

Acyclic Butadiene–Iron Tricarbonyl Complexes in Organic Synthesis

René Grée

Laboratoire de Chimie Organique Biologique, Unité associée CNRS n° 704, Ecole Nationale Supérieure de Chimie de Rennes, Avenue du Général Leclerc, 35700 Rennes-Beaulieu, France

The synthetic uses of acyclic butadiene–iron tricarbonyl complexes are reviewed. The main advantages of these organometallic reagents include their easy access (even in chiral form), the efficiency of the $\text{Fe}(\text{CO})_3$ moiety in protecting 1,3-dienes, and its use as a stereodirecting group in various types of reactions. Furthermore, these complexes lead to many polyfunctionalized, eventually optically active, dienes which are themselves of much current interest in organic synthesis.

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1. Introduction

Butadiene–iron tricarbonyl complexes have been known for more than 50 years,¹ but it is only recently that organic chemists have become interested in the possible use of such organometallic complexes in synthesis. The purpose of this review is to describe the progress that has recently been made in the use of *acyclic* butadiene–iron tricarbonyl complexes in organic synthesis. The complexes obtained from cyclic derivatives such as cyclohexadienes² or tropone,³ for instance, and also bismethylene exocyclic systems⁴ will not be included in this review.

Although the general principles and background of the use of transition metal complexes in synthesis have already been described,^{5–7} it is worth while pointing out, briefly, the main advantages of the butadiene–iron tricarbonyl complexes, since these compounds are remarkably versatile organometallic intermediates:

- These complexes are easily accessible, even on a large scale (10–100 g), usually starting from inexpensive reagents;⁸ furthermore, they may be handled under standard laboratory conditions.
- They can stabilize, in complexed form, very unstable molecules;⁹ for instance, two examples that will be described later are dienes bearing electron withdrawing groups in the 2-position and pentadienyl cations.
- They can be obtained in optically active form¹⁰ and, thus, are useful in the synthesis of chiral compounds.
- The butadiene–iron tricarbonyl moiety itself, being stable towards a large variety of chemical reagents, can be utilized to protect, temporarily and very efficiently in a selective fashion, two conjugated double bonds.
- Finally, it is usually possible to carry out the decomplexation reaction under very mild conditions, thus giving an interesting entry into polyfunctionalized, eventually chiral, dienes, which are of much current interest in organic synthesis.

The preparation and the spectral properties of these complexes have been described in a recent book¹⁰ and will not be discussed

here. Much attention has recently been paid to asymmetric synthesis, so aspects relating to the chirality of these complexes will be considered first. Reactions in which the organometallic part of the molecule is directly involved will be examined next, and finally, consideration will be given to reactions in which the organometallic moiety mainly acts as a protecting and stereodirecting group.

2. Preparation and Properties of Chiral Acyclic Butadiene–Iron Tricarbonyl Complexes

Complexes of the general type **1** and **1'** are chiral (except if $\text{R}^1 = \text{R}^3$ and $\text{R}^2 = \text{H}$) and are accessible in optically active form.¹¹

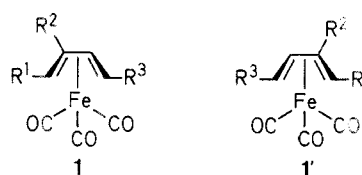


Table 1 indicates the derivatives that have been resolved by classical methods using either fractional crystallization or chromatography of diastereoisomeric mixtures.

Table 1. The Chiral Butadiene–Iron Tricarbonyl Complexes Obtained by Resolution

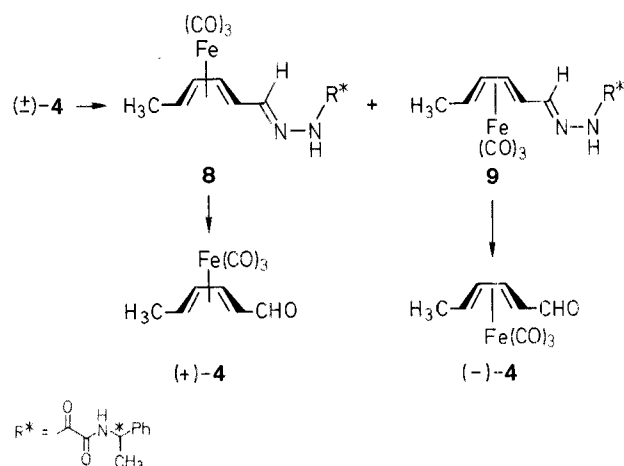
Compound	R ¹	R ²	R ³	Method ^a	Ref.
2	CH ₃	H	CO ₂ H	A	12
3	H	H	CO ₂ H	A	12
4	CH ₃	H	CHO	A B	12 14
5	CO ₂ Me	H	CHO	A A	16 17
6	H	CHO	H	B	15
7	H	H	CHO	B	16

^a Method A: fractional crystallization of diastereoisomers.
Method B: chromatographic separation of diastereoisomers.

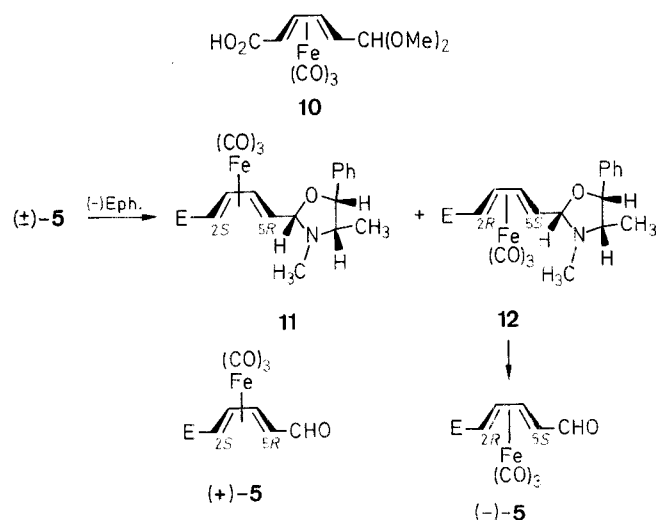
The resolution of acids **2** and **3** was achieved by separation of their α -methylbenzylamine salts.¹² In the case of **2** the optical purity of the corresponding methyl ester was determined by NMR.¹³

The resolution of **4** was first performed via fractional crystallization of the corresponding pyrrolidinium salts having *d*-camphor sulfonate¹² as the optically active anion. More recently a very efficient method, using chromatographic separation of the diastereoisomers of the chiral semi-oxamazones **8** and **9** has been described.¹⁴

This method was later extended to the 2-formylcomplex **6**¹⁵ and to the monosubstituted derivative **7**.¹⁶ In each case excellent optical purity was achieved for these compounds.



The bifunctional derivative (+)-**5** was first obtained via fractional crystallization of the brucine salt of acid **10**,¹⁷ but a more direct route, via the diastereoisomeric oxazolidines **11** and **12**, which gives the complexes (+)-**5** and (-)-**5** in optically pure form and in excellent overall yield, was later introduced.¹⁸



E = CO₂Me

A different strategy has been described recently in the case of the methyl sorbate complex ($R^1 = \text{CH}_3$; $R^2 = \text{H}$; $R^3 = \text{CO}_2\text{Me}$). The chirality transfer from several optically active butadiene-iron tricarbonyl complexes to this diene gives the desired compound, but only in relatively low yields ($\leq 50\%$) and with small ee's ($\leq 19\%$).¹⁹

All the chiral complexes in Table 1 bear functionalities and can, thus, be used for the preparation of other derivatives. Table 2

gives examples of the chiral compounds that have been prepared in such a way and some of them have proved to be useful intermediates in organic synthesis; **14** and **18** for instance were used in the enantiospecific synthesis of hemicalonaldehydes, and **17** in the preparation of (-)-verbenalol, as described later.

Table 2. Optically Active Butadiene – Iron Tricarbonyl Complexes Prepared by Synthesis

Com- pound	R ¹	R ²	R ³	Ref.
13	CH ₃	H	COCH ₃	12
14	CH ₃	H	CH=CHCO ₂ Me (<i>E</i> and <i>Z</i>)	14
15	CO ₂ Me	H	CH=CHCO ₂ Me (<i>E</i>)	17
16	CO ₂ Me	H	CH=C(CO ₂ Me) ₂	18
17	CO ₂ Me	H		20
18	CO ₂ Me	H	CH=C(CH ₃) ₂	21
19	CO ₂ Me	H	CH(OH)CH ₃	22
20	CO ₂ Me	H	CH(OH)CH ₃ ^a	23
21	H	H	CH ₃	16
22	CH ₃	H	COCH ₃	16
23	CH ₃	H	COCH ₂ CH ₃	16
24	CH ₃	H	CO(CH ₂) ₃ CO ₂ Me	16
25	CH ₃	H	CH ₃ C(OH)Ph	16
26	CH ₃	H	CH ₃ C(OH)CH ₂ CH ₃	16
27	CH ₃	H	CH(OH)(CH ₂) ₃ CO ₂ Me	16
28	CH ₃	H		16

^a Derivative with a *E,Z*-configuration of the complexed diene system.

A knowledge of the absolute configuration of the starting material and the conditions for its racemization are two important factors that must be studied before designing the synthesis of chiral derivatives. Complex **5** appears to be the only example where the absolute configuration has been established unambiguously; the X-ray diffraction analysis of **11** gives a *2S,5R* configuration for this compound and also for the corresponding aldehyde (+)-**5**.¹⁸

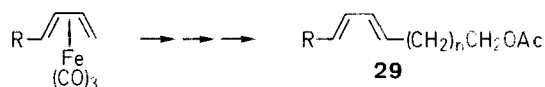
A preliminary study of the circular dichroism of some butadiene-iron tricarbonyl complexes suggested that the sign and the magnitude of the d-d transition at long wavelengths could be related to the absolute configuration of these compounds.¹² This is a point that has to be established on more examples and where progress might be expected in the near future, since many chiral complexes are now easily accessible.

