# Efficient Synthesis of Tricarbonyliron–Diene Complexes — Development of an Asymmetric Catalytic Complexation†

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*Received March 10, 2000*

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## *I. Introduction*

The application of transition metals to organic synthesis has been one of the most active research areas in organic chemistry over the past decades.[1−9] The progress which has been achieved in the field of synthetic organometallic chemistry is of course also based on the increased *know how* in the handling of air- and moisture-sensitive organometallic compounds on a scale useful for synthetic purposes.[10,11] Transition metal carbonyl $\pi$-complexes of unsaturated hydrocarbons have played a pivotal role in this tremendous development. They are generally prepared by either photochemical or thermal reaction of the transition metal carbonyl with the unsaturated hydrocarbon. Especially the tricarbonyl($\eta^4$-diene)iron complexes have found versatile applications to the regio-, diastereo-, and enantioselective synthesis of organic compounds including biologically active natural products and as a protecting group for labile diene systems.[12−30]

† Part 60 of Transition Metal Complexes in Organic Synthesis. For part 59, see: Knölker, H.-J.; Baum, E.; Reddy, K. R. *Chirality* **2000**, *12*, 526.

Hans-Joachim Knölker was born in Rehren, Germany, in 1958. He studied chemistry at the universities of Göttingen and Hannover, where he received his diploma degree in Chemistry in 1983 and his Ph.D. degree in 1985 with Professor E. Winterfeldt. He became interested in organometallic chemistry during his postdoctoral studies in 1986 in the research group of Professor K. P. C. Vollhardt at the University of California in Berkeley. In 1987 he returned to the University of Hannover and finished his habilitation in 1990. Since 1991 he has been Full Professor of Organic Chemistry at the University of Karlsruhe. His research interests include organotransition metal chemistry, organosilicon chemistry, isocyanate chemistry, and the synthesis of fluorescent imidazole derivatives.

This review describes selective procedures for the efficient synthesis of tricarbonyliron−diene complexes as starting materials for organic synthesis with the main focus on cyclohexadiene ligands. The tricarbonyl($\eta^4$-cyclopentadienone)iron complexes and the tricarbonyl($\eta^4$-cyclobutadiene)iron complexes, which both are usually not obtained from the corresponding free ligands,[1−6] are not covered. Beginning with the classical procedures for the preparation of tricarbonyliron−diene complexes from the corresponding dienes, the development of tricarbonyliron transfer reagents and the catalytic complexation of dienes by the tricarbonyliron fragment are described. Finally, the asymmetric catalytic complexation of prochiral cyclohexa-1,3-dienes is highlighted.

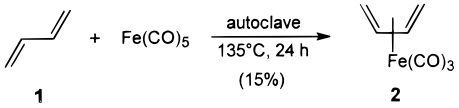
## *II. Classical Preparation of Tricarbonyl($\eta^4$-1,3-diene)iron Complexes*

The classical procedure for the preparation of tricarbonyliron−diene complexes is based on the complexation of dienes by direct reaction with the binary carbonyliron compounds pentacarbonyliron, nonacarbonyldiiron, or dodecacarbonyltriiron using either thermal or photolytic conditions. Reihlen et al.

10.1021/cr990267k CCC: $35.00 
Published on Web 07/12/2000

described the first synthesis of the parent complex, ($\eta^4$-buta-1,3-diene)tricarbonyliron **(2)**, by thermal reaction of an excess of buta-1,3-diene **(1)** with pentacarbonyliron in an autoclave and obtained complex **2** in 15% yield based on pentacarbonyliron (Scheme 1).[31] This was the first report of a transition

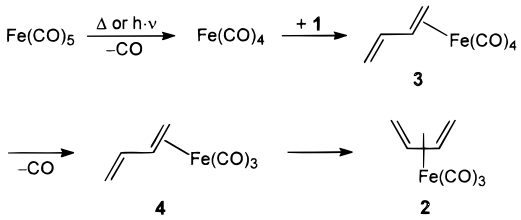
**Scheme 1**




metal−diene complex, which represents a highly useful class of organometallic compounds.

