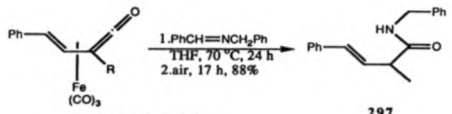
156

157 a R= Me (51%)
b R= ^{t}Bu (84%)

The i.r., ^{1}H n.m.r., MS and m.p. obtained for complexes (156 a, b) and (157 a, b) showed good agreement with the literature data.[44]

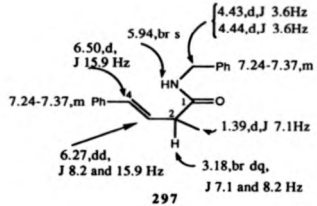
The (vinylketene)Fe(CO)$_4$ complexes (157) were then reacted with an imine, in an attempt to reproduce the conversion of the postulated chromium ketene intermediate (267) to β-lactams (page 119).

To a solution of (1-methyl-3-phenylvinylketene)Fe(CO)$_4$ (157 a) in THF under nitrogen at 0 °C, a solution of *N*-benzylidenebenzylamine (prepared from benzaldehyde and benzylamine in dichloromethane)[111] in THF was added dropwise. The orange reaction mixture obtained was allowed to warm to room temperature and then stirred at 70 °C for 24 h. The dark reaction mixture obtained was filtered through alumina and evaporation of the solvent gave a dark orange oil. Since the characterisation of this oil proved to be difficult due to its instability, it was dissolved in diethyl ether and stirred in the presence of air for 17 h. The 'rusty' reaction mixture was filtered through alumina to remove iron residues and the orange solution obtained was evaporated under vacuum to give an orange oil. Purification by column chromatography on silica gel yielded *N*-benzyl-2-methyl-4-phenyl-3-butenamide (297), identified on the basis of ^{1}H n.m.r., ^{13}C n.m.r. and mass spectroscopy.



157 a R= Me (51%) **297**

The 400 MHz ^{1}H n.m.r. data obtained for (297) in $CDCl_3$ is indicated in the diagram below.

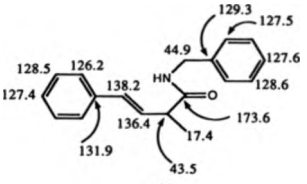


297

The methyl group α to the carbonyl group appears as a three-proton doublet (J 7.1 Hz) at δ 1.39 and is coupled to the adjacent proton 2-H, which gives a broad superimposed doublet of quartets (J 7.2 and 8.2 Hz). The protons 1'-H give two distinct doublets at δ 4.43 and δ 4.44 (J 3.6 Hz) due to coupling to the NH proton, which appears as a very broad singlet at δ 5.94, and to restricted rotation about the carbon-nitrogen bond of the amide. The vinylic proton 3-H gives a

one-proton doublet of doublets at δ 6.27 (J 8.2 and 15.9 Hz) and 4-H shows a one-proton doublet at δ 6.50 (J 15.9 Hz). A ten-proton multiplet at δ 7.24-7.37 accounts for the two phenyl groups.

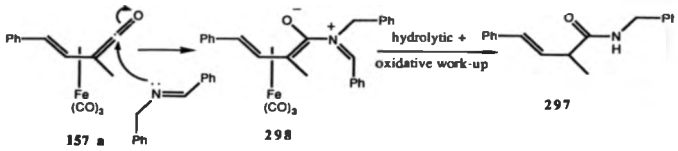
The ^{13}C n.m.r. spectrum of (297) is indicated in the diagram below.



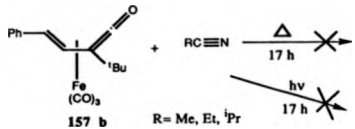
297

The EI mass spectrum of (297) showed a molecular ion M⁺ peak at *m/z* 265 (10%). A peak at *m/z* 131 (100%) was assigned to M⁺-CONHCH$_2$Ph and a 80% intensity peak at *m/z* 91 was attributed to the CH$_2$Ph fragment.

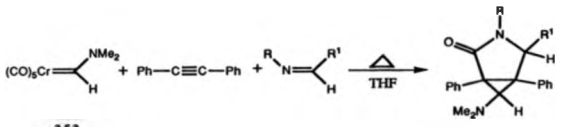
Thus the reaction of vinylketene complex (157 a) with *N*-benzylidenebenzylamine appears to have proceeded by nucleophilic attack of the imine onto the ketene to give intermediate (298) which is analogous to intermediate (268) postulated in the chromium ketene chemistry. Cyclisation of intermediate (298) to give either a 4- or 6-membered nitrogen heterocycle, however, did not occur under the reaction conditions used, and the subsequent air oxidation and hydrolysis led to hydrolytic cleavage of the carbon-nitrogen double bond to give the isolated amide product (297).



The (1-^{t}butyl-3-phenylvinylketene)tricarbonyliron(0) complex (**157 b**) was reacted with nitriles under thermal and photochemical conditions. In a typical procedure, the ketene complex was dissolved in the nitrile (excess) and refluxed for 17 h under N_2. Alternatively, the solution of ketene complex in nitrile under N_2 was irradiated for 17 h with two 100 watt lamps. The reaction mixture obtained was filtered through alumina and the solvent evaporated to yield a dark orange-brown oil. Analysis of the oils obtained from reaction of the (vinylketene)$Fe(CO)_3$ complex (**157 b**) with acetonitrile, propionitrile or butyronitrile showed that no appreciable reaction had occurred, and that the starting material (**157 b**) was the major component of the isolated oils.



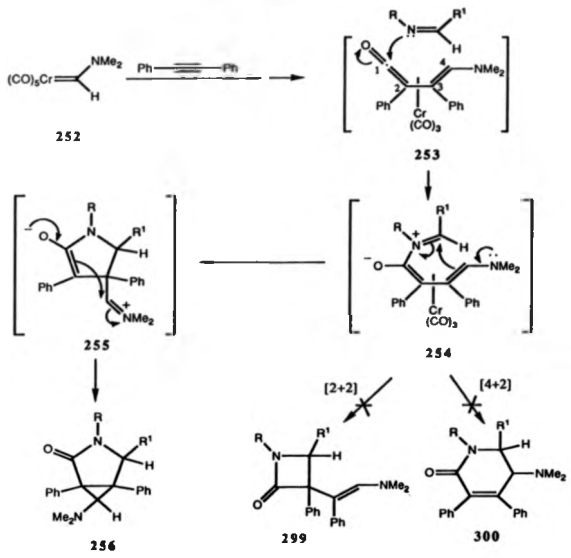
Thermal reactions of chromium aminocarbene complexes with alkynes were recently postulated to proceed *via* addition of imines to a (vinylketene) tricarbonylchromium intermediate.[119] Hence heating a mixture of ((dimethylamino)methylene)pentacarbonylchromium complex (252), diphenylacetylene and an imine in THF at 80 °C for 1-2 days produced bicyclo[3.1.0] lactams (256) in reasonable yields.



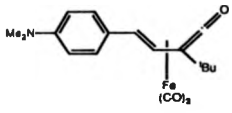
252

256 a R= ^{t}Bu; R^1= H (75%)
b R= Me; R^1= Ph (77%)
c R= $PhCH_2$; R^1= OMe (49%)

The mechanism proposed for this reaction involves the formation of a chromium-coordinated enaminoketene complex (253) which undergoes nucleophilic attack at the ketene carbon by the imine to give the addition intermediate (254). A two-step cyclisation leads to the bicyclic lactam products (256) rather than the expected [2 + 2] or [4 + 2] cycloaddition products (299) and (300).