Thermal racemization has been studied in the case of **5** and **15**. The measured rates were $2.37 \times 10^{-4} \text{ min}^{-1}$ and $2.70 \times 10^{-4} \text{ min}^{-1}$ at 119.4°C giving ΔG^\ddagger close to 130 kJ · mole⁻¹.¹⁷ This signifies that the upper temperature limit for the use of these complexes in asymmetric synthesis is around 90–100°C.

3. Reactions Occurring on the Organometallic Moiety

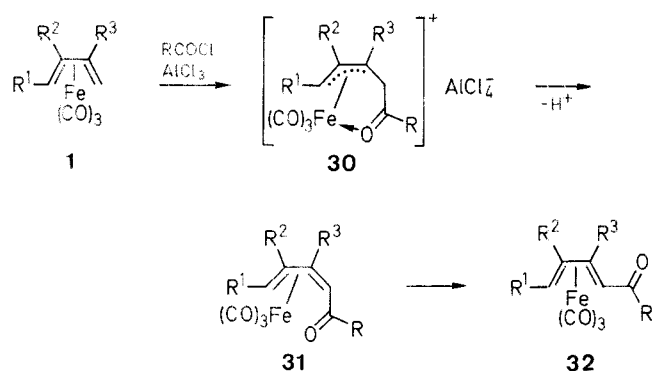
3.1. Reactions with Electrophiles

It is well known that butadiene-iron tricarbonyl complexes are reactive towards electrophiles.²⁴ Friedel-Crafts type reactions, which give synthetically useful functionalization of the diene system, have been the most thoroughly studied. An example is its use as the key step in the stereospecific synthesis of several insect pheromones **29**.²⁵



a: R = H, n = 7; **b:** R = CH₃CH₂, n = 7; **c:** R = CH₃, n = 6;
d: R = CH₃(CH₂)₂, n = 8

The reaction mechanism involves an electrophilic attack of the complex at the terminal position to give cation **30**; such cations have been isolated and characterized by X-ray crystallography in a few cases.²⁶ The primary product on deprotonation is the complexed dienone **31**, which has the *anti* stereochemistry. This may be isolated in good stereochemical purity, although it is readily converted to its *syn* isomer **32** under basic, acidic, or thermal conditions.²⁷

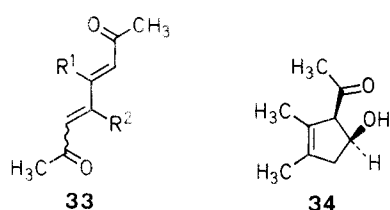


The following are the main characteristics of the reaction:

- The presence of the iron-carbonyl moiety facilitates the Friedel-Crafts reaction. However, it has been found that it is not due to an "activation" by the complex, but more to a "control" of the reaction, since uncomplexed dienes are usually polymerized under these reaction conditions.²⁸ Furthermore, in one case the electrophilic reaction occurred preferentially on free carbon-carbon double bonds.²⁹

- The reaction occurs without racemization.¹⁶ It always occurs on the terminal non-substituted carbon, mainly for steric reasons.

- The substituents in positions 2 and 3 have usually relatively small effects on the regioselectivity of the reaction.²⁸ Electron-withdrawing groups deactivate the complex and inhibit the reaction.²⁸ However, it has been found recently that a second acylation is possible, under different reaction conditions, with complexes bearing silyl³⁰ and even carbon³¹ substituents at position 2. This yields interesting 2,4-diene-1,6-diones such as **33**, which are difficult to prepare by other methods. This route is also useful for the synthesis of 2-acyl-3-cyclopentenols **34** by a reductive photodecomplexation procedure.³¹ Other electrophiles have been used, and it is interesting to note that formylation of diene-Fe(CO)₃ complexes proceeds only in modest yields using dichloromethyl methyl ether/aluminum trichloride.³²



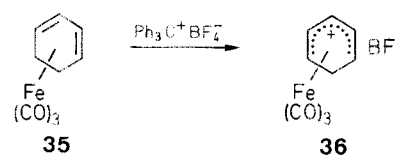
a: R¹ = SiEt₃, R² = H; **b:** R¹ = H, R² = CH₃; **c:** R¹ = R² = CH₃

A new synthesis of polysubstituted 2-cyclopenten-1-ones, by reaction of butadiene-iron tricarbonyl complexes with aluminum trichloride eventually under carbon monoxide pressure, has been described recently.¹⁶ In the case of the acyclic derivatives, however, the yields are relatively low and drastic reaction conditions are usually necessary.¹⁶

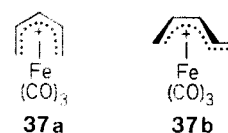
The protonation of butadiene-iron tricarbonyl complexes leads to π -allylic derivatives, whose structures have been studied in detail.³³ However, these compounds have not been used extensively in organic synthesis.

3.2. Pentadienyl-Iron Tricarbonyl Cations

It is well known that the complexation by Fe(CO)₃ strongly stabilizes conjugated pentadienyl cations. The derivative **36**, for instance, is not only easily accessible from the complex **35**, but is even stable in water.³⁴ The cyclohexadienyl complexes have found many applications in synthesis.²

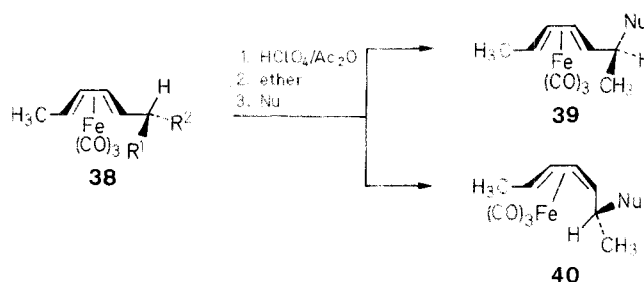


In the *acyclic* series, although somewhat less stable, the corresponding cations are also usually isolable compounds. In this case, the stereochemical problem is more complex due to the fact that two different forms, "*cisoid*" **37a** or "*transoid*" **37b** need to be considered both from the structural and the reactivity point of view.



Furthermore, for each of them, depending upon the nature and position of substituents, *cis* and *trans* derivatives can exist. It is, then, not surprising that much work has been devoted to these cations in order to establish their structures³⁵ and study their reactivity towards nucleophiles. Only the most significant aspects from the synthetic point of view will be considered here.

The cations are usually prepared by reaction of alcohols such as **38a** or **38b** with strong acids (HClO₄ or HBF₄) in acetic anhydride followed by addition of anhydrous ether. These crystalline cations react with various nucleophiles giving adducts of the type **39** or **40** or mixtures of both.

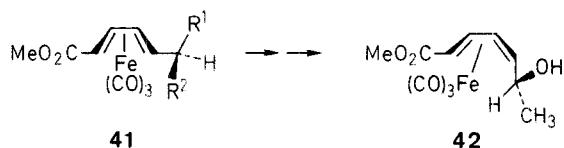


a: R¹ = CH₃, R² = OH; **b:** R² = OH, R¹ = CH₃
 Nucleophiles = ROH, RNH₂, PR₃, R₂Cd, electron-rich aromatics, hydride donors

The nature of the nucleophile has a strong influence upon the reaction pathway: water, alcohols,³⁶ and electron-rich aromatic compounds³⁷ give rise exclusively to the *E,E* derivatives **39**, while phosphines³⁸ and organocadmium reagents,³⁹ lead only to the *E,Z* complexes **40**. Reduction is strongly dependent on the hydride donor. Sodium cyanoborohydride yields complex **40**,^{40,41} whereas lithium ethoxyborohydride⁴⁰ gives *E,E* derivatives **39**. In the case of amines, the result depends upon their pK:⁴² strongly basic amines give the complexes **40**, while the arylamines with pK between 10 and 13 lead to the *E,E* compounds **39**. Aniline and *p*-toluidine lead to mixture of both **39** and **40**.

It is important to note that in each case the reaction is *stereoselective* and gives only one diastereoisomer in both type **39** and **40** derivatives.

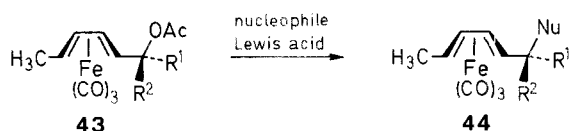
The nature of the substituents on the diene⁴³ also has an important effect on the reaction pathway. Under the same conditions as described for **38**, complex **41** gives almost exclusively (95% stereoselectivity) **42**,²³ instead of the *E,E* complex obtained from **38**.



a: R¹ = CH₃, R² = OH; **b:** R¹ = OH, R² = CH₃

This reaction, performed with optically active derivatives, established for the first time that acyclic pentadienyl cations complexed to Fe(CO)₃ could be used in a chiral form.

The synthetic applications of such isolated cations are particularly useful for carbon-heteroatom bond formation, but there are considerable limitations with regard to C-C bond formation.⁴⁴ A recent development involves the *in situ* use of iron-tricarbonyl cations.⁴⁵ The reaction of acetates **43** with nucleophiles in the presence of a Lewis acid leads directly, and stereospecifically, to the desired compound **44**. In agreement with the pioneering studies of Clinton and Lillya on the solvolysis of dinitrobenzoates,⁴⁶ this reaction occurs with retention of configuration. Allyl silanes, trialkylaluminums, and enol silyl ethers have all been successfully used as nucleophiles in the synthesis of type **44** derivatives.