The coordination of the diene to the tricarbonyliron fragment is initiated by the loss of carbon monoxide from pentacarbonyliron, which can be induced in a thermal or photolytic reaction (Scheme 2). The re-

**Scheme 2**




sulting tetracarbonyliron fragment represents a 16-electron species with a vacant coordination site, which thus binds to an olefinic double bond of the diene **1** to provide the ($\eta^2$-buta-1,3-diene)tetracarbonyliron complex **(3)**. A further loss of a carbon monoxide ligand affords the coordinatively unsaturated complex **4**. After conversion of the butadiene from the *s-cis* into the *s-trans* conformation, a haptotropic migration ($\eta^2$ to $\eta^4$) of the metal fragment provides complex **2**.

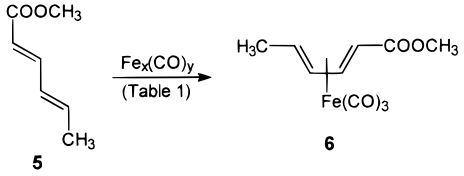
A broad range of tricarbonyliron−butadiene complexes was obtained based on the original procedure of Reihlen by thermal reaction of pentacarbonyliron with the corresponding butadienes.[32−35] However, to generate the coordinatively unsaturated tetracarbonyliron fragment by direct thermal reaction from pentacarbonyliron, energy is required which corresponds to a temperature of about 135−140 °C (xylene at reflux). Side reactions take place to a large extent under these reaction conditions, especially with reactive diene systems. Therefore, organometallic chemists were seeking milder conditions providing the tricarbonyliron−butadiene complexes with higher selectivity. Using pentacarbonyliron, this can be achieved by a photolytic induction of the reaction. Lower temperatures in the thermal reaction are feasible with the more labile but also more expensive carbonyliron cluster compounds nonacarbonyldiiron and dodecacarbonyltriiron, for which 60−80 °C is sufficient to achieve complexation of the diene. A large variety of substituents and functional groups is tolerated for the coordination of the buta-1,3-diene to the metal fragment, and nonconjugated butadienes generally undergo an isomerization to provide the ($\eta^4$-buta-1,3-diene)tricarbonyliron complexes.[32−35] The

**Table 1. Complexation of Methyl Sorbate (5) by Direct Reaction with a Binary Carbonyliron Compound**

| $Fe_x(CO)_y$ | reaction conditions | **6**, yield [%] | ref |
|---|---|---|---|
| $Fe(CO)_5$ (1.1 eq) | **5**, *n*-$Bu_2O$, 142 °C, 8 h | 43 | 37 |
| $Fe(CO)_5$ (1.1 eq) | **5**, *n*-$Bu_2O$, $AlCl_3$ (5%), 142 °C, 8 h | 62 | 37 |
| $Fe_2(CO)_9$ (1.1 eq) | **5**, benzene, ultrasound, 1 h | 100 | 38, 39 |

development of more selective techniques for the synthesis of tricarbonyliron−butadiene complexes is demonstrated for the complexation of methyl sorbate **(5)**, as an example (Scheme 3, Table 1).

**Scheme 3**




Stone and co-workers first reported the synthesis of the tricarbonyliron complexes of sorbic acid derivatives including ethyl sorbate by heating the appropriate diene with dodecacarbonyltriiron in benzene at reflux.[36] However, no yields were given. A widely used method for the synthesis of tricarbonyliron−diene complexes is the direct reaction of dienes with pentacarbonyliron by heating in di-*n*-butyl ether at reflux, first described by Cais and Maoz.[37] Using these conditions, methyl sorbate **(5)** was transformed to complex **6** in 43% yield. These authors also reported that the yields for the complexation of butadiene carboxylic acid esters are significantly increased if catalytic amounts of Lewis acids, like aluminum trichloride or boron trifluoride, are added. Thus, complex **6** could be obtained in 62% yield in the presence of anhydrous aluminum trichloride (5 wt %).[37] An interesting procedure is the ultrasound-promoted complexation of 1,3-dienes with nonacarbonyldiiron at room temperature reported by Ley and co-workers.[38,39] This method proved to be most efficient for buta-1,3-dienes, and in the case of methyl sorbate **(5)**, sonication with nonacarbonyldiiron in benzene provided complex **6** quantitatively.