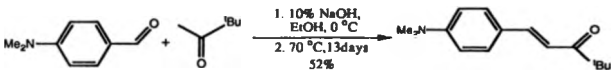


The requirement of an electron-donating group at the ketene C-4 position to promote cyclisation of the intermediate (254) suggested the preparation of the ((dimethylaminobenzyl)vinylketene)tricarbonyliron(0) complex (301).



The first step in the synthesis of (301) was the preparation of (dimethylaminophenyl)vinyl ketone (302).

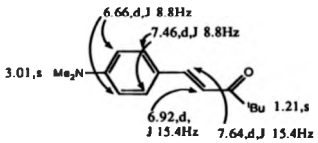
Commercially available ^{t}butylmethyl ketone was condensed with 4-dimethylaminobenzaldehyde in a 2:1 ethanol:water solution by adding a 10% w/v aqueous sodium hydroxide solution at low temperature (0 °C). The reaction mixture was allowed to warm to room temperature and then heated at 70 °C for 13 days. Extraction with dichloromethane and column chromatography on silica gel led to the isolation of a yellow crystalline solid (m.p. 74-75 °C) identified as the new compound 1-^{t}butyl-3-(para-*N,N*-dimethylaminophenyl)vinylketone (302) on the basis of i.r., ^{1}H n.m.r., ^{13}C n.m.r., mass spectroscopy and microanalysis.



302

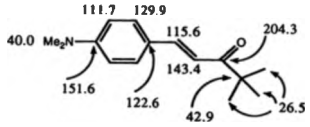
The i.r. spectrum of the vinylketone (302) in hexane showed a sharp, medium intensity peak at 1 668 cm^{-1}, attributed to C=O stretching and an intense peak at 1 579 cm^{-1} identified as a C=C absorption band.

The 400 MHz ^{1}H n.m.r. data obtained for (302) is indicated below.



302

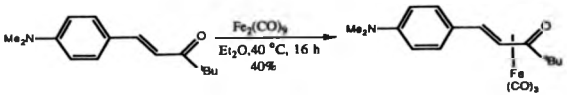
The proton decoupled 100 MHz ^{13}C n.m.r. data for (302) are given in diagram II.2.2.-4.



302

The high resolution EI mass spectrum obtained for the vinylketone (302) showed a molecular ion peak M† at m/z 231 (15%) and a 100% intensity peak at *m/z* 174 attributed to the loss of the ^{t}Bu group from M†.

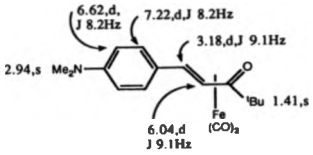
Reaction of the vinylketone (302) with nonacarbonyldi-iron(0) (2 equiv.) according to a previously described procedure (*e.g.* see page 134),[88] yielded the new complex (1-^{t}butyl-3-(para-*N,N*-dimethylaminobenzyl)vinylketone)Fe(CO)$_3$ (303) as a red crystalline solid, identified by i.r., ^{1}H n.m.r., ^{13}C n.m.r., mass spectroscopy and microanalysis.



302 **303**

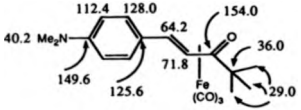
The i.r. spectrum of (303) in hexane includes three sharp and very intense peaks at 2 059, 1 999 and 1 980 cm^{-1} due to the iron-bound C≡O groups.

The 400 MHz ^{1}H n.m.r. spectrum of (303) in $CDCl_3$ showed the chemical shifts and coupling constants indicated below.



303

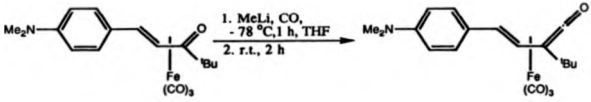
The ^{13}C n.m.r. spectrum of (303) contained resonances at δ 154.0, 71.8 and 64.2 assigned to C-1, C-2 and C-3, respectively, in addition to resonances due to the dimethylaminobenzyl and *t*-butyl groups (diagram II.2.2-6).



303

The mass spectrum of (303) contained a MH^+ peak at *m/z* 372 (10%) and a fragmentation pattern corresponding to successive loss of three CO units (*m/z* 344 (24%), 289 (19%) and 259 (9%)). The maximum intensity peak (100%) observed at *m/z* 232 was attributed to the loss of the $Fe(CO)_3$ unit (MH^+-3CO-Fe).

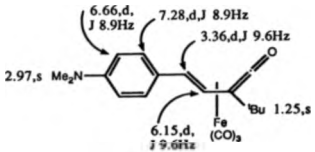
With the aim of preparing the vinylketene complex (301), (1-^{t}butyl-3-(*para*-*N*,*N*-dimethylaminophenyl)vinylketone)$Fe(CO)_3$ (303) was reacted with methyllithium (1.1 equiv.) at -78 °C under a carbon monoxide atmosphere.[19] Filtration through alumina followed by column chromatography yielded the new (vinylketene)tricarbonyliron(0) complex (301) as a yellow crystalline solid (m.p. 107-111 °C, decomp.) identified on the basis of i.r., ^{1}H n.m.r., ^{13}C n.m.r., mass spectroscopy and microanalysis.



303 301

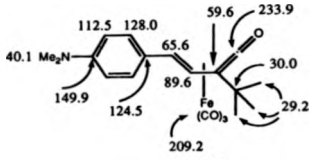
The i.r. spectrum of (301) showed three intense bands at 2 054, 1 994 and 1 987 cm^{-1}, attributed to the iron-bound C≡O groups, and a less intense band at 1 784 cm^{-1}, due to the ketene C=O stretching.

The 400 MHz ^{1}H n.m.r. spectrum of (301) showed the chemical shifts and coupling constants indicated below.



301

The ^{13}C n.m.r. data obtained for the (vinylketene)$Fe(CO)_3$ complex (301) is indicated in the diagram below.

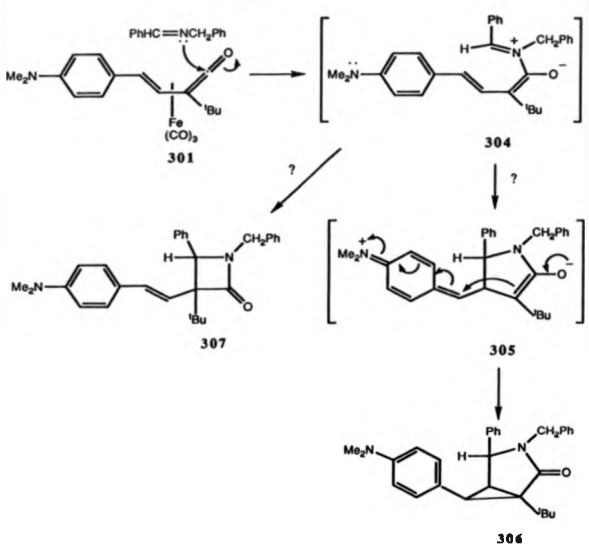


301

The chemical shift values obtained for the (vinylketene)$Fe(CO)_4$ skeleton are in good agreement with ^{13}C n.m.r. data published for other analogous complexes.[44]

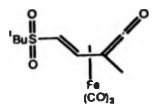
The FAB mass spectrum of (301) shows peaks at *m/z* 384 (29%), attributed to the molecular ion MH^+, and at *m/z* 356 (23%), 327 (15%), 299 (100%) and 271 (73%), due to successive loss of four CO groups. A medium intensity peak at *m/z* 215 (38%) was assigned to the M^+-4CO-Fe fragment.