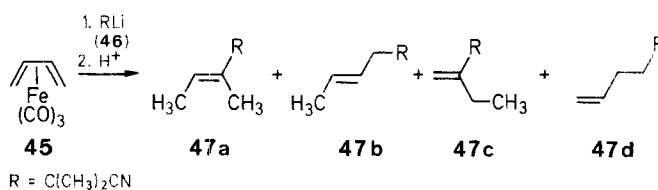
a: R¹ = H, R² = CH₃; **b:** R¹ = CH₃, R² = H

3.3. Reactions with Nucleophiles

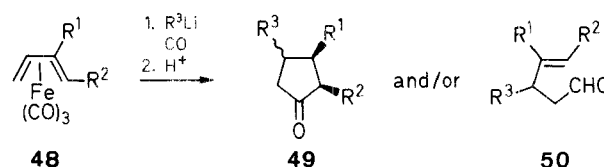
The reaction of butadiene-iron tricarbonyl complexes with nucleophiles has not been so well studied as the addition of electrophiles. The reaction of complex **45** with anion **46** gives a mixture of olefins **47**.⁴⁷

Detailed mechanistic studies, including deuterium labelling experiments, have been performed on this reaction and indicate the formation of η^3 -allylic complexes and that transient ferroclobutanes are formed as intermediates.⁴⁸ If the addition

of the nucleophilic is carried out in the presence of carbon monoxide (1.5 atm), cyclopentanones **49** or aldehydes **50** are obtained.

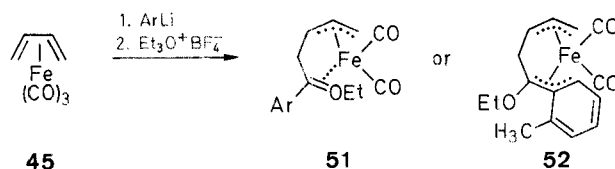


R = C(CH₃)₂CN



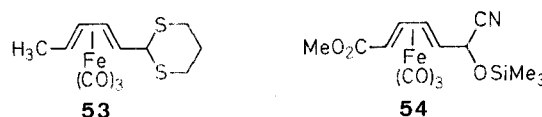
The reaction pathway adopted depends, strongly, upon the nature of the complex **48**: cyclopentanone formation is efficient only with monosubstituted derivatives (R¹ or R² = H), while for the sterically more hindered complexes (R¹, R² = alkyls) aldehydes **50** are obtained.⁴⁹

The main limitation of these reactions lies in the nature of the nucleophile and only some stabilized carbanions (α -cyano or carboxy, cyanohydrins or dithianes, for instance) appear to be synthetically useful. Simple organomagnesium and organolithium reagents show a tendency to attack at the carbon monoxide ligand⁴⁷ as has been clearly established in the case of aryllithium derivatives: after trapping of the acylmetalate intermediates with Meerwein's salt, carbene type complexes **51** or **52** were obtained.⁵⁰



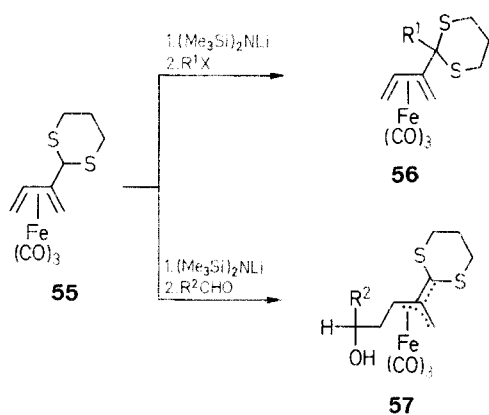
3.4. Miscellaneous Reactions

In contrast to the complexed pentadienyl cations, little is known about carbanions that are adjacent to the butadiene-iron tricarbonyl moiety. Attempts to use stabilized anions derived from **53**⁵¹ or **54**⁵² failed irrespective of the temperature, the base, or the electrophile employed.



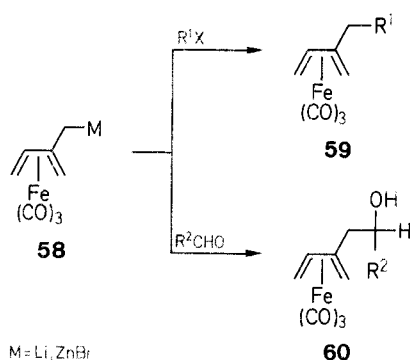
In most cases decomposition and decomplexations occurred. More successful were reactions with carbanionic species at position 2 of the complex. Metalation of **55** leads to stable anion, which, depending upon the electrophile, gives **56** or **57**.

Alkyl and allyl halides give the butadienyl derivatives **56** and aldehydes lead to the complexes **57** of the trimethylenemethane type.⁵¹

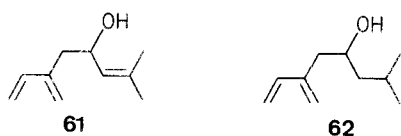


$R^1 = \text{CH}_3, \text{CH}_2\text{CH}=\text{CH}_2$; $R^2 = \text{Ph}, \text{CH}=\text{C}(\text{CH}_3)_2, \text{CH}(\text{CH}_3)_2$

Similar problems of rearrangement to a trimethylenemethane derivative have been observed with the isoprene anion equivalent **58**; however, a careful choice of the reaction conditions resulted in the formation of the desired compounds **59** or **60**.⁵³

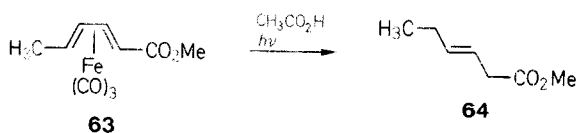


The role of the metal is very important, and the zinc derivative appears particularly useful in terms of stability and reactivity. This approach has allowed a very short synthesis, in racemic form, of the pheromones **61** and **62**.⁵³



It is interesting to note that no enolate linked to a butadiene-iron tricarbonyl complex has been described,⁵⁴ in spite of the numerous publications dealing with acyclic stereocontrol using aldol type condensations. Thus, the preparation and the potential use of such species in stereoselective synthesis remains an open question.

The decomplexation reaction is usually achieved with good chemoselectivity using oxidizing reagents. However an interesting new method has recently been reported. UV irradiation in acetic acid of complexes bearing electron-withdrawing substituents, such as **63**, occurs cleanly to give **64** of exclusive *E* configuration in an unusual 1,4-reduction process.⁵⁵ It has been established, using cyclic models, that the two hydrogen atoms are added in a *cis* manner.



4. The Organometallic Complex as a Protecting and Stereodirecting Group

4.1. Reaction of Nucleophiles with Carbonyl Derivatives

A large variety of organometallic nucleophiles have been reacted with butadiene-iron tricarbonyl complexes bearing an aldehyde function. The reaction is quite general and leads in almost every case, in good overall yield, to a mixture of the ψ -*exo*⁵⁶ **65** and the ψ -*endo* **66** alcohols. These diastereoisomers are usually very easily separated by chromatography, and in two cases, their stereochemistry has been established unambiguously by X-Ray crystallography.^{57,58}

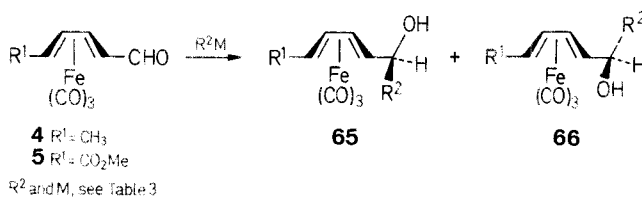
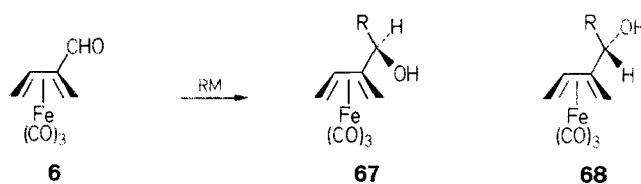


Table 3. Reaction of Organometallic Nucleophiles with Complexes **4** and **5**

R^1	R^2M	Yield (%)		Ref.
		65	66	
CO_2Me	CH_3MgI	80	60 : 40	59, 22
CO_2Me	CH_3Li	85	80 : 20	59
CH_3	CH_3MgI	57	53 : 47	60
CO_2Me	PhLi	94	66 : 34	59
CH_3	PhMgBr	91	75 : 25	60
CO_2Me	$\text{EtO}_2\text{CCH}_2\text{Li}$	88	86 : 14	59
CO_2Me	<i>t</i> -BuO ₂ CCH ₂ Li	94	66 : 34	61
CO_2Me	PhSCH_2Li	88	72 : 28	59
CO_2Me	$\text{CH}_3(\text{CH}_2)_2\text{C}\equiv\text{CLi}$	96	70 : 30	62
CO_2Me	$\text{LiO}_2\text{C}(\text{CH}_2)_2\text{C}\equiv\text{CLi}$	42	60 : 40	59
CO_2Me	$\text{BrMgO}(\text{CH}_2)_2\text{C}\equiv\text{CMgBr}$	87	70 : 30	59
CO_2Me	$\text{CH}_3\text{Ti}(\text{OPr-}i)_3$	94	25 : 75	59
CO_2Me	" $\text{HC}\equiv\text{CCH}_2\text{Al}_{2/3}\text{Br}$ "	94	25 : 75	59
CO_2Me	" $\text{CH}_2=\text{C}=\text{C}(\text{Al}_{2/3}\text{Br})(\text{CH}_2)_4\text{CH}_3$ "	80	43 : 57	59