Cyclic dienes readily afford the corresponding tricarbonyliron complexes. The first example was described by Hallam and Pauson in 1958. They prepared tricarbonyl($\eta^4$-cyclohexa-1,3-diene)iron **(8)** in 21% yield using the original procedure of Reihlen, by heating pentacarbonyliron with an excess of cyclohexa-1,3-diene **(7a)** in an autoclave (Scheme 4,

**Scheme 4**

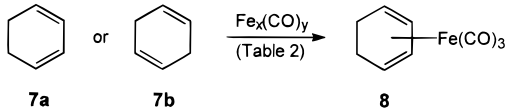



Table 2).[40] The simple quantitative hydride abstraction with triphenylmethyl tetrafluoroborate to tricarbonyl($\eta^5$-cyclohexadienylium)iron tetrafluoroborate reported by Fischer in 1960[41] and the resulting

**Table 2. Complexation of Cyclohexadiene 7 by Direct Reaction with a Binary Carbonyliron Compound**

| $Fe_x(CO)_y$ | reaction conditions | **8**, yield [%][a] | ref |
|---|---|---|---|
| $Fe(CO)_5$ | **7a** (1.5 equiv), autoclave, 135−140 °C, 24 h | 21 | 40 |
| $Fe(CO)_5$ | **7b** (3.3 equiv), benzene, h·$\nu$ (125 W, Hg), 50 h | 56 | 43 |
| $Fe(CO)_5$ | **7b** (0.7 equiv), *n*-$Bu_2O$, 142 °C, 18 h | 23 | 45 |
| $Fe_2(CO)_9$ | **7a** (3.0 equiv), 1,2-dimethoxyethane, 85 °C, 16 h | 21 | 46 |
| $Fe_2(CO)_9$ | **7a** (1.2 equiv), tetrahydrofuran, 65 °C, 6 h | 22 | 46, 47 |
| $Fe_2(CO)_9$ | **7a** (excess), tetrahydrofuran, ultrasound | 16 | 46 |
| $Fe(CO)_5$ | **7a** (1.5 equiv), hexane, h·$\nu$ (150 W, Hg), 24 h | 77 | 47 |

[a] All yields are based on the tricarbonyliron equivalents, except in entry 3, where the yield is based on **7b** for a single-stage procedure.

**Table 3. Complexation of Methoxycyclohexadiene 9 by Direct Reaction with a Binary Carbonyliron Compound**

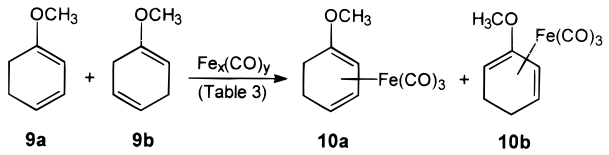
| $Fe_x(CO)_y$ | reaction conditions | **10**, yield [%][a] | ref |
|---|---|---|---|
| $Fe_3(CO)_{12}$ | **9a**/**9b** (3.4 equiv), benzene, 80 °C, 4 h | 30 | 43 |
| $Fe_3(CO)_{12}$ | **9b** (3.4 equiv), benzene, 80 °C, 4 h | 32 | 43 |
| $Fe_2(CO)_9$ | **9b** (excess), $Et_2O$, 35 °C, 7 h | 10 | 43 |
| $Fe(CO)_5$ | **9b** (1.1 equiv), *n*-$Bu_2O$, 142 °C, 55 h | 42 | 44, 45, 48 |
| $Fe_2(CO)_9$ | **9b** (2.0 equiv), 1,2-dimethoxyethane, 85 °C, 15 h | 24 | 46 |
| $Fe_2(CO)_9$ | **9b** (1.5 equiv), tetrahydrofuran, 65 °C, 15 h | 32 | 46 |

[a] All yields refer to the mixture of the regioisomers **10a** and **10b** and are based on the tricarbonyliron equivalents.