The reactivity of (1-*t*butyl-3-(*para*-*N*,*N*-dimethylaminophenyl)vinylketene) tricarbonyliron(0) (301) towards nucleophilic addition of imines was investigated as follows. The ketene complex (301) was dissolved in dry THF, under nitrogen and the resulting yellow solution was cooled to 0 °C. A solution of *N*-benzylidenebenzylamine in dry THF was added dropwise and the reaction mixture was allowed to warm to room temperature. The reaction mixture was then stirred at 70 °C for 24 h. The dark orange reaction mixture obtained was cooled to room temperature. Its i.r. spectrum showed intense bands at 2 053, 1 993 and 1 986 cm^{-1} and a less intense band at 1 784 cm^{-1}, all attributed to unreacted vinylketene complex (301). Medium intensity bands at 1 751 and 1 718 cm^{-1} could be attributed to carbonyl groups in the expected four- and five- ring lactams as (307) and (306), but no further evidence for the presence of these compounds was obtained. The starting material (301) was recovered from the reaction mixture in 72% yield.



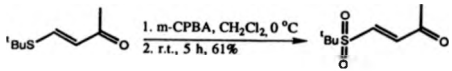
As attempts to cyclise relatively electron-rich vinylketene complexes with the electron-rich *N*-benzylidenebenzylamine had been unsuccessful, the reactivity between an electron-poor vinylketene complex and *N*-benzylidenebenzylamine was investigated.

Due to the availability of suitable precursors, (1-methyl-3-^{t}butylsulphonylvinylketone)tricarbonyliron(0) (308) was chosen as the target molecule for reaction with the imine.



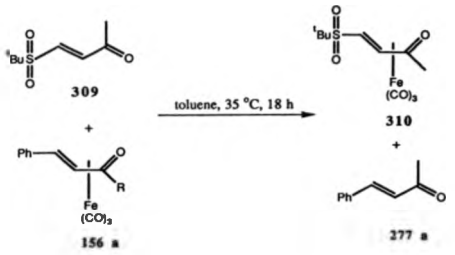
308

The first step in the preparation of (308) is the synthesis of 1-methyl-3-^{t}butylsulphonyl vinyl ketone (309).[111] Readily available 1-methyl-3-^{t}butylthiovinylketone was dissolved in dichloromethane and the yellow solution obtained was cooled to 0 °C. A solution of *m*-chloroperbenzoic acid in dichloromethane was added dropwise and the reaction mixture was allowed to warm to room temperature. Stirring was continued until no trace of the starting thiovinylketone was detected by t.l.c. (10% EtOAc-petroleum ether 40-60 °C). Extraction with aqueous sodium hydroxide solution and evaporation of the solvent yielded the sulphonyl vinyl ketone (309) which was identified by comparison of its ^{1}H n.m.r. with literature data.[111]



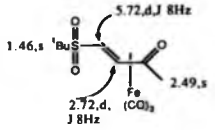
309

Complexation of the vinylketone (309) was achieved by reacting it with (1-methyl-3-phenylvinylketone)Fe(CO)$_3$ (156 a), according to a procedure developed by Thomas and co-workers.[8] A solution of the ^{t}butylsulphonyl vinylketone (309) in toluene was heated with the tricarbonyliron(0) complex (156 a) under N_2 at 35 °C for 18 h. Filtration through alumina followed by column chromatography on silica gel (40% EtOAc-petroleum ether 40-60 °C) led to the isolation of a yellow crystalline solid identified as the (sulphonylvinyl ketone)Fe(CO)$_3$ complex (310) by i.r., ^{1}H n.m.r. and mass spectroscopy.



The i.r. spectrum of (310) in hexane showed three intense bands at 2 082, 2 028 and 2 010 cm^{-1}, attributed to the three C≡O ligands. A weaker band at 1 308 cm^{-1} was attributed to the sulphonyl S=O stretching.

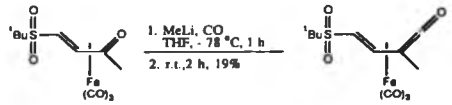
The 220 MHz ^1H n.m.r. data obtained for (310) is indicated in the diagram below.



310

The FAB mass spectrum of (310) included peaks at *m/z* 331 (MH^+, 100%), 307 (MH^+-CO+4H, 64), 275 (MH^+-2CO, 92), and 247 (MH^+-3CO, 95).

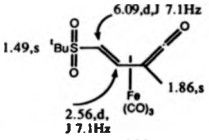
Preparation of the vinylketene complex (308) from the vinylketone complex (310) was then undertaken by reacting it with methyllithium under a carbon monoxide as previously described.[49] Purification by column chromatography (3% EtOAc petroleum ether 40-60 °C) followed by crystallisation from *n*-pentane gave a yellow crystalline solid in 19% yield which was identified as the new complex (1-methyl-3-^{t}butylsulphonylvinylketone) tricarbonyliron(0) (308) on the basis of its i.r., ^{1}H n.m.r., ^{13}C n.m.r., mass spectra and microanalysis.



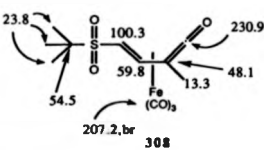
310 308

The i.r. spectrum of (308) in hexane showed intense peaks at 2 087, 2 041 and 2 013 cm^{-1}, attributed to the iron-bound C≡O groups, and the medium intensity band at 1 797 cm^{-1}, assigned to the ketene C=O stretching.

The 400 MHz ^{1}H n.m.r. and ^{13}C n.m.r. data for (308) are indicated in the diagrams below.



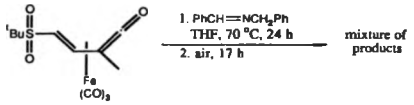
308



308

CO units (100, 83 and 57%, respectively). A medium intensity peak at *m/z* 174 (51%) was attributed to M^+-4CO-Fe.

The *t*-butylsulphonylvinylketene (308) was then heated with *N*-benzylidenebenzylamine in THF at 70 °C for 24 h. The orange reaction mixture obtained was cooled to room temperature and the solvent evaporated to give a dark orange oil. I.r. and ^{1}H n.m.r. analysis of this oil showed it to be a mixture of products, including unreacted imine and (^{t}butylsulphonylvinylketene)Fe(CO)$_3$ (308) as major components.



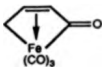
308

Thus the results obtained on reacting both electron-rich and electron-poor vinylketene complexes (301) and (308) with *N*-benzylidenebenzylamine, suggest that neither react cleanly with imines.

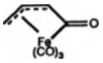
II.3 CONCLUSIONS

The results described in the previous section reveal that (vinylketene)tricarbonyliron(0) complexes do not react readily with electron rich multiple bonds to give cycloaddition products. This contrasts strongly with the reactivity reported for 'free' vinylketenes (see section II.1.1). The difference of reactivity is probably a result of the importance of structures **B** and **C** together with structure **A** in the description of a $Fe(CO)_3$ - bound vinylketene (**311**).[44]

311 A



311 B



311 C

II.4 EXPERIMENTAL

All reactions involving metal complexes were performed using standard vacuum line techniques[7,8] under an atmosphere of nitrogen.

