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PHOTOINITIATED COUPLING OF DIENES AND MONOOLEFINS WITH PENTACARBONYLIRON

A thesis submitted to the Council for National Academic Awards in partial fulfilment of the requirements for the degree of Doctor of Philosophy

by

Ibrahim Hamed Ibrahim Salama

The Polytechnic of
North London
and
Max-Planck-Institut
für Strahlenchemie

September 1984

To

my Mother and in loving
memory of my Father, the
late Dr.med. Hamed Salama

My wife Anette

My family

John Charalambous:

Without you, this work might not have been accomplished.

Declaration

Whilst registered as a candidate for this degree the author has not been a registered candidate for any other award.

I.H.I. Salama

Ibrahim Hamed Ibrahim Salama

Photoinitiated coupling of dienes and monoolefins with pentacarbonyliron

Abstract

The photoreaction of pentacarbonyliron with 1,3-diene/monoolefin mixtures results in C-C coupling of the two organic substrates, forming a six-carbon chain which is coordinated to the $Fe(CO)_3$ moiety in a 1-σ,4-6-η^3 fashion. Using various 1,3-dienes and monoolefins carrying methyl and carboalkoxy substituents, the wide applicability of this process is demonstrated.

The reaction is regio- and stereo-selective to some extent yielding a limited number of isomeric (σ,η^3-organo)-$Fe(CO)_3$ complexes. The product distributions are correlated with steric and electronic factors due to the influence of the substituents. In all cases the original configurations of the organic components are retained in the final products. The structures of the (σ,η^3-organo)$Fe(CO)_3$ isomers are established on the basis of their IR, ^1H- and ^{13}C-NMR spectroscopic data. In one case the structure was confirmed by an X-ray crystal structure investigation, carried out by Krüger et.al.

The reaction sequence involves several photochemical and thermal steps. Photolytic detachment of carbonyl ligands provides the free coordination sites at the metal which are required to accomodate both the diene and olefin substrates prior to C-C bond formation. The reaction proceeds via the (η^4-diene)-$Fe(CO)_3$ and (η^2-olefin)$Fe(CO)_4$ complexes; in two cases a (η^4-diene)(η^2-olefin)$Fe(CO)_2$ complex has been isolated and shown to be the key intermediate involved in the C-C bond formation. This coupling process can be interpreted in terms of oxidative cyclization. It does not require the action of light but is, like the subsequent take-up of a CO ligand, a thermal process.

The reactivity of the (σ,η^3-organo)$Fe(CO)_3$ complexes is also examined. The photolysis of these compounds results in (i) formation of other (σ,η^3-organo)$Fe(CO)_3$ isomers, (ii) cleavage of the previously formed C-C bond with liberation of the olefinic component and formation of (η^4-diene)$Fe(CO)_3$, and (iii) hydrogen migration with formation of either 1,3- or 1,5-diene derivatives, depending on the particular substituents at the C_6-chain. Treatment of (σ,η^3-organo)$Fe(CO)_3$ complexes with carbon monoxide at elevated pressure and temperature results in displacement of the metal (formation of pentacarbonyliron) and incorporation of one CO molecule in the organic moiety yielding cycloheptenone derivatives.

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I should like to thank most sincerely my supervisors *Dr. John Charalambous* of the Polytechnic of North London and *Dr. Friedrich-Wilhelm Grevels* of the Max-Planck-Institut für Strahlenchemie for their constant encouragement, guidance, advice, and attention given to me during the period this work was carried out.

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The support of the directors of the Max-Planck-Institut, *Prof. Dr. K. Schaffner*, *Prof. Dr. O.E. Polansky*, and *Prof. Dr. Schulte-Frohlinde*, which enabled me to carry out this research, is gratefully acknowledged.

In conclusion I would like to express my love to my wife, not only for her patience in typing this thesis, but also for her encouragement throughout the study.

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Abbreviations

The following is a list of abbreviations employed in this text.

BD	buta-1,3-diene
Et	ethyl, C_2H_5
DEF	diethyl fumarate
DMF	dimethyl fumarate
DEM	diethyl maleate
DMM	dimethyl maleate
MA	methyl acrylate
MC	methyl crotonate
Me	methyl, CH_3
MSo	methyl sorbate
NBD	norbornadiene
Z	methyl or ethyl ester group ($-CO_2R$; R = Me or Et)

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CHAPTER ONE

PENTACARBONYLIRON: REACTIONS WITH MONOOLEFINS AND DIENES

1.1. Pentacarbonyliron

Pentacarbonyliron, $Fe(CO)_5$, was first reported by *Mond*, *Quincke* {1}, and *Langer* {2} in 1891 as the discovery of tetracarbonylnickel {3} encouraged them to expand their research to other transition-metals. *Berthelot* was also successful in preparing this substance {4} using the same method, i.e. the direct reaction of metallic iron with carbon monoxide at high pressure and temperature. This method is still used for the industrial production of pentacarbonyliron.

For some time, pentacarbonyliron was considered to have advantages compared to tetraethyl lead as an anti-knock agent for motor fuels {5}. Iron, as well as nickel, may be purified by forming the metal carbonyl complex and then heating to its decomposition temperature (reaction 1.1)

$$Fe(impure) + CO \longrightarrow Fe(CO)_5 \xrightarrow{>250\ ^\circ C} Fe(pure)$$

(reaction 1.1)

A gas phase electron diffraction study of pentacarbonyliron, carried out by *Davis* and *Hanson* {6}, showed that its structure is trigonal-bipyramidal in the vapour state (Figure 1.1).

The compound also has a trigonal-bipyramidal structure in the solid state as established by a single crystal X-ray analysis at ca. -80 $^\circ$C. This study was carried out by *Davis* and

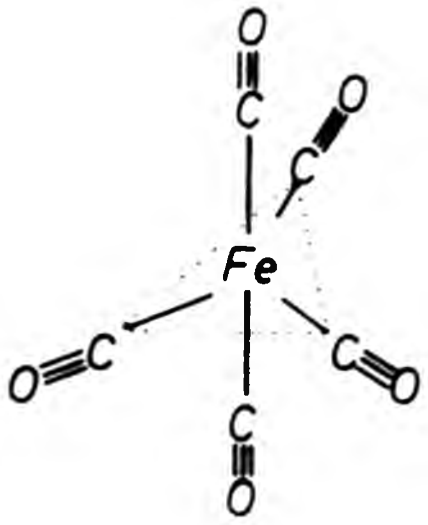


Figure 1.1: Molecular structure of $Fe(CO)_5$

Hanson, who reported that the axial Fe-C bonds were shorter than the equatorial ones by 0.045 Å {6,7}, however, this has been disputed by other workers {8,9,10}.

A single resonance was observed in the ^{13}C-NMR spectrum of $Fe(CO)_5$ at room temperature {11}. On cooling a solution in ether no change was observed in the spectrum indicating that all of the five carbonyl ligands were stereochemically non-rigid on the NMR time scale {12}. Apparently, the activation barrier for the exchange of axial and equatorial CO ligands is low in this compound as *Meakin* and *Jesson* {13} have observed that the ^{13}C-NMR spectra of a solution of $Fe(CO)_5$ remains a sharp singlet down to ca. -170 °C. The interpretation of this rearrangement is based on the *Berry pseudo*-rotation mechanism which was first proposed for PX_5 molecules {14}.

Gray et.al. {15} investigated the UV-spectrum of $Fe(CO)_5$. As in other metal carbonyls, the CT bands and the d-d bands were not clearly resolved at room temperature. However, the spectra at ca. -195 °C showed a better resolution. One result which is relevant to the photochemistry of $Fe(CO)_5$ is the assignment of the lowest energy absorption at 35.450 cm^{-1} to a ligand field transition. A simplified diagram illustrating this transition is shown in Figure 1.2. As a result of such electronic excitation, it loses one CO molecule with high quantum yield {16,17} to form nonacarbonyldiiron (reaction 1.2) {18}, thus accounting for its well known light sensitive character {2,19}.

ground state **excited state**

Figure 1.2: Simplified d-orbital diagram for trigonal-bipyramidal (TBP) d^8 complexes.

$$2Fe(CO)_5 \xrightarrow{h\nu} Fe_2(CO)_9 + CO$$

(reaction 1.2)

1.2. Monoolefin Carbonyliron Complexes

Complexes of type (η^2-olefin)Fe(CO)$_4$ may be regarded as substituted products of pentacarbonyliron in which one of the equatorial carbonyl groups is replaced by a *dihapto*-coordinated olefin. Stable complexes of this type are known mainly for olefins containing electron-withdrawing substituents.

The first olefin-tetracarbonyliron complex to be prepared was the acrylonitrile derivative, (η^2-CH_2=CH-CN)Fe(CO)$_4$. This was reported by *Kettle* and *Orgel* in 1960 {20}. In 1963, a group of workers at the *European Cyanamid Research Institute* {21} developed general conditions for reactions of electronegatively substituted olefins (i.e. maleic, fumaric, acrylic, methacrylic and cinnamic acids and their derivatives) with $Fe_2(CO)_9$ in benzene at 40-45 °C. The corresponding η^2-olefin iron tetracarbonyl derivatives were obtained in good yields (60-93 %) according to reaction 1.3. Similar thermal reactions were subsequently used to prepare the tetracarbonyliron complexes of ethylene {22}, tetramethoxyethylene {23}, and various *cis*- and *trans*-dihaloethylenes {24}.

$$Fe_2(CO)_9 + \text{olefin} \xrightarrow{\Delta} (\text{olefin})Fe(CO)_4 + Fe(CO)_5$$

(reaction 1.3)

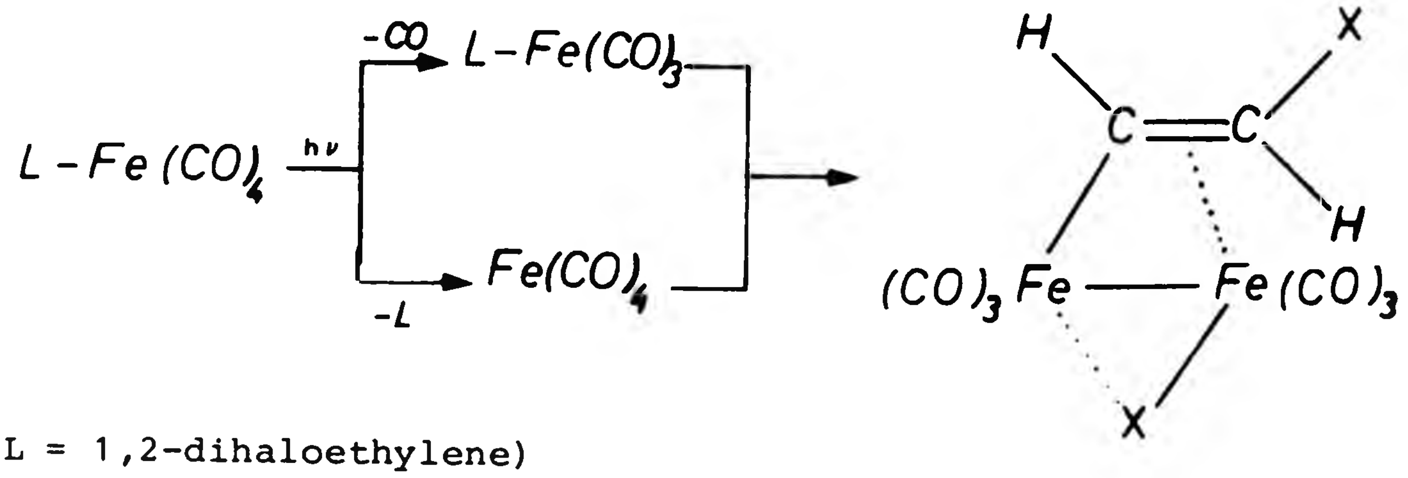
Photochemical methods have been used to prepare a wide range of (η^2-olefin)Fe(CO)$_4$ complexes (reaction 1.4), (e.g. maleic anhydride, dimethyl maleate, dimethyl fumarate {25}, methyl acrylate, vinyl acetate {26}, vinyl chloride, styrene, propylene, and vinyl ethyl ether {27}). The effectiveness of this method arises from the ability to dissociate one of the carbonyl groups from $Fe(CO)_5$ without heating the system to a temperature above the decomposition temperature of the resulting (olefin)$Fe(CO)_4$ derivative.

$$Fe(CO)_5 + \text{olefin} \xrightarrow{h\nu} (\text{olefin})Fe(CO)_4 + CO$$

(reaction 1.4)

Koerner von Gustorf et.al. {26} have pointed out two advantages of the photochemical synthesis of (η^2-olefin)$Fe(CO)_4$ complexes compared with their thermal synthesis from nonacarbonyldiiron reported by *Weiss* et.al. {21}. These advantages are (*i*) the reactions can proceed at low temperature, and (*ii*) it is possible to carry out the reaction using the parent iron carbonyl compound, $Fe(CO)_5$, as the starting material. This is because the nonacarbonyldiiron required is obtainable photochemically from pentacarbonyliron. Thus one step is saved and the route is more economical than the thermal one.

The photochemical method may be less appropriate for the preparation of η^2-olefin iron tetracarbonyl complexes when the latter compounds react further photochemically. *Grevels* and *Koerner von Gustorf* have reported an example where electronic excitation of (η^2-1,2-dihaloethylene)$Fe(CO)_4$ leads to the elimination of the olefinic ligand or CO (Scheme 1.1), finally resulting in the formation of μ-[1-η:1,2-η-(*trans*-2-halovinyl)]-μ-halobis(tricarbonyliron)(Fe-Fe) complexes {28}.



(L = 1,2-dihaloethylene)

(Scheme 1.1)

The structural characterisation of (η^2-olefin)tetracarbonyliron complexes has received considerable attention. Soon after the reported preparation of the acrylonitrile derivative, *Luxmoore* and *Truter* undertook an X-ray analysis {29,30} to establish the mode of bonding of the olefin. The molecule contains five ligands arranged about the iron in the form of a trigonal bipyramid as depicted in Figure 1.3. The equatorial plane

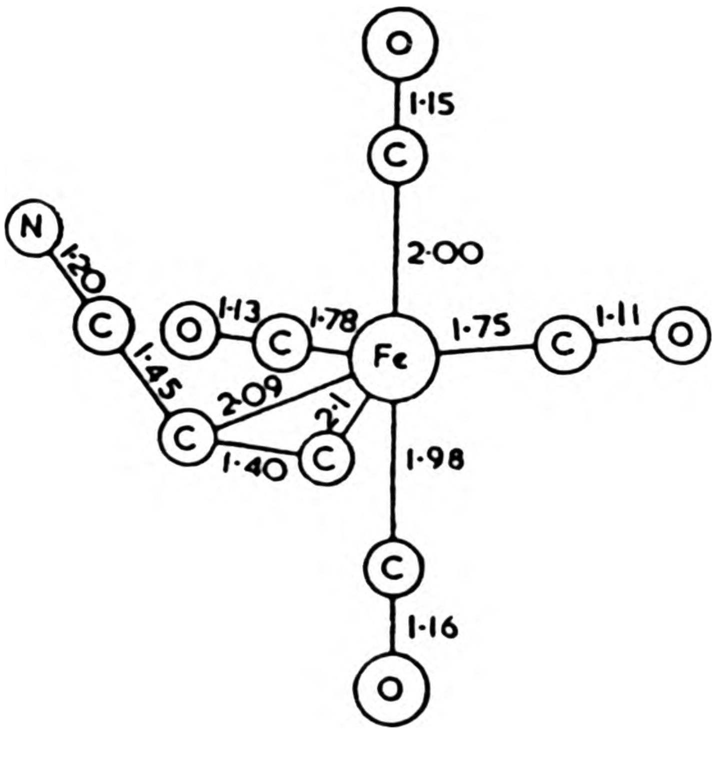


Figure 1.3: (η^2-acrylonitrile)tetracarbonyliron, bond lengths in Å. {29,30}

of the trigonal bipyramid contains the iron atom, two carbonyl groups and the olefinic carbon atoms of the acrylonitrile ligand. As predicted by *Kettle* and *Orgel* from a study of the infrared spectrum {20}, only the olefin group of the acrylonitrile molecule is coordinated to the iron and the cyano group is not bound to the metal.

Infra-red spectroscopy has been used extensively to examine the complexation of the olefins to transition metals. As a result of the π(olefin)→metal and metal→π*(olefin) bonding interactions (Figure 1.4) the C=C double bond is weakened and, consequently, the ν(C=C) vibration is shifted to lower frequency by 120 - 160 cm^{-1} {20,31,32}.

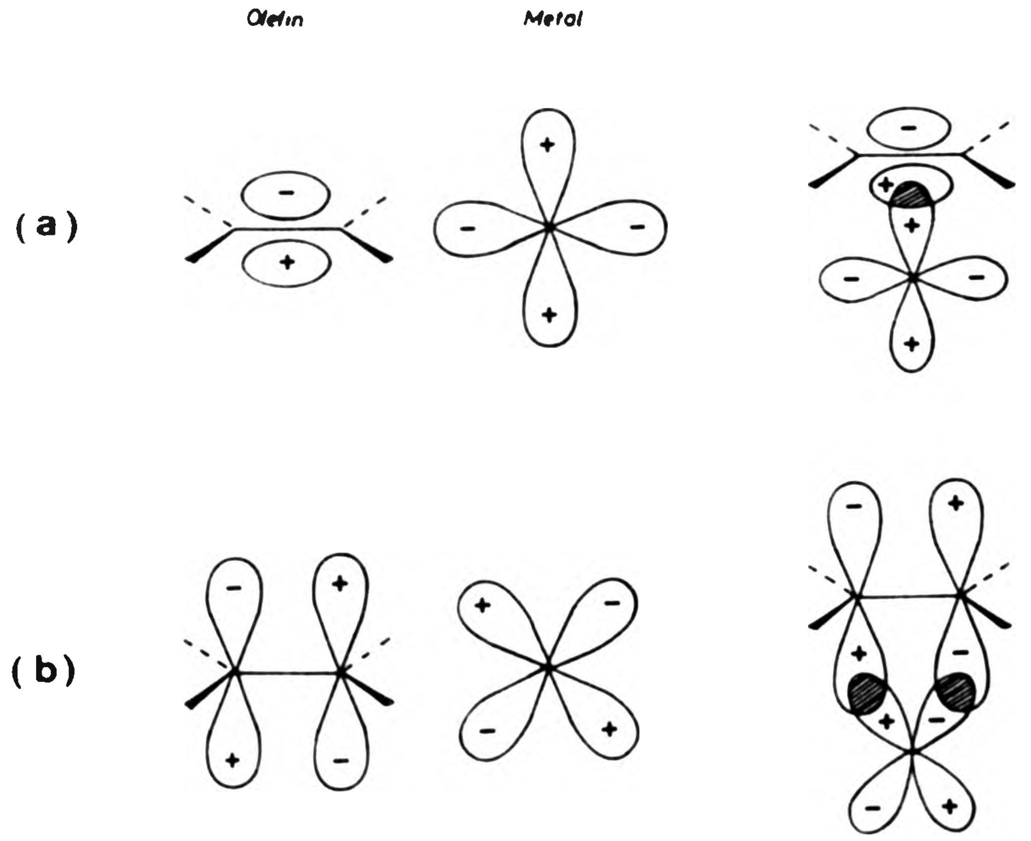


Figure 1.4: Schematic representation of the metal-olefin bond: (a) π(olefin)→metal and (b) metal→π*(olefin) interactions.

In olefin substituted metal carbonyl complexes the ν(CO) vibrations reflect the donor/acceptor properties of the olefinic ligand: the more electron density is donated from the olefin to the metal, the stronger becomes the metal→π^*(CO) interaction (Figure 1.5) thus leading to weakening of the CO bond and consequently, to shift of the ν(CO) vibration to a lower frequency {23,24,33}.

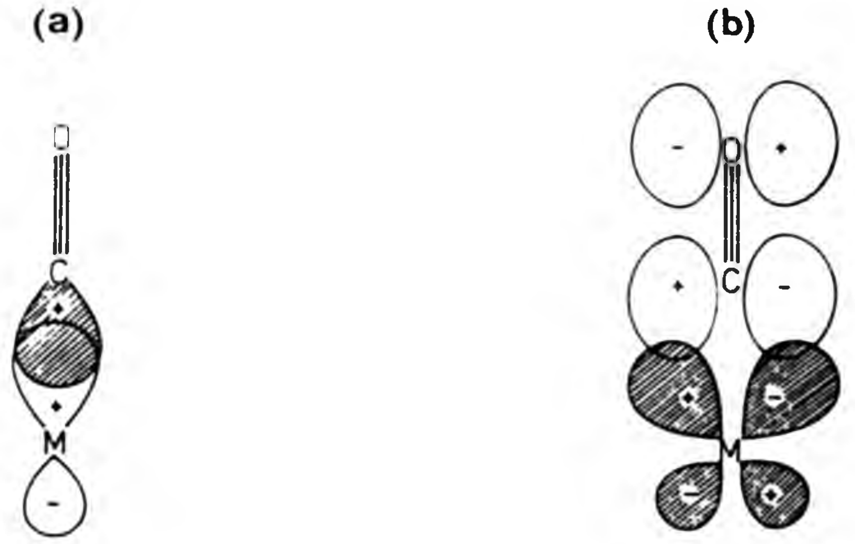


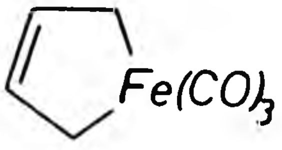
Figure 1.5: Schematic representation of the metal-CO bond: (a) lone pair (CO)→ metal and (b) metal → π^*(CO) interactions.

As discussed before, the ^{13}C-NMR spectrum of $Fe(CO)_5$ shows an extremely low activation barrier towards intramolecular rearrangement of its five carbonyl groups {11,12,13}. The substitution of a carbonyl group by a monoolefin (e.g., diethyl maleate, diethyl fumarate, methyl acrylate) {34,35} raises appreciably this activation barrier. The low temperature limiting ^{13}C-NMR spectra of such (η^2-olefin)$Fe(CO)_4$ complexes are consistent with a trigonal bipyramidal structure having the olefin in the equatorial plane. Thus, in the case of diethyl maleate complex, three lines are observed of relative intensity 2:1:1, for equatorial and non-equivalent axial carbonyl groups. In the case of the diethyl fumarate two lines of equal intensity are observed. For the ethyl acrylate complex, a four-line-pattern is observed with relative intensity 1:1:1:1. The high temperature limiting spectrum with a single ^{13}CO signal, in all cases, indicates averaging of the carbonyl group positions. It is obvious that simple olefin rotation is not solely responsible for the averaging of the carbonyl groups, since such a process would not exchange axial carbonyl groups with equatorial ones.

1.3. Diene Carbonyliron Complexes

1,3-Dienes upon coordination with iron carbonyl form (η^4-diene)tricarbonyliron complexes. This class of compound {36,37, 38,39,40} has been known for many years and continues to receive attention {41,42}.

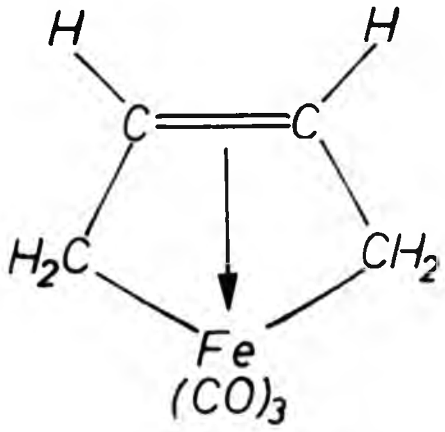
The first example of a 1,3-diene-tricarbonyliron was reported by Reihlen and his co-workers {43}. These authors obtained a complex of stoichiometry $(C_4H_6)Fe(CO)_3$ by reaction of buta-1,3-diene with pentacarbonyliron in a sealed tube at 135-150 °C. They suggested the structure 1 which represents a 16e complex.



1

2

In 1947, carbonyliron complexes of buta-1,3-diene, 2-methylbuta-1,3-diene (isoprene), and 2,3-dimethylbuta-1,3-diene were patented as anti-knock agents for motor fuels {44}. *Pauson*, together with *Hallam* reexamined {45} the early (buta-1,3-diene)tricarbonyliron previously studied by *Reihlen* and co-workers, and formulated the product as the π-complex 2. This structure represents an 18e complex, e.g. the metal has a *pseudo*-noble gas configuration. *Green*, *Pratt* and *Wilkinson* have suggested the structural formula 3, which also represents an 18e complex {46}.



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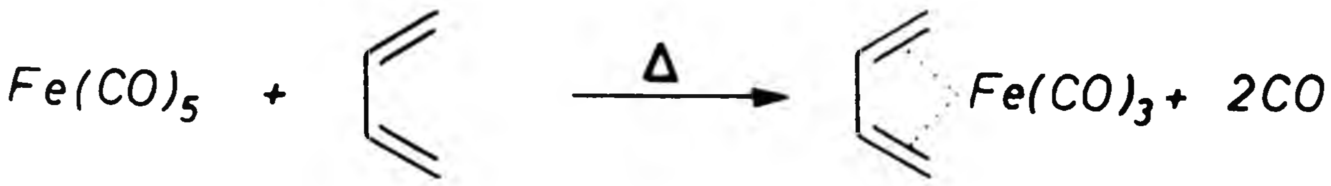
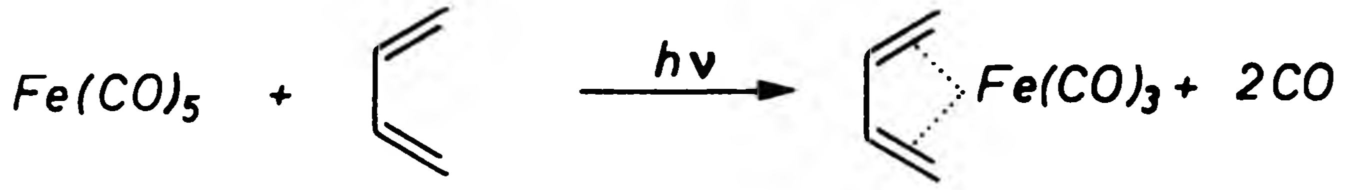
General methods for the preparation of diene-iron-tricarbonyl complexes are summarized below:

1. Thermally, from pentacarbonyliron and the diene {43,47,48}.



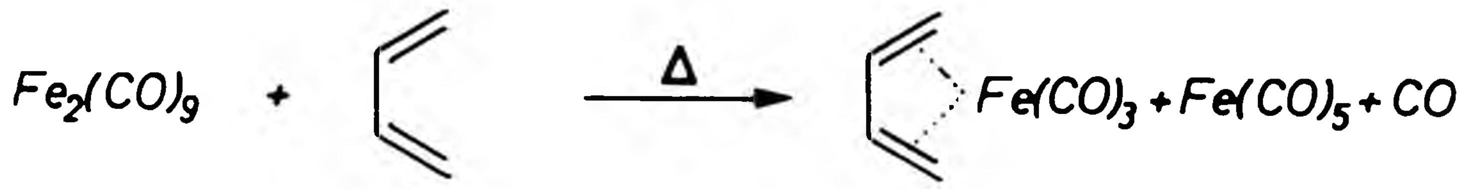
(reaction 1.5)

2. Photochemically, from pentacarbonyliron and the diene {47,48, 49}.



(reaction 1.6)

3. Thermally, from $Fe_2(CO)_9$ and the diene {50}.

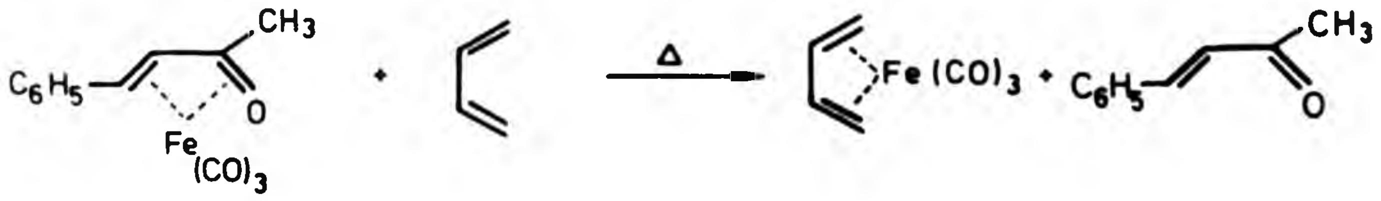


(reaction 1.7)

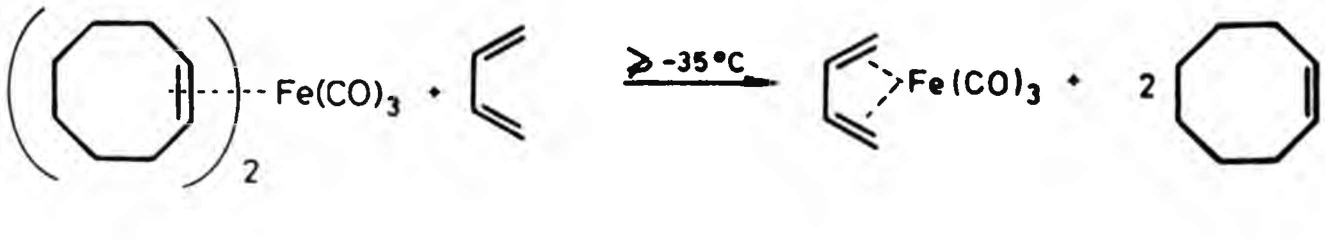
4. Thermally, from $Fe_3(CO)_{12}$ and the diene {47}.

(reaction 1.8)

5. Using ligand exchange reactions {51,52,53}.



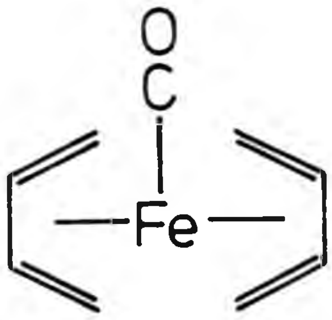
(reaction 1.9)



(reaction 1.10)

The thermal formation of the (1,3-diene)$Fe(CO)_3$ complexes often requires severe conditions, which can lead to side reactions. Thus in the case of isoprene dimerization, resulting in formation of dipentene, takes place {47}. As noted earlier, the photochemical reaction of $Fe(CO)_5$ with 1,3-diene is advantageous over the thermal one. *Reihlen* conducted the reaction in 24 hours and reported 17 % yield of the (buta-1,3-diene)tricarbonyliron {43}. The analogous photochemical reaction performed by *Koerner von Gustorf, Pfaijfer* and *Grevels* {49}, afforded the product in 65 % yield.

It was shown that prolonged irradiation of buta-1,3-diene with pentacarbonyliron can subsequently lead to displacement of two additional carbonyl groups from the 1,3-diene carbonyl complex to give bis(buta-1,3-diene)monocarbonyliron **4** {54,55}. It is



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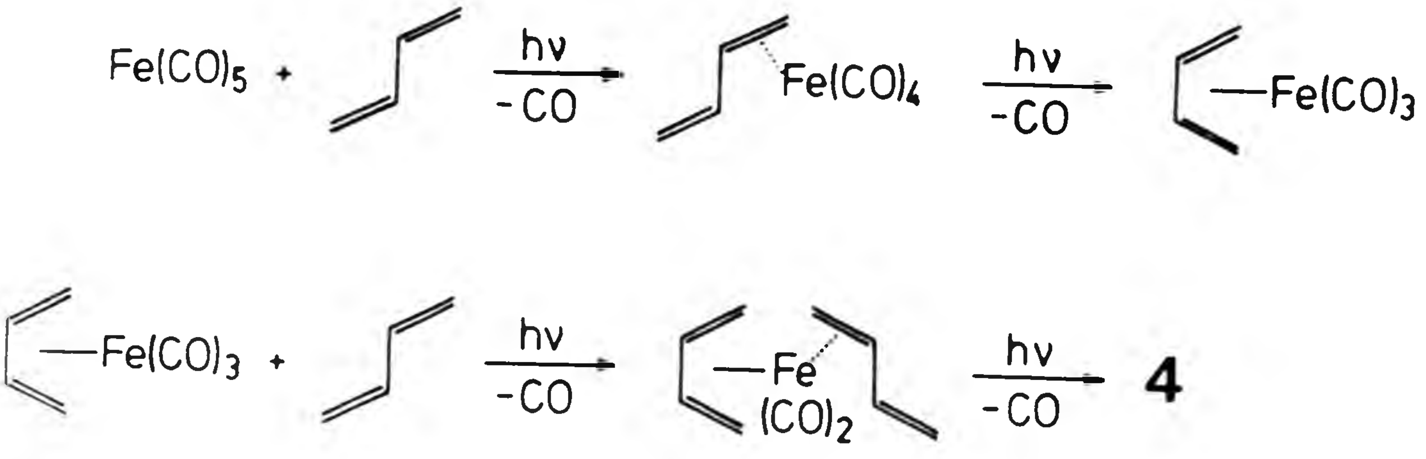
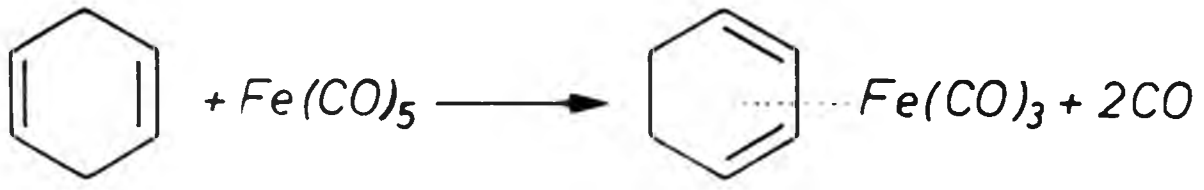
noted that compound **4** was not observed in the thermal reaction of $Fe(CO)_5$ with buta-1,3-diene. The formation of **4** is illustrated in Scheme 1.2.

In some cases, formation of the (diene)$Fe(CO)_3$ complex is accompanied by isomerization of the diene. Non-conjugated dienes, in general, are isomerized to yield (η^4-1,3-diene)$Fe(CO)_3$

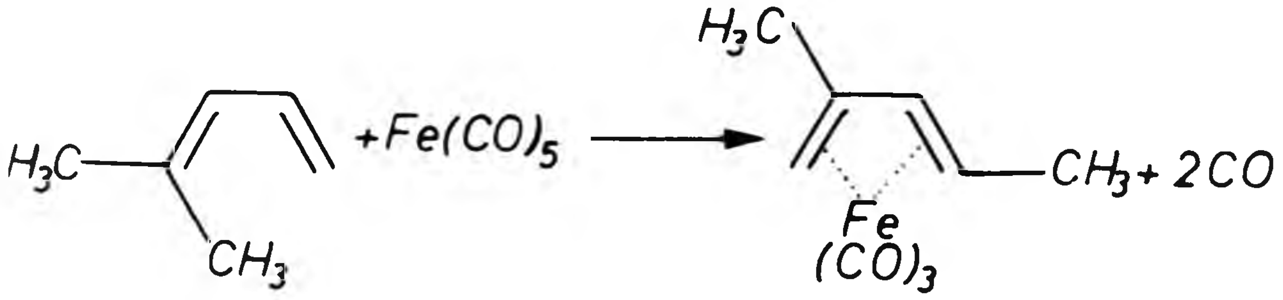


(Scheme 1.2)

complexes (reaction 1.11) {56}. In other cases, the isomerization seems to be due to steric factors: 4-methyl-1,3-pentadiene, for example, reacts with $Fe(CO)_5$ to form (2-methyl-1,3-pentadiene)tricarbonyliron (reaction 1.12) {38}.

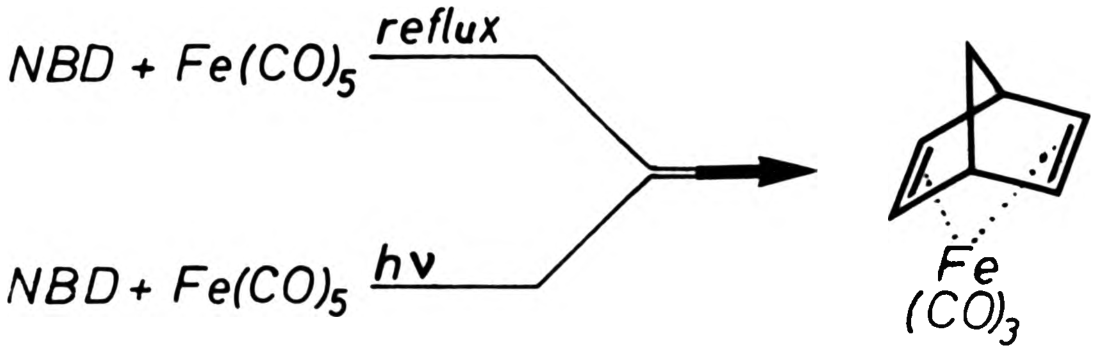


(reaction 1.11)



(reaction 1.12)

Hallam and *Pauson* suggested that conjugation of the double bonds is an essential feature for formation of metal-π-bonds {45}. However, *Pettit* successively isolated (norbornadiene)$Fe(CO)_3$ complex from the reaction of NBD with pentacarbonyliron (reaction 1.13). This led him to conclude (*i*) that conjugation is not an essential factor for coordination of the diene to the metal and (*ii*) that the spatial arrangement of the ligand is important for interaction and effective overlap with the metal orbitals {48}.



(reaction 1.13)

The structure of (η^4-buta-1,3-diene)tricarbonyliron was established by X-ray crystallography {57,58}. The structure found (Figure 1.6, see also 5c) is essentially that suggested by *Hallam* and *Pauson* with buta-1,3-diene in the *cisoid* arrangement.

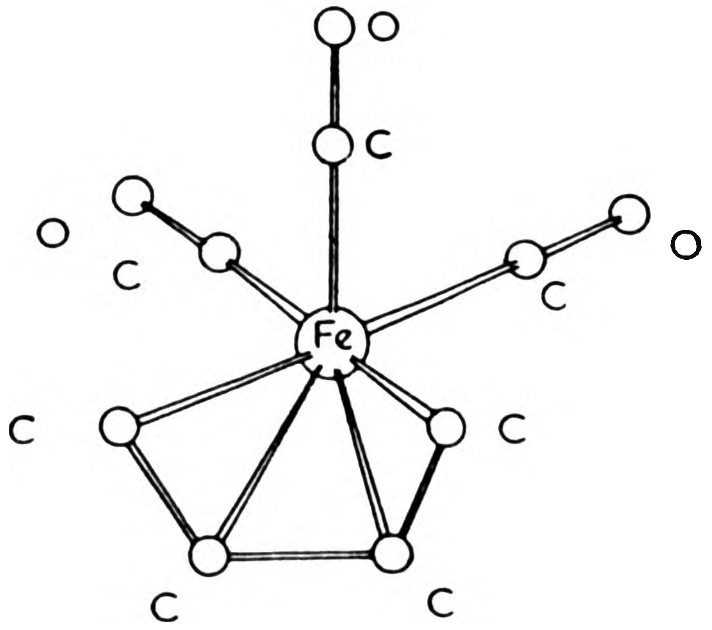
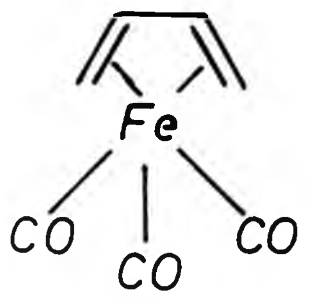


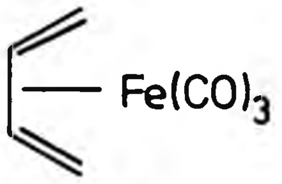
Figure 1.6: Schematic representation of the molecular geometry of (BD)Fe(CO)$_3$. {58}

The iron atom lies approximately equidistant from the four carbon atoms. The coordination geometry about the iron can be described as square pyramidal, the base of the pyramid being formed by two of the carbons of the carbonyls and the terminal carbon atoms of the buta-1,3-diene. The third carbonyl group occupies the apical position.

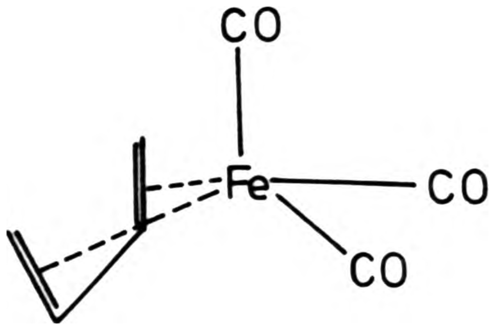
Three types of representation for (η^4-diene)tricarbonyliron complexes are found in the literature. For convenience, formulae of type **5b** are mostly used. Formulae such as **5a** are useful when it is desirable to indicate which double bonds in a polyene complex are coordinated.



5a



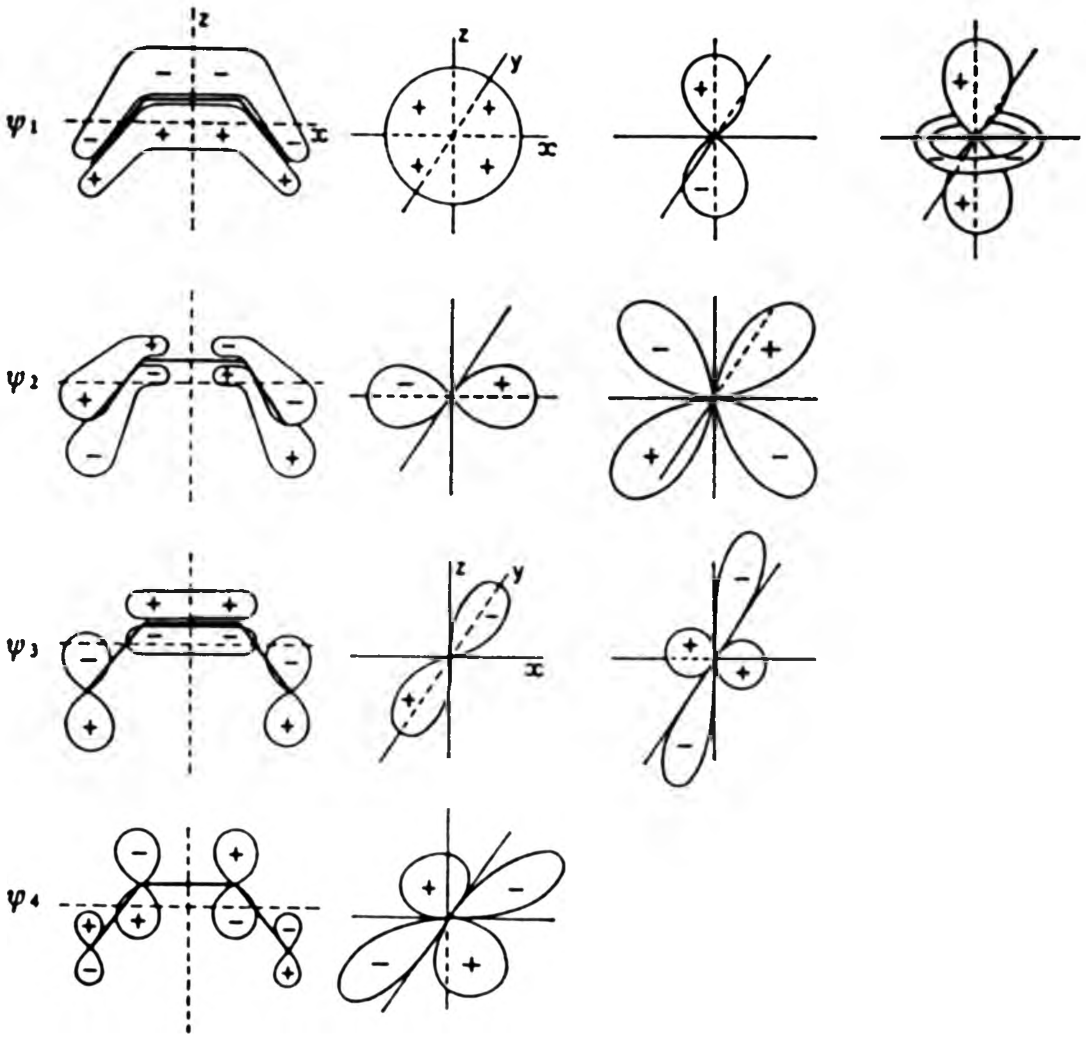
5b



5c

The description of the bonding between the diene and the metal atom is analogous to the *Dewar-Chatt-* and *Duncanson* model for monoolefin complexes. In a (conjugated diene)tricarbonyliron complex, electrons are donated from the occupied molecular orbitals ψ_1, ψ_2 of the ligand π-electron system to vacant metal orbitals. Electron back-donation from occupied metal d-orbitals into vacant ligand antibonding molecular orbitals (ψ_3, ψ_4) allows charge compensation resulting in the formation of a stable complex.

Scheme 1.3 shows the four molecular orbitals of a 1,3-diene π-system together with the metal orbitals of corresponding symmetries. For the donor character of the diene, it is essentially the ψ_2-orbital which may be considered, and for the acceptor character the ψ_3-orbital.



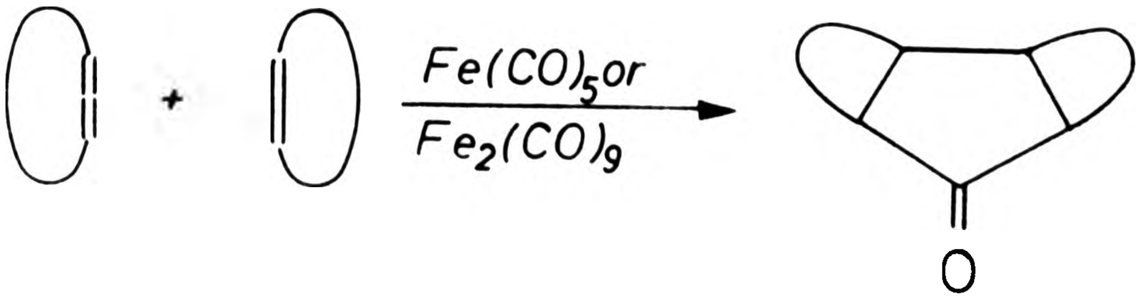
(Scheme 1.3) (taken from ref. {36})

Two early reports appeared on the ^{13}C-NMR spectrum of (η^4-buta-1,3-diene)tricarbonyliron {59}. These were concerned only with the question whether 2 or 3 was a better representation of the bonding. No attempt was made to rationalize the observation of a single sharp resonance for the three carbonyl groups, which is clearly inconsistent with either 2 or 3 and the known tetragonal pyramidal geometry of the complex {57,58} in the solid state. Nor was a variable temperature study carried out to verify whether the single line was due to accidental coincidence or nonrigid behaviour. Investigations by *Takats* et.al. {60,61,62} and *Kreiter* et.al. {63} on the variable temperature ^{13}C-NMR spectra of diene-$Fe(CO)_3$ complexes have shown that in fact intramolecular rearrangement is responsible for the single ^{13}CO resonance observed at room temperature. The low temperature limiting spectra are consistent with a square pyramidal arrangement for the diene-tricarbonyliron complexes having one apical and two equivalent basal CO groups.

1.4. Carbonyliron-mediated coupling of olefinic ligands

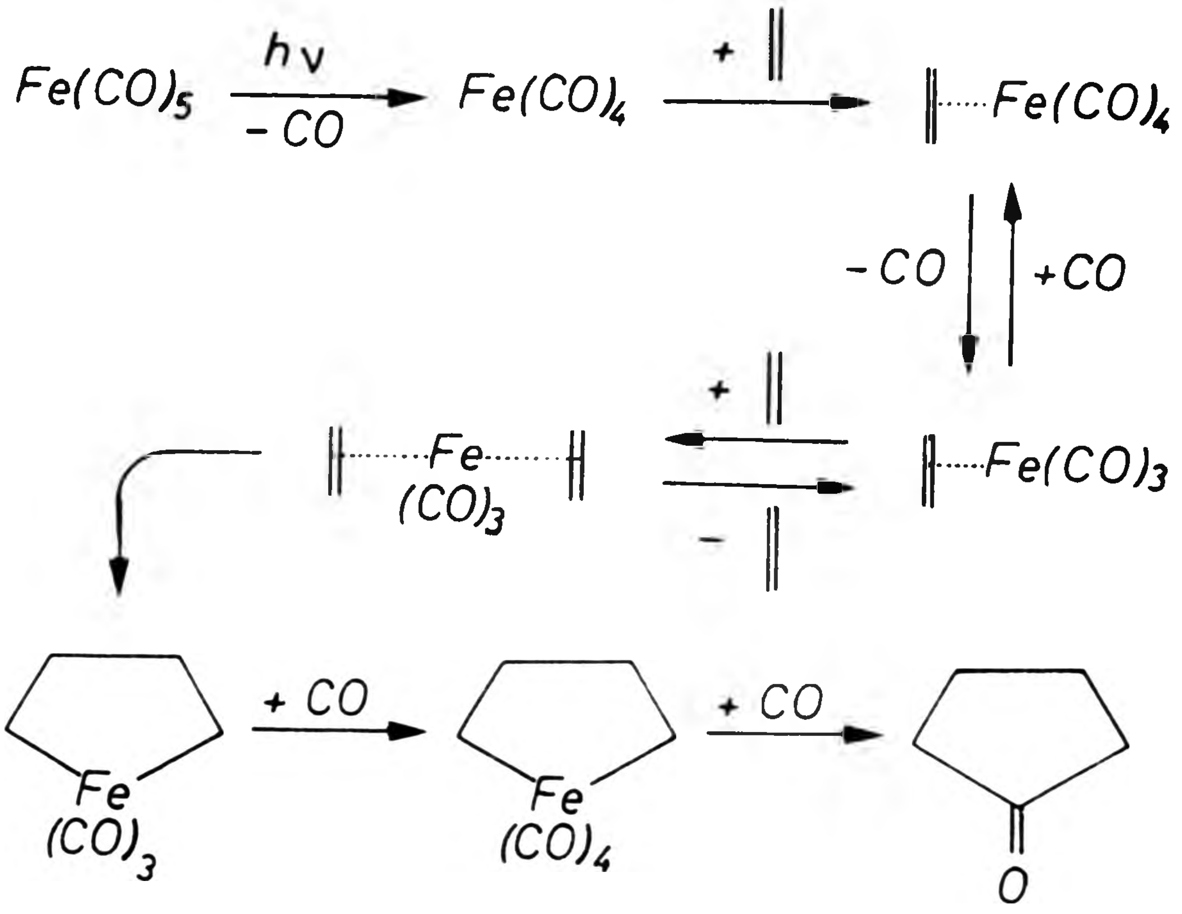
The role of iron carbonyls in organic synthesis and in metal-induced carbonylation reactions has received considerable attention.

A process leading to cyclic ketones, which has been extensively studied, is a coupling reaction in which olefin cycloaddition takes place with carbonyl insertion to generate cyclopentanones. Strained cyclic olefins such as norbornenes and cyclobutenes exhibit a pronounced tendency to react with carbonyliron complexes to form cyclopentanone derivatives {64 and refs therein} (e.g. reaction 1.14).



(reaction 1.14)

A mechanism for the formation of such cyclopentanones (Scheme 1.4) was proposed by *Weissberger* {64}. The initiating step involves occupancy by an olefin of a vacant coordination site on the metal available by prior loss of CO. In other words, the olefin coordination is subsequent to the transient presence of Fe(CO)$_4$. The reaction should continue via a series of coordinatively saturated and unsaturated iron complexes according to *Tolman's* "16 and 18 electron rule" {65}.



(Scheme 1.4)

Important species involved in the suggested mechanism are the bis(olefin)Fe(CO)$_3$ and tetracarbonylferracyclopentane complexes. The metallacyclopentane ring closure by oxidative coupling {65, of two olefins with a transition metal has been classified by *Pearson* {66,67} as a symmetry-allowed process. The basic idea is that two electrons are transferred from the metal into the symmetric combination of the olefinic LUMO (π^*) orbitals to form the carbon-carbon σ-bond. The olefinic π-electrons are used to form the two carbon-metal σ-bonds. In other words, this reaction is considered as a 2+2+2 cycloaddition reaction (Figure 1.7). The metal loses, formally, two electrons and has to take up one more ligand in order to complete its coordination sphere. However, in contrast to the above, *Weissberger* {64} was unable to isolate or detect neither the (η^2-olefin)$_2$Fe(CO)$_3$ nor the carbonylferracyclopentane species.

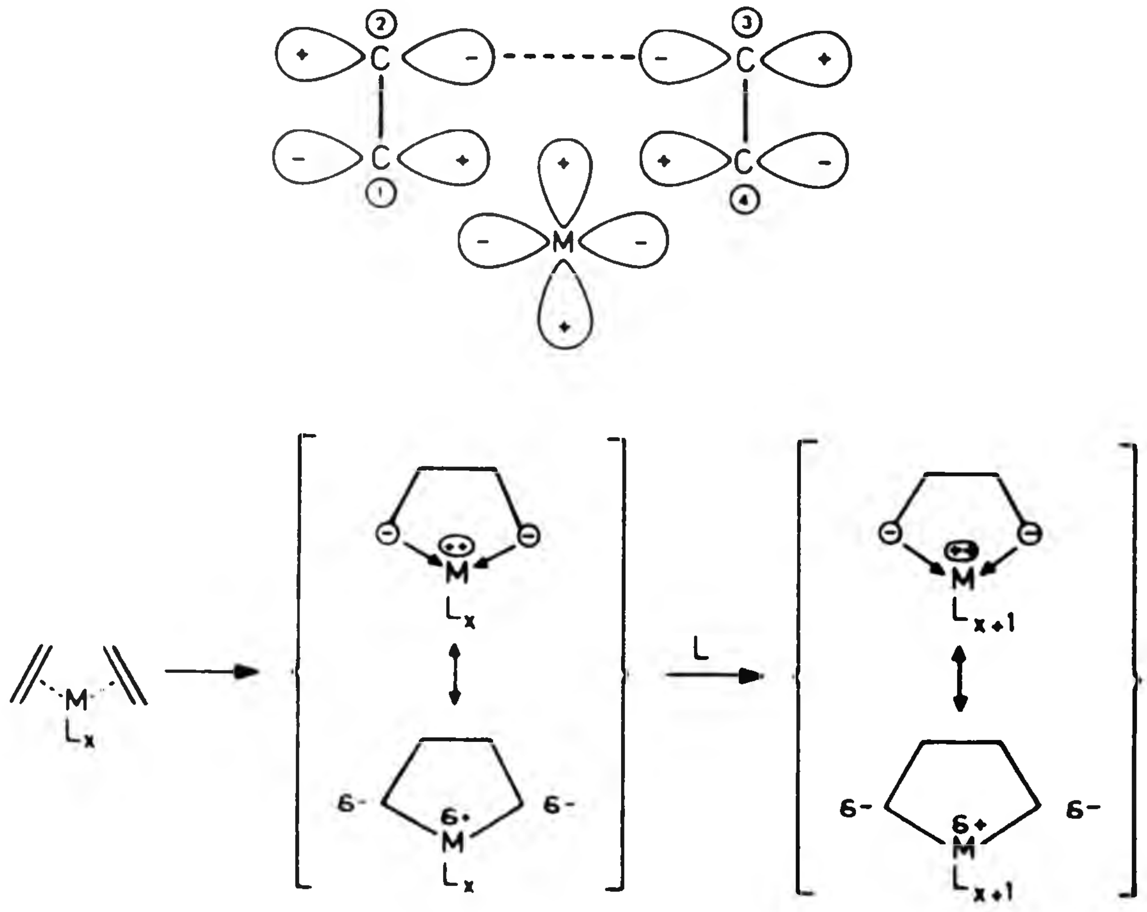
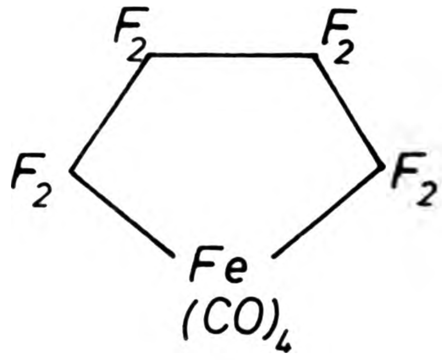


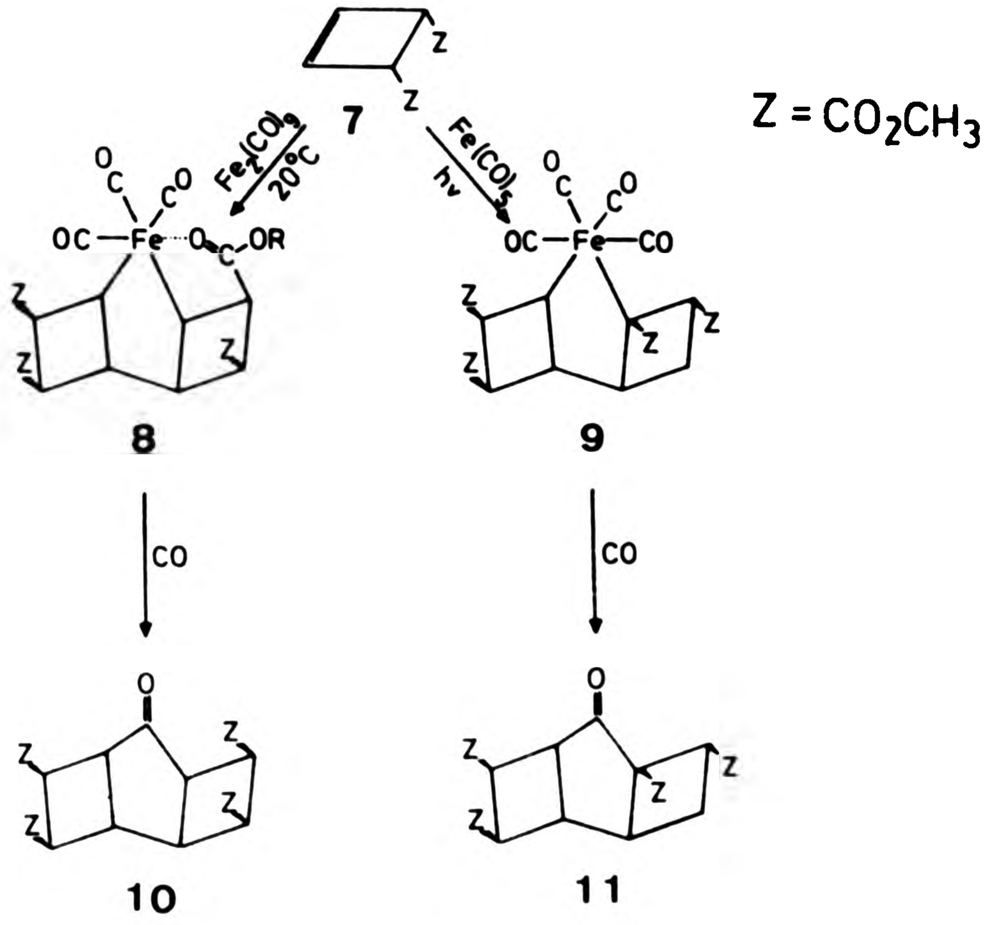
Figure 1.7: Oxidative coupling of two olefins with a metal atom

Watterson and *Wilkinson* obtained a fluorocarbon carbonyliron complex from the reaction of tetrafluorethylene with $Fe_3(CO)_{12}$ {68}. Initially it was thought that the compound was the bis-olefin derivative $(C_2F_4)_2Fe(CO)_3$. However, subsequent work showed that the compound is the ferracyclopentane derivative 6, i.e. that the olefin groups have coupled {69,70}. An acrylonitrile complex, originally thought to be (η^2-acrylonitrile)$_2$Fe(CO)$_3$ {71}, was later re-formulated as [(acrylonitrile)Fe(CO)$_3$]$_2$ {72}, where, according to an X-ray crystallographic study {73}, acrylonitrile acts as a bridging ligand.



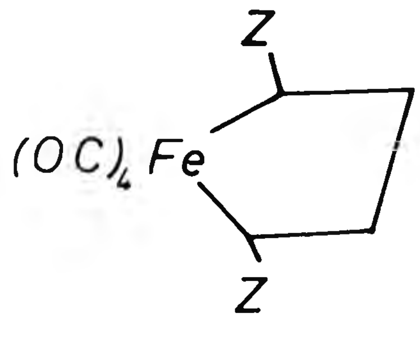
6

Thermal and photochemical reactions of the cyclobutene diester 7 with iron carbonyls (Scheme 1.5) also failed to yield complexes of type bis(η^2-olefin)Fe(CO)$_3$. Thus, thermal reaction of 7 with $Fe_2(CO)_9$ gives the tricyclic ferracyclopentane complex 8 which has the carbonyl group of one ester function occupying a coordination site {74}. The photoreaction of 7 with $Fe(CO)_5$ leads to a similar product 9. Complexes 8 and 9 give the cyclopentanones 10 and 11, respectively, {74} on treatment with carbon monoxide.

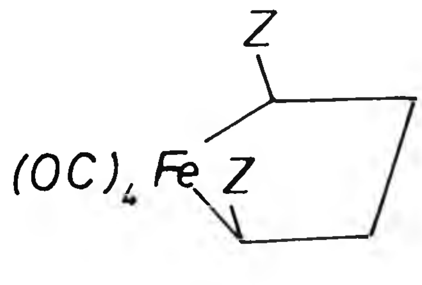


(Scheme 1.5)

Photoreactions of an iron carbonyl complex, (η^2-MA)-Fe(CO)$_4$, with methyl acrylate provided the first example where both, the metallacyclopentane derivative and the bis(η^2-olefin) metal complex, were isolated {75,76}. Irradiation of (η^2-methyl acrylate)Fe(CO)$_4$ with excess methyl acrylate in n-hexane at room temperature resulted in the formation of the tetracarbonylferracyclopentane complex 12. Two isomers, 12a and 12b, were obtained. The structure of the *trans*-disubstituted isomer 12a {77} (Figure 1.8) was established using X-ray crystallography.



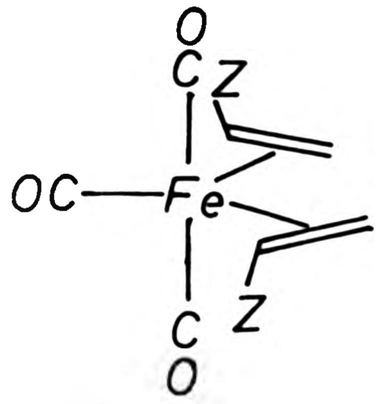
12a



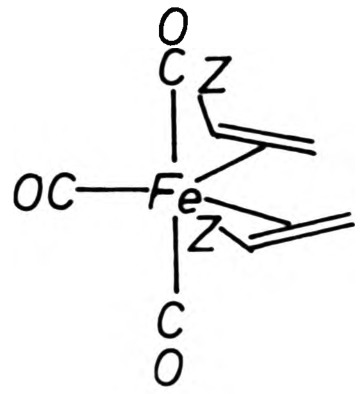
12b

$Z = CO_2CH_3$

The oxidative coupling was prevented by performing the photoreaction at lower temperature, -30 °C. Under these conditions, the (η^2-methyl acrylate)$_2$Fe(CO)$_3$ complex 13 was obtained instead of 12. The ^{1}H-NMR data indicated the presence of two stereoisomers, 13a and 13b. Hence it was concluded



13 a



13 b

$Z = CO_2CH_3$

that at room temperature 13 undergoes oxidative coupling to form the ferracycle. This regiospecific carbon-carbon bond formation between the two CH_2 groups is in accordance with the π^* orbital (LUMO) coefficients of methyl acrylate {78,79}

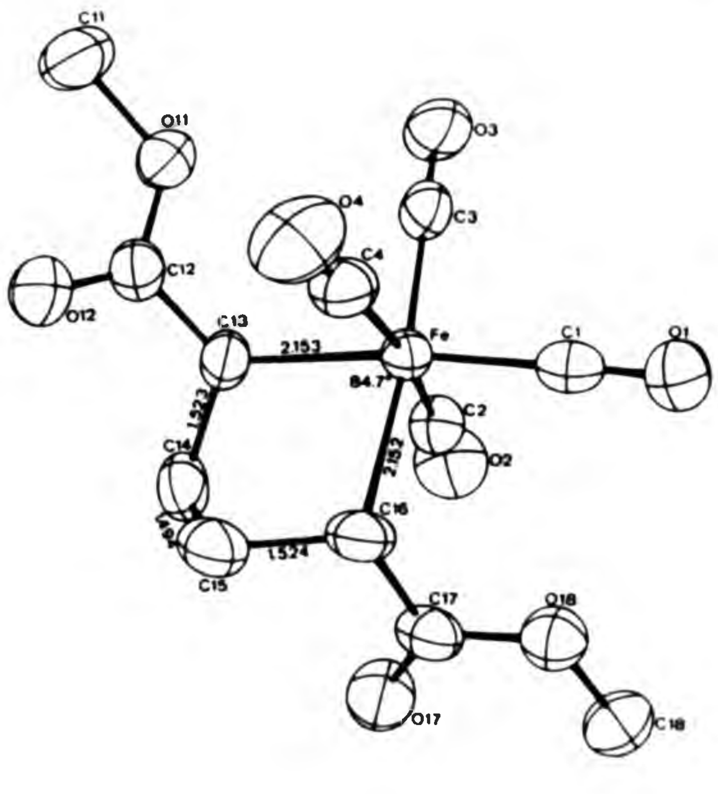
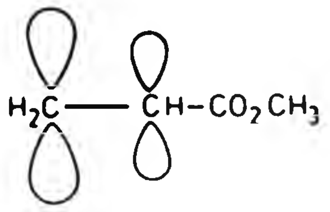


Figure 1.8: Molecular structure of tetracarbonyl-*trans*-2,5-dicarbomethoxy-ferracyclopentane {77}.