reactivity toward nucleophiles made complex **8** to a versatile starting material for organic synthesis.[12−16,20−25,27,29,30] Several alternative procedures for the synthesis of complex **8** by direct reaction with a binary carbonyliron compound were described (Table 2). Arnet and Pettit found that cyclohexa-1,4-diene **(7b)** and pentacarbonyliron react with concomitant isomerization of the diene to provide complex **8**.[42] On the basis of this observation, Lewis and co-workers showed that the photolytic reaction of cyclohexa-1,4-diene **(7b)** with pentacarbonyliron in benzene using a 125 W mercury lamp afforded complex **8** in 56% yield.[43] Birch and his group used the method of Cais and Maoz[37] for the synthesis of tricarbonyliron complexes of cyclic dienes.[44] Thus, heating cyclohexa-1,4-diene **(7b)** with an excess of pentacarbonyliron in di-*n*-butyl ether under reflux provided complex **8** in about 23% yield (single-stage procedure).[45] The authors reported that the yield is about twice as high by resubmission of the excess starting materials (**7b** and pentacarbonyliron) to the reaction conditions. Alternatively, complex **8** can be prepared at lower temperatures in up to 22% yield based on iron by heating nonacarbonyldiiron with an excess of cyclohexa-1,3-diene **(7a)** in either 1,2-dimethoxyethane or tetrahydrofuran under reflux.[46,47] The application of Ley's ultrasound-promoted complexation[38,39] to the reaction of cyclohexa-1,3-diene **(7a)** with nonacarbonyldiiron afforded complex **8** in only 16% yield along with large amounts of dodecacarbonyltriiron.[46] An increase of the yield for complex **8** using the photochemical reaction, earlier applied by Lewis to the 1,4-diene **7b**,[43] was achieved with the conjugated isomer **7a** as starting material.[47] Irradiation of pentacarbonyliron with an excess of cyclohexa-1,3-diene **(7a)** in hexane using a 150 W mercury lamp provided complex **8** in 77% yield (Scheme 5, Table 3).

The complexation of dihydroanisole **(9)** by the tricarbonyliron fragment was reported first by Lewis and his group.[43] This reaction usually leads to a regioisomeric mixture of tricarbonyl($\eta^4$-1-methoxycyclohexa-1,3-diene)iron **(10a)** and tricarbonyl($\eta^4$-2-methoxycyclohexa-1,3-diene)iron **(10b)**. Heating of dodecacarbonyltriiron with either a mixture of 1-methoxycyclohexa-1,3-diene **(9a)** and 1-methoxycyclohexa-1,4-diene **(9b)** or pure **9b** in benzene under reflux afforded a mixture of the regioisomeric tricarbonyliron complexes **10a** and **10b** in up to 32% yield. Reaction of 1-methoxycyclohexa-1,4-diene **(9b)** with nonacarbonyldiiron in diethyl ether under reflux provided the regioisomeric complexes **10** in only 10% yield.[43] An application of the method of Cais and Maoz[37] to the complexation of 1-methoxycyclohexa-1,4-diene **(9b)** was reported by the groups of Birch[44,45] and Ireland.[48] Thus, heating pentacarbonyliron with **9b** in di-*n*-butyl ether under reflux for more than 2 days afforded the regioisomeric complexes **10** in 42% yield.[48] The yield for the complexation of 1-methoxycyclohexa-1,4-diene **(9b)** using nonacarbonyldiiron could be increased by heating in either 1,2-dimethoxyethane or tetrahydrofuran under reflux, which afforded the regioisomeric mixture of **10** in 24% and 32% yield, respectively.[46]

**Scheme 5**

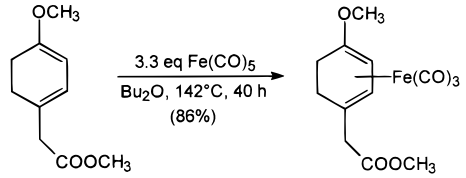



Since a variety of substituted cyclohexa-1,4-dienes is available by the Birch reduction of the corresponding benzene derivatives, this reaction opened up the way to the synthesis of a broad range of tricarbonyl($\eta^4$-cyclohexa-1,3-diene)iron complexes. The subsequent complexation in most cases was achieved using the method of Cais and Maoz[37] as modified by Birch,[44,45] which became a standard procedure. Using this two-step reaction sequence, many alkylbenzenes, alkoxybenzenes, alkoxyalkylbenzenes, and benzoic acid derivatives were transformed to the corresponding tricarbonyliron−cyclohexa-1,3-diene complexes, mainly by the groups of Birch and Pearson. However, the yields of the complexation step were usually only

moderate (30−50%).[44,48−55] This is, at least in some cases,[45] due to the high volatility of the cyclohexa-1,4-dienes and because of the harsh reaction conditions (heating for many hours at 142 °C) which promote side reactions for the reactive dienes. However, for some dienes considerably better results could be obtained.

