Synthesis and reactivity of iron tricarbonyl complexes of vinylketenes, vinylketenimines and vinylallenes

Lawrence Hill, Christopher J. Richards, Stephen P. Saberi and Susan E. Thomas*

Department of Chemistry, Imperial College, South Kensington, London SW7 2AY

Abstract - (Vinylketene)tricarbonyliron complexes are synthesised from readily-available (vinylketone)tricarbonyliron complexes. They react with isonitriles to give (vinyl-ketenimine)tricarbonyliron complexes and with phosphonoacetate anions to give (vinylallene)tricarbonyliron complexes. Nucleophiles add to C-1 of the vinylketene complexes to produce β,γ-unsaturated carbonyl derivatives whilst, in contrast, nucleophiles add to C-2 of the vinylketenimine complexes to give β,γ-unsaturated carbonyl derivatives containing α quaternary centres. Addition of nucleophiles to optically pure vinylketenimine complexes generates optically pure quaternary centres. Oxidation of the vinylallene complexes leads to 5,5-disubstituted 2(5H)-furanones.

INTRODUCTION

Vinylketenes complexed to a range of transition metals including iron, vandium, manganese, cobalt and molybdenum have been isolated and characterised over the last thirty years (ref. 1). Although many of these complexes were found to be highly stable and easy to manipulate, very few investigations of their reactivity have been carried out probably reflecting the fact that many of the synthetic methods used to generate them were low-yielding and/or lengthy. We recently discovered a new and direct route to (vinylketene)tricarbonyliron complexes and this has enabled us to carry out extensive studies of their reactivity. Experiments executed to date, described below, have shown that the vinylketene complexes may be converted directly into tricarbonyliron complexes of vinyl*ketenimines* (including optically pure vinylketenimine complexes) and tricarbonyliron complexes of vinyl*allenes*. Also discussed below are reactions which release the vinylketene, vinylketenimine and vinylallene ligands to give organic products, some of which have been produced in homochiral form.
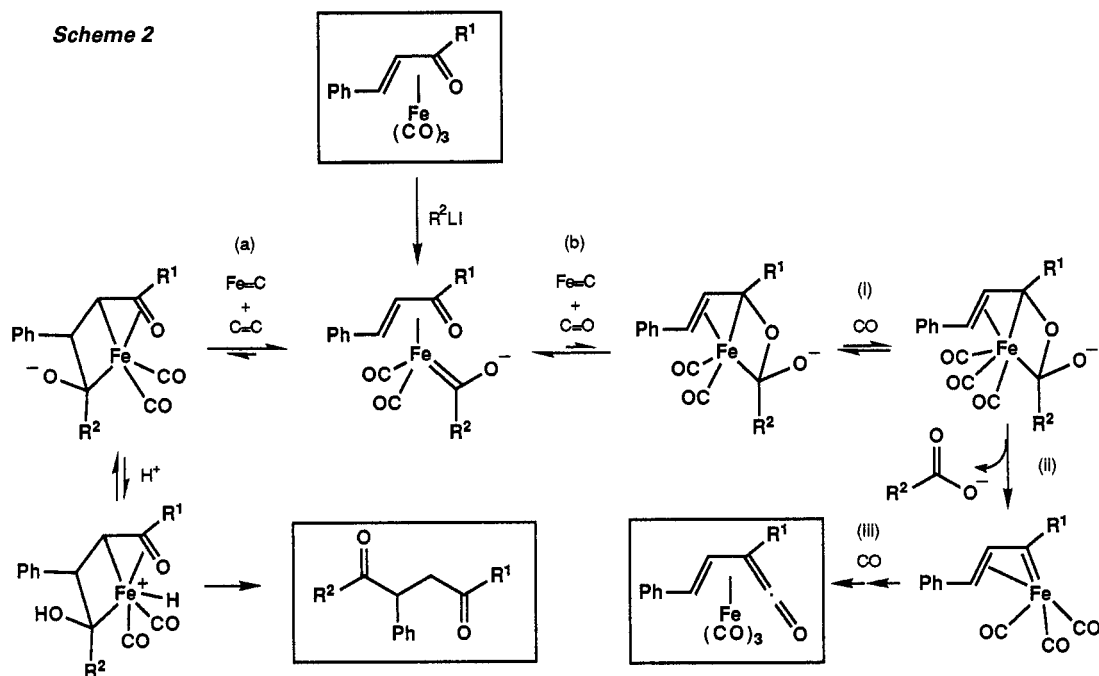
SYNTHESIS OF (VINYLKETENE) TRICARBONYLIRON COMPLEXES