R and M , see Table 4

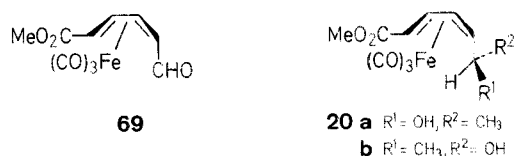
Table 4. Reaction of Organometallic Nucleophiles with Complex **6**¹⁵

RM	Yield (%)	Diastereoselectivity ^a
CH_3MgI	97	63 : 37
PhMgBr	88	50 : 50
<i>i</i> -PrMgBr	80	63 : 37
CH_3Li	98	80 : 20
$\text{CH}_3\text{Li}(\text{LiBr})$	85	91 : 9
<i>n</i> -BuLi	90	92 : 8
$\text{CH}_3\text{Ti}(\text{OPr-}i)_3$	100	42 : 58
$(\text{CH}_3)_2\text{CuLi}$	40	< 10 : > 90

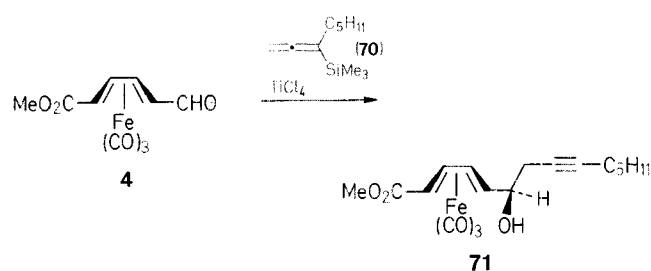
^a The stereochemistry of the resulting alcohols (**67** or **68**) has not been definitely established.¹⁵ The numbers correspond to the ratios of the more polar to the less polar diastereoisomer (easily separated by chromatography).

The diastereoselectivity of the reaction has been studied in detail using complexes **4**, **5**, and **6**, and representative examples are given in Tables 3 and 4.

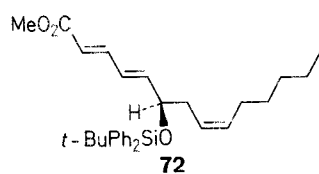
With Grignard reagents the reaction shows a low selectivity, but it is more selective with lithium derivatives, especially methyl lithium–lithium bromide complex. Nucleophiles derived from second-row metals (Ti, Cu, Al) exhibit an inversion of the diastereoselectivity. Interestingly, similar results have been obtained in the case of the *E,Z*-dienyl complex **69** during the formation of alcohols **20a** and **20b** on reaction with various organometallics.⁶³



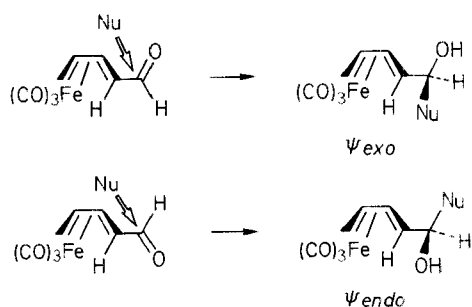
The addition of the allenyl silane **70**⁶⁵ is also noteworthy. Reaction of **70** with the complex **4** in the presence of titanium(IV) chloride gives, exclusively (in 65% yield), the ψ -endo derivative **71**.⁶⁴



This compound is useful for the preparation, in a chiral form, of a key intermediate in the synthesis of leukotriene B₄ (**72**).⁶⁶

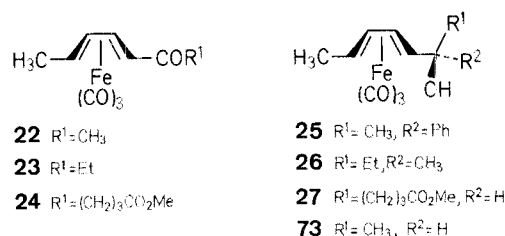


The diastereoselectivity of these reactions appears to be highly dependent upon the temperature, the nature of the metal, and the assistance, or not, of electrophiles. All these factors influence the conformer population of the aldehyde group; if it is assumed that the nucleophile reacts only on the face opposite to the bulky Fe(CO)₃ moiety, then the *s-cis* conformer leads to the ψ -exo derivative and the *s-trans* gives the ψ -endo product.



However, it has been suggested that for the copper and titanate derivatives the reaction could occur “endo” through addition to iron or to a carbonyl ligand.¹⁵ Thus, more work has to be carried out on these reactions in order to obtain a clear picture of the detailed reaction pathway.

The reactions of the corresponding complexed ketones are much less common. Reduction of **22**⁵⁶ and **24**¹⁶ is stereospecific and leads exclusively to the ψ -endo isomers **73** and **27**.



Similar results were obtained during the addition of organolithium reagents giving only **25** starting from **22**, and **26** from **23**.¹⁶ This stereospecificity has been attributed to a preferred *s-cis* conformation of the complexed dienones and reaction of the nucleophiles *anti* to Fe(CO)₃.⁵⁶

The key feature of these reactions is that it is possible, starting from an optically active complex, to control the absolute configuration at the secondary or tertiary alcohol carbon atom. This gives, after decomplexation, dienes bearing chiral substituents of predictable absolute configuration. Due to the presence of the alcohol function a careful choice of the decomplexation reagent has to be made. Ce(NH₄)₂(NO₃)₆ in methanol,^{22,23} hydrogen peroxide under basic conditions,¹⁶ and interestingly, 3-chloroperoxybenzoic acid¹⁶ prove to be efficient, but with trimethylamine-*N*-oxide, complex mixtures containing ketonic derivatives were obtained.⁵⁹ Most importantly *no racemization* could be detected during these decomplexations, since compounds with optical purities higher than 95% were usually obtained. Representative examples of such dienes are given in Table 5.

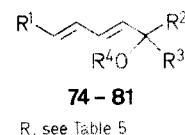


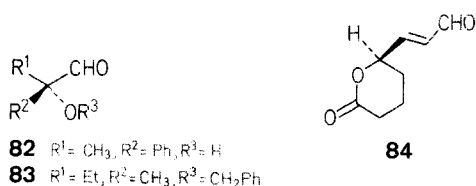
Table 5. Optically Active Dienes Prepared via Their Iron-Tricarbonyl Complexes

Compound	R ¹	R ²	R ³	R ⁴	Ref.
74	CO ₂ Me	CH ₃	H	H	22
75	CO ₂ Me	CH ₃	H	CH ₃	22
76	CO ₂ Me	CH ₃	H	H ^a	23
77	CO ₂ Me	CH ₃	H	COCH ₂ CO ₂ Et	67
78	CH ₃	CH ₃	Ph	H	16
79	CH ₃	CH ₃ CH ₂	CH ₃	H	16
80	CH ₃	(CH ₂) ₃ CO ₂ H	H	H	16
81	CH ₃		H	H	16

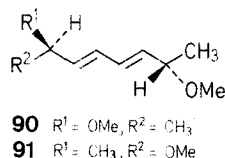
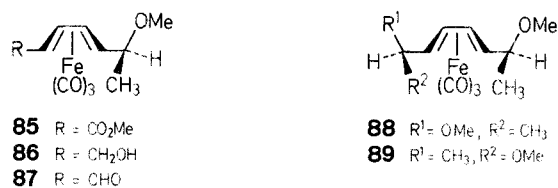
^a Diene with an *E, Z* configuration.

These functionalized dienes are themselves useful intermediates in organic synthesis, as it has already been demonstrated in several examples.

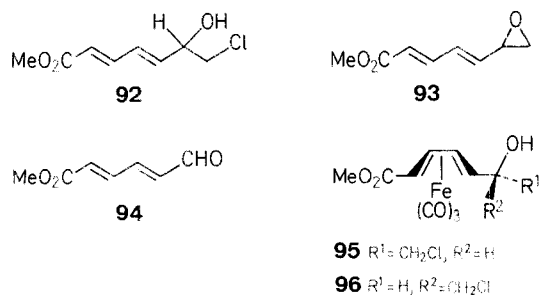
Ozonolytic cleavage of the diene leads to formyl derivatives. Thus, starting from **78** and **79** optically active α -hydroxy- and α -alkoxy aldehydes **82** and **83** were obtained.¹⁶ Interestingly, in the presence of pyridine only a partial ozonolysis was observed and chiral enal **84** was obtained from diene **81**.¹⁶



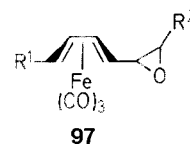
These organometallic complexes also offer a unique opportunity to control the relative (and, possibly, the absolute) configuration and the 1 and 6 position of a conjugated diene, as has been shown, for instance, in the case of **90** and **91**.⁶⁸ The complex **85**, easily obtained from **4**, is transformed into the aldehyde **87** via the alcohol **86**. After addition of the methyl Grignard, separation of the diastereoisomers and protection of the alcohols, the bis ethers **88** and **89** are obtained. The structure of these compounds has been unambiguously established by NMR utilizing the high symmetry of **88**. After decomplexation, the corresponding dienes **90** and **91** were used to test the cooperativity principle during Diels-Alder cycloadditions.⁶⁸



The organometallic complex proved to be a useful protecting group in the synthesis of chlorohydrin **92** and epoxide **93**.⁶⁹ The reaction of chloromethyl lithium with **94** gave only a low yield of **92**, but a similar reaction with **4** provided a 76% yield of the complexes **95** and **96**, which are easily separated by chromatography.