Thus, Pearson described the complexation of methyl (4-methoxycyclohexa-1,3-dienyl)acetate **(11)** by heating with 3.3 equiv of pentacarbonyliron in di-*n*-butyl ether under reflux for 40 h, which provides the corresponding tricarbonyliron complex **12** in 86% yield (Scheme 6).[56]

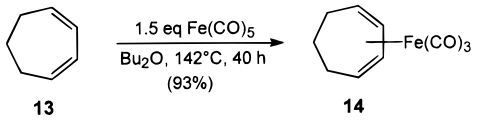
**Scheme 6**




**11** **12**

The optimized procedure for the complexation of cyclohepta-1,3-diene **(13)** reported by Pearson proceeds in high yield.[57] Heating of **13** with 1.5 equiv of pentacarbonyliron in di-*n*-butyl ether under reflux for 44 h led in 93% yield to tricarbonyl($\eta^4$-cyclohepta-1,3-diene)iron **(14)** (Scheme 7), which exhibits useful reactivity.[57]

**Scheme 7**

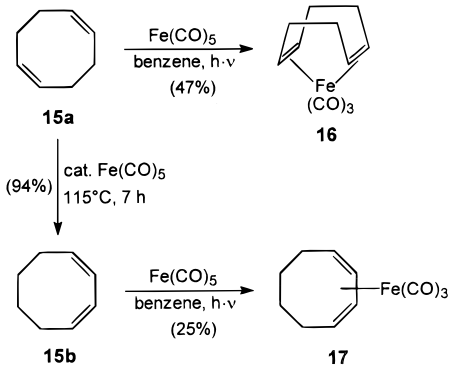



**13** **14**

As mentioned above, the complexation of nonconjugated butadienes and cyclohexadienes to the tricarbonyliron fragment generally occurs with concomitant isomerization of the diene to provide the tricarbonyliron complex of the corresponding conjugated diene. An exception represents the tricarbonyliron complex of norbornadiene (bicyclo[2.2.1]hepta-2,5-diene),[58,59] where such an isomerization is not possible.

In this context, the reaction between cycloocta-1,5-diene **(15a)** and pentacarbonyliron was investigated with the objective to extend the series of nonconjugated diene−tricarbonyliron complexes (Scheme 8).[36,42,60] It was reported that on heating **15a** with pentacarbonyliron, no organometallic complex was formed but a quantitative isomerization to cycloocta-1,3-diene **(15b)** occurred.[42] This isomerization can even be effected with catalytic amounts of pentacarbonyliron. After some original structural assignments[36] were questioned,[34] Koerner von Gustorf and Hogan unequivocally established the structures of the metal complexes which derive from **15a** using alternative reaction conditions.[60] Thus, the photochemical reaction of pentacarbonyliron with an excess of cycloocta-1,5-diene **(15a)** provided tricarbonyl($\eta^4$-cycloocta-1,5-diene)iron **(16)**. This reaction was shown to proceed via the intermediate tetracarbonyl($\eta^2$-