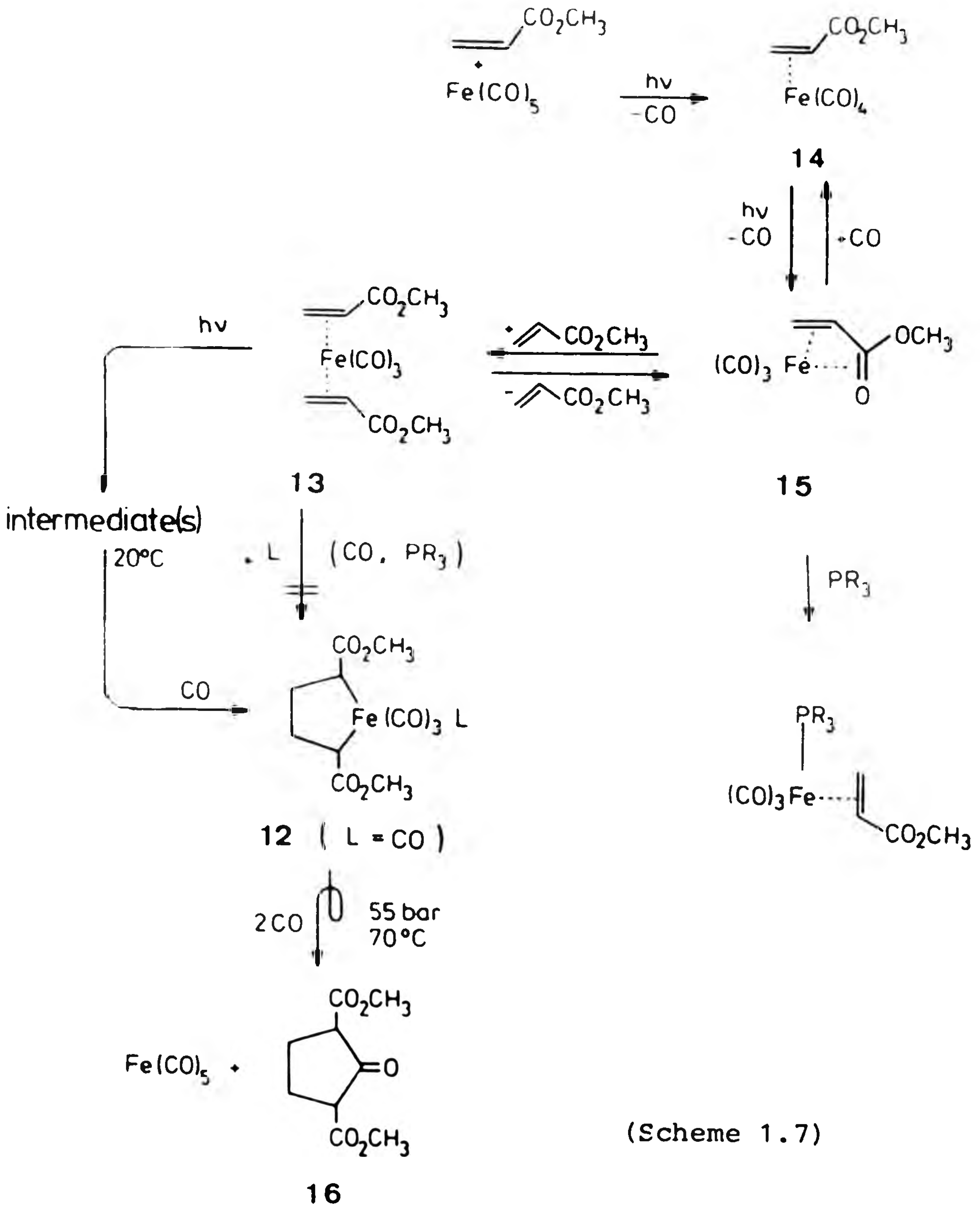
(Scheme 1.6). However, later it was shown that highly purified 13 , on treatment with carbon monoxide or triphenylphosphine as the required additional ligand, does not give any ferracyclopentane products. Instead, one of the methyl acrylate ligands is quantitatively displaced to yield (η^2-methyl acrylate)Fe(CO)$_3$L (L = CO, 14; PR$_3$), presumably via the equilibrium



π^*	0.67	- 0.47	HMO - Coefficients
π	0.43	0.33	

(Scheme 1.6)

involving the species 15 with methyl acrylate coordinated in a η^4-1-oxadiene fashion (Scheme 1.7). From these new results {76,80} it is obvious that the ring closure of 13 does not occur directly but that other intermediate(s) are involved. The nature of these intermediate species is currently being investigated {80}. It seems that ferracyclopentane formation is not a generally applicable reaction but is restricted to some special cases. For example, dimethyl maleate and dimethyl fumarate afforded the (η^2-olefin)Fe(CO)$_4$ complexes but further conversion to either (η^2-olefin)$_2$Fe(CO)$_3$ or ferracyclopentane products was not observed.



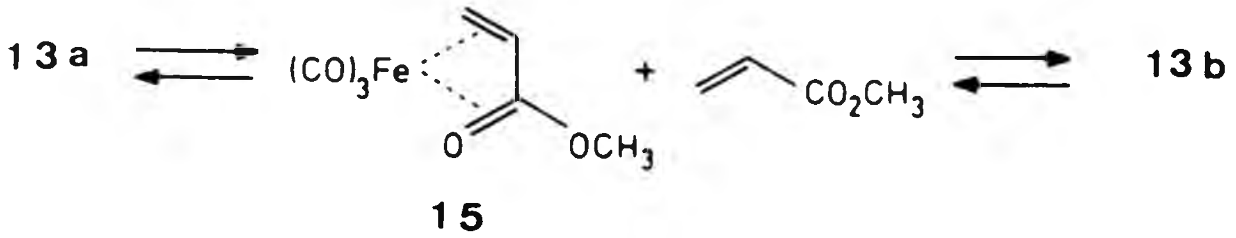
(Scheme 1.7)

Complexes of type $(\eta^2\text{-olefin})_2Fe(CO)_3$ of *cis*-cyclooctene {53}, *trans*-cyclooctene {81}, and 1,5-dimethylen-2,6-dimethyl cyclooctane {82} are known. The structures {81,82} are suitable for ring closure since the olefinic double bonds occupy two positions in the equatorial plane of the trigonal-bipyramidal complexes. However, none of these complexes has been converted to a ferracyclopentane derivative. Moreover, *Hoffmann* and co-workers, in a recent theoretical treatment {83} of (η^2-ethene)$_2$Fe(CO)$_3$ came to the conclusion that ferracyclopentane ring closure of this complex, with retention of symmetry, is a forbidden reaction.

Treatment of 12 with carbon monoxide under pressure at elevated temperature (Scheme 1.7) resulted in the formation of the expected cyclopentanone derivative 16. As summarized in Scheme 1.7, this compound is the final result of several carbonyliron mediated coupling reactions. However, unlike the analogous carbonylnickel-catalyzed process {84}, it is not possible to combine these particular steps to a catalytic cycle: the undesirable backward reaction of 13 with CO (→ 14) requires removal of liberated carbon monoxide whereas in the last step (12 → 16) CO at high pressure is required.

1.5. Ligand exchange and C-C coupling

Grevels {76} has examined the possibility that bis-(methyl acrylate)Fe(CO)$_3$, 12, may serve as a source of the tricarbonyliron unit. Particular attention was paid to the following questions (*i*) whether other unsaturated organic substrates (olefins, alkynes, 1,3-dienes) may be introduced via the equilibrium 13⇄15 (reaction 1.15) and (*ii*) subsequent

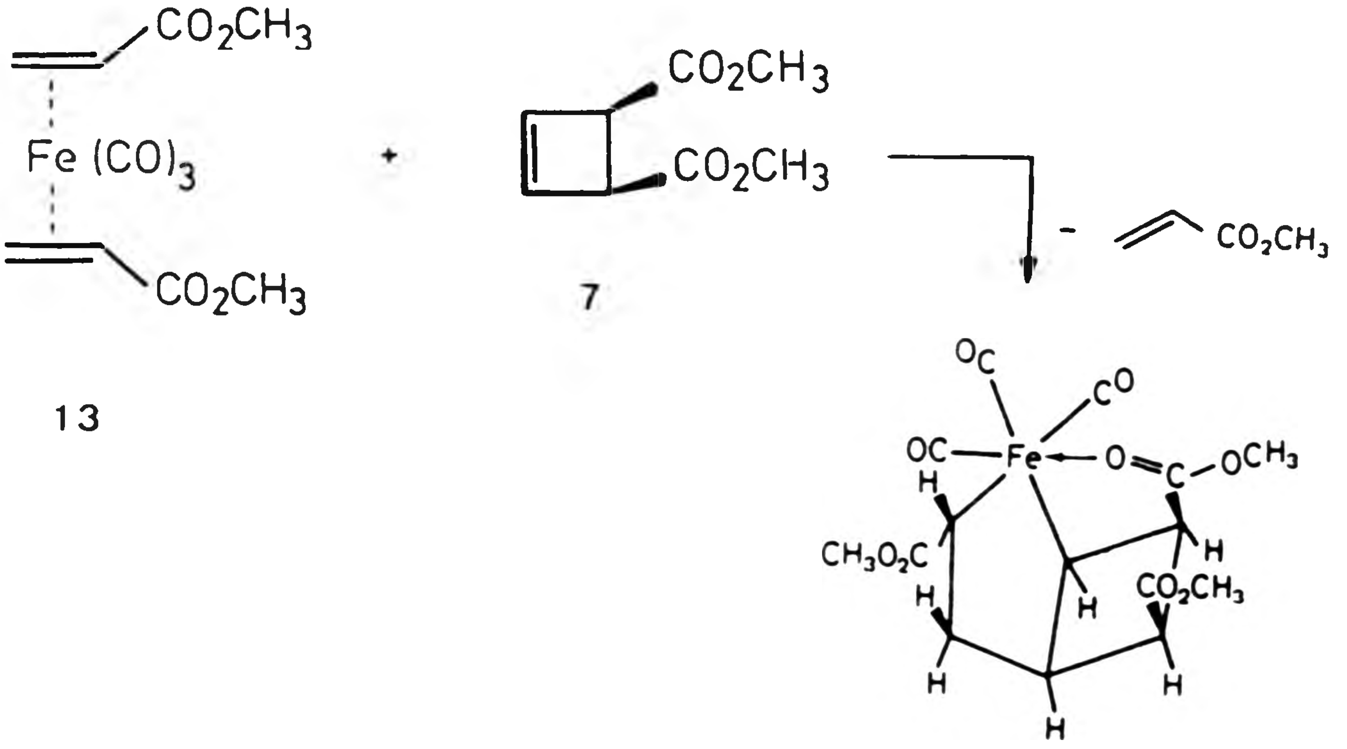


15

(reaction 1.15)

cyclization may lead to the corresponding mixed coupled products.

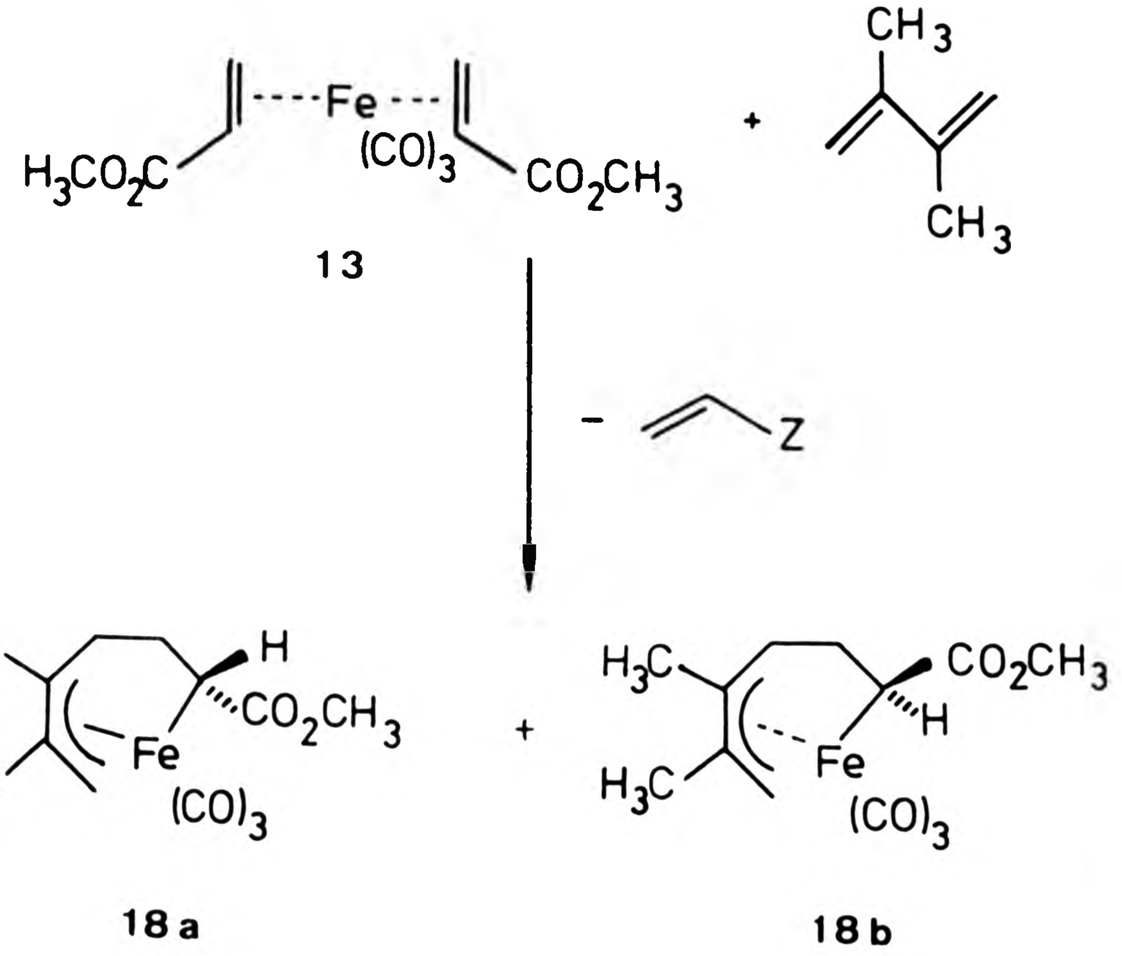
Significantly,bis(η²-methyl acrylate)Fe(CO)$_3$, 13, was found {76} to undergo ligand exchange and C-C coupling with cyclobutene-*cis*-3,4-dimethyl ester, 7. This afforded, in 5-10 % yield, the unsymmetrically substituted ferracyclopentane derivative, 17 (reaction 1.16), whose coordination geometry resembles that of 8 (Scheme 1.5).



(reaction 1.16) 17

The analogous reactions of 13 with various alkynes {76} did not afford any mixed coupling products but gave mixtures of merely alkyne-derived organocarbonyliron compounds such as the well-known {85} ferroles and cyclopentadienone complexes.

Reaction of bis(η²-methyl acrylate)tricarbonyliron, 13, with 2,3-dimethylbuta-1,3-diene provided another example of a mixed coupling product, 18 (reaction 1.17). The diene and the olefin are linked together to form a six-carbon chain which is coordinated to the Fe(CO)$_3$ moiety in a 1,4,5,6-*tetra-hapto* fashion. The C-C bond formation occurs regiospecifically at the CH$_2$ position of the acrylate component. However, the possibility of two different orientations of the ester group at the σ-bonded carbon atom gives rise to two stereoisomers (18a, 18b) which have been isolated in 3:1 to 5:1 ratio {76, 86}.

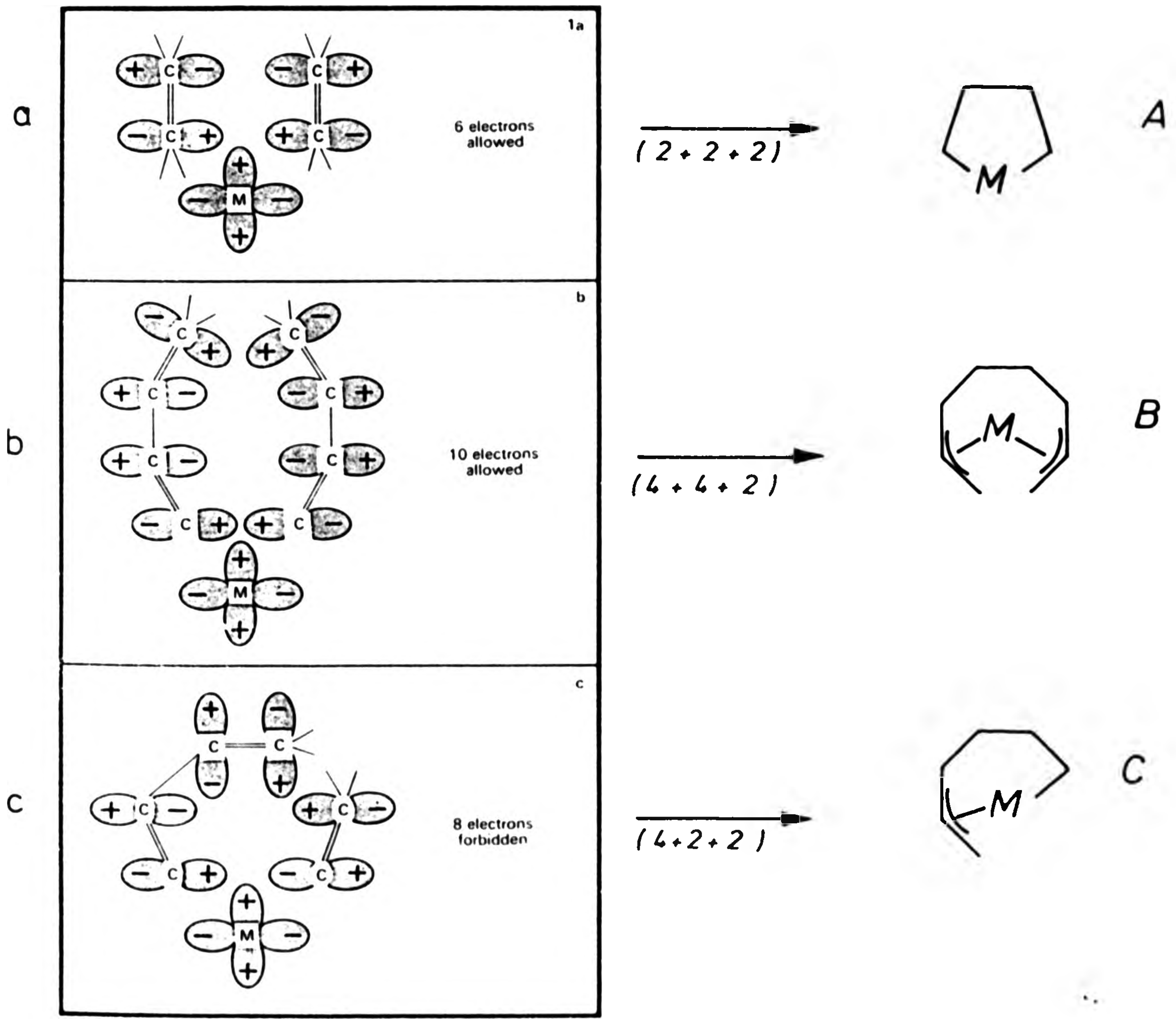


(reaction 1.17)

1.6. Statement of the problem and aim of the present study

This project is concerned with the photoinitiated coupling of dienes and monoolefins with pentacarbonyliron.

Pearson {66,67} has considered the oxidative cyclization of unsaturated organic compounds with transition metals and noted that the cyclization is accomplished using both the π-electrons of the organic moieties, and two electrons supplied by the metal. He also proposed that only the $4n+2$ reactions should be allowed (Scheme 1.8).



(taken from ref. {66})

(Scheme 1.8)

Grevels et.al. {75,76,80} have investigated olefin-olefin coupling reactions of the complex bis(η^2-methyl acrylate) tricarbonyliron (reaction type *a*, Scheme 1.8). They showed that, although cyclization occurs to give a product of type *A*, this is not a direct reaction but involves further intermediate steps.

These workers have also shown that (η^4-1,3-diene)$_2$-FeCO complexes on treatment with carbon monoxide under pressure at elevated temperature afforded Fe(CO)$_2$ complexes of type *B*, thus verifying *Pearson's* type *b* cyclization route {87}.

The aim of the present investigation is the study of diene-olefin coupling reactions (type c, Scheme 1.8) using carbonyliron complexes. In spite of *Pearson's* suggestion that this type of reaction is not allowed, some Fe(CO)$_3$ complexes of type C have been isolated, e.g. 18 (for further examples see Chapter two). However, at the outset of this project, no mechanistic investigations regarding their formation had been reported.

CHAPTER TWO

PHOTOINDUCED COUPLING REACTIONS OF DIENES, MONOOLEFINS, AND PENTACARBONYLIRON.

FORMATION AND STRUCTURAL CHARACTERIZATION OF (1-σ,4-6-η^3-ORGANO)-TRICARBONYLIRON COMPLEXES

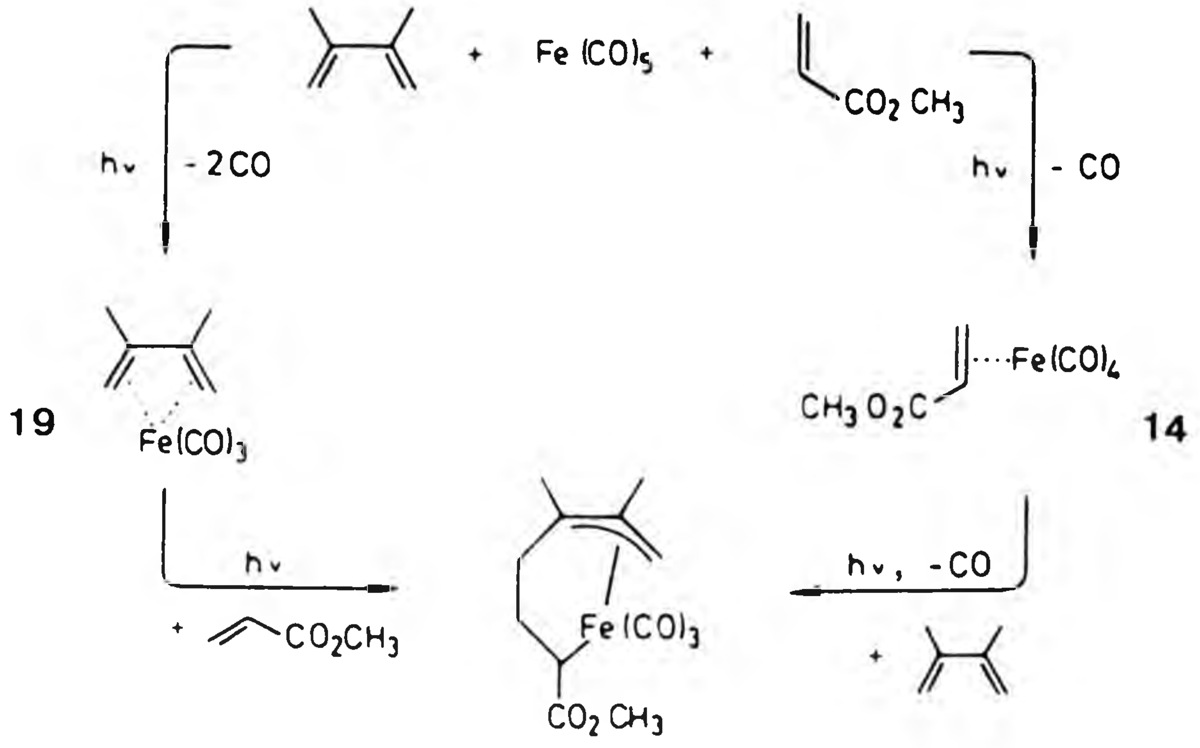
2.1. (σ,η^3-Organo)tricarbonyliron complexes

In (1,3-diene/olefin)tricarbonyliron adducts of type 18 the organic moiety is coordinated to the $Fe(CO)_3$ group in a 1,4,5,6-*tetrahapto* fashion, e.g. the six-carbon chain is bound to the metal by a σ- and a η^3-allyl type bond. Henceforth in this thesis the name (1-σ,4-6-η^3-organo)tricarbonyliron or its abbreviated presentation (σ,η^3-organo)$Fe(CO)_3$ will be used.

Such complexes were initially obtained by addition of fluoroolefins to (η^4-1,3-diene)$Fe(CO)_3$ complexes {88-90} and later on from analogous reactions of fluoroalkynes {91,92}. A preliminary communication reported that a (σ,η^3-organo)$Fe(CO)_3$ complex results from the photolysis of (η^4-buta-1,3-diene)$Fe(CO)_3$ and ethene but no details concerning this reaction or the structure of the product were given {93}.

Grevels et.al. obtained and characterized the isomeric (σ,η^3-organo)$Fe(CO)_3$ complexes 18a and 18b from the reaction of (η^2-methyl acrylate)$_2Fe(CO)_3$ with 2,3-dimethylbuta-1,3-diene {76, 86}. This group of workers also developed a much simpler procedure for the synthesis of these complexes, whereby pentacarbonyliron was photolysed in the presence of 2,3-dimethylbuta-1,3-diene and methyl acrylate {76,86}. Using this "one pot" procedure the analogous coupling of isoprene and buta-1,3-diene with methyl acrylate was also achieved {76,86}.

These "one pot" reactions proceed via the initial formation of both the (η^4-1,3-diene)Fe(CO)$_3$ (cf. reaction 1.6) and (η^2-methyl acrylate)Fe(CO)$_4$ (cf. reaction 1.4) complexes which on continued irradiation react further with the respective other organic substrate to form the (σ,η^3-organo)Fe(CO)$_3$ products (Scheme 2.1).



18

(Scheme 2.1)

The "one pot" reaction has preparative advantages and in the case of 18 leads to higher overall yield than reaction of (η^2-methyl acrylate)$_2$Fe(CO)$_3$ with the diene {86}.

During the present work an extensive study of the "one pot" reaction and of the products was undertaken. A wide range of both symmetric and unsymmetric 1,3-dienes and monoolefins were used (Table 2.1). Related reactions, e.g. the reaction of mono-

Table 2.1: 1,3-Dienes, monoolefins and iron complexes used to study the coupling reactions

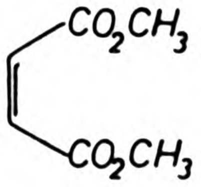
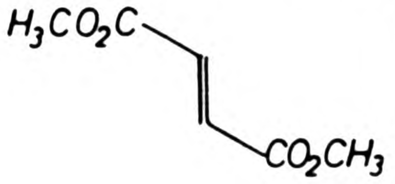
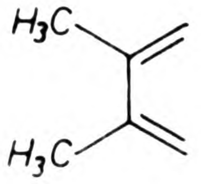
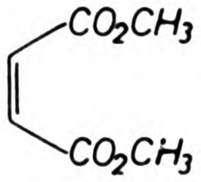
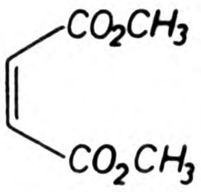
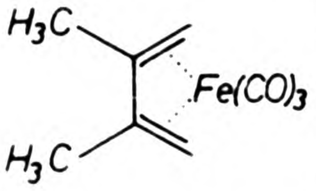
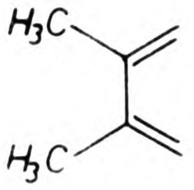
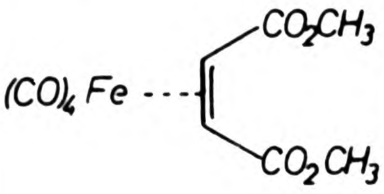
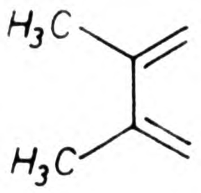
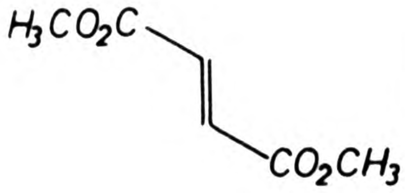
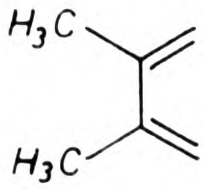
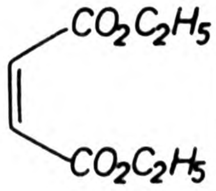
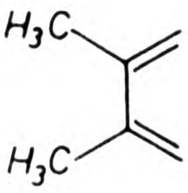
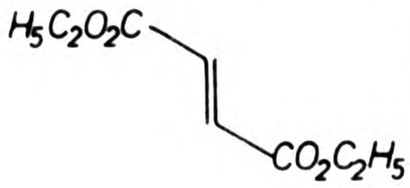
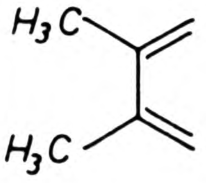
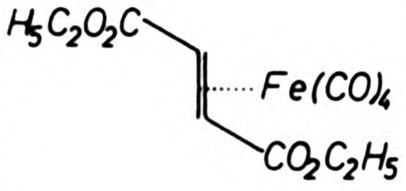
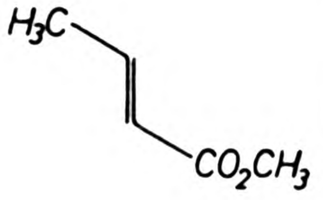
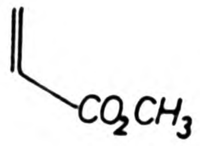
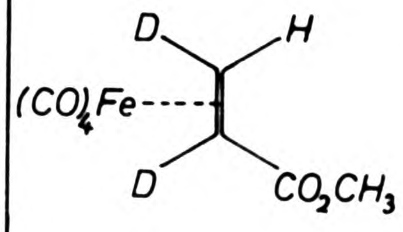
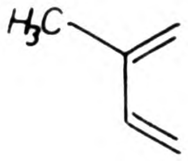
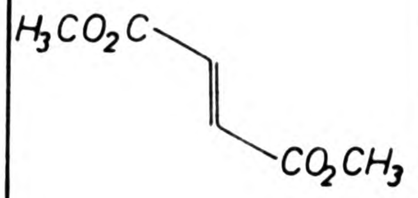
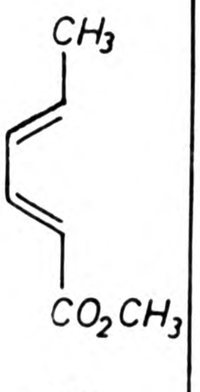
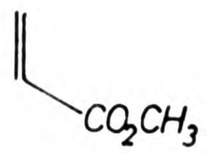
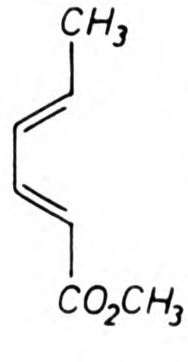
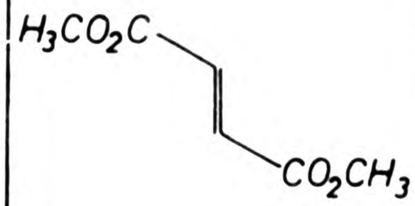
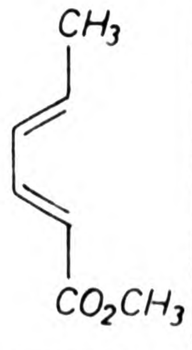
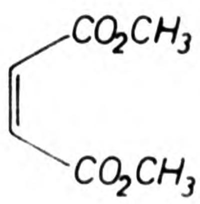
Diene	Mono-olefin	Metal -Complex
		$Fe(CO)_5$
		$Fe(CO)_5$
		$Fe(CO)_5$
		
		
		$Fe(CO)_5$
		$Fe(CO)_5$
		$Fe(CO)_5$

Table 2.1 (contd.):

		
		$Fe(CO)_5$
		$Fe(CO)_5$
		
		$Fe(CO)_5$
		$Fe(CO)_5$
		$Fe(CO)_5$
		$Fe(CO)_5$

olefins with (η^4-1,3-diene)Fe(CO)$_3$ complexes, were also examined.

The main aims of the work described in this chapter are outlined below:

(*i*) To determine whether the "one pot" reaction is more generally applicable for the synthesis of (σ,η^3-organo)Fe(CO)$_3$ complexes, and to examine how this type of reaction relates to *Pearson's* predictions (Scheme 1.8).

(*ii*) To assess further the preparative advantages of the "one pot" reaction.

(*iii*) To determine the structures of the (σ,η^3-organo)Fe(CO)$_3$ complexes arising from such reactions and to investigate how the structures relate to those of the monoolefins and 1,3-dienes used. Mechanistic aspects of these studies are presented in chapter three.

2.2. The photochemical coupling reactions of iron carbonyl complexes with 1,3-dienes and monoolefins - General synthetic and spectroscopic aspects

According to scheme 2.1 irradiation of pentacarbonyliron in the presence of a 1,3-diene and a monoolefin could lead to a coupling reaction resulting in the formation of a (σ,η^3-organo)-Fe(CO)$_3$ complex of type **18**. The present work has shown that this is indeed the case for a wide range of 1,3-diene/monoolefin pairs (Table 2.1).

During this study it was found that the best solvent for these photoreactions was diethyl ether. Each of the reaction systems examined afforded complex mixtures of products. These included the expected (σ,η^3-organo)$Fe(CO)_3$ products (which in general were mixtures of isomers) and the respective (η^2-olefin)-$Fe(CO)_4$ and (η^4-1,3-diene)$Fe(CO)_3$ complexes. Some reactions were performed in n-hexane as solvent. In these cases the same types of carbonyliron complexes resulted. However, compared with alkane solvents diethyl ether has the particular advantage that the amounts of insoluble by-products deposited on the inner wall of the irradiation apparatus are substantially smaller.

In general, the reaction mixtures were irradiated for an extended period of time (4 - 400h), depending on the starting carbonyliron complex and on the amount of material used. The progress of the reaction was monitored by means of infrared spectroscopy, and the irradiation was stopped (in order to avoid unnecessary decomposition of products) as soon as no further product formation could be detected.

In order to promote the photosubstitution of CO for the organic substrates in the initial steps of the reaction sequence (Scheme 2.1), the carbon monoxide evolved was removed from the system by purging the solution with a slow stream of argon.

The separation of the products arising from the reactions was accomplished using combinations of various techniques, most frequently sublimation/distillation, crystallization, and column chromatography. Chromatographic separations were carried out at 20 °C or, in the case of labile intermediate products, at -30 °C. Because of the complexity of the separation procedures loss in yields often resulted. In some cases, complete separation and isolation of all the isomeric (σ,η^3-organo)Fe(CO)$_3$ products of a reaction could not be achieved, although these products were detectable in the reaction mixture by means of IR and/or NMR spectroscopy.

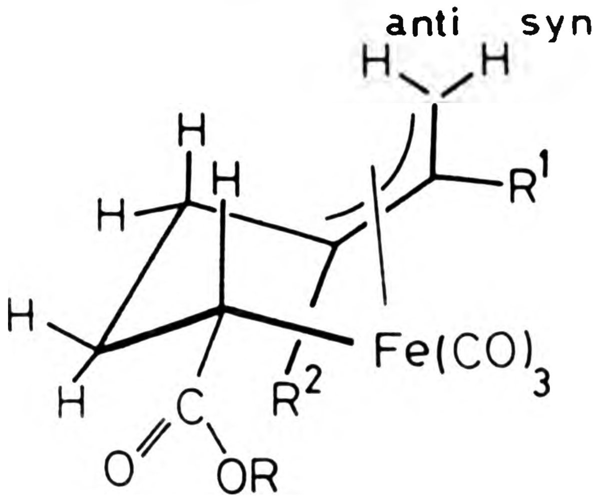
The (σ,η^3-organo)Fe(CO)$_3$ complexes obtained during this study were characterized using IR, mass, and NMR spectroscopic techniques. Their stereochemistry was established using both ^{1}H- and ^{13}C-NMR spectroscopy. In most cases, IR spectroscopy was used as a convenient method for the tentative assignment and identification of the particular compounds.

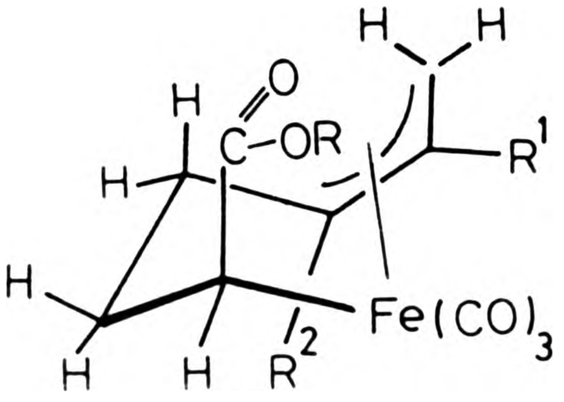
Grevels et.al., in their investigations of (σ,η^3-organo)Fe(CO)$_3$ complexes derived from methyl acrylate and 1,3-diene (Table 2.2) {76,86}, recognized an empirical correlation between the structure and infrared data of these compounds. In each of these cases, the complex exists in two isomeric forms which they labelled as $\underline{\underline{a}}$ and $\underline{\underline{b}}$ isomers.

Using NMR spectroscopy and in two cases X-ray crystallography {76,86}, they established that in isomers of type $\underline{\underline{a}}$ the ester group is directed away from the η^3-allyl group (*exo*-orientation) whereas in isomers of type $\underline{\underline{b}}$ the arrangement is *endo*. These workers noted that in the infrared spectra the ester carbonyl and the metal carbonyl frequencies are higher in the $\underline{\underline{a}}$ isomers than in the corresponding $\underline{\underline{b}}$ isomers. Another characteristic feature is the larger difference between the CO stretching bands (2) and (3) in the case of compounds of type $\underline{\underline{a}}$ compared with those of type $\underline{\underline{b}}$.

As will be shown later, most of the compounds prepared in this work also obeyed these empirical correlations.

Table 2.2: Infrared and ^{1}*H-NMR spectroscopic data {76} of* *(σ,η^{3}-organo)Fe(CO)$_3$ complexes {76,86}*





complex	$\tilde{\nu}$/cm^{-1} (1)	(2)	(3)	(ester)	δ/ppm H^{anti}	H^{syn}
$R^1=R^2=CH_3$						
isomer $\underline{\underline{a}}$ ($\underline{\underline{18a}}$)	2062.5	2006.5	1984	1709	1.81	2.95
isomer $\underline{\underline{b}}$ ($\underline{\underline{18b}}$)	2058	1999	1982	1694	3.00	2.79
$R^1=H, R^2=CH_3$						
isomer $\underline{\underline{a}}$	2064.5	2008	1990	1707.5	1.77	2.85
isomer $\underline{\underline{b}}$	2060	2000	1989	1701	3.11	2.89
$R^1=R^2=H$						
isomer $\underline{\underline{a}}$	2068.5	2012.5	1995	1708	1.86	2.89
isomer $\underline{\underline{b}}$	2064.5	2005	1994.5	1701	3.25	3.00

2.3. The photochemical coupling reactions of iron carbonyl complexes with symmetric dienes and monoolefins

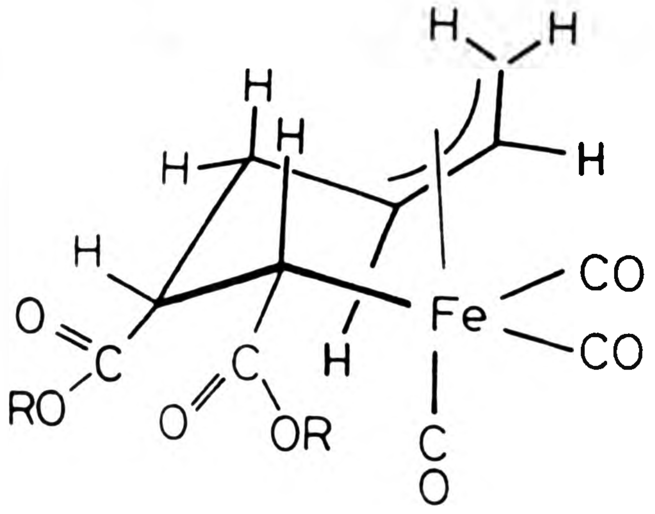
In this part of the study, reactions involving buta-1,3-diene or 2,3-dimethylbuta-1,3-diene with olefinic diesters (dimethyl maleate, dimethyl fumarate, diethyl maleate, and diethyl fumarate) or with methyl crotonate were investigated. The previously reported study {86} of the reaction involving buta-1,3-diene and methyl acrylate has been extended and the related system involving *cis*-d_2-methyl acrylate has been investigated.

2.3.1. Reaction involving buta-1,3-diene and maleic or fumaric esters

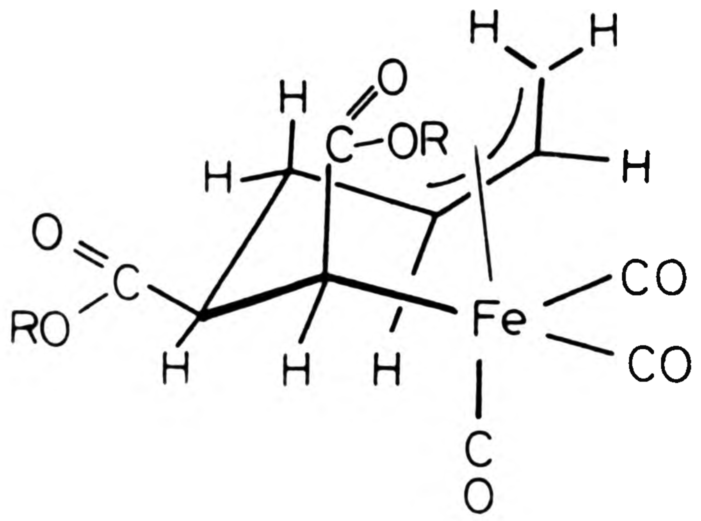
Extended photolysis of pentacarbonyliron in the presence of buta-1,3-diene and dimethyl maleate (1:2:2 molar ratio, in diethyl ether) resulted in the formation of two isomeric (σ,η^3-organo)Fe(CO)$_3$ coupling products: *tricarbonyl{1,4,5,6-*η^4*-[cis-1(endo),2-dicarbomethoxy-hex-4-en-1,6-diyl]}iron*, 20b, and *tricarbonyl{1,4,5,6-*η^4*-[cis-1(exo),2-dicarbomethoxy-hex-4-en-1,6-diyl]}iron*, 20a. The latter isomer was obtained in fair yield (33 %) but the yield of the former was very poor (3 %). This reaction also afforded two other products, the complexes (η^4-BD)Fe(CO)$_3$ and (η^2-DMM)Fe(CO)$_4$.

From the analogous reaction involving dimethyl fumarate only one (σ,η^3-organo)Fe(CO)$_3$ complex was isolated (28 % yield) and characterized: *tricarbonyl{1,4,5,6-*η^4*-[trans-1(exo),2-dicarbomethoxy-hex-4-en-1,6-diyl]}iron*, 21a. The infrared spectra of the mother liquors from the crystallization of 21a indicated that the second isomer, 21b (ν(CO) = 2068, 2010, 1999 cm^{-1}; (ester-CO)

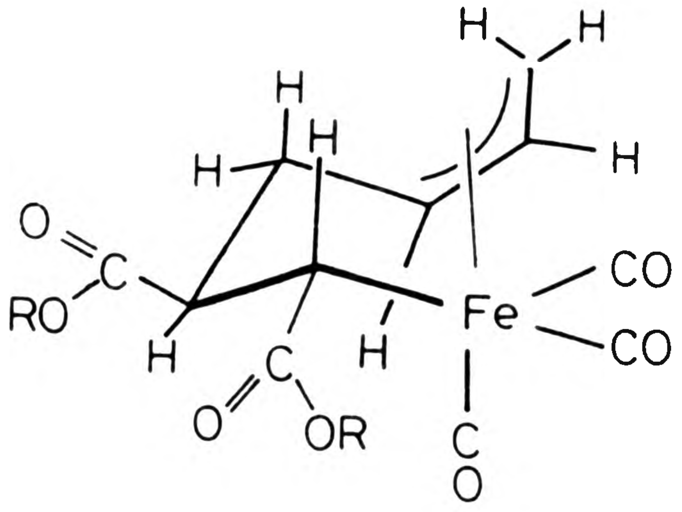
1737, 1701 cm^{-1}, in n-hexane), was present in minor amounts. The reaction also afforded the complexes (η^4-BD)Fe(CO)$_3$ and (η^2-DMF)-Fe(CO)$_4$.



20a



20b



21a

R= CH_3

Both the mass and infrared spectra of the complexes 20a, 20b, and 21a showed the presence of the tricarbonyliron unit.

The mass spectra of these compounds did not show peaks corresponding to the molecular ion at m/e 338 but included peaks corresponding to the ions $[M-nCO]^+$ (n = 1-3) and $[M-OCH_3]^+$ (Figure 2.1).

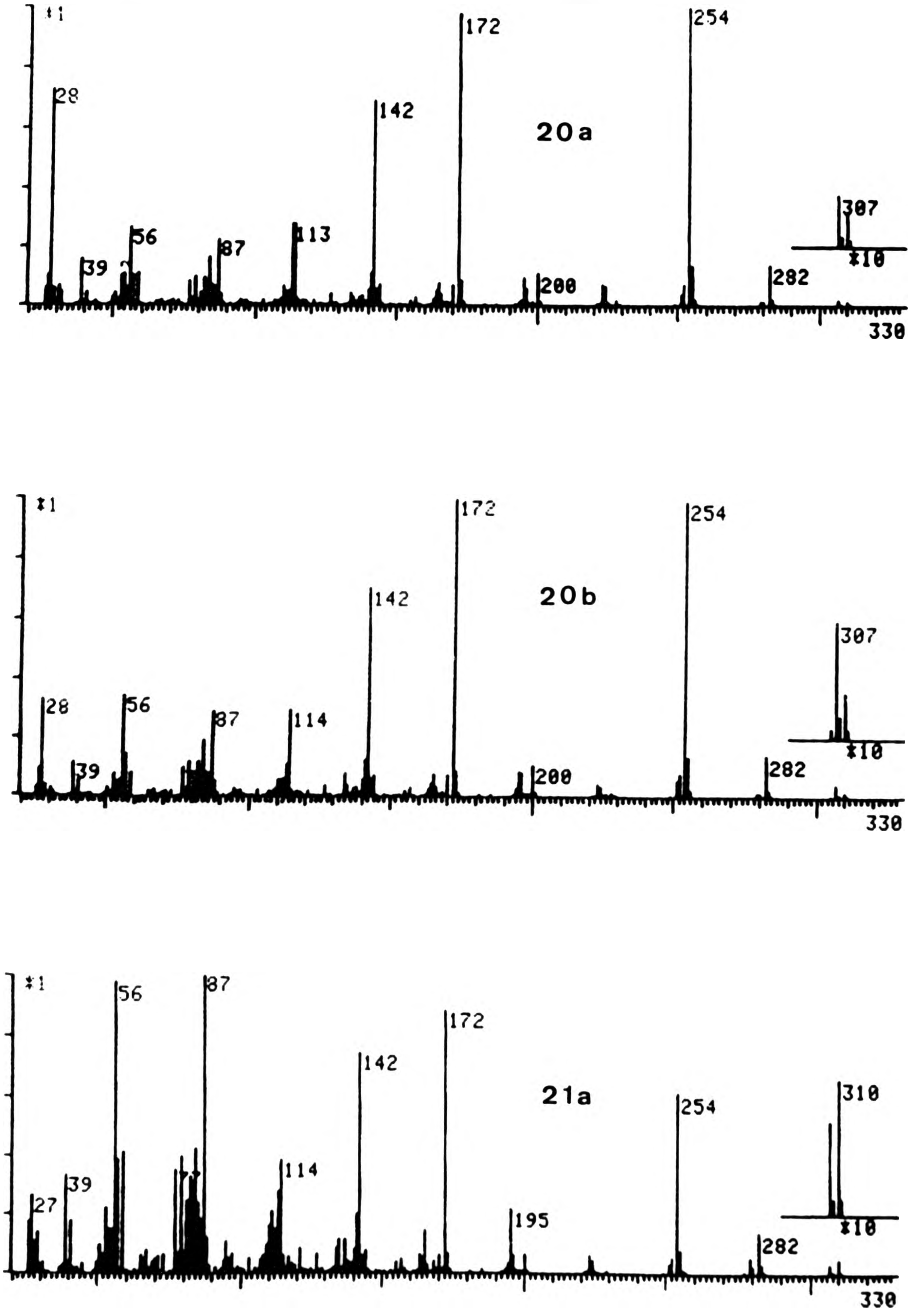


Figure 2.1: Mass spectra of 20a, 20b and 21a.

The IR spectra (Table 2.3, Figure 2.2) showed the typical CO stretching vibration pattern of the pyramidal $Fe(CO)_3$ group {94}, i.e. three bands of comparable intensities in the 2000 cm^{-1} region. The infrared spectra also included two bands at ca. 1750 and 1700 cm^{-1} due to the ester carbonyl vibrations. The band at the lower wavenumber can be assigned to the ester group attached to the α-carbon atom, i.e. the carbon atom which is σ-bonded to the metal (cf. compounds listed in Table 2.2).

Table 2.3:IR-data (cm^{-1}, n-hexane) for (cis- and trans-dimethyl ester substituted monoolefin/buta-1,3-diene)$Fe(CO)_3$ adducts.

complex	$\tilde{\nu}$(CO)			$\tilde{\nu}$(ester-CO)	
	(1)	(2)	(3)	(β)	(α)
20a	2072.0	2017.0	2000.4	1749.9	1708.0
20b	2069.1	2011.4	1996.7	1746.6	1698.2
21a	2072.0	2017.3	1999.3	1743.4	1712.0

The stereochemistry of the complexes 20a, 20b and 21a was established using ^1H- and ^{13}C-NMR spectroscopy. The ^1H-NMR spectra of all the complexes showed, in addition to two singlets associated with the two methyl ester groups, a number of multiplets due to the remaining eight protons (H^1, H^4-H^{10}). Furthermore the coupling pattern confirmed the coupling of the buta-1,3-diene with the olefin.

The ^1H-NMR spectrum of compound 20a is shown in Figure 2.3. Detailed analysis of the spectrum was confirmed by a series of double resonance experiments and the results, summarized in Table 2.4, are consistent with the proposed structure. The

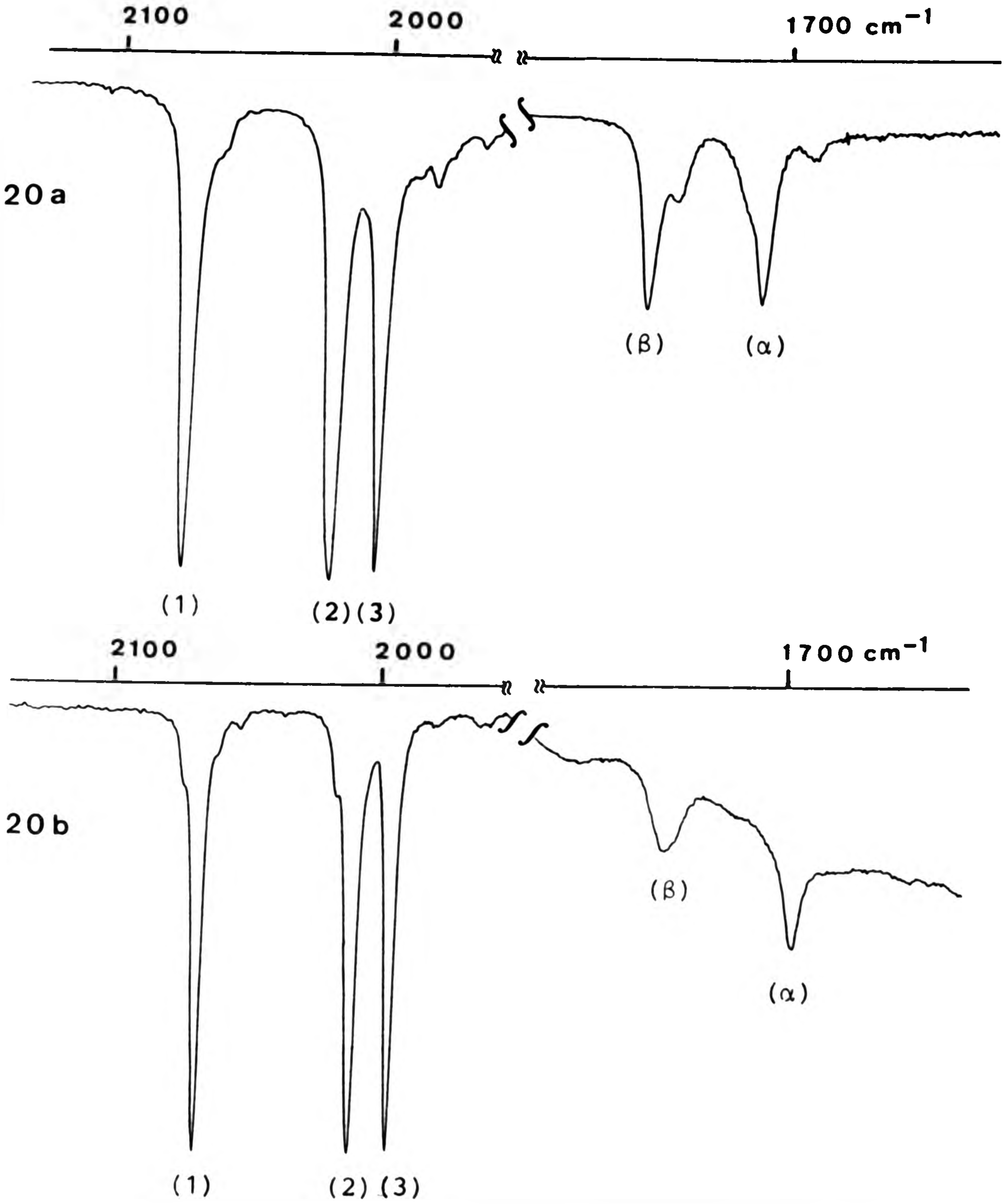


Figure 2.2: Infrared spectra (CO stretching vibrational region) of 20a and 20b.

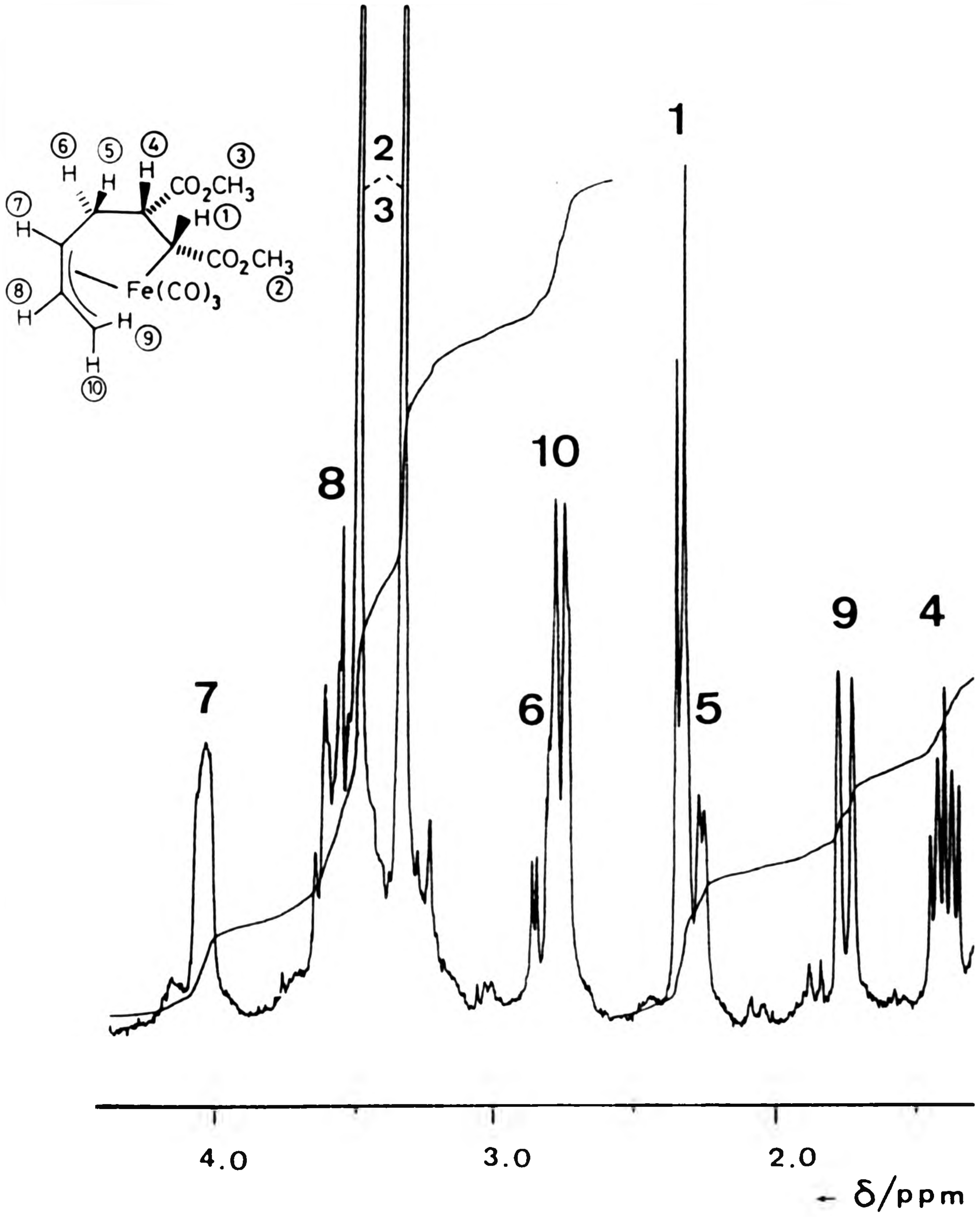


Figure 2.3: ^{1}H-NMR spectrum of *tricarbonyl{1,4,5,6-*η^4*-cis-1(exo), 2-dicarbomethoxy-hex-4-en-1,6-diyl}iron* 20a (small splittings, not visible in this figure, were taken from expanded scale spectra, cf. Table 2.4); in C_6D_6, 27 °C ±1, Bruker WH 270.

Table 2.4: ^{1}H-NMR-data for DMM/BD and DMF/BD(σ,η^3-organo)Fe(CO)$_3$ adducts a)

		20a	**20b**	**21a**
δ/ppm b)				
	H^1	2.35	3.12	1.99
	H^2 }	3.35	3.29	3.22
	H^3 }	3.50	3.41	3.58
	H^4	1.40	2.96	3.56
	H^5	2.30	1.99	0.70
	H^6	2.82	2.14	1.90
	H^7	4.04	~4.08	~4.01
	H^8	3.56	~4.13	~4.05
	H^9	1.76	2.78	2.01
	H^{10}	2.77	3.06	2.91
J/Hz				
	(1,4)	7.1	6.6	12.1
	(4,5)	6.3	13.2	12.9
	(4,6)	13.7	6.0	6.0
	(5,6)	13.2	13.2	13.0
	(6,7)	4.7	7.0	8.0
	(7,5)	~2.5	7.7	7.0
	(7,10)	~0.5	1.5	1.9
	(9,10)	2.0	1.5	1.9
	(8,9)	13.3	11.4	12.0
	(8,10)	9.2	6.6	7.2
	(1,6)	-	1.5	-
	(7,8)	9.5	8.0	~8.0

a) *in benzene-d$_6$, Bruker WH 270, at 27 °C ±1.*

b) *for assignments of the protons, cf. Figures 2.3, 2.4, and 2.5.*

spectrum shows the characteristic features of a η^3-allyl system {95-100}. A doublet of doublets centred at δ 1.76 ppm is assigned to the inner (*anti*) terminal proton H^9. The outer (*syn*) terminal allyl proton H^{10} appears at δ2.77 ppm exhibiting coupling with protons H^9, H^8 and H^7. The central allylic proton H^8 appears at δ 3.56 ppm and the remaining allylic proton H^7 as a multiplet centred at δ 4.04 ppm.

In double resonance experiments with irradiation at H^9 or H^{10}, the resonance assigned to H^8 collapsed into a triplet or a doublet of doublets, respectively. Irradiation at H^8 collapsed H^9 and H^{10} into doublets.

The methylene protons H^5 and H^6 appear as multiplets centred at δ 2.30 and δ 2.82 ppm, respectively. The aliphatic proton H^4 resonates as an apparent quintet centred at δ 1.40 ppm. The other remaining proton, H^1, attached to the σ-bonded carbon atom resonates as a doublet centred at δ 2.35 ppm.

The two carbomethoxy groups (H^2 and H^3) appeared at δ 3.35 and δ 3.50 ppm, respectively, but no definite assignment of each could be made.

The spectrum of compound 20$\underline{\underline{b}}$ (Figure 2.4) was analyzed in a similar manner and the results are listed in Table 2.4. The coupling pattern of the η^3-allylic protons, H^7-H^{10}, resembles that in isomer 20$\underline{\underline{a}}$.

The coupling between H^7 and H^8 (9.5 Hz and 8.0 Hz in 20$\underline{\underline{a}}$ and 20$\underline{\underline{b}}$, respectively) indicates that these protons in

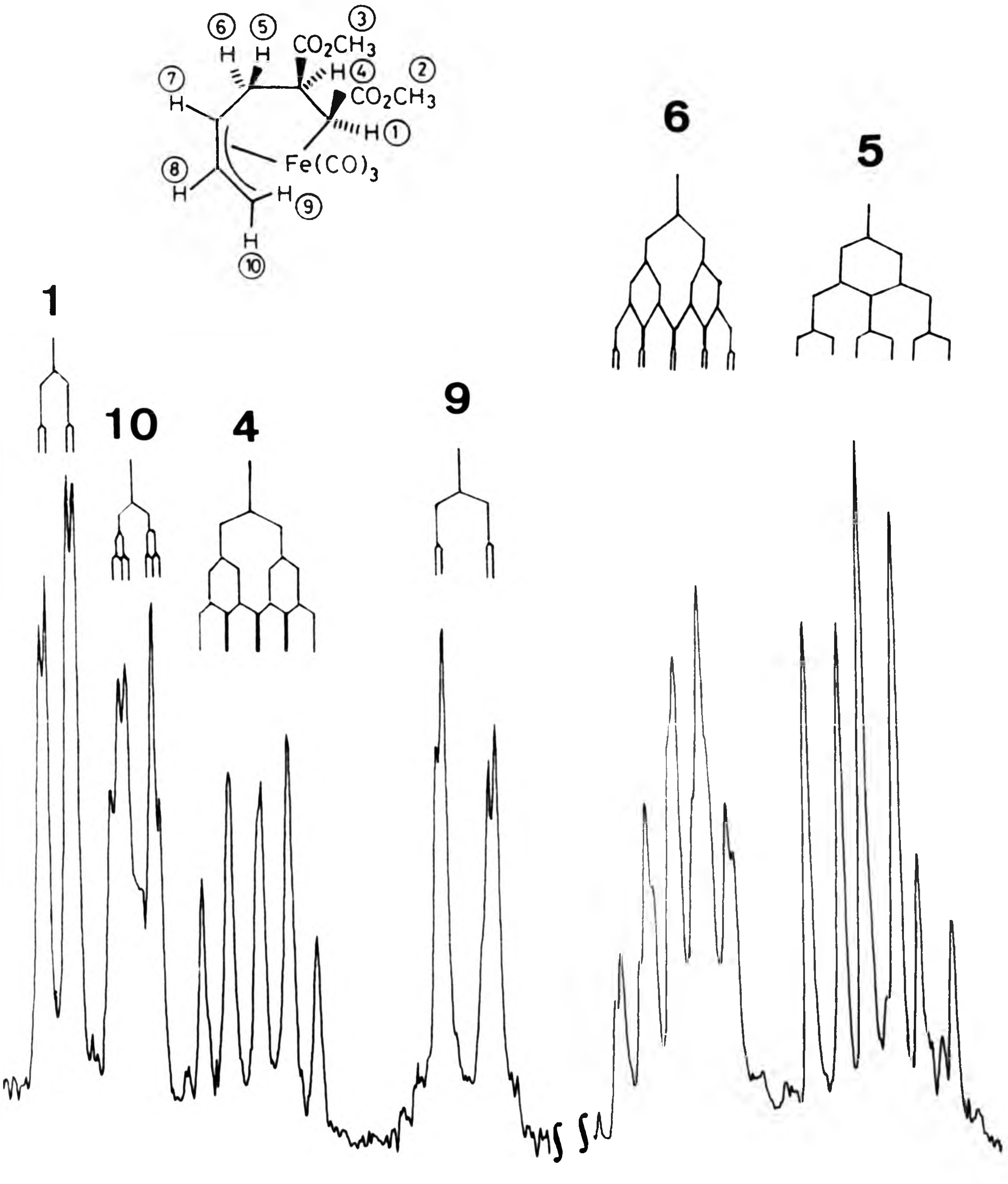


Figure 2.4: Proton resonances and coupling patterns of the individual protons of $20\underline{\underline{b}}$; in C_6D_6 at 27 °C ±1, Bruker WH 270.

both compounds are *cis* to each other. Accordingly, a long range coupling of the so-called "W" type is observed between H^7 and H^{10}. Hence it follows that the aliphatic part of the six-carbon chain is attached to the η^3-allyl moiety via the *anti*-position.

Furthermore, for both compounds $J(H^1\text{-}H^4)$ is typical of a *gauche*-coupling, corresponding to the *cis*-arrangement of these protons in the starting olefin, dimethyl maleate. In **20b**, H^4 exhibits a *trans*-coupling with H^5 and a *gauche*-coupling with H^6 whereas the reverse is observed for isomer **20a**.

An important feature of **20b** is the observation of the long range coupling $J(H^1\text{-}H^6) = 1.5$ Hz which is absent in **20a**. This indicates that in **20b** H^1 and H^6 adopt a so-called "W" arrangement which is possible only if H^1 is directed away from the η^3-allyl moiety, i.e. if the ester group attached to the σ-bonded carbon atom (α-position) is in the *endo*-orientation.