Tetrahydrofuran was distilled under nitrogen from sodium benzophenone ketyl. *Diethyl ether* and *toluene* were dried over sodium wire. *Methyllithium* (1.4 M in diethyl ether) was purchased from Aldrich and its concentration checked before each utilization by titration against diphenylacetic acid.[9] *Propargyl bromide* was used as a 80 wt. % solution in toluene (Aldrich). *Benzophenone* (99%), *dibenzoylmethane*, *5-hexen-2-one*, *benzaldehyde*, *phenylmagnesium bromide* (3.0 M in Et_2O), *tert-butyl methyl ketone*, *4-dimethylaminobenzaldehyde* (98%), and *benzylamine* were also obtained from Aldrich. *m-Chloroperbenzoic acid* was purchased from Aldrich (50-60%) and purified by washing with 8 ml 0.2 M NaH_2PO_4 - 42 ml 0.2M Na_2HPO_4 aqueous solution (3 x 50 ml/ 10 g *m*-CPBA) in diethyl ether. All other chemicals were used as obtained from commercial sources. *Nonacarbonyldi-iron* was prepared by a published procedure.[10]

Column chromatography was performed on SiO_2 (Merck, Art. 9385, 40-63 μm)[11] and thin layer chromatography (t.l.c.) was performed on glass based SiO_2 plates (20 cm x 20 cm x 1 mm; Merck, Art. 7747, 60 PF_{254}). The Al_2O_3 used for filtrations was deactivated with H_2O (Brockmann grade 4, Al_2O_3 : H_2O = 10:1 w/w).

Melting points were determined on a Gallenkamp MF B 595 010 M melting point apparatus and are uncorrected. The melting points of complexes were measured in nitrogen filled capillaries, and subsequent examination by t.l.c. was used to establish whether decomposition had taken place.

Elemental analysis were performed by MEDAC Limited.

I.r. spectra were recorded on Perkin Elmer 580B and 1720X instruments.

^{1}H n.m.r. spectra were recorded on Perkin Elmer R34 (220 MHz) and Bruker WH400 (400 MHz) spectrometers. ^{13}C n.m.r. spectra were recorded on a Bruker WH400 instrument operating at 100.6 MHz. All chemical shifts are quoted in ppm relative to a TMS standard.

Mass spectra were recorded on a Kratos MS 80 instrument using FAB (*m*-nitrobenzyl alcohol as matrix[18]), CI (NH_3 as reactant gas), and EI (70 eV) techniques.

II.4.1 Synthesis of vinylketones (280), (284), (290), (302) and (309)

1-Methyl-3,3-diphenylvinylketone (280).[188]

A mixture of propargyl bromide (19.0 g, 128 mmol) and benzophenone (14.9 g, 82 mmol) was dissolved in dry THF (30 ml). This solution was added dropwise to a stirred suspension of zinc (7.0 g, 107 mmol, washed with 5% HCl, water, MeOH, dry THF) in dry THF (30 ml) under nitrogen at 0 °C, to prevent too vigorous of a reaction. After stirring for 0.5 h, the grey solution was poured into ice water (200 ml). A white precipitate formed which was dissolved by adding 20% w/v acetic acid until acidic. The mixture was extracted with diethyl ether, and the extracts were washed with water, 5% w/v $NaHCO_3$, and dried over $MgSO_4$. Removal of the solvent gave 1,1-diphenyl-but-3-yn-1-ol (279) as a yellow oil (12.2 g, 67%); δ_H (220 MHz; CCl_4) 3.04 (2 H, d, J 1 Hz, -CH_2C≡CH), 3.51 (1 H, m, -CH_2C≡C*H*), 4.89 (2 H, d, J 6, -*CH*=C=CH_2), 5.85 (1 H, t, J 7 Hz, -CH=C=C*H*$_2$), and 7.05 - 7.55 (10 H, m, - CH_2CPh_2OH) (lit.[188] δ_H (CCl_4) 1.90 (1 H, t, J 1 Hz, -CH_2C≡C*H*), 3.10 (2 H, d, J 1 Hz, -CH_2C≡CH), and 7.0 -8.0 (10 H, m, CH_2CPh_2OH).

Concentrated sulphuric acid (0.1 ml) was added to a solution of 1,1-diphenyl-but-3-yn-1-ol (279) (2.0 g, 9.0 mmol) in acetic acid (8.1 ml). The dark brown reaction mixture was heated at 70 °C for 40 minutes, poured into ice water (50 ml), and extracted with dichloromethane. The extracts were washed with water, saturated $NaHCO_3$, and dried over $MgSO_4$. Removal of the solvent gave the title vinylketone (280) as a dark orange oil (1.45 g, 49% overall); ν_{max} (neat) 1 694 and 1 663 (C=O, two isomers), 1 592 and 1 575 cm^{-1} (C=C) (lit.[188] ν_{max} (neat) 1 695, 1 670, and 1 590 cm^{-1}); δ_H (220 MHz; CCl_4) 1.70 (3 H, s, Me), 6.44 (1 H, s, -*CH*=CPh$_2$), and 7.10-7.40 (10 H, m, -CH=C*Ph*$_2$) (lit.[188] δ_H (CCl_4) 1.73 (3 H, s, Me), 6.43 (1 H, s, -*CH*=CPh$_2$), and 7.1-7.5 (10 H, m, -CH=C*Ph*$_2$).

1,3,3-Triphenylvinylketone (284).

Dibenzoylmethane (0.715 g, 3.12 mmol) was dissolved in dry THF (4 ml) under nitrogen and cooled to 5 °C. Phenylmagnesium bromide (2.1 ml, 6.24 mmol) was

added dropwise. The reaction mixture became gradually green. The cooling bath was removed and the mixture allowed to warm to room temperature. It was then warmed to 60 °C and stirred at this temperature for 16 h. The yellow reaction mixture obtained was poured into ice water (30 ml). A white precipitate formed which was dissolved by adding 20% w/v acetic acid until acidic. The mixture was extracted with diethyl ether, and the extracts were washed with water, saturated NaCl aqueous solution, and dried over $MgSO_4$. Removal of the solvent yielded 1,1,3-triphenyl-1-hydroxy-propan-3-one (283) as a yellow oil (0.89 g, 94%); δ_H (220 MHz; $CDCl_3$) 3.97 (2 H, s, -CH_2CPh$_2$OH), 5.50 (1 H, s, -CPh$_2$O*H*), and 7.20 - 8.10 (15 H, m, *Ph*COCH$_2$C*Ph*$_2$OH).

Concentrated sulphuric acid (2 ml) was added to a solution of 1,1,3-triphenyl-1-hydroxy-propan-3-one (283) (1.90 g, 6.28 mmol) in acetic acid (50 ml). The dark brown reaction mixture was heated at 80 °C for 1 h, poured into ice water (100 ml), and extracted with dichloromethane. The extracts were washed with water, saturated $NaHCO_3$ aqueous solution, and dried over $MgSO_4$. Removal of the solvent gave the title vinyl ketone (284) as an orange oil (1.74 g, 97%); $\nu_{max.}$ ($CHCl_3$) 1 688 cm^{-1} (C=O); δ_H (220 MHz; $CDCl_3$) 5.62 (1 H, s, -C*H*=CPh$_2$), and 7.18 - 8.05 (15 H, m, *Ph*COCH=C*Ph*$_2$).

(E)-1-Phenyl-1,6-heptadien-3-one (291).