Some time ago, during a study of the reactivity of iron tricarbonyl complexes of vinylketones, we found that addition of alkyl-lithium reagents to these complexes under a nitrogen atmosphere generated 1,4-diketones in good yield (ref. 2). Replacing the nitrogen atmosphere with a carbon monoxide atmosphere, however, led to the production of organometallic compounds identified as (vinylketene)tricarbonyliron complexes (ref. 3) (scheme 1). Thus a range of (vinylketene)tricarbonyliron complexes are available in a two-step synthesis from vinylketones in overall yields of between 28% (R^1 = Me) and 74% (R^1 = Bu^t).
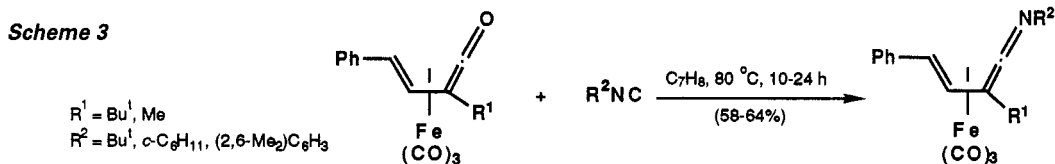
Scheme 1
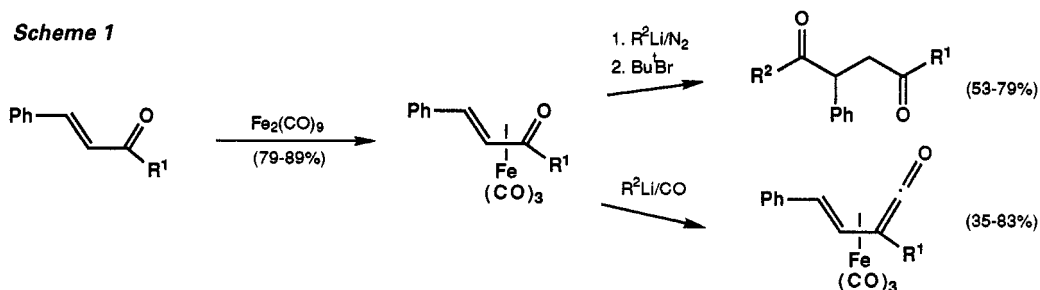
Mechanisms to account for the conversion of (vinylketone)tricarbonyliron complexes to 1,4-diketones under nitrogen and (vinylketene)tricarbonyliron complexes under carbon monoxide are illustrated in scheme 2. In a common first step, the alkyl-lithium reagent adds to a metal-carbonyl ligand to give a metal-carbene. It is proposed that the iron-carbon double bond thus generated may then undergo the first step of a metathesis-type reaction with either (a) the carbon-carbon double bond of the vinylketone ligand ultimately leading to the 1,4-diketone on work-up, or (b) the carbon-oxygen double bond of the vinylketone ligand leading to the vinylketene complex *via* (i) carbonylation, (ii) completion of the metathesis reaction forming a new iron-carbon double bond in a vinylcarbene complex and a new carbon-oxygen double bond in a liberated molecule of alkanoate, and (iii) a second carbonylation step. It is of note that we have isolated the proposed alkanoate by-product (ref. 3) and that the carbonylation of (vinylcarbene)tricarbonyliron complexes to (vinylketene)tricarbonyliron complexes has been observed previously (ref. 4-5).
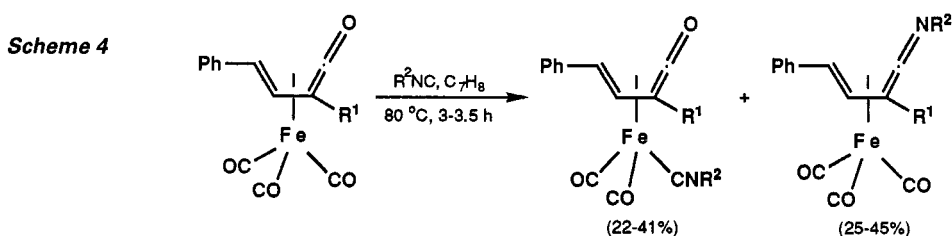
Scheme 2