The chemical shift of the *anti*-allylic proton H^9 provides further evidence for this structural assignment. In the above-mentioned $(\sigma,\eta^3\text{-organo})Fe(CO)_3$ complexes investigated by *Grevels* et.al. {76,86} (Table 2.2) H^{anti} experiences a significant (~ 1 ppm) downfield shift in going from isomer **a** to isomer **b** type of complexes. This can be explained in terms of the magnetic anisotropic effect of the α-ester group which, in type **b** isomers, is situated closely to the hydrogen H^9 (H^{anti}). As shown in Table 2.4, the chemical shifts of H^9

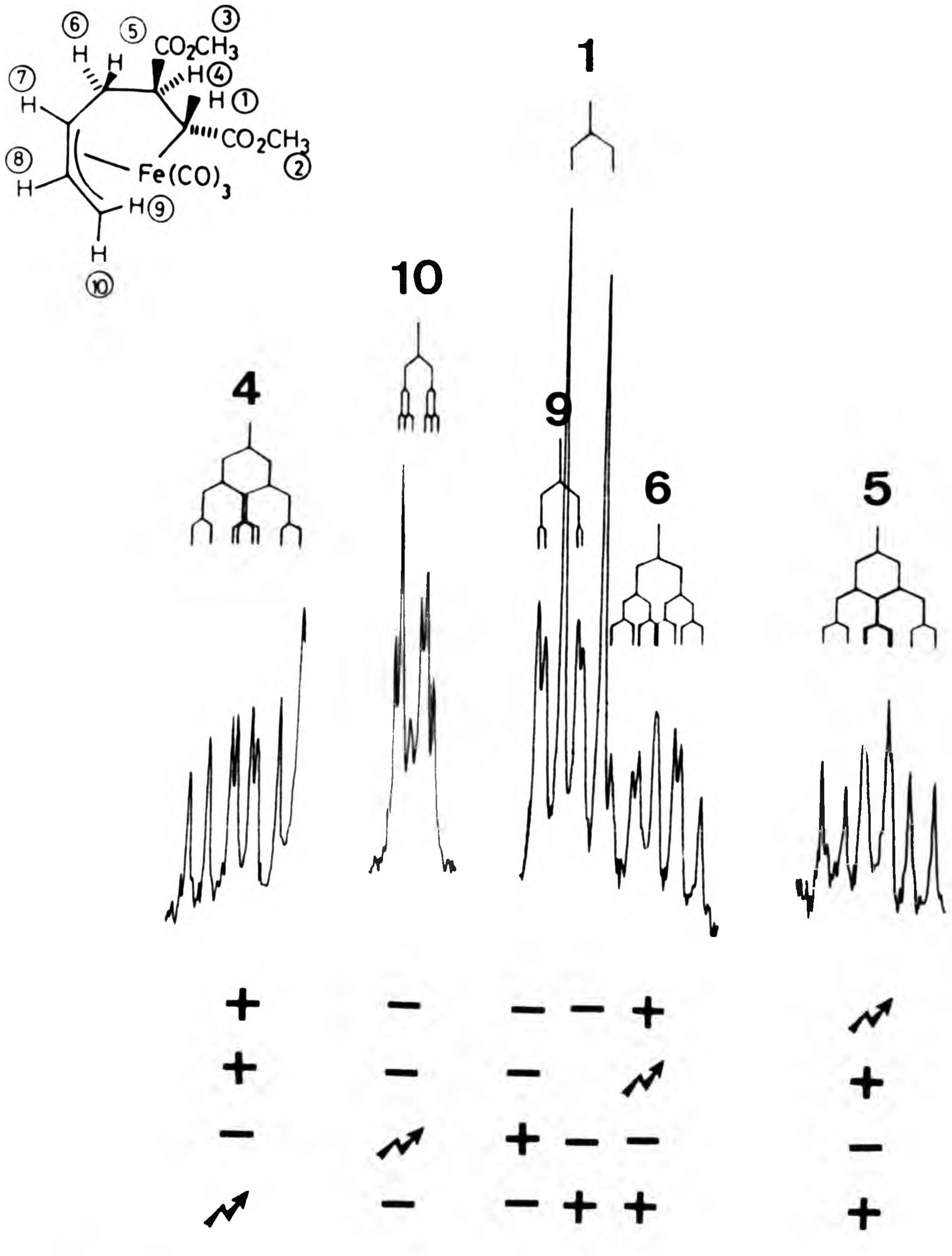
in the isomers 20a and 20b follow the same tendency, thus indicating that in 20b the α-ester group is *endo*-oriented.

The ^{1}H-NMR data of 21a are listed in Table 2.4. The appearance of the H^1, H^4-H^6, H^9 and H^{10} is shown in Figure 2.5. This Figure also shows the results of some decoupling experiments which confirm the particular assignments. The coupling pattern is nearly identical to that of 20b with two exceptions: the coupling constant $\{J(H^1-H^4) = 12.1$ Hz$\}$ is large, characteristic of *trans* coupling, and long-range "W"-type coupling, between H^6 and H^1, has disappeared.

Thus, the two ester groups are situated in a *trans*-arrangement and, since H^1 is *endo*-oriented, the ester group attached to the σ-bonded carbon atom is in the *exo*-position. Accordingly, H^9 (see Table 2.4) appears at higher field, i.e. the chemical shift between H^9 and H^{10} is in the range of 1 ppm as it is observed in 20a.

An essential conclusion drawn from the ^{1}H-NMR spectra of 20a, 20b and 21a, is that the *cis*- or *trans*-configuration of the olefin component is retained in the coupling product.

The ^{13}C-NMR spectra of compounds 20a, 20b (Figure 2.6 and 2.7; Table 2.5) and 21b (Table 2.5) confirm the σ,η^3-coordination of the C_6-chain of the diene-olefin adducts. The particular assignments of the ^{13}C-NMR resonances (Table 2.5) of the three different isomers were derived either directly



↯ = double irradiation

+ = change observed in the appearance of the signal

− = no change observed

Figure 2.5: Proton resonances and coupling patterns of 21a. Assignment confirmed by decoupling experiments.

Table 2.5: ^{13}C-NMR-data for (DMM-BD)Fe(CO)$_3$ and (DMF-BD)Fe(CO)$_3$ adducts a)

b)	c)	20a		20b		21a	
		d)	e)	d)	e)	d)	e)
C^1 f)	q	50.5	147	50.0	146	50.5	145
C^2	s	180.6	-	179.6	-	179.1	-
C^3	d	37.5	140,(8)*	34.1	135,(9)*	41.2	138,(10)*
C^4	s	211.7	-	213.3	-	211.5	-
C^5	s	211.3	-	209.4	-	210.2	-
C^6	s	205.3	-	205.0	-	204.7	-
C^7	t	56.6	163,(10)*	55.7	162,(10)*	57.5	157,(10)*
C^8	d	93.3	156,(11)*	100.4	159	98.7	160
C^9	-	-	-	-	-	-	-
C^{10}	d	85.2	157	83.8	159	82.4	163,(9)*
C^{11}	-	-	-	-	-	-	-
C^{12}	t	35.3	135	29.3	130	30.8	128
C^{13}	d	42.7	125	59.8	125	59.1	134
C^{14}	s	173.5	-	172.1	-	172.5	-
C^{15} f)	q	51.0	147	50.9	146	50.9	145

a) *in toluene-d$_8$, Bruker WH 270, at 27 °C ±1.*

b) *for numbering of the carbon atoms, see Figures 2.6 and 2.7.*

c) *multiplicity, q = quartet, t = triplet, s = singlet.*

d) *chemical shift δ/ppm.*

e) *coupling constant J/Hz.*

f) *tentative assignments by comparison with the (MA-BD)Fe(CO)$_3$ adducts {76}.*

*) *^2J(C-H) long range coupling.*

from the signal multiplicities (Figure 2.7) and $^1J(C-H)$ coupling constants or from comparison with the spectra of various methyl substituted derivatives described in the following sections.

Three of the carbon atoms of the C_6-chain show $^1J(C-H)$ coupling constants characteristic of sp^3 hybridized C-atoms {101,102,103}, two of which appear as doublets (C^{13} and C^3) while the third one, C^{12}, appears as a triplet (Figure 2.7). It is interesting to note that the resonance of C^{12} in 21a and 20b is shifted upfield relative to that in compound 20a. A similar phenomenon was observed for the resonances of H^5 and H^6 in the ^{1}H-NMR spectra of these compounds. This may be attributed to the influence of the β-ester group which in 21a and 20b points towards these atoms.

In all spectra, two ester carbonyl resonances (C^2, C^{14}) were observed at ca. δ 180 and δ 173 ppm, respectively, which were assigned by comparison with the analogous methyl acrylate adducts {76}. In the latter compounds, *exo*- and *endo*-(MA-BD)Fe(CO)$_3$, the signal of the sole ester carbonyl group appeared at δ 180.7 and δ 180.8 ppm, respectively. Hence it follows that of the afore-mentioned two ester carbonyl signals the one at ca. δ 180 ppm is assigned to α-ester group (C^2) and that at ca. δ 173 ppm to the β-ester group (C^{14}). Surprisingly, on going from 20a to 20b there is no significant change in the chemical shift of C^2 despite the characteristic frequency shift of that ester carbonyl in the IR spectra (cf. Table 2.3).

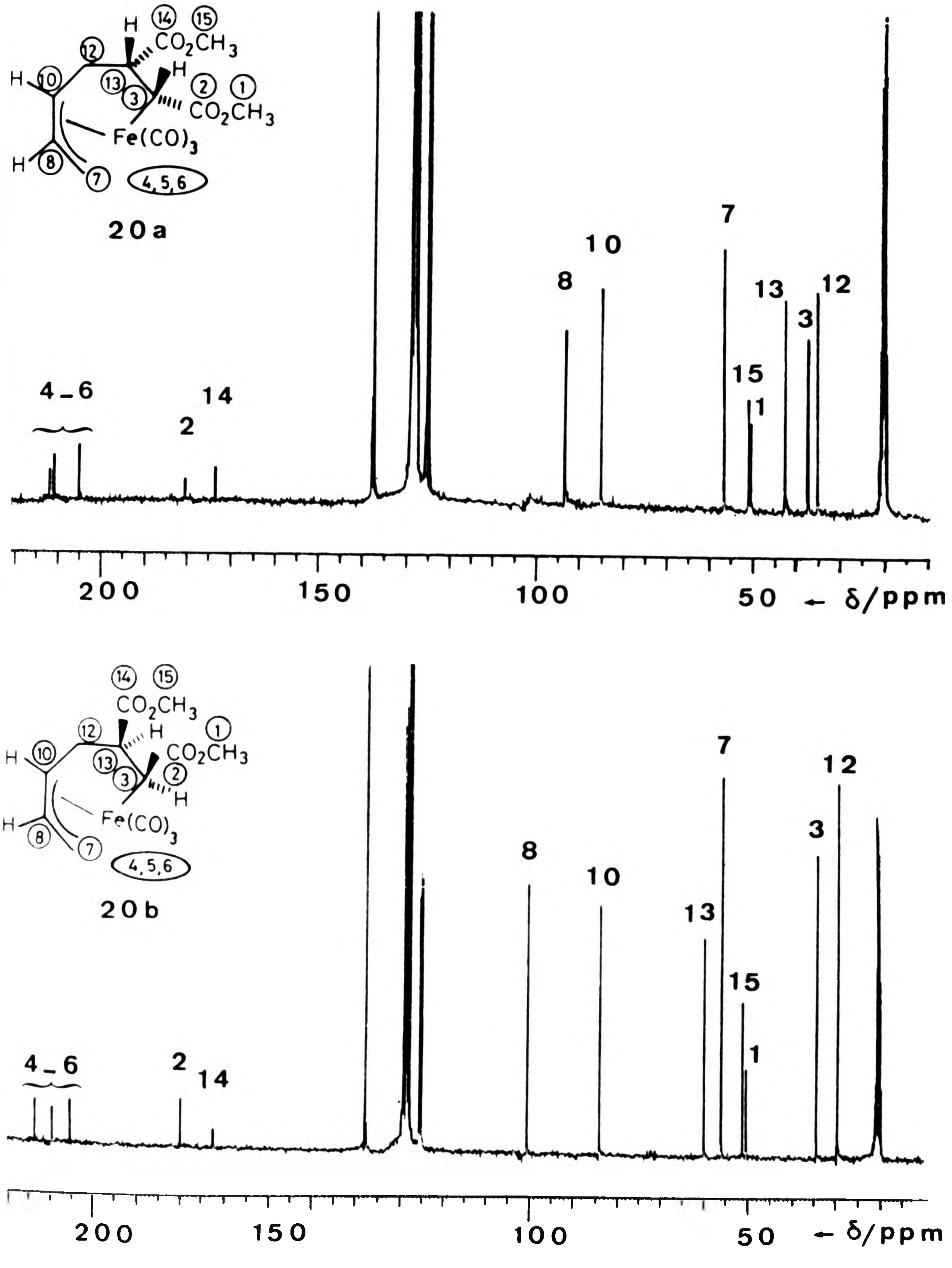


Figure 2.6: Comparative $^{13}C-\{^{1}H\}$-NMR spectra of *exo*- and *endo*-(DMM-BD)Fe(CO)$_3$ adducts, 20a and 20b, in C_7D_8, Bruker WH 270, at 27°C ± 1.

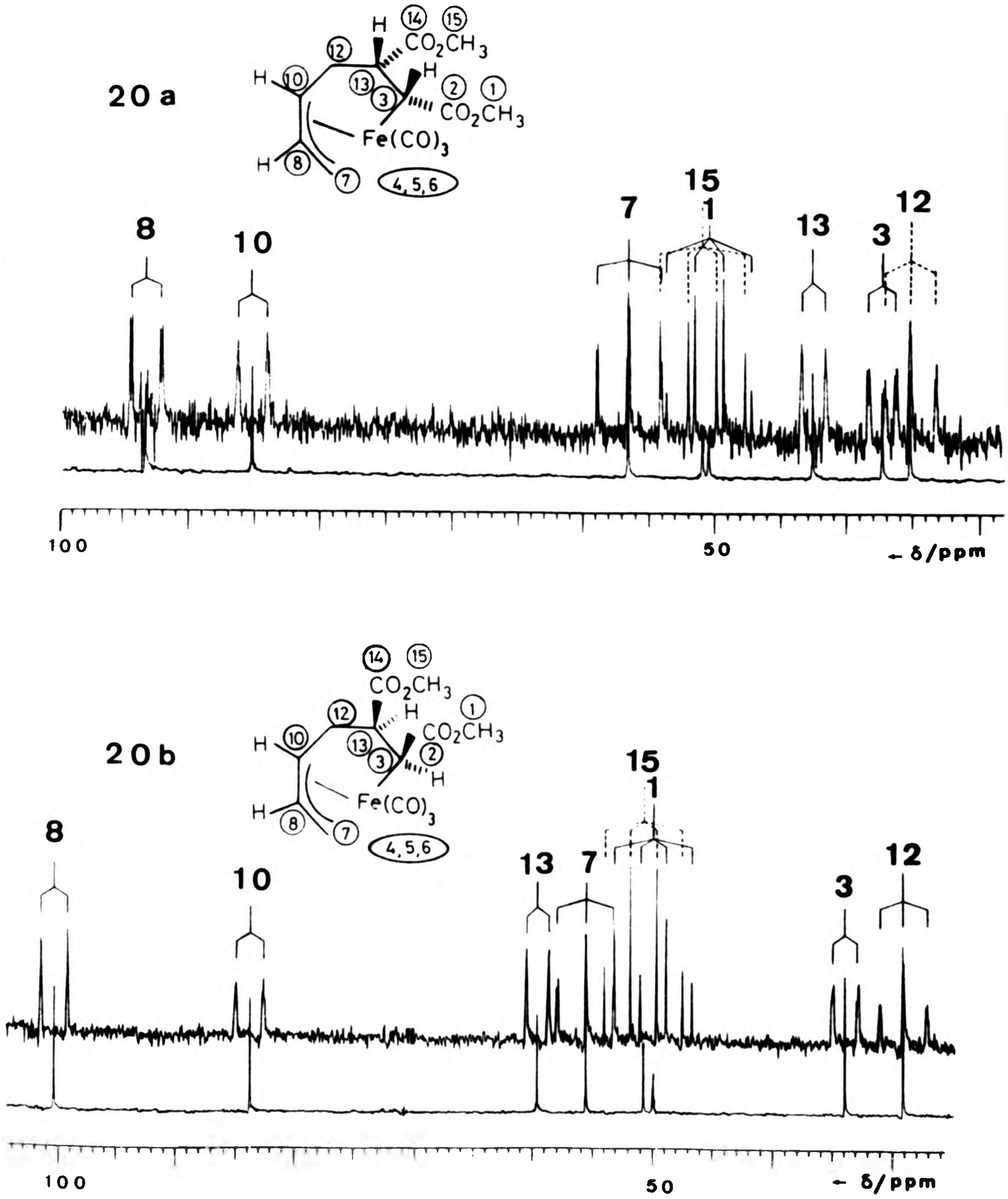


Figure 2.7: Comparative ^{13}C- and ^{13}C-{^{1}H}-NMR spectra of 20a and 20b in D_7D_8, Bruker WH 270, at 27°C ±1.

The remaining three carbon atoms (C^8, C^7, and C^{10}) of the C_6-chain exhibit $^1J(C-H)$ coupling constants characteristic for sp^2 hybridization and thus are assigned to the η^3-allyl groups. The carbon atom C^8, being the centre of an allylic moiety coordinated to the metal, appears as a doublet at lower field than the other allyl carbon atoms (C^7 and C^{10}) which appear as a doublet (C^{10}) and a triplet (C^7), respectively. Notably, C^{10} in all these compounds resonates at distinctly lower field than C^7, due to the fact that C^{10} is linked to the next carbon atom of the organic moiety whereas C^7 is in a terminal position (cf. the effect of methyl substituents at the η^3-allyl group, Table 2.16).

In contrast to the fluxional (η^4-diene)Fe(CO)$_3$ complexes {61,62,63,104,105} these (σ,η^3-organo)Fe(CO)$_3$ compounds exhibit, at room temperature, three distinctly observable ^{13}C signals for the three carbonyl ligands. This indicates that, due to the Fe-C σ-bond, these complexes either have a rigid structure or the carbonyl ligand scrambling is at least slow enough not to be observable on the NMR time scale.

The ^{13}C-signals of the three carbonyl ligands appear (Figure 2.6) in the typical range of metal carbonyl resonances. The one observed at highest field (δ 204-205 ppm) is tentatively assigned to the C^6O group oriented in a *trans*-position relative to the (Fe-C)σ-bond as implied by comparison with the ^{13}C-NMR data obtained for ferracyclopentane compound, 12, {76}. The two other resonances due to C^4 and C^5 could not be specifically assigned.

2.3.2. Reactions involving 2,3-dimethylbuta-1,3-diene and maleic and fumaric esters

The coupling of 2,3-dimethylbuta-1,3-diene (DMB) with the olefinic diesters, dimethyl maleate, dimethyl fumarate, diethyl maleate, and diethyl fumarate was investigated under various conditions.

Photoreaction of $(\eta^4\text{-DMB})\text{Fe(CO)}_3$ with dimethyl maleate (DMM) in n-hexane afforded the $(\sigma,\eta^3\text{-allyl})\text{Fe(CO)}_3$ adduct, 22b. This compound was also obtained in a high yield from the photoreaction of $(\eta^2\text{-DMM})\text{Fe(CO)}_4$ with 2,3-dimethylbuta-1,3-diene. The "one-pot" photoreaction of Fe(CO)_5 with DMB and DMM provided an even better route to the complex 22b. It involves the initial formation of both of the afore said carbonyliron complexes, $(\eta^4\text{-DMB})\text{Fe(CO)}_3$ and $(\eta^2\text{-DMM})\text{Fe(CO)}_4$, which then react further with the respective other compound (cf. Scheme 2.1). However, these complexes are not completely converted to the final product 22b and are present in considerable quantities in the reaction mixture.

The synthetic advantage of the "one-pot" method is illustrated in Table 2.6 where the direct and overall yields of 22b are contrasted. The "one-pot" synthesis was found to be the most convenient method for the preparation of 22b, affording significantly higher yield because under these conditions both of the organic substrates, the 1,3-diene and the olefin, are in excess with respect to the iron carbonyl. From the manipulative view, the three methods involve similar operations and all of them afforded only one of the possible (σ,η^3-allyl)$Fe(CO)_3$ isomers, namely complex 22b with the *endo*-oriented α-ester group.

Table 2.6: Comparative yields for complex 22b

Method of Preparation	Direct Yields (%) a)	Overall Yield (%) b)
$(DMB)Fe(CO)_3/DMM$	14	9 c)
$(DMM)Fe(CO)_4/DMB$	37	25 d)
"one-pot" $DMM+DMB+Fe(CO)_5$	48	48

a) *Based on iron compound used.*

b) *Based on* $Fe(CO)_5$.

c) *Calculated on the basis of the reaction sequence:*

$$Fe(CO)_5 \xrightarrow{62\ \%} (DMB)Fe(CO)_3 \xrightarrow{14\ \%} 22b$$

d) *Calculated on the basis of the reaction sequence:*

$$Fe(CO)_5 \xrightarrow{90\ \%} Fe_2(CO)_9 \xrightarrow{74\ \%} (DMM)Fe(CO)_4 \xrightarrow{37\ \%} 22b$$

The "one-pot" reaction also provided satisfactory routes to the (σ,η^3-allyl)$Fe(CO)_3$ complexes 23a, 24b and 25a derived from 2,3-dimethylbuta-1,3-diene and dimethyl fumarate, diethyl maleate or diethyl fumarate. The yields are summarized in Table 2.7. These reaction systems also afforded (η^4-DMB)$Fe(CO)_3$ and the respective (η^2-olefin)$Fe(CO)_4$ complexes.

In the case of the reaction involving diethyl fumarate, the isomer 25a was isolated in 19 % yield and the isomer 25b was formed in minor quantities. The latter isomer was detected by IR spectroscopy [$\tilde{\nu}$(CO) = 2063.4, 2006.1, 1988.5 cm^{-1};

$\tilde{\nu}$(ester-CO) = 1735.0, 1685 cm^{-1}; in n-hexane] but could not be isolated. Furthermore, the reaction also afforded complex 37 in substantial amount, thus accounting for the relatively low yield of 25a. The infrared spectrum of 37 [$\tilde{\nu}$(CO) = 2034.0, 2030.0, 1990.0, and 1979.0 cm^{-1}; $\tilde{\nu}$(ester-CO) = 1713 cm^{-1}; in n-hexane] is distinctly different from the spectra of the (σ,η^3-organo)Fe(CO)$_3$ coupling products. The elemental analysis and the mass spectrum suggested the empirical formula $C_{16}H_{22}FeO_6$ which implies that both the diene and the fumarate moieties are present. These results suggested the formulation (η^4-DMB)-(η^2-DEF)Fe(CO)$_2$. However, for a complex of this type one would expect only two CO stetching vibrations. Further investigations on 37 and on the analogous dimethyl fumarate complex, 38, will be described in Chapter three. The isolation and further reaction of these (η^4-diene)(η^2-olefin)Fe(CO)$_2$ complexes proved to be of great significance with respect to the mechanism of the formation of the (σ,η^3-organo)Fe(CO)$_3$ coupling products.

The complex 25a was also obtained from the reaction of 2,3-dimethylbuta-1,3-diene with (η^2-DEF)Fe(CO)$_4$ (Table 2.7). Another product obtained from this reaction was the complex (η^4-DMB)Fe(CO)$_3$.

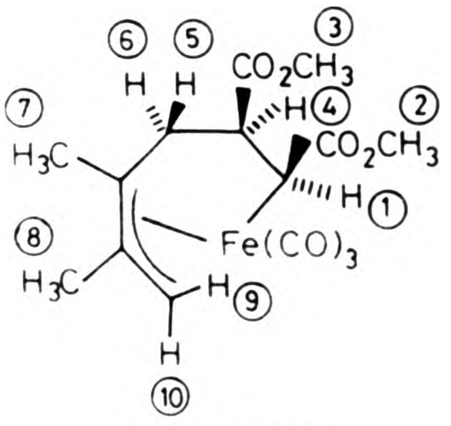
The complexes 22b, 23a, 24b, and 25a were characterized by elemental analysis and by various spectroscopic techniques. The mass spectra of these complexes did not show molecular ions but included peaks corresponding to the ion

$[M\text{-}nCO]^+$ (n = 1-3), and $[M\text{-}OR]^+$.

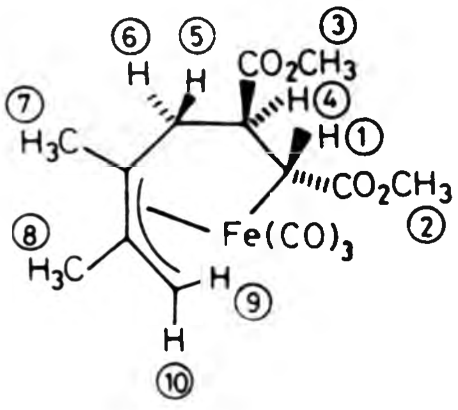
Table 2.7: Yields for (σ,η^3-organo)Fe(CO)$_3$ complexes derived from 2,3-dimethylbuta-1,3-diene and maleic and fumaric esters

Method of Preparation	Coupling Product	Yield (%)
DMB+DMF+Fe(CO)$_5$	23a	25
DMB+DEM+Fe(CO)$_5$	24b	27
DMB+DEF+Fe(CO)$_5$	25a	19[a)]
DMB+(DEF)Fe(CO)$_4$	25a	21

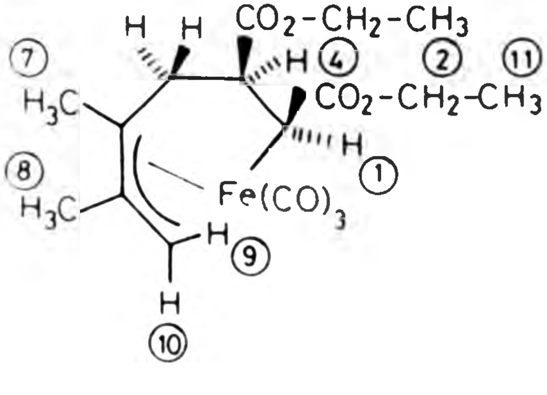
a) *In addition, the complex (η^4-DMB)(η^2-DEF)Fe(CO)$_2$ (37, see text) was isolated in 16 % yield.*



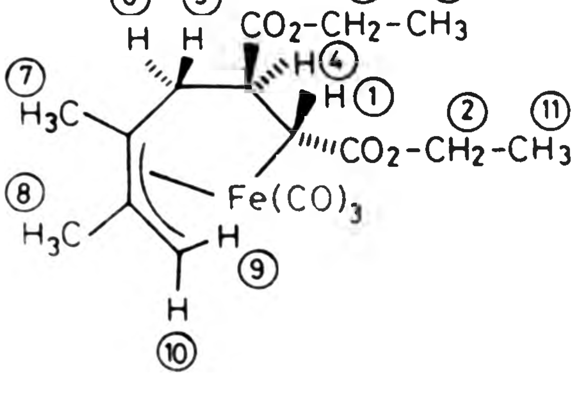
22 b



23 a



24b



25a

The complexes were assigned type **a** or **b** structures (Table 2.8) on the basis of their infrared data (cf. Table 2.2). These assignments were confirmed by the study of their NMR spectra.

Table 2.8: IR-data (cm^{-1}, in n-hexane) for (DMB-olefin)Fe(CO)$_3$ adducts

complex	$\tilde{\nu}$(CO)			$\tilde{\nu}$(ester-CO)	
	(1)	(2)	(3)	(β)	(α)
22b	2061.0	2001.8	1985.8	1745.3	1695.7
23a	2065.9	2010.6	1988.6	1740.8	1704.5
24b	2060.3	2000.8	1984.0	1740.0	1690.0
25a	2065.4	2009.9	1988.4	1737.4	1705.4

The ^{1}H-NMR data are shown in Table 2.9a for dimethyl ester adducts and Table 2.9b for the diethyl ester adducts. In general, the spectra of these complexes are simpler than those of the respective complexes derived from buta-1,3-diene (**20**,**21**) due to the presence of two methyl groups (H^7, and H^8) attached to the fourth and fifth carbon atom in the C$_6$-carbon chain. However, assignment of these methyl resonances could not be made due to the proximity of their chemical shifts.

The coupling constant between H^1 and H^4 was again used to deduce information about the orientation of the two ester groups relative to each other: *cis*-arrangement in **22b** {J(H^1-H^4) = 6.5 Hz} and **24b** {J(H^1-H^4) = 6.0 Hz}; *trans*-arrangement in **23a** {J(H^1-H^4) = 12.0 Hz} and **25a** {J(H^1-H^4) = 12.0 Hz}. As previously (Section 2.3.1), coupling constants J(H^4-H^5),

Table 2.9a: ^{1}*H-NMR data for tricarbonyl{1,4,5,6-η^4-(1,2-dicarbomethoxy-4,5-dimethylhex-4-en-1,6-diyl)}iron complexes.*[a)]

22**b**							23**a**	
Solvent %	C_6D_6	$C_6D_6/CDCl_3$			$CDCl_3$	J/Hz	C_6D_6	J/Hz
δ/ppm		75/25	50/50	25/75				
H^1	2.11	2.0	2.94	2.89	2.96	(1,4)= 6.5	2.13	(1,4)=12.0
H^2	3.33	3.35	3.33	3.37	3.54	-	3.30	-
H^3	3.46	3.44	3.39	3.41	3.55	-	3.59	-
H^4	~3.2	3.16	3.13	3.14	3.31	(4,5)=12.5	3.89	(4,5)=13.9
H^5	2.20	~2.0	1.94	1.89	1.98	(5,6)=13.0	0.92	(5,6)=13.0
H^6	2.10		1.98	2.01	2.10	(6,4)= 5.5 (6,1)= 1.5	1.80	(6,4)= 5.0
H^7	1.31	1.50	1.56	1.69	1.99	-	1.34	-
H^8		1.48	1.53	1.65	1.92	-	1.29	-
H^9	2.71	2.58	2.50	2.47	2.59	(9,10)=2.0	1.87	(9,10)=1.9
H^{10}	2.94	3.02	3.06	3.14	3.38	-	2.83	-

a) *spectra measured on Bruker WH 270, at 27 °C ±1.*

Table 2.9a: ^{1}H-NMR data for tricarbonyl{1,4,5,6-η^4-(1,2-dicarbomethoxy-4,5-dimethylhex-4-en-1,6-diyl)}iron complexes.$^{a)}$

22b							23a	
Solvent %	C_6D_6	$C_6D_6/CDCl_3$			$CDCl_3$	J/Hz	C_6D_6	J/Hz
δ/ppm		75/25	50/50	25/75				
H^1	2.11	2.0	2.94	2.89	2.96	(1,4)= 6.5	2.13	(1,4)=12.0
H^2	3.33	3.35	3.33	3.37	3.54	-	3.30	-
H^3	3.46	3.44	3.39	3.41	3.55	-	3.59	-
H^4	~3.2	3.16	3.13	3.14	3.31	(4,5)=12.5	3.89	(4,5)=13.9
H^5	2.20	~2.0	1.94	1.89	1.98	(5,6)=13.0	0.92	(5,6)=13.0
H^6	2.10		1.98	2.01	2.10	(6,4)= 5.5 (6,1)= 1.5	1.80	(6,4)= 5.0
H^7	1.31	1.50	1.56	1.69	1.99	-	1.34	-
H^8		1.48	1.53	1.65	1.92	-	1.29	-
H^9	2.71	2.58	2.50	2.47	2.59	(9,10)=2.0	1.87	(9,10)=1.9
H^{10}	2.94	3.02	3.06	3.14	3.38	-	2.83	-

a) spectra measured on Bruker WH 270, at 27 °C ±1.

Table 2.9b: ^{1}H*-NMR data for tricarbonyl{1,4,5,6-η⁴-(1,2-dicarboethoxy-4,5-dimethylhex-4-en-1,6-diyl)}iron complexes.*[a)]

	24b	**25a**
δ/ppm		
H^1	3.18	2.15
$H^2 + H^{2'}$	~3.9	3.92
$H^3 + H^{3'}$	4.05	4.19
H^4	3.25	3.90
H^5	2.23	0.92
H^6	2.14	1.84
H^7	1.34	1.32
H^8	1.33	1.28
H^9	2.74	1.87
H^{10}	2.95	2.83
H^{11}	0.96	0.93
H^{12}	1.10	1.15
J/Hz		
(1,4)	6.0	12.0
(4,5)	12.5	12.5
(4,6)	6.0	5.0
(5,6)	12.8	12.5
(9,10)	2.0	2.0
(1,6)	1.5	-
(2,11)	7.0	7.0
(3,12)	7.0	7.0

[a)] *in benzene-*d_6*, Bruker WH 270, at 27 °C ±1.*

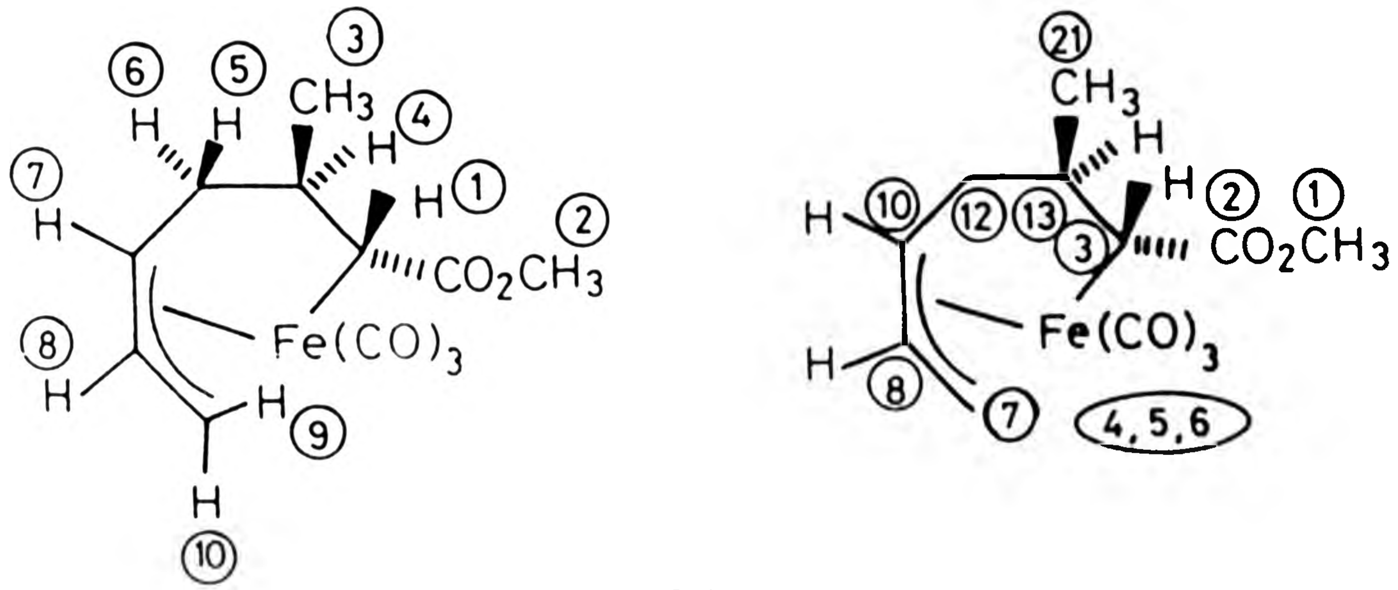
$J(H^4-H^6)$, and $J(H^1-H^6)$ were used to determine the stereo-orientation of the β-ester group relative to the iron atom.

The chemical shifts of protons H^9 and H^{10} are in agreement with the orientation of the α-ester group: *endo*-orientation (complex type b) causes a shift of H^9 to lower field.

Comparison of proton magnetic resonance data for 22b and 23a with the analogous compounds 20b and 21a confirms the assignments made here. In accordance with the results obtained in the previous section (2.3.1) the *cis*- and *trans*-configuration, respectively, of the olefinic component is retained in the resulting $(\sigma,\eta^3\text{-organo})Fe(CO)_3$ coupling products.

2.3.3. Reaction of buta-1,3-diene with methyl crotonate and pentacarbonyliron

Photolysis of buta-1,3-diene, methyl crotonate, and pentacarbonyliron afforded the $(\sigma,\eta^3\text{-organo})Fe(CO)_3$ complex 26a together with $(\eta^4\text{-BD})Fe(CO)_3$ and minor amount of $(\eta^2\text{-MC})$-$Fe(CO)_4$ and $(\eta^4\text{-BD})_2FeCO$.



26a

The spectral data of 26a are in agreement with the proposed formula. Its mass spectrum shows successive loss of three carbonyl ligands followed by loss of the buta-1,3-diene. The IR spectrum (Table 2.10) includes three bands in the metal carbonyl region and an ester carbonyl vibration at 1711.7 cm^{-1}. The latter value indicates that the ester group is attached to the α-carbon atom of the σ,η^3-organo ligand, i.e. C-C bond formation with buta-1,3-diene involves the methyl substituted carbon atom of the crotonate unit. Furthermore, the ester carbonyl frequencies suggest that the complex has type a structure, i.e. *exo*-orientation of the ester group (cf. Table 2.2).

The ^{1}H-NMR spectrum showed an 11.8 Hz coupling between H^1 and H^4 which is indicative of a *trans*-configuration (Table 2.10). In addition, comparison of couplings $J(H^4-H^5)$ and $J(H^4-H^6)$ with those of compound 21a also indicates that compound 26a has a structural configuration similar to that of 21a. The methyl group (H^3) showed no coupling with the proton (H^1) attached to the σ-bonded carbon atom. On the other hand the proton H^4, attached to the β-carbon atom, is coupled to the methyl group, H^3, with $J(H^3-H^4) = 6.3$ Hz. Hence it follows that the methyl group is situated at the β-position and, consequently, the ester group at the α-position of the six-carbon chain. This result thus obtained is in agreement with the afore-mentioned IR data.

Detailed analysis of the ^{13}C-NMR spectra of compound 26a was carried out and the resulted data are summarized in Table 2.10. The chemical shifts of the carbon atoms of this

Table 2.10: Spectroscopic data for 26a.[a,b,c]

a)

$\tilde{\nu}$(CO)			$\tilde{\nu}$(ester-CO)
2068.9	2013.4	1995.9	1711.7

b)

δ/ppm	
H^1	1.21
H^2	3.59
H^3	0.70
H^4	2.82
H^5	0.20
H^6	1.45
H^7	4.29
H^8	4.16
H^9	1.98
H^{10}	3.04
J/Hz	
(1,4)	11.8
(4,5)	12.6
(4,6)	6.3
(5,6)	12.5
(6,7)	6.3
(7,5)	7.7
(7,10)	1.5
(9,10)	1.5
(8,9)	12.5
(8,10)	7.4
(7,8)	7.8
(3,4)	6.3

c)

C^1	50.1 (q,146)
C^2	179.1 (s, -)
C^3	49.8 (d,131,6)
C^4	211.7 (s, -)
C^5	211.2 (s, -)
C^6	205.0 (s, -)
C^7	56.7 (t,161,8)
C^8	98.3 (d,161)
C^9	- -
C^{10}	85.5 (d,155)
C^{11}	- -
C^{12}	35.4 (t,128)
C^{13}	52.7 (d,133)
C^{21}	21.7 (q,128)

a) Infrared data (cm^{-1}, in n-hexane).

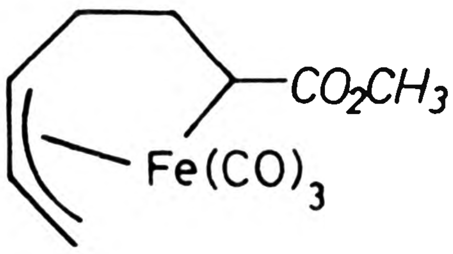
b) ^{1}H-NMR data, in benzene-d_6, Bruker WH 270, at 27 °C ±1.

c) ^{13}C-NMR data, in toluene-d_8, Bruker WH 270, at 27 °C ±1.

compound are nearly identical with those of 21a (cf. Table 2,5), except for C^3 and C^{13}.

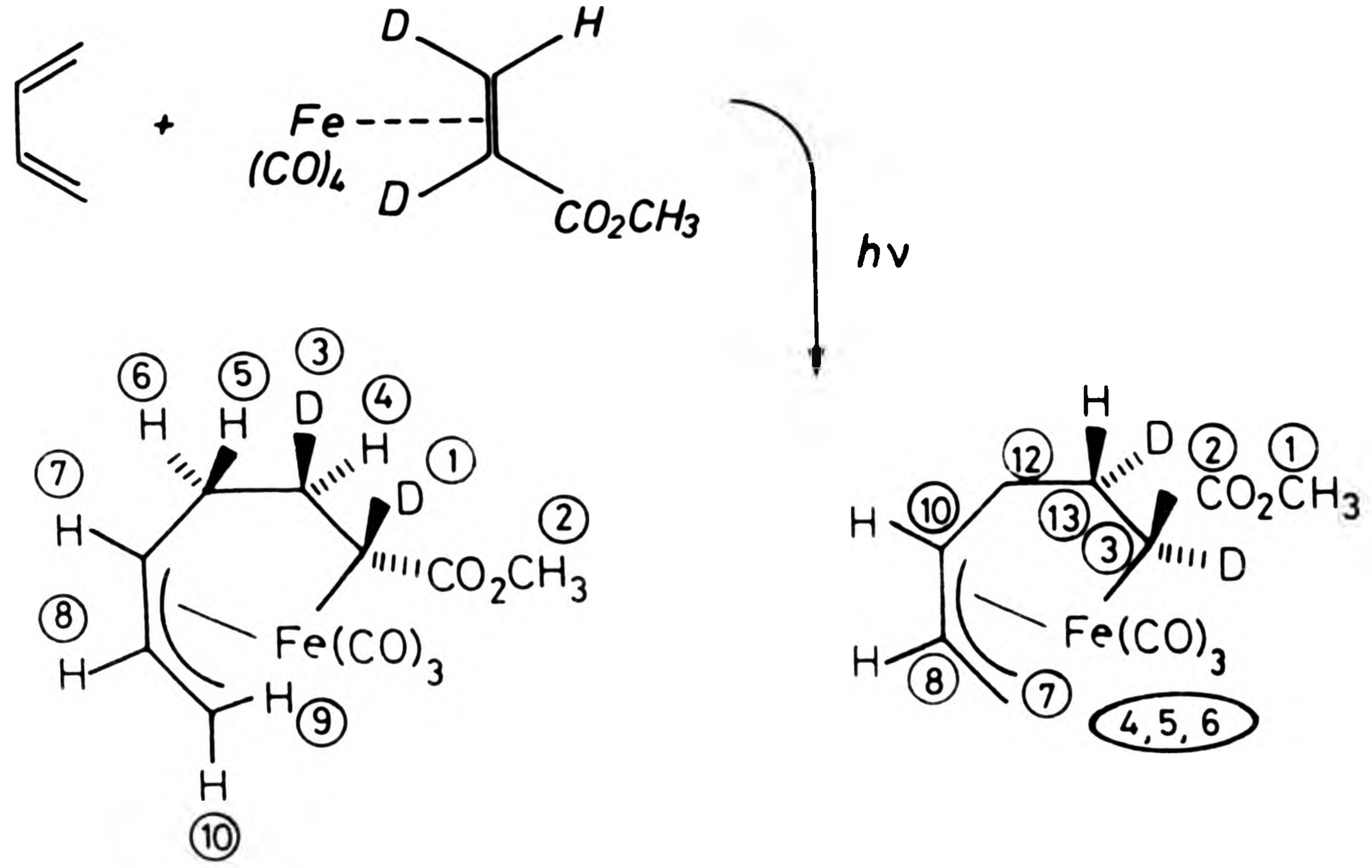
2.3.4. Reaction involving buta-1,3-diene and *cis*-d_2-methyl acrylate

The photoreaction of pentacarbonyliron, buta-1,3-diene and methyl acrylate has been reported previously {86}. This system afforded (η^2-MA)Fe(CO)$_4$, (η^4-BD)Fe(CO)$_3$ and the isomeric (σ,η^3-organo)Fe(CO)$_3$ complexes, 27a and 27b. When this system was reexamined during the present study, these products were obtained in similar yields but in addition, another minor product, *tricarbonyl*{η^4-[*1-carbomethoxy-hexa-1(E),3(E)-diene*]}*iron*, 43, was isolated. The isolation of this product was very significant because it was suggestive of a photoreaction of (σ,η^3-organo)Fe(CO)$_3$ complexes. This type of photoreaction is discussed in Chapter four where the structure of 43 is also considered.



27

During this study the coupling system involving buta-1,3-diene and deuterium-labelled methyl acrylate (*cis*-d_2) was also examined. Reaction of *cis*-d_2-methyl acrylate {106} with nonacarbonyldiiron gave tetracarbonyl[η^2-(*cis*-2,3-dideuterio-methyl acrylate)]iron. The purity of the latter compound was checked by ^{1}H-NMR (80 % of *cis*-d_2-MA, and 20 % of *trans*-d_2-MA). Photochemical reaction of this compound with buta-1,3-diene afforded the two (σ,η^3-organo)Fe(CO)$_3$ complexes, **28a** and **28b**, in 12 % and 8 % yield, respectively, (Scheme 2.2) together with (η^4-BD)Fe(CO)$_3$ and unreacted (η^2-*cis*-d_2-MA)Fe(CO)$_4$.



28a (Scheme 2.2) **28b**

The (σ,η^3-organo)Fe(CO)$_3$ isomers were characterized spectroscopically (mass, IR and NMR). Their stereochemistry was established using the IR data given in Table 2.11, the criteria discussed earlier and by comparison with the respective non-deuterated compounds {86}.

The ^{1}H-NMR spectra of both **28a** (Figure 2.8) and **28b** (Table 2.12) are in agreement with those of the non-deuterated

Table 2.11: IR-data (cm^{-1}, in n-hexane) for tricarbonyl(cis-d$_2$-methyl acrylate/buta-1,3-diene)iron

complex	$\tilde{\nu}$(CO)			$\tilde{\nu}$(ester-CO)
	(1)	(2)	(3)	(α)
28a	2068.2	2012.4	1995.9	1708.3
28b	2063.6	2004.3	1995.3	1700.7

compounds {76,86}. The signal associated with H^1 [$\delta \sim 1.75$ ppm {76,86}] is missing which indicates complete deuteration in this position. The signal integrals of H^3 and H^4 are reduced, compared with the other protons, to ~ 20 % and ~ 80 % of the value expected for one proton, in agreement with the distribution of deuteration in the starting (η^2-d$_2$-methyl acrylate)-Fe(CO)$_4$. Hence it follows that during the formation of the adduct complex 28a the steric configuration of the olefin is retained, as it was in the products derived from maleate, fumarate, and crotonate. Analogous changes in the corresponding signal integrals are observed for 28b.

As a useful cross-check, the ^{2}D-NMR spectrum of each of the two isomeric products 28a and 28b (Figure 2.9) showed the presence of two deuterium atoms in each molecule. The chemical shifts of the two deuterium atoms appear at δ 1.03 ppm (D^3) and δ 1.70 ppm (D^1) for 28a, and δ 1.17 ppm (D^3) and δ 2.42 ppm (D^1) for 28b. The expected low intensity (~20 %) signals in position four could not be clearly recognized due to overlapping with other signals (see Figure 2.9, footnotes). Chemical shifts agree with the proton data for the non-deuterated (buta-1,3-diene/methyl acrylate)Fe(CO)$_3$ adducts {86}.

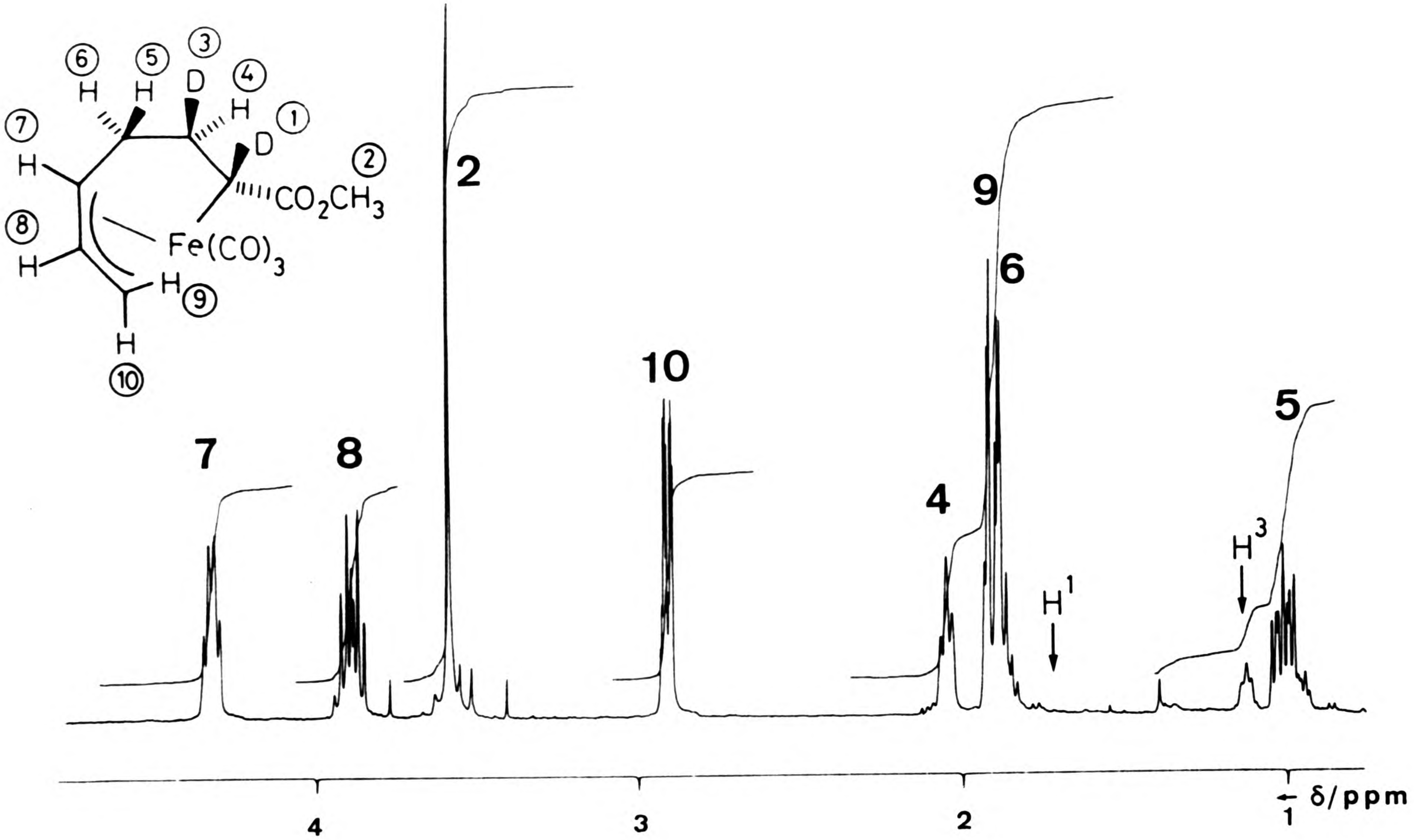


Figure 2.8: ^{1}H-NMR spectrum of compound 28a, in benzene-d$_6$, Bruker WH 400, at 27°C ± 1.

Table 2.12: ^{1}H-NMR data for tricarbonyl{1,4,5,6-η^4-(1-carbomethoxy-cis-1,2-dideuteriohex-4-en-1,6-diyl)}iron[a)]

δ/ppm	28a	28b
H^1	(1.75)[b)]	(2.52)[b)]
H^2	3.59	3.55
H^3	1.13 (~20 %)[c)]	~1.3[d)]
H^4	2.05 (~80 %)[c)]	
H^5	1.01	1.73
H^6	1.90	1.44
H^7	4.32	4.19
H^8	3.89	3.81
H^9	1.91	3.27
H^{10}	2.91	3.00

[a)] *in benzene-d_6, Bruker WH 400, at 27 °C ±1.*

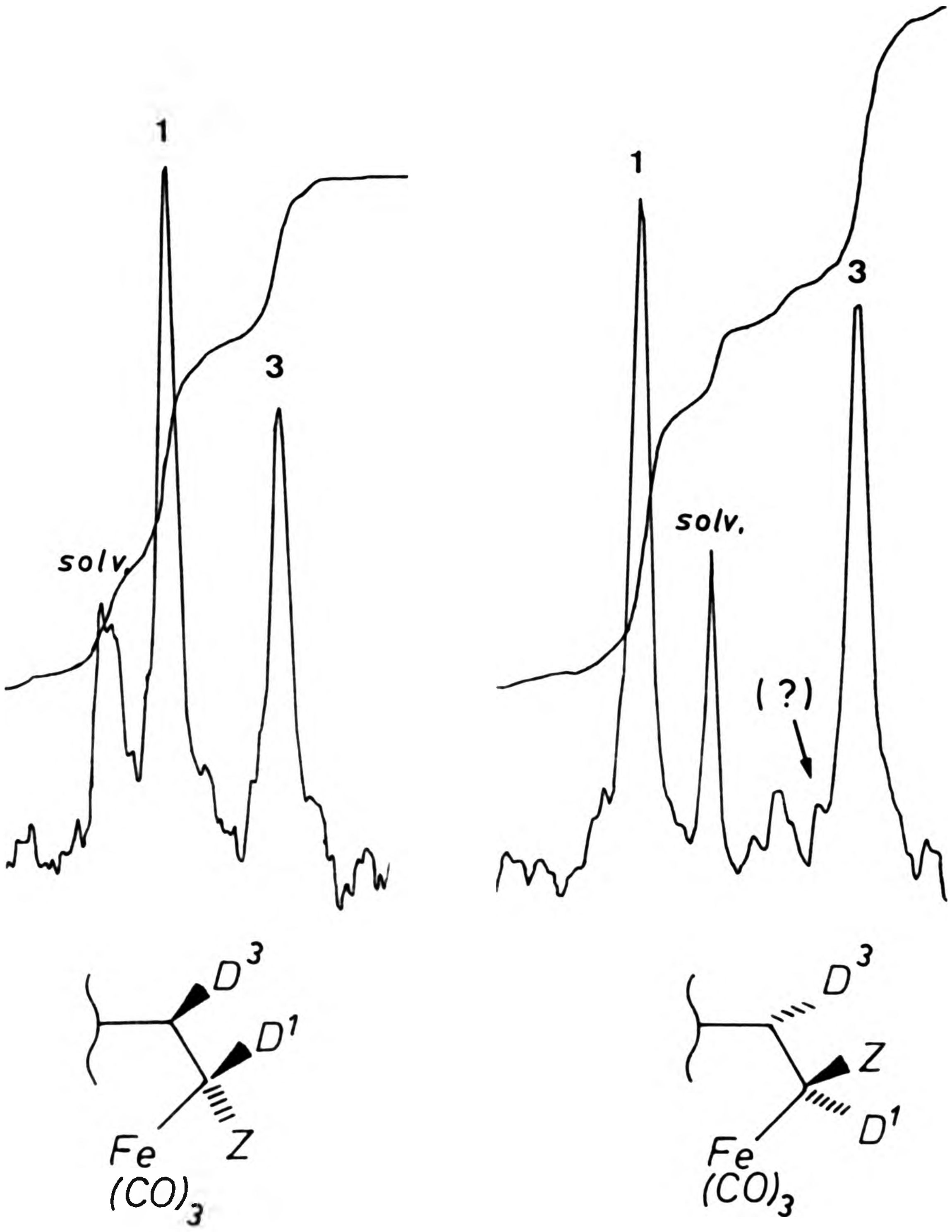
[b)] *not observed due to 100 % deuteration.*

[c)] *reduced intensity due to partial deuteration.*

[d)] *integral sums up to 1 proton.*

Thus it was confirmed that the deuterium atoms are attached to the α- and β-carbon atoms, and in both isomers are in *cis*-configuration to each other.

The ^{13}C-NMR data of both compounds 28a and 28b are summarized in Table 2.13. The spectra of both compounds 28a (Figure 2.10) and 28b (Figure 2.11) can be compared with those of the two isomeric products 20a and 20b derived from (buta-1,3-diene/dimethyl maleate)Fe(CO)$_3$ (Figure 2.7, Table 2.5). They



δ/ppm

D-position	28a	28b
1	1.70	2.42
3	1.03	1.17
4	~ 2.01 a)	(?) b)

Figure 2.9: ^{2}D-NMR spectra of 28a and 28b, chemical shifts relative to toluene-d_8, Bruker WH 270. a) overlapping with solvent signal; b) position not clearly recognized due to overlapping with D^3.

are in agreement with those of the two non-deuterated compounds, apart from the fact that the resonance due to C^3 in 28a and 28b appear as a triplet (intensity ratio 1:1:1) due to the $^1J(C-D)$ coupling. Accordingly, C^{13} appears as a doublet of triplets to the $^1J(C-H)$ and $^1J(C-D)$ couplings (Table 2.13). The latter is still observable in the $^{13}C-\{^1H\}$-NMR spectra.

Table 2.13: ^{13}C-NMR data for tricarbonyl{1,4,5,6-η^4-(1-carbomethoxy-cis-1,2-dideuteriohex-4-en-1,6-diyl)}iron[a)]

		28a		28b	
	multiplicity	δ/ppm	$^1J(C-H)$	δ/ppm	$^1J(C-H)$
C^1	q	50.3	147	49.8	147
C^2	s	180.6	-	180.7	-
C^3	t	39.1	21[b)]	32.3	21[b)]
C^4	s	212.1	-	214.0	-
C^5	s	211.5	-	211.4	-
C^6	s	205.2	-	205.6	-
C^7	t	56.8	160, (10)[c)]	57.7	161, (10)[c)]
C^8	d	96.3	158	96.0	155
C^9	-	-	-	-	-
C^{10}	d	90.5	153	89.5	153
C^{11}	-	-	-	-	-
C^{12}	t	30.6	128	33.0	129
C^{13}	t,d	35.2	19[b)], 122	29.8	18[b)], 122

[a)] *in toluene-d_8, Bruker WH 270, at 27 °C ±1.*

[b)] *$^1J(C-D)$.*

[c)] *long range coupling.*

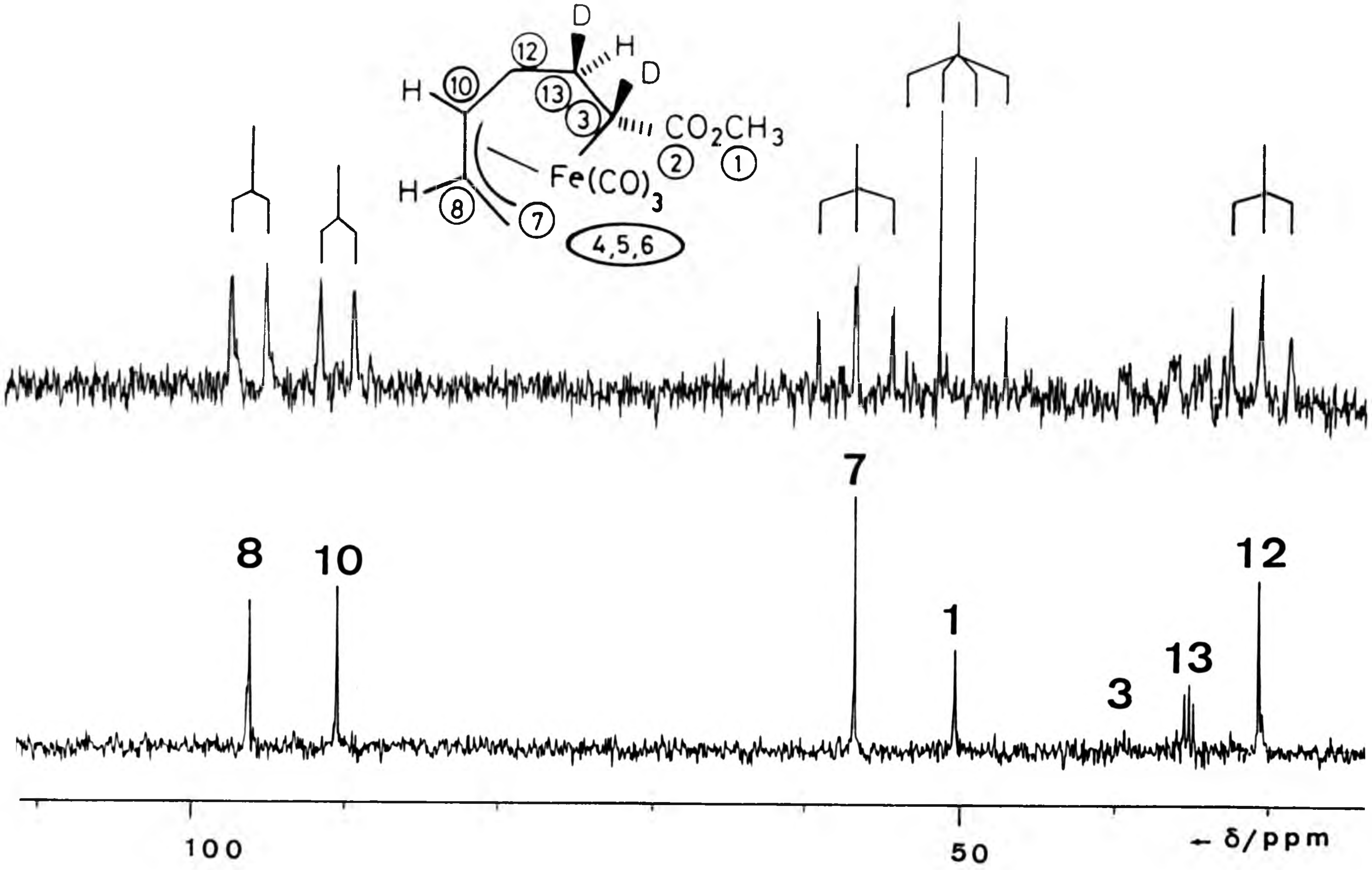


Figure 2.10: The ^{13}C- and ^{13}C-{^{1}H}-NMR spectra of compound 28a, in toluene-d_8, Bruker WH 270, at 27°C ± 1.

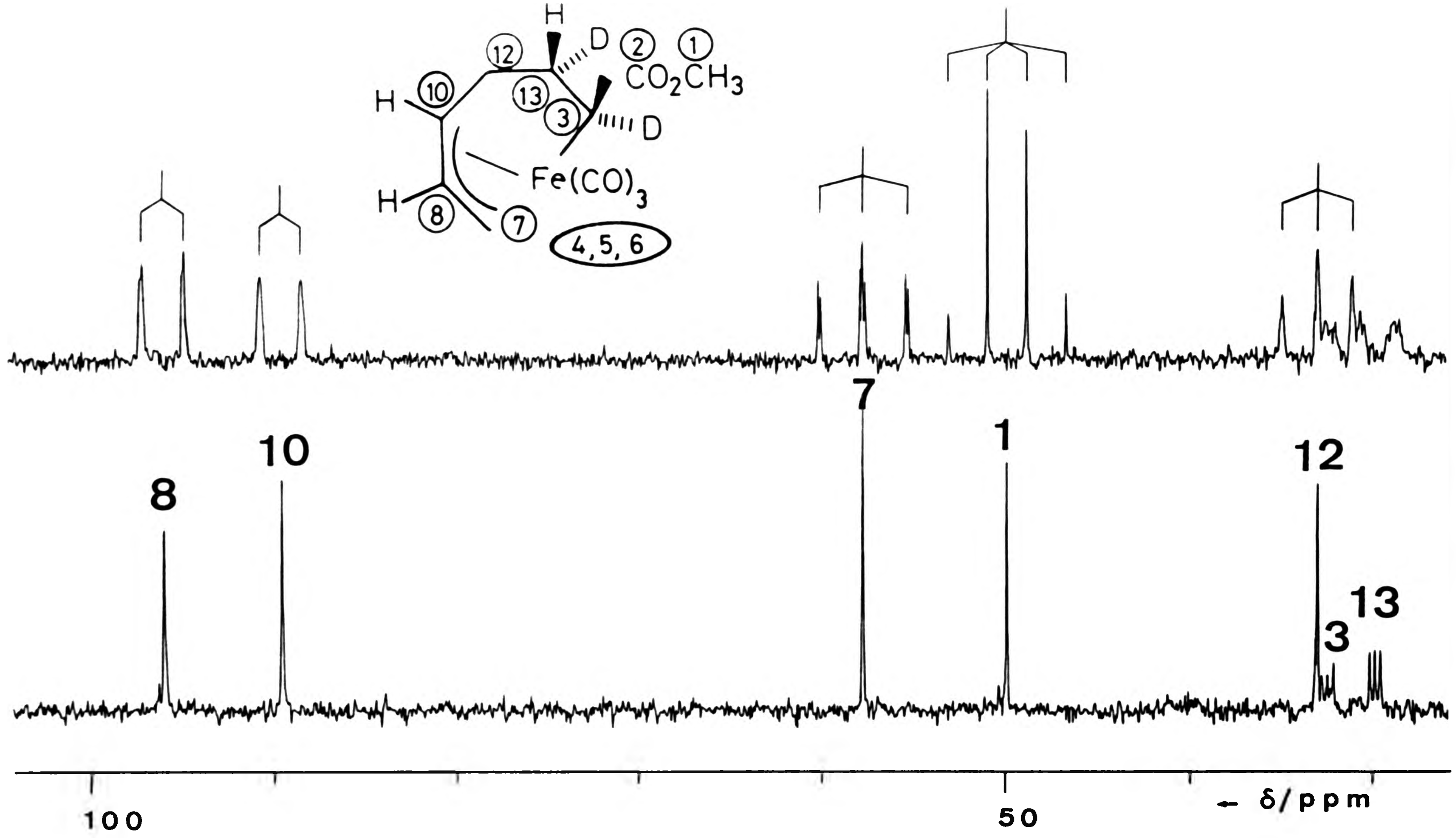


Figure 2.11: The ^{13}C- and ^{13}C-{^1H}-NMR spectra of compound 28b, in toluene-d_8, Bruker WH 270, at 27°C ± 1.