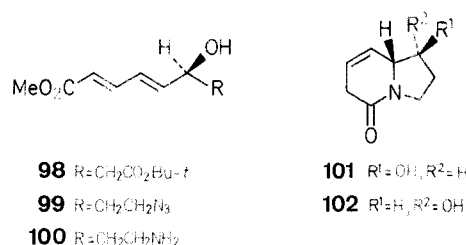


After decomplexation of **95** and **96**, the chlorohydrin **92** was smoothly converted into the epoxide **93**. In contrast, the complexed chlorohydrins **95** and **96** proved to be particularly reluctant to cyclization: irrespective of the reaction conditions used, only the starting material was recovered. In fact, it is interesting to point out that no example of epoxide of general structure **97** has been described to date.⁷⁰



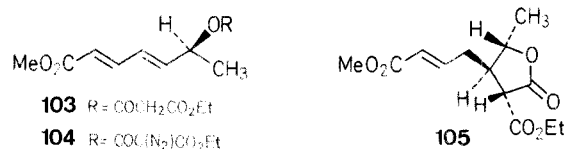
Such derivatives would be of much interest, because they are close to the basic skeleton of some natural products (leukotriene A_4 , for instance,⁷¹ and also because the organometallic moiety should modify the regio- and stereoselectivity of the ring opening of the epoxide. The synthesis and stability of type **97** epoxide remains, then, an open question.

The presence, after decomplexation, of the diene unit also offers attractive possibilities for intramolecular reactions. Thus, the diene **98**, obtained by decomplexation of **65** or **66** ($R^1 = \text{CO}_2\text{Me}, R^2 = \text{CH}_2\text{CO}_2\text{Bu}-t$), is the starting material for a new indolizidine synthesis.⁶¹ It is first transformed, in several steps, into the azide **99**, which is then reduced under mild and chemoselective conditions ($\text{Ph}_3\text{P}, \text{H}_2\text{O}$, room temperature)⁷² to the amine **100**.

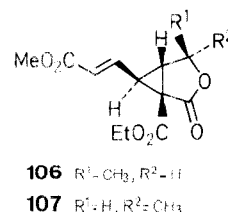


This intermediate first undergoes a 1,6-Michael-type addition, and then a second cyclization on the ester group to give the indolizidines **101** and **102** with good stereoselectivity (**101/102** = 80:20). In this reaction the organometallic complex plays a key role. First, starting from the corresponding chiral derivative, it would afford a possible control of the absolute configuration of the secondary alcohol functionality in **98**, and secondly, it directly introduces the electrophilic diene necessary for the intramolecular addition. The indolizidines **101** and **102** appear to be interesting starting materials for the synthesis of several alkaloids.

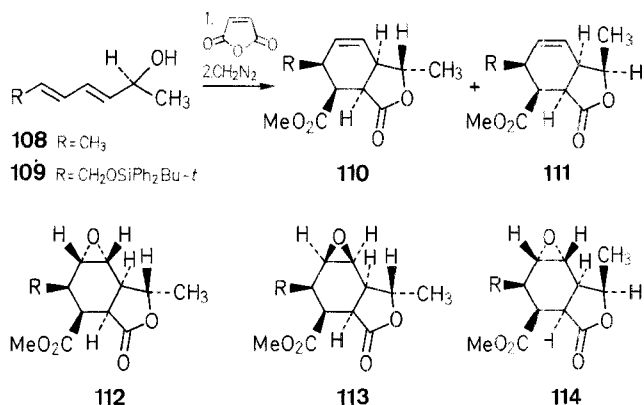
A similar 1,6-Michael-type addition is observed with the malonic ester derivative **103**. Reaction with DBU in acetonitrile leads, with a high diastereoselectivity, to the lactone **105** (in racemic form).⁶⁷



On the other hand, the intramolecular carbene type reaction of **104** in the presence of copper powder shows no selectivity in giving a 1:1 mixture of the racemic electrophilic⁷³ cyclopropanes **106** and **107**.⁶⁷



Intramolecular Diels–Alder cycloadditions⁷⁴ have also been described. The diene **108** reacts with maleic anhydride to give, after esterification, a 1 : 1 mixture of lactones **110** and **111**, which were separated by chromatography.



The epoxidation of **110** is highly stereoselective giving a 95 : 5 mixture of **112** and **113**. The reaction is stereospecific in the case of **111**, giving only **114**.⁷⁵ Diene **109** gave the same intramolecular Diels–Alder and epoxidation sequence.⁷⁵ These reactions were until now done only in racemic form; however, it appears that starting from an optically active complex, it would be possible to control in a short sequence *seven* asymmetric carbon atoms in these highly functionalized molecules.

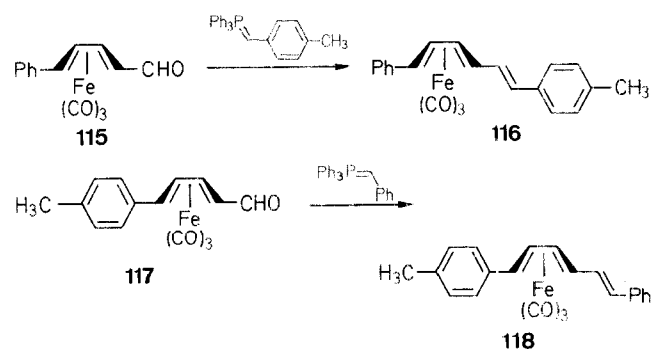
In conclusion, because of the easy access to different chiral butadiene–iron tricarbonyl complexes and the large variety of substituents that can be introduced by nucleophilic reactions, this approach affords a general entry into optically active and polyfunctionalized dienes, which are extremely useful building blocks in organic synthesis.

4.2. Regioselective Synthesis of Complexed Linear Polyenes

The presence in the same molecule of both “free” double bonds and a 1,3-diene temporarily protected as an iron tricarbonyl complex also offers excellent opportunities in organic synthesis, as will be described later. However, the regioselective preparation and the thermal stability of such molecules must be considered before describing their use in synthesis.

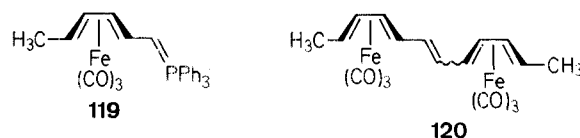
The direct complexation of trienes or higher polyenes does not appear to be very useful. Mixtures of positional isomers are commonly obtained, and in some cases, isomerism caused by the complexing agent and formation of polynuclear complexes (with two or more iron atoms) have also been observed.⁷⁶

The best approach is, thus, to use an olefination procedure. The Wittig-type reaction of complexed aldehydes with phosphoranes

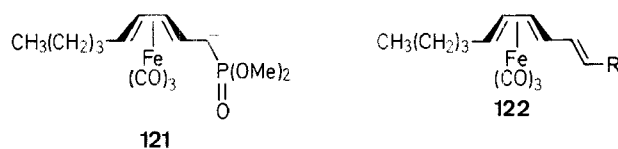


is efficient and occurs without bond-shift isomerization: complex **115**, for instance, gives only **116**, and **117** leads exclusively to **118**.⁷⁷ Stabilized^{17,18} and non-stabilized phosphoranes as well as phosphonate carbanions¹⁴ have been used in this type of reaction.

The inverse reaction, i.e. addition of complexed phosphoranes or phosphonate carbanions to aldehydes, has also recently been described. The stable ylide **119** reacts with **4** to give a mixture (*E/Z* = 3) of olefins **120**.³⁸



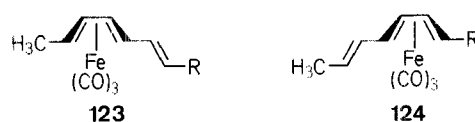
A systematic study has been carried out on the synthesis and reactivity of phosphonate **121**.⁷⁹ Condensation with various aldehydes gave the corresponding olefins **122** (exclusively *E*) in good to excellent yields.



R = Ph, 4-MeOC₆H₄, (CH₂)₄CH₃, CH=CH(CH₂)₂CH₃ (*E*),
 CH=CHCH=CH(CH₂)₂CH₃ (*E,E*)

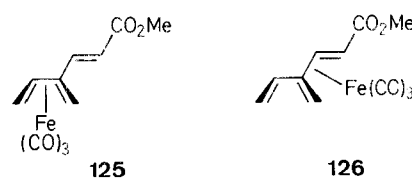
Sterically hindered aldehydes and ketones, however, do not react with **121**. Experiments with 1-²H-hexanal excluded any bond shift during this reaction.

Cope–Knoevenagel condensations also gave the expected olefins without isomerization.^{18,20,80} A different result, however, was obtained recently in the synthesis of several triene complexes.⁸⁰ The reaction of aldehyde **4** with acetone under *strongly* basic conditions does not give the expected compound **123**, but the bond shift isomer **124a** instead.



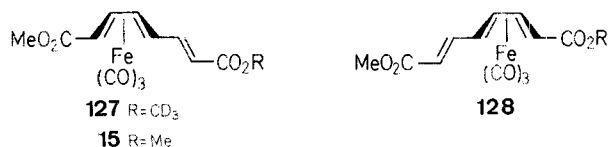
a: R = COCH₃; **b**: R = CN; **c**: R = CO₂Et

In the same way, LiCH₂CN and LiCH₂CO₂Et also lead to type **124** derivatives. By analogy with the mechanism proposed for the *syn-anti* isomerization of the butadiene–iron tricarbonyl complexes,²⁷ the first step in the reaction giving this bond shift could be the addition of the nucleophile to the iron. Isomerism has also been catalyzed by a Lewis acid. Complex **125** is smoothly converted into **126** on treatment with ether–borontrifluoride complex.⁸¹

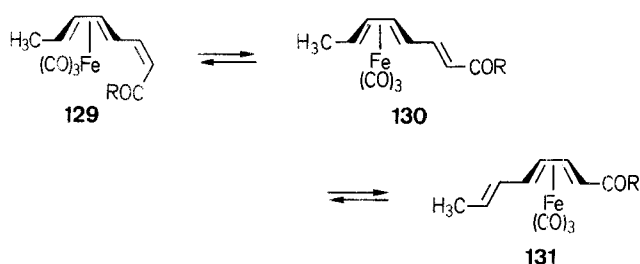


Thus, the structure of the complexed polyenes must be carefully established in each case, especially when strong nucleophiles or electrophiles are used.