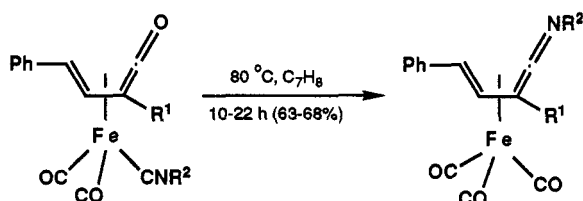## SYNTHESIS OF (VINYLKETENIMINE) TRICARBONYLIRON COMPLEXES

The first reaction of the vinylketene complexes that we investigated was their reaction with isonitriles. We found that simply heating (vinylketene)tricarbonyliron complexes with isonitriles at 80 °C led directly to (vinylketenimine)tricarbonyliron complexes (scheme 3) (ref. 3).

Scheme 3

$R^1 = Bu^t, Me$
$R^2 = Bu^t, c-C_6H_{11}, (2,6-Me_2)C_6H_3$

This unprecedented reaction was examined more closely. Firstly, as monitoring the reactions depicted in scheme 3 by t.l.c. had revealed the appearance and disappearance of an intermediate, several of the reactions were halted after 3-3.5 h. The product mixtures contained not only (vinylketenimine)tricarbonyliron complexes but also compounds identified as (vinylketene)dicarbonylisonitrile complexes (scheme 4). These complexes were isolated and converted to (vinylketenimine)tricarbonyliron complexes under the reaction conditions used for the ketene-ketenimine transformation (scheme 5) (ref. 3).
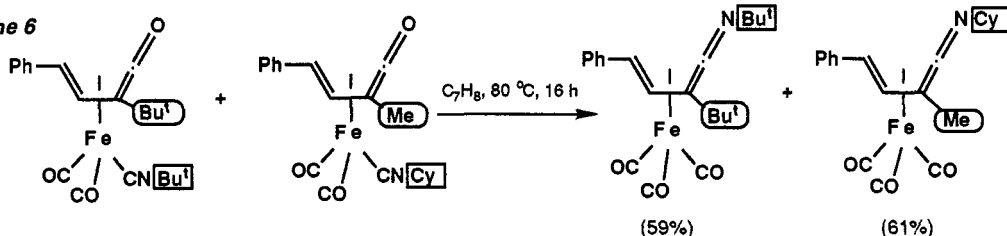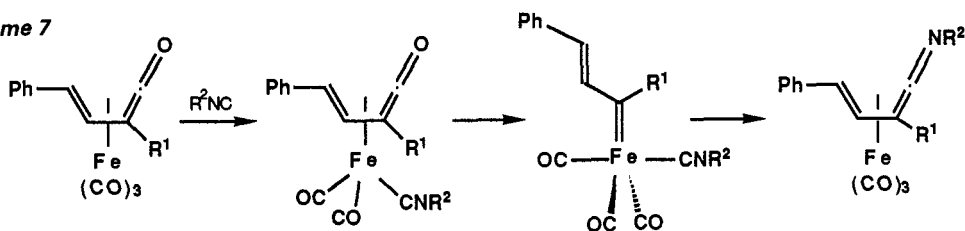
Scheme 4

Scheme 5

Secondly, the two (vinylketene)dicarbonylisonitrileiron complexes depicted in scheme 6 were heated in the same reaction vessel. This gave a product mixture from which the corresponding (vinylketenimine)tricarbonyliron complexes were isolated in yields consistent with those yields recorded previously for this reaction. We were unable to detect any evidence for the generation of cross-over products during the experiment and this suggests that the carbonyl/isonitrile exchange occurs intramolecularly (ref. 3).

Scheme 6

A reaction pathway consistent with these observations is outlined in scheme 7. It is of note that conversion of the (vinylketene)dicarbonylisonitrileiron complex to the (η^1-vinylcarbene)tricarbonylisonitrileiron species is consistent with the observation (depicted in scheme 8) that heating a (vinylketene)tricarbonyliron complex at 60 °C transforms it into an (η^3-vinylcarbene)tricarbonyliron complex (ref. 5).
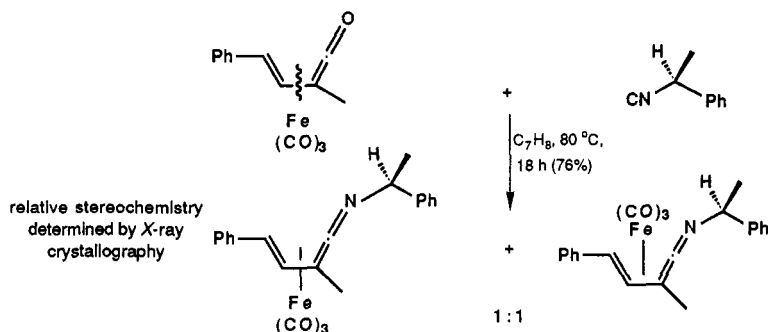
Scheme 7