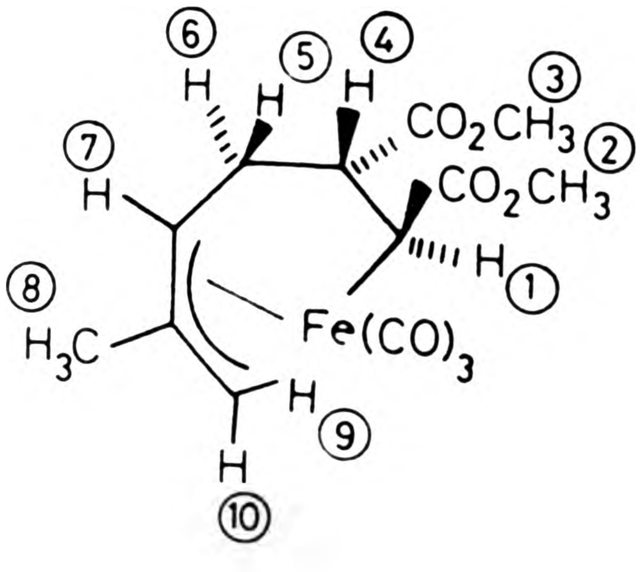
2.4. The photochemical coupling reaction of pentacarbonyliron with unsymmetrical dienes, and symmetrical or unsymmetrical monoolefins

The coupling reaction of pentacarbonyliron with an unsymmetrical diene, and a symmetrical or unsymmetrical monoolefin could give rise to several isomeric $(\sigma,\eta^3\text{-organo})\mathrm{Fe(CO)}_3$ species. If the olefin is symmetrical four isomers could arise provided that the stereo-configuration of the olefinic component is retained. However, if both the diene and the olefin are unsymmetrical, the reaction could lead to eight isomers.

In this study, reactions involving two unsymmetrical dienes (2-methylbuta-1,3-diene and methyl sorbate) and both symmetrical (dimethyl fumarate and dimethyl maleate) and unsymmetrical (methyl acrylate) olefins were examined. A particular aim of this investigation was to establish the role of the electronic and/or steric effects of the hydrocarbon ligand substituents on the number of isomers formed and their relative yields.

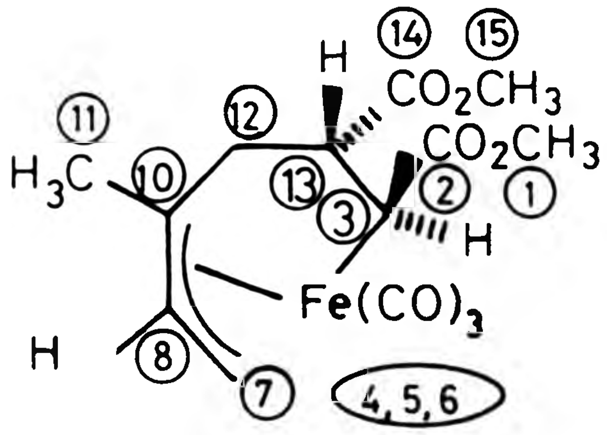
2.4.1. Reaction of 2-methylbuta-1,3-diene with dimethyl fumarate and pentacarbonyliron

Photolysis of pentacarbonyliron with 2-methylbuta-1,3-diene, and dimethyl fumarate afforded all possible $(\sigma,\eta^3\text{-organo})$-$\mathrm{Fe(CO)}_3$ isomeric products (29b, 29a, 30b, 30a) and the complexes $(\eta^2\text{-DMF})\mathrm{Fe(CO)}_4$ and $(\eta^4\text{-DMB})\mathrm{Fe(CO)}_3$. The separation of the products arising from this reaction proved to be difficult. However three of the isomers (29b, 30b, and 29a) were obtained in a pure state, giving very satisfactory elemental analysis. A mixture of isomers 29a and 30a was also obtained, but attempts to separate the components of this mixture by various methods were unsuccessful. Unfortunately, the multi-step separation and purification procedures led to severe loss of products and therefore the yields of the products were rather low.



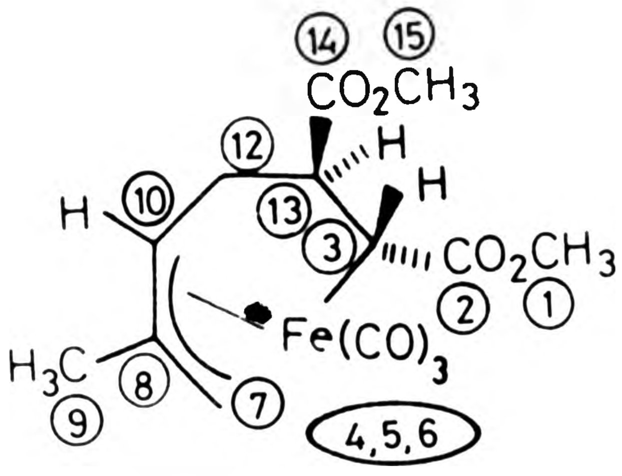
29b, 2 %

(5-methyl, *endo* α-ester)



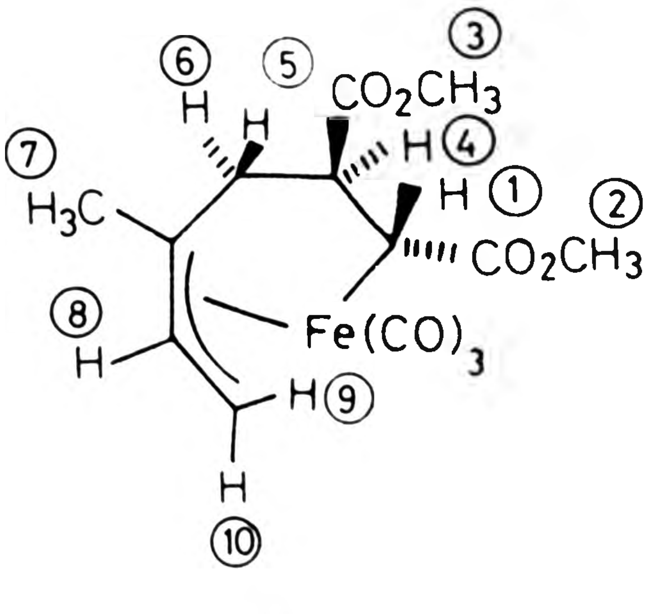
30b, 1 %

(4-methyl, *endo* α-ester)



29a, 6 %

(5-methyl, *exo* α-ester)



30a, 2 %

(yield estimated from ^{1}H-NMR spectra of 29a/30a mixtures)

(4-methyl, *exo* α-ester)

The mass spectra of the three isomers isolated in a pure state and that of the mixture of isomers 29a and 30a did not show peaks corresponding to the molecular ion $[M]^+$ but included peaks corresponding to the ions $[M\text{-}nCO]^+$ (n = 1-3) and $[M\text{-}OCH_3]^+$.

IR-spectral data (1700-2100 cm^{-1}) for the four isomers are given in Table 2.14.

Table 2.14: Infrared spectroscopic data (cm^{-1}, in n-hexane) for tricarbonyl{1,4,5,6-η^4-trans-1,2-dicarbomethoxymethylhex-4-en-1,6-diyl}iron compounds.

complex	$\tilde{\nu}$(CO)			$\tilde{\nu}$(ester-CO)	
	(1)	(2)	(3)	(β)	(α)
29b	2065.8	2008.0	1996.0	1740.0	1703.8
30b	2064.0	2006.3	1994.9	1738.9	1704.0
29a	2069.8	2015.5	1995.3	1744.0	1712.2
30a*	2069	2015	1995	1743	1711

*) *approximate values taken from the spectrum of a mixture which, according to its ^{1}H-NMR spectrum, contained* 30a *and* 29a.

As previously, the classification of compounds into a or b type is made on the basis of the α-ester carbonyl vibrations (Section 2.3, cf. also Table 2.2), and as found previously (Section 2.3.2), there is a larger difference between the second and third bands of series a relative to series b. Noteably, the position of the methyl substituent at the central (*meso*) or at a terminal position of the η^3-allyl moiety (29a/b or 30a/b) has almost no influence on the CO-stretching vibrations, i.e. the frequencies of these bands are nearly the same in 29a compared with 30a and in 29b compared with 30b.

Unlike the infrared spectra, the ^{1}H-NMR coupling patterns (Table 2.15) clearly allowed to distinguish whether the methyl substituent at the η^3-allyl group is situated at the fourth carbon (30b, 30a) or fifth carbon atom (29b, 29a) of the six-carbon chain. Therefore, 30a in a solution mixture contaminated with 29a was clearly recognizable by ^{1}H-NMR, although isomers 29a and 30a could not be clearly distinguished on the basis of IR.

All four compounds showed two resonances between δ 3.24 and δ 3.59 ppm, which correspond to the two methoxy groups (protons H^2 and H^3). In addition, a high field resonance, characteristic of a methyl group, was also observed in each case. In both 29b and 29a, the methyl singlet occurs at higher field than in 30a or 30b. This is consistent with the methyl group occupying the *meso* position of the η^3-allyl moiety. For all four compounds, the remaining signals are assigned to seven coupled protons as detailed below.

The ^{1}H-NMR spectrum of *tricarbonyl{1,4,5,6-*η^4*-[trans-1(endo),2-dicarbomethoxy-5-methylhex-4-en-1,6-diyl]}iron*, 29b, is consistent with the proposed structure. Detailed analysis of the spectrum was based upon double resonance experiments (Figure 2.12). A *geminal* coupling $J(H^9-H^{10})$ = 3.0 Hz was the

Table 2.15: *^{1}H-NMR data for tricarbonyl{1,4,5,6-η^4-(trans)-1,2-dicarbomethoxy-methylhex-4-en-1,6-diyl}iron compounds*[a]

	29b	**30b**	**29a**	**30a**[b]
α-ester	endo	endo	exo	exo
methyl	5-CH_3	4-CH_3	5-CH_3	4-CH_3
δ/ppm				
H^1	2.99	2.95	2.07	1.90
H^2	3.24	3.24	3.27	3.27
H^3	3.58	3.56	3.59	3.51
H^4	2.58	2.56	3.68	3.55
H^5	~2.18	2.12	0.77	0.95
H^6	~2.18	2.08	2.02	1.75
H^7	3.87	1.40	3.98	1.48
H^8	1.17	3.75	1.18	4.31
H^9	3.42	3.32	2.09	1.92
H^{10}	2.94	2.80	2.95	3.04
J/Hz[c]				
(1,4)	11.0	12.0	12.0	12.0
(4,5)	8.0	7.0	13.0	13.5
(4,6)	11.5	12.9	5.5	5.5
(5,6)	15.0	16.0	13.0	12.0
(6,7)	5.0	-	7.8	-
(7,5)	4.0	-	7.4	-
(7,10)	1.5	-	1.9	-
(9,10)	3.0	3.0	1.9	2.0
(8,9)	-	13.8	-	12.8
(8,10)	-	9.2	-	8.0

[a] *in benzene-d_6, Bruker WH 270, at 27 °C, ±1.*

[b] *analytically pure sample was not obtained, assignment was tentatively carried out from a mixture of both 29a and 30a.*

[c] *coupling is, in part, deduced from spectra in different solvents.*

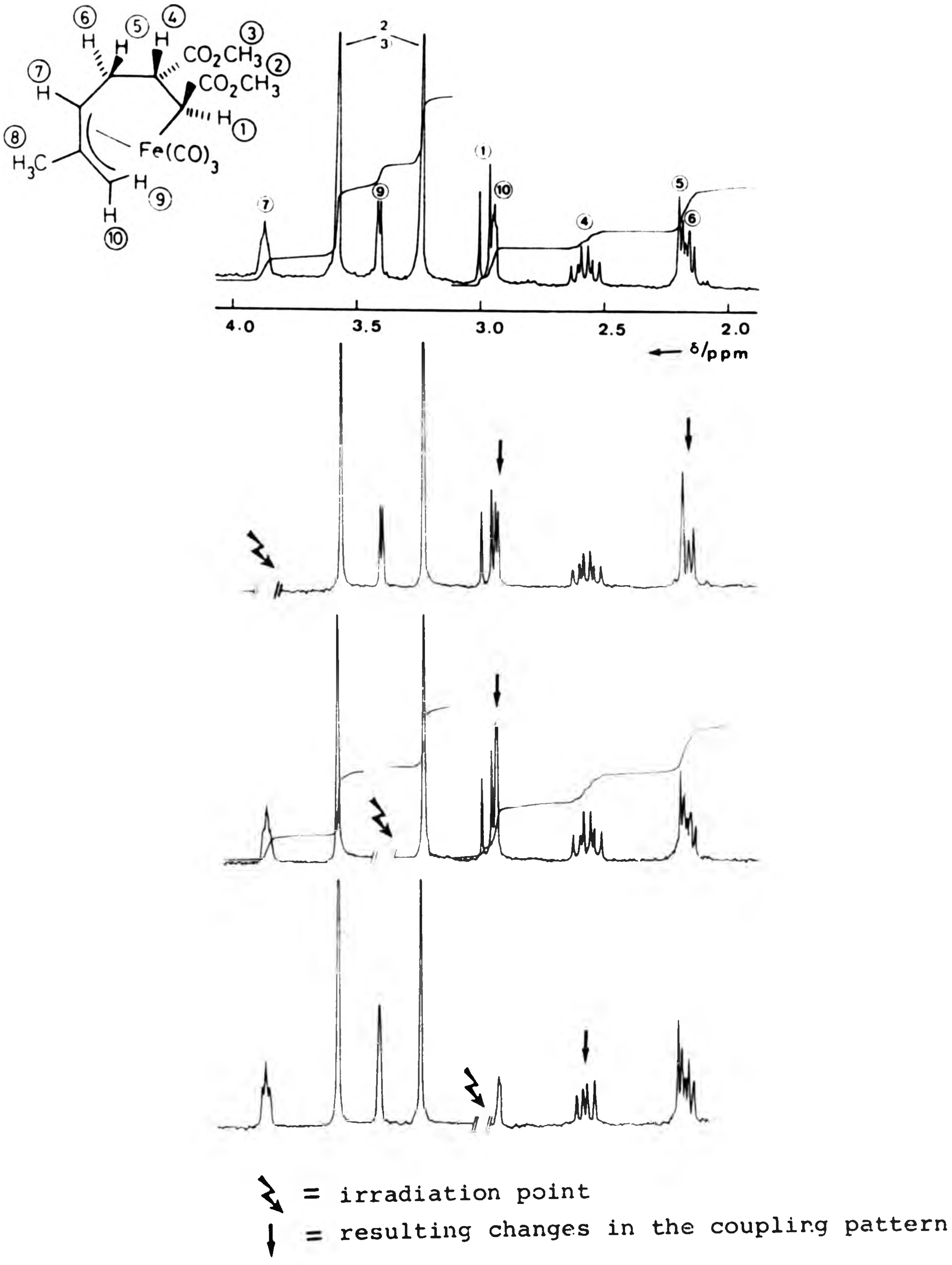


Figure 2.12: ^{1}H-NMR spectrum and double resonance experiments of 29b, in C_6D_6, Bruker WH 270, at 27 °C ±1.

sole coupling observed for proton H^9. The coupling $J(H^7-H^{10}) = 1.5$ Hz is typical of a W-type coupling over three carbon atoms. No coupling was observed between either H^{10} or H^9 with a neighbouring proton, thus indicating that the methyl group is in the *meso*-position of the allylic moiety. The chemical shifts of both allylic protons H^9 (*anti*) and H^{10} (*syn*) were used to confirm the orientation of the α-ester group (cf. Section 2.3.1). Since the doublet due to H^9 appears at lower field than H^{10}, the α-ester group is assigned to an *endo*-position with respect to the allyl group. The coupling constant between H^1 and H^4 is consistent with a *trans*-configuration of these protons and, consequently, of the ester groups.

In an additional double resonance experiment (Figure 2.13) irradiation at H^9 gave a *Nuclear Overhauser* enhancement of H^4 indicating a through-space interaction between these protons. Such an effect is only expected if the proton H^4 is directed towards the η^3-allyl group. Thus the orientation of the β-methyl ester group is confirmed.

The ^{1}H-NMR spectrum of **30b** (Figure 2.14) has been analysed in a similar way. The chemical shifts and coupling patterns of protons H^1 and H^6 are similar to those found for the corresponding protons in **29b** (Table 2.15), hence the α-ester group is also assigned to an orientation which is *endo* with respect to the η^3-allyl moiety and *trans* to the β-ester group. This was confirmed by the observation that the inner proton, H^9, resonates at lower field than the outer proton, H^{10}.

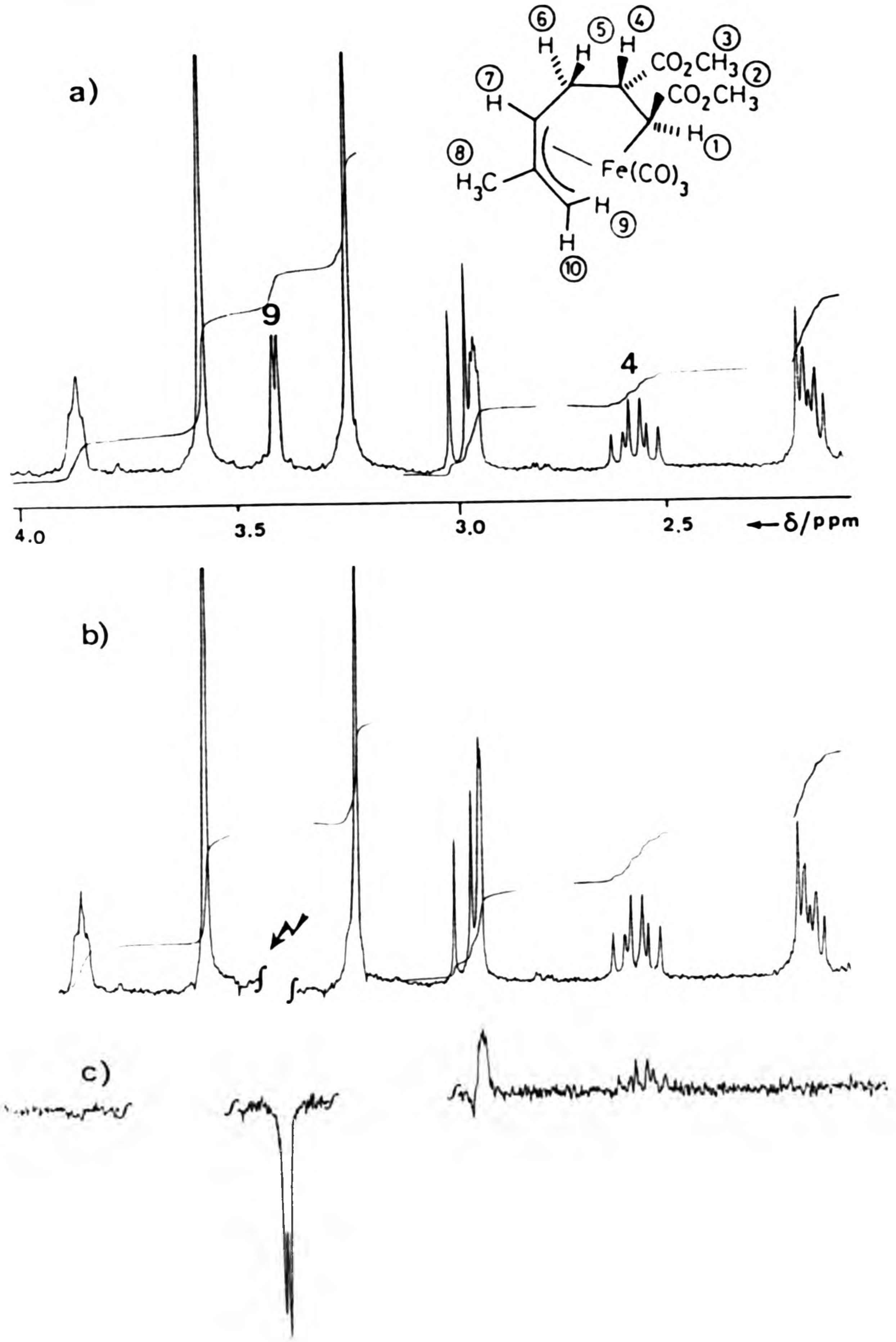


Figure 2.13: Nuclear Overhauser effect in 29b, Bruker WH 270, 27 °C ±1.

a) normal spectrum

b) irradiation at H^9

c) difference spectrum (b-a)

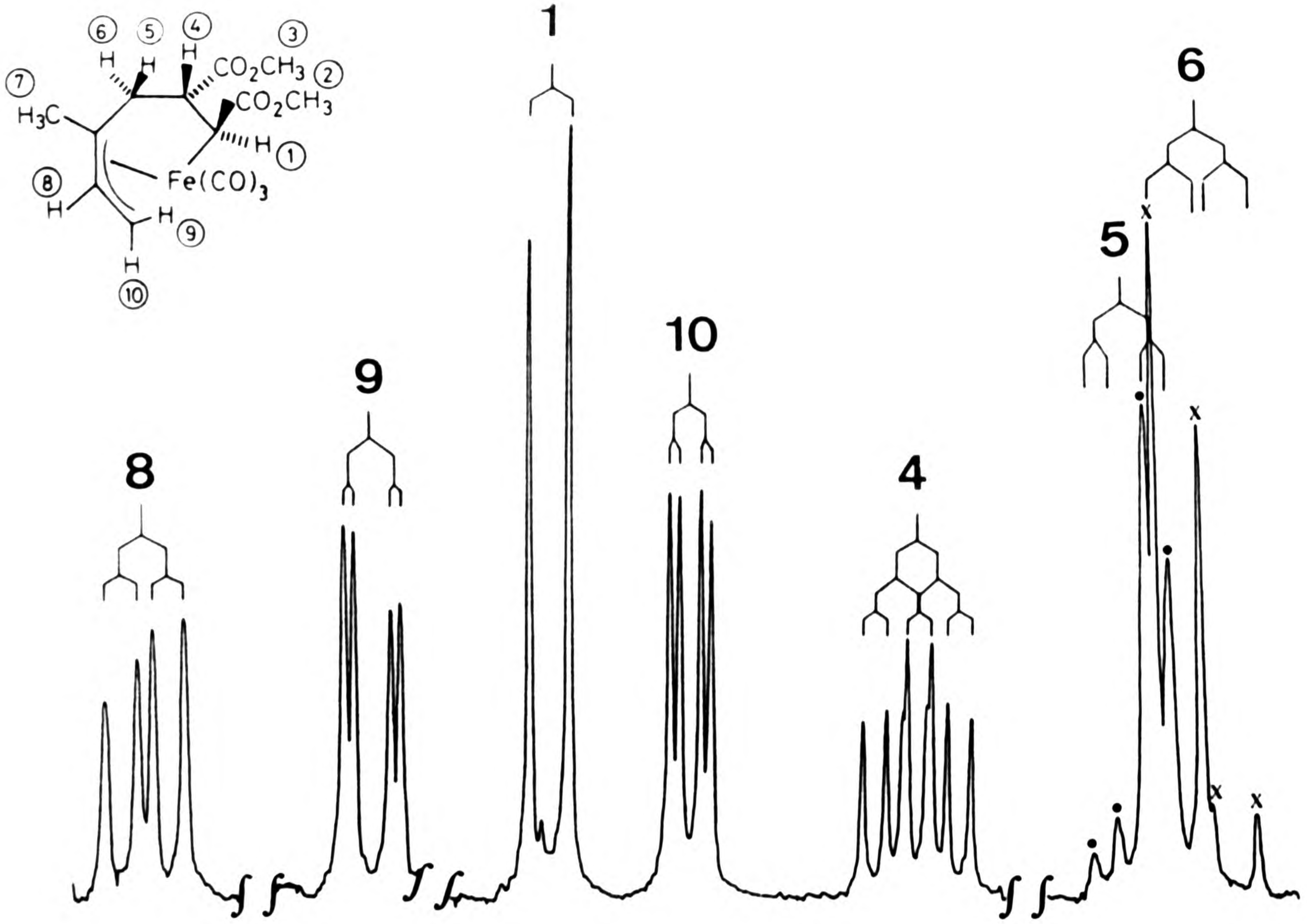


Figure 2.14: Coupling patterns of the individual protons of 30b, in C_6D_6, Bruker WH 270, at 27 °C ±1.

The splitting patterns of H^8, H^9, and H^{10} are typical of a vinylic group {100}. H^8 appears as a doublet of doublets centred at δ 3.75 ppm with $J(H^8-H^9)$ = 13.8 Hz (*trans*) and $J(H^8-H^{10})$ = 9.2 Hz (*cis*). Protons H^9 and H^{10} each appear as doublets of doublets centred at δ 3.32 ppm and δ 2.80 ppm, respectively, with $J(H^9-H^{10})$ = 3 Hz. As expected, the *meso* proton, H^8, resonates at lower field than protons H^9 and H^{10} (*anti* and *syn*).

The structure of **29a** has been elucidated by comparison with compound **21a** (Section 2.3.1). The ^{1}H-NMR signals of relevant protons of **29a** in CD_2Cl_2 are shown in Figure 2.15. In this solvent the signals are well separated (cf. data in C_6D_6, Table 2.15, with substantial overlapping of H^1, H^6, and H^9). Proton H^9 appears as a doublet centred at δ 2.64 ppm with $J(H^9-H^{10})$ = 1.9 Hz. Proton H^{10}, however, shows an additional small allylic coupling $J(H^7-H^{10})$ = 1.9 Hz. Proton H^7 shows two larger, almost equal couplings of 7.4 and 7.8 Hz with H^5 and H^6, respectively, as well as the allylic coupling with H^{10}. It is evident, therefore, that the methyl group (H^8) is attached to the central carbon atom of the allylic group. As with the **b** isomers, $J(H^1-H^4)$ = 12.0 Hz indicates a *trans* configuration of the two ester groups. This, together with $J(H^4-H^5)$ = 13.0 Hz and $J(H^4-H^6)$ = 5.5 Hz (Table 2.15) indicates that the α-ester group is in an *exo*-orientation relative to the η^3-allyl moiety. This assignment is confirmed by the reverse ordering of the chemical shifts of protons H^9 and H^{10} with respect to those compounds having an *endo*-configuration. Double resonance expe-

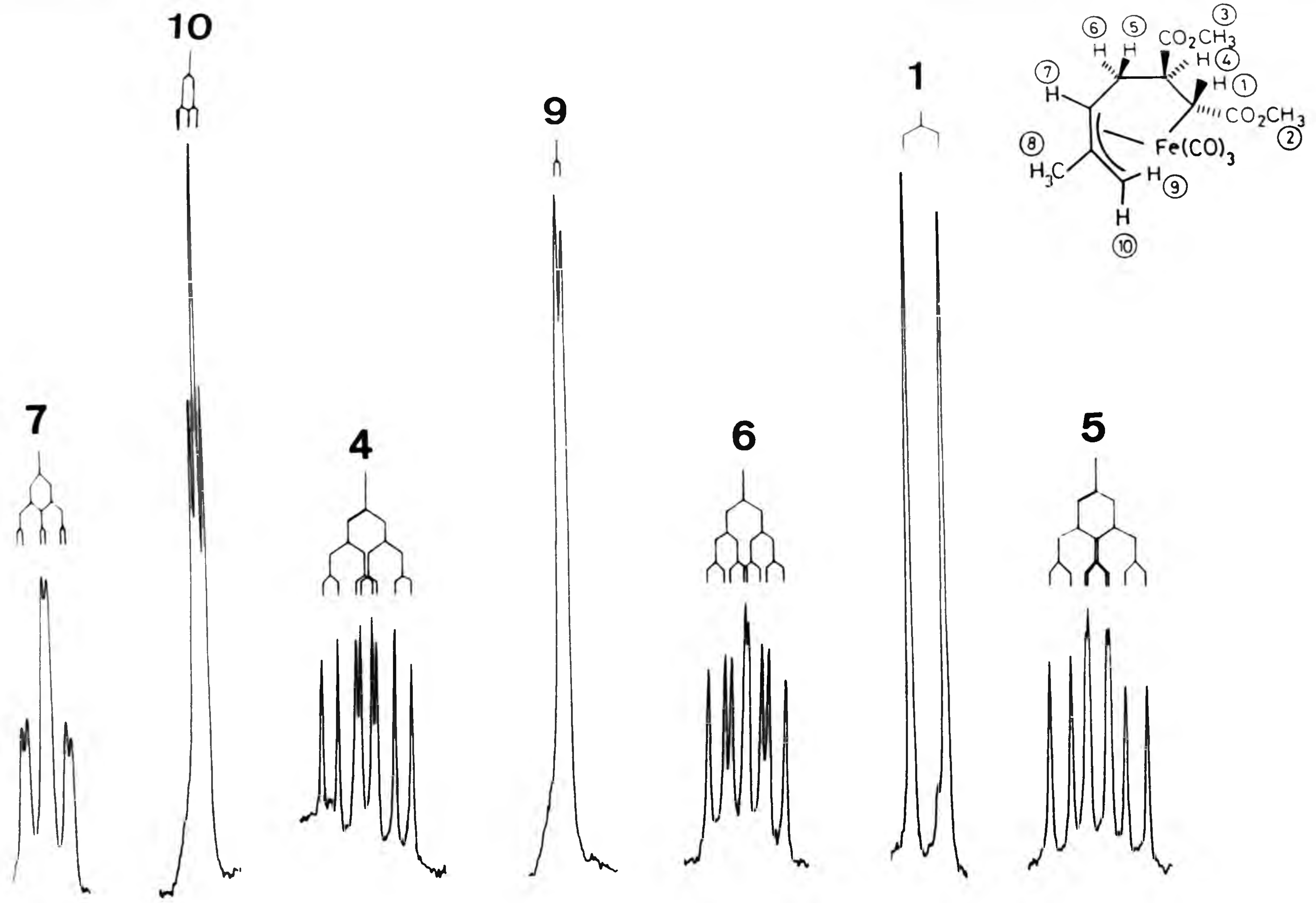


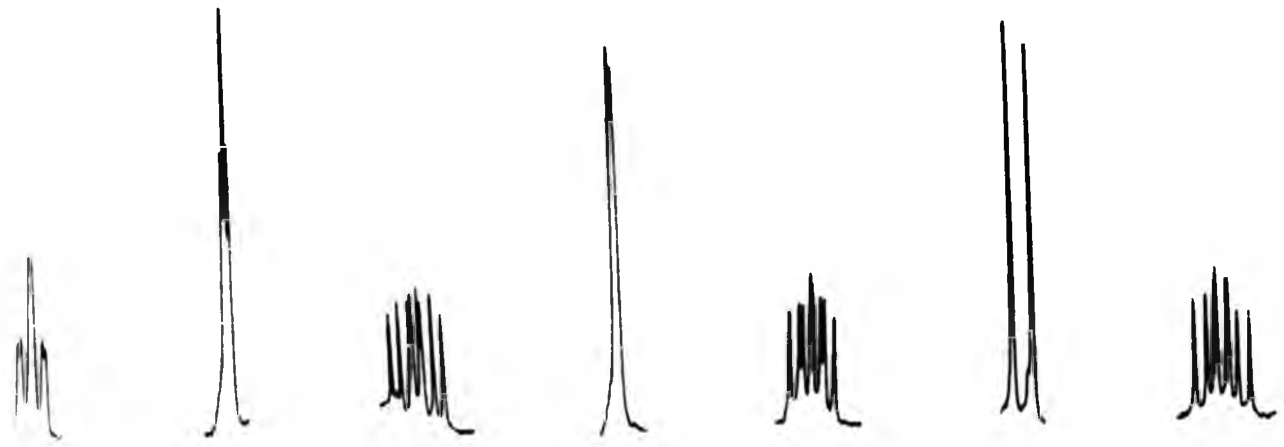
Figure 2.15: ^{1}H-NMR signals of selected protons from compound 29a, in CD_2Cl_2, Bruker WH 270, at 27 °C ±1.

riments were also carried out as a final confirmation of the assignment and the results are shown in Figure 2.16.

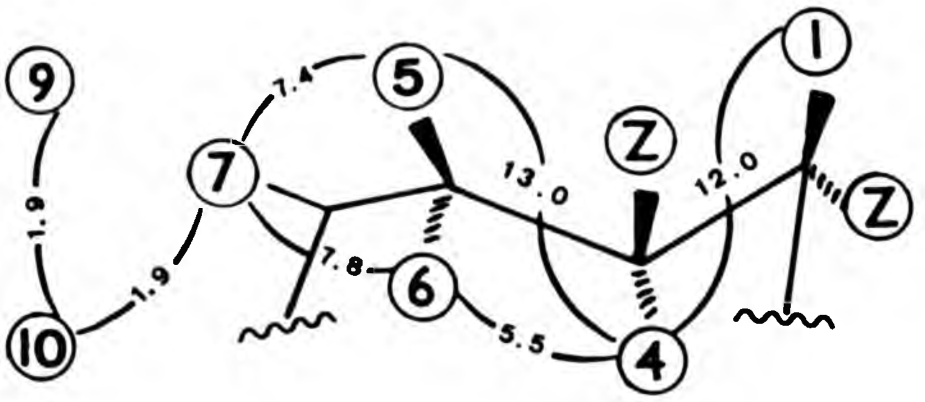
The fourth isomer 30a was identified in a mixture containing 29a. The chemical shifts and coupling constants are directly compared with the other isomers in Table 2.15. Using the arguments discussed previously, the compound 30a was assigned to a *trans-exo*-ester/4-methyl structure as shown above.

^{13}C-NMR spectroscopic data for compounds 29b, 30b, and 29a are given in Table 2.16, and the spectra of compounds 30b and 29a are shown in Figure 2.17. In all three complexes, two ester carbonyl resonances were observed; the one at lower field was assigned to C^2 and the other to C^{14}. This assignment was based on comparison with other examples (cf. 2.3.1, and Table 2.5). The only singlet observed in each of the non-decoupled spectra must be associated with the carbons C^8, C^{10}, and C^8 in 29b, 30b and 29a, respectively, which carry the methyl substituent. Three doublets in the spectrum of compound 30b were assigned to C^3, C^8 and C^{13} on the basis of their chemical shifts and coupling constants by analogy with other examples (Section 2.3.1). The remaining resonances showed no unusual features and were assigned as shown.

The spectra of compounds 29a and 29b were assigned in a similar way. The spectrum of the mixture containing the fourth isomer, 30a, did not prove amenable to analysis due to the presence of many overlapping signals.



	7	10	4	9	6	1	5	
δ	4.78	3.73	3.35	2.64	2.33	1.75	0.95	ppm
	+	−	+	−	+	−	↯	
	−	−	+	−	−	↯	−	
	+	−	+	−	↯	−	+	
	−	−	↯	−	+	+	+	
	+	↯	−	+	−	−	−	
	↯	+	−	−	+	−	+	



↯ = double irradiation

+ = change observed in the appearance of the signal

− = no change observed

Figure 2.16: Confirmation of the assignment of the proton signals of 29a by ^{1}H-NMR-decoupling experiments, in CD_2Cl_2.

Table 2.16: ^{13}*C-NMR data for tricarbonyl{1,4,5,6-η^4-(trans)-1,2-dicarbomethoxy-methylhex-4-en-1,6-diyl}iron compounds.*[a]

	29b	**30b**	**29a**
C^1	50.1 (q,145)	50.1 (q,144)	50.4 (q,144)
C^2	180.1 (s, -)	180.4 (s, -)	178.8 (s, -)
C^3	34.1 (d,133)	32.1 (d,133)	43.5 (d,136)
C^4	212.9 (s, -)	212.8 (s, -)	211.1 (s, -)
C^5	210.6 (s, -)	211.0 (s, -)	210.1 (s, -)
C^6	205.5 (s, -)	206.1 (s, -)	205.0 (s, -)
C^7	58.9 (t,158)	53.5 (t,161)	59.9 (t,155)
C^8	112.1 (s, -)	96.5 (d,158)	116.0 (s, -)
C^9	29.7 (q,128)	-	27.4 (q,128)
C^{10}	82.1 (d,150)	100.4 (s, -)	81.6 (d,155)
C^{11}	-	29.9 (q,128)	-
C^{12}	37.5 (t,127)	42.3 (t,129)	33.2 (t,128)
C^{13}	44.4 (d,130)	43.7 (d,130)	58.4 (d,133)
C^{14}	174.4 (s, -)	169.4 (s, -)	172.9 (s, -)
C^{15}	51.3 (q,146)	51.3 (q,147)	51.0 (q,147)

[a] *in toluene-d_8, Bruker WH 270, at 27 °C ±1, in brackets $^{1}J(C-H)/Hz$*

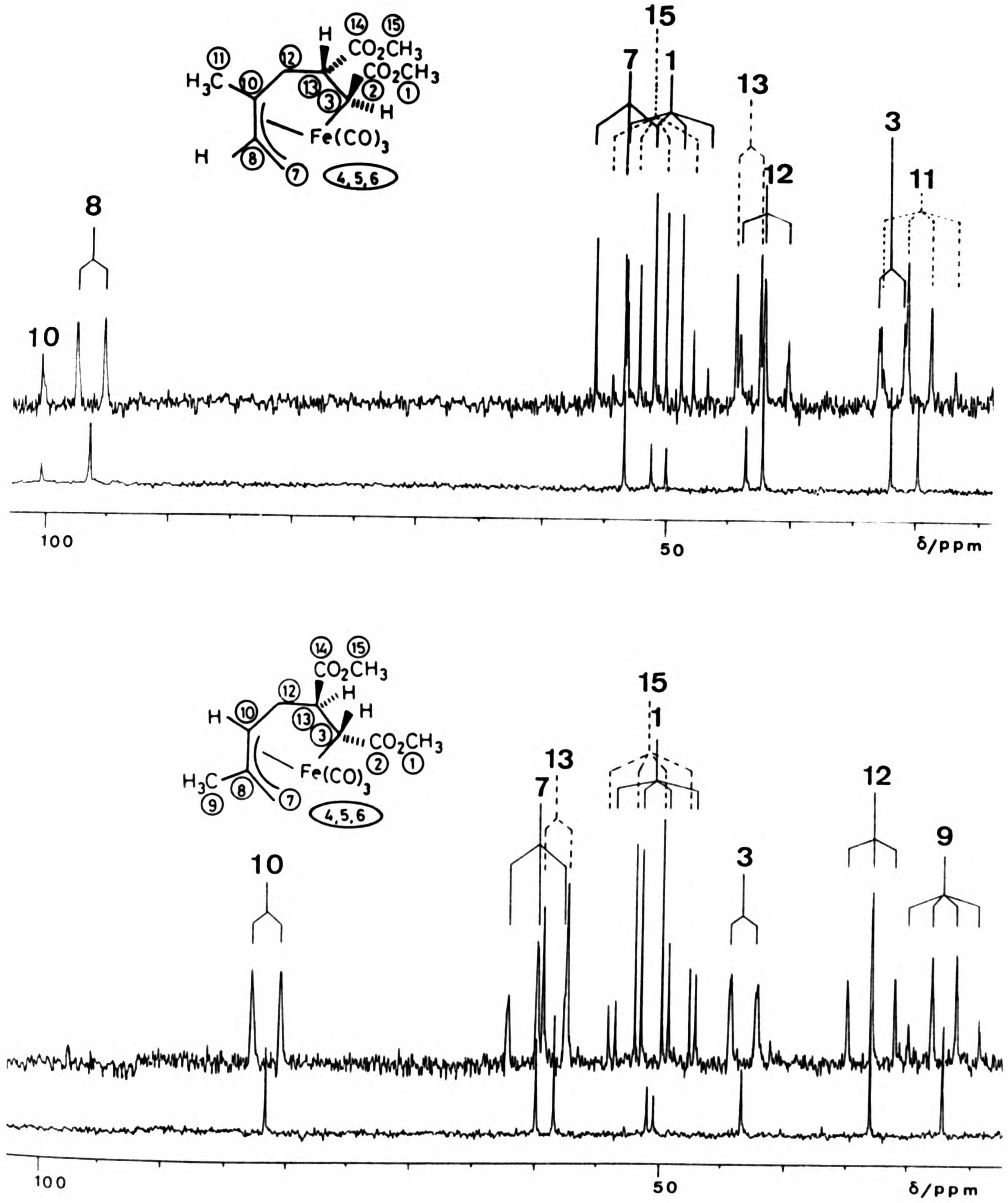
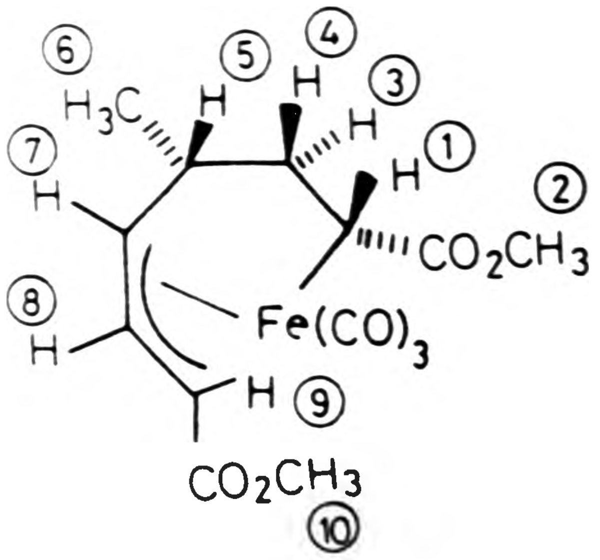


Figure 2.17: Comparative non-decoupled ^{13}C- and ^{13}C-{^{1}H}-NMR spectra of 30b and 29a.

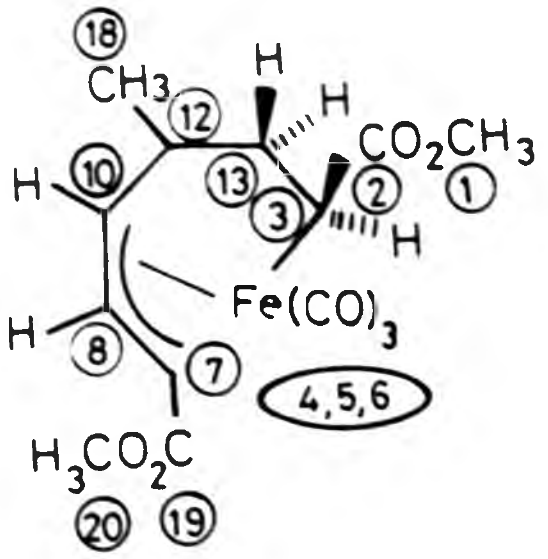
The results show that all four isomers retain the *trans*-arrangement of the fumarate ester group. In addition, the α-ester group (attached to the σ-bonded carbon atom) is in an *endo*-orientation for compounds 29b and 30b and an *exo*-orientation for compounds 29a and 30a. The difference between the compounds of either series a or b is the position of the methyl group on the η^3-allyl moiety. In compounds 29a and 29b the methyl group is on the fifth carbon atom (*meso*-position of the allylic group) whereas in 30a and 30b, it is on the fourth carbon atom.

2.4.2. Reaction of methyl sorbate with methyl acrylate and pentacarbonyliron

This reaction afforded two isomeric $(\sigma,\eta^3\text{-allyl})Fe(CO)_3$ complexes, 31a (21 %) and 31b (7 %). In addition, $(\eta^2\text{-MA})Fe(CO)_4$, $(\eta^4\text{-MSo})Fe(CO)_3$ and two organic products, 32-Z and 32-E, were obtained.



31 a



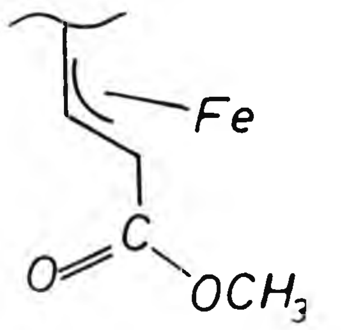
31 b

The mass spectra of both isomers 31**a** and 31**b** showed the molecular ion and peaks corresponding to the ions $[M-nCO]^+$ (n = 1-3). These compounds were classified as **a** or **b** type on the basis of the α-ester carbonyl vibration in their IR spectra (Table 2.17).

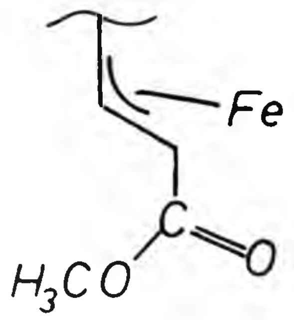
Table 2.17: IR-data (cm^{-1}, in n-hexane) for tricarbonyl(MA/MSo) iron compounds

complex	ν̃(CO)				ν̃(ester-CO)	
31**a**	2077.5	2021.1	(2010.8 sh)	2011.0(w)	1725.0	1713.5
31**b**	2073.3	2020.7	(2017.8 sh)	2008.0	1722.9	1697.8

The observation of more than the expected three bands in the metal carbonyl region could possibly be due to the presence of different conformers where an ester carbonyl group adopts different conformations, e.g. *s-cis* and *s-trans*. A similar phenomenon has been reported for, e.g. (η^2-dimethyl maleate)$Ru(CO)_4$ {107} which exhibits more than four metal carbonyl bands.



(s-cis-conformation)



(s-trans- conformation)

The ^{1}H-NMR spectra of isomers **31a** and **31b** are shown in Figure 2.18, and the data are summarized in Table 2.18. In both isomers, the coupling pattern of H^5 with H^3, H^4, H^7 and the methyl protons (H^6) together with that involving $J(H^1-H^3)$, $J(H^1-H^4)$, indicate that the former acrylate ester group is situated at the σ-bonded α-carbon atom and the methyl substituent is on the γ-carbon atom of the six-carbon chain, i.e. the C-C coupling has occured between the methylenic carbon atom of the olefin and the methyl substituted carbon atom of the diene component.

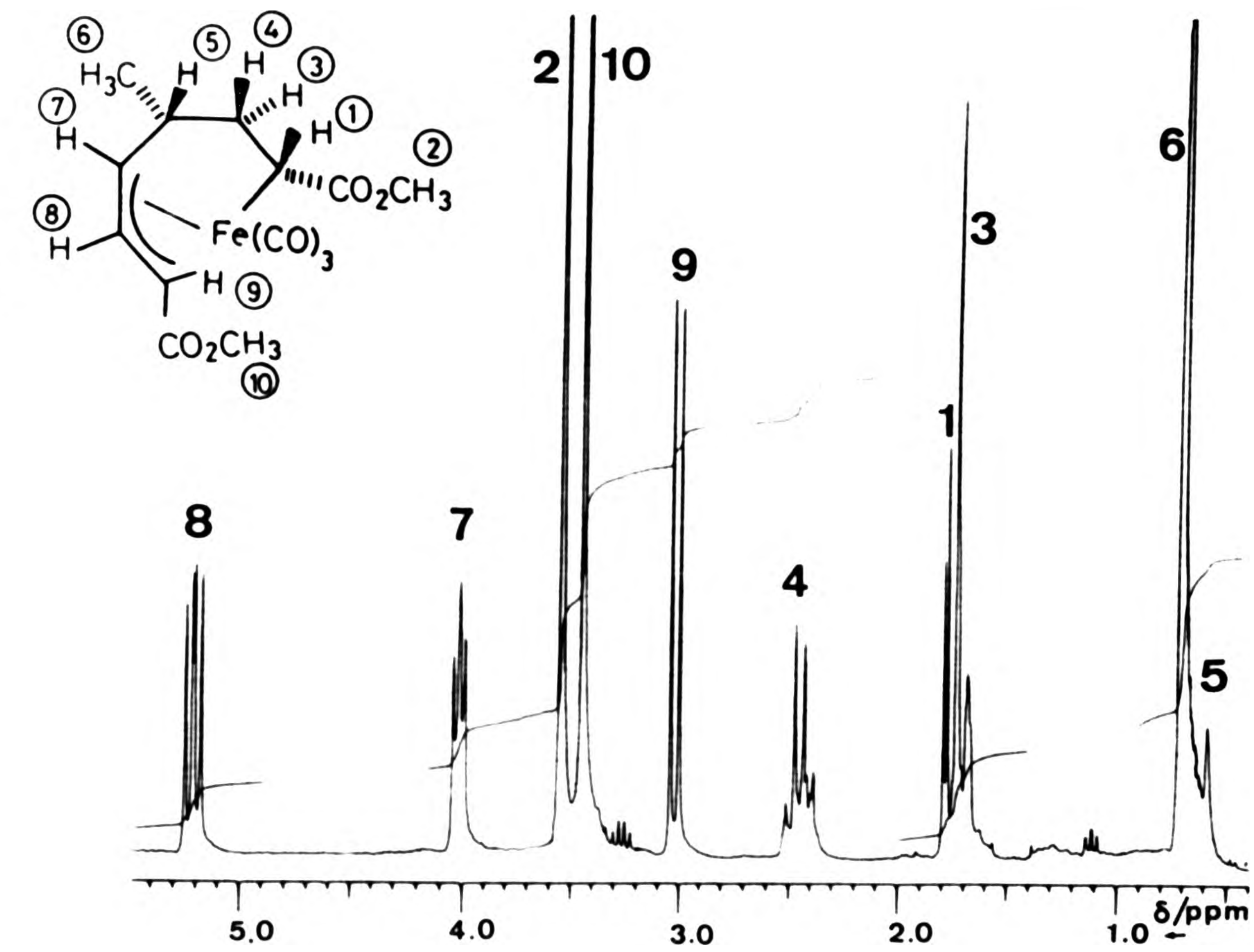
In both isomers, the presence of H^8, as a doublet of doublets, at lower field than H^9 is consistent with the order of an η^3-allylic system {95}. The coupling constant of H^8-H^9 (11.5 and 11.4 Hz for **31a** and **31b**, respectively) is indicative of a *trans*-configuration of these two protons, i.e. the methyl ester group (H^{10}) is at *syn* position of the η^3-allyl moiety.

H^9 appears as a doublet at higher field in **31a** than in **31b** due to the anisotropic effect of the methyl ester group attached to the σ-bonded carbon, C^3. This indicates that compound **31a** is an *exo*-isomer and compound **31b** is an *endo*-isomer.

Double resonance experiments were carried out and the results confirmed both the assignment of signals and the structural configuration made here.

^{13}C-NMR data for **31a** and **31b** are given in Table 2.19. Comparative ^{13}C-NMR spectra of both **31a** and **31b** are shown in

31 a



31 b

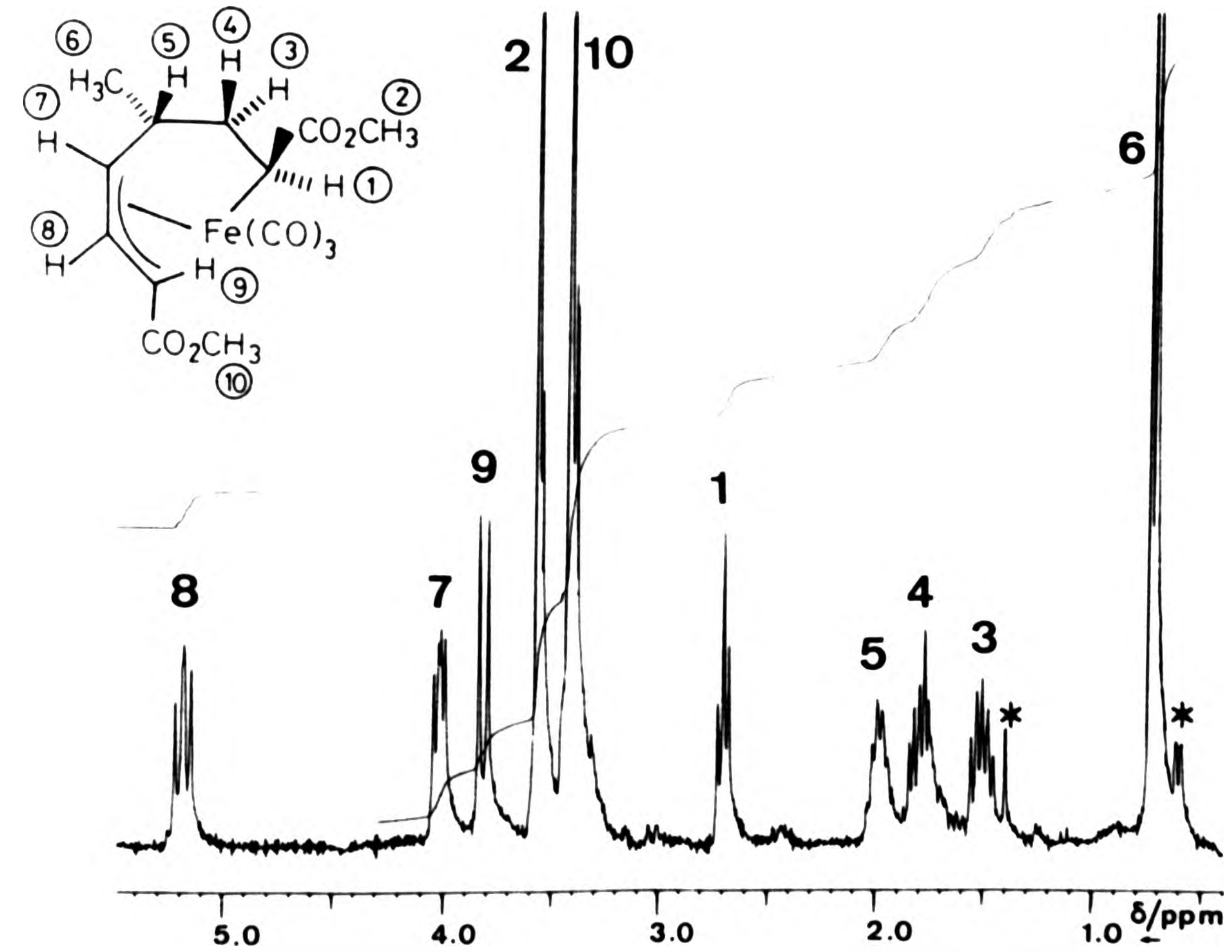


Figure 2.18: Comparative ^{1}H-NMR spectra of 31a and 31b in C_6D_6, Bruker WH 270, 27 °C ±1.

Table 2.18: ^{1}H-NMR data for (methyl/sorbate methyl acrylate)Fe(CO)$_3$ compounds.[a)]

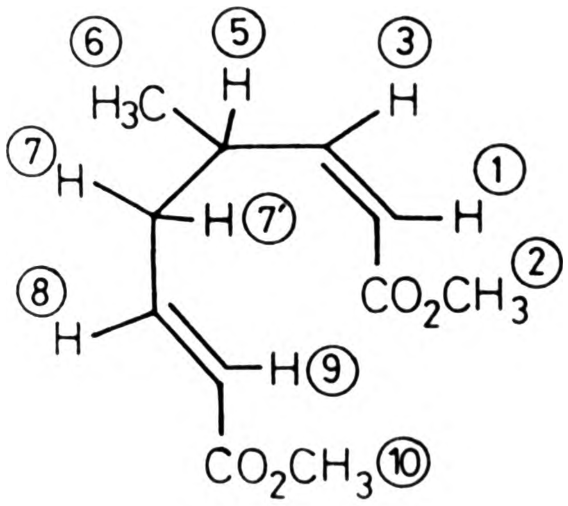
31a								31b	
Solvent δ/ppm	$CDCl_3$	$CDCl_3/C_6D_6$				C_6D_6	J/Hz	C_6D_6	J/Hz
		80/20	60/40	40/60	20/80				
H^1	1.91	1.82	1.78	1.77	1.74	1.72	(1,4)=12.5	2.69	(1,4)= 6.3
H^2 b)	3.69	3.63	3.59	3.57	3.55	3.55	-	3.57	-
H^3	2.01	1.90	1.85	1.77	1.74	1.72	(3,1)= 4.0	1.50	(3,1)= 6.3
H^4	2.47	2.42	2.39	2.36	2.39	2.43	(4,3)=12.9	1.78	(4,3)=13.5
H^5	1.36	1.17	1.11	0.88	0.76	0.67	(5,4)=12.8	1.97	(5,4)= 6.2
H^6	1.18	1.03	0.95	0.88	0.80	0.69	(6,5)= 6.2	0.72	(6,5)= 6.6
H^7	4.97	4.69	4.52	4.37	4.20	4.02	(7,5)= 7.4	4.02	(7,5)= 5.5
H^8	5.66	5.50	5.40	5.33	5.26	5.22	(8,7)= 8.0	5.19	(8,7)= 8.5
H^9	3.31	3.19	3.13	3.08	3.04	3.02	(9,8)=11.5	3.82	(9,8)=11.4
H^{10} b)	3.83	3.71	3.64	3.58	3.52	3.45	-	3.42	-

a) spectra measured on Bruker WH 270, at 27 °C ±1.

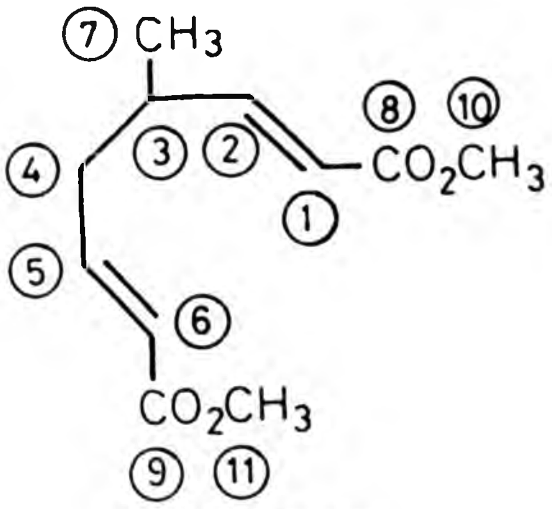
b) tentative assignments by comparison with previous examples (cf. Tables 2.4, 2.10, and 2.15).

Figure 2.19. The two allylic carbon atoms C^8 and C^{10} are distinguished from C^7 on the basis of the chemical shift and comparison with other examples. The remaining two doublets in the non-decoupled spectrum of each isomer were assigned to C^3 and C^{12}. The chemical shifts and coupling constants of C^3 and C^{12} are consistent with an sp^3 hybridized carbon atom. The assignment of C^1 and C^{20} was achieved by comparison with previously discussed compounds.

The two organic products, 32-Z and 32-E, arising from the reaction involving methyl sorbate and methyl acrylate were obtained in very low yield and in an impure form. The mass spectrum of each of the products suggested a molecular weight of 212 corresponding to a (methyl sorbate-methyl acrylate) adduct, but in both cases the elemental analyses were not satisfactory.



32 – Z



32 – E

Table 2.19: ^{13}C-NMR data for tricarbonyl(methyl sorbate-olefin) iron adducts.$^{a)}$

	31a	31b	33a	35b
C^1	50.3 (q,146)	50.2 (q,144)	50.5 (q,147)	50.5 (q,147)
C^2	179.3 (s, -)	180.6 (s, -)	178.6 (s, -)	179.4 (s, -)
C^3	38.6 (d,139)	36.3 (d,130)	39.4 (d,142)	36.3 (d,130)
C^4	210.0 (s, -)	213.2 (s, -)	210.0 (s, -)	212.3 (s, -)
C^5	209.5 (s, -)	209.0 (s, -)	208.7 (s, -)	207.8 (s, -)
C^6	201.9 (s, -)	202.3 (s, -)	201.9 (s, -)	202.3 (s, -)
C^7	61.6 (d,165,9*)	60.7 (d,168,9*)	62.5 (d,164,8*)	62.0 (d,168,9*)
C^8	99.5 (d,160)	98.8 (d,161)	99.6 (d,167)	100.0 (d,164)
C^{10}	97.3 (d,153)	98.0 (d,153)	90.6 (d,161)	90.8 (d,161)
C^{12}	35.6 (d,132,6*)	31.4 (d,139,6*)	38.7 (d,128)	33.9 (d,137,6*)
C^{13}	53.5 (t,129)	46.5 (t,128)	66.3 (d,142)	64.5 (d,128)
C^{14}	-	-	172.5 (s, -)	172.4 (s, -)
C^{15}	-	-	50.9 (q,147)	50.8 (q,147)
C^{18}	20.7 (q,128)$^{b)}$	21.4 (q,127)$^{b)}$	21.3 (q,128)$^{b)}$	22.1 (q,128)$^{b)}$
C^{19}	172.3 (s, -)	173.0 (s, -)	171.9 (s, -)	171.6 (s, -)
C^{20}	51.5 (q,146)	51.4 (q,147)	51.6 (q,147)	51.4 (q,147)

a) in toluene-d_8, Bruker WH 270, at 27 °C +1.

b) partially hidden by solvent signal.

*) ^2J(C-H) long range coupling.

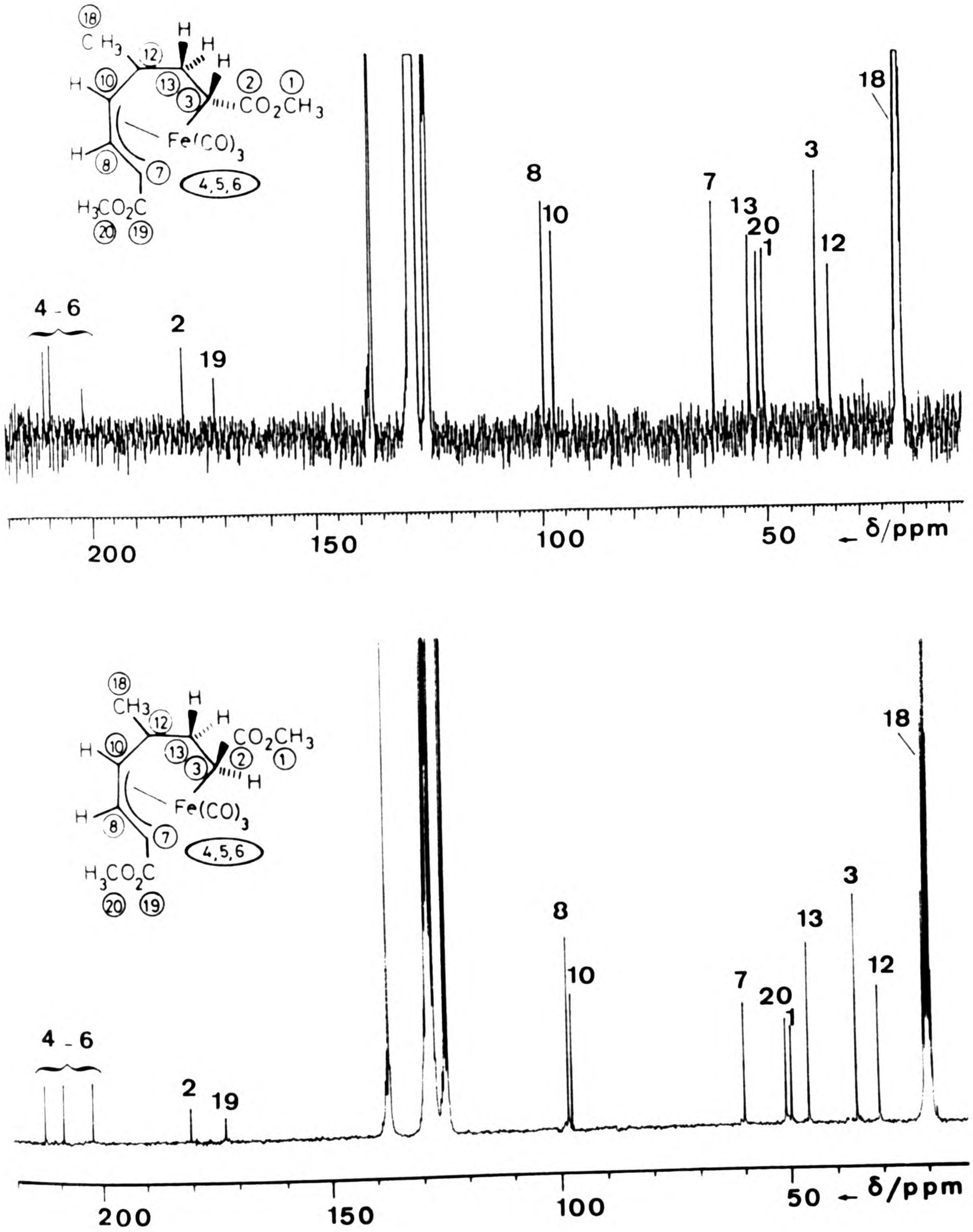


Figure 2.19: Comparative ^{13}C-{^{1}H}-NMR spectra of 31a and 31b in C_7D_8, Bruker WH 270, at 27 °C ±1.

The formulation of 32-Z and 32-E was accomplished using both ^{1}H- and ^{13}C-NMR spectroscopy. Furthermore, it is indirectly supported by the isolation in a pure form and the characterisation of an analogous product 34-E from the reaction of methyl sorbate with dimethyl fumarate and pentacarbonyliron (see Section 2.4.3). As discussed in Chapter four, these two isomeric hexa-1,5-diene derivatives arise from a secondary photoreaction of the respective (σ,η^3-organo)Fe(CO)$_3$ complexes.

The ^{1}H-NMR data for 32-Z are shown in Figure 2.20 and are summarized for both isomers in Table 2.20. Assignments of the signals and coupling constants were based on double resonance experiments. The spectra exhibit in addition to the two methyl ester singlets, six aliphatic protons (three signals with 3:2:1 intensity ratio) and four signals in the region characteristic of olefinic protons.

The appearance of proton H^5 as a multiplet resulting from coupling with the methyl group (H^6), the methylene group ($H^7/H^{7'}$), and the olefinic proton (H^3), together with the presence of coupling patterns corresponding to $J(H^1-H^3)$, and $J(H^8-H^9)$ indicate that in both compounds, 32-Z and 32-E, the two double bonds are in terminal positions, i.e. the compounds are hexa-1,5-diene derivatives.