The *thermal* bond shift of several polyene-iron tricarbonyl complexes has also been studied.⁷⁶ An activation energy of $138 \text{ kJ} \cdot \text{mole}^{-1}$ was measured for the transformation **116** \rightleftharpoons **118**.⁸² Similar results were obtained in the case of **127** and **128** and it was established on these models that racemization [$(-)-\mathbf{15} \rightarrow (\pm)\text{-}\mathbf{15}$] is 2.6 times slower than the bond shift.¹⁷



Interestingly, it was also observed, recently, that the *cis-trans* isomerization of double bonds vicinal to the organometallic complex (i.e. **129** \rightleftharpoons **130**) occurs *before* the bond shift (**130** \rightleftharpoons **131**).⁷⁸



a: R = OMe; b: R = Ph

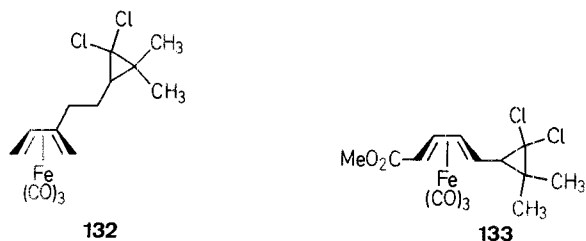
Thus, many polyenes, selectively, complexed in the desired position, are now easily accessible by any of these routes.

4.3. Reactions on the Uncoordinated Double Bonds in the Iron Tricarbonyl Complexes of Polyenes

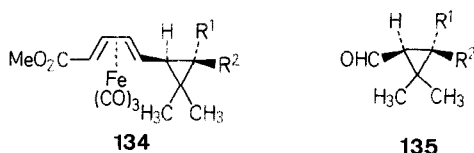
4.3.1. Cycloadditions

2 + 1: Carbenes

Dichlorocarbene addition to tricarbonyl complexes of polyenes have been described. The complex of myrcene, for instance, leads to **132**;⁸³ similarly, under phase-transfer-catalytic conditions, complex **18** gives the substituted cyclopropane **133**.^{18,84}



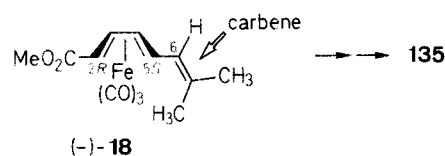
The carbene from methyl diazoacetate also reacts with $(-)-\mathbf{18}$ to give a 1:1 mixture of cyclopropanes **134a** and **134b**, which were separated by chromatography.



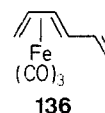
a: R¹ = CO₂Me, R² = H; b: R¹ = H, R² = CO₂Me

After decomplexation and ozonolysis, optically pure hemicaldonaldehydes **135** are obtained.²¹ It is important to note that for these cyclopropanations, as well as for many of the following reactions, *only one diastereoisomer is obtained at the C-C bond vicinal to the organometallic complex*.

Correlation between the absolute configuration (*2R,5S*) of the starting complex $(-)-\mathbf{18}$ and that of the product hemicaldonaldehydes (*3S*) implies an attack of the carbene *anti* to the Fe(CO)₃, if an *s-trans* configuration is assumed at the C₅-C₆ position, as indicated.



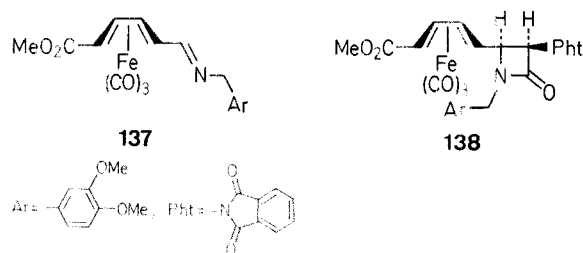
Although the Simmons-Smith reagent adds to the cycloheptatriene-iron tricarbonyl complex,⁸⁵ it does not react with the hexatriene **136**.⁸⁶



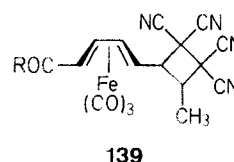
No nitrene addition on polyene-iron carbonyl complexes has yet been reported.

2 + 2: Ketene or Electrophilic Olefin

Only two examples of such reactions have been described. The cycloaddition of phthalimidoketene, generated *in situ*, with imine **137** gives the β -lactam **138** (52% yield)⁸⁷ and the polar addition of tetracyanoethylene (TCNE) to complexes **129** leads to cyclobutanes **139**.⁷⁸



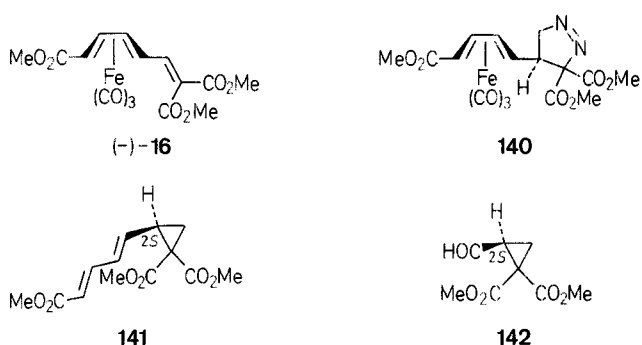
Although the stereochemistry of these adducts has not been fully established, it is interesting to note that in each case only one diastereoisomer has been obtained.



a: R = OMe; b: R = Ph

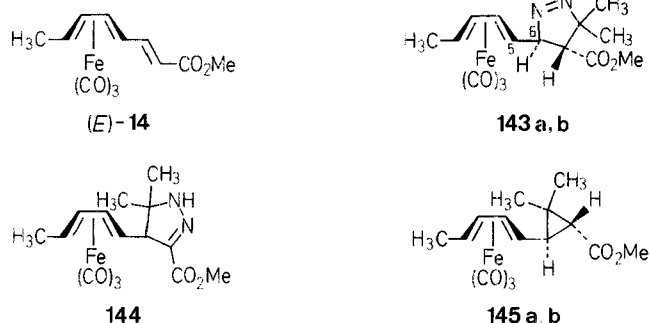
3 + 2: 1,3-Dipolar Cycloadditions

The use of temporarily protected polyenes has proven to be very fruitful in this type of cycloaddition. Reaction of diazomethane with $(-)-\mathbf{16}$ leads exclusively to pyrazoline **140**, which on reaction with Ce(NH₄)₂(NO₃)₆ gave the cyclopropane **141** directly.^{18,88}

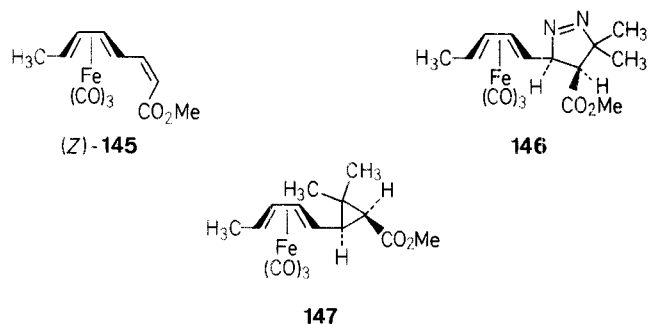


After ozonolysis, the optically pure derivative **142** was obtained. In agreement with the stereochemical outcome previously discussed, the *2S* absolute configuration of **142** indicates an addition of diazomethane *anti* to $\text{Fe}(\text{CO})_3$.

Cycloaddition of 2-diazopropane with complexes (*E*)-**14** and (*Z*)-**14** is also the key step in a chiral synthesis of hemicaronaldehydes.¹⁴ Reaction of the diazocompound with (+)-(*E*)-**14**⁸⁹ leads to the pyrazolines **143a** and **143b** (diastereoisomers at the C₅-C₆ bond), together with some Δ^2 -pyrazoline **144**. Thermolysis of **143a** and **143b** gave the cyclopropanes **145a** and **145b**, respectively.

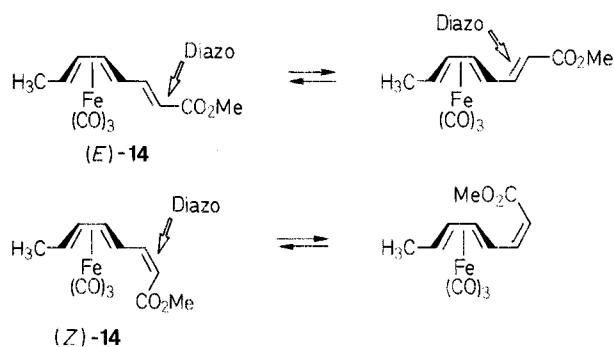


After decomplexation and ozonolysis pure (*1R,3R*)-hemicaronaldehyde was obtained.¹⁴ The same approach was used starting from (*Z*)-**14**: 2-diazopropane cycloaddition gave pyrazoline **146** (only one diastereoisomer) together with some Δ^2 -pyrazoline **144**.