A mixture of 5-hexen-2-one (2.3 ml, 20 mmol), benzaldehyde (2.4 ml, 24 mmol), water (2.7 ml) and ethanol (7.8 ml) was cooled to 0 °C, and a 10% w/v sodium hydroxide aqueous solution (2.0 ml, 5.2 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature and then heated at 70 °C for 18 h. To the reaction mixture water (100 ml) was added and the solution obtained was extracted with dichloromethane (2 x 75 ml). The yellow organic extracts were washed with saturated NaCl aqueous solution and dried ($MgSO_4$), and evaporation of the solvent afforded the title vinylketone (291) as a yellow oil (3.45 g, 93%); $\nu_{max.}$ ($CHCl_3$) 1 686 (C=O), 1 654 (C=C), and 1 609 (C=C); δ_H (220 MHz;

$CDCl_3$) 2.36 - 2.54 (2 H, m, $-CH_2CH_2CH=CH_2$), 2.68 - 2.86 (2 H, m, $-CH_2CH_2CH=CH_2$), 4.92 - 5.20 (2H, m, $-CH=CH_2$), 5.70 - 6.03 (1 H, m, $-CH=CH_2$), 6.78 (1 H, d, J 17 Hz, -CH=CHPh), and 7.20 - 7.70 (6 H, m, -CH=CHPh) (lit.[116] δ_H (270 MHz; $CDCl_3$) 2.39 (2 H, br t, J 7 Hz, $-CH_2CH_2CH=CH_2$), 2.81 (2 H, t, J 7.4 Hz, $-CH_2CH_2CH=CH_2$), 4.72 (1 H, br s, $-CH=CH_2$), 4.76 (1 H, br s, $-CH=CH_2$), 6.76 (1 H, d, J 16 Hz, -CH=CHPh), and 7.3-7.6 (6 H, m, -CH=CHPh)); *m/z* (EI) 186 (M^+, 6.2%), 131 (M^+-$CH_2CH_2CH=CH_2$, 100), and 103 (M^+-$COCH_2CH_2CH=CH_2$, 26) (lit.[116] *m/z* (EI) 200 (M^+, 5%), 132 (MH^+-$CH_2CH_2CH=CH_2$, 26), 131 (M^+-$CH_2CH=CH_2$, 100), 104 (MH^+-$COCH_2CH_2CH=CH_2$, 20), and 103 (M^+-$COCH_2CH_2CH=CH_2$, 82)).

1-[t]Butyl-3-(para-N,N-dimethylaminophenyl)vinylketone (302).

A mixture of *tert*-butyl methyl ketone (2.9 g, 28 mmol), 4-dimethylaminobenzaldehyde (3.4 g, 23 mmol), water (5 ml) and ethanol (11 ml) was cooled to 0 °C, and a 10% w/v sodium hydroxide aqueous solution (28.6 ml, 11 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature and then heated at 70 °C for 13 days. To the reaction mixture water (150 ml) was added and the solution obtained was extracted with dichloromethane (2 x 100 ml). The orange organic extracts were washed with saturated NaCl aqueous solution, dried ($MgSO_4$) and the solvent evaporated to yield a dark orange oil. Column chromatography on SiO_2, 10% EtOAc-30% CH_2Cl_2-60% petroleum ether 40-60 °C gave the title vinylketone (302) as a yellow solid (2.79 g, 52%), m.p. 74-75 °C (hexane) (Found: C, 77.85; H, 9.13; N, 5.98. $C_{15}H_{21}NO$ requires C, 77.88; H, 9.15; N, 6.05%); ν_{max} ($CHCl_3$) 1668 (C=O), 1579 (C=C), and 1525 (C=C); δ_H (400 MHz; $CDCl_3$) 1.21 (9 H, s, [t]Bu), 3.01 (6 H, s, NMe_2), 6.66 (2 H, d, J 8.8 Hz, $-C_6H_4NMe_2$, *meta*), 6.92 (1 H, d, J 15.4 Hz, $-CH=CHC_6H_4NMe_2$), 7.46 (2 H, d, J 8.8 Hz, $-C_6H_4NMe_2$, *ortho*), and 7.64 (1 H, d, J 15.4 Hz, $-CH=CHC_6H_4NMe_2$); δ_C {[1]H} (100.6 MHz; $CDCl_3$) 26.5 ($-CMe_3$), 40.0 (NMe_2), 42.9 ($-CMe_3$), 111.7 ($-C(CH)_4CNMe_2$, *meta*), 115.6 ($-CH=CHC_6H_4NMe_2$), 122.6

(-*C*(CH)$_4$CNMe$_2$), 129.9 (-C(CH)$_4$CNMe$_2$, *orto*), 143.4 (-*CH*-CHC$_6$H$_4$NMe$_2$) 151.6 (-C(CH)$_4$*C*NMe$_2$), and 204.3 (C=O); *m/z* (EI) 231 (M†, 15%), and 174 (M†-CMe$_2$, 100).

1-Methyl-3-^{t}butylsulphonylvinylketone (309).[188]

1-Methyl-3-^{t}butylthiovinylketone (2.0 g, 12.6 mmol) was dissolved in dichloromethane (50 ml) and the yellow solution obtained was cooled to 0 °C. A solution of *m*-chloroperbenzoic acid (5.44 g, 31.5 mmol) in dichloromethane (60 ml) was added dropwise and the reaction mixture was allowed to warm to room temperature. The reaction was monitored by t.l.c. (10% EtOAc-petroleum ether 40-60 °C) and stirring was continued until no trace of the starting thiovinylketone was found (*c.* 5 h). Dichloromethane (150 ml) was added and the yellow mixture was washed successively with 10% sodium hydroxide aqueous solution (3 x 200 ml), water, brine, and then dried ($MgSO_4$). The solvent was evaporated under reduced pressure to yield the sulphonylvinylketone (309) as a yellow solid (1.47 g, 61%); δ_H (220 MHz; $CDCl_3$) 1.41 (9 H, s, Bu^t), 2.42 (3 H, s, Me), and 7.08-7.33 (2 H, m, -*CH*=*CH*COMe) (lit.[189] δ_H (400 MHz; $CDCl_3$) 1.41 (9 H, s, Bu^t), 2.41 (3 H, s, Me), 7.07 (1 H, d, J 15.4 Hz, -CH=C*H*COMe), and 7.22 (1 H, d, J 15.4 Hz, -*CH*=CHCOMe)).

II.4.2 Synthesis of (vinylketone)Fe(CO)$_4$ complexes (156), (285) and (303)

General method[188]

The vinylketone was heated with nonacarbonyldi-iron(0) (2 equiv.) in dry diethyl ether (5 ml/g $Fe_2(CO)_9$) at 35 °C, under N_2, for 16-18 h. The reaction mixture was cooled to room temperature and filtered through alumina to remove iron residues. The solvent was evaporated under vacuum and the dark orange/red oil or

solid obtained was purified by column chromatography to yield the (vinylketone) $Fe(CO)_3$ complexes as yellow/orange crystalline solids.

(1,3,3-Triphenylvinylketone)tricarbonyliron(0) (**215**).

1,3,3-Triphenyl vinyl ketone (**214**) (0.50 g, 1.76 mmol), $Fe_2(CO)_9$ (1.28 g, 3.52 mmol), Et_2O (7.5 ml). Reaction time: 16 h. Chromatography on SiO_2, 5% EtOAc-15% Et_2O-petroleum ether 40-60 °C gave (**215**) as a unstable orange oil (0.51 g, 68%); $\nu_{max.}$ (hexane) 2 067, 2 010, and 1 994 (C≡O), 1 671 cm^{-1} (C=O); δ_H (220 MHz; $CDCl_3$) 7.13-8.16 (16 H, m, *Ph*COC*H*=C*Ph*$_2$); *m/z* (FAB) 340 (M^+-3CO, 34%), 285 (MH^+-$Fe(CO)_3$, 100%), and 263 (M^+-3CO-Ph, 73).

((E)-1-Methyl-3-phenylvinylketone)tricarbonyliron(0) (**156 a**).