In both isomers, the large coupling $J(H^8-H^9)$ = 15.4 Hz characteristic of *trans* arrangement is indicative of E-configuration of the methyl ester group at C^6. An important

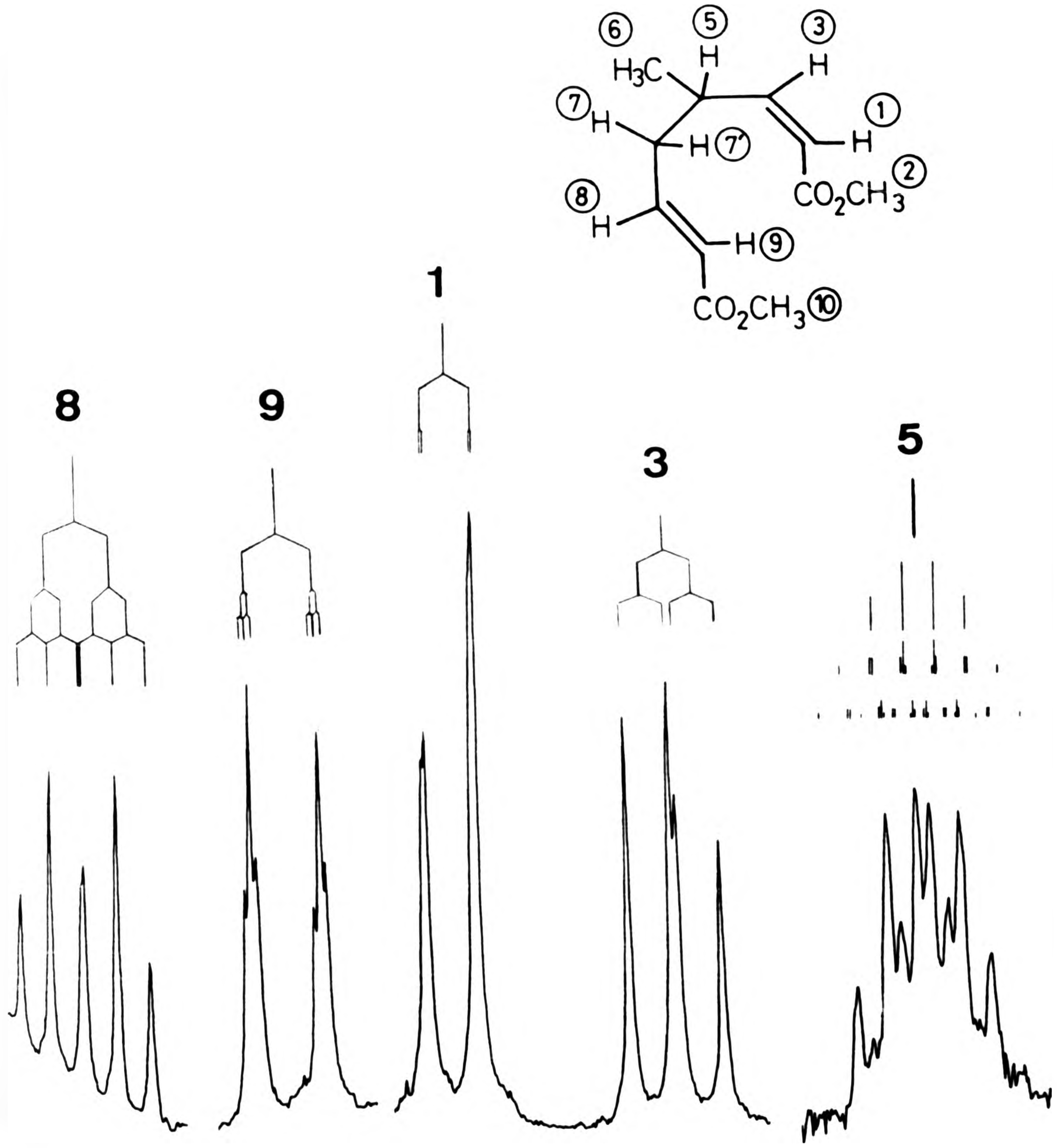


Figure 2.20: Parts of the ^{1}H-NMR spectrum of compound 32-Z and coupling patterns, in C_6D_6, Bruker WH 270, at 27 °C ±1.

Table 2.20: ^{1}H-NMR data for di- and tri-carbomethoxy-3-methylhexa-1,5-diene compounds.[a]

		32-Z	32-E	34-E
δ/ppm				
	H^1	5.64	5.69	6.60
	H^2	3.38	3.39	3.35
	H^3	5.45	6.79	-
	H^4	-	-	3.24
	H^5	3.79	~1.50	4.04
	H^6	0.76	0.59	1.15
	H^7	~1.80	~1.60	2.57
	$H^{7'}$		~1.80	2.25
	H^8	6.96	6.77	7.04
	H^9	5.82	5.71	5.89
	H^{10}	3.33	3.38	3.29
J/Hz				
	(9,8)	15.4	15.4	15.4
	(8,7)	7.5	7.6	7.7
	(8,7')	7.4	7.5	7.5
	(7,7')	?	?	14.2
	(7,5)	7.4	?	7.3
	(7',5)	7.4	?	7.0
	(6,5)	6.6	7.0	7.0
	(5,3)	9.9	7.2	-
	(3,1)	11.4	15.6	-
	(9,7)	1.5	1.5	1.5
	(9,7')	1.5	1.5	1.5

[a] *in benzene-d_6, Bruker WH 270, at 27 °C ±1.*

feature used to distinguish these two isomers is the smaller coupling constant between H^1 - H^3 in 32-Z (11.4 Hz) suggesting Z-configuration of the methyl ester at C^1 whereas, in 32-E, the coupling constant is larger {$J(H^1\text{-}H^3)$ = 15.6 Hz} typical of *trans* arrangement of these two protons and, hence the methyl ester group attached to C^1 is assigned to E-configuration.

^{13}C-NMR data (Table 2.21) for 32-Z and 32-E are in agreement with the structure derived from the ^{1}H-NMR data. The

Table 2.21: ^{13}C-NMR data for 1,6-dicarbomethoxy-3-methylhex-1,5-diene compounds$^{a)}$

		32-Z		32-E	
	$^{b)}$	δ/ppm	^1J(C-H)/Hz	δ/ppm	^1J(C-H)/Hz
C^1	d	154.3	155	152.4	154
C^6	d	146.6	152	146.0	149
C^2	d	123.4	156	123.3	162
C^5	d	119.4	156	120.5	159
C^3	d	32.1	142	35.6	129
C^4	t	39.4	132	38.2	128
C^7	q	20.5	127*	18.7	127
C^8	s	166.5	-	166.3	-
C^9	s	162.2	-	166.0	-
C^{10}	q	50.8	145	50.8	145
C^{11}	q				

$^{a)}$ in toluene-d_8, Bruker WH 270, at 27 °C ±1.

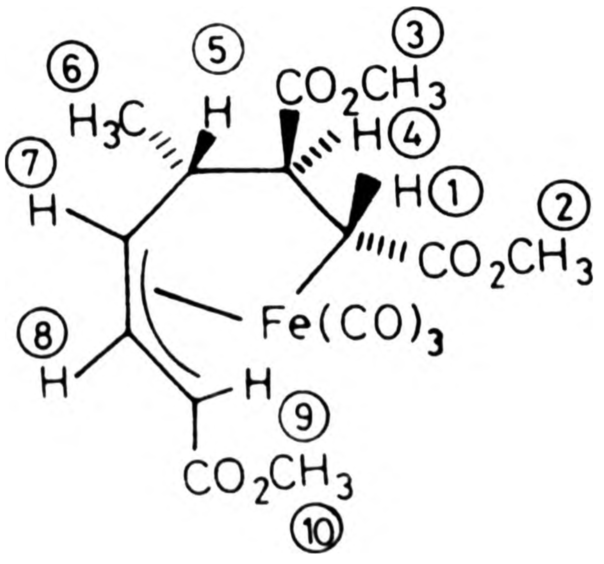
$^{b)}$ multiplicity.

$^{*)}$ partially hidden by the solvent signal.

spectra of both isomers showed resonances assignable to the methyl, ester carbonyl, and methoxy groups. Carbons C^8 and C^9 resonate almost together, therefore no further assignment of each could be made. Five resonances appear as doublets and are assigned on the basis of chemical shifts and coupling constants. The one at highest field was assigned to C^3. Another pair of doublets were assigned to C^2 and C^5. The remaining two doublets were assigned to either C^1 or C^6. The only triplet in the spectrum was assigned to C^4.

2.4.3. Reaction of methyl sorbate with dimethyl fumarate and pentacarbonyliron

The photochemical reaction of pentacarbonyliron with methyl sorbate and dimethyl fumarate gave only one (σ,η^3-organo)-$Fe(CO)_3$ isomer, the complex 33a in 28 % yield. None of the other possible isomers could be detected. The reaction also afforded the complexes (η^4-MSo)-$Fe(CO)_3$, (η^2-DMF)$Fe(CO)_4$ and (η^4-MSo)$_2$FeCO. Furthermore, the organic compound 34-E was obtained. This compound is analogous to the products 32-E and 32-Z obtained from the corresponding reaction involving methyl acrylate.



33a

Although the mass spectrum of 33a did not show a molecular ion $[M]^+$, the presence of peaks in the spectrum corresponding to the fragments [M-nCO] (n = 1-3) and $[M-OCH_3]^+$ indicate the molecular weight 410. The IR spectrum (Table 2.22) suggested that the compound has a type a structure.

Table 2.22: IR-data (cm^{-1}, in n-hexane) for (cis-/and trans-dimethyl ester substituted monoolefin-methyl sorbate)-Fe(CO)$_3$ adducts[a]

complex	$\tilde{\nu}$(CO)			$\tilde{\nu}$(ester-CO)		
						(α)
33a	2079.3	2024.9[b]	2017.9(w)	1746.2	1724.0	1714.1
35b	2076.3	2025.2	2010.2	1753.9	1724.0	1700.3

[a] *(MSo-DMF)Fe(CO)$_3$, (MSo-DMM)Fe(CO)$_3$.*

[b] *shoulders at 2030 and 2023 cm^{-1}.*

The ^1H-NMR spectroscopic data, shown in Table 2.23, are consistent with the proposed structure and were used to derive the steric arrangement of the substituents. Double resonance experiments were carried out and the results confirm the assignment made here. The essential features of the coupling pattern were $J(H^1-H^4) = 12.1$ Hz, $J(H^4-H^5) = 12.1$ Hz, $J(H^5-H^7) = 7.7$ Hz, and $J(H^8-H^9) = 11.0$ Hz. Hence it follows, by analogy with the data obtained for previously discussed compounds (Section 2.3.1, 2.4.2), that compound 33a was assigned to series a, that is, the α-ester group is in an *exo*-position relative to the η^3-allyl group, and is in *trans*-configuration with the β-ester group. Conclusively, the ^1H-NMR data of 33a show that the compound retains the stereo-configuration of

Table 2.23: ^{1}*H-NMR data for (methyl sorbate-olefin)Fe(CO)*$_3$ *adducts.*$^{a)}$

	33a	**35b**
δ/ppm		
H^1	2.27	3.25
H^2	3.49	3.54
H^3	3.25	3.30
H^4	3.47	2.67
H^5	1.14	2.30
H^6	0.84	1.15
H^7	3.76	3.61
H^8	5.19	5.21
H^9	3.21	3.57
H^{10}	3.41	3.37
J/Hz		
(1,4)	12.1	7.0
(4,5)	12.1	12.1
(5,6)	6.3	6.3
(7,5)	7.7	7.4
(8,9)	11.0	10.7
(7,8)	7.9	7.7

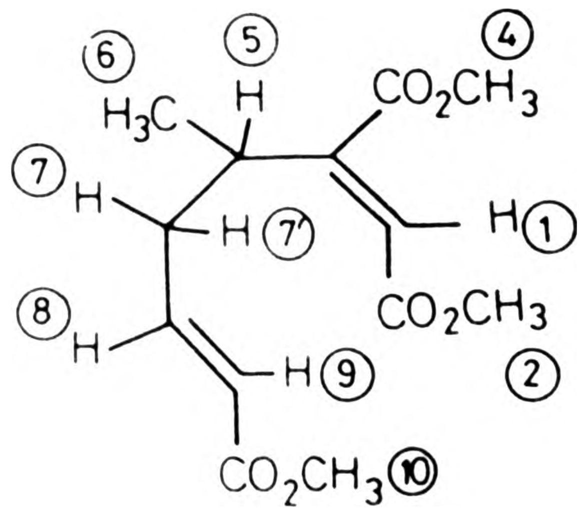
$^{a)}$ *in benzene-d*$_6$*, Bruker WH 270, at 27 °C ±1.*

both the olefinic and the diene components.

^{13}C-NMR spectra of compound 33a are in agreement with the structure deduced by ^{1}H-NMR. The data are summarized in Table 2.19. Figure 2.21 illustrates both ^{13}C- and ^{13}C-{^{1}H}-NMR spectra. Assignment of resonances was made by analogy with previous compounds and the data are consistent with the poposed structure.

In contrast to compounds 32-E and 32-Z compound 34-E was obtained in a very satisfactory state of purity. Its mass spectrum showed the molecular ion at m/e 270.

The ^{1}H-NMR data (Table 2.20) for the product 34-E are consistent with a structure similar to those of 32.



34-E

Three resonances of carbomethoxy groups, a doublet indicative of the methyl group, and six other proton resonances were observed. A singlet resonating at δ 6.60 ppm was assigned to H^{1}, and the other five protons were assigned and confirmed by double resonance experiments (Figure 2.22). The methyl ester group, H^{10}, was assigned to a *trans*-geometry relative to

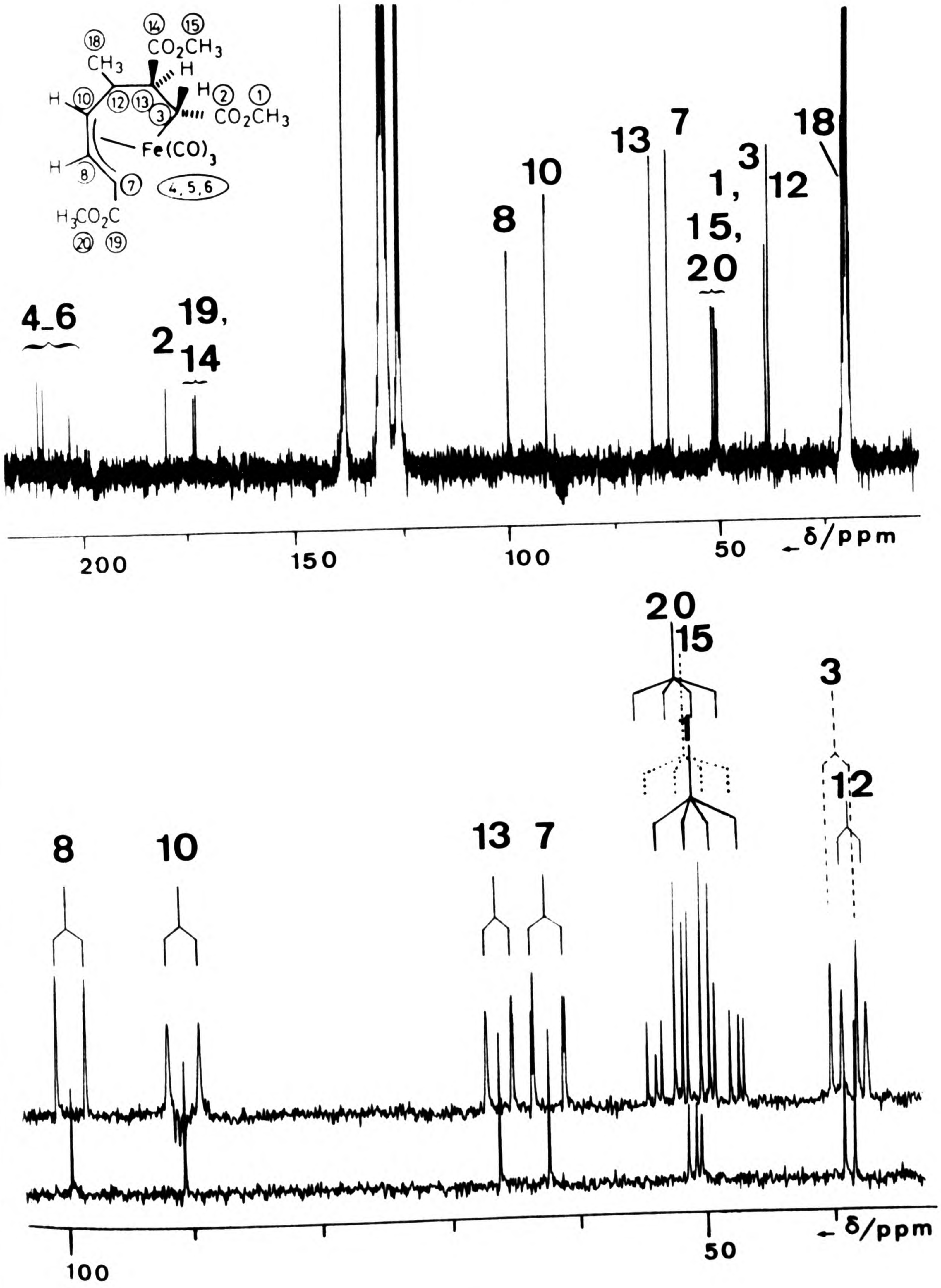
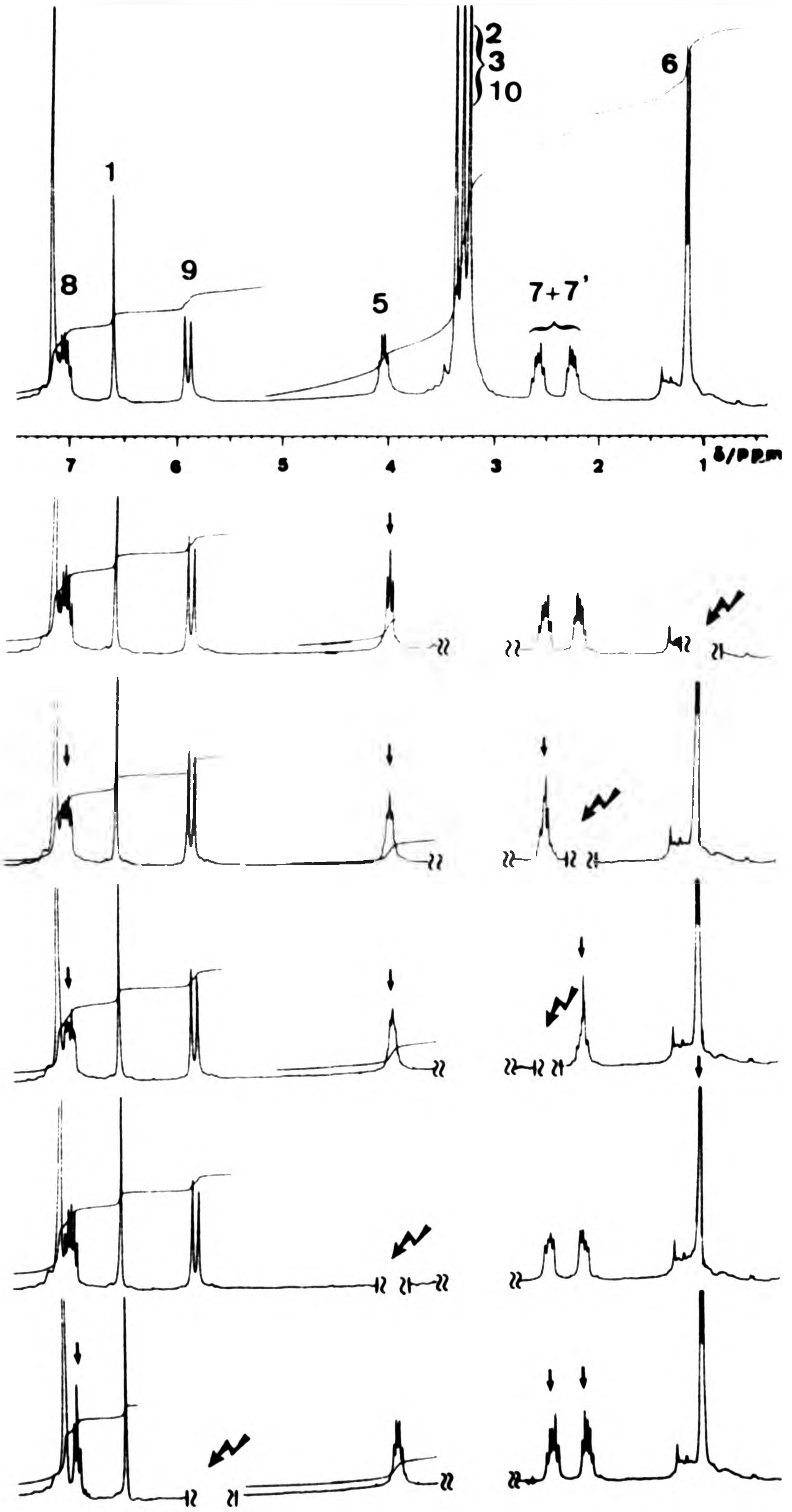


Figure 2.21: Non-decoupled ^{13}C and $^{13}C-\{^{1}H\}$-NMR spectra of compound 33a.

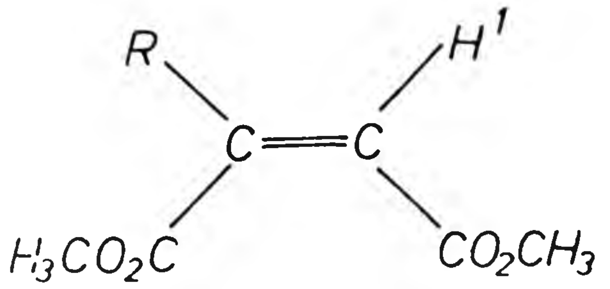


↯ = irradiation point , ↓ = resulting change in the coupling pattern

Figure 2.22: ^{1}H-NMR spectrum and decoupling experiments of compound 34-E, in C_6D_6, Bruker WH 270, at 27°C ± 1.

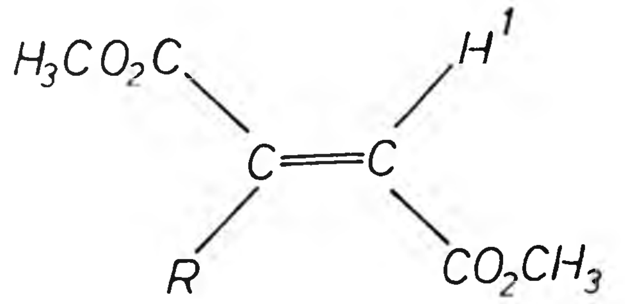
the rest of the chain indicated by the large coupling, 15.4 Hz, between H^8 and H^9. This, together with the position of the singlet resonance corresponding to H^1, clearly indicates that the two double bonds are situated in terminal positions, i.e. the compound 34-E is a hexa-1,5-diene derivative.

The two methyl ester groups, H^2 and H^4, were assigned to E-configuration on the basis of the chemical shift of H^1 (δ 6.60 ppm): comparison with various related compounds {108} indicates that in 34-E the terminal olefinic proton H^1 is *cis* to the vicinal ester group.



H^1: δ 6.16 ppm (R=H)

H^1: δ 5.79 ppm (R=CH_3)

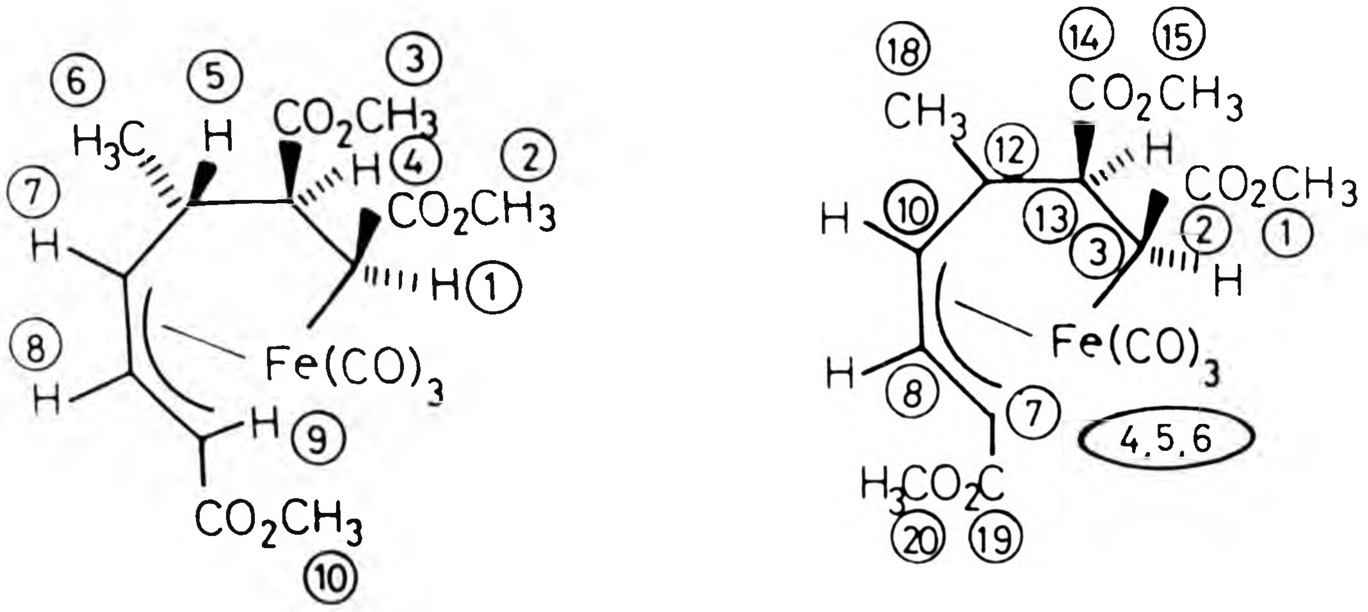


H^1: δ 6.86 ppm (R=H)

H^1: δ 6.62 ppm (R=CH_3)

2.4.4. Reaction of methyl sorbate with dimethyl maleate and pentacarbonyliron

This reaction, as in the case of the analogous reaction involving dimethyl fumarate, afforded only one (σ,η^3-organo)$Fe(CO)_3$ isomer, 35b (38 % yield), together with the complexes (η^4-MSo)$Fe(CO)_3$ and (η^2-DMM)$Fe(CO)_4$. However, in this case no organic product of the 1,2,6-tricarbomethoxy-3-methylhex-1,5-diene type, i.e. a product analogous to 34-E, was isolated. This is either due to experimental separation problems or most probably to the relatively short irradiation period used (47h in the case of DMM compared with 171h or 350h for the DMF and MA systems, respectively).



35b

The mass spectrum of 35b showed peaks corresponding to $[M-nCO]^+$ (n = 1-3) and $[M-OCH_3]^+$. The IR spectrum (Table 2.22) suggested, on the basis of the α-ester carbonyl frquency, that the compound has a type b structure.

The ^1H-NMR data for 35b (Table 2.23) were compared with those of compounds 20b and 21a and confirmed that the complex was of type b with the two former maleate ester groups in a *cis*-arrangement. The down field chemical shift of proton H^9 in 35b relative to 33a indicates that the α-ester group in 35b was in an *endo*-orientation relative to the η^3-allyl moiety. This has been confirmed by an X-ray structural analysis (see Section 2.5).

^{13}C-NMR data are shown in Table 2.19 together with data for other complexes of the same type. The carbon resonances were assigned on the basis of chemical shift and coupling constant data as described in previous sections.

As with other $(\sigma,\eta^3$-adducts$)\mathrm{Fe(CO)}_3$ type, the compound 35b was found to retain the stereochemistry of the olefin substrate. In addition, products 31a, 31b, 33a, and 35b involving methyl sorbate as the diene component (cf. 2.4.2, 2.4.3, and 2.4.5) resulted in C-C bond formation at the methyl substituted atom of the diene system.

2.5 Discussion

This section is concerned with a general discussion of the work described in the previous sections of this chapter, of its relationship with other relevant work, and its wider implications. For convenience, the discussion is presented under the following headings:

Evaluation of the "one pot" reaction.

The structural characterization of the $(\sigma,\eta^3$-organo$)\mathrm{Fe(CO)}_3$ complexes.

General spectroscopic trends in the $(\sigma,\eta^3$-organo$)\mathrm{Fe(CO)}_3$ complexes.

Factors affecting the nature and stereochemistry of $(\sigma,\eta^3$-organo$)\mathrm{Fe(CO)}_3$ complexes.

^{13}C-NMR data are shown in Table 2.19 together with data for other complexes of the same type. The carbon resonances were assigned on the basis of chemical shift and coupling constant data as described in previous sections.

As with other (σ,η^3-adducts)Fe(CO)$_3$ type, the compound 35b was found to retain the stereochemistry of the olefin substrate. In addition, products 31a, 31b, 33a, and 35b involving methyl sorbate as the diene component (cf. 2.4.2, 2.4.3, and 2.4.5) resulted in C-C bond formation at the methyl substituted atom of the diene system.

2.5 Discussion

This section is concerned with a general discussion of the work described in the previous sections of this chapter, of its relationship with other relevant work, and its wider implications. For convenience, the discussion is presented under the following headings:

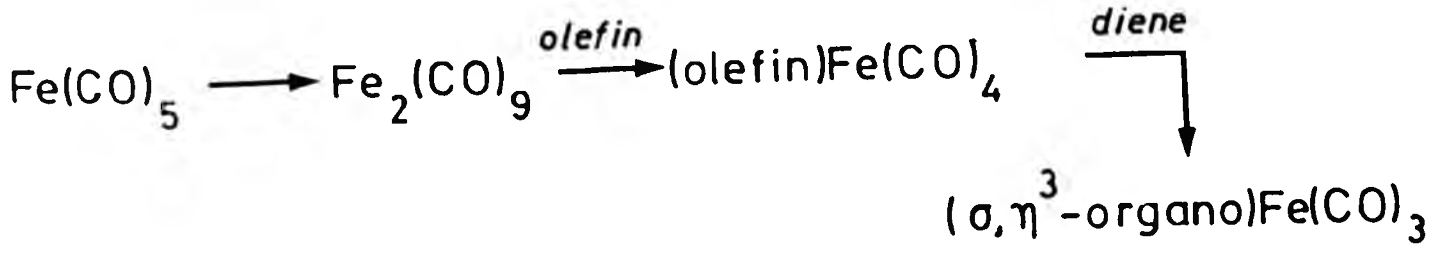
1. Evaluation of the "one pot" reaction.
2. The structural characterization of the (σ,η^3-organo)Fe(CO)$_3$ complexes.
3. General spectroscopic trends in the (σ,η^3-organo)Fe(CO)$_3$ complexes.
4. Factors affecting the nature and stereochemistry of (σ,η^3-organo)Fe(CO)$_3$ complexes.

2.5.1. Evaluation of the "one pot" reaction

The studies carried out during this work demonstrate the wide applicability of the "one pot" synthesis of $(\sigma,\eta^3$-organo$)Fe(CO)_3$ complexes. Generally this method affords the $(\sigma,\eta^3$-organo$)Fe(CO)_3$ complexes in moderate yields. However, in comparison with other methods {88-90} for the synthesis of $(\sigma,\eta^3$-organo$)Fe(CO)_3$ complexes (e.g. reactions 2.1 and 2.2) the overall yields of the complexes obtainable by the "one pot" procedure are significantly higher, based on $Fe(CO)_5$, than those obtainable when other synthetic routes are used. Furthermore the "one pot" route involves only one step whereas the other routes require at least two. In the course of the "one pot" reaction, it was found that $(\eta^2$-olefin$)Fe(CO)_4$ was largely consumed after a sufficiently long period of irradiation, whereas a considerable amount (30-50 %) of $(\eta^4$-diene$)$-$Fe(CO)_3$ remained apparently (cf. Chapter four) unchanged in the reaction mixture.

$$Fe(CO)_5 \xrightarrow{diene} (diene)Fe(CO)_3 \xrightarrow{olefin} (\sigma,\eta^3\text{-organo})Fe(CO)_3$$

(reaction 2.1)

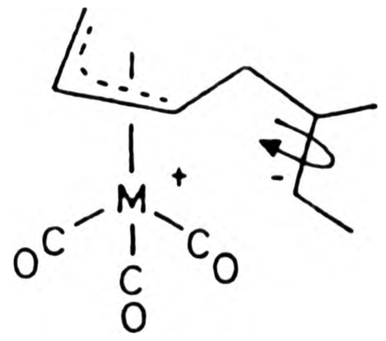


(reaction 2.2)

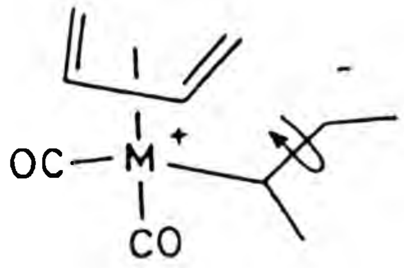
In the "one pot" synthesis the formation of (σ,η^3-organo)Fe(CO)$_3$ complexes proceeds via two different routes, i.e. via the initial formation of (η^2-olefin)Fe(CO)$_4$, as well as via (η^4-1,3-diene)Fe(CO)$_3$ (cf. Scheme 2.1). This has been established in detail, during the present study, using 2,3-dimethylbuta-1,3-diene and dimethyl maleate as the coupling components. In any of the steps involved, the intrinsic photoreaction is the creation of free coordination site(s) by detachment of carbon monoxide ligand(s) in order to accommodate the olefin and/or the diene at the metal prior to C-C bond formation. In principle, detachment of CO could also be accomplished thermally. However, this would require rather severe conditions which eventually may lead to extensive decomposition of the (σ,η^3-organo)Fe(CO)$_3$ products. Therefore, photosubstitution is the method of choice as it can be performed under thermally mild conditions.

The (σ,η^3-organo)Fe(CO)$_3$ complexes formed by the "one pot" procedure are accompanied by various other complexes and often by organic products. These are either their precursors,i.e. (η^2-olefin)Fe(CO)$_4$ and (η^4-1,3-diene)Fe(CO)$_3$ or species which arise by their photolysis,e.g. 44 and 32-E (cf. Chapter four for a discussion of the photolysis products of (σ,η^3-organo)Fe(CO)$_3$ complexes). These further reactions of (σ,η^3-organo)Fe(CO)$_3$ greatly affect their yields and in addition, the presence of these "by-products" complicate the work-up of the "one pot" reaction mixtures and generally the isolation of (σ,η^3-organo)Fe(CO)$_3$ complexes is not an easy operation. However, the other synthetic routes also suffer from similar separation problems.

The detailed structural characterization of the various (σ,η^3-organo)Fe(CO)$_3$ complexes demonstrates that in each case the product retains the stereo configuration of the respective olefin substrate. Thus in the (σ,η^3-organo)Fe(CO)$_3$ complexes arising from fumaric and crotonic esters, the substituents are in "*trans*" (*anti*) arrangements, in those arising from maleic esters in "*cis*" (*gauche*) arrangements, and in the product originating from d_2-acrylic ester, the two deuterium labels are also "*cis*" (*gauche*) to each other. Hence it is unlikely that intermediates are involved in which rotation about the former olefinic double bond is possible, such as zwitterionic species of type (A) or (B). Such intermediate species have been suggested in the addition of fluoroalkynes to (η^4-diene)Fe(CO)$_3$ complexes {92}.

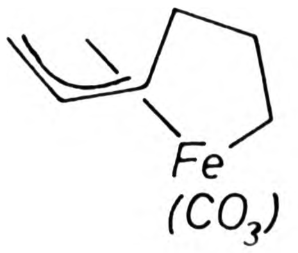


(A)

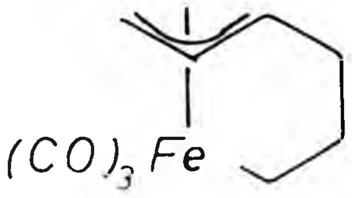


(B)

Another general feature, which emerges from the structural study of (σ,η^3-organo)Fe(CO)$_3$ complexes is that the η^3-allyl group is linked to the rest of the six-carbon chain via the *anti* position rather than via the *syn* position. In this respect their structure resembles the *s-cis* geometry of a η^4-coordinated diene.



anti-linkage



syn-linkage
(not observed)

2.5.2. The structural characterization of the (σ,η^3-organo)-Fe(CO)$_3$ complexes

During this study, the structural characterization of the (σ,η^3-organo)Fe(CO)$_3$ complexes has been accomplished using IR and NMR spectroscopic methods. The validity of this approach and the correctness of the proposed structures is strongly supported by two X-ray crystallographic studies of (σ,η^3-organo)Fe(CO)$_3$ complexes resulting (*i*) from the coupling reaction of methyl acrylate with buta-1,3-diene {86} and with 2,3-dimethylbuta-1,3-diene {76,110}, and (*ii*) from the coupling of dimethyl maleate with methyl sorbate which has been investigated during this work {109}.

The crystallographically determined structure of 35b is shown in Figure 2.23. The coordination geometry about the iron atom may be considered as a slightly distorted octahedron, in which the σ-bonded carbon atom occupies one site, the η^3-allyl group two sites, and the carbonyl ligands the other three coordination sites in a *fac*-arrangement. Alternatively, the coordination geometry at the iron atom may be considered as a trigonal bipyramid (Figure 2.23). The allylic ligand with its good acceptor character occupies an equatorial position, and the other two equatorial sites are occupied by two carbonyl groups. The σ-bonded α-carbon atom, C_4, has no acceptor ability, and, as expected from a donor ligand, occu-

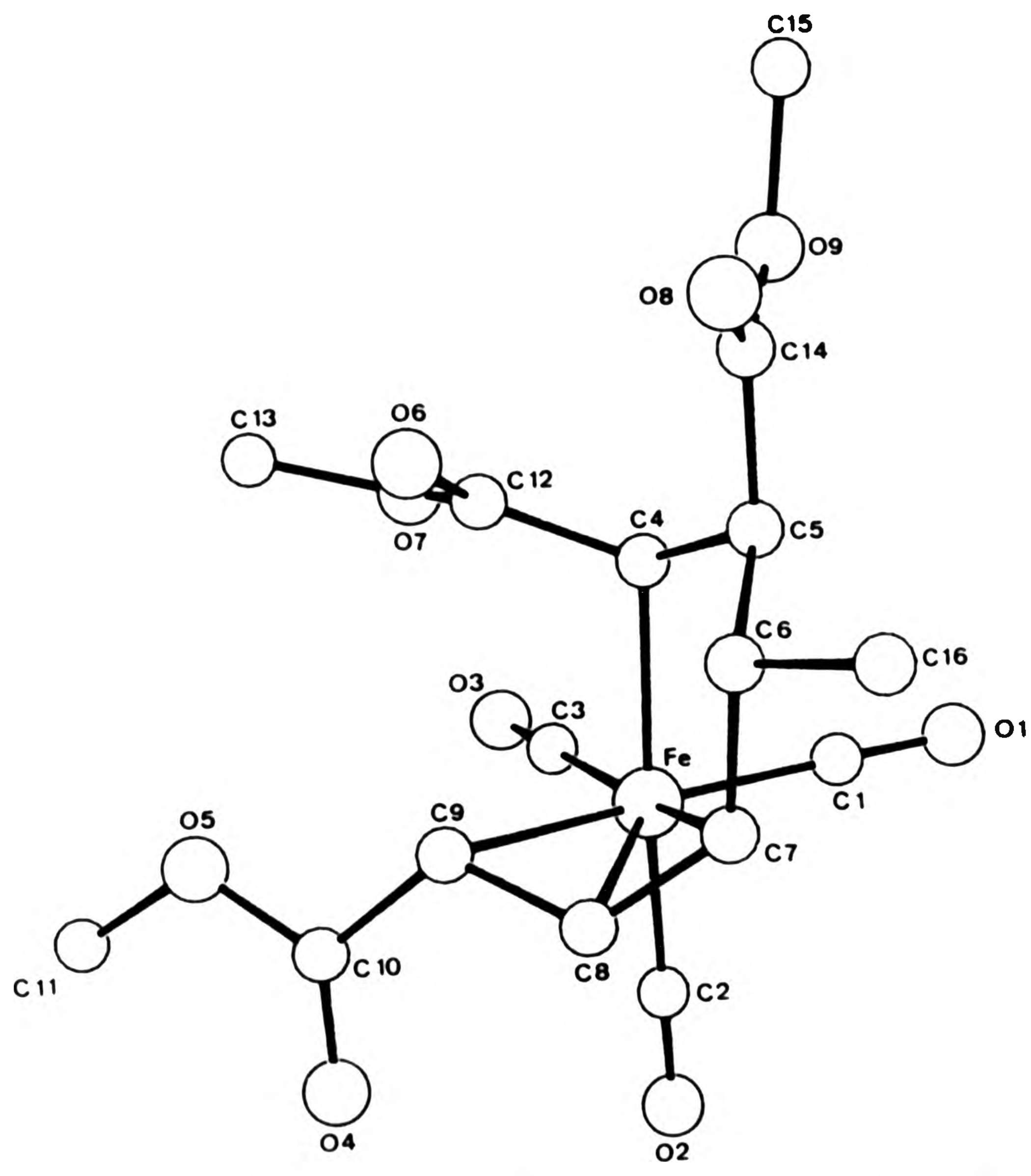


Figure 2.23: X-ray structure of *tricarbonyl* {1,4,5,6-η^4-[*cis*-1(*endo*),2,6-*tricarbomethoxy*-3-*methyl*-*hex*-4-*en*-1,6-*diyl*]}*iron*, 35$\underline{\underline{b}}$.

pies an axial coordination site. The axis C_4-Fe-C_2 is slightly tilted away from the allylic moiety (∡ 173.5 °). This axis is almost perpendicular to the equatorial plane: C_1-Fe-C_4 = 83.6 ° and C_3-Fe-C_4 = 86.7 °. The iron-carbon σ-bond length (2.147 Å) is slightly shorter than those reported for the ferracyclopentane complex, **12**, {77} (Figure 1.8).

The structure confirms that C-C coupling (C_5-C_6) with the maleate has occurred at the methyl substituted carbon atom of the former diene. The η^3-allyl group is connected to the rest of the carbon chain via the *anti*-position. The α-ester group attached to C_4 is *endo*-oriented with respect to the η^3-allyl unit. The two ester groups are in a *cis*-configuration and the carbomethoxy group of the former diene is in the *syn* position of the allylic moiety, i.e. the compound **35b** retains the stereo-configuration of both of the starting organic ligands.

Similar features are shown by the other two compounds (Figures 2.24 and 2.25).

2.5.3. General spectroscopic trends in the (σ,η^3-organo)Fe(CO)$_3$ complexes

Some general observations and trends concerning the spectroscopic data are summarized below.

(*i*) Infrared spectra:

The CO stretching vibrational pattern of the various

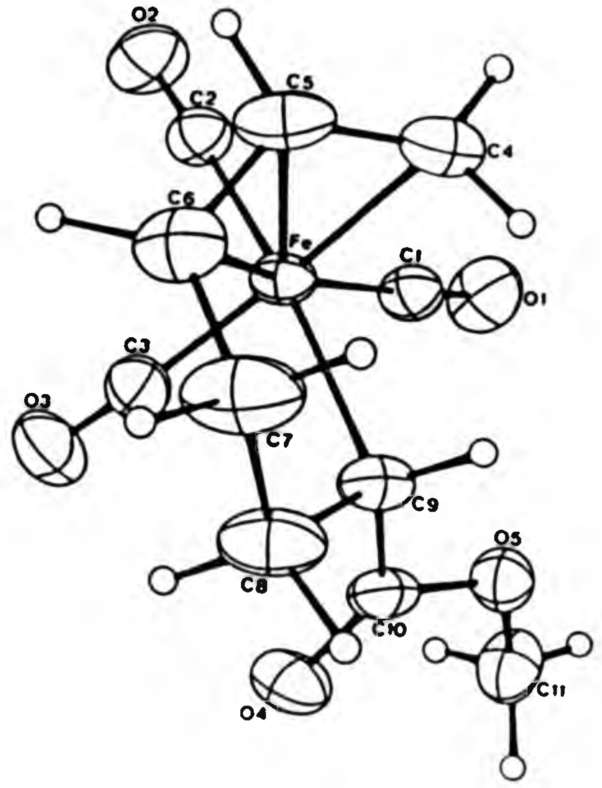


Figure 2.24: (σ,η^3-Organo)Fe(CO)$_3$ derived from methyl acrylate and buta-1,3-diene {86}.

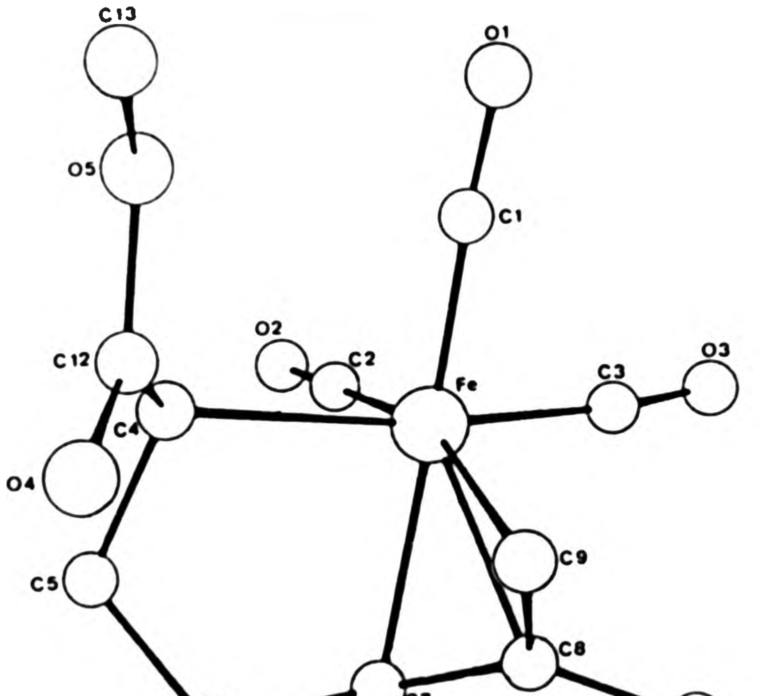
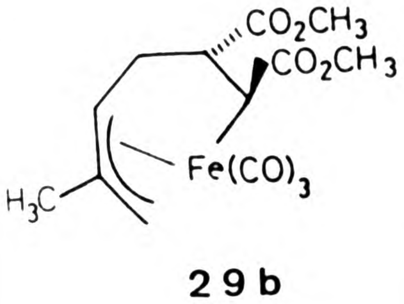
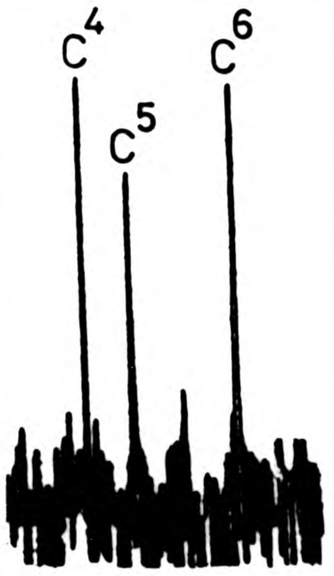
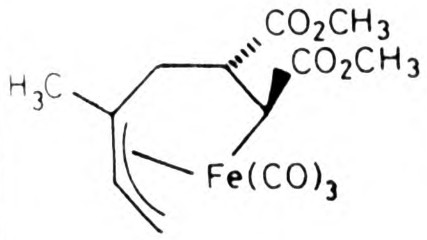
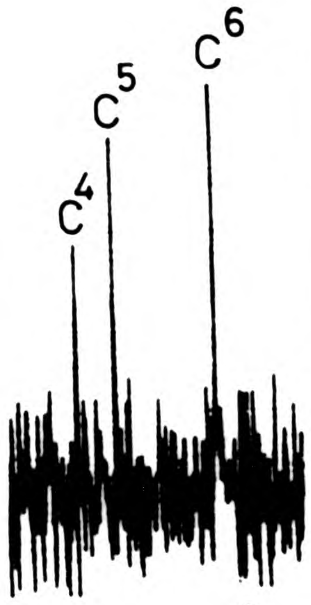
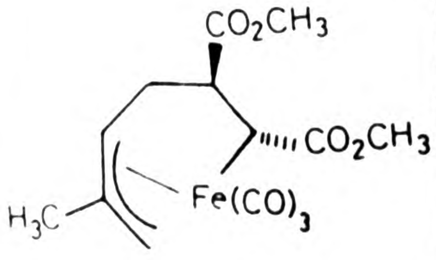
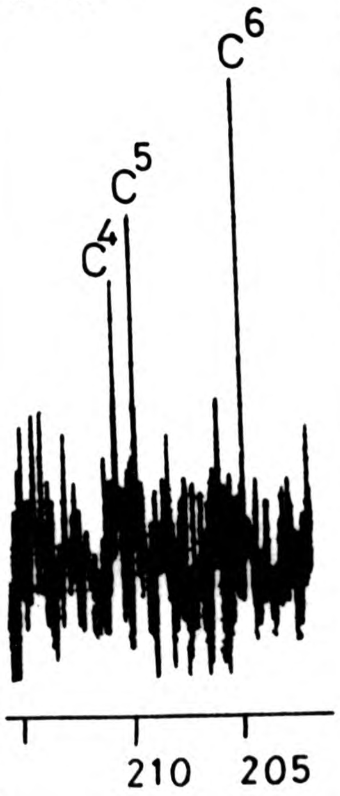


Figure 2-25: (σ,η^3-Organo)Fe(CO)$_3$ derived from methyl acrylate and 2,3-dimethylbuta-1,3-diene {76,110}.

$(\sigma,\eta^3$-organo)Fe(CO)$_3$ complexes are typical of a *fac*-M(CO)$_3$ group. There are small, albeit significant differences between those complexes in which the ester group at the σ-bonded (α-position) carbon atom is *exo*-oriented (type **a**) and those in which it is *endo*-oriented (type **b**). Type **a** complexes exhibit a larger difference between the second and the third metal carbonyl bands (cf. Tables 2.2 and, e.g. 2.8) and a higher frequency for the α-ester carbonyl band than type **b** complexes. In other words, all *endo*-compounds (series **b**) have a carbonyl ester frequency at about 1705 cm^{-1} or below, whereas all *exo*-compounds (series **a**) have a carbonyl ester band at higher frequency (Table 2.24). At this stage, there is no explanation for these trends.

In both series **a** and **b** complexes the frequencies of the metal carbonyl bands are affected by the nature of the substituent(s) at the η^3-allyl group. Compared with the unsubstituted η^3-allyl moiety (cf. **20** and **21**, derived from buta-1,3-diene), an electron-withdrawing substituent (cf. **33**) causes a high frequency shift whereas an electron-releasing substituent (cf. **22**, **23**, derived from 2,3-dimethylbuta-1,3-diene; **29**, **30**, derived from isoprene) causes a low frequency shift. The comparison of isomers such as **29a** and **30a**, or **29b** and **30b**, shows that the attachment of a substituent (CH$_3$) to different positions of the η^3-allyl moiety does not significantly alter the appearance of the CO bands.

complex	IR in n-hexane cm^{-1} $\tilde{\nu}$(ester-CO)	^{1}H-NMR in C_6D_6 δ/ppm		^{13}C-NMR in C_7D_8 δ/ppm
		H^9	H^{10}	
 **29b**	1740.0, 1703.8	3.42	2.94	
 **30b**	1738.9, 1704.0	3.32	2.80	
 **29a**	1744.0, 1712.2	2.09	2.95	

(Table 2.24)

(*ii*) ^{1}H-NMR spectra:

The assignment of *anti* (H^9) and *syn* (H^{10}) protons of the allylic moiety was achieved by comparison of the data for different complexes and was used as further evidence for structural assignments. In type $\underline{\underline{a}}$ complexes, H^9 appears at higher field than H^{10} (Table 2.24) in accordance with the order usually found for η^3 complexes {97,111}. Compared to this, in type $\underline{\underline{b}}$ complexes, H^9 experiences a shift to lower field by ca. 1.3 ppm whereas H^{10} appears at nearly the same position as in the respective $\underline{\underline{a}}$ isomer. This is interpreted in terms of the magnetic anisotropic effect of the α-ester group which in the type $\underline{\underline{b}}$ complexes (cf. Figure 2.23) is oriented towards the *anti*-hydrogen atom at C^9 (H^9). In some cases, a significant solvent dependency of chemical shifts was observed and hence was used to elucidate the coupling patterns and confirm the structural assignments (cf. Tables 2.9a, 2.15, and 2.18).

(*iii*) ^{13}C-NMR spectra:

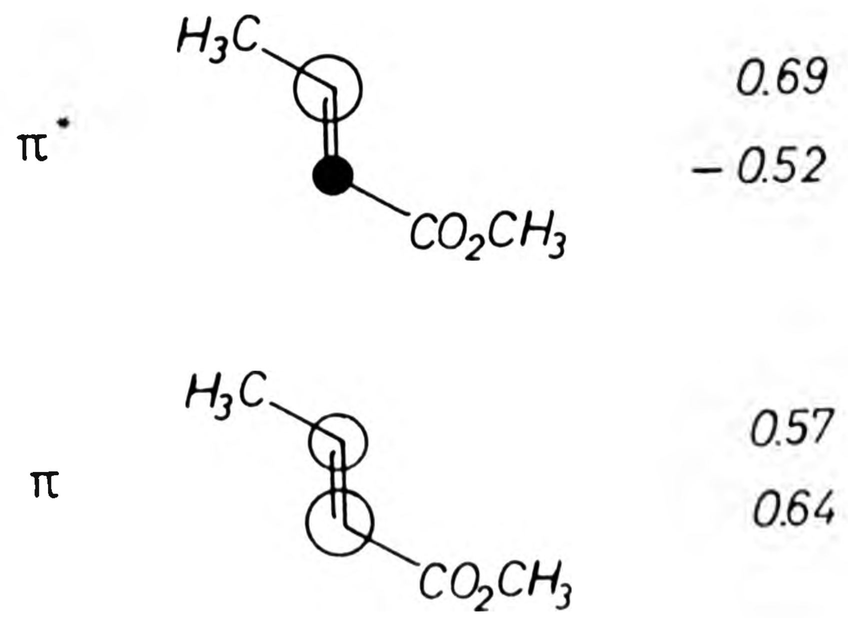
The ^{13}C-NMR spectroscopic data, in general, did not provide direct evidence for the stereo configuration of the (σ,η^3-organo)$Fe(CO)_3$ complexes, but were in accordance with the proposed structures deduced from the IR and ^{1}H-NMR spectra. The $Fe(CO)_3$ group in the (σ,η^3-organo)$Fe(CO)_3$ complexes gives rise to three distinct ^{13}CO signals (Table 2.24). This contrasts the behaviour of (η^4-1,3-diene)$Fe(CO)_3$ {51-63} and suggests that scrambling does not occur at ambient temperature. Among the three signals, that at highest field (C^6) was assigned to the CO group *trans* to the Fe-C σ-bond (C^2O^2 in Figure 2.23). A characteristic feature of the spectra is the observation that the difference in chemical shifts between the other two resonances (C^4/C^5) is significantly smaller in type a complexes than in type b compounds. This may be explained by the fact that in the former case the α-ester group is nearly equidistant from these two carbonyl ligands (cf. BD/MA-Fe$(CO)_3$ adduct {86}), whereas in the latter case, the ester group is nearer to one of the two carbonyl groups (C^3O^3 in Figure 2.23). This effect can probably be used as a general empirical criterion to distinguish between type a or type b isomers.

2.5.4. Factors affecting the nature and stereochemistry of $(\sigma,\eta^3$-organo)Fe$(CO)_3$ complexes

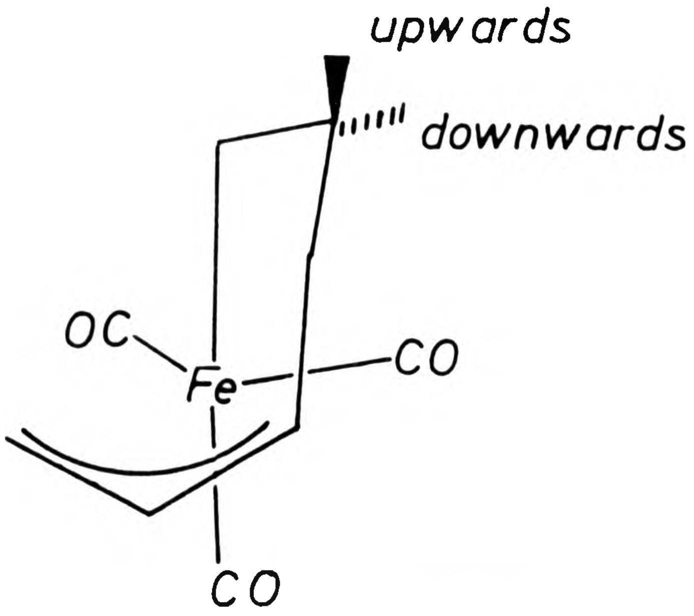
The present studies of the reactions of pentacarbonyliron with both symmetrical or unsymmetrical dienes and olefins illustrate the electronic and steric factors which determine the nature and stereochemistry of the $(\sigma,\eta^3$-organo)-Fe$(CO)_3$ products.

Methyl acrylate (in 31 and 27) and *cis*-d_2-methyl acrylate (in 28) underwent coupling at the CH_2 and CHD group, respectively. This parallels the coupling behaviour of bis(η^2-methyl acrylate)Fe$(CO)_3$ {75,36} and of the methyl acrylate/2,3-dimethylbuta-1,3-diene/Fe$(CO)_5$ system {76,86}. The calculated orbital coefficients of the π^* orbital (LUMO) of the methyl acrylate is larger at the unsubstituted carbon atom (cf. Scheme 1.6), hence the C-C coupling should occur regioselectively at the CH_2 position. The results obtained thus indicate that the coupling site of the olefin is determined by the electronic factor. However, the orientation of the sole ester group, attached to the α-carbon atom, is determined by steric factors. In the major products of these reactions, i.e. the *exo*-isomers, this ester group is directed away from the η^3-allylic moiety where it experiences less steric hindrance than in the *endo*-isomers which result in lower yields.

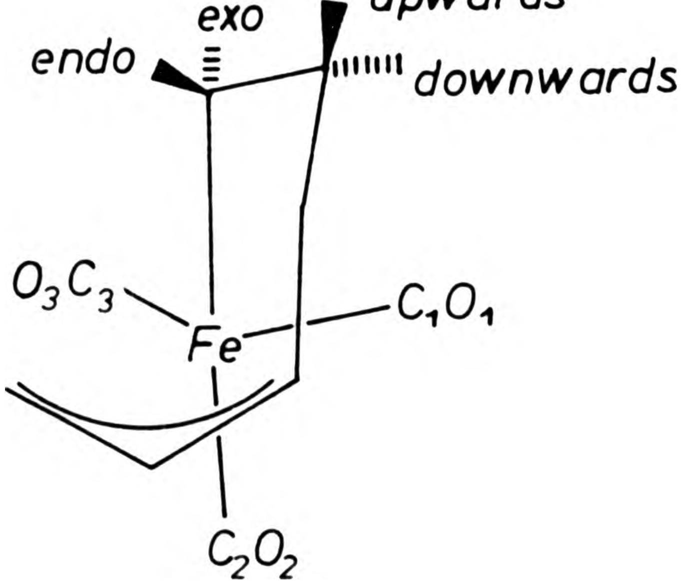
Likewise, the reaction involving buta-1,3-diene and methyl crotonate afforded a $(\sigma,\eta^3$-organo)$Fe(CO)_3$ compound of type a (26a), in which the coupling occurred at the methyl substituted carbon atom of the latter. The formation of this compound is influenced by both electronic and steric factors. Firstly, coupling of the olefin at this position is consistent with the interpretation of C-C bond formation in terms of



oxidative cyclization because it is the olefinic π*-orbital which has the larger HMO coefficient at the methyl substituted carbon atom {112}. As no products with the ester substituted carbon atoms at the β-position of the six-carbon chain were formed in this reaction, it emerges that the π*- and not the π-orbital is responsible for the C-C bond formation, i.e. the results confirm the basic principle of oxidative cyclization. Secondly, steric factors are important in determining the orientation of the substituents. It seems likely that a substituent at the β-carbon atom, if it is "upwards" oriented, has almost no steric hindrance from other substituents (see below). Providing that the *trans*-arrangement of the former olefin is retained, the ester group attached to the σ-bonded carbon atom is thus oriented away from the η^3-allylic unit (*exo*-position).

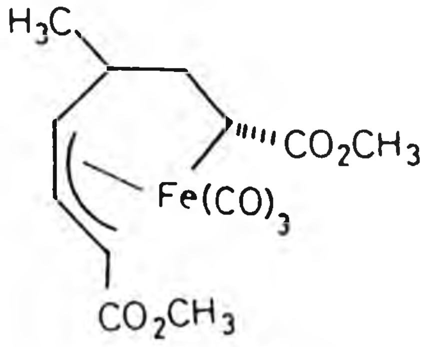


For symmetrically disubstituted olefins there is no coupling site preference. However, the geometry of $(\sigma,\eta^3$-organo)Fe(CO)$_3$ arising from such olefins can be affected by the olefin substituents. In the case of fumarate (*trans*-olefin), two arrangements of the ester groups are possible. These are either α-*exo*,β-upwards, or α-*endo*,β-downwards (see below). In the latter case the ester groups in both positions are more sterically hindered than in the former case. Accordingly, in

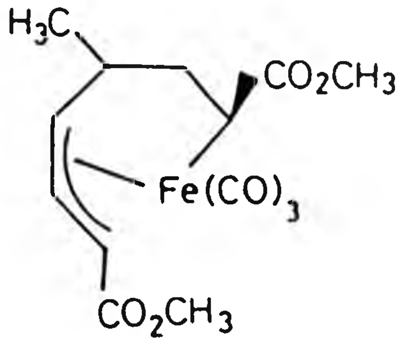


the (σ,η^3-organo)Fe(CO)$_3$ complexes arising from reactions involving fumarate the *exo*-isomers are by far the major products. In the case of maleate (*cis*-olefin), two geometries are also possible, namely: α-*endo*,β-upwards, or α-*exo*,β-downwards. Obviously there are two counteracting effects in each of the two cases. However, in all cases investigated in the present study, the major product has an α-*endo*-configuration whereas the α-*exo*-product is formed in minor amounts, e.g. the yield of 20$\underline{\underline{b}}$ is 33 % whereas the yield of 20$\underline{\underline{a}}$ is only 3 %. The steric environment of the β-carbon atom affects the arrangement of other parts of the molecule. Thus the upwards oriented substituent at the β-carbon atom forces the substituent at the α-carbon atom into the less favourable *endo*-position. This is illustrated in Figure 2.23 which shows the structure of 35b as a typical example.

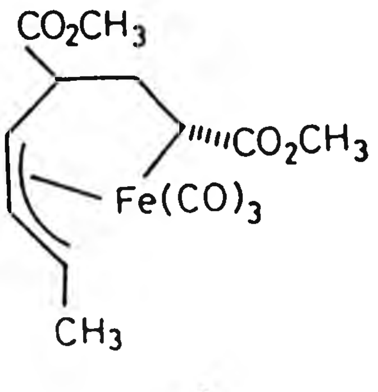
Electronic and steric effects resulting from the substituents at the 1,3-diene are also important. In the case of coupling between methyl acrylate and methyl sorbate, both of which are unsymmetrical, eight isomeric products are possible in principle. However, as discussed earlier, acrylate undergoes coupling only at the methylene carbon atom. Thus, only the four isomers, 31a, 31a', 31b and 31b' are likely products of the reaction involving methyl acrylate and methyl sorbate. Experimentally, it was found that coupling of the 1,3-diene



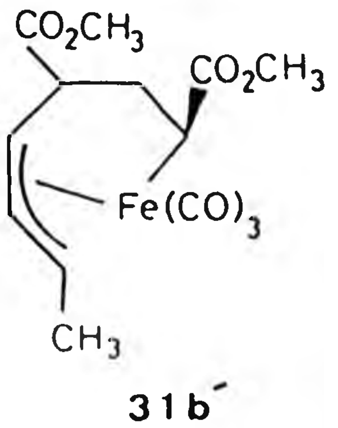
31 a



31 b

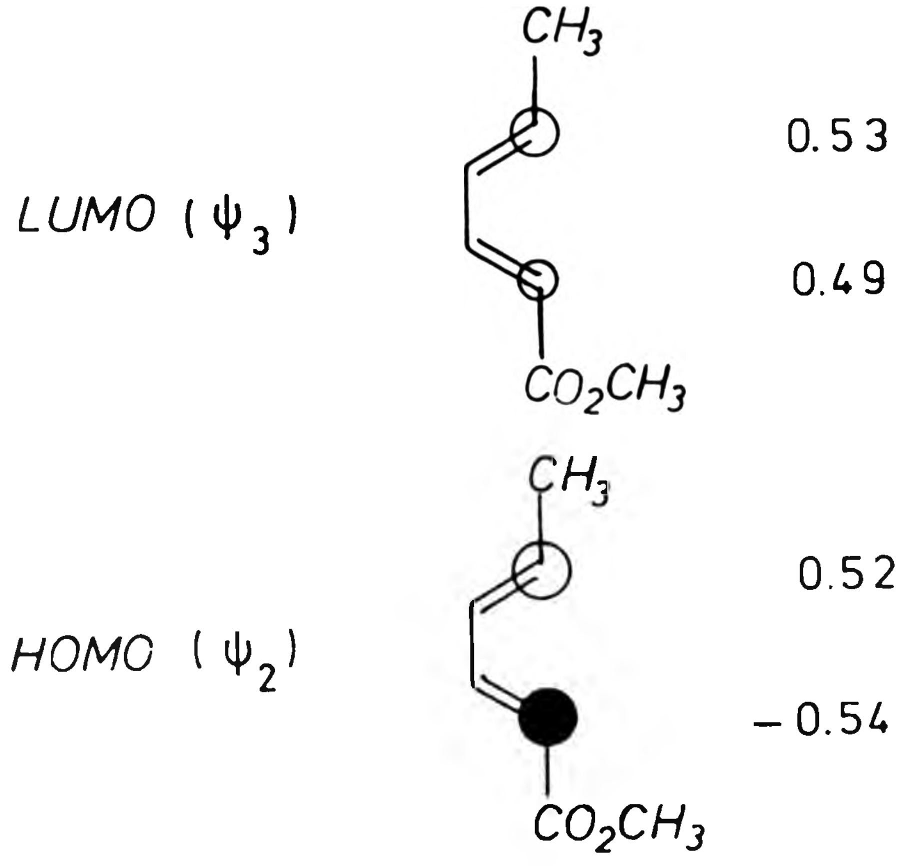


31 a'



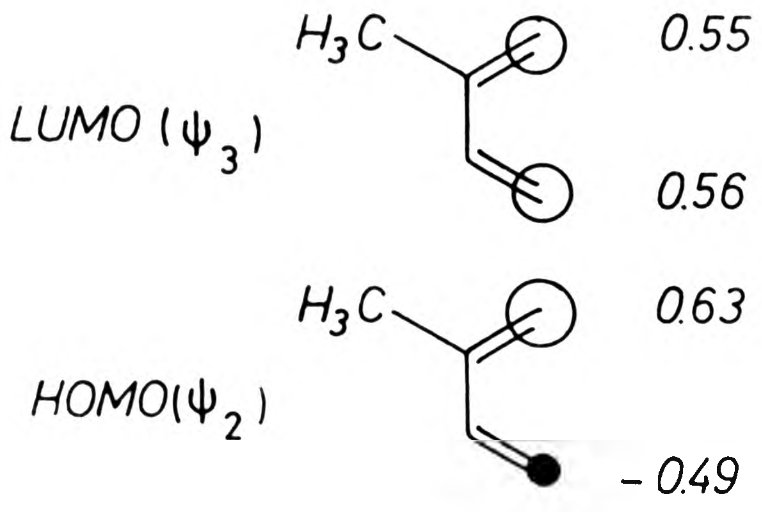
31 b'

occurs exclusively at the carbon atom which carries the methyl substituent togive 31a and 31b. Not even traces of the products 31a' and 31b', whose formation involves coupling at the ester substituted carbon atom, could be detected. This can be rationalized, at least in part, in terms of the calculated ψ_3 (LUMO) orbital coefficients for methyl sorbate {112} which indicate a preference for C-C bond formation, by oxidative cyclization, at the methyl substituted carbon atom. Furthermore, as the methyl group is smaller than the ester group



the preference for C-C bond formation at the methyl-substituted carbon atom is also favoured for steric reasons. Likewise, the systems involving methyl sorbate and *trans*- or *cis*-diester olefins (methyl fumarate or maleate) afforded exclusively products where coupling occurred at the methyl substituted carbon atom of the diene.