Scheme 8
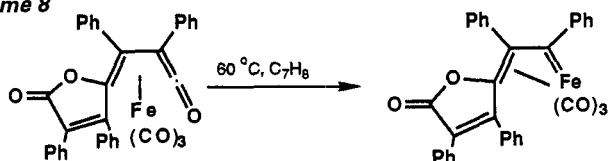
The use of an optically pure isonitrile in the vinylketenimine synthesis appeared to be a promising approach to optically pure vinylketenimine complexes. Accordingly (S)-(-)-α-methylbenzyl isonitrile (ref. 6) was heated with a vinylketene complex as depicted in scheme 9 (ref. 7). This gave a 1:1 mixture of diastereoisomeric vinylketenimine complexes which it proved possible to separate by column chromatography. The relative stereochemistry of the slower moving diastereoisomer was determined by X-ray crystallography and the optical purity of the diastereoisomers was proven to be >92% by derivatisation (see below).

Scheme 9

relative stereochemistry
determined by X-ray
crystallography

## SYNTHESIS OF (VINYLALLENE) TRICARBONYLIRON COMPLEXES

The first example of a (vinylallene)tricarbonyliron complex was reported as recently as 1988 and was synthesised by irradiating an allenic lactone in the presence of $Fe(CO)_5$ (ref. 8) (scheme 10). This gave a mixture of several products including the (vinylallene)tricarbonyliron complex which was characterised by X-ray crystallography.

Scheme 10

(15%)
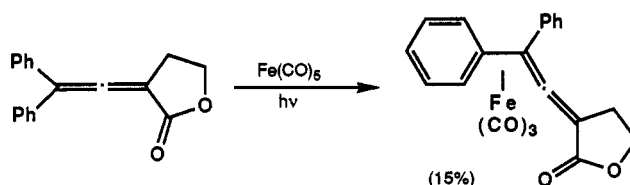
We considered that if (vinylketene)tricarbonyliron complexes could be directly converted into (vinylallene)tricarbonyliron complexes, then this would constitute a complementary and potentially more versatile approach to this relatively new class of complex. Attention initially focussed on the reaction between vinylketene complexes and the anion derived from trimethyl phosphonoacetate. Gratifyingly these reactions did produce vinylallene complexes as indicated in scheme 11 but, rather disappointingly, each product contained two stereoisomers in approximately equal amounts.

Scheme 11
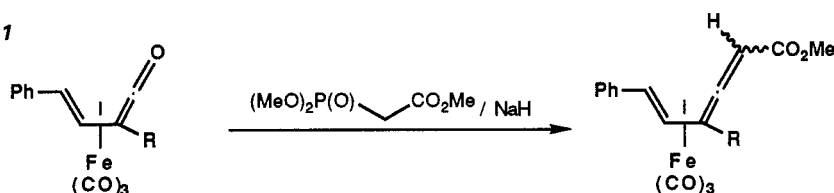
R	Stereoisomeric Ratio Major:Minor	Yield of Analytically Pure Major Stereoisomer (%)
Me	69:31	25
Bu^n	50:50	38
Bu^t	70:30	30