1-Methyl-3-phenylvinylketone (**277 a**) (1.0 g, 6.77 mmol), $Fe_2(CO)_9$ (4.95 g, 13.6 mmol), Et_2O (25 ml). Reaction time: 18 h. Chromatography on SiO_2, 10% EtOAc-petroleum ether 40-60 °C gave (**156 a**) as an orange crystalline solid (1.41 g, 73%), m.p. 86-89 °C (decomp.) (lit.[188] m.p. 88-89 °C); $\nu_{max.}$ (cyclohexane) 2 060, 2 000, and 1 985 cm^{-1} (C≡O) (lit.[188] $\nu_{max.}$ (cyclohexane) 2 065, 2 000, and 1 985 cm^{-1} (C≡O)); δ_H (220 MHz; $CDCl_3$) 2.56 (3 H, s, Me), 3.14 (1 H, d, J 10 Hz, -CH=C*H*Ph), 6.13 (1 H, d, J 10 Hz, -C*H*=CHPh), and 7.2 - 7.5 (5 H, m, Ph) (lit.[188] δ_H (60 MHz; $CDCl_3$) 2.50 (3 H, s, Me), 3.10 (1 H, d, J 9 Hz, -CH=C*H*Ph), 6.02 (1 H, d, J 9 Hz, -C*H*=CHPh), and 7.27 (5 H, m, Ph)); *m/z* (FAB) 287 (MH^+, 32%), 259 (MH^+-CO, 28), and 202 (M^+-3CO, 100) (lit.[72] *m/z* (FAB) 287 (MH^+, 38%), 259 (MH^+-CO, 20), 231 (MH^+-2CO, 16), 203 (MH^+-3CO, 45), and 202 (M^+-3CO, 100)).

((E)-1-^{t}Butyl-3-phenylvinylketone)tricarbonyliron(0) (**156 b**).

1-^{t}Butyl-3-phenylvinylketone (**277 b**) (0.75 g, 3.98 mmol), $Fe_2(CO)_9$ (2.90 g, 7.97 mmol), Et_2O (15 ml). Reaction time: 16 h. Chromatography on SiO_2, 3% EtOAc-petroleum ether 40-60 °C gave the title vinylketone (**156 b**) as a red

crystalline solid (0.98 g, 75%), m.p. 86-89 °C (decomp.) (lit.[118] m.p. 86-88 °C); $\nu_{max.}$ (cyclohexane) 2 060, 2 000, and 1 985 cm^{-1} (C≡O) (lit.[118] $\nu_{max.}$ (cyclohexane) 2 080, 2 020, and 1 990 cm^{-1} (C≡O)); δ_H (220 MHz; $CDCl_3$) 1.42 (9 H, s, ^tBu), 3.08 (1 H, d, J 9 Hz, -CH=C*H*Ph), 6.13 (1 H, d, J 9 Hz, -C*H*=CHPh), and 7.20-7.45 (5 H, m, Ph) (lit.[118] δ_H (220 MHz; $CDCl_3$) 1.40 (9 H, s, ^tBu), 3.05 (1 H, d, J 9 Hz, -CH=C*H*Ph), 6.10 (1 H, d, J 9 Hz, -C*H*=CHPh), and 7.20-7.35 (5 H, m, Ph)); *m/z* (FAB) 329 (MH^+, 18%), 301 (MH^+-CO, 13), 272 (M^+-2CO, 23), and 244 (M^+-3CO, 100) (lit.[118] *m/z* 329 (MH, 40%), 301 (MH^+-CO, 21), 273 (MH^+-2CO, 22), and 244 (M^+-3CO, 100)).

(1-^{t}Butyl-3-(para-N,N-dimethylaminophenyl)vinylketone)tricarbonyliron(0) (303).

1-^{t}Butyl-3-(para-N,N-dimethylaminophenyl)vinylketone (302) (0.60 g, 2.59 mmol), $Fe_2(CO)_9$ (1.88 g, 5.19 mmol), Et_2O (9.5 ml). Reaction time: 16 h. Chromatography on SiO_2, 10% EtOAc-30% Et_2O-petroleum ether 40-60 °C, gave the title vinylketone (303) as a red crystalline solid (0.38 g, 40%), m.p. 99-102 °C (decomp.) (Found: C, 58.20; H, 5.65; N, 3.70. $C_{18}H_{21}FeNO_4$ requires C, 58.24; H, 5.70; N, 3.77%); $\nu_{max.}$ (hexane) 2 059, 1 999, and 1 980 (C≡O), 1 611 cm^{-1} (C=O); δ_H (400 MHz; $CDCl_3$) 1.41 (9 H, s, ^tBu), 2.94 (6 H, s, NMe_2), 3.18 (1 H, d, J 9.1 Hz, -CH=C*H*$C_6H_4NMe_2$), 6.04 (1 H, d, J 9.1 Hz, -*CH*=CH$C_6H_4NMe_2$), 6.62 (2 H, d, J 8.3 Hz, -$C_6H_4NMe_2$, *meta*), and 7.22 (2 H, d, J 8.3 Hz, -$C_6H_4NMe_2$, *orto*); δ_C [^{1}H] (100.6 MHz; $CDCl_3$) 29.0 (-*C*Me_3), 36.0 (-*C*Me_3), 40.2 (NMe_2), 64.2 (-CH=*C*H$C_6H_4NMe_2$), 71.8 (-*C*H=CH$C_6H_4NMe_2$), 112.4 (-C(CH)$_4$CNMe$_2$, *meta*), 125.6 (-*C*(CH)$_4$CNMe$_2$), 128.0 (-C(CH)$_4$CNMe$_2$, *orto*), 149.6 (-C(CH)$_4$*C*NMe$_2$), and 154.0 (C=O); *m/z* (FAB) 372 (MH^+, 10%), 344 (MH^+-CO, 24), 289 (MH^+-2CO, 19), 259 (MH^+-3CO, 9), and 232 (MH^+-3CO-Fe, 100).

II.4.3 Synthesis of ((E)-1-methyl-3-^{t}butylsulphonylvinylketone)Fe(CO)$_3$ (310)[188]

1-Methyl-3-^{t}butylsulphonylvinylketone (309) (0.25 g, 1.31 mmol) was dissolved in toluene, under N_2, and to the yellow solution obtained (1-methyl-3-phenylvinyl ketone)Fe(CO)$_3$ (156 a) (0.49 g, 1.71 mmol) was added. The red reaction mixture was heated at 35 ^oC for 18 h. The dark reaction mixture was cooled to room temperature and filtered through alumina to remove iron residues. The solvent was evaporated and column chromatography of the dark orange oil obtained (SiO_2, 40% EtOAc-petroleum ether 40-60 ^oC) yielded the (sulphonylvinylketone)Fe(CO)$_3$ complex (310) as a yellow crystalline solid (0.32 g, 74%); ν_{max} (hexane) 2 082, 2 028, and 2 010 (C=O), 1 308 cm^{-1} (S=O) (lit.[188] ν_{max} (hexane) 2 085, 2 025 and 2 010 cm^{-1} (C=O)); δ_H (220 MHz; $CDCl_3$) 1.46 (9 H, s, ^{t}Bu), 2.49 (3 H, s, Me), 2.72 (1 H, d, J 8 Hz, -CH=C*H*COMe), and 5.72 (1 H, d, J 8 Hz, -C*H*=CHCOMe) (lit.[188] δ_H (220 MHz; $CDCl_3$) 1.46 (9 H, s, ^{t}Bu), 2.50 (3 H, s, Me), 2.72 (1 H, d, J 8 Hz, -CH=C*H*COMe), and 5.71 (1 H, d, J 7 Hz, -C*H*=CHCOMe)); *m/z* (FAB) 331 (MH^+, 100%), 307 (MH^+-CO+4H, 64), 275 (MH^+-2CO, 92), and 247 (MH^+-3CO, 95) (lit.[188] *m/z* (FAB) 331 (MH^+, 2.7%), and 307 (MH^+-CO+4H, 17)).