**Scheme 8**

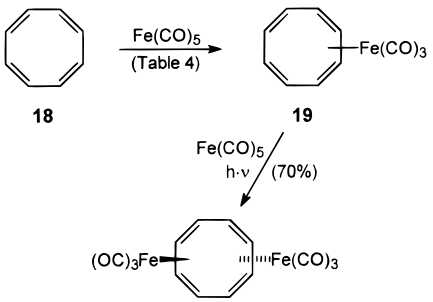



**15a** **16** **15b** **17**

cycloocta-1,5-diene)iron complex. Tricarbonyl($\eta^4$-cycloocta-1,3-diene)iron **(17)** was formed by the photochemical reaction of pentacarbonyliron with an excess of cycloocta-1,3-diene **(15b)**. Complex **17** is thermally less stable than complex **16**. This is explained by the conformational strain resulting from the conjugated double bonds which are forced into one plane because of the coordination to the metal fragment. Generally the reaction of pentacarbonyliron with nonconjugated dienes causes an isomerization and affords the conjugated diene as the stable tricarbonyl($\eta^4$-1,3-diene)iron complex. In the present case, however, the low thermal stability of complex **17** rationalizes that under thermal reaction conditions, only catalytic amounts of pentacarbonyliron are required for the isomerization of **15a** to **15b**, as found by Pettit and co-workers.[42]

The synthesis of the cyclooctatetraene−tricarbonyliron complex was reported independently by three research groups in 1959 (Scheme 9, Table 4).[61−64]

**Scheme 9**




**18** **19** **20**

From the thermal reaction of cyclooctatetraene **(18)** with pentacarbonyliron, tricarbonyl[(1−4-$\eta$)-cyclooctatetraene]iron **(19)** was obtained as the major product (60% yield) along with the cyclooctatetraene-hexacarbonyldiiron complex **20** as byproduct (8% yield).[61,62] The photochemical reaction of pentacarbonyliron with a slight excess of **18** provided exclusively complex **19** in 72% yield.[63] Increasing the amount of pentacarbonyliron led to the formation of complex **20** at the expense of complex **19**.[63,64] Moreover, it was demonstrated that the photochemical reaction of complex **19** with an excess of pentacarbonyliron led to the cyclooctatetraene-hexacarbonyldiiron complex **20** in 70% yield.[63] An X-ray crystal structure determination of complex **19** revealed that

**Table 4. Complexation of Cyclooctatetraene (18) by Direct Reaction with a Binary Carbonyliron Compound**

| $Fe(CO)_5$ | reaction conditions | **19**, yield [%] | ref |
|---|---|---|---|
| 1.4 equiv | **18**, ethylcyclohexane, 132 °C, 24 h | 60 | 61, 62 |
| 0.9 equiv | **18**, hexane, h·$\nu$, 24 h | 72 | 63 |
| 2.0 equiv | **18**, THF, $Me_3NO$ (4.0 equiv), 0 °C, then 65 °C, 1 h | 80 | 67 |

the tricarbonyliron fragment is coordinated to a 1,3-diene unit,[65] in contrast to one of the earlier structural assignments.[64] In the dinuclear complex **20**, the two tricarbonyliron fragments are each coordinated to a different 1,3-diene unit with the two metals oriented anti to each other, as confirmed by X-ray analysis.[66]

The first step of the coordination of a diene to the tricarbonyliron fragment in the reaction with pentacarbonyliron is the generation of a 16-electron tetracarbonyliron fragment by loss of a carbon monoxide ligand (see Scheme 2). This process can be initiated either thermally, by heating at 135−140 °C, or photolytically, by irradiation using UV light, or chemically, by oxidation with trimethylamine *N*-oxide as shown by Shvo and Hazum.[67] Trimethylamine *N*-oxide represents a versatile oxidizing reagent which can promote substitution reactions at metal carbonyl complexes.[68−70] Alper and Edward showed that amine *N*-oxides are reduced to the corresponding amines on reaction with pentacarbonyliron.[71] In this reaction, a carbon monoxide ligand is oxidized to carbon dioxide. On the basis of this conversion, Shvo and Hazum developed a novel procedure for the demetalation of tricarbonyl($\eta^4$-diene)iron complexes to the free ligands by treatment with 8 equiv of trimethylamine *N*-oxide.[72] The reverse reaction, the trimethylamine *N*-oxide-promoted complexation of 1,3-dienes by the tricarbonyliron fragment on reaction with pentacarbonyliron, was reported by the same authors.[67] This transformation is achieved by treatment of the diene with 2 equiv of pentacarbonyliron in the presence of 4 equiv of trimethylamine *N*-oxide in an inert solvent at 0 °C and subsequently for 1 h under reflux to complete the reaction. Application of this method to the complexation of cyclooctatetraene **(18)** afforded complex **19** in 80% yield.[67] The mechanism proposed for this reaction involves the tetracarbonyliron−trimethylamine complex, which could be isolated from the reaction of pentacarbonyliron with trimethylamine *N*-oxide in tetrahydrofuran at −30 °C.[73] It is known that tetracarbonyliron−amine complexes can dissociate at room temperature and thus represent a convenient source for the 16-electron tetracarbonyliron fragment.[69] In fact, reaction of the tetracarbonyliron−trimethylamine complex with an equimolar amount of cyclooctatetraene **(18)** in benzene at 60 °C provided complex **19** in 55% yield.[73] However, a further intermediate, a tetracarbonyliron−dimethylamine complex, which would be related to those intermediates found for the demetalation reaction using trimethylamine *N*-oxide,[74,75] might be involved as well.