We thus proposed that an increase in the steric demands of the phosphonoacetate should lead to improved stereoselectivity. The reactions recorded in scheme 11 were repeated using the anion derived from *tert*-butyl diethyl phosphonoacetate and, as may be seen in scheme 12, these reactions did indeed occur more selectively and produced predominantly one stereoisomer (ref. 9).
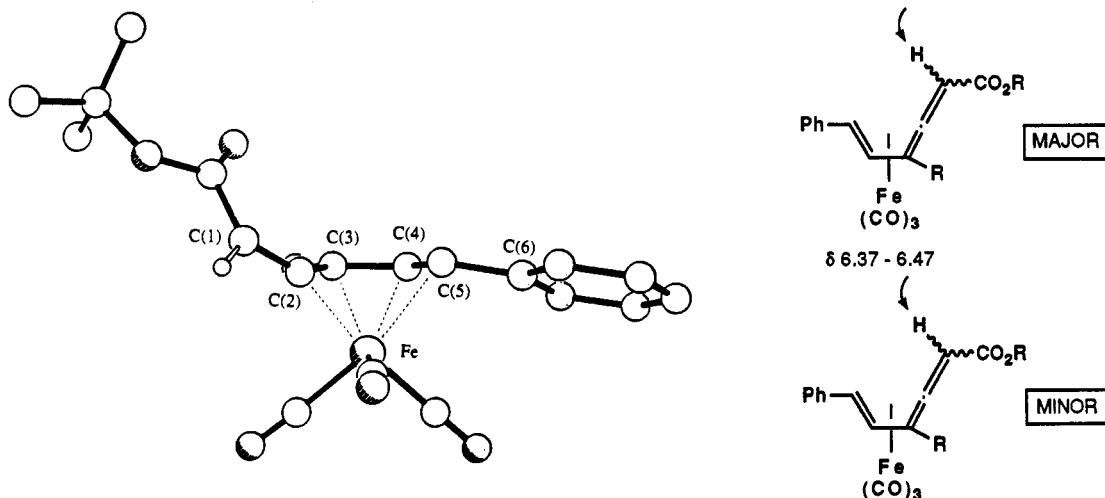
Scheme 12
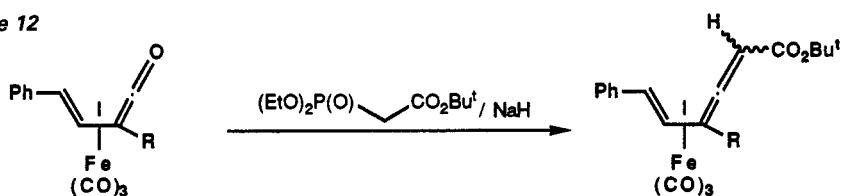
R	Stereoisomeric Ratio Major:Minor	Yield of Analytically Pure Major Stereoisomer (%)
Me	98:2	71
Bu^n	82:18	43
Bu^t	86:14	39

The relative stereochemistry of the major and minor stereoisomers of the vinylallene complexes was determined by an X-ray crystal structure analysis of the major stereoisomer of the product obtained from the reaction between the methyl-substituted vinylketene and the *tert*-butyl diethyl phosphonoacetate anion (scheme 13). This revealed that in the major stereoisomer, the bulky carboalkoxy group is directed away from the tricarbonyliron unit. Comparison of the ^{1}H NMR shift values of the proton attached to the allene terminus in the major and minor stereoisomers of all the vinylallene complexes formed revealed that all the major stereoisomers had the same relative stereochemistry.