II.4.4 Synthesis of (vinylketene)Fe(CO)$_3$ complexes

General method[44]

The (vinylketone)Fe(CO)$_3$ complex was dissolved in dry THF, under nitrogen. The nitrogen atmosphere was substituted by carbon monoxide (1.1 atm) and the solution cooled to -78 ^oC. Methyllithium (1.1 equiv.) was added dropwise and the reaction mixture was stirred at -78 ^oC for 1 h. The cooling bath was then removed and the reaction mixture was stirred at room temperature for 2 h. The resultant dark brown mixture was filtered through alumina to remove iron residues and the solvent evaporated under vacuum to give a dark yellow oil. Column chromatography on silica gel yielded the (vinylketene)Fe(CO)$_3$ complexes as yellow crystalline solids.

((E)-1-Phenyl-1,6-heptadien-3-ketene)tricarbonyliron(0) (290).

(1-Phenyl-1,6-heptadien-3-ketone)$Fe(CO)_3$ (292) (0.29 g, 0.89 mmol), MeLi (0.66 ml, 0.98 mmol), THF (8 ml). Chromatography on SiO_2, 10% Et_2O-petroleum ether 40-60 °C, gave (290) (0.121 g, 40%), m.p. 64-66 °C (hexane); ν_{max} (hexane) 2 061, 2 003, and 1 995 (C≡O), and 1 786 cm^{-1} (C=O); δ_H (400 MHz; $CDCl_3$) 2.08-2.16 (1 H, m, $-CH_2CH_2CH=CH_2$), 2.30-2.48 (3 H, m, $-CH_2CH_2CH=CH_2$), 3.22 (1 H, d, J 9.3 Hz, -CH=C*H*Ph), 5.09 (1 H, br d, J 10.2 Hz, $-CH=CH_2$, *trans*), 5.14 (1 H, d, J 17.0 Hz, *cis*), 5.82-5.92 (1 H, m, $-CH=CH_2$), 6.34 (1 H, d, J 9.3 Hz, -C*H*=CHPh), and 7.32-7.39 (5 H, m, Ph); δ_C {^{1}H} (100.6 MHz; $CDCl_3$) 27.4 ($-CH_2CH_2CH=CH_2$), 33.0 ($-CH_2CH_2CH=CH_2$), 49.4 (*C*=C=O), 59.5 (-CH=*C*HPh), 95.0 (-*C*H=CHPh), 116.4 ($-CH=CH_2$), 126.4 (Ph, C-*ortho*), 127.4 (Ph, C-*para*), 129.0 (Ph, C-*meta*), 136.2 ($-CH=CH_2$), 138.0 (Ph, C-*ipso*), 207.8 br (C≡O), and 234.2 (C=*C*=O); *m/z* (FAB) 339 (MH^+, 8%), 283 ($M^+-(CH_2)_2CH=CH_2$, 11), 254 ($M^+-(CH_2)_2CH=CH_2-CO-H$, 15), 226 ($M^+-(CH_2)_2CH=CH_2-2CO-H$, 100), and 191 ($M^+-(CH_2)_2CH=CH_2-4CO-H$, 7).

(E)-1-Methyl-3-phenylvinylketene)tricarbonyliron(0) (157 a).

(1-Methyl-3-phenylvinylketone) $Fe(CO)_3$ (156 a) (0.50 g, 1.75 mmol), MeLi (1.42 ml, 1.92 mmol), THF (18 ml). Chromatography on SiO_2, 10% EtOAc-petroleum ether 40-60 °C gave (157 a) (0.267 g, 51%); ν_{max} (cyclohexane) 2 064, 2 005, and 1 996 (C≡O), 1 793 cm^{-1} (C=O) (lit.[44] ν_{max} (cyclohexane) 2 067, 2 006, and 1 995 (C≡O), 1 791 cm^{-1} (C=O)); δ_H (220 MHz; $CDCl_3$) 1.94 (3 H, s, Me), 3.22 (1 H, d, J 9 Hz, -CH=C*H*Ph), 6.42 (1 H, d, J 9 Hz, -C*H*=CHPh), and 7.3-7.5 (5 H, m, Ph) (lit.[44] δ_H (220 MHz; $CDCl_3$) 1.94 (3 H, s, Me), 3.22 (1 H, d, J 9 Hz, -CH=C*H*Ph), 6.43 (1 H, d, J 9 Hz, -C*H*=CHPh, and 7.31-7.47 (5 H, m, Ph)); *m/z* (FAB) 299 (MH^+, 40%), 270 (M^+-CO, 36), 242 (M^+-2CO, 48), 214 (M^+-3CO, 100), and 184 (M^+-4CO-2H, 56) (lit.[44] *m/z* (FAB) 299 (MH^+, 43%), 270 (M^+-CO, 40), 242 (M^+-2CO, 48), 214 (M^+-3CO, 100), and 186 (M^+-4CO, 49).

((E)-1-^{t}Butyl-3-phenylvinylketene)tricarbonyliron(0) (**157 b**).

(1-^{t}Butyl-3-phenylvinylketone)Fe(CO)$_3$ (**156 b**) (0.240 g, 0.731 mmol), MeLi (0.82 ml, 0.804 mmol), THF (9 ml). Chromatography on SiO_2, 3% EtOAc-petroleum ether 40-60 °C, gave (**157 b**) (0.210 g, 84%), m.p. 109-113 °C (decomp.) (lit.[44] m.p. 127-129 °C); ν_{max} (cyclohexane) 2 059, 1 998, and 1 992 (C≡O), 1 783 cm^{-1} (C=O) (lit.[44] ν_{max} (cyclohexane) 2 065, 2 001, and 1 995 (C≡O), 1 785 cm^{-1} (C=O)); δ_H (220 MHz; $CDCl_3$) 1.28 (9 H, s, Bu), 3.13 (1 H, d, *J* 9 Hz, -CH=C*H*Ph), 6.33 (1 H, d, *J* 9 Hz, -C*H*=CHPh), and 7.28 - 7.47 (5 H, m, Ph) (lit.[44] δ_H (220 MHz; $CDCl_3$) 1.29 (9 H, s, ^{t}Bu), 3.14 (1 H, d, *J* 9 Hz, -CH=C*H*Ph), 6.34 (1 H, d, *J* 9 Hz, -C*H*=CHPh), and 7.31 - 7.48 (5 H, m, Ph)); *m/z* (FAB) 341 (MH^+, 47%), 312 (M^+-CO, 29), 284 (M^+-2CO, 28), 256 (M^+-3CO, 100), and 228 (M^+-4CO, 99) (lit.[44] *m/z* (FAB) 341 (MH^+, 33%), 313 (MH^+-CO, 16), 284 (M^+-2CO, 24), 256 (M^+-3CO, 88), and 228 (M^+-4CO, 100)).

(1-^{t}Butyl-3-(para-N,N-dimethylaminophenyl)vinylketene)tricarbonyliron(0) (**301**).