## *III. Complexation of Dienes Using Tricarbonyliron Transfer Reagents*

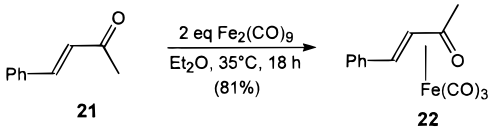
The classical procedure for the synthesis of tricarbonyl($\eta^4$-1,3-diene)iron complexes, as described in the previous section, involves either thermal or photochemical reaction of the diene with a binary carbonyliron compound, $Fe(CO)_5$, $Fe_2(CO)_9$, or $Fe_3(CO)_{12}$. However, complexations are achieved under much milder reaction conditions and thus generally with higher selectivity by using tricarbonyliron transfer reagents.[76] Tricarbonyliron transfer reagents are complexes of the tetracarbonyliron or the tricarbonyliron fragment with ligands which show only a relatively weak coordination to the metal. Because of the lability of these complexes, they readily generate 16-electron species which can then bind to one of the double bonds of a 1,3-diene. This coordination initiates the transfer of the metal fragment to the 1,3-diene, which provides the thermodynamically more stable tricarbonyl($\eta^4$-1,3-diene)iron complex. Therefore, tricarbonyliron transfer reagents offer a useful alternative, especially for the preparation of tricarbonyliron complexes of dienes which are sensitive toward heat or UV light.

It should be noted that the tetracarbonyliron−trimethylamine complex mentioned above[73] represents such a tricarbonyliron transfer reagent as demonstrated by the transfer to cyclooctatetraene. Thus, the trimethylamine *N*-oxide-promoted complexation of 1,3-dienes with pentacarbonyliron[67] may be regarded as an in situ generation of this transfer reagent.

### 1. Tricarbonyl($\eta^4$-1-oxabuta-1,3-diene)iron Complexes

The tricarbonyl($\eta^4$-1-oxabuta-1,3-diene)iron complexes, first reported by Weiss in 1964,[77] were introduced as tricarbonyliron transfer reagents for the first time by Lewis in 1972.[78] The standard reagent is ($\eta^4$-benzylideneacetone)tricarbonyliron, (bda)$Fe(CO)_3$,[76,78] which was obtained from benzylideneacetone by thermal reaction with 1 equiv of nonacarbonyldiiron (toluene, 60 °C, 4−5 h; 32% yield).[78−80] Alternatively, the photochemical reaction of 2.8 equiv of pentacarbonyliron with benzylideneacetone affords ($\eta^2$-benzylideneacetone)tetracarbonyliron,[81] which on subsequent thermal reaction (benzene, 60 °C) is converted to (bda)$Fe(CO)_3$ in 60% yield as described by Brookhart.[82−84] A more convenient method reported by Thomas involves heating of benzylideneacetone **(21)** with 2 equiv of nonacarbonyldiiron in diethyl ether under reflux and provides (bda)$Fe(CO)_3$ **(22)** in 81% yield based on benzylideneacetone (Scheme 10).[85,86] However, one has to consider that nonacarbonyldiiron is the more expen-

**Scheme 10**



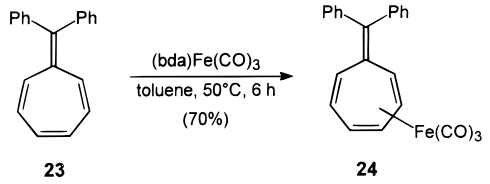

21 22

sive component and that the yield of (bda)Fe(CO)$_3$ based on the tricarbonyliron equivalents is only 20%.