Scheme 13

δ 5.71-5.87

MAJOR

δ 6.37 - 6.47

MINOR

## NUCLEOPHILIC ADDITION TO (VINYLKETENE)- AND (VINYLKETENIMINE) TRICARBONYLIRON COMPLEXES

The reactions of the vinylketene complexes with a range of nucleophiles have been examined. As depicted in scheme 14, addition of sulphur, carbon, oxygen and nitrogen nucleophiles occurs at C-1 to give β,γ-unsaturated carbonyl products (ref. 10).
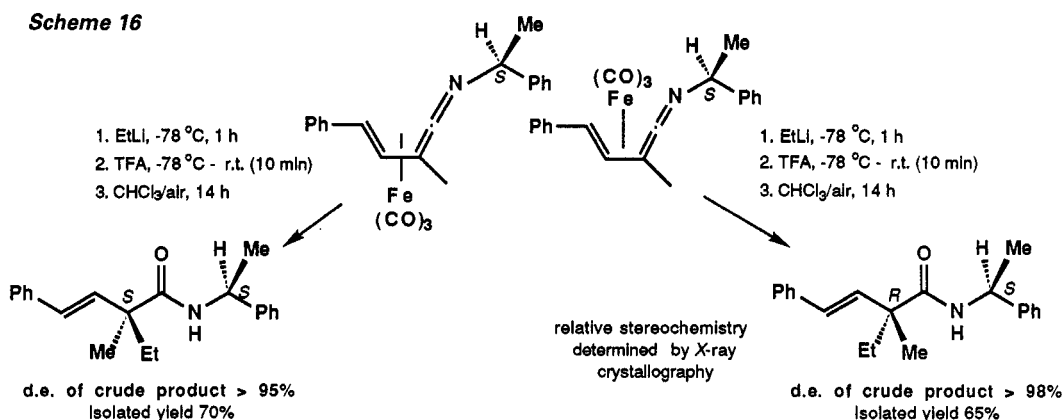
Scheme 14
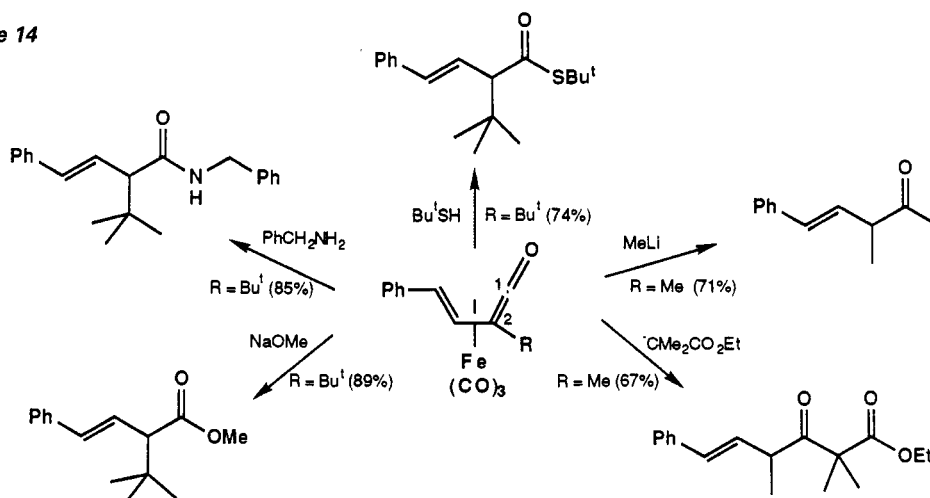
Nucleophilic attack on vinylketenimine complexes has also been examined. It was discovered that alkyl-lithium reagents attack these complexes at C-2 to give, after stirring briefly (10 min) with acid and an oxidative work-up, β,γ-unsaturated amides containing an α quaternary centre (scheme 15) (ref. 10).
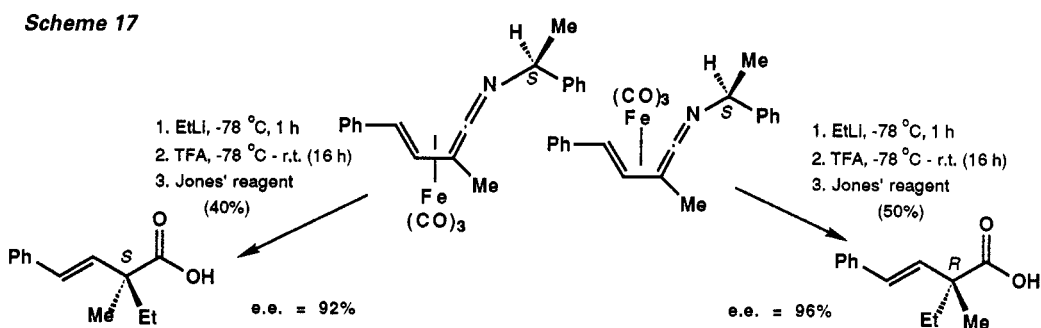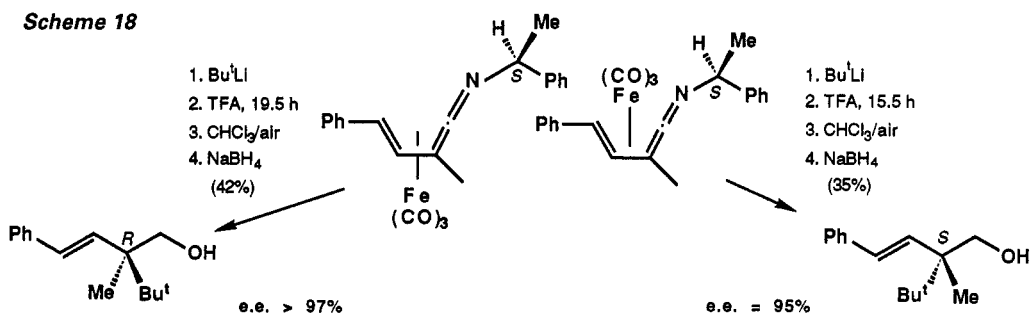
Scheme 15
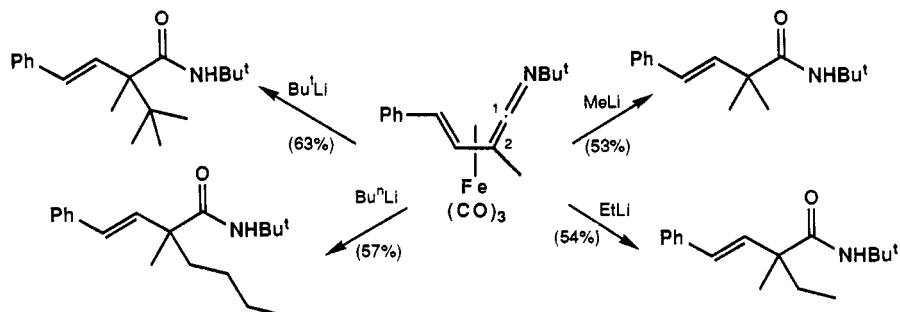
The stereospecificity and direction of nucleophilic attack on the vinylketenimine complexes was determined by adding ethyl-lithium to diastereoisomerically pure samples of the vinylketenimine complexes derived from (S)-(-)-α-methylbenzyl isonitrile (scheme 16). Analysis of the β,γ-unsaturated amide products revealed that in each case the nucleophile approached the vinylketenimine complex exclusively from its *exo* face *i.e.* the face not shielded by the tricarbonyliron unit (ref. 7).