In the case of the system involving isoprene and dimethyl fumarate, the separation and purification of the products was accomplished with considerable loss of material. Nevertheless, the relative yields indicate clearly that the amounts of products formed by the coupling at the unsubstituted end of the coordinated diene (compounds 29a and 29b) are higher than those of the products formed by coupling at the substituted end (compounds 30a and 30b) by a factor of ca. 2.5. The behaviour of this system parallels that of related systems. Thus, for example, *Green* et.al. noted that in the coupling of isoprene with fluoroethylene, the products arising by coupling at the unsubstituted end of isoprene predominate over those arising by coupling at the substituted end by a factor of 5 {113}. Similarly, for the system involving isoprene and fluoroalkyne, the coupling at the unsubstituted end is predominant by a factor of 2.5 {92}. The present results and the findings of the other workers described above cannot be interpreted in terms of electronic effects for isoprene since the orbital coefficients {79} are almost equal for both ends in the ψ_3 (LUMO) orbital. Clearly, in these cases, steric factors control the mode of coupling and determine the product distribution. The product distribution in the isoprene-dimethyl fumarate system correlates also closely with the arrangement of the substituents in the (σ,η^3-organo)$Fe(CO)_3$ products. When the substituents are well separated the product achieves high stability. Thus the arrangement in 29a (α-*exo*, β-upwards/5-methyl, i.e. coupling occurred at the unsubstituted



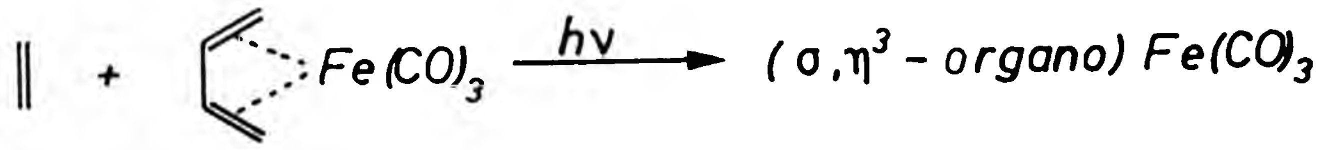
end of isoprene), which implies little steric hindrance, accounts for its relatively high yield of 6 %. On the other hand, when these two influences are counteracting (29b: α-*endo*, β-downwards/methyl at the unsubstituted end; 30a: α-*exo*,β-upwards/methyl at the substituted end) the yields are lowered to 2 % in each of these two cases. The maximum steric hindrance is shown in compound 30b because the two afore said factors (α-*endo*,β-downwards/methyl at the substituted end) are strongly pronounced, and account for its low yield (1 %).

CHAPTER THREE

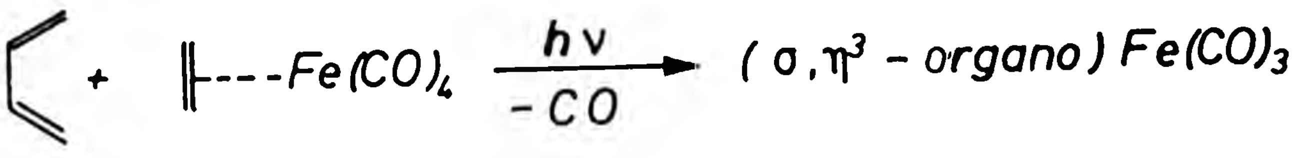
ISOLATION AND CHARACTERIZATION OF DICARBONYL(η^4-2,3-DIMETHYL-BUTA-1,3-DIENE)(η^2-DIMETHYL FUMARATE)IRON AS AN INTERMEDIATE INVOLVED IN THE PHOTO-INDUCED COUPLING REACTION BETWEEN 1,3-DIENE, MONOOLEFIN AND CARBONYLIRON

3.1 Introduction

In the previous chapter (Section 2.1) it was noted that the formation of (1-σ,4-6-η^3-organo)$Fe(CO)_3$ complexes from the photolytic reaction of pentacarbonyliron with a diene and an olefin proceeds via the initial formation of the complexes (η^2-olefin)$Fe(CO)_4$ and (η^4-diene)$Fe(CO)_3$ (Scheme 2.1). The formation of these complexes has been indicated by monitoring the reaction mixture using IR spectroscopy. Furthermore, it has been established by separate irradiation reactions that (η^4-diene)($Fe(CO)_3$-olefin or (η^2-olefin)$Fe(CO)_4$-diene afford (σ,η^3-organo)$Fe(CO)_3$ (e.g. reaction 3.1 and 3.2; cf. Section 2.3.2) {88,89,90,113}.



(reaction 3.1)

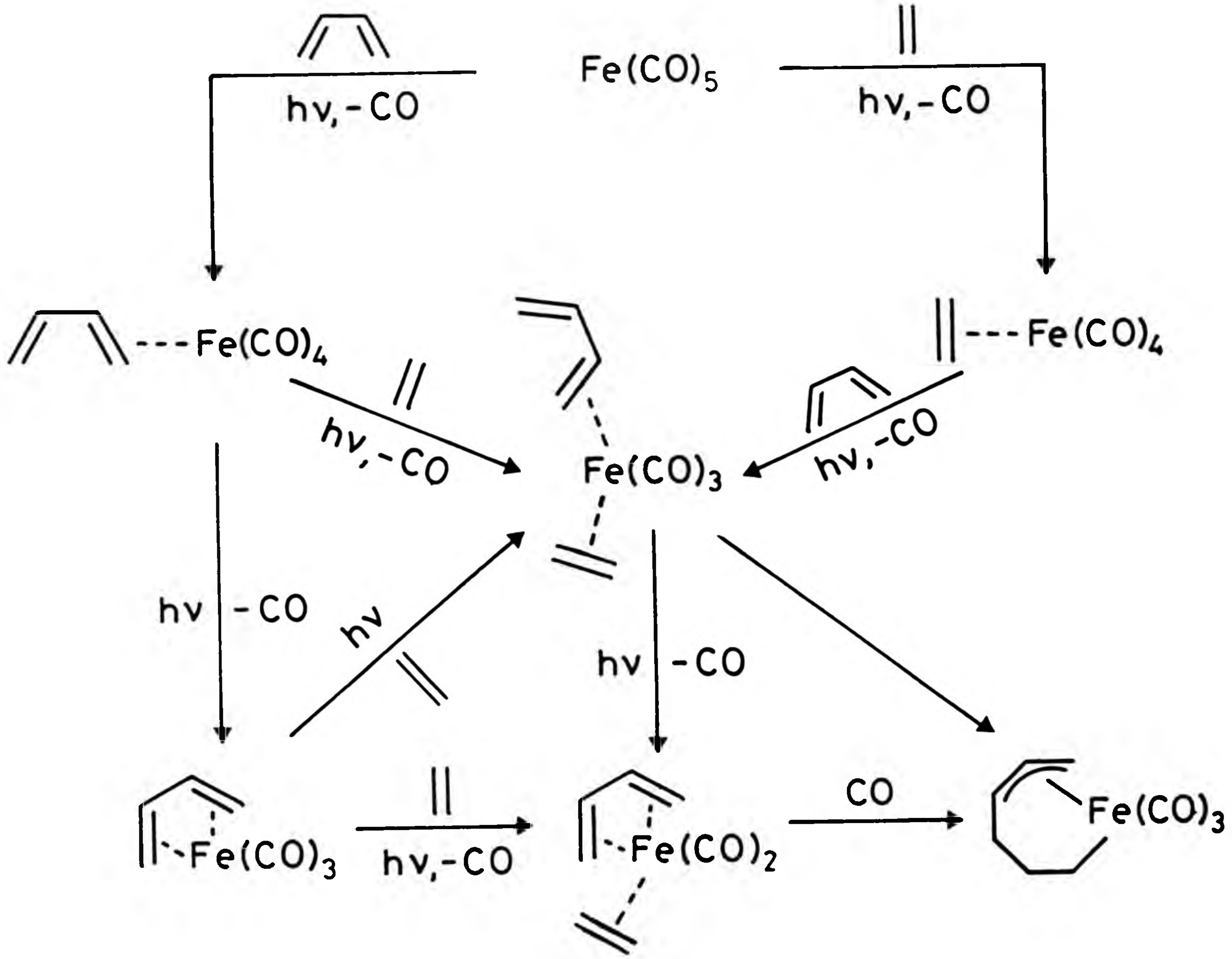


(reaction 3.2)

The reactions outlined in Scheme 2.1 provide a reasonable but incomplete picture of the routes leading to the formation of (σ,η^3-organo)Fe(CO)$_3$ complexes. A more detailed description of the possible routes to such complexes is illustrated in Scheme 3.1. According to this Scheme two other types of complex, namely the (η^2-diene)(η^2-olefin)Fe(CO)$_3$ or (η^4-diene)-(η^2-olefin)Fe(CO)$_2$ complexes, are involved as intermediates. The complex (η^2-diene)(η^2-olefin)Fe(CO)$_3$ may arise from three routes, either from the (η^4-1,3-diene)Fe(CO)$_3$ by photolytic detachment of one double bond of the diene followed by addition of the olefin, or from (η^2-olefin)Fe(CO)$_4$ by photolytic dissociation of CO and η^2-coordination of the diene, or from the analogous reaction of a (η^2-diene)Fe(CO)$_4$ species (cf. Scheme 1.2) with the olefin. The complex (η^4-diene)(η^2-olefin)Fe(CO)$_2$ may arise from the (η^2-diene)(η^2-olefin)Fe(CO)$_3$ complex by further loss of CO or directly from the reaction of (η^4-diene)Fe(CO)$_3$ with the olefin.

The involvement of the (η^4-diene)(η^2-olefin)Fe(CO)$_2$ complex as an intermediate is strongly suggested by the isolation, during the present and parallel studies, of complexes of this type from the reaction of pentacarbonyliron with, e.g. 2,3-dimethylbuta-1,3-diene and diethyl fumarate (cf. 2.3.2), or from the reaction of (methyl acrylate)Fe(CO)$_4$ with 2,3-dimethylbuta-1,3-diene {114}

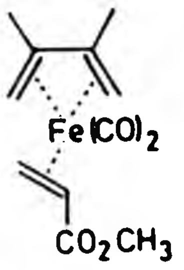
The work described in this chapter was carried out with the aims (*i*) of preparing, characterizing, and extending the knowledge of complexes of type (η^4-diene)(η^2-olefin)Fe(CO)$_2$, and (*ii*) of evaluating their significance as intermediates in the formation of (σ,η^3-organo)Fe(CO)$_3$ complexes.


Fe(CO)5
hν,-CO
hν,-CO
---Fe(CO)4
---Fe(CO)4
Fe(CO)3
hν,-CO
hν,-CO
hν -CO
hν
hν -CO
Fe(CO)3
hν,-CO
Fe(CO)2
CO
Fe(CO)3

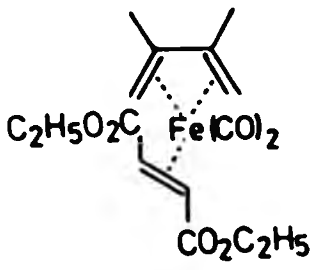
(Scheme 3.1)

3.2. The preparation and characterization of (η^4-diene)(η^2-olefin)Fe(CO)$_2$ complexes

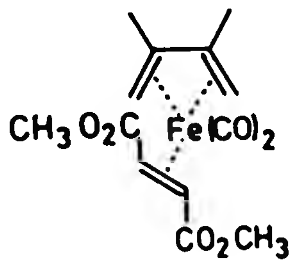
In this section three (η^4-diene)(η^2-olefin)Fe(CO)$_2$ complexes, 36, 37, and 38 are considered. The methyl acrylate



36



37



38

complex 36 has been prepared and characterized by *Grevels* et. al. {114} in a parallel study. The preparation and characterization of the diethyl fumarate complex 37 has been described earlier (Section 2.3.2). The analogous dimethyl fumarate complex 38 was isolated in moderate yield (19 %) from the mixture arising from the "one pot" reaction of pentacarbonyliron with 2,3-dimethylbuta-1,3-diene and dimethyl fumarate at 0 °C. However, the yield could be improved (37 %) by photolysing (η^2-DMF)Fe(CO)$_4$ with an excess of 2,3-dimethylbuta-1,3-diene in diethyl ether. Like 36, the fumarate complexes 37 and 38 are moderately stable at room temperature, but are sensitive towards air and react readily with carbon monoxide (cf. Section 3.4). Therefore, the preparation of 38 required strict exclusion of air, removal of the carbon monoxide evolved during its formation with a strong stream of argon, and work-up of the reaction mixture at a low temperature (ca. -45 °C). Pure 38, isolated by recrystallization as an amorphous yellow solid which melts at ca. -20 °C, can be stored at low temperature (ca. -80 °C) without decomposition.

The elemental analyses for 37 and 38 are in accord with the proposed formulations. Their mass spectra do not exhibit the molecular ions but show peaks corresponding to $[M-CO]^+$ and $[M-2CO]^+$.

NMR studies on 38 (see following Section) and 36 {114} show that the olefin and diene moieties are not linked.

The infrared spectra of 37 (Section 2.3.2) and 38 (see Figure 3.1) indicate that both compounds exist as mixtures

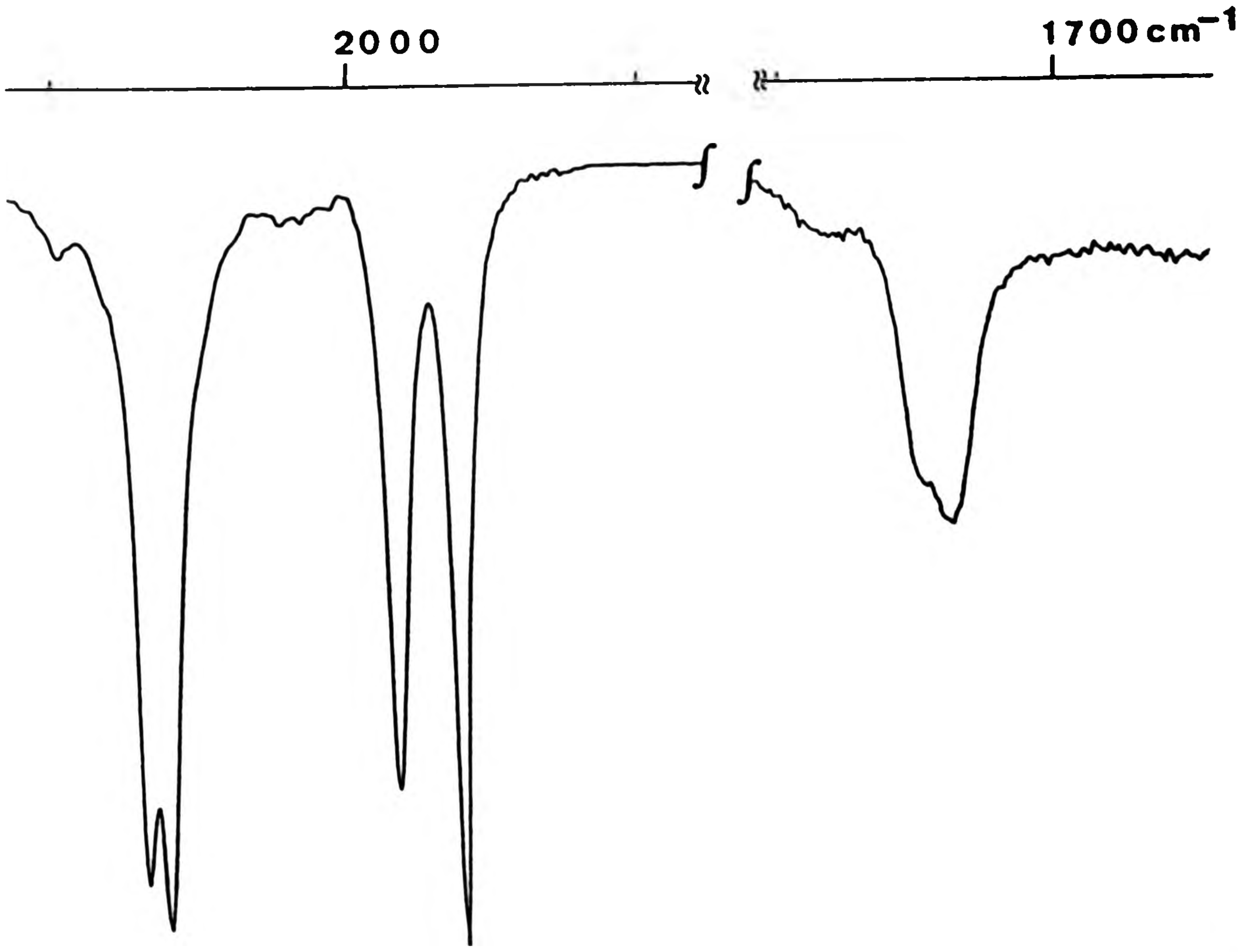


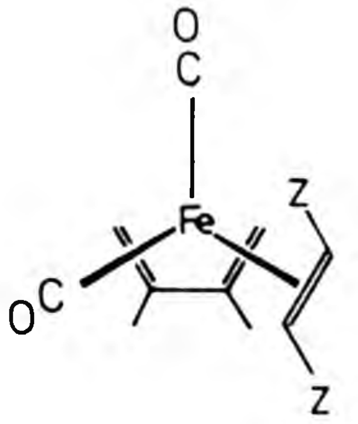
Figure 3.1: CO stretching vibration bands in the IR spectrum of 38 (2033.4, 2030.9, 1991.4, 1979.8, 1719.0 cm^{-1} in n-hexane, calibrated with DCl {115}.

of two species: in both cases, the metal carbonyl region exhibits two pairs of bands (i.e., a total number of four bands) whereas only two CO stretching bands can be expected for a single dicarbonyl metal complex. The position of these bands is similar to those reported for dicarbonyl(η^4-cyclobuta-diene)-(η^2-olefin)iron complexes {116}.

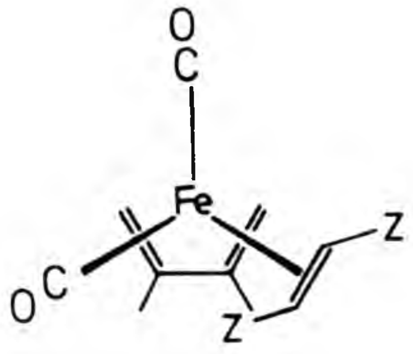
Previous studies on (η^4-diene)Fe(CO)$_3$ and (η^4-diene)$_2$-FeCO complexes have shown that such compounds have square-pyramidal structures {117,118}. The C=C double bonds occupy basal positions (cf. Figure 1.6) in agreement with the general coordination site preference in complexes of this geometry {120}. Furthermore, the related complex (η^2-methyl acrylate)(η^4-norbornadiene)Fe(CO)$_2$ was shown by X-ray crystallography {119} to adopt a slightly distorted square-pyramidal geometry where the C=C double bonds of the diene and the olefin occupy three basal positions. Hence it is reasonable to suggest that the complexes 36, 37, and 38 possess an analogous structure, although it was not possible to confirm this suggestion by means of X-ray crystallography since attempts to obtain suitable crystals of either 36 {76}, 37, or 38 were unsuccessful.

39

In a structure of type 39, a *trans*-substituted olefin such as dimethyl or diethyl fumarate can adopt two different orientations. Thus, two different isomeric complexes, 39a and 39b, are possible, each of which should exhibit two CO stetching bands in the infrared spectrum, in agreement with

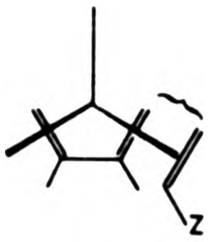


39 a

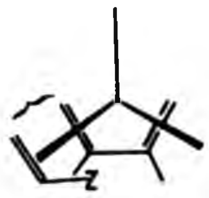


39 b

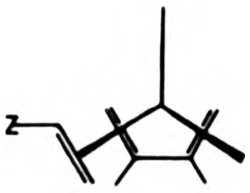
the observed total number of four bands in the cases of 37 and 38. Accordingly, a monosubstituted olefin such as methyl acrylate can adopt four different orientations of the single substtuent with respect to the rest of the complex. Indeed, the IR



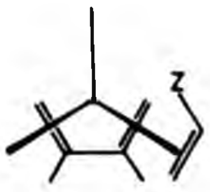
36 a



36 b



36 c



36 d

spectrum of 36 shows a total of five bands, some of which are slightly broadened, in the metal carbonyl region (n-hexane: 2023, 2018, 1981, 1977.5, 1968 cm^{-1}). This indicates that the complex exists as a mixture of at least three or perhaps four different species {76}.

3.3. NMR spectroscopic studies of dicarbonyl(η^4-2,3-dimethylbuta-1,3-diene)(η^2-dimethyl fumarate)iron

The ^{1}H-NMR spectrum of 38 at low temperature, -55 °C, (Figure 3.2, Table 3.1) is consistent with the presence of an η^4-2,3-dimethylbuta-1,3-diene and an η^2-dimethyl fumarate ligand which are not linked together. The spectrum exhibits one set of signals for each half of the diene in agreement with an unsymmetrical structure.

Table 3.1: ^{1}H-NMR data for dicarbonyl(η^4-2,3-dimethylbuta-1,3-diene)(η^2-dimethyl fumarate)iron$^{a)}$, 38.

	-55 °C	+47 °C
δ/ppm		
H^1	4.09	~3.5
H^4	3.02	
H^2	3.44	3.39
H^3	3.27	
H^5	1.73	1.81
H^{10}	0.60	0.63
H^6	-0.03	0.05
H^9	-0.50	-0.41
H^7	2.09	2.10
H^8	1.90	1.98

$^{a)}$ *in toluene-d_8, Bruker WH 400.*

Likewise, two signals are observed for the two fumarate ester groups, and the fumarate olefinic protons appear as an AB system. On warming up, coalescence is observed for the fumarate signals. The two methyl ester singlets broaden and

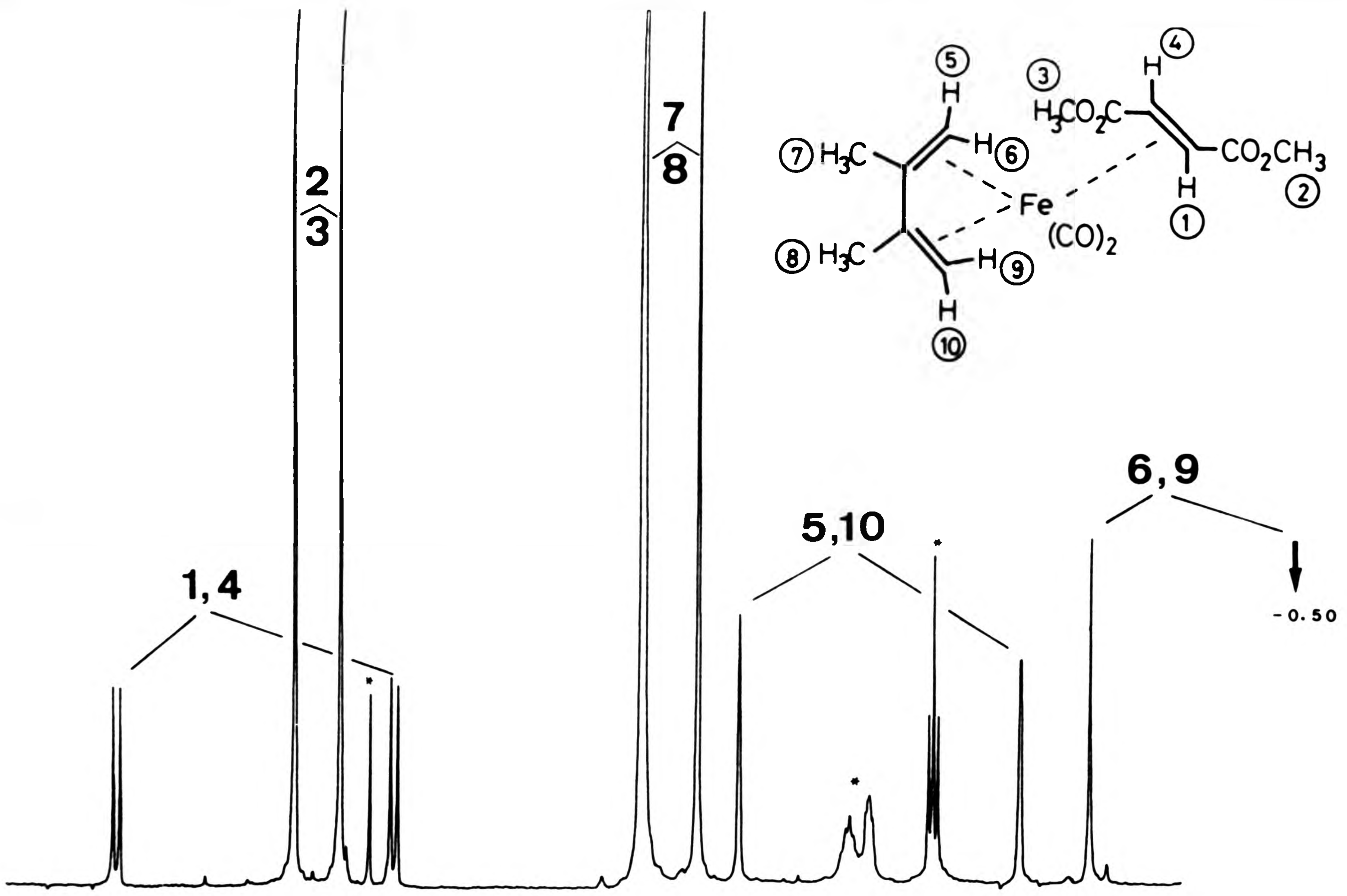
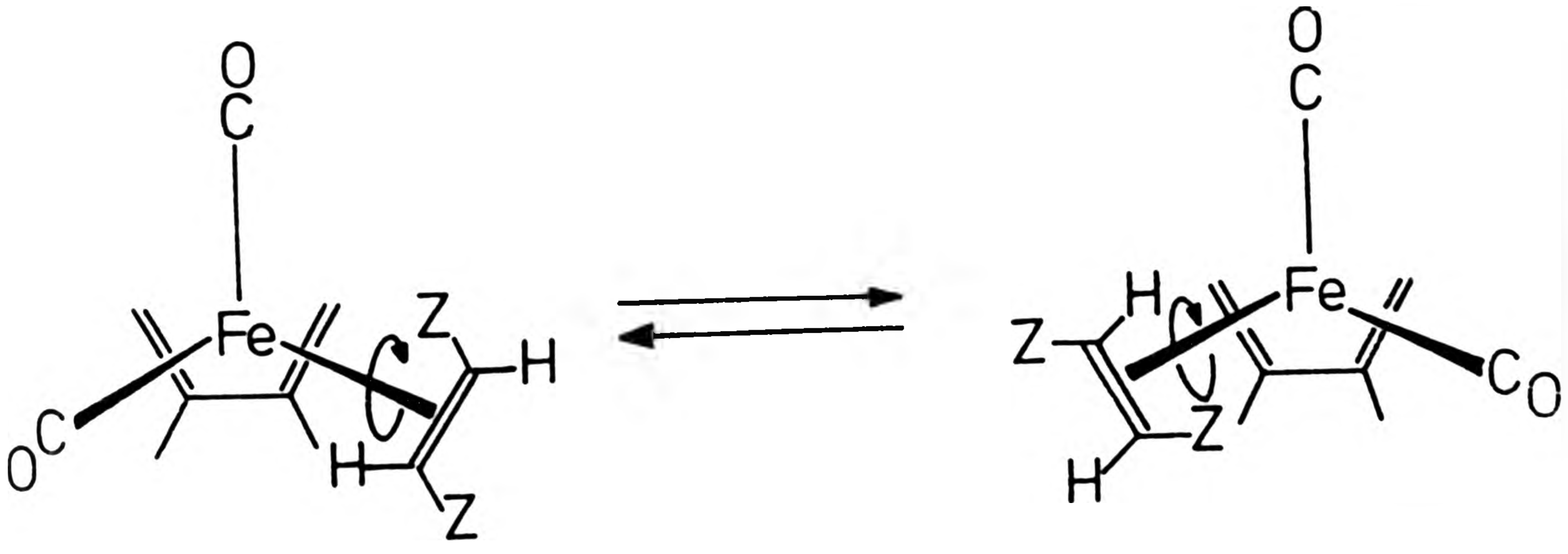


Figure 3.2: ^{1}H-NMR spectrum of compound 38, in toluene-d_8, Bruker WH 400, at -55 °C ±1.

above room temperature give rise to one sharp singlet. Concomitantly, the two doublets of the olefinic AB systems become broad, however, the re-sharpening of these signals could not be observed, up to +45 °C, due to the larger distance of the resonances in the low temperature spectrum. These spectral changes are readily interpreted in terms of rotation, about the metal-olefin bond, which is a degenerate process equilibrating the two halves of the fumarate ligand.

By contrast, rotation about the diene-metal bond is not a degenerate process. Therefore, this motion cannot equilibrate the two halves of the diene but it interconverts the two different species 38a and 38b, as shown in Scheme 3.2.



38a

38b

(Scheme 3.2)

Freezing out this process should double the number of signals. However, down to -80 °C no changes were observed apart from small shifts of the diene signals. Hence it follows that the latter process has a significantly lower activation barrier than metal-olefin rotation, in accordance with the fact that the carbonyl scrambling in (η^4-diene)Fe(CO)$_3$ generally stops only at lower temperature {105} than, e.g. in (η^2-olefin)Fe(CO)$_4$ complexes.

The ^{13}C-NMR spectrum at 0 °C showed the expected signals due to the olefin and the diene. The resonances of the former showed coalescence and split at lower temperatures. The number of resonances observed in the ^{13}C-{^{1}H}-decoupled spectrum at -80 °C is consistent with the given unsymmetrical formula (Figure 3.3). Two resonances appeared at δ 221.7 and 207.4 ppm which are typical of metal-carbonyl groups and are assigned to C^4 and C^5 accordingly. No further assignment of each resonance could be made. No scrambling of these two carbonyl resonances was observed, even at temperatures up to 50 °C. Both carbonyl ester groups, C^2 and C^{14}, appeared almost overlapped at δ 173.8 and 173.6 ppm. The two singlets appearing at δ 113.2 and 92.0 ppm are assigned to the internal carbon atoms of the diene, C^{10} and C^8. The further assignments are based on the multiplicities and ^1J(C-H) coupling constants taken from the non-decoupled spectrum of 38 at -80 °C (Figure 3.4). Chemical shifts, signal multiplicities, and coupling constants are given in Table 3.2.

Two doublets centred at δ 55.5 and 51.1 ppm, each with ^1J(C-H) = 161.7 Hz were assigned to either C^3 or C^{13}. The carbon atoms C^7 and C^{12} appeared as triplets centred at δ 47.7 and 52.9 ppm with ^1J(C-H) = 161.0 and 161.7 Hz, respectively. Two quartets at δ 50.6 and δ 51.6 ppm (^1J(C-H) = 146.6)

Table 3.2: ^{13}C-NMR *data for dicarbonyl(*η^4*-2,3-dimethylbuta-1,3-diene)(*η^2*-dimethyl fumarate)iron.*[a)]

	δ/ppm	multiplicity	J/Hz
C^1	50.6	q	147
C^{15}	51.6	q	147
C^2	173.8	s	-
C^{14}	173.6	s	-
C^3	55.5	d	162
C^{13}	51.1	d	162
C^4	221.7	s	-
C^5	207.4	s	-
C^6	-	-	-
C^7	47.7	t	161
C^{12}	52.9	t	160
C^8	92.0	s	-
C^{10}	113.2	s	-
C^9	17.5	q	128
C^{11}	~19.6	q	128[b)]

[a)] *in toluene-*d_8*, Bruker WH 270, at -80 °C.*

[b)] *partially hidden by solvent signal.*

are assigned to either C^1 or C^{15}. Finally the methyl carbons C^9 and C^{10} are assigned to two quartets at δ 17.5 and 19.5 ppm (^{1}J(C-H) = 128).

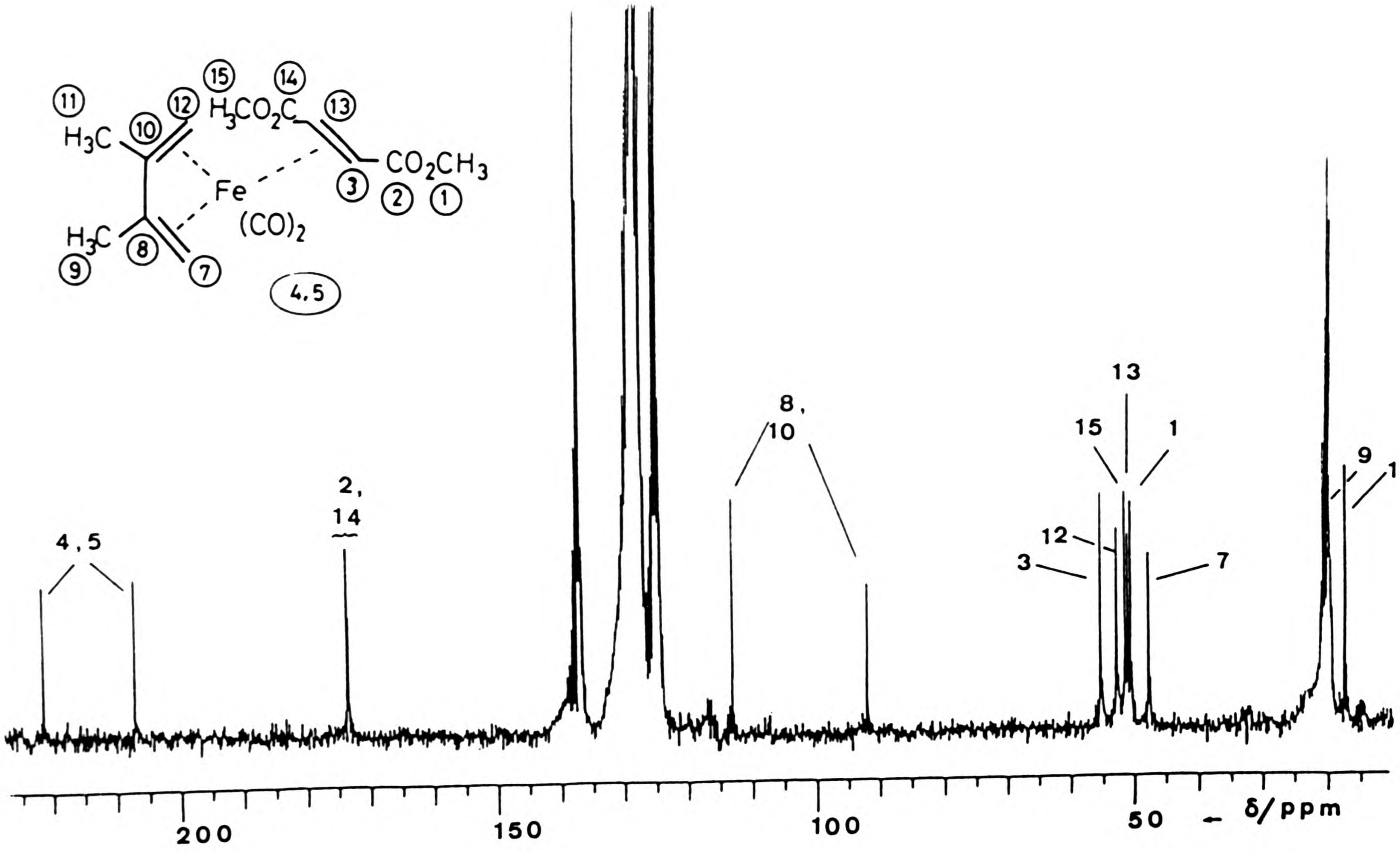


Figure 3.3: The ^{13}C- {^{1}H} -NMR spectrum of 38, in toluene-d$_8$, Bruker WH 270, at -80 °C.

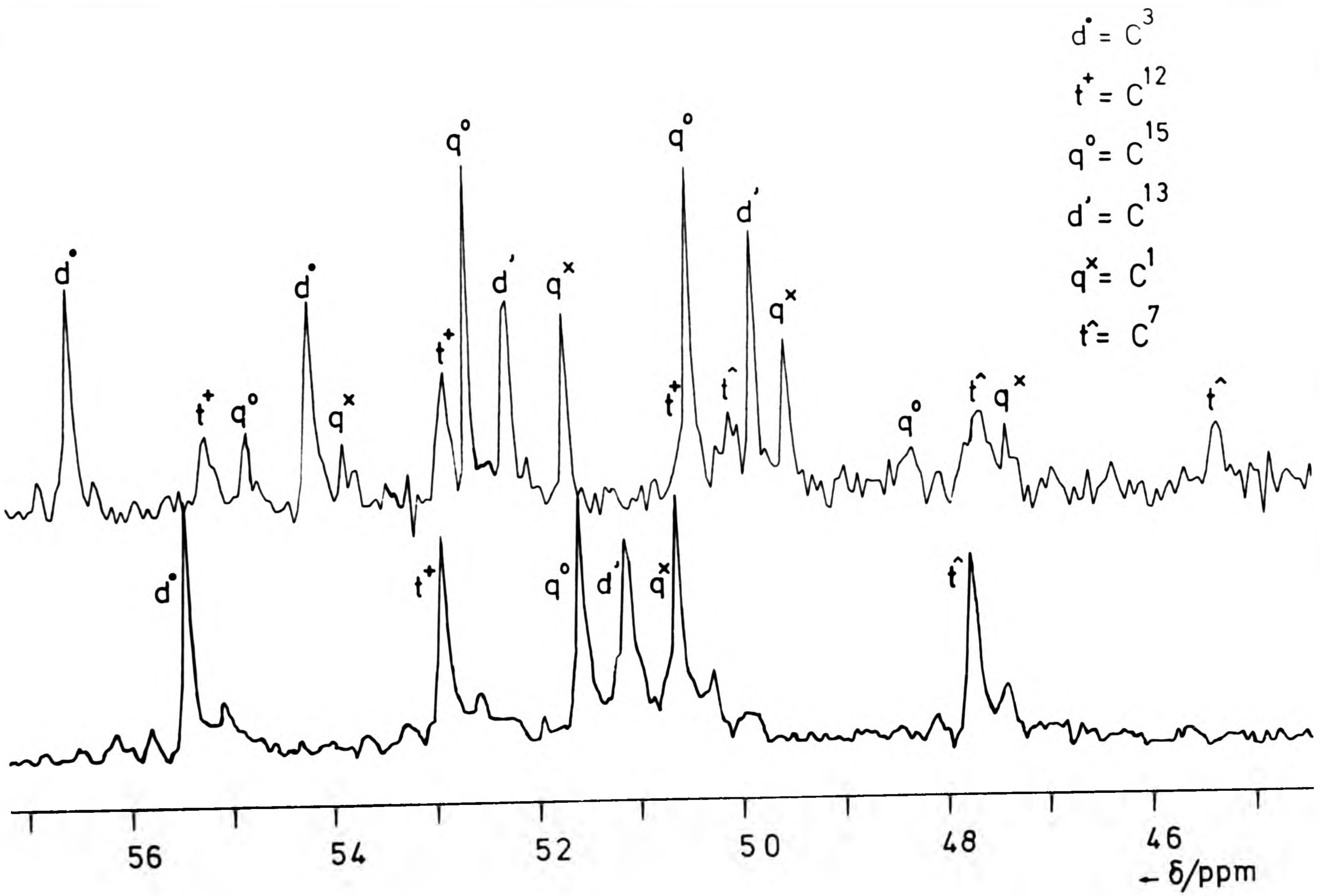


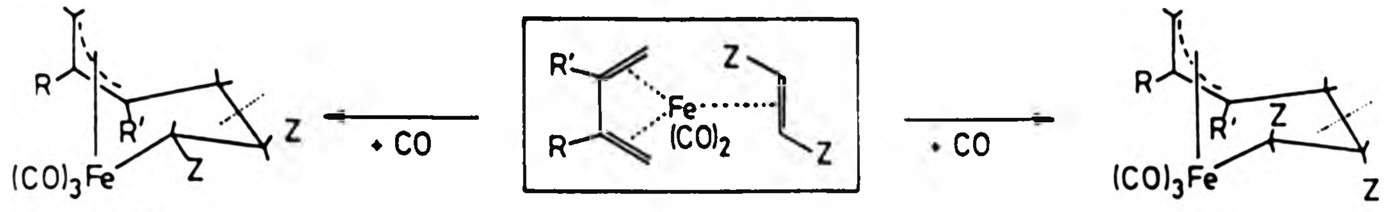
Figure 3.4: ^{13}C- and ^{13}C-{^{1}H}-NMR spectra of 38 in toluene-d_8, Bruker WH 270, at -80 °C.

The synthesis and isolation of the compound 38 is of considerable importance since the NMR study of this compound has clarified the behaviour of these types of compounds whereas the intricate ^{1}H-NMR spectra of compound 36 and the changes involved were not completed even at -80 °C. Thus the question about the number of species involved and their structure remained unanswered.

3.4. The reaction of (η^4-diene)(η^2-olefin)$Fe(CO)_2$ complexes with carbon monoxide and their involvement as key intermediates in the formation of the (σ,η^3-organo)$Fe(CO)_3$ complexes

During the present study it has been found that the reaction of (η^4-2,3-dimethylbuta-1,3-diene)(η^2-diethyl fumarate)-$Fe(CO)_2$, 37, with carbon monoxide at ca. 25 °C results in C-C linkage of the two organic ligands to yield the (σ,η^3-organo)-$Fe(CO)_3$ complex 25. The ratio of the two isomers 25a and 25b is similar to that found for the "one pot" reaction (Section 2.3.2). The *exo*-isomer 25a is obtained as the main product together with small amounts of the *endo*-isomer 25b. This reaction does not require the action of light but is a thermal process which occurs in the dark.

The conversion of 37 to 25a and 25b is effectively quantitatively (reaction 3.3); no (η^4-diene)$Fe(CO)_3$ is formed, i.e. CO does not displace the olefin ligand, in contrast to the corresponding reaction of (η^2-methyl acrylate)$_2Fe(CO)_3$ (cf. Scheme 1.7).



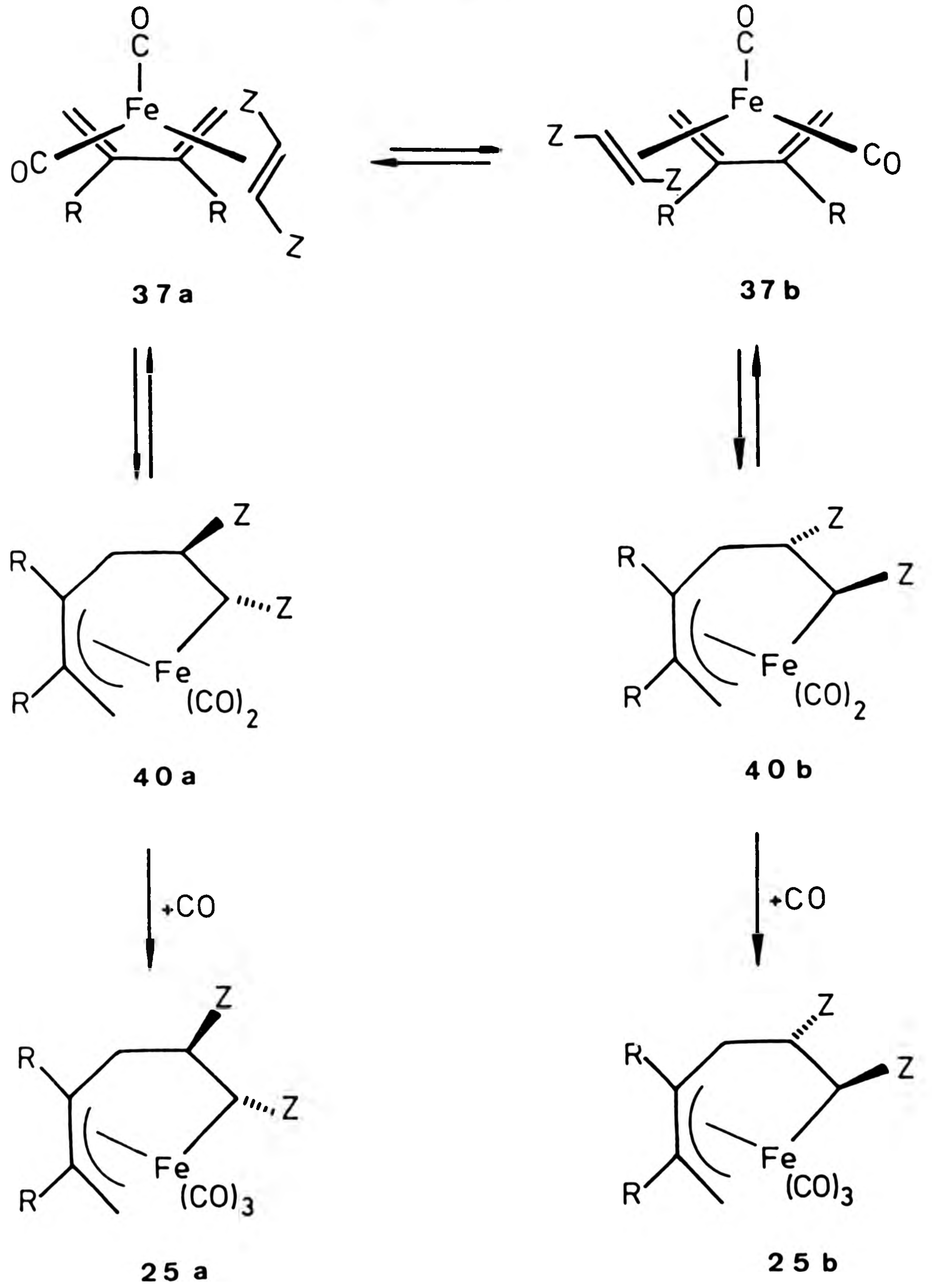
25a **37** **25b**

(reaction 3.3)

Similar results were obtained in a parallel study involving the analogous methyl acrylate complex, **36**, {114}. In this case, the reaction starts at ca. -30 $^{\circ}$C. At this temperature, the *endo*-isomer, **18b**, is eminent whereas at room temperature the *exo*-isomer, **18a**, is the major product.

The findings outlined above confirm that the $(\eta^4\text{-diene})(\eta^2\text{-olefin})\mathrm{Fe(CO)_2}$ complexes are intermediates in the formation of $(\sigma,\eta^3\text{-organo})\mathrm{Fe(CO)_3}$ complexes in the coupling reaction involving 1,3-dienes, monoolefin, and pentacarbonyliron.

In the case of complex **37**, its reaction with carbon monoxide can be rationalized as indicated in Scheme 3.3. Based on the infrared and NMR spectroscopic results it is assumed that $(\eta^4\text{-diene})(\eta^2\text{-olefin})\mathrm{Fe(CO)_2}$ complex exists as a mixture of two isomeric species. These should first undergo oxidative cyclization to form the respective "16 electron" $(\sigma,\eta^3\text{-organo})$-$\mathrm{Fe(CO)_2}$ species **40a** and **40b** which subsequently, in order to complete the coordination sphere, should take up a carbon monoxide yielding the $(\sigma,\eta^3\text{-organo})\mathrm{Fe(CO)_3}$ isomers **25a** and **25b**. This proposal is in accord with the generally accepted alternation of 18-16-18 electron species in organometallic reactions {65}. It also provides some basis for rationalizing the relative yields of **25a** and **25b**. Obviously, the ratio of these



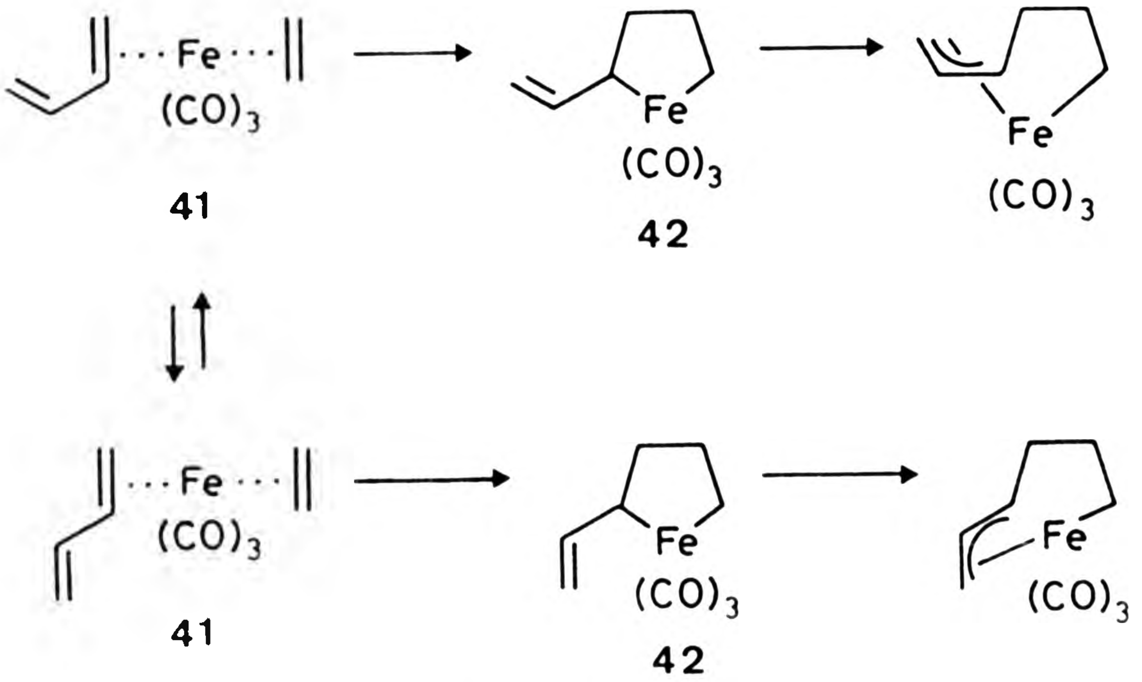
$R = CH_3$

$Z = CO_2C_2H_5$

(Scheme 3.3)

two isomers is not determined by the equilibrium ratio of the two respective precursors 37a and 37b. According to the infrared spectrum (see Figure 3.1 , which shows the analogous spectrum of the methyl ester complex, 38), these two species are present in comparable amounts whereas the observed product ratio 25a : 25b is >> 1. Consequently, this product ratio must be determined by the coupling reaction itself and not by the equilibrium of the precursors. It seems likely that the first coupling step 37 → 40 is more sterically hindered by the *endo*-oriented α-ester group in 37b than by the *exo*-oriented α-ester group in 37a. However, the reverse effect can be expected for the second step 40 → 25 . In the case of the analogous (σ,η^3-organo)$Fe(CO)_2$ species derived from methyl acrylate, it was shown by detailed low temperature matrix isolation study {121} that the incoming CO ligand is seriously hindered in the case of the a isomer but not for the b isomer. In other words, the α-ester group has two counteracting steric effects. It seems that the latter one, i.e. hindrance of the incoming CO ligand, becomes kinetically more important at lower temperatures, thus increasing the relative yield of the type b product.

Although it is evident from these results that the (η^4-diene)(η^2-olefin)$Fe(CO)_2$ complex(es) are in fact involved as intermediate(s) in the formation of (σ,η^3-organo)$Fe(CO)_3$ coupling products, other possibilities cannot be strictly excluded. Various alternative coupling mechanisms have been outlined by *Green* and co-workers {92} to account for the photoinduced addition of fluoroalkynes to (η^4-1,3-diene)Fe(CO)$_3$ complexes which may be used here analogously. One of these proposals involves the intermediacy of a (η^2-diene)(η^2-olefin)-Fe(CO)$_3$ species, 41, which could undergo oxidative cyclization, via the 16-electron vinyl substituted ferracyclopentane species, 42, to form the (σ,η^3-organo)Fe(CO)$_3$ complex (Scheme 3.4). However, this proposal has two serious drawbacks; firstly, it is analogous to the oxidative cyclization of a (η^2-olefin)$_2$-Fe(CO)$_3$ complex which has been disproven theoretically by *Hoffmann* et.al. {83} and experimentally by *Grevels* et.al. {76, 80} (cf. Section 1.4). Secondly, free rotation of the vinyl group is possible, thus giving rise to two (σ,η^3-organo)Fe(CO)$_3$ isomeric products, i.e. the η^3-allylic moiety could be linked to the rest of the six-carbon chain via the *anti* or the *syn* position. However, in all cases investigated in this thesis, only (1-σ,4-6-η^3-*anti*-organo)Fe(CO)$_3$ was found. Hence it follows that an intermediate of type (dihapto coordinated diene)-(dihapto coordinated olefin)dicarbonyliron is unlikely.



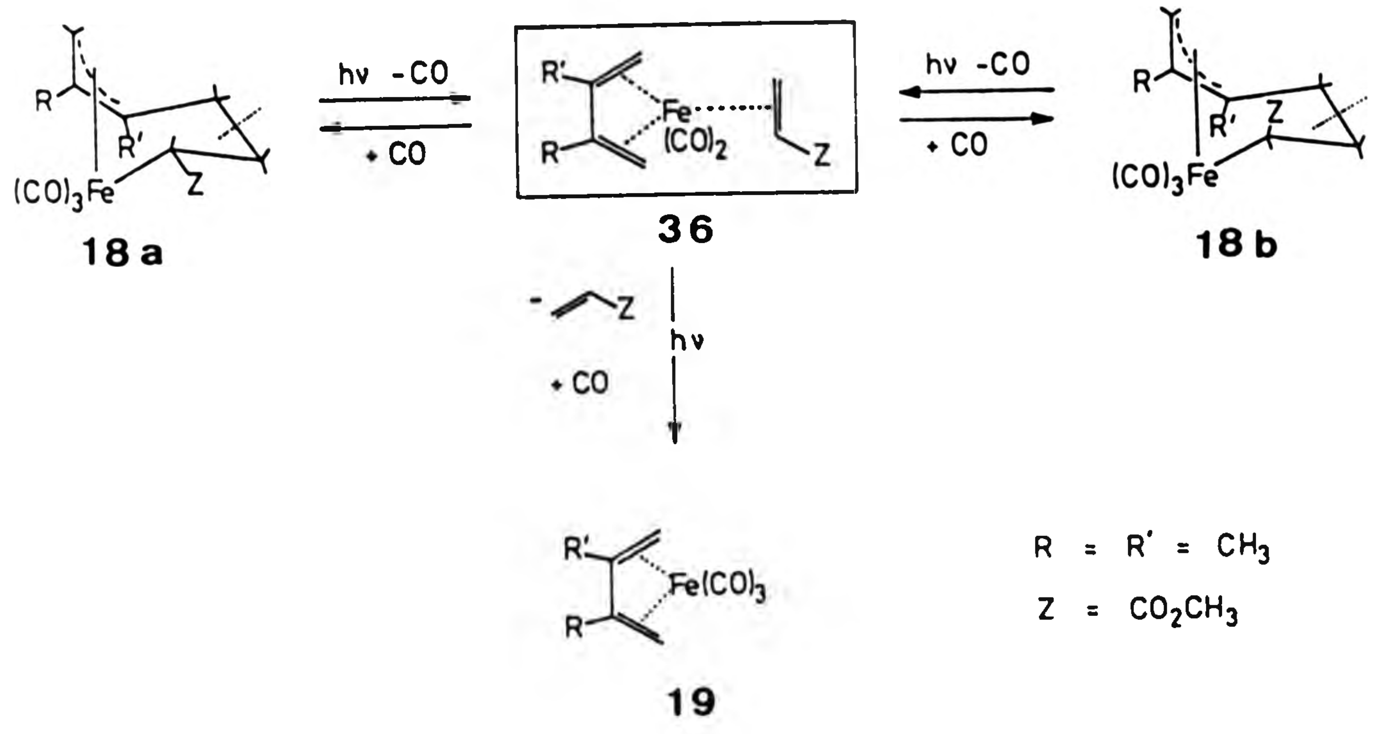
(Scheme 3.4)

CHAPTER FOUR

PHOTOREACTIONS OF (1-σ,4-6-η^3-ORGANO)Fe(CO)$_3$ COMPLEXES

4.1. Introduction

(σ,η^3-Organo)Fe(CO)$_3$ complexes undergo various types of photoreactions. *Grevels* et.al. have shown that e.g. on photolysis the isomers 18a and 18b undergo (*i*)isomerization and (*ii*) loss of methyl acrylate to give (η^4-DMB)Fe(CO)$_3$. The latter process may account, at least in part, for the observation that in the "one pot" reaction substantial amounts of (η^4-diene)Fe(CO)$_3$ remain present in the reaction mixture even after extended irradiation. It has been established that these reactions of 18 involve photoinduced loss of carbon monoxide {121} and C-C cleavage yielding the complex (η^4-DMB)(η^2-MA)Fe(CO)$_2$, 36, {122} as a common intermediate in both processes (Scheme 4.1).



(Scheme 4.1)

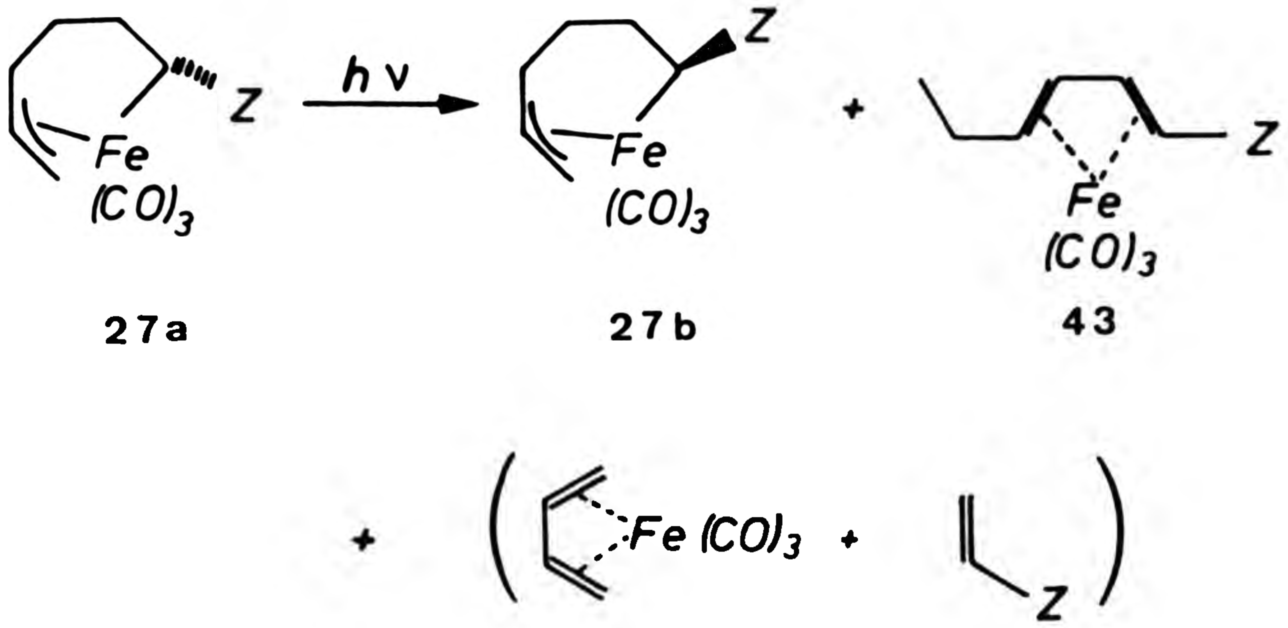
Some other interesting photoreactions of $(\sigma,\eta^3$-organo)Fe(CO)$_3$ complexes have been indicated by the observations made during the present study. For example, hexa-1,5-diene compounds 32-E and 32-Z, and 34-E have been isolated from the "one pot" reactions involving methyl sorbate as the diene component. The (hexa-1,3-diene)Fe(CO)$_3$ complex of type 43 has been observed as a by-product of the $(\sigma,\eta^3$-organo)Fe(CO)$_3$ complex 27, which is derived from buta-1,3-diene and methyl acrylate. The formation of these linear diene products may be due to photoinduced rearrangements of the respective $(\sigma,\eta^3$-organo)Fe(CO)$_3$ complexes.

The work described in the following sections of this Chapter was carried out with the aim of investigating, with emphasis on mechanistic aspects, such photoreactions of the $(\sigma,\eta^3$-organo)Fe(CO)$_3$ complexes.

4.2. Photoreactions of tricarbonyl(buta-1,3-diene/methyl acrylate)iron and tricarbonyl(buta-1,3-diene/*cis*-d_2-methyl acrylate)iron

Photolysis of *tricarbonyl{1,4,5,6-*η^4*-[1(exo)-carbomethoxy-hex-4-en-1,6-diyl]}iron*,27a, afforded the *endo*-isomer, 27b, and a second product 43 in 11 % and 16 % yields, respectively. Some of the starting isomer was recovered (19 %) and $(\eta^4$-buta-1,3-diene)Fe(CO)$_3$ was detected by infrared spectroscopy but was neither isolated nor determined quantitatively (Scheme 4.2).

The product 43 was shown by elemental analysis and mass spectroscopy {m/e 280, 252, 224, 196; [M-nCO]$^+$,



(Scheme 4.2)

n = 0, 1, 2, 3} to be another isomer of 27a. The infrared spectrum showed three bands of comparable intensities (2061.4, 2001.5, and 1987.0 cm $^{-1}$, in n-hexane) in the metal carbonyl region, thus indicating the presence of the tricarbonyliron unit. The ester carbonyl band appears at higher frequency (1725 cm $^{-1}$) than in 27a and 27b (1708 and 1702 cm^{-1}, respectively). It may be compared with the ester band of (η^4-methyl sorbate)Fe(CO)$_3$ ($\tilde{\nu}$ ester-CO = 1723.5 cm^{-1}), thus indicating that 43 may possess analogous structure.