(1-^{t}Butyl-3-(*para*-*N*,*N*-dimethylaminophenyl)vinylketone)Fe(CO)$_3$ (**303**) (0.200 g, 0.539 mmol), MeLi (0.34 ml, 0.593 mmol), THF (7 ml). Chromatography on SiO_2, 5% CH_2Cl_2-15% Et_2O-petroleum ether 40-60 °C, gave (**301**) (0.130 g, 63%), m.p. 107-111 °C (decomp.) (Found: C, 59.36; H, 5.61; N, 3.60. $C_{19}H_{21}FeNO_4$ requires C, 59.55; H, 5.52; N, 3.65%); ν_{max} (hexane) 2 054, 1 994, and 1 987 (C≡O), 1 784 cm^{-1} (C=O); δ_H (400 MHz; $CDCl_3$) 1.25 (9 H, s, ^{t}Bu), 2.97 (6 H, s, Me), 3.36 (1 H, d, *J* 9.6 Hz, -CH=C*H*C$_6$H$_4$NMe$_2$), 6.15 (1 H, d, *J* 9.6 Hz, -C*H*=CHC$_6$H$_4$NMe$_2$), 6.66 (2 H, d, *J* 8.9 Hz, -C$_6$H$_4$NMe$_2$, *meta*), and 7.28 (2 H, d, *J* 8.9 Hz, -C$_6$*H*$_4$NMe$_2$, *ortho*), δ_C {^{1}H} (100.6 MHz; $CDCl_3$) 29.2 (*C*Me$_3$), 30.0 (C*Me*$_3$), 40.1 (NMe$_2$), 59.6 (-C^{t}BuCO), 65.6 (-CH=CHC$_6$H$_4$NMe$_2$), 89.6 (-CH=CHC$_6$H$_4$NMe$_2$), 112.5 (-C(CH)$_4$CNMe$_2$, *meta*), 124.5 (-*C*(CH)$_4$CNMe$_2$), 128.0 (-C(CH)$_4$C*N*Me$_2$, *ortho*), 149.9 (-C(CH)$_4$*C*NMe$_2$), 209.2 br (C≡O), and 233.9 (C=*C*=O); *m/z* (FAB) 384 (MH^+, 29%), 356 (MH^+-CO, 23), 327 (M^+-2CO, 15), 299 (M^+-3CO, 100), 271 (M^+-4CO, 73), and 215 (M^+-4CO-Fe, 38).

((E)-1-Methyl-3-^{t}butylsulphonylvinylketene)tricarbonyliron(0) (308).

(1-Methyl-3-^{t}butylsulphonylvinylketone)Fe(CO)$_{3}$ (310) (0.260 g, 0.79 mmol), MeLi (0.59 ml, 0.87 mmol), THF (4 ml). Crystallisation from *n*-pentane gave (308) as a yellow crystalline solid (0.050 g, 19%), m.p. 103-107 °C (decomp.) (Found: C, 41.84; H, 4.14. $C_{12}H_{14}FeO_6S$ requires C, 42.12; H, 4.12%); ν_{max} (hexane) 2 087, 2 041, and 2 013 (C≡O), and 1 797 cm^{-1} (C=O); δ_H (400 MHz; $CDCl_3$) 1.46 (9 H, s, ^{t}Bu), 1.86 (3 H, s, Me), 2.56 (1 H, d, J 7.1 Hz, -C*H*=CHSO$_2{}^{t}$Bu), and 6.09 (1 H, d, J 7.1 Hz, -CH=C*H*SO$_2{}^{t}$Bu); δ_C {^{1}H} (100.6 MHz; $CDCl_3$) 13.3 (Me), 23.8 (*C*Me$_3$), 48.1 (*C*=C=O), 54.5 (*C*Me$_3$), 59.8 (-*C*H=CHSO$_2{}^{t}$Bu), 100.3 (-CH=*C*HSO$_2{}^{t}$Bu), 207.2 br (C≡O), and 230.9 (C=*C*=O); *m/z* (FAB) 343 (MH^+, 95%), 287 (MH^+-2CO, 100), 259 (MH^+-3CO, 83), 230 (M^+-4CO, 57), and 174 (M^+-4CO-Fe, 51).

11.4.5 Synthesis of *N*-benzylidenebenzylamine[311]

A solution of benzaldehyde (5 ml, 0.0483 mmol) in dichloromethane (72 ml) was cooled to 0 °C with stirring. Benzylamine (5.3 ml, 0.0483 mmol) was added dropwise for 15 min., and the reaction mixture was stirred at 0 °C for 0.5 h. Anhydrous $MgSO_4$ (2.5 g, 0.21 mmol) was added, and the reaction mixture was allowed to warm to room temperature and was stirred for an additional 2 h. The reaction mixture was stirred and the solvent removed under vacuum to give *N*-benzylidenebenzylamine as a yellow liquid (7.21 g, 76%); ν_{max} ($CHCl_3$) 1 643 cm^{-1} (C=N); δ_H (220 MHz; $CDCl_3$) 4.83 (2 H, s, -C*H*$_2$Ph), 7.16-7.55 (8 H, m, *Ph*CH$_2$N=CH*Ph*), 7.73-7.86 (2 H, m, -N=CH*Ph ortho*), and 8.41 (1 H, s, -N=C*H*Ph).

11.4.6 Reaction of ((*E*)-1-methyl-3-phenylvinylketene)Fe(CO)$_3$ (157 a) with *N*-benzylidenebenzylamine

A solution of (1-methyl-3-phenylvinylketene)Fe(CO)$_3$ (157 a) (0.139 g, 0.466 mmol) in THF (5 ml) under nitrogen was cooled to 0 °C.

N-Benzylidenebenzylamine (0.100 g, 0.513 mmol) in THF (2 ml) was added dropwise and the orange reaction mixture was allowed to warm to room temperature. The mixture was then stirred at 70 °C for 24 h. The dark reaction mixture obtained was cooled to room temperature and stirred in the presence of air for 17 h. The 'rusty' reaction mixture was filtered through alumina to remove iron residues and the orange solution obtained was evaporated under vacuum to give an orange oil. Chromatography on SiO_2, 1 : 1 EtOAc-petroleum ether 40-60 °C, gave *N*-benzyl-2-methyl-4-phenyl-3-butenamide (**297**) as a pale yellow oil (0.109 g, 88%); δ_H (400 MHz; $CDCl_3$) 1.39 (3 H, d, J 7.1 Hz, Me), 3.18 (1 H, br dq, J 7.1 and 8.2 Hz, -*CH*CH_2CH=CHPh), 4.43 (1 H, d, J 3.6 Hz, -NHC*H*$_2$Ph), 4.44 (1 H, d, J 3.6 Hz, -NHC*H*$_2$Ph), 5.94 (1 H, br s, NH), 6.27 (1 H, dd, J 8.2 and 15.9 Hz, -*CH*=CHPh), 6.50 (1 H, d, J 15.9 Hz, -CH=*CH*Ph), and 7.24-7.37 (10 H, m, 2 Ph); δ_C {^{1}H} (100.6 MHz; $CDCl_3$) 17.4 (*Me*), 43.5 (-*C*HMe-), 44.9, (-NH*C*H$_2$Ph), 126.2 (-CH=CH*Ph*, *orto*), 127.4 (-CH=CH*Ph*, *para*), 127.5 (-NHCH$_2$*Ph*, *orto*), 127.6 (-NHCH$_2$*Ph*, *para*), 128.5 (-CH=CH*Ph*, *meta*), 128.6 (-NHCH$_2$*Ph*, *meta*), 129.3 (-NHCH$_2$*Ph*, *ipso*), 131.9 (-CH=*CH*Ph, *ipso*), 136.4 (-*CH*=CHPh), 138.2 (-CH=*CH*Ph), and 173.6 (*C*=O); *m/z* (EI) 265 (M$^+$, 10%), 131 (M$^+$-CONHCH$_2$Ph, 100), and 91 (CH$_2$Ph, 80).

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