Scheme 16

1. EtLi, -78 °C, 1 h
2. TFA, -78 °C - r.t. (10 min)
3. CHCl₃/air, 14 h

1. EtLi, -78 °C, 1 h
2. TFA, -78 °C - r.t. (10 min)
3. CHCl₃/air, 14 h

relative stereochemistry
determined by X-ray
crystallography

d.e. of crude product > 95%
Isolated yield 70%

d.e. of crude product > 98%
Isolated yield 65%

The enantiomeric purity of the quaternary centres produced by this approach was then determined. Once again ethyl-lithium was added to samples of each diastereoisomeric complex but this time the work-up conditions were altered to produce β,γ-unsaturated carboxylic acids (scheme 17). The enantiomeric excesses of the carboxylic acids were measured and found to be 92% and 96%. Given that the e.e. of the chiral amine used to prepare the chiral isonitrile was 96%, the optical purity of the products appears only to be limited (within experimental error) to the purity of the chiral amine used.

Scheme 17

1. EtLi, -78 °C, 1 h
2. TFA, -78 °C - r.t. (16 h)
3. Jones' reagent
(40%)

1. EtLi, -78 °C, 1 h
2. TFA, -78 °C - r.t. (16 h)
3. Jones' reagent
(50%)

e.e. = 92%

e.e. = 96%

This approach to homochiral quaternary centres has also been used to generate essentially optically pure molecules containing two contiguous quaternary centres (scheme 18).

Scheme 18

1. BuᵗLi
2. TFA, 19.5 h
3. CHCl₃/air
4. NaBH₄
(42%)

1. BuᵗLi
2. TFA, 15.5 h
3. CHCl₃/air
4. NaBH₄
(35%)

e.e. > 97%

e.e. = 95%

OXIDATION OF (VINYLALLENE) TRICARBONYLIRON COMPLEXES

The reactivity patterns of (vinylallene)tricarbonyliron complexes are essentially unknown. (The single reported reaction to date involved stirring a vinylallene complex with tetracyanoethylene which led to decomplexation and isolation of the free allene (ref. 8).) Our attention focussed on the outcome of oxidising the vinylallene complexes produced as described above. We found that stirring these complexes with $FeCl_3$ and work-up led to the isolation of 5,5-disubstituted 2(5H)-furanones (scheme 19, ref. 11), and that the yield obtained in each case was inversely proportional to the bulk of the vinylallene substituent R^1.