The ^{1}H-NMR spectrum of 43 shown in Figure 4.1 is consistent with the proposed formulation, *tricarbonyl*{η^4-[*1-carbomethoxy-hexa-1(E),3(E)-diene*]}*iron*. The chemical shifts of the four olefinic protons are in accord with the general order of (η^4-diene)Fe(CO)$_3$ complexes {96,97}. The coupling constant J(H^5-H^6) = 8.1 Hz {123,124,125} together with the low field shift of H^5, due to the anisotropic effect of the ester group, provide evidence for E-configuration at the ester substituted double bond. Likewise, the coupling constant

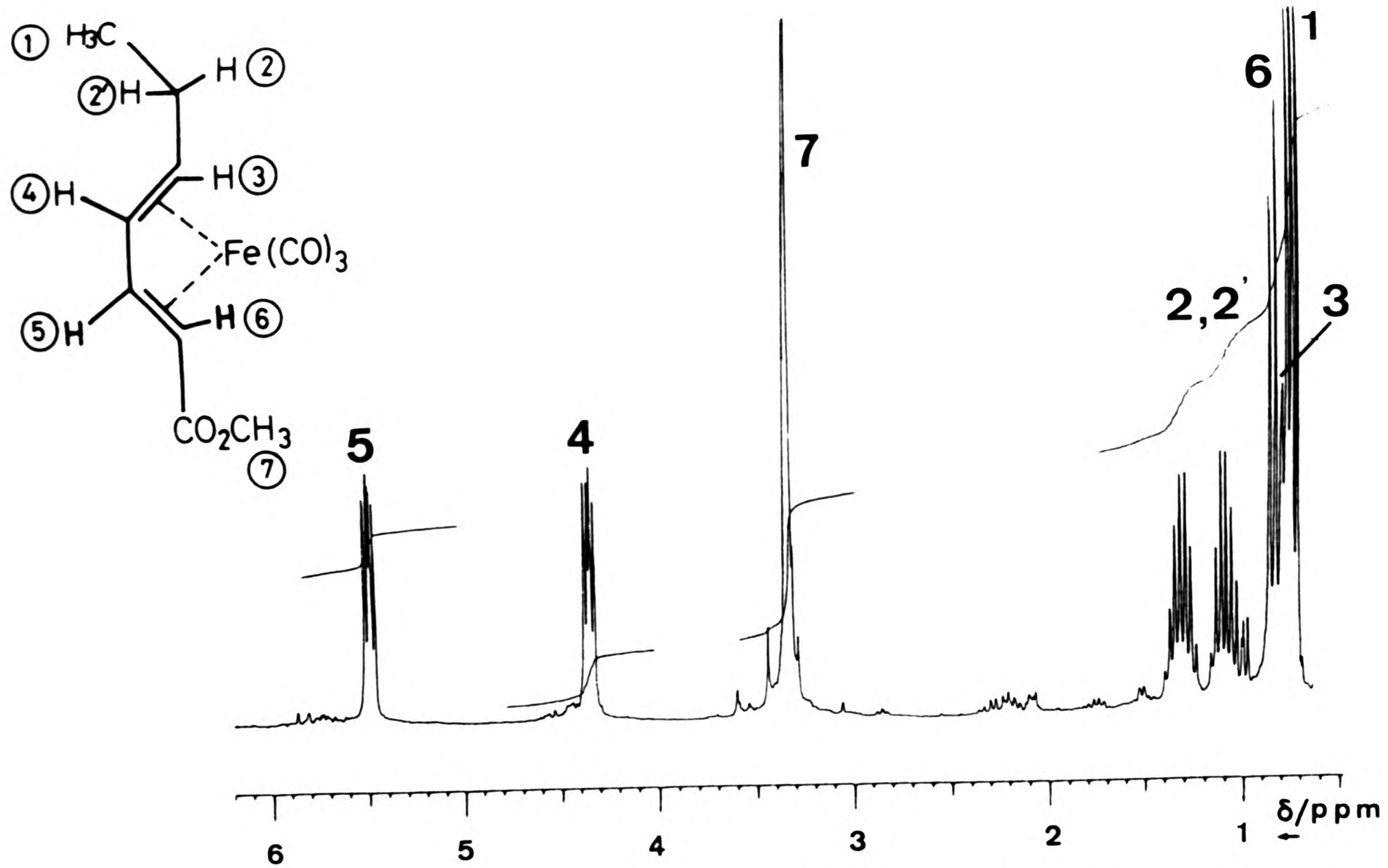
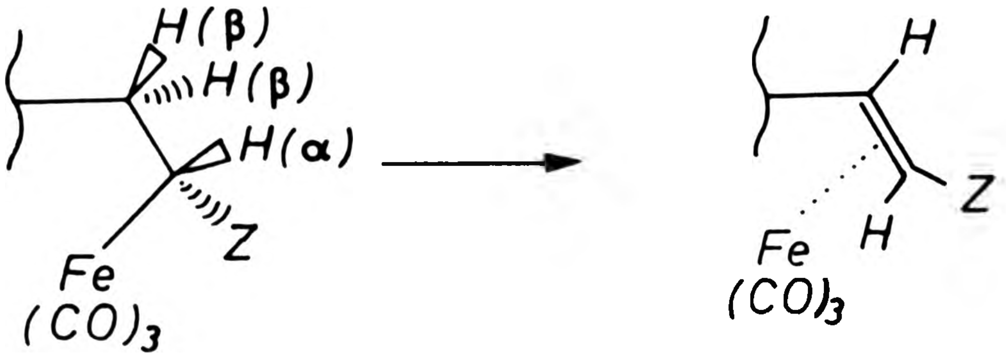


Figure 4.1: ^{1}H-NMR spectrum of *tricarbonyl* {η^4-[*1-carbomethoxy-hexa-1(E), 3(E)-diene*]} *iron* 43, in benzene-d_6, Bruker WH 270, at 27 °C ±1; {δ in ppm = 5.49 (H^5), 4.36 (H^4), 3.33 (H^7), 1.31/1.09 ($H^2/H^{2'}$), 0.86 (H^6), 0.74 (H^1), and 0.76 (H^3)}.

$J(H^3-H^4)$ = 8.2 Hz shows that the ethyl substituted double bond has also *E*-configuration {123,124,125}.

The conversion of 27a into 43 involves β-hydrogen abstraction and addition of this hydrogen to the terminal allylic carbon atom. At this stage, however, it is not clear which of the two β-hydrogen atoms is transferred (Scheme 4.3).

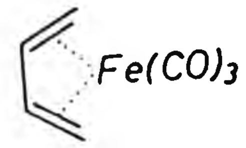
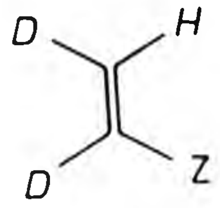
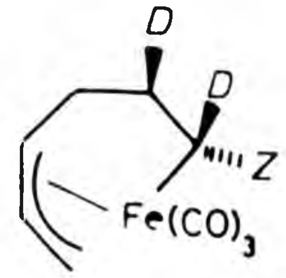
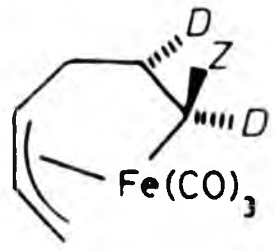
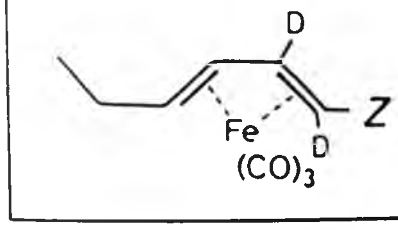


(Scheme 4.3)

In order to elucidate this particular feature of this process, the reaction was repeated with a specifically deuterium labelled complex, 28a (for synthesis and characterization of this compound, cf. Section 2.3.4). Like 27a, the labelled complex underwent C-C bond cleavage with formation of (buta-1,3-diene)-Fe(CO)$_3$ and loss of acrylate, isomerization to 28b and rearrangement to 44 (Table 4.1). The progress of the reaction during irradiation was monitored by means of infrared spectroscopy (Figure 4.2).

The mass and infrared spectra of 44 are very similar to those of 43. The $[M-nCO]^+$ peaks (n = 0, 1, 2 ,3; m/e 282, 254, 226, 198) in the mass spectrum indicate the incorporation of two deuterium atoms. The position of the deuterium atoms

Table 4.1: Infrared data (cm^{-1}, in n-hexane) of compounds resulting from photolysis of 28a.

compound	$\tilde{\nu}$ (CO)	$\tilde{\nu}$(ester-CO)
x 	2056.2, 1990.1, 1980.2	
o 		1740.0
a  **28a**	2068.2, 2012.4, 1995.9	1708.3
b  **28b**	2063.6, 2004.3, 1995.3	1700.7
 **44**	2061.4, 2001.5, 1987.0	1723.7

in the complex was established using ^{1}H-NMR spectroscopy. The ^{1}H-NMR spectrum of 44 (Figure 4.3) is similar to that of 43 except the H^{6} signal at δ 0.86 ppm is completely missing and the resonance due to H^{5} at δ 5.49 ppm is almost diminished. The residual (H^{5}) signal (ca. 20 %) is due to the fact that in 28a the D-label at the β-carbon atom was distributed over the positions H^{3}/H^{4} in a ca. 4:1 ratio (see Table 2.12). Thus the

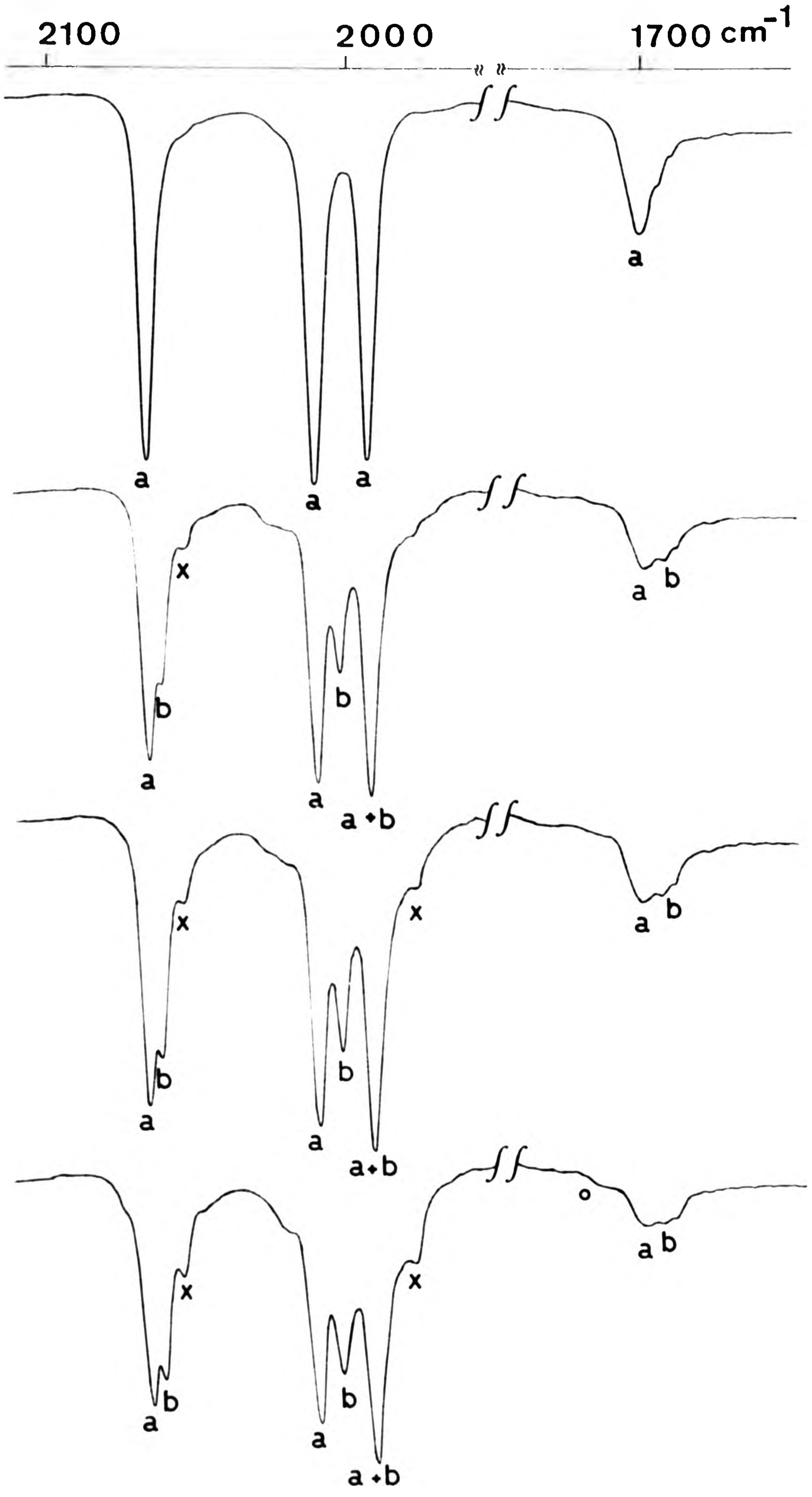


Figure 4.2: Infrared spectral changes associated with photolysis of compound 28a; (for assignments of bands see Table 4.1).

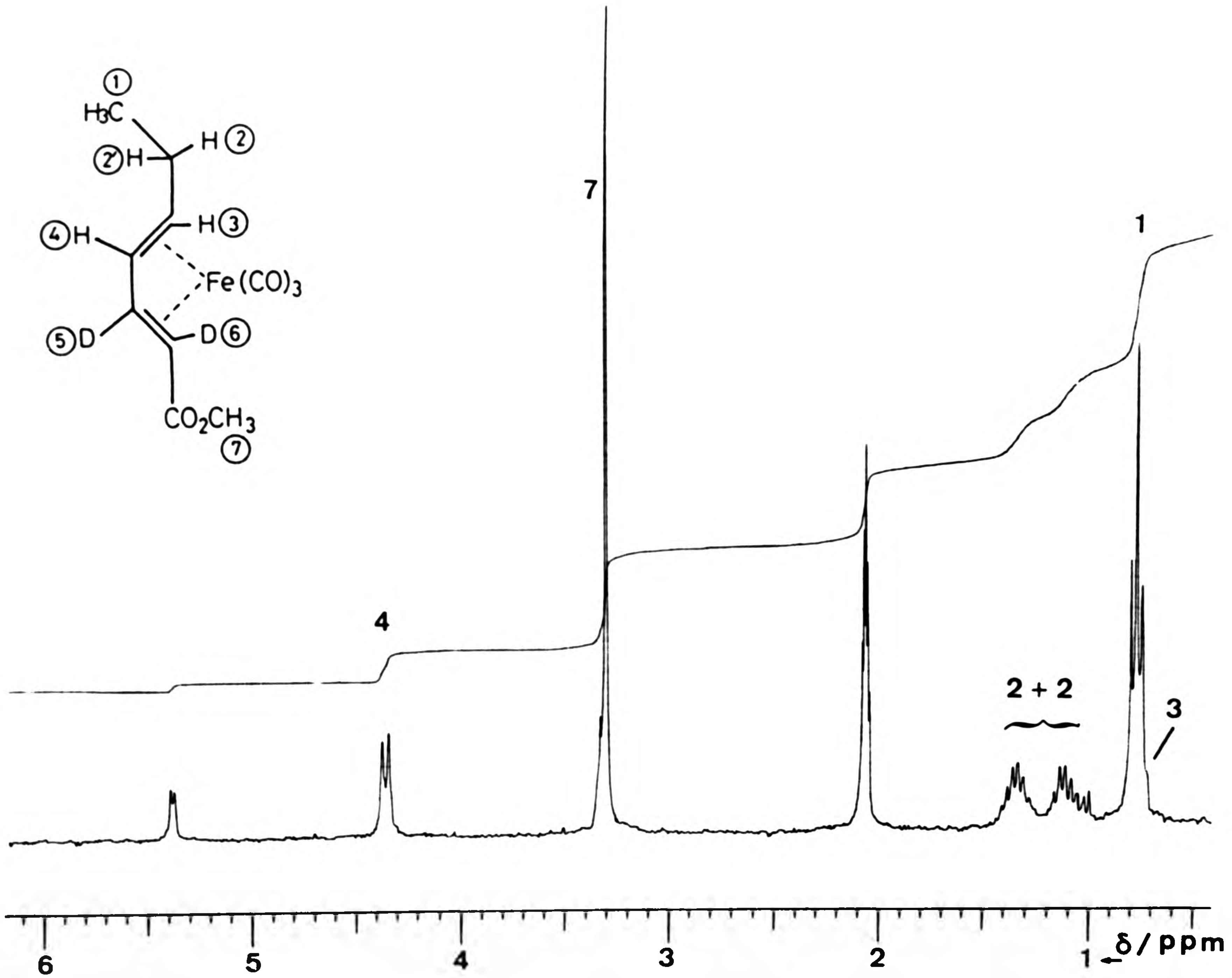
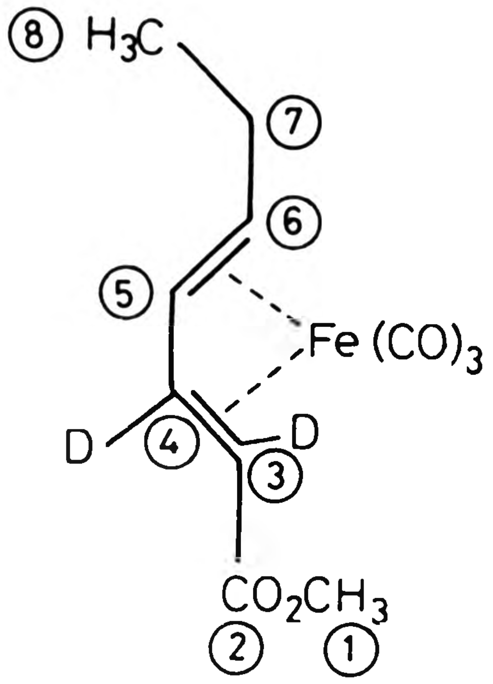


Figure 4.3: ^{1}H-NMR spectrum of *tricarbonyl* {η^4[*1-carbomethoxy-1,2-dideuterio-hexa-1(E), 3(E)-diene*]}*iron* 44, in toluene-d_8, Bruker WH 270, at 27 °C $\pm$1; (cf. Figure 4.1)

compound 44 is formulated as *tricarbonyl{η^4 [1-carbomethoxy-1,2-dideuteriohexa-1(E),3(E)-diene]}iron*, the d_2-analogue of 43.

The ^{13}C-NMR spectrum of 44 is consistent with the given structure. A summary of the data is given in Table 4.2. The carbon atoms C^4 and C^3 carrying a deuterium and being an sp^2-hybridized centre, resonate as triplets centred at δ 45.6 ppm and δ 30.3 ppm, respectively, with typical $^1J(C-D)$ coupling constants of 21.0 Hz and 20.0 Hz {126}.



44

Hence it follows from the ^{1}H- and ^{13}C-NMR data that formation of compound 44 upon photolysis of compound 28a is accomplished by hydrogen-migration, not deuterium migration, from the β-position. This leads to the suggestion that the transferred hydrogen atom is stereoselectively abstracted from one of the two β-H positions, provided that the kinetic H-D isotope effect possibly operating {127}is not pronounced. Although it cannot be entirely excluded,this latter possibility seems to be unlikely particularly because the residual (20 %) H^5 signal is in good agreement with the above-mentioned 4:1 ratio of the D-label in the β-hydrogen positions.

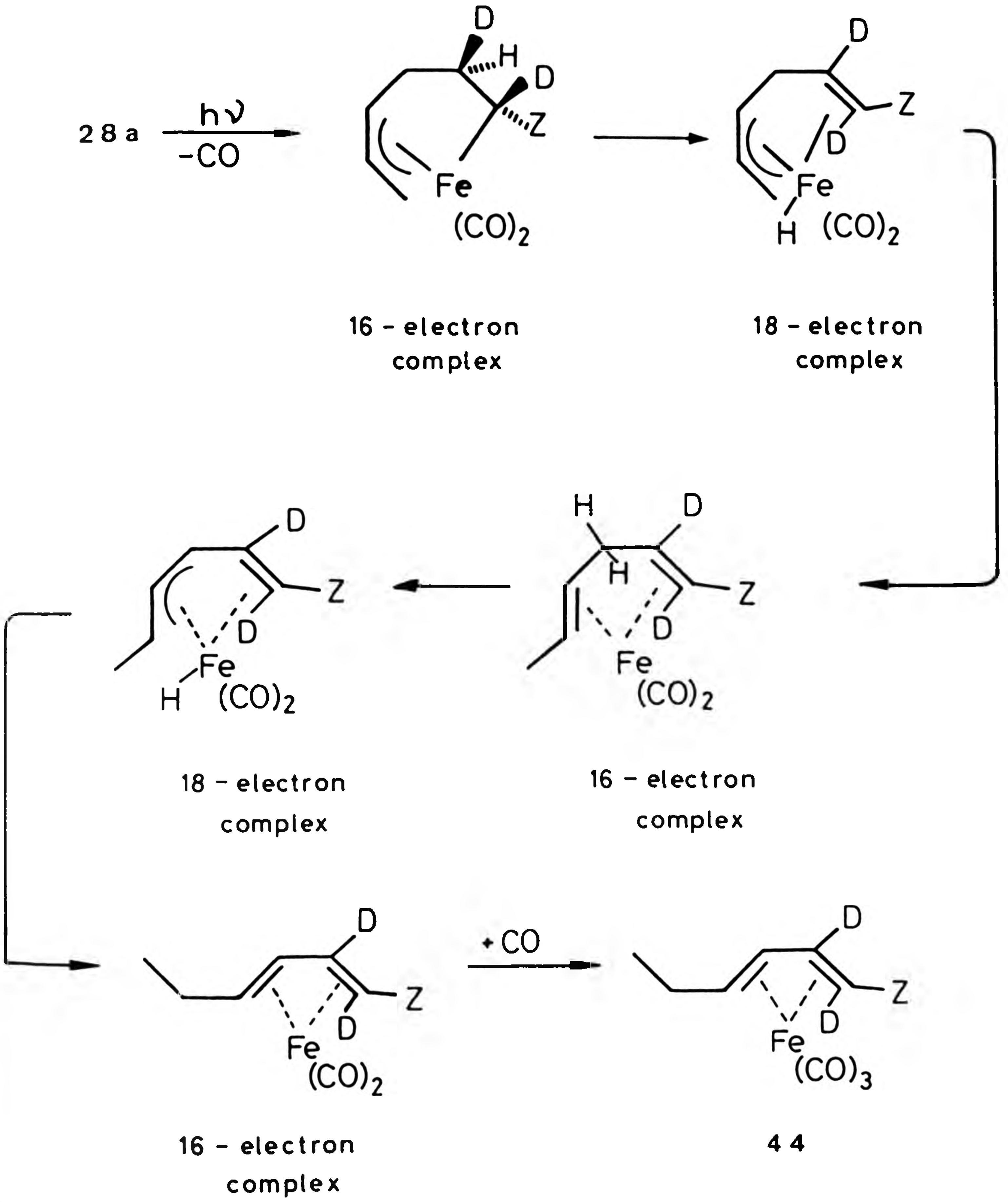
Table 4.2: ^{13}C-NMR data for compound 44.[a]

	δ/ppm	multi-plicity	^1J(C-H)/Hz
C^1	51.1	q	147
C^2	172.0	s	-
C^3	30.3	t	20[b]
C^4	45.6	t	21[b]
C^5	86.9	d	155
C^6	67.8	d	167
C^7	27.5	t	127
C^8	16.1	q	128
C^9	212.5	s	-
C^{10}	210.8	s	-
C^{11}	208.6	s	-

[a] *in toluene-d_8, Bruker WH 270, at 27 °C ±1.*

[b] *^1J(C-D).*

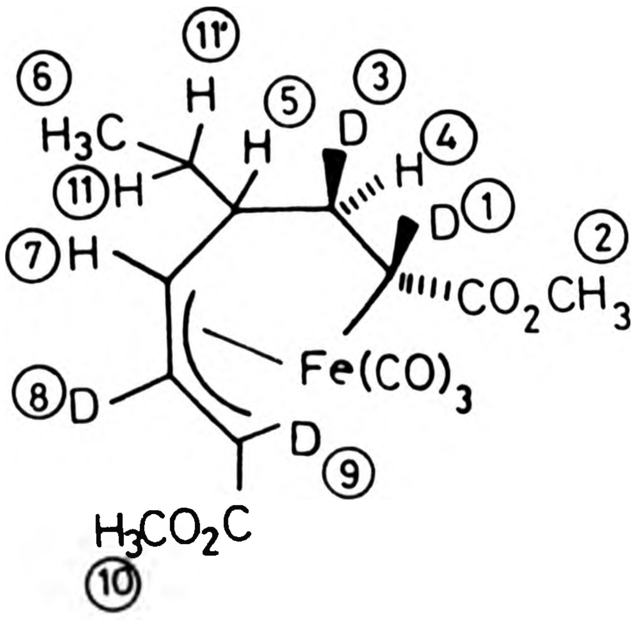
The formation of product 44 from the photoreaction of 28a can be rationalized as shown in Scheme 4.4. The initial, photochemical step is the detachment of one carbonyl ligand. Such detachment was previously established by photolysis of the (σ,η^3-organo)Fe$(CO)_3$ complex 18a derived from DMB/MA, carried out under low-temperature matrix isolation conditions [121]. The resulting 16 electron dicarbonyl species may subsequently


28a
hν
-CO
D
H
D
Z
Fe
(CO)$_2$
16 - electron complex
D
Z
D
Fe
H
(CO)$_2$
18 - electron complex
H
D
H
Z
D
Fe
(CO)$_2$
16 - electron complex
D
Z
D
Fe
H
(CO)$_2$
18 - electron complex
D
Z
D
Fe
(CO)$_2$
16 - electron complex
+CO
D
Z
D
Fe
(CO)$_3$
44

(Scheme 4.4)

undergo β-hydrogen abstraction to give an 18 electron metal hydride species. Similar abstraction has been observed in the photochemical reactions of alkyl iron complexes in low temperature matrix {128}. The hydrogen should then be transferred to the allylic moiety with formation of a 1,4-diene complex. Analogously, the second hydrogen transfer from the γ-position, formulated via a sequence of 18- and 16-electron species in accordance with *Tolman's* rule {65}, results in the formation of the 1,3-diene moiety. The last step involves re-uptake of a carbonyl ligand to give the final product 44.

In addition to the main products 44 and 28b, the photoreaction of 28a affords another tricarbonyliron complex, 45a, in low yield. The mass spectrum of this compound {m/e 342, 314, 286, $[M-nCO]^+$ (n=1,2,3); m/e 339 $[M-OCH_3]^+$} indicates that it is derived from one buta-1,3-diene, two d_2-methyl acrylate and one $Fe(CO)_3$ units. The infrared spectrum is very similar in the metal carbonyl region [ν (CO): 2075.9, 2020.3,



45a

2017.3, 2010.0 cm^{-1}; $\tilde{\nu}$ ester(CO): 1722.2, 1710.9 cm^{-1}] to that of the $(\sigma,\eta^3$-organo)$Fe(CO)_3$ complex **31a**, derived from methyl sorbate and methyl acrylate (cf. Table 2.17), thus suggesting an analogous structure.

The ^{1}H-NMR data (Table 4.3) of **45a** confirm the proposed structure. It relates to the spectrum of **31a** with regard to the methyl ester signals (H^2 and H^{10}) and to H^4, H^5, H^7.

Table 4.3: Comparative ^{1}H-NMR-data for compounds **45a** and **31a**.[a)]

δ/ppm	45a	31a
H^1	Deut	1.72
H^2	3.59	3.55
H^3	(ca. 20 %)[b)]	1.72
H^4	2.42	2.43
H^5	0.42	0.67
H^6	0.64	0.69
H^7	4.00	4.02
H^8	(ca. 20 %)[b)]	5.22
H^9	Deut	3.02
H^{10}	3.48	3.45
H^{11} $H^{11'}$	$\}$ ~1.06	-

a) *in benzene-d_6, Bruker WH 270, at 27 °C ±1.*

b) *intensity is reduced due to partial deuteration.*

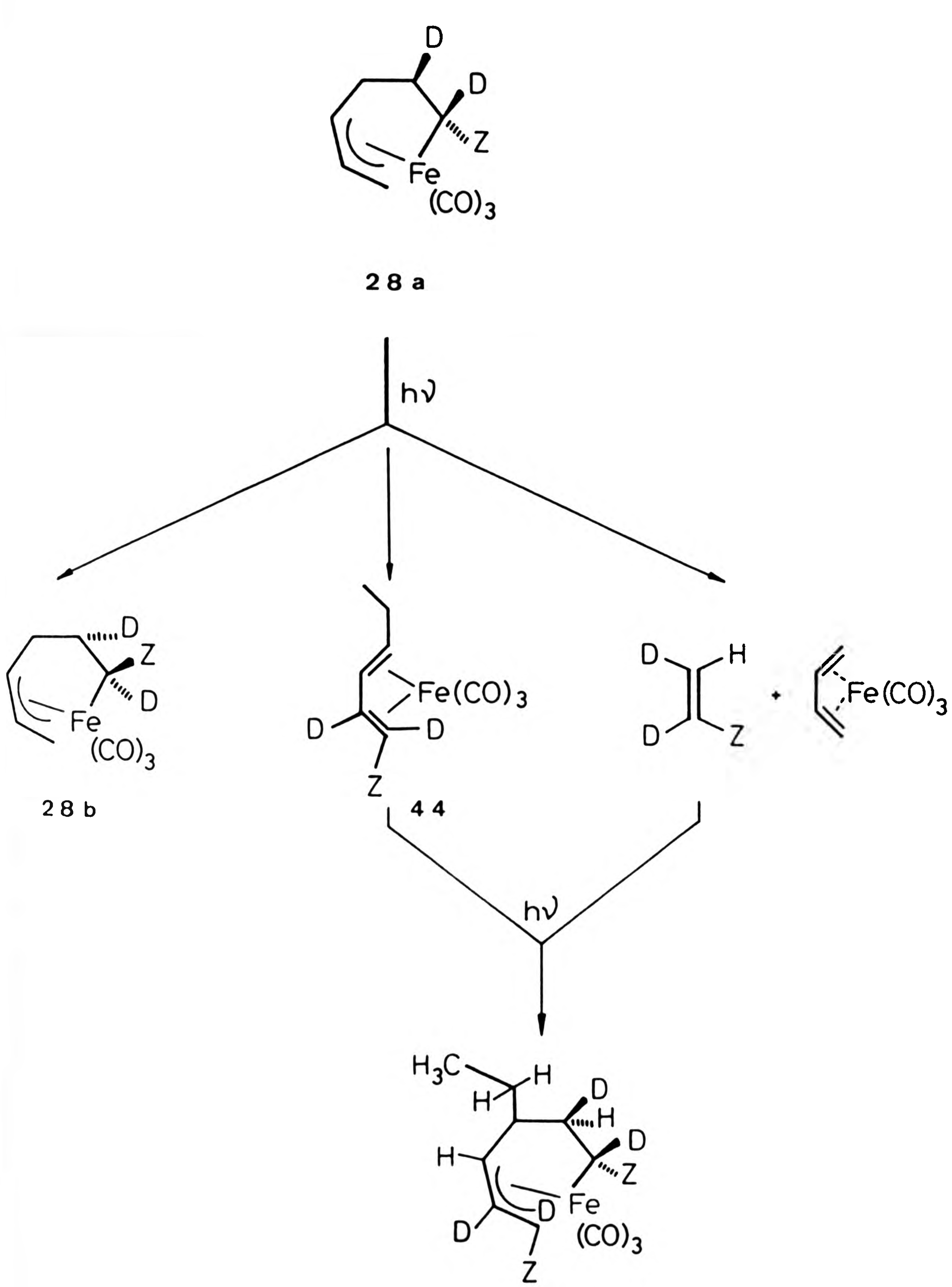
The ethyl group (which replaces the methyl substituent of **31a**) is clearly characterized {$J(H^6-H^{11}) = 7.2$ Hz}. As indicated in Table 4.3, the signals of H^1, H^3, H^8 and H^9 are missing or exhibit reduced intensity, due to the deuterium content.

The formation of this compound can be rationalized as shown in Scheme 4.5, i.e. by the coupling of the initial photoreaction product **44** and *cis*-d_2-methyl acrylate. This coupling reaction parallels those of methyl sorbate and other 1,3-dienes described in Chapter two. The observed distribution of the deuterium labels is in accordance with this proposal.

4.3. Photolytic cleavage and isomerization reactions of tricarbonyl{1,4,5,6-η^4-(1(*exo*),6(*trans*)-dicarbomethoxy-3-methylhex-4-en-diyl)}iron

As discussed in Chapter two (Section 2.4.2) the photochemical reaction of methyl sorbate, methyl acrylate, and pentacarbonyliron gave two organic products which have been identified as isomeric hexa-1,5-diene derivatives, **32-Z** and **32-E**, in low yield, in addition to the (σ,η^3-organo)Fe(CO)$_3$ isomers **31a** and **31b** and the olefin- and diene-iron carbonyl products. It was thought that **32-Z** and **32-E** are photoreaction products of **31a** and **31b**, respectively. In order to check this hypothesis the photolytic behaviour of **31a** was examined.

The photolysis of compound **31a** was carried out in n-hexane/diethyl ether using the irradiation apparatus described in Figure 6.1. The changes upon photolysis were monitored using infrared spectroscopy by the observation of the sharp and characteristic bands in the metal-carbonyl region. The

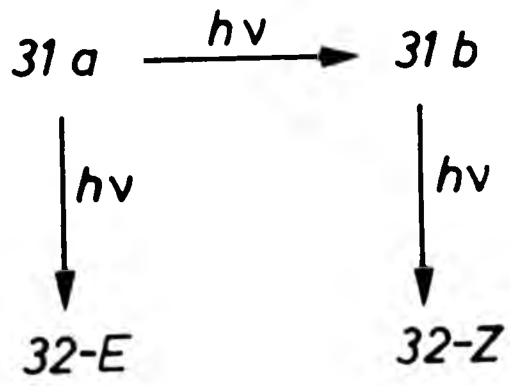

D
D
Z
Fe
(CO)3
28 a
hν
D
Z
D
Fe
(CO)3
28 b
Fe(CO)3
D
D
Z
44
D
H
D
Z
+
Fe(CO)3
hν
H3C
H
H
D
H
D
H
Z
D
Fe
D
(CO)3
Z
45 a

(Scheme 4.5)

infrared spectra of the reaction mixture showed the bands of 31a together with its isomerization product 31b. In addition, bands due to the C-C bond cleavage product, (methyl sorbate)-$Fe(CO)_3$, were also observed (2063, 2003, 1988 and 1725 cm^{-1}).

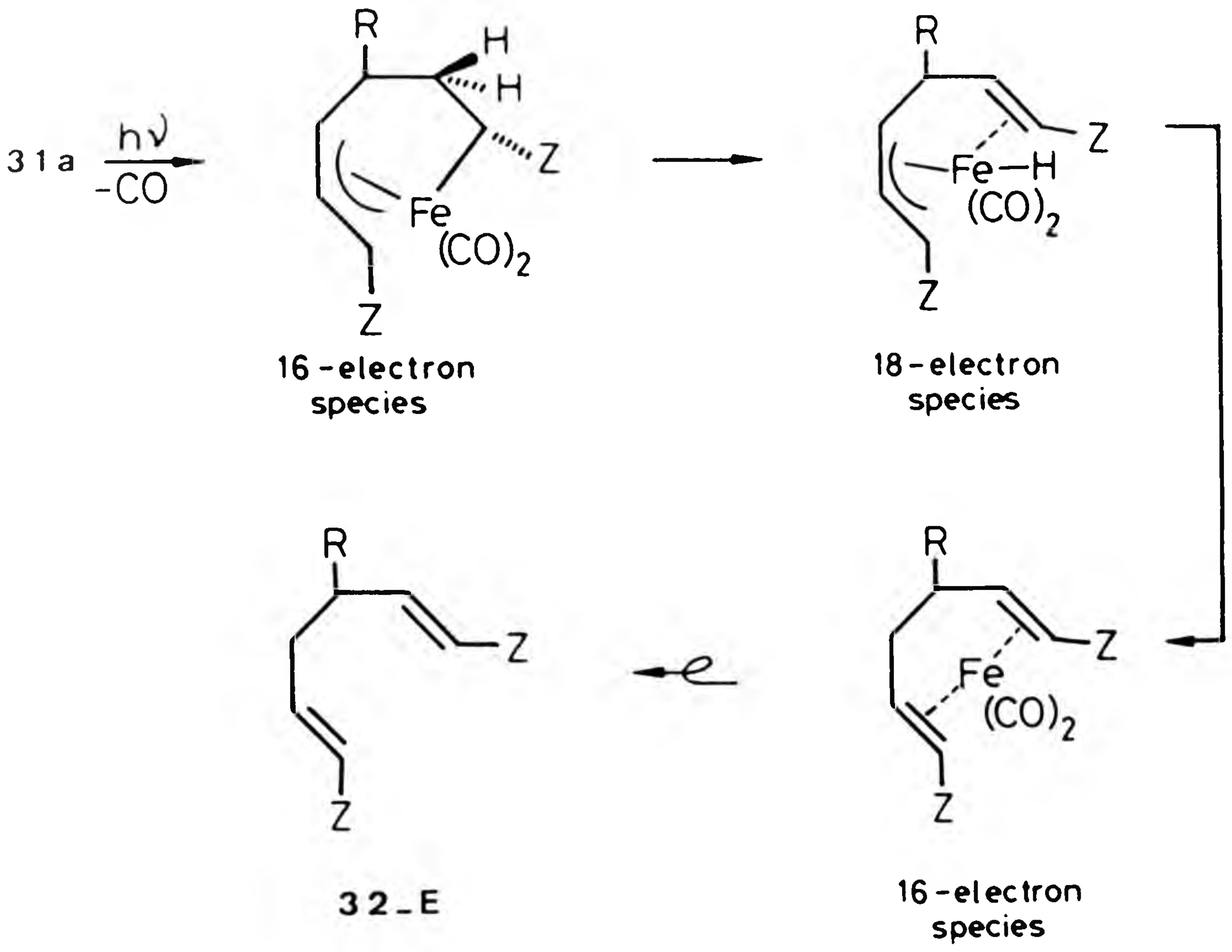
Chromatographic separation of the reaction mixture gave unreacted 31a (12 % recovery), its isomer 31b (11 %), $(\eta^4$-MSo)$Fe(CO)_3$ (40 %), 32-E (9 %) and 32-Z (1 %). The separated products were characterized using IR- and/or ^{1}H-NMR-spectroscopy.

Thus it is proven that the $(\sigma,\eta^3$-organo)$Fe(CO)_3$ complex 31a not only undergoes photoinduced isomerization and C-C cleavage with loss of MA, but also rearrangement involving hydrogen transfer takes places. It is assumed that the compounds 32-E and 32-Z arise from 31a and 31b, respectively by photolysis (Scheme 4.6).



(Scheme 4.6)

Mechanistically the formation of the hexa-1,5-dienes 32-E and 32-Z can be rationalized as exemplified in Scheme 4.7 for 32-E. The initial step involves loss of CO to give a 16-electron species {121}. This is followed by β-hydrogen abstrac-



(Scheme 4.7)

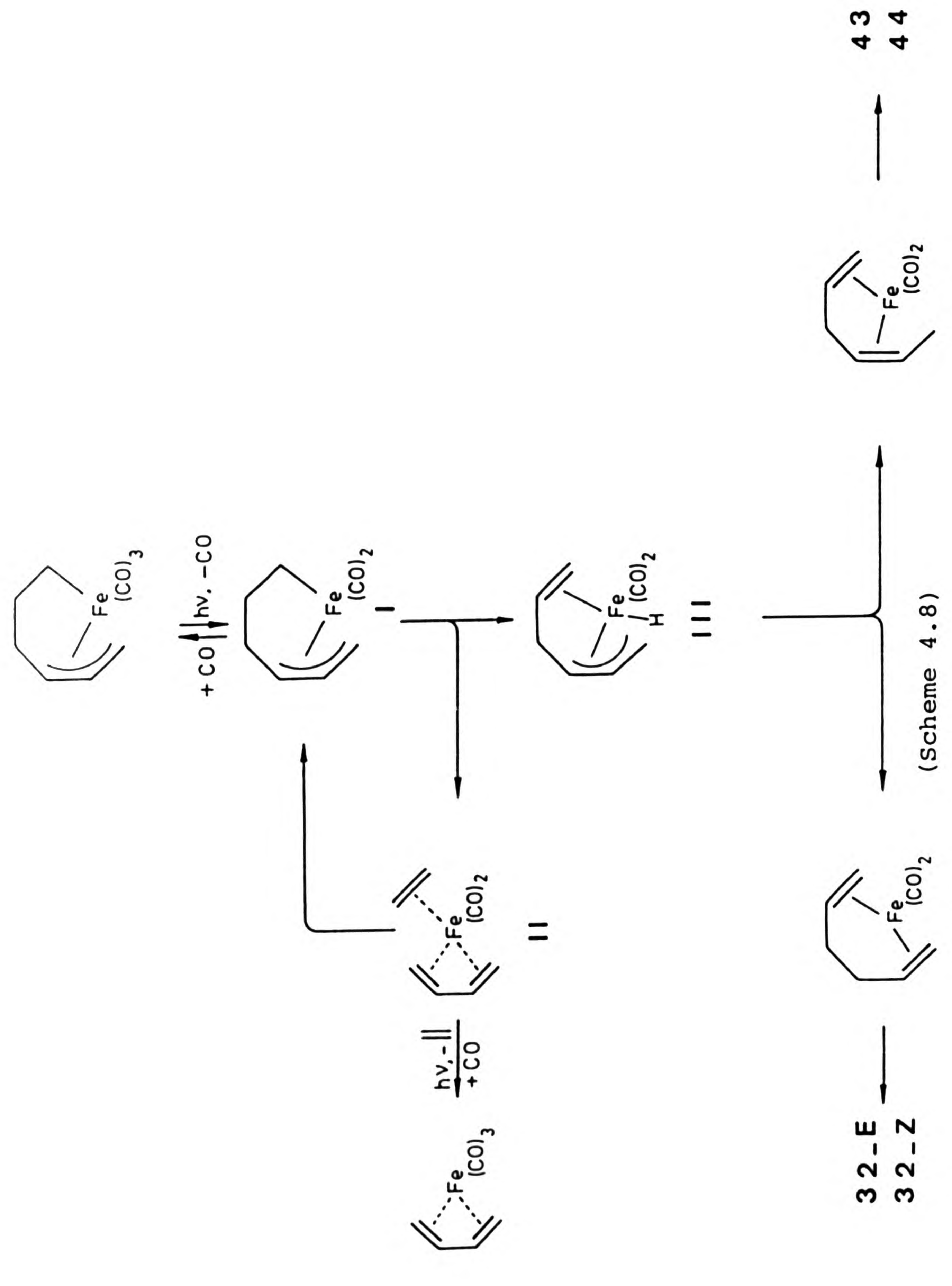
tion and formation of a metal-hydride 18-electron species. The subsequent hydrogen transfer from the metal does not occur to the terminal site of the allylic moiety as with the previous case (cf. Scheme 4.4), but to the δ-position in the C_6-chain (Scheme 4.7). Thus the two terminal double bonds are situated in conjugation with the ester carbonyl groups to yield a 16-electron species which then yields 32-E by loss of the dicarbonyliron unit.

4.4. Conclusions

The results obtained from the present study demonstrate that (σ,η^3-organo)$Fe(CO)_3$ complexes can undergo a variety of photoreactions, and also it has been shown that the isomerization and C-C cleavage reactions, which were originally established for the (MA/DMB) adduct {122}, are also shown by other (σ,η^3-organo)$Fe(CO)_3$ complexes. Furthermore, it has been demonstrated that the complexes can undergo photoreactions involving H-shift probably via metal-hydride intermediates to give (diene)$Fe(CO)_3$ and novel (σ,η^3-organo)$Fe(CO)_3$ complexes, and hexa-1,5-dienes.

The overall photochemical behaviour of (σ,η^3-organo)-$Fe(CO)_3$ complexes is illustrated in Scheme 4.8. The complexity of the photoreaction behaviour is related to the effect of the different substituents on the C_6-carbon skeleton. Upon irradiation of such a complex cleavage of one carbonyl ligand occurs leading to the 16-electron (σ,η^3-organo)$Fe(CO)_2$ complex I. Complex I may then undergo reductive cleavage to give II or hydrogen abtraction to give III in order to achieve an 18-electron configuration.

Complex II can (*i*) give the original (σ,η^3-organo)-$Fe(CO)_3$ complex or its isomer, or (*ii*) undergo olefin photosubstitution to give (η^4-diene)$Fe(CO)_3$. In the latter case, the formation of (η^4-1,3-diene)$Fe(CO)_3$ (cf. Scheme 4.1) requires two photons: one for the formation of (σ,η^3-organo)dicarbonyliron, I, and a second photon to exchange the olefin


Fe
(CO)3
+CO
hν, -CO
Fe
(CO)2
I
Fe
(CO)2
H
III
hν, -||
+CO
Fe
(CO)3
Fe
(CO)2
II
Fe
(CO)2
IV
43
44
(Scheme 4.8)
Fe
(CO)2
V
32-E
32-Z

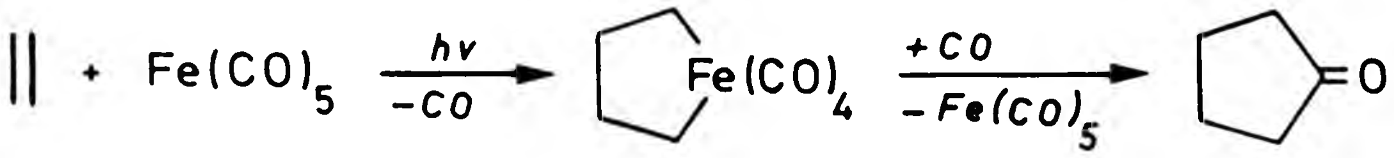
for a carbonyl ligand.

The metal hydride complex III can also undergo a variety of reactions. The hydride atom can be transferred to the allyl moiety at two different sites, depending upon the substituents at the C_6-chain, thus giving rise to compounds of type IV or V. In the former case, subsequent 1,3-hydrogen shift yields a conjugated diene complex. This has been observed for compounds derived from buta-1,3-diene, i.e. where the η^3-allyl moiety is unsubstituted (cf. Scheme 4.4). The latter compound, whose olefinic double bonds are in conjugation with ester carbonyl groups, has been observed when methyl sorbate was used.

CHAPTER FIVE

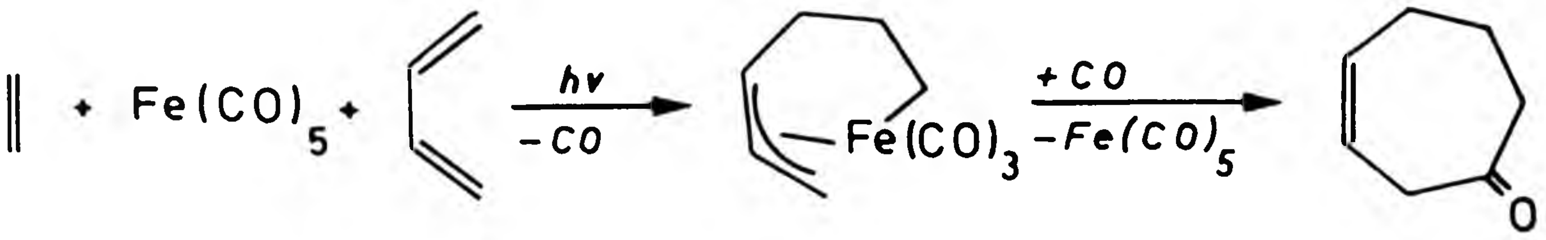
CARBONYLATION OF TRICARBONYL(1-σ,4-6-η^3-ORGANO)IRON COMPLEXES

As discussed in Chapter One (Section 4) the role of iron carbonyls in carbonylation reactions is very significant. In such reactions ferracyclo derivatives are involved as illustrated by the cyclopentanone synthesis outlined in reaction 5.1 (cf. also Scheme 1.4).



(reaction 5.1)

Grevels et.al. have shown that the (σ,η^3-organo)Fe(CO)$_3$ complex 18a reacts with carbon monoxide under pressure to give a cycloheptenone of type 46 together with pentacarbonyliron and other products {114}. This observation indicates a useful preparative reaction sequence to cycloheptenones (reaction 5.2).



46

(reaction 5.2)

The successful synthesis of several (σ,η^3-organo)-Fe(CO)$_3$ complexes accomplished during this study provided the necessary substrates for the further examination of the carbonylation behaviour of (σ,η^3-organo)Fe(CO)$_3$ complexes. Thus

CARBONYLATION OF TRICARBONYL(1-σ,4-6-η^3-ORGANO)IRON COMPLEXES

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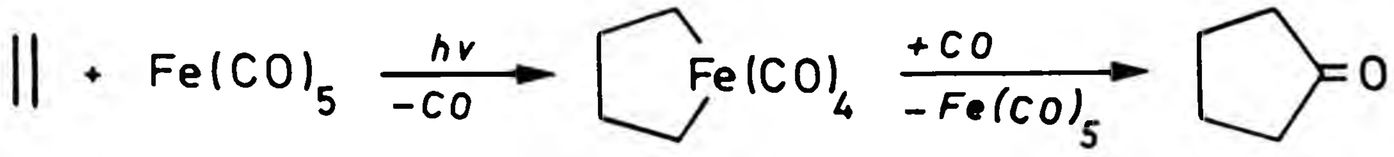

(reaction 5.1)

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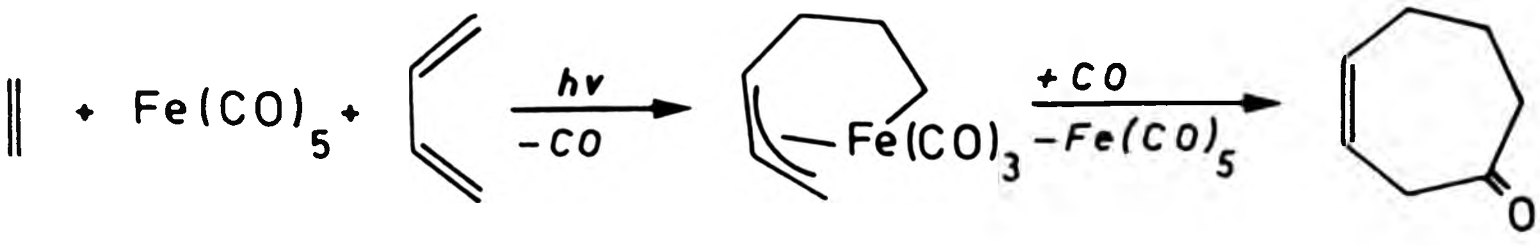

46

(reaction 5.2)

The successful synthesis of several (σ,η^3-organo)-Fe(CO)$_3$ complexes accomplished during this study provided the necessary substrates for the further examination of the carbonylation behaviour of (σ,η^3-organo)Fe(CO)$_3$ complexes. Thus the behaviour of three compounds, 20b, 22b, and 23a, was studied with two principal aims. These were (*i*) to examine the generality of the carbonylation reactions noted by *Grevels* et.al. and (*ii*) to establish the reaction conditions which afford maximum yield of cycloheptenones.

The carbonylation of *tricarbonyl{1,4,5,6-*η^4*-[cis-1-(endo),2-dicarbomethoxy-4,5-dimethylhex-4-en-1,6-diyl]}iron*, 22b, was examined under various conditions. These are summarized in Table 5.1, where the products arising from the reaction are also given. When the reaction was carried out in n-hexane/diethyl ether (2:1) at 50 ^{o}C and under pressure of 50 bar of carbon monoxide, most of the starting material was recovered. However, when the reaction was carried out at 70 ^{o}C and 45 bar pressure, an organic product 47 resulted together with pentacarbonyliron, (η^4-DMB)Fe(CO)3, and dimethyl maleate. The same product resulted in a most satisfactory yield of ca. 60 % when the reaction was carried out in methyl acetate at ca. 70 ^{o}C and 90 bar. Under similar conditions the compounds 48 and 49 were obtained in comparable yields from (σ,η^3-organo)Fe(CO)$_3$ complexes 23a and 20b, respectively.

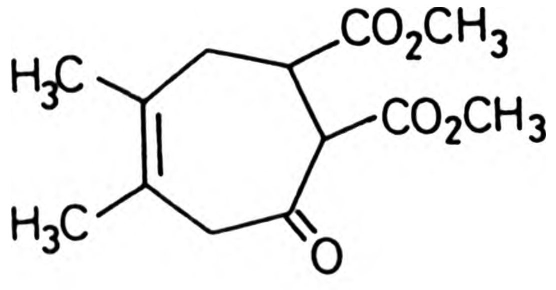

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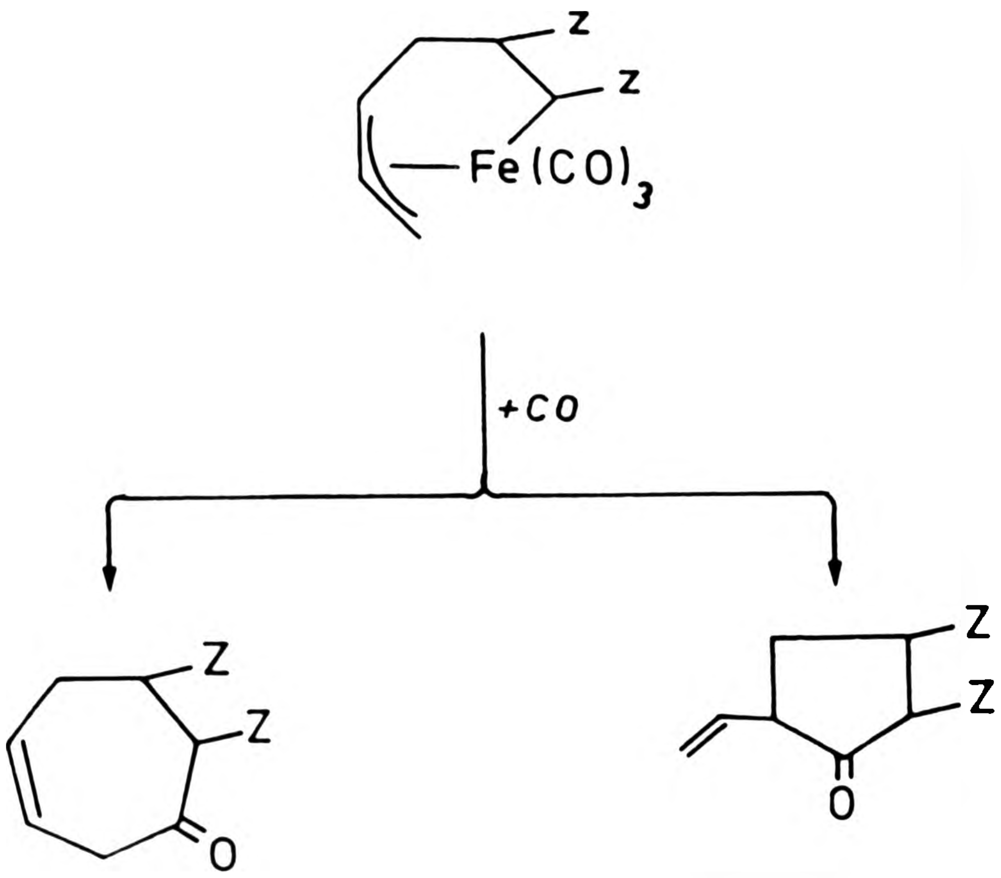
Table 5.1: Carbonylation behaviour of $(\sigma,\eta^3\text{-organo})Fe(CO)_3$ compounds.

Compound	Solvent	CO pressure (bar)	t (^oC)	Carbonylation product(s) %	Other products
22b	n-Hexane 2 $(C_2H_5)_2O$ 1	50	50	-	22b recovered (88 %), no other products detected.
	n-Hexane 2 $(C_2H_5)_2O$ 1	45	70	21[a]	$Fe(CO)_5$, $(\eta^4\text{-DMB})Fe(CO)_3$, DMM
	Methyl acetate	90	70	60[a]	$Fe(CO)_5$, $(\eta^4\text{-DMB})Fe(CO)_3$, $(\eta^2\text{-DMM})Fe(CO)_4$, DMM
23a	Methyl acetate	90	70	52[a]	$Fe(CO)_5$, $(\eta^4\text{-DMB})Fe(CO)_3$, $(\eta^2\text{-DMF})Fe(CO)_4$, DMF
20b	Methyl acetate	110	70	69[a]	$Fe(CO)_5$, $(\eta^4\text{-BD})Fe(CO)_3$, $(\eta^2\text{-DMM})Fe(CO)_4$, DMM

[a] mixture of several isomers.

The elemental analysis of the organic product obtained from the carbonylation of 22b was in excellent agreement with the proposed cycloheptenone structure 47. The mass spectrum of this product showed the expected molecular ion and peaks at m/e 223 = $[M\text{-}OCH_3]^+$, and m/e 195 = $[M\text{-}COOCH_3]^+$. Furthermore its IR spectrum showed keto and ester carbonyl bands at 1746 and 1720 cm^{-1} together with a C=C stretching vibration at 1655 cm^{-1}. However, ^{1}H-NMR spectra of the product revealed that it was a mixture of several components. Combined GC/MS-examination of the trimethylsilyl derivative of 47, obtained by treatment with N,N-bis-trimethylsilyl-trifluoro acetamide, showed the presence of five components of identical composition ($C_{13}H_{17}O_5\text{-}Si(CH_3)_3$) thus indicating that the product was a mixture of at least five isomers. The ^{1}H-NMR spectrum of the product also indicated that it was a mixture of isomers but analysis of the spectrum and characterization of the isomers could not be made due to its complexity.

As in the case of the carbonylation product 47 and in analogous fashion it was established that each of the products 48 and 49 was also a mixture of isomers. The presence of several isomers in each of the products 47, 48 and 49 is not really unexpected. The carbonylation reaction (Scheme 5.1) could lead to several cycloheptenone derivatives having (*i*) the double bond at different positions of the ring, or (*ii*) different orientation (*cis*- and/or *trans*-) of the ring substituents. Furthermore, the reaction may lead to vinyl substituted cyclopentanone isomers. However, the formation of cyclo-



(Scheme 5.1)

pentanone isomers is not considered to be significant as *Grevels* et.al. have shown, using ^{1}H-NMR that the product of the carbonylation reaction of the (σ,η^3-organo)Fe$(CO)_3$ complex 18a has a cycloheptenone structure {114}.

In conclusion the results presented in this chapter coupled with the wide applicability of the "one pot" route to (σ,η^3-organo)Fe$(CO)_3$ complexes established during this study (*i*) demonstrate the value of these complexes in the synthesis of cycloheptenones, and (*ii*) show that these coupling products can be formed in good yield using the readily available reagents: 1,3-diene, monoolefin, pentacarbonyliron, and carbon monoxide.

CHAPTER SIX

EXPERIMENTAL

6.1. General considerations

(i) Argon atmosphere

The reactions investigated in this work, including the work-up procedures, were carried out under argon (99.997 %, Messer Griesheim) atmosphere, unless specifically stated otherwise.

(ii) Procedure and general precautions

Metal carbonyls are toxic compounds and were treated accordingly. All reactions were carried out in a fume cupboard.

The isolated pure compounds were protected from decomposition by covering their glass containers with aluminium foil and/or by storing them in a refrigerator at -28 °C or -78 °C.

(iii) Solvents

The solvents diethyl ether and benzene were dried by passing them through an aluminium oxide column (Woelm, neutral or basic) and were distilled before use. n-Pentane (Merck, min. 99 %) and n-hexane (Merck, min. 96 %) were refluxed and distilled over $LiAlH_4$ and kept under argon. All solvents were freed from any remaining air by extended flushing with argon. Prior to use the deuterated solvents: benzene-d_6 (Merck, Darmstadt), chloroform-d_1 (Merck, Darmstadt), dichloromethane-d_2 (Merck, Darmstadt), and toluene-d_8 (Merck, Darmstadt) were freed from dissolved air by repeated freeze-pump-thaw cycles with argon.

(*iv*) *Starting materials and reagents*

Pentacarbonyliron was a gift from BASF Aktiengesellschaft (Ludwigshafen, W. Germany) and if necessary, was filtered before use. The following reagents were obtained from commercial sources and were used as received: dimethyl maleate (Fluka), dimethyl fumarate (Merck-Schuchardt), diethyl maleate (Merck-Schuchardt), diethyl fumarate (Merck-Schuchardt), methyl acrylate (Merck-Schuchardt), methyl crotonate (Fluka), 2,3-dimethylbuta-1,3-diene (Fluka), 2-methylbuta-1,3-diene (Merck-Schuchardt), buta-1,3-diene (Matheson), N,N-bis-trimethylsilyl-trifluoro acetamide (Macherey Nagel & Co.), and carbon monoxide (Messer Griesheim).

The following reagents were prepared by methods described in the literature and their purity was checked prior to use.

Reagent	References
1. Tetracarbonyl[η^2-(*cis*-2,3-dideuterio-methyl acrylate)]iron.[a)]	{21,106}

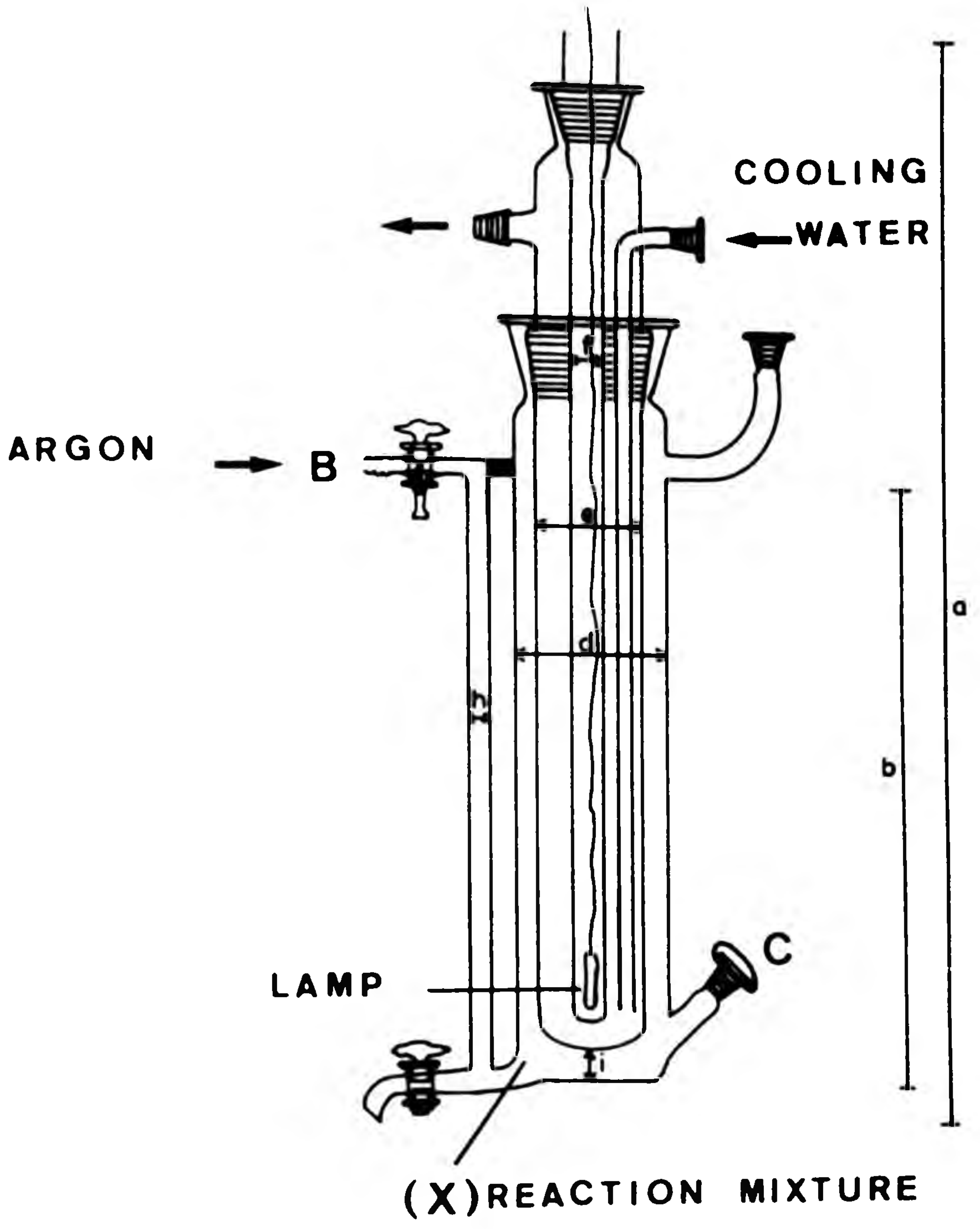
Reagent	References
2. Tricarbonyl(η^4-2,3-dimethylbuta-1,3-diene)iron.[b)]	{47-49}
3. Tetracarbonyl(η^2-dimethyl maleate)-iron.[b)]	{21}
4. Tetracarbonyl(η^2-dimethyl fumarate)-iron.[b)]	{21}
5. Tetracarbonyl(η^2-diethyl fumarate)-iron.[b)]	{21}

[a)] *estimated 80% cis-d_2-MA, and 20% of trans-d_2-MA.*

[b)] *estimated ⩾ 95% by ^{1}H-NMR.*

(v) *Photochemical reactions*

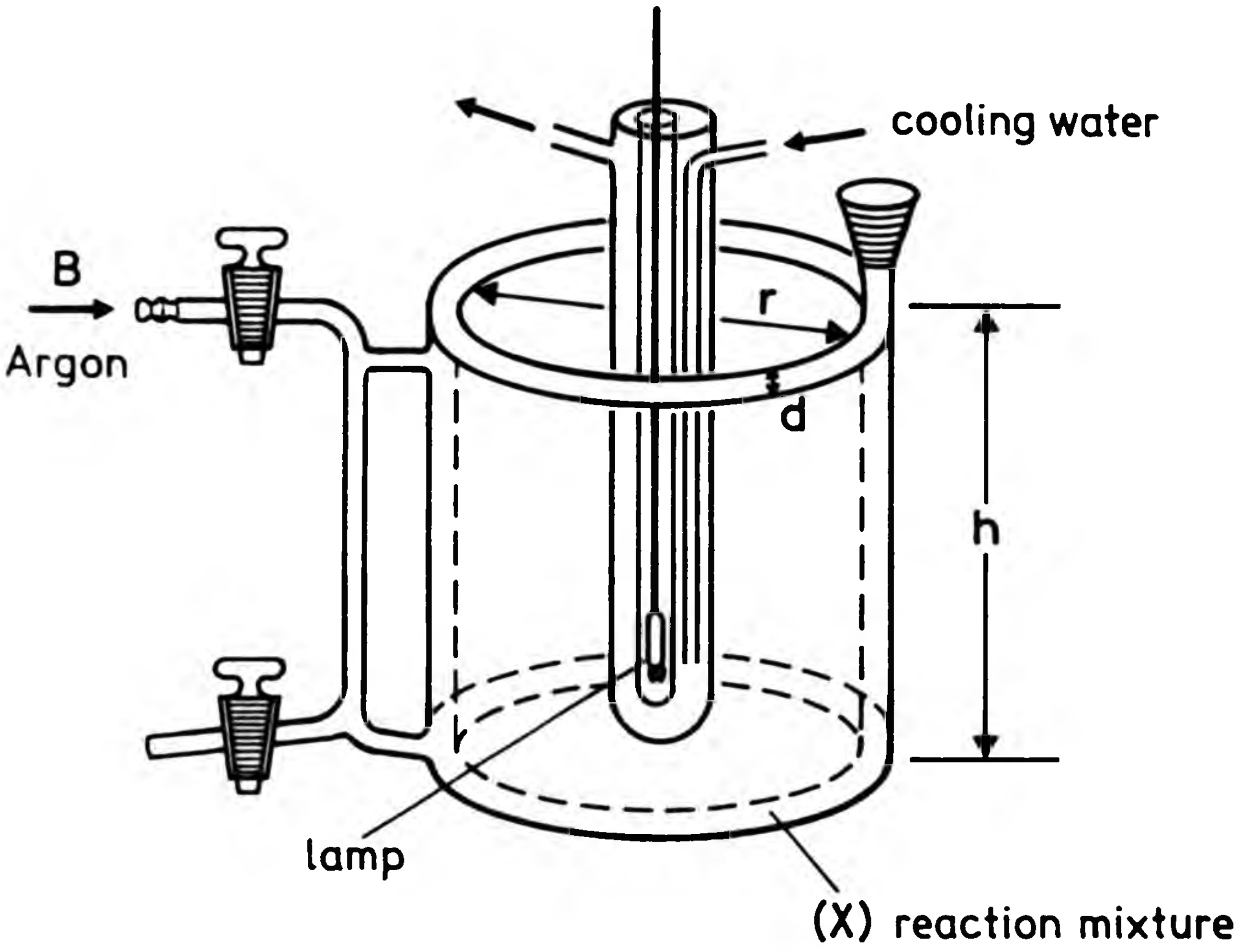
General.- The photochemical syntheses were carried out under argon and in argon-saturated solvents. Irradiations were performed in a *Pyrex* glass immersion lamp apparatus (Figure 6.1) using a medium pressure mercury lamp (Philips HPK 125 W). Large scale reactions were performed in the apparatus illustrated in Figure 6.2.



a	b	c	d	e	f	h	i (in mm)
420	160	-	50	40	20	10	15
500	240	-	60	48	22	10	15
500	240	-	65	48	22	10	15
500	240	-	70	48	22	10	15

Figure 6.1: Immersion lamp irradiation apparatus

Procedure.- The diene, olefin and pentacarbonyliron reactants were placed with the solvent in the photochemical reaction vessel (X). The solution was purged with argon before irradiation for 10-15 min. Cooling was achieved with water, or, for the low temperature photolyses, with methanol using an ULTRA KRYTOMAT K 120 or K 50 W (Lauda). The reactions were monitored by means of infrared spectroscopy by withdrawing samples through the serum cap (C).



r = 17cm; h = 29 cm; d = 2 cm

Figure 6.2: Large scale irradiation apparatus

(vi) Reactions under pressure

These reactions were carried out in a stainless steel autoclave. The $(\sigma,\eta^3\text{-organo})Fe(CO)_3$ complex was dissolved and transferred to the autoclave with concomitant passage of argon. Carbon monoxide was repeatedly passed into the system (ca. 60 bar), then ejected. The solution was then heated for several hours under the required carbon monoxide pressure.