Thermolysis of **146** gave a mixture of cyclopropanes **147** and **145b**, which were separated by chromatography. Decomplexation of **147**, followed by ozonolysis, gave optically pure (*1S,3R*)-hemicaronaldehyde.¹⁴

An important point to consider here is the diastereoselectivity of the cycloaddition. The reaction is only stereoselective in the case of (*E*)-**14**, but stereospecific for (*Z*)-**14**. This has been rationalized in terms of conformational equilibria.^{15,60}



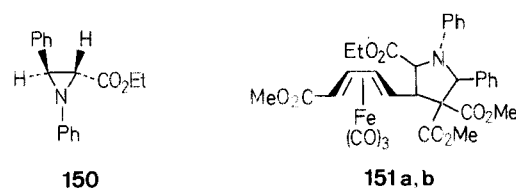
For (*E*)-**14**, the difference in energy between the two conformers is not large enough, and 2-diazopropane can react *anti* to $\text{Fe}(\text{CO})_3$ on *both* conformers to give a diastereoisomeric mixture of pyrazolines **143a** and **143b**. For (*Z*)-**14**, the equilibrium lies very much to the left, and the cycloaddition occurs only on this conformer giving a single pyrazoline **146**.

Similar results have been obtained in the case of **125**, which has a "free" double bond with an *E* configuration.

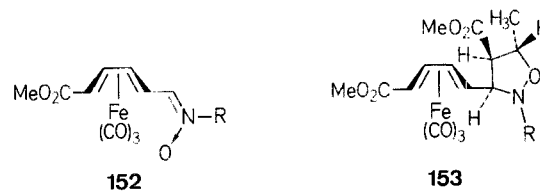


In this case 2-diazopropane gave a 4:1 mixture of pyrazolines **148a** and **148b**, whose thermolysis afforded the corresponding cyclopropanes **149**.¹⁵

An azomethine ylide, obtained by thermal ring opening of aziridine **150**, has also been added. Reaction with complex **16** leads to two pyrrolidines **151a** and **151b**.⁸⁷ The stereochemistry of these compounds, however, could not be established unambiguously.



Finally, nitrones **152** are examples of 1,3-dipoles directly linked to a butadiene-iron tricarbonyl complex.⁹⁰

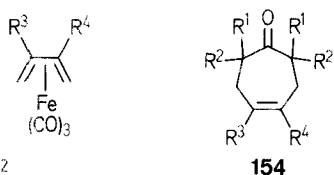


a: R = CH₃; b: R = Ph

Reaction with methyl crotonate gave isoxazolidine **153** whose stereochemistry (established by X-Ray analysis⁸⁷) is again in agreement with an addition of the dipolarophile *anti* to $\text{Fe}(\text{CO})_3$. Cycloadditions of **152** with dimethyl fumarate have also been reported.⁹⁰

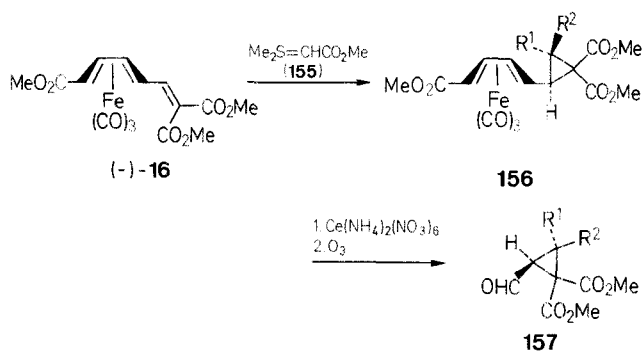
It should be noted that no examples of Diels-Alder or hetero-Diels-Alder reactions on complexed acyclic polyenes have been described, only unsuccessful attempts having been reported.⁸⁶ This may be due eventually to the fact that high temperatures are often necessary for these cycloadditions. Although the possibility of Lewis acid catalysis exists for this reaction, aluminum trichloride, for instance, is known to react directly with the $\text{Fe}(\text{CO})_3$ moiety,⁹¹ thus probably rendering this route impracticable.

Various butadiene-iron tricarbonyl complexes react with α,α' -dibromoketones to give cycloheptenones of the type **154** in a 4 + 3 cyclocoupling condensation.⁹²



4.3.2. Nucleophilic Additions

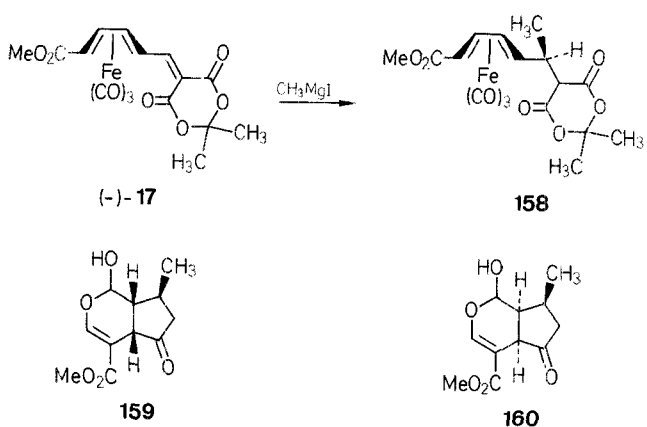
Addition of the sulfur ylide **155** to complex (-)-**16** gives a 45:55 mixture of cyclopropanes **156a** and **156b**, which were separated by chromatography.



a: $\text{R}^1 = \text{CO}_2\text{Me}$, $\text{R}^2 = \text{H}$; b: $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{CO}_2\text{Me}$

After decomplexation and ozonolysis, optically pure formylcyclopropanes **157** were obtained.¹⁸ The (2*S*,3*S*) configuration established in the case of **157b** is again in agreement with addition of the ylide *anti* to $\text{Fe}(\text{CO})_3$.⁸⁷

The 1,4-addition of methyl Grignard to complex (-)-**17** is also stereospecific *anti* to $\text{Fe}(\text{CO})_3$, giving enantiomerically pure complex **158**.

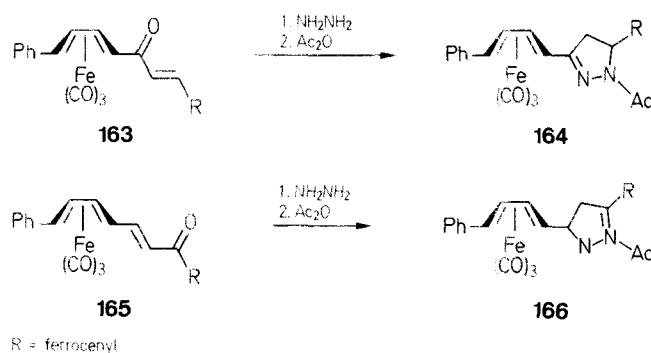


This reaction efficiently controls the absolute configuration of the carbon atom vicinal to the butadiene-iron tricarbonyl moiety. It is the first step in the total synthesis of (-)-verbenalol **159** and (-)-epiverbenalol **160**.²⁰

A 1,4-addition of the nitromethane anion was also observed in the case of complex **161** giving adduct **162**.⁸⁰



The asymmetric induction in the synthesis of pyrazolines carrying butadiene-iron tricarbonyl substituents has also been studied.⁹³

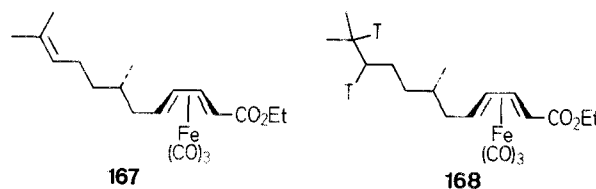


Better diastereoselectivity was found during the formation of **166**, where the asymmetric carbon is closer to the $\text{Fe}(\text{CO})_3$ moiety.

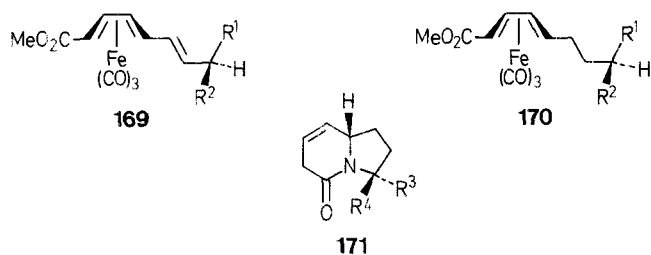
4.3.3. Miscellaneous Reactions

Iron tricarbonyl is an efficient protecting group for a diene system during remote hydrogenation of double or triple bonds. It has been used, for example, in the selective hydrogenation of a side-chain double bond in a complexed steroid.⁹⁴ The same methodology was recently followed in the synthesis of a tritium labelled hydroprene with high specific activity.

Homogeneous tritiation of **167** using a three-fold molecular excess of Wilkinson catalyst gave **168** in 93% yield; after decomplexation, the desired labelled insect growth regulator was obtained.⁹⁵

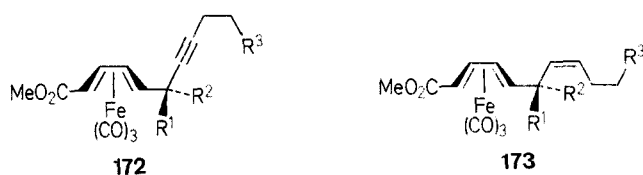


It is interesting to note that for reduction of double bonds homogeneous catalysts are necessary, since reduction of several polyenic complexes were unsuccessful using Pt or Pd on charcoal.⁹⁴⁻⁹⁶ Complexes **169a** and **169b** appear to be the only known exceptions probably due to the allylic alcohol function. Reduction of the double bond was carried out using platinum and hydrogen (5 bar), giving **170a** and **170b**. These complexes were intermediates for the preparation (in racemic form) of indolizidines **171**.⁶¹



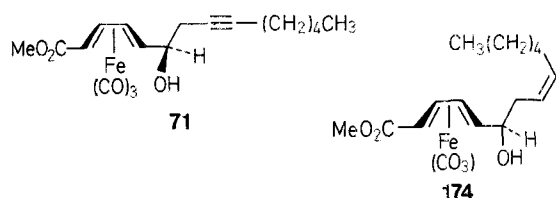
a: $R^1 = H, R^2 = OH$; **b:** $R^1 = OH, R^2 = H$; **c:** $R^3 = CH_3, R^4 = H$;
d: $R^3 = H, R^4 = CH_3$