Scheme 19
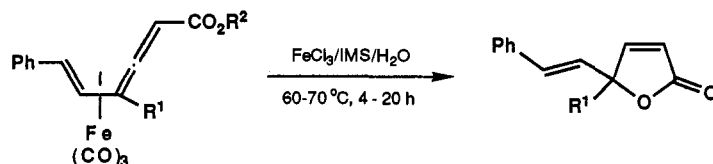
R^1	R^2	Yield (%)
Me	Me	82
Bu^t	Me	18
Me	Bu^t	96
Bu^n	Bu^t	54

More work is required to delineate a detailed mechanism for the oxidation of the vinylallene complexes to the 2(5H)-furanones. It may be postulated, however, that the first step is an $FeCl_3$-mediated one-electron oxidation of the vinylallene complex to give a cationic species (route a, scheme 20). Subsequent internal nucleophilic attack on the η^3-allyl ligand by the carboalkoxy group leads to an intermediate which under the acidic reaction conditions will give rise to the product 2(5H)-furanones by protonation of the iron centre followed by reductive elimination and hydrolysis of the $C=O^+R$ group. An alternative mechanism (route b, scheme 20), in which the $FeCl_3$ leads to complete decomplexation and generates the free vinylallene ligand, cannot be discounted as uncomplexed 1-carboethoxyallenes have been reported to cyclise to 2(5H)-furanones under acidic conditions (ref. 12). Investigations to distinguish between the two types of mechanism using optically pure vinylallene complexes are in hand.

Scheme 20
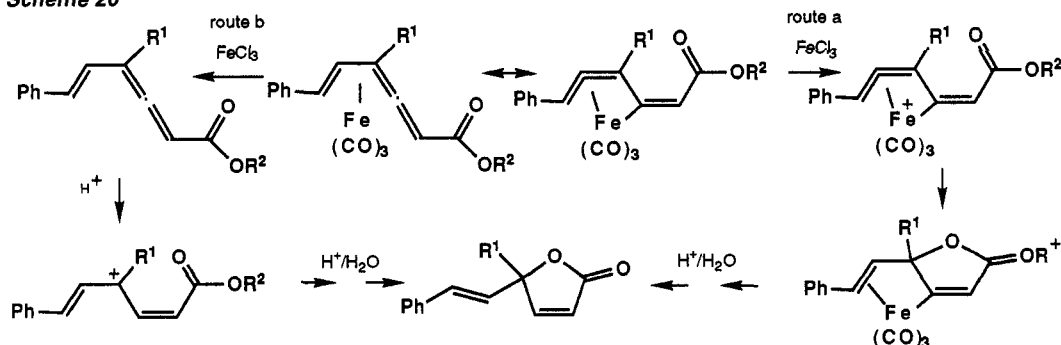
REFERENCES

1. G.L. Geoffroy and S.L. Bassner, *Adv. Organomet. Chem. 28*, 1-83 (1988).
2. T.N. Danks, D. Rakshit and S.E. Thomas, *J. Chem. Soc., Perkin Trans. 1* 2091-2093 (1988).
3. N.W. Alcock, C.J. Richards and S.E. Thomas, *Organometallics 10*, 231-238 (1991).
4. T.A. Mitsudo, H. Watanabe, T. Sasaki, Y. Takegami, Y. Watanabe, K. Kafuku and K. Nakatsu, *Organometallics 8*, 368-378 (1989).
5. J. Klimes and E. Weiss, *Angew. Chem., Int. Ed. Engl. 21*, 205-205 (1982).
6. S. Terashima, K. Takashima, T. Sato and S-I. Yamada, *Chem. Pharm. Bull. 21*, 1135-1139 (1973).
7. N.W. Alcock, G.A. Pike, C.J. Richards and S.E. Thomas, *Tetrahedron: Asymmetry 1*, 531-534 (1991).
8. L.S. Trifonov, A.S. Orahovats, R. Prewo and H. Heimgartner, *Helv. Chim. Acta 71*, 551-561 (1988).
9. L. Hill, S.P. Saberi, A.M.Z. Slawin, S.E. Thomas and D.J. Williams, *J. Chem. Soc., Chem. Commun.* in press.
10. L. Hill, C.J. Richards and S.E. Thomas, *J. Chem. Soc., Chem. Commun.* 1085-1086 (1990).
11. S.P. Saberi and S.E. Thomas, submitted for publication in *J. Chem. Soc., Perkin Trans. 1*.
12. G. Aksnes and P. Froyen, *Acta Chem. Scand. 22*, 2347-2352 (1968).