(vii) Work-up and general techniques

All operations were performed using *Schlenck* techniques {129,130} under a static atmosphere of argon.

All glassware was heated in an oven to 90 °C and then immediately evacuated and filled with argon before use.

A silicone lubricant, Siliconfett (Wacker-Chemie GmbH), high vacuum grease, was used on all glass joints.

Filtrations were carried out using the inverse filtration technique under argon pressure (Figure 6.3). The

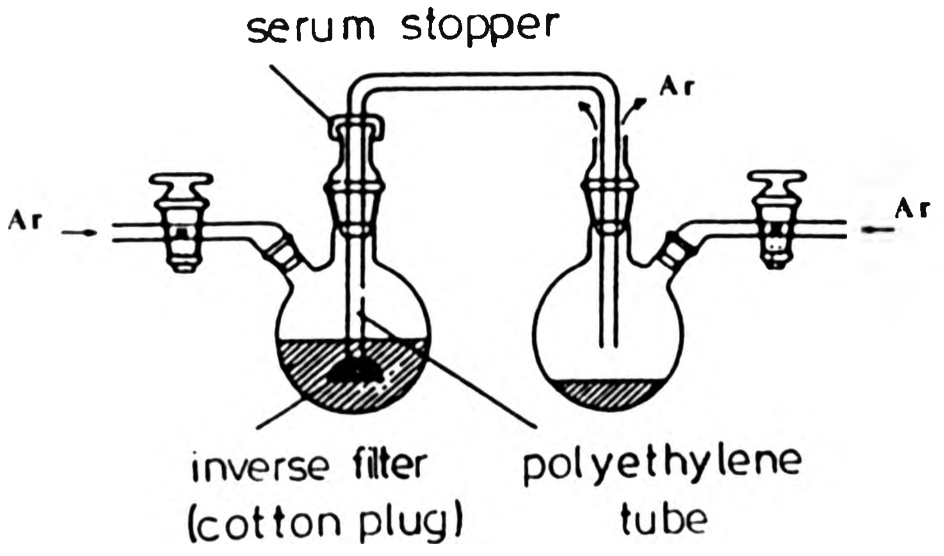


Figure 6.3: Inverse Filtration apparatus

solution mixture was filtered using a cotton or glass wool plug inverse filter attached to a polyethylene tube. The filtrates were concentrated to dryness at a reduced pressure of about 15 Torr.

The distillation and/or sublimation of products, e.g. diene and olefin complexes, was carried out under vacuum (0.1 - 0.001 Torr) using the apparatus illustrated in Figure 6.4.

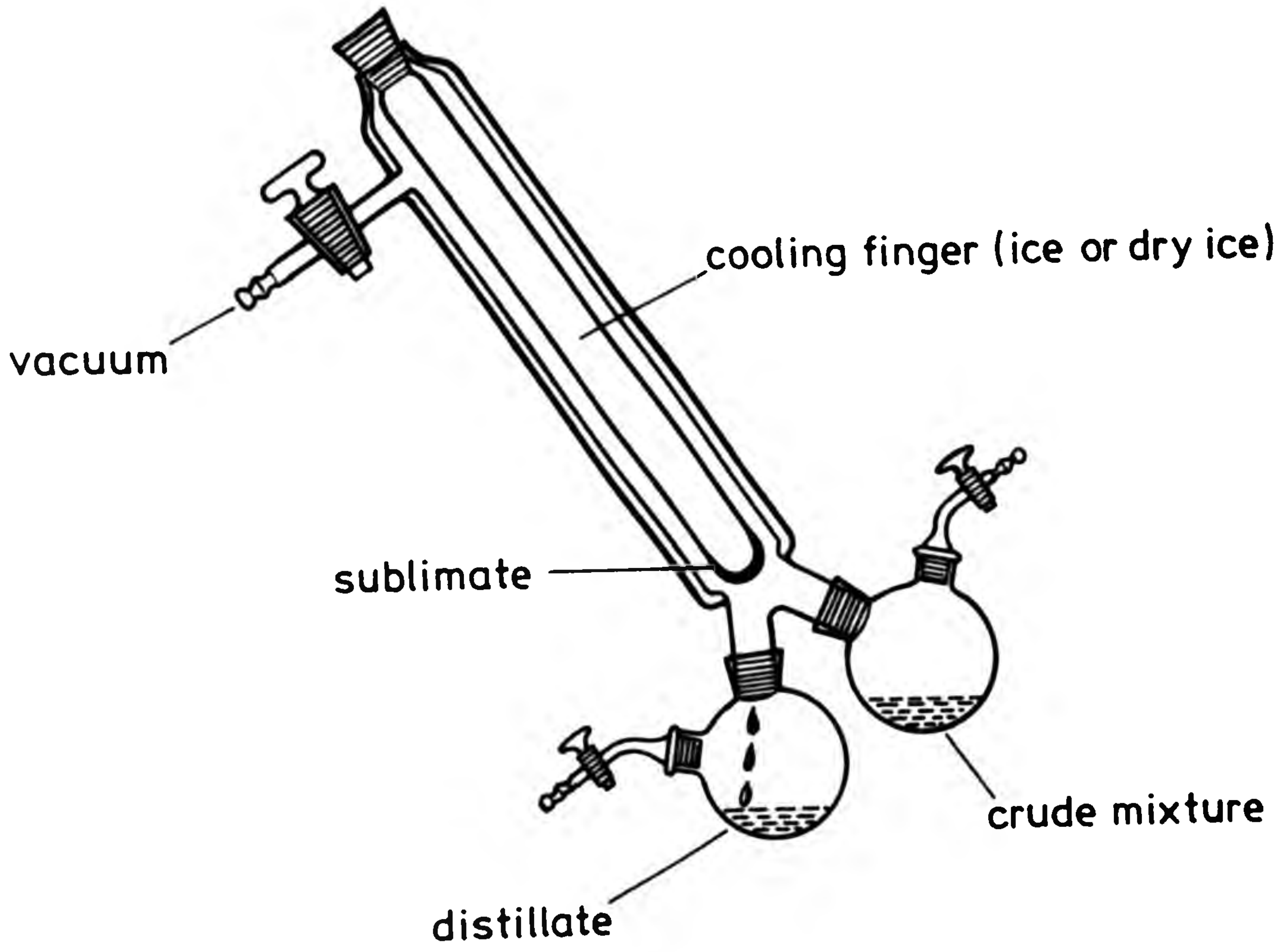


Figure 6.4: Distillation and/or sublimation apparatus

Column chromatography was performed using silica gel 60 (Merck, 0.040 - 0.063 mm) which was degassed, saturated with argon, suspended in a dry solvent, and packed into the column under argon. Elution of the column was carried out under an argon atmosphere.

Isolated by-product compounds, e.g. (η^4-1,3-diene)tricarbonyliron and (η^2-monoolefin)tetracarbonyliron, were identified by infrared and ^{1}H-NMR spectroscopy. In some experiments, TLC was also used to identify these compounds.

The term "crystallization at 20 °C/-78 °C" means that the compound to be purified was dissolved at 20 °C, then crystallised by cooling the solution to -78 °C.

(viii) *Analytical and spectroscopic data*

Elemental analyses and molecular weight determination (cryoscopic in benzene) were performed by *Dornis* and *Kolbe*, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, W. Germany.

Melting points were determined using a *Reichert Kofler* apparatus.

Mass spectra were recorded on a MAT CH-5 instrument, operating at 70 eV. The samples were introduced into the ion source using the direct inlet technique.

GC/MS-combination employed a Varian MAT CH-7A mass spectrometer and a Perkin-Elmer F-22 gas chromatograph.

Gas chromatogramms were run on Siemens L 350 chromatograph using a 15 m column and a flow rate of argon of 6 °C min^{-1} at 60 - 160 °C.

Infrared spectra were measured using 0.05 or 0.1 mm CaF_2 and KBr cells on a Perkin-Elmer 257 instrument, or in n-hexane solution using a Perkin-Elmer 580 instrument. The spectra recorded in solution were calibrated with DCl {115}. The frequencies quoted are accurate within 2 cm^{-1} (PE 257) and 0.5 cm^{-1} (PE 580), respectively.

Proton magnetic resonance spectra were recorded on Bruker WH 270 (27 °C, ±1 °C) and Bruker WH 400 (20 °C) spectrometers using sealed or serum-capped NMR tubes. Variable temperature spectra (dynamic NMR studies) on compound 38 were carried out on the Bruker WH 400 spectrometer.

^{1}H-NMR assignments were confirmed with double irradiation experiments where possible. The ^{1}H-NMR chemical shifts were measured in δ/ppm relative to TMS or to the solvent resonance. The following conversions were used {131}:

$$\delta_{TMS}(^1H) = \delta_{C_6D_6} - 7.15$$

$$\delta_{TMS}(^1H) = \delta_{CDCl_3} - 7.24$$

$$\delta_{TMS}(^1H) = \delta_{CD_2Cl_2} - 5.32$$

$$\delta_{TMS}(^1H) = \delta_{C_7D_8(CH_3)} - 2.03$$

Carbon-13 nuclear magnetic resonance spectra were recorded on a Bruker WH 270 spectrometer operating at 67.89 MHz. The ^{13}C-NMR chemical shifts were measured in δ/ppm relative to the TMS or to the internal solvent resonance. In the latter

In the latter case, the following conversion was used {132,133}:

$$\delta_{TMS}(^{13}C) \quad = \quad \delta_{C_7D_8}(CH_3) \quad - \quad 20.4$$

The preparation of sealed samples for the NMR studies was carried out using the following procedure: The sample was transferred to a *Schlenck* tube and dissolved in the appropriate solvent. The solution was then transferred into the NMR tube, fitted with a three way stop-cock, using the inverse filtration procedure as shown in Figure 6.3. The NMR tube was placed in liquid nitrogen in order to freeze the solution, evacuated using high vacuum (ca. 10 min) and then sealed.

6.2. Reactions

6.2.1. Photoreaction of pentacarbonyliron with buta-1,3-diene and dimethyl maleate in diethyl ether at ambient temperature

A solution of buta-1,3-diene (27.9 g, 0.5 mol), pentacarbonyliron (49.0 g, 0.25 mol), and dimethyl maleate (72.0 g, 0.5 mol) in diethyl ether (2 l) was irradiated at ca. 20 °C for 113 h. Filtration gave an intractable solid (8.0 g) (ill-defined IR). Evaporation of the filtrate under reduced pressure gave a brown solid (131.5 g), which was column chromatographed on silica gel. n-Hexane/diethyl ether (4:1) eluted (η^4-buta-1,3-diene)tricarbonyliron (21.2 g, 44 %) (identical IR, NMR and TLC with authentic sample) followed by tetracarbonyl(η^2-dimethyl maleate)iron (14.7 g, 19 %) (identical IR, NMR and TLC with authentic sample). n-Hexane/diethyl ether (3:2) eluted a two-component mixture (34.0 g) which was rechromatographed on silica gel. n-Hexane followed by a gradual change to n-hexane/diethyl ether (4:1) eluted two fractions which gave a dark yellow and a pale yellow solid on evaporation of the solvent. Crystallization of the dark yellow solid from n-hexane at 20 °C/-78 °C gave *tricarbonyl* {*1,4,5,6-*η^4*-[cis-1(endo),2-dicarbomethoxy-hex-4-en-1,6-diyl]*} *iron*, **20b**, (28.1 g, 33 %), m.p. 100.5 - 102 °C (Found: C, 46.19; H, 4.21; Fe, 16.58; mol.wt., 340. $C_{13}H_{14}FeO_7$ requires C, 46.18; H, 4.17; Fe, 16.52 %; mol.wt., 338.1). Crystallization of the pale yellow solid from diethyl ether at 20 °C/

-28 °C gave *tricarbonyl{1,4,5,6-*η^4*-[cis-1(exo),2-dicarbomethoxy-hex-4-en-1,6-diyl]}iron*, **20a**, (2.2 g, 3 %), m.p. 118.5 - 119.5 °C (Found: C, 46.25; H, 4.26; Fe, 16.69; mol.wt., 341. $C_{13}H_{14}FeO_7$ requires C, 46.18; H, 4.17; Fe, 16.52 %, mol.wt., 338.1).

6.2.2. Photoreaction of pentacarbonyliron with buta-1,3-diene and dimethyl fumarate in diethyl ether at ambient temperature

A solution of buta-1,3-diene (4.7 g, 87 mmol), pentacarbonyliron (6.9 g, 35 mmol), and dimethyl fumarate (12.5 g, 87 mmol) in diethyl ether (400 ml) was irradiated at ca. 20 °C for 27 h. The solvent was evaporated, and the brown residue (23.6 g) was chromatographed on silica. n-Pentane eluted (η^4-buta-1,3-diene)tricarbonyliron (identical IR and TLC with authentic sample) followed by tetracarbonyl(η^2-dimethyl fumarate)iron (identical IR and TLC with authentic sample). Elution with n-pentane/diethyl ether (3:1) followed by evaporation of the solvent from the eluate gave a solid residue (19.4 g) (mixture by IR). The residue was heated at 50 °C/0.01 Torr in the apparatus illustrated in Figure 6.4. A mixture of dimethyl fumarate and tetracarbonyl(η^2-dimethyl fumarate)iron was collected as a sublimate (6.2 g) (components identified by IR and TLC) and a pale yellow solid was left as a residue (10 g) which by successive crystallization from diethyl ether/n-hexane (5:1) at 20 °C/-28 °C gave *tricarbonyl{1,4,5,6-*η^4*-[trans-1(exo),2-dicarbomethoxy-hex-4-en-1,6-diyl]}* *iron*, 21a, (3.3 g, 28 %), m.p. 109 - 110 °C (Found: C, 46.21; H, 4.20; Fe, 16.61; mol.wt., 335. $C_{13}H_{14}FeO_7$ requires C, 46.18; H, 4.17; Fe, 16.52 %; mol.wt., 338.1).

6.2.3. Photoreaction of pentacarbonyliron with 2,3-dimethylbuta-1,3-diene and dimethyl maleate in diethyl ether at ambient temperature

A solution of 2,3-dimethylbuta-1,3-diene (20.5 g, 0.25 mol), pentacarbonyliron (9.4 g, 0.05 mol), and dimethyl maleate (30.0 g, 0.21 mol) in diethyl ether (400 ml) was irradiated at ca. 20 °C for 30 h. The reaction mixture was filtered, and evaporation of the filtrate under reduced pressure gave a yellow oil (31.4 g). A mixture of tricarbonyl(η^4-2,3-dimethylbuta-1,3-diene)iron and dimethyl maleate (15.1 g) (components of mixture identified by IR and TLC) was distilled from the mixture by heating at 40 °C/0.01 Torr in the apparatus illustrated in Figure 6.4 leaving a dark brown residue (13.9 g) which was chromatographed on silica. Benzene/diethyl ether (7:3) eluted a mixture of tricarbonyl(η^4-2,3-dimethylbuta-1,3-diene)iron, dimethyl maleate, and tetracarbonyl(η^2-dimethyl maleate)iron (1.9 g) (components identified by IR and TLC). Benzene/diethyl ether (6:4) eluted a yellow solid (10.0 g) which by successive crystallization from n-hexane at 20 °C/-78 °C gave *tricarbonyl{1,4,5,6-*η^4*-[cis-1(endo),2-dicarbomethoxy-4,5-dimethylhex-4-en-1,6-diyl]}iron*, 22b, (8.1 g, 48 %), m.p. 94-95 °C (Found: C, 49.80; H, 5.00; Fe, 15.32; mol.wt., 351. $C_{15}H_{18}FeO_7$ requires C, 49.20; H, 4.96; Fe, 15.25 %; mol.wt., 336.16).

6.2.4. Photoreaction of tricarbonyl(η^4-2,3-dimethylbuta-1,3-diene)iron with dimethyl maleate in n-hexane at ambient temperature

A solution of tricarbonyl(η^4-2,3-dimethylbuta-1,3-diene)iron (2.25 g, 10 mmol) and dimethyl maleate (1.47 g, 10 mmol) in n-hexane (250 ml) was irradiated at ca. 20 °C for 45 h. Filtration of the reaction mixture gave an intractable brown solid residue (0.50 g) (ill-defined IR). Evaporation of the filtrate under reduced pressure gave a yellow solid (1.69 g) which was chromatographed on silica. Benzene/diethyl ether (4:1) eluted tricarbonyl(η^4-2,3-dimethylbuta-1,3-diene)-iron (0.40 g, 18 % recovery) (identical IR with authentic sample). Benzene/diethyl ether (3:2) eluted a two-component mixture (0.96 g), which was rechromatographed on silica. Elution with benzene/diethyl ether (initially 9:1, gradual change to 7:3) gave tricarbonyl(η^4-2,3-dimethylbuta-1,3-diene)-iron (0.10 g, 5 %) and then a yellow solid (0.75 g). Crystallization of the yellow solid from n-hexane at 20 °C/-78 °C and successive crystallization of the mother liquor at -78 °C gave *tricarbonyl{1,4,5,6-*η^4*[cis-1(endo),2-dicarbomethoxy-4,5-dimethylhex-4-en-1,6-diyl]}iron*, **22b**, (0.52 g, 14 %), m.p. 92-93 °C (Found: C, 49.98; H, 5.12; Fe, 16.02. $C_{15}H_{18}FeO_7$ requires C, 49.20; H, 4.96; Fe, 15.25 %).

6.2.5. Photoreaction of tetracarbonyl(η^2-dimethyl maleate)iron with 2,3-dimethylbuta-1,3-diene in n-hexane at ambient temperature

A solution of tetracarbonyl(η^2-dimethyl maleate)iron (3.15 g, 10 mmol) and 2,3-dimethylbuta-1,3-diene (3.78 g, 46 mmol) in n-hexane (200 ml) was irradiated at ca. 20 °C for 20 h. Filtration gave a brown solid residue (ill-defined IR). The filtrate was kept at -78 °C for five days and filtered at -70 °C to give a yellow filtrate containing tricarbonyl(η^4-2,3-dimethylbuta-1,3-diene)iron (identified by IR with authentic sample) and a dark yellow solid (1.9 g) which was chromatographed on silica. Benzene/diethyl ether (4:1) eluted a mixture of tricarbonyl(η^4-2,3-dimethylbuta-1,3-diene)iron and tetracarbonyl(η^2-dimethyl maleate)iron (0.22 g) (components identified by IR and TLC). Benzene/diethyl ether (7:3) eluted a yellow solid (1.57 g) which on crystallization from n-hexane (40 ml) at 20 °C/-78 °C gave *tricarbonyl{1,4,5,6-*η^4*-[cis-1(endo),2-dicarbomethoxy-4,5-dimethylhex-4-en-1,6-diyl]}iron*, 22$\underline{\underline{b}}$, (1.37 g, 37 %), m.p. 92-93 °C (Found: C, 49.83; H, 4.70; Fe, 15.90. $C_{15}H_{18}FeO_7$ requires C, 49.20; H, 4.96; Fe, 15.25 %).

6.2.6. Photoreaction of pentacarbonyliron with 2,3-dimethylbuta-1,3-diene and dimethyl fumarate in diethyl ether at ambient temperature

A solution of 2,3-dimethylbuta-1,3-diene (6.1 g, 74 mmol), pentacarbonyliron (14.7 g, 75 mmol), and dimethyl fumarate (10.8 g, 75 mmol) in diethyl ether (1.5 l) was irradiated at ca. 20 °C for 51 h. Filtration gave a solid residue (3.0 g) (ill-defined IR). Evaporation of the filtrate under reduced pressure gave a dark yellow solid (25.1 g), which was chromatographed on silica. Elution with benzene gave tricarbonyl(η^4-2,3-dimethylbuta-1,3-diene)iron (7.3 g, 44 %) (identical IR and TLC with authentic sample), followed by a multi-component mixture (13.3 g). This mixture on heating at 50 °C/0.001 Torr gave a mixture of dimethyl fumarate (est. 2.2 g, 21 %) and tetracarbonyl(η^2-dimethyl fumarate)-iron (est. 2.2 g, 10 %) (components identified by IR and TLC) as sublimate and a solid residue (7.2 g). The residue was shaken with benzene (160 ml) and filtered successively until a clear solution was obtained. Chromatography of the clear filtrate on silica using benzene as eluant gave first tetracarbonyl(η^2-dimethyl fumarate)iron (0.8 g, 4 %) (identical IR and TLC with authentic sample) and then yellow fractions which gave a yellow solid on evaporation of the solvent. Crystallization of this solid from n-hexane at 20 °C/-78 °C gave *tricarbonyl{1,4,5,6-*η^4*-[trans-1(exo),2-dicarbomethoxy-4,5-dimethylhex-4-en-1,6-diyl]}iron*, **23a**, (6.9 g, 25 %), m.p. 100-101 °C (Found: C, 49.68; H, 5.15; Fe, 16.72; mol.wt., 342. $C_{15}H_{18}FeO_7$ requires C, 49.20; H, 4.96; Fe, 15.25 %; mol.wt., 366.16).

6.2.7. Photoreaction of pentacarbonyliron with 2,3-dimethylbuta-1,3-diene and diethyl maleate in n-hexane at ambient temperature

A solution of 2,3-dimethylbuta-1,3-diene (10.2 g, 124 mmol), pentacarbonyliron (24.8 g, 127 mmol), and diethyl maleate (21.5 g, 125 mmol) in n-hexane (2 l) was irradiated at ca. 20 °C for 93 h. Evaporation of the solvent under reduced pressure gave a brown oil (44.7 g), which was stirred with n-hexane (800 ml). Filtration of the resultant mixture gave a brown insoluble residue (1.0 g) (ill-defined IR). The filtrate was kept at -78 °C for 24 h. Filtration gave a yellow solid (30.5 g) and a filtrate containing tricarbonyl(η^2-2,3-dimethylbuta-1,3-diene)iron (identified by IR and TLC) and tetracarbonyl(η^2-diethyl maleate)iron (identified by IR and TLC). The yellow solid, on heating at 50 °C/0.001 Torr in the apparatus shown in Figure 6.4, gave a mixture of tricarbonyl(η^4-2,3-dimethylbuta-1,3-diene)iron, diethyl maleate, and tetracarbonyl(η^2-diethyl maleate)iron as distillate or sublimate and a brown viscose residue (25.2 g), which was column chromatographed on silica (elution with n-hexane/diethyl ether, 2:1). A mixture of tricarbonyl(η^4-2,3-dimethylbuta-1,3-diene)iron and tetracarbonyl(η^2-diethyl maleate)iron was eluted first (components identified by IR and TLC), followed by a yellow brown solid which was crystallized from n-hexane at 20 °C/-78 °C to give *tricarbonyl{1,4,5,6-*η^4*-[cis-1(endo),2-dicarboethoxy-4,5-dimethylhex-en-1,6-diyl]}iron*, **24b**, (13.1 g, 27 %), m.p. 60-61 °C (Found: C, 51.80; H, 5.55; Fe, 14.18;

mol.wt., 376. $C_{17}H_{22}FeO_7$ requires C, 51.80; H, 5.63; Fe, 14.17 %; mol.wt., 394.21).

6.2.8. Photoreaction of pentacarbonyliron with 2,3-dimethylbuta-1,3-diene and diethyl fumarate in diethyl ether at ambient temperature

A solution of 2,3-dimethylbuta-1,3-diene (8.1 g, 99 mmol), pentacarbonyliron (9.8 g, 50 mmol), and diethyl fumarate (17.2 g, 100 mmol) in diethyl ether (2 l) was irradiated at ca. 20 °C for 81 h. Successive filtration gave a brown residue (11.0 g) (ill-defined IR). Evaporation of the filtrate under reduced pressure gave a thick brown oil (19 g), which was column chromatographed on silica. Elution with n-hexane/diethyl ether (2:1) gave successively (*i*) tricarbonyl(η^4-2,3-dimethylbuta-1,3-diene)iron (2.5 g, 23 %) (identical IR and TLC with authentic sample), (*ii*) tetracarbonyl(η^2-diethyl fumarate)iron (7.1 g, 42 %) (identical IR and TLC with authentic sample), (*iii*) a yellow fraction which gave a yellow oil (3.4 g) upon evaporation of the solvent under reduced pressure. Attempted crystallization from n-hexane at -78 °C gave an amorphous solid which became an oil at ca. -20 °C. Chromatography of the oil on silica (elution with n-hexane/diethyl ether, 2:1) gave *dicarbonyl*(η^4-*2,3-dimethylbuta-1,3-diene*)(η^2-*diethyl fumarate*)*iron*, 37, (3.0 g, 16 %) (Found: C, 52.95; H, 6.11; Fe, 13.25; mol.wt., 337. $C_{16}H_{22}FeO_6$ requires C, 52.48; H, 6.06; Fe, 15.25 %; mol.wt., 366.2), and (*iv*) a yellow fraction which after concentration and crystallization from n-hexane at 20 °C/-78 °C gave *tricarbonyl {1,4,5,6-*η^4*-[trans-1(exo),2-dicarboethoxy-4,5-dimethylhex-4-en-1,6-diyl]}iron*, 25a, (3.7 g, 19 %), m.p. 43-44 °C (Found: C, 51.95; H, 5.60; Fe, 14.06; mol.wt., 378. $C_{17}H_{22}FeO_7$ requires C, 51.80; H, 5.63; Fe, 14.17 %; mol.wt., 394.21). The mother liquor contained isomer 25b (traces; ca. 0.1 g) (identified by IR) which could not be isolated in a pure state.

6.2.9. Photoreaction of tetracarbonyl(η^2-diethyl fumarate)iron with 2,3-dimethylbuta-1,3-diene in n-hexane at ambient temperature

A solution of tetracarbonyl(η^2-diethyl fumarate)iron (3.43 g, 10.99 mmol) and 2,3-dimethylbuta-1,3-diene (4.07 g, 49.5 mmol) in n-hexane (500 ml) was irradiated at ca. 20 °C for 4.5 h. The turbid reaction mixture was filtered, and the brown residue was discarded. Tricarbonyl(η^4-2,3-dimethylbuta-1,3-diene)iron (identified by IR) was partially removed together with the solvent by evaporating the filtrate at 40 °C/ 0.01 Torr leaving a yellow oily residue (2.60 g). The latter was column chromatographed on silica. Benzene eluted tricarbonyl(η^4-2,3-dimethylbuta-1,3-diene)iron (0.71 g, 32 %) (identical IR and TLC with authentic sample). Benzene/diethyl ether (4:1) eluted a yellow fraction which upon evaporation of the solvent under reduced pressure gave a mixture of diethyl fumarate and tetracarbonyl(η^2-diethyl fumarate)iron (0.49 g) (components identified by IR and TLC). Benzene/diethyl ether (7:3) eluted mixtures containing diethyl fumarate, tetracarbonyl(η^2-diethyl fumarate)iron and *tricarbonyl{1,4,5,6-*η^4*-[trans-1(exo),2-dicarboethoxy-4,5-dimethylhex-4-en-1,6-diyl]}iron*, **25a** (components identified by TLC). The combined mixtures on crystallization from n-hexane at 20 °C/-78 °C gave *tricarbonyl{1,4,5,6-*η^4*-[trans-1(exo),2-dicarboethoxy-4,5-dimethylhex-4-en-1,6-diyl]}iron*, **25a** (0.92 g, 21 %), m.p. 43-44 °C (Found: C, 51.70; H, 5.34; Fe, 13.81. $C_{17}H_{22}FeO_7$ requires C, 51.80; H, 5.63; Fe, 14.17 %).

6.2.10. Photoreaction of pentacarbonyliron with buta-1,3-diene and *trans*-butenoic acid methyl ester (methyl crotonate) in diethyl ether at ambient temperature

A solution of buta-1,3-diene (12.3 g, 230 mmol), pentacarbonyliron (9.8 g, 50 mmol) and *trans*-butenoic acid methyl ester (20.0 g, 200 mmol) in diethyl ether (300 ml) was irradiated at ca. 20 °C for 77 h. The reaction mixture was filtered, and the insoluble brown residue (ill-defined IR) was discarded. Evaporation of the solvent under reduced pressure gave a brown-reddish oil (18.6 g), which was chromatographed on silica. Elution with n-pentane gave successively (*i*) (η^4-buta-1,3-diene)tricarbonyliron (4.0 g, 41 %) (identical IR with authentic sample), (*ii*) bis(η^4-buta-1,3-diene)monocarbonyliron (0.6 g, 6 %) (identical IR with authentic sample), (*iii*) tetracarbonyl(η^2-methyl crotonate)iron (1.5 g, 11 %) (identical IR with authentic sample), and (*iv*) a brown-reddish oil (5.1 g) which was crystallized twice from n-hexane/diethyl ether (1:1) at 20 °C/-28 °C to yield orange crystalline *tricarbonyl{1,4,5,6-*η^4*-[trans-1(exo)-carbomethoxy,2-methylhex-4-en-1,6-diyl]}iron*, 26a, (4.0 g, 27 %), m.p. 53.5 - 54 °C (Found: C, 48.88; H, 4.72; Fe, 18.95; mol.wt., 297. $C_{12}H_{14}FeO_5$ requires C, 49.01; H, 4.80; Fe, 18.99 %; mol.wt., 294.09).

6.2.11. Photoreaction of pentacarbonyliron with buta-1,3-diene and tetracarbonyl[η^2-(*cis*-2,3-dideuterio-methyl acrylate)]iron in diethyl ether at ambient temperature

A solution of buta-1,3-diene (7.92 g, 150 mmol) and tetracarbonyl[η^2-(*cis*-2,3-dideuterio-methyl acrylate)]iron (7.50 g, 29 mmol) in diethyl ether (400 ml) was irradiated at ca. 20 °C for 3.6 h. Evaporation of the solvent under reduced pressure gave a brown oily residue (5.6 g). The residue was heated at 35 °C/0.01 Torr in the apparatus illustrated in Figure 6.4. A mixture of (η^4-buta-1,3-diene)tricarbonyliron and tetracarbonyl[η^2-(*cis*-2,3-dideuterio-methyl acrylate)]iron was collected as a distillate (1.5 g) (components identified by IR and NMR), leaving behind a brown oily residue (3.7 g), which was column chromatographed on silica. n-Hexane/diethyl ether (9:1) eluted (η^4-buta-1,3-diene)tricarbonyliron (0.5 g, 9 %) (identical IR, NMR, and TLC with authentic sample). n-Hexane/diethyl ether (4:1) eluted (*i*) *tricarbonyl{1,4,5,6-*η^4*-[1(endo)-carbomethoxy-cis-1,2-dideuterio-hex-4-en-1,6-diyl]}iron*, 28a, (0.97 g, 12 %), (Found: C, 46.73; H + D, 4.81; Fe, 19.78; mol.wt., 292. $C_{11}H_{10}D_2FeO_5$ requires C, 46.84; H + D, 4.99; Fe, 19.80 %; mol.wt., 282.05) as a yellow oil which could not be crystallized (using various solvents and at different temperatures, and (*ii*) a yellow solid which on crystallization from n-hexane at 20 °C/-28 °C gave yellow crystals of *tricarbonyl{1,4,5,6-*η^4*-[1(exo)-carbomethoxy-cis-1,2-dideuterio-hex-4-en-1,6-diyl]}iron*, 28b, (0.66 g, 8 %), m.p. 61 - 61.5 °C (Found: C, 46.91; H + D, 4.75; Fe, 19.86; mol.wt., 285. $C_{11}H_{10}FeO_5$ requires C, 46.84; H + D, 4.99; Fe, 19.80 %; mol.wt., 282.05).

6.2.12. Photoreaction of pentacarbonyliron with 2-methylbuta-1,3-diene (isoprene) and dimethyl fumarate in diethyl ether at ambient temperature

A solution of 2-methylbuta-1,3-diene (61.2 g, 0.9 mol), pentacarbonyliron (88.2 g, 0.45 mol), and dimethyl fumarate (64.2 g, 0.45 mol) in diethyl ether (2 l) was irradiated at ca. 20 °C for 274 h. The reaction mixture was filtered to give an intractable brown solid (ill-defined IR) which was discarded. Evaporation of the filtrate under reduced pressure gave a brown solid (141.4 g). This solid was heated at 45 - 50 °C/0.01 Torr in the apparatus illustrated in Figure 6.4. Tricarbonyl(η^4-2-methylbuta-1,3-diene)iron (45.1 g, 48 %) (identical IR and TLC with authentic sample) was collected as a distillate, tetracarbonyl(η^2-dimethyl fumarate)iron (10.7 g, 8 %) (identical IR and TLC with authentic sample) was collected as a sublimate, and a brown solid (81.7 g) remained as a residue. The residue was stirred with diethyl ether (1.5 l) and filtered to give a dark brown solid (10.5 g) (ill-defined IR) and a yellow filtrate. Removal of the solvent from the filtrate under reduced pressure afforded a yellow solid 12.1 which was column chromatographed on silica as shown in Table 6.1.

Table 6.1: The chromatographic separation of solid 12.1.

Eluting solvent (n-Hexane/diethyl ether)	Code	Weight (g)	Component(s)	Found(%)			(Found)
				C	H	Fe	Mol.wt.
9:1	1	28.8	(DMF)Fe(CO)$_4$ [a)]				
4:1	2	4.1	29b [b,c)]	47.68	4.47	15.88	349
7:3	3	2.0	30b [c,d)]	47.65	4.41	15.73	355
3:2	4	7.5	29a [c,e)]	47.66	4.64	15.77	346
1:1	5	6.0	29a,30a [f)]				

[a)] Identical IR with authentic sample.

[b)] Light brown crystals of *tricarbonyl{1,4,5,6-η⁴-[trans-1(endo),2-dicarbomethoxy-5-methylhex-4-en-1,6-diyl]}iron*, 29b, (3.3 g, 2 %), m.p. 99.5 - 100 °C obtained by crystallization of oil 2 from n-hexane/diethyl ether (2:1) (40 ml) at 20 °C/-78 °C; mother liquor contained 29b and one unidentified substance (by TLC).

[c] $C_{14}H_{16}FeO_7$ requires C, 47.75; H, 4.58; Fe, 15.86 %; mol.wt., 352.13.

[d] Dark yellow crystals of *tricarbonyl{1,4,5,6-*η^4*-[trans-1(endo),2-dicarbomethoxy-4-methylhex-4-en-1,6-diyl]}iron*, 30b, (1.3 g, 1 %), m.p. 67-68 °C obtained by crystallization of solid 3 from n-hexane/diethyl ether (2:1) (30 ml) at 20 °C/-78 °C; mother liquor contained 30b and one unidentified substance (by TLC).

[e] Yellow crystals of *tricarbonyl{1,4,5,6-*η^4*-[trans-1(exo),2-dicarbomethoxy-5-methylhex-4-en-1,6-diyl]}iron*, 29a, (3.1 g, 2 %), m.p. 101-102 °C obtained as precipitate by dissolving 3 in n-hexane/diethyl ether (2:1) (200 ml) and cooling the solution to -28 °C (12 h); mother liquor contained 29a, 30a and one unidentified substance (by TLC).

[f] Solid 5 combined with mother liquor from e; mixture dried and resultant residue (10.5 g) extracted with n-hexane/diethyl ether (2:1) (500 ml) to give 29a (6.0 g, 4 %) (identified by IR and NMR) and filtrate which contained 29a and *tricarbonyl{1,4,5,6-*η^4*-[trans-1(exo),2-dicarbomethoxy-4-methylhex-4-en-1,6-diyl]}iron*, 30a, (est. 3.7 g, 2 %) (identified by IR and NMR; see text) and one unidentified substance (by TLC). Attempts to separate the components of this filtrate by crystallization or chromatography were unsuccessful.

6.2.13. Photoreaction of pentacarbonyliron with (*trans*,*trans*)-hexa-2,4-dienoic acid methyl ester (methyl sorbate) and methyl acrylate in diethyl ether at ambient temperature

A solution of methyl sorbate (50.4 g, 0.4 mol), pentacarbonyliron (39.2 g, 0.2 mol), and methyl acrylate (34.4 g, 0.4 mol) in diethyl ether (2 l) was irradiated at ca. 20 °C for 350 h. The turbid reaction mixture was filtered. Evaporation of the filtrate under reduced pressure gave a reddish-brown oil (98.8 g). This was heated in the apparatus shown in Figure 6.4 at 50 °C/0.01 Torr. A mixture of tricarbonyl(η^4-methyl sorbate)iron, unchanged methyl sorbate, and tetracarbonyl(η^2-methyl acrylate)iron was collected as a distillate (17.4 g) (components of mixture identified by IR, NMR, and TLC). The thick, dark brown oily residue (76.1 g) was stirred with n-hexane (1 l) and filtered to give yellow *tricarbonyl{1,4,5,6-*η^4*-[1(exo),6(trans)-dicarbomethoxy-3-methylhex-4-en-1,6-diyl]}iron*, **31a**, (10.5 g; additional 3.9 g were isolated from the filtrate, *vide infra*, resulting in a total yield of 14.4 g, 21 %), m.p. 119-120 °C (recrystallized from n-hexane/diethyl ether (9:1) at 20 °C/-28 °C) (Found: C, 47.82; H, 4.61; Fe, 15.81; mol.wt., 353. $C_{14}H_{16}FeO_7$ requires C, 47.75; H, 4.58; Fe, 15.86 %; mol.wt., 352.16). Cooling of the filtrate to -28 °C precipitated **31a** (1.7 g). The filtrate obtained after removal of the precipitate gave on evaporation of the solvent under reduced pressure a yellow solid 13.1, which was chromatographed on silica as shown in Table 6.2.

Table 6.2: The chromatographic separation of solid 13.1.

Eluting solvent (n-Hexane/diethyl ether)	Code	Weight (g)	Components
4:1	1	4.3	(η^4-MSo)Fe(CO)$_3$ and (η^2-MA)Fe(CO)$_4$[a]
7:3	2	10.9	31b[b] and 32-Z[c]
3:2	3	7.0	31a[d] and 32-E[e]

[a] Components of mixture identified by IR, ^{1}H-NMR and TLC.

[b] Yellow crystals of *tricarbonyl{1,4,5,6-η⁴-[1(endo),6(trans)-dicarbomethoxy-3-methylhex-4-en-1,6-diyl]}iron*, 31b, (4.6 g, 7 %), m.p. 44-45 °C (Found: C, 47.65; H, 4.68; Fe, 15.76; mol.wt., 356. $C_{14}H_{16}FeO_7$ requires C, 47.75; H, 4.58; Fe, 15.86 %; mol.wt., 352.16) obtained by successive crystallization of oil 2 from diethyl ether/n-hexane (5:1) at 20 °C/ -28 °C.

[c] Impure *1-Z,6-E-dicarbomethoxy-3-methylhexa-1,5-diene*, 32-Z, (0.8 g, 2 %) (Found: C, 59.36; H, 6.26. $C_{11}H_{16}O_4$ requires C, 62.25; H, 7.60 %) obtained as oil by concentration of the mother liquor from *b)* and subsequent distillation at 35-40 °C/ 0.001 Torr.

d) Yellow crystals of *tricarbonyl{1,4,5,6-*η^4*-[1(exo),6(trans)-dicarbomethoxy-3-methylhex-4-en-1,6-diyl]}iron*, 31a, (2.2 g; see above) obtained by successive crystallization of oil 3 from diethyl ether/n-hexane (5:1) at 20 °C/-28 °C.

e) Impure *1-E,6-E-dicarbomethoxy-3-methylhexa-1,5-diene*, 32-E, (2.5 g, 6 %) (Found: C, 53.05; H, 5.96. $C_{11}H_{16}O_4$ requires C, 62.25; H, 7,60 %) obtained as oil by concentration of the mother liquor from *d)* and subsequent distillation at 35-40 °C/0.001 Torr.

6.2.14. Photoreaction of pentacarbonyliron with (*trans,trans*)-hexa-2,4-dienoic acid methyl ester (methyl sorbate) and dimethyl fumarate in diethyl ether/n-hexane at ambient temperature

A solution of methyl sorbate (25.2 g, 0.2 mol), pentacarbonyliron (19.6 g, 0.1 mol), and dimethyl fumarate (28.8 g, 0.2 mol) in diethyl ether/n-hexane (2:1) (2 l) was irradiated at ca. 20 °C for 171 h. The reaction mixture was filtered and the insoluble brown residue (ill-defined IR) was discarded. Evaporation of the filtrate under reduced pressure gave a brown solid (43.8 g), which was stirred with n-hexane (500 ml). The resultant mixture was filtered successively until a clear yellow solution was obtained. This was cooled at -28 °C for 12 h and then filtered to give a bright yellow precipitate (22.5 g). The precipitate on heating at 50 °C/0.001 Torr in the apparatus illustrated in Figure 6.4 gave dimethyl fumarate (6.6 g) (identical m.p., IR and NMR with authentic sample) and a yellow residue (15.5 g), which on successive crystallization from n-hexane at 20 °C/-78 °C gave *tricarbonyl{1,4,5,6-*η^4*-[trans-1(exo),2,6-tricarbomethoxy-3-methylhex-4-en-1,6-diyl]}iron*, 33a, (10.6 g, additional 0.8 g were isolated from the filtrate, *vide infra*, resulting in a total yield of 11.4 g, 28 %), m.p. 124-125 °C (Found: C, 46.78; H, 4.38; Fe, 13.65; mol.wt., 405. $C_{16}H_{18}FeO_9$ requires C, 46.85; H, 4.42; Fe, 13.62 %; mol.wt., 410.16). The filtrate was concentrated and column chromatographed on silica. n-Hexane/diethyl ether (9:1) eluted tricarbonyl[η^4-(*trans,trans*)-hexa-2,4-dienoic acid methyl ester]iron (1.8 g, 8 % recovery) (identical IR, NMR and TLC with authentic sample). n-Hexane/diethyl ether (4:1) eluted a mixture (0.9 g) of dimethyl fumarate and tetracarbonyl (η^2-dimethyl fumarate)iron (components of mixture identified by IR, NMR and TLC). n-Hexane/diethyl ether (7:3) eluted a pale yellow fraction which on heating at 35-40 °C/0.001 Torr gave *1-E,2,6-E-tricarbomethoxy-3-methylhexa-1,5-diene*, 34-E, (0.9 g, 3 %) (Found: C, 57.60; H, 6.39. $C_{13}H_{18}O_6$ requires C, 57.77; H, 6.71 %). n-Hexane/diethyl ether (3:2) eluted bis[η^4-(*trans,trans*)-hexa-2,4-dienoic acid methyl ester]monocarbonyliron (0.2 g, 1 %) (identical IR, NMR and TLC with authentic sample). n-Hexane/diethyl ether (2:3) eluted 33a, (0.8 g) (identified by IR and NMR).

6.2.15. Photoreaction of pentacarbonyliron with (*trans,trans*)-hexa-2,4-dienoic acid methyl ester (methyl sorbate) and dimethyl maleate in diethyl ether at ambient temperature

A solution of methyl sorbate (25.2 g, 0.2 mol), pentacarbonyliron (19.6 g, 0.1 mol), and dimethyl maleate (28.8 g, 0.2 mol) in diethyl ether (1.7 l) was irradiated at ca. 20 °C for 47 h. The reaction mixture was filtered and the brown residue (ill-defined IR) was discarded. Evaporation of the filtrate under reduced pressure gave a brown oil (51.9 g), which was stirred with n-hexane (500 ml). The resultant mixture was filtered successively until a clear yellow solution was obtained. This was cooled at -28 °C for 12 h and then filtered to give *tricarbonyl{1,4,5,6-*η^4*-[cis-1(endo),2,6-tricarbomethoxy-3-methylhex-4-en-1,6-diyl]}iron*, **35b**, (9.4 g; additional 6.2 g were isolated from the filtrate, *vide infra*, resulting in a total yield of 15.6 g, 38 %), m.p. 105 - 105.5 °C (recrystallized from n-hexane at 20 °C/-10 °C) (Found: C, 46.84; H, 4.36; Fe, 13.61; mol.wt., 408. $C_{16}H_{18}FeO_9$ requires C, 46.85; H, 4.42; Fe, 13.62 %; mol.wt., 410.16). The filtrate was concentrated and column chromatographed on silica. n-Hexane/diethyl ether (initially 4:1, gradual change to 3:2) eluted a mixture of tricarbonyl[η^4-(*trans,trans*)-hexa-2,4-dienoic acid methyl ester]iron, dimethyl maleate and tetracarbonyl(η^2-dimethyl maleate)iron (14.8 g) (components identified by IR, NMR and TLC). n-Hexane/diethyl ether (3:7) eluted *tricarbonyl{1,4,5,6-*η^4*-[cis-1(endo),2,6-tricarbomethoxy-3-methylhex-4-en-1,6-*

diyl]}iron, 35b, (6.2 g) (identified by IR and NMR).

6.2.16. Photoreaction of pentacarbonyliron with 2,3-dimethylbuta-1,3-diene and dimethyl fumarate in diethyl ether at 0 °C

A solution of 2,3-dimethylbuta-1,3-diene (8.2 g, 0.1 mol), pentacarbonyliron (19.6 g, 0.1 mol), and dimethyl fumarate (14.4 g, 0.1 mol) in diethyl ether (2 l) was irradiated at 0 °C for 217 h. The reaction mixture was filtered and the brown filtrate (ill-defined IR) was discarded. Evaporation of the filtrate under reduced pressure gave a thick brown oil (23.3 g), which was chromatographed on silica. n-Hexane eluted tricarbonyl(η^4-2,3-dimethylbuta-1,3-diene)iron (3.7 g, 17 %) (identical IR and TLC with authentic sample). n-Hexane/diethyl ether (4:1) eluted a mixture of dimethyl fumarate and tetracarbonyl(η^4-dimethyl fumarate)iron (5.0 g) (components of mixture identified by IR and TLC). n-Hexane/diethyl ether (7:3) eluted a dark yellow fraction which gave a yellow oil (mixture by TLC) upon evaporation of the solvent under reduced pressure, which on further chromatography and subsequent crystallization at 20 °C/-28 °C from n-hexane gave yellow amorphous *dicarbonyl(η^4-2,3-dimethylbuta-1,3-diene)(η^2-dimethyl fumarate)iron*, 38, (6.3 g, 19 %), m.p. ca. -20 °C (Found: C, 49.68; H, 5.31; Fe, 16.38; mol.wt., 336. $C_{14}H_{18}FeO_6$ requires C, 49.73; H, 5.37; Fe, 16.52 %; mol.wt., 338.14). n-Hexane/diethyl ether (3:2, gradual change to diethyl ether) eluted yellow fractions which gave a yellow solid on evaporation of the solvent under reduced pressure. Crystallization of this solid from n-hexane/diethyl ether (9:1) at 20 °C/-28 °C gave *tricarbonyl{1,4,5,6-η^4-[trans-1(exo),2-dicarbomethoxy-4,5-dimethylhex-4-en-1,6-diyl]}iron*, 23a (4.0 g, 11 %) (identical m.p., IR and NMR with authentic sample).

6.2.17. Photoreaction of tetracarbonyl(η^2-dimethyl fumarate)-iron with 2,3-dimethylbuta-1,3-diene in diethyl ether at ambient temperature

A solution of tetracarbonyl(η^2-dimethyl fumarate)iron (2.0 g, 6.4 mmol) and 2,3-dimethylbuta-1,3-diene (1.1 g, 12.8 mmol) in diethyl ether (1.2 l) was irradiated under a strong concomitant stream of argon at ca. 20 °C for 1 h. The reaction mixture was filtered, and the brown precipitate was discarded. Evaporation of the filtrate under reduced pressure gave a brown oil (1.9 g), which was column chromatographed on silica at -45 °C. n-Hexane/diethyl ether (9:1) eluted tricarbonyl(η^4-2,3-dimethylbuta-1,3-diene)iron (0.6 g, 42 %) (identical IR and TLC with authentic sample). n-Hexane/diethyl ether (7:3) eluted a yellow fraction which upon evaporation of the solvent under reduced pressure gave a yellow oil. Attempts to crystallize this oil from n-hexane at -80 °C gave amorphous *dicarbonyl(η^4-2,3-dimethylbuta-1,3-diene)(η^2-dimethyl fumarate)iron*, 38, (0.8 g, 37 %), m.p. ca. -20 °C (Found: C, 49.66; H, 5.53; Fe, 16.46; mol.wt., 346. $C_{14}H_{18}FeO_6$ requires C, 49.73; H, 5.37; Fe, 16.52 %; mol.wt., 338.14). Diethyl ether eluted a mixture (0.1 g) of unreacted dimethyl fumarate, tetracarbonyl(η^2-dimethyl fumarate)iron, and *tricarbonyl{1,4,5,6-η^4-[trans-1(exo),* *2-dicarbomethoxy-4,5-dimethylhex-4-en-1,6-diyl]}iron*, 23a (component identified by IR).

6.2.18. Reaction of dicarbonyl(η^4-2,3-dimethylbuta-1,3-diene)(η^2-diethyl fumarate)iron with carbon monoxide in n-hexane at ambient temperature

Dicarbonyl(η^4*-2,3-dimethylbuta-1,3-diene*)(η^2*-diethyl fumarate*)*iron*, 37, (0.6 g, 1.6 mmol) was transferred to a *Schlenck* tube, and dissolved in n-hexane (30 ml). The tube was placed in liquid nitrogen, then evacuated under vacuum (3 x freeze-pump-thaw cycles). The solution was then stirred under carbon monoxide for 18 h. Two isomers of the type tricarbonyl{1,4,5,6-η^4-1,2-dicarboethoxy-4,5-dimethylhex-4-en-1,6-diyl}iron complex were detected (IR). On cooling to -78 °C the solution gave bright yellow crystals of *tricarbonyl{1,4,5,6-*η^4*-[trans-1(exo),2-dicarboethoxy-4,5-dimethylhex-4-en-1,6-diyl]}iron*, 25a, (0.2 g, 32 %) (identical IR, m.p. with authentic sample) and a mother liquor containing 25a and 25b (components identified by IR).

6.2.19. Photolysis of tricarbonyl{1,4,5,6-η^4-[1(exo)-carbomethoxy-hex-4-en-1,6-diyl]}iron in n-hexane at ambient temperature

A solution of *tricarbonyl{1,4,5,6-*η^4*-[1(exo)-carbomethoxy-hex-4-en-1,6-diyl]}iron*, 27a (2.8 g, 10 mmol) in n-hexane (290 ml) was irradiated at 20 °C for 5 h. The reaction was monitored by means of infrared spectroscopy. The turbid reaction mixture was filtered and evaporation of the filtrate under reduced pressure gave a brown oil (1.8 g). Column chromatography on silica gel (elution with n-hexane/diethyl ether, 9:1) gave successively:

(*i*) A mixture of several components (0.2 g) (ill-defined IR),

(*ii*) *tricarbonyl*{η^4-*[1-carbomethoxy-hexa-1(E),3(E)-diene]*}*iron*, 43, (0.46 g, 16 %) (Found: C, 47.12; H, 4.34; Fe, 19.73; mol.wt., 273. $C_{11}H_{12}FeO_5$ requires C, 47.18; H, 4.32; Fe, 19.94 %; mol.wt., 280.06),

(*iii*) *tricarbonyl*{*1,4,5,6*-η^4-*[1(endo)-carbomethoxy-hex-4-en-1,6-diyl]*}*iron*, 27b (0.3 g, 11 %) (identical IR and NMR with authentic sample), and

(*iv*) unchanged *tricarbonyl*{*1,4,5,6*-η^4-*[1(exo)-carbomethoxy-hex-4-en-1,6-diyl]*}*iron*, 27a (0.52 g, 19 % recovery).

6.2.20. Photolysis of tricarbonyl{1,4,5,6-η^4-[1(exo)-carbomethoxy-*cis*-1,2-dideuteriohex-4-en-1,6-diyl]}iron in n-hexane/diethyl ether at ambient temperature

A solution of *tricarbonyl*{*1,4,5,6*-η^4-*[1(exo)-carbomethoxy-cis-1,2-dideuteriohex-4-en-1,6-diyl]*}*iron*, 28a, (0.96 g, 3.40 mmol) in n-hexane (200 ml) was irradiated at ca. 20 °C for 2.5 h. The reaction was monitored by means of infrared spectroscopy. The turbid reaction mixture was filtered. Evaporation of the solvent from the filtrate under reduced pressure also removed (η^4-buta-1,3-diene)tricarbonyliron and left a brown oil (0.9 g) as residue. Column chromatography of the oil on silica (elution with n-hexane/diethyl ether, 9:1) gave successively:

(*i*) *tricarbonyl*{η^4-[*-carbomethoxy-1,2-dideuteriohexa-1(E),3(E)-diene*]}*iron*, 44, (0.18 g, 19 %) (Found: C, 46.76; H + D, 4.92; Fe, 19.94; mol.wt., 284. $C_{11}H_{10}D_2FeO_5$ requires C, 46.84; H + D, 4.99; Fe, 19.80 %; mol.wt., 282.05).

(*ii*) *tricarbonyl*{*1,4,5,6*-η^4-[*1(endo)-carbomethoxy-cis-1,2-dideuterichex-4-en-1,6-diyl*]}*iron*, 28b (0.17 g, 18 %) (identified by IR and NMR),

(*iii*) *tricarbonyl*{*1,4,5,6*-η^4-[*1(exo)-carbomethoxy-cis-1,2-dideuteriohex-4-en-1,6-diyl*]}*iron*, 28a (0.36 g, 38 % recovery) (identified by IR and NMR), and

(*iv*) *tricarbonyl*{*1,4,5,6*-η^4-[*1(exo),6(trans)-dicarbomethoxy-cis-1,2-dideuterio-3-ethylhex-4-en-1,6-diyl*]}*iron*, 45a (traces) (identified by IR and NMR).

6.2.21. Photolysis of tricarbonyl{1,4,5,6-η^4-[1(exo),6(*trans*)-dicarbomethoxy-3-methylhex-4-en-1,6-diyl]}iron in n-hexane/diethyl ether at ambient temperature

A solution of *tricarbonyl*{*1,4,5,6*-η^4-[*1(exo),6(trans)-dicarbomethoxy-3-methylhex-4-en-1,6-diyl*]}*iron*, 31a, (3.5 g, 10 mmol) in n-hexane/diethyl ether (1:1) (600 ml) was irradiated at ca. 20 °C for 11.5 h. The reaction was monitored by means of infrared spectroscopy. After filtration the brown precipitate was discarded (0.3 g) (ill-defined IR). Evaporation of the filtrate under reduced pressure gave an oily residue (2.4 g). Column chromatography of the oil on silica gel (elution with n-hexane/diethyl ether, initially 9:1, changed to 4:1) gave successively:

(*i*) tricarbonyl[η^4-(*trans*,*trans*)-hexa-2,4-dienoic acid methyl ester]iron, (0.9 g, 40 %) (identical IR and NMR with authentic sample),

(*ii*) *1-Z,6-dicarbomethoxy-3-methylhexa-1,5-diene*, 32-Z, (0.03 g, 1%) (identified by NMR),

(*iii*) *tricarbonyl{1,4,5,6-*η^4*-[1(endo),6-dicarbomethoxy-3-methylhex-4-en-1,6-diyl]}iron*, 31b, (0.4 g, 11 %) (identified by IR and NMR),

(*iv*) 1-E,6-E-dicarbomethoxy-3-methylhex-1,5-diene, 32-E, (0.2 g, 9 %) (identified by NMR), and

(*v*) unchanged *tricarbonyl{1,4,5,6-*η^4*-[1(exo),6-dicarbomethoxy-3-methylhex-4-en-1,6-diyl]}iron*, 31a (0.44 g, 12 % recovery) (identified by IR and NMR).

6.2.22. Reaction of tricarbonyl{1,4,5,6-η^4-[*cis*-1(endo),2-dicarbomethoxy-4,5-dimethylhex-4-en-1,6-diyl]}iron with carbon monoxide in n-hexane/diethyl ether (2:1) at 50 °C and 50 bar

Tricarbonyl{1,4,5,6-η^4*-[cis-1(endo),2-dicarbomethoxy-4,5-dimethylhex-4-en-1,6-diyl]}iron*, 22b, (2.4 g, 6.6 mmol) in n-hexane/diethyl ether (2:1) (150 ml) was heated at 50 °C under a carbon monoxide pressure of 50 bar for 16 h. Evaporation of the solvent from the mixture under reduced pressure also removed pentacarbonyliron (identical IR with authentic sample) leaving a red solid residue (2.3 g) which on crystallization from n-hexane/diethyl ether (2:1) at 20 °C/-78 °C gave 22b (2.1 g, 88 % recovery) (identical m.p., IR and TLC with authentic sample).

6.2.23. Reaction of tricarbonyl{1,4,5,6-η^4-[*cis*-1(endo),2-dicarbomethoxy-4,5-dimethylhex-4-en-1,6-diyl]}iron with carbon monoxide in n-hexane/diethyl ether (2:1) at 70 °C and 45 bar

Tricarbonyl{1,4,5,6-η^4-[cis-1(endo),2-dicarbomethoxy-4,5-dimethylhex-4-en-1,6-diyl]}iron, 22b, (2.1 g, 5.7 mmol) in n-hexane/diethyl ether (2:1) (150 ml) was heated at 70 °C under a carbon monoxide pressure of 45 bar for 48 h. Evaporation of the solvent from the mixture under reduced pressure also removed pentacarbonyliron (identical IR with authentic sample) leaving a red oil (1.6 g) which was chromatographed on silica gel. Elution with benzene/diethyl ether (4:1) gave a mixture of tricarbonyl(η^4-2,3-dimethylbuta-1,3-diene)iron and dimethyl maleate (0.4 g) (components of mixture identified by IR and TLC) followed by a mixture of 22b, 47, tricarbonyl(η^4-2,3-dimethylbuta-1,3-diene)iron, and dimethyl maleate. Thin layer chromatography (silica gel plates 20 x 20 cm) of the latter mixture using dichloromethane as eluant gave yellow and colourless bands which on extraction afforded 22b (0.05 g, 2 % recovery) (identical IR, NMR and TLC with authentic sample), and 47 (0.3 g, 21 %), [m/e 254 (M^+), 223 and 195], respectively.

6.2.24. Reaction of tricarbonyl{1,4,5,6-η^4-[*cis*-1(endo),2-dicarbomethoxy-4,5-dimethylhex-4-en-1,6-diyl]}iron with carbon monoxide in methyl acetate at 70 °C and 90 bar

Tricarbonyl{1,4,5,6-η^4-[cis-1(endo),2-dicarbomethoxy-4,5-dimethylhex-4-en-1,6-diyl]}iron, 22b, (5.0 g, 13.7 mmol) in methyl acetate (100 ml) was heated at 70 °C under a carbon monoxide pressure of 90 bar for 48 h. Evaporation of the solvent from the mixture under reduced pressure also removed pentacarbonyliron (identical IR with authentic sample) leaving a red oily residue (3.6 g). Distillation of this oil under vacuum gave successively:

(*i*) a mixture of tricarbonyl(η^4-2,3-dimethylbuta-1,3-diene)iron, tetracarbonyl(η^2-dimethyl maleate)iron, and dimethyl maleate (0.1 g) (b.p. 50 °C/0.001 Torr) (components of mixture identified by IR and TLC),

(*ii*) a similar mixture (0.2 g) (b.p. 68 °C/0.001 Torr) (identified by IR and TLC), and

(*iii*) thick-oily 47 (2.1 g, 60 %) (b.p. 98-103 °C/0.001 Torr) (Found: C, 61.49; H, 7.10; mol.wt., 248. $C_{13}H_{18}O_5$ requires C, 61.41; H, 7.14 %; mol.wt., 254.28) [m/e 254 (M^+), 223 and 195]. Sylilation of compound 47 with excess N,N-bis-trimethylsilyl-trifluoro acetamide at room temperature was carried out (multicomponent by GC; relative proportions of two main components and combined minor components 45:38:17, respectively) [m/e 326 (M^+), 311, 296 and 281].

6.2.25. Reaction of tricarbonyl{1,4,5,6-η⁴-[*trans*-1(exo),2-dicarbomethoxy-4,5-dimethylhex-4-en-1,6-diyl]}iron with carbon monoxide in methyl acetate at 70 °C and 90 bar

Tricarbonyl{1,4,5,6-η⁴-[trans-1(exo),2-dicarbomethoxy-4-5-dimethylhex-4-en-1,6-diyl]}iron, **23a**, (5.8 g, 15.8 mmol) in methyl acetate (100 ml) was heated at 70 °C under a carbon monoxide pressure of 90 bar for 72 h. Evaporation of the solvent from the mixture under reduced pressure also removed pentacarbonyliron (identical IR with authentic sample) leaving a thin reddish oil residue (4.4 g). Distillation of this oil under vacuum gave two fractions:

(*i*) a mixture of tricarbonyl(η⁴-2,3-dimethylbuta-1,3-diene)iron, tetracarbonyl(η²-dimethyl fumarate)-iron, and dimethyl fumarate (1.8 g) (b.p. 70 - 73 °C/0.001 Torr) (components identified by IR and TLC), and

(*ii*) an oil (2.2 g) (b.p. 100 °C/0.001 Torr) which on redistillation gave 48 as a thick oil (2.1 g, 52 %) (Found: C, 61.29; H, 7.04; mol.wt., 249. $C_{13}H_{18}O_5$ requires C, 61.41; H, 7.14 %; mol.wt., 254.28) [m/e 254 (M^+), 223 and 195]. Silylation of compound 48 with N,N-bis-trimethylsilyl-trifluoro acetamide at room temperature was carried out (multicomponent by GC; relative proportions of two main components and combined minor components 37:12:51, respectively) [m/e 326 (M^+), 311, 296 and 281].

6.2.26. Reaction of tricarbonyl{1,4,5,6-η^4-[*cis*-1(endo),2-dicarbomethoxy-hex-4-en-1,6-diyl]}iron with carbon monoxide in methyl acetate at 70 °C and 110 bar

Tricarbonyl{1,4,5,6-η^4-[cis-1(endo)2,dicarbomethoxy-hex-4-en-1,6-diyl]}iron, 20b, (4.1 g, 12.1 mmol) in methyl acetate (100 ml) was heated at 60 °C under a carbon monoxide pressure of 90 bar for 60 h. Evaporation of the solvent under reduced pressure also removed pentacarbonyliron (identical IR with authentic sample) leaving a thin reddish oil residue (3.5 g) (IR showed incomplete conversion). The residue was redissolved in methyl acetate (100 ml) and heated at 70 °C under a carbon monoxide pressure of 110 bar for 60 h. A thin reddish oil resulted (3.1 g). Distillation of this oil under vacuum gave successively:

(*i*) a mixture of (η^4-buta-1,3-diene)tricarbonyliron, tetracarbonyl(η^2-dimethyl maleate)iron, and dimethyl maleate (0.3 g) (b.p. 38 °C/0.001 Torr) (components identified by IR, NMR and TLC), and

(*ii*) a thick oily 49, (1.9 g, 69 %) (b.p. 88-90 °C/0.001 Torr) (Found: C, 59.46; H, 6.48. $C_{11}H_{14}O_5$ requires C, 58.40; H, 6.24 %) [m/e 226 (M^+), 195, and 167]. Silylation of compound 49 with N,N-bistrimethylsilyl-trifluoro acetamide at room temperature was carried out (multicomponent by GC; relative proportion of a main and combined minor components 86:14,respectively) [m/e 298 (M^+), 283, and 268].

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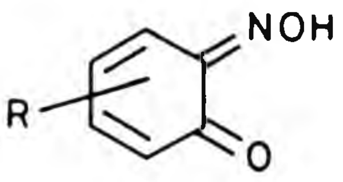
APPENDIX

APPENDIX

One of the initial aims of this study was to examine photoinitiated coupling of olefins with heterodienes of type 1 in the presence of pentacarbonyliron. Both thermal and photochemical reactions involving methyl acrylate, pentacarbonyliron and the heterodiene 2 showed that the main reaction product is the iron(II) chelate 3. This was obtained in > 95 % yield (based on 2). Several organic products were also formed but in very low yield. All products corresponded very closely in nature and yield to those obtained from the reaction of 2 with pentacarbonyliron. As no coupling occurred between 2 and methyl acrylate, no further studies were undertaken.



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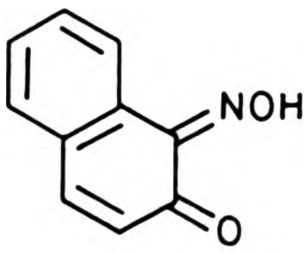

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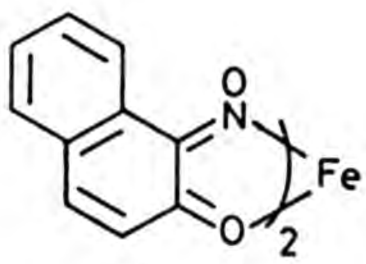

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