On the other hand, semihydrogenation of triple bonds is usually very efficient using heterogeneous catalysts. Reaction of complexes **172** with hydrogen in the presence of palladium on charcoal stops cleanly at the *Z* olefinic systems **173**, irrespective of the *ψ-exo* or *ψ-endo* stereochemistry of the starting complex.^{59,62}

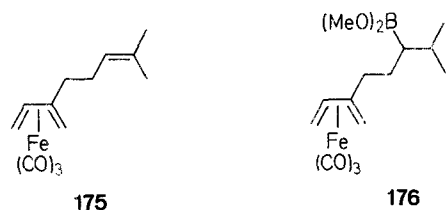


a: $R^1 = H, R^2 = OH, R^3 = OH$; **b:** $R^1 = OH, R^2 = H, R^3 = OH$;
c: $R^1 = H, R^2 = OH, R^3 = CH_3$; **d:** $R^1 = OH, R^2 = H, R^3 = CH_3$

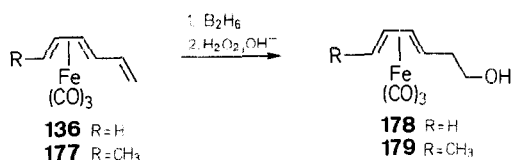
The synthesis of the leukotriene B_4 precursor **71** required semireduction of alkyne **71**;⁶⁴ this could not be done using Lindlar catalyst, but it was achieved, in a very good yield, using Nickel P2 catalyst.⁹⁷



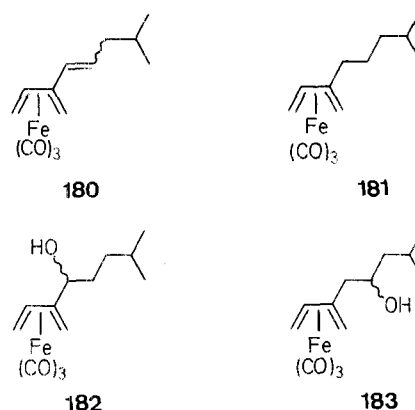
Diimide reduction of the free double bond was also achieved in the case of complex **175**, albeit in a relatively low yield (23%).⁹⁶ The same complex reacted with diborane to give, after treatment with methanol, adduct **176**.⁹⁶



Hydroboration of complexes **136** and **177** yielded, regioselectively, alcohols **178** and **179**.^{86,98}

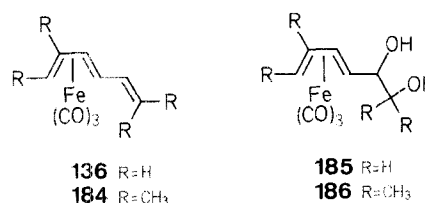


Surprising results were obtained in the case of complex **180**, where, depending upon the reaction conditions, either the reduced derivative **181** or a mixture of **181** along with the alcohols **182** and **183** was isolated.¹⁵

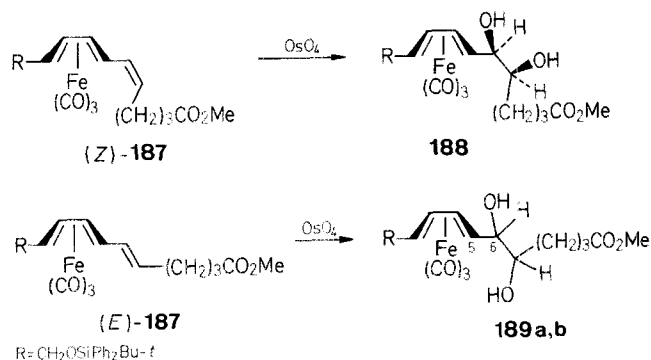


Of particular interest is the fact that, for all these hydroborations, an *oxidative work-up* (H_2O_2/OH^-) could be used without decomplexation.

Two other reagents, which proved to be compatible with the iron carbonyl moiety, are noteworthy because of their synthetic value. Osmylation of complexes **136** or **184** gave the corresponding glycols **185** and **186**.⁸⁶

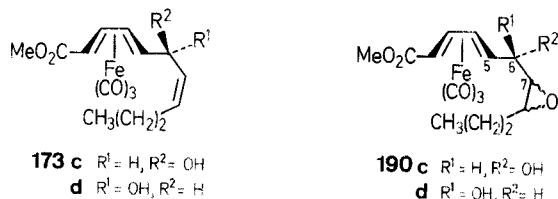


This reaction was successfully applied in the preparation of glycols **188** and **189**.⁹⁹



In agreement with the results previously described during the 2-diazopropane cycloaddition with complexes (*Z*)-**14** and (*E*)-**14**, the osmylation of (*Z*)-**187** is stereospecific and leads only to glycol **188** by reaction of OsO_4 *anti* to $Fe(CO)_3$. However, reaction of (*E*)-**187** is only highly stereoselective, giving a mixture (ca. 90:10) of glycols **189a** and **189b** diastereoisomeric at the C_5-C_6 bond.⁹⁹ The glycols **188** and **189** are key intermediates for the stereoselective synthesis of 5,6-DiHETES, which are leukotriene A_4 metabolites.¹⁰⁰

The Sharpless method of epoxidation $[\text{VO}(\text{acac})_2 + t\text{-BuOOH}]$ is also compatible with the butadiene-iron tricarbonyl complexes.¹⁰¹

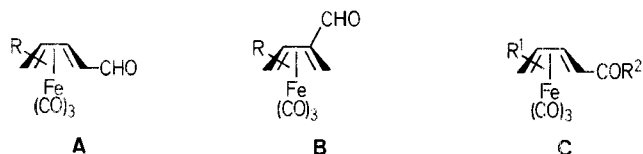


Reaction with allylic alcohols **173c** or **173d** gave epoxides **190c** and **190d** in excellent overall yields; in each case a 3:2 mixture of diastereoisomers at C₆-C₇ was obtained.⁶² These compounds appear to be interesting models in studying the influence of the organometallic moiety on the regio- and stereoselectivity of the epoxide ring opening.

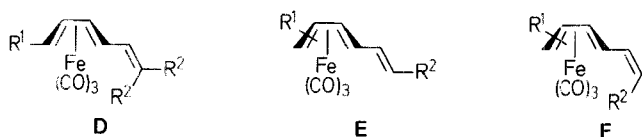
5. Conclusion

Acyclic butadiene-iron tricarbonyl complexes are easily accessible and versatile organometallics. The high stability of the $\text{Fe}(\text{CO})_3$ moiety towards many chemical reagents makes it particularly useful as a protecting group for 1,3-dienes. Being very bulky, $\text{Fe}(\text{CO})_3$ is also a good stereodirecting group; the diastereoselectivity of the reactions depending essentially upon the structure and the conformational properties of the starting complexes.

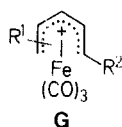
The main points can be summarized as follows: for type **A** and type **B** aldehydes, nucleophilic addition gives, in almost every case, a mixture of two diastereoisomers easily separated by chromatography, whilst reactions of type **C** ketones are stereospecific.



In the case of complexes bearing free double bonds, the results are strongly dependent upon the terminal substituents. The reactions are stereospecific in type **D** and **F** complexes, but only stereoselective for the type **E** derivatives.



Addition of nucleophiles to type **G** pentadienyl cations is also found to be stereospecific at the newly created asymmetric centre, whatever the *E,Z* or the *E,E* configuration of the butadienyl-iron tricarbonyl complexes obtained.

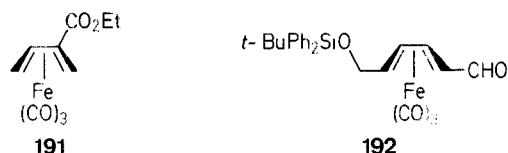


Finally, these complexes offer an unique opportunity of preparing 1,3-dienes of various types by controlling not only the nature of the substituents, but also, often in a predictable fashion, the

stereochemistry of the asymmetric centers. Some of these dienes have already proved to be useful intermediates in organic synthesis, and it is to be expected that these acyclic butadiene-iron tricarbonyl complexes will find many more applications in the future.

Addenda

Two other complexes have been obtained in pure chiral form: the 2-ethoxycarbonyl derivative **191** has been resolved using pig liver esterase, and its absolute configuration was unambiguously established by X-Ray analysis.¹⁰²



The bifunctional complex **192** has also been resolved via the formation of distereoisomeric imidazolidines;¹⁰³ in the case of (-)-**192**, the absolute configuration could be established by correlation with the (2*S*,5*R*) complex (+)-**5**.¹⁰⁴

The chiral complex of sorbic acid (-)-**2** proved to be also itself an efficient resolving agent for some allylic alcohols, which are useful precursors of fatty acid metabolites.¹⁰⁵

Several studies have dealt with the synthetic uses of complexed pentadienyl cations. Alkynyl nucleophiles react exclusively at the non-substituted terminus to afford (η^4 -*trans*, *cis*-1,3,6-dienyne) $\text{Fe}(\text{CO})_3$ complexes, which appear as interesting intermediates in the field of icosanoids.¹⁰⁶ Different results, however, were obtained with cations derived from **41**: phosphorus nucleophiles¹⁰⁷ and also malonic anions¹⁰⁸ lead, at least in part, to σ - π allyl derivatives through reaction on a non-terminal atom of the complexed cation.

Finally, it is interesting to point out that type **97** epoxides have been prepared recently for the first time in Franck-Neumann's group.¹⁰⁹

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