The (bda)Fe(CO)$_3$ complex **(22)** serves as a convenient source of the tricarbonyliron fragment for the synthesis of tricarbonyl($\eta^4$-1,3-diene)iron complexes under mild conditions. The reaction of complex **22** and 1,3-dienes generally occurs at 50−60 °C with smooth transfer of the metal fragment to the 1,3-diene and provides the corresponding tricarbonyliron complex in high yield.

Heating a solution of 8,8-diphenylheptafulvene **(23)** in toluene with a slight excess of (bda)Fe(CO)$_3$ **(22)** at 50 °C for 6 h provides the tricarbonyliron complex **24** in 70% yield (Scheme 11).[78] In this case, the

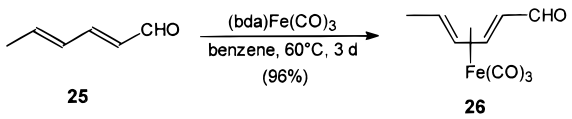
**Scheme 11**




carbonyliron compounds Fe(CO)$_5$ and Fe$_3$(CO)$_{12}$ could not be used because of the sensitivity of the free ligand to both heat and UV light, while Fe$_2$(CO)$_9$ afforded an unstable hexacarbonyldiiron complex.

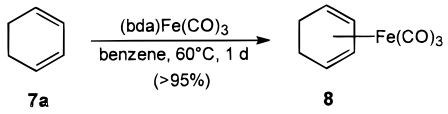
Acyclic 1,3-dienes can be transformed to the corresponding ($\eta^4$-buta-1,3-diene)tricarbonyliron complexes using (bda)Fe(CO)$_3$ as shown by Brookhart.[84] Thus, reaction of (bda)Fe(CO)$_3$ with 1.2 equiv of *trans*,*trans*-hexa-2,4-dienal (sorbic aldehyde) **(25)** in benzene at 60 °C for 3 days afforded complex **26** almost quantitatively (Scheme 12).

**Scheme 12**




Cyclohexa-1,3-diene **(7a)** on reaction with 1 equiv of (bda)Fe(CO)$_3$ **(22)** provided the tricarbonyliron complex **8** also almost quantitatively (Scheme 13).[83,84]

**Scheme 13**




This transformation clearly demonstrated the synthetic utility of (bda)Fe(CO)$_3$ as a mild and highly selective reagent for the transfer of the tricarbonyliron fragment to sensitive dienes in high yields. The result is superior to those obtained for the complexation of **7a** by direct reaction with a binary carbonyliron compound as described in Table 2.

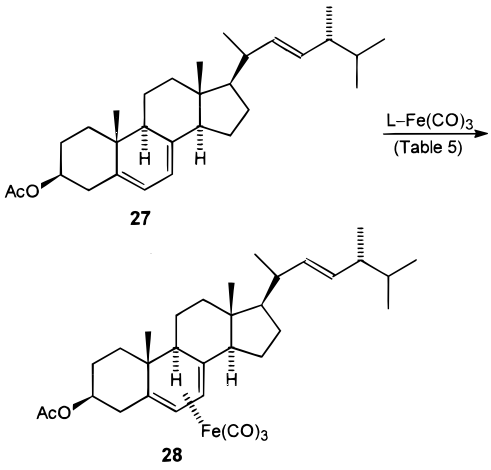
The transfer reagent (bda)Fe(CO)$_3$ was used for the selective protection of the diene moiety in the steroid B-ring of ergosterol derivatives by coordination to the tricarbonyliron fragment.[87,88] The tricarbonyliron-protected ergosterols were used for chemoselective reactions (hydroboration, dihydroxylation, and hydrogenation) at the 22,23-double bond. Thus, heating

**Table 5. Complexation of Ergosteryl Acetate (27) by Reaction with 1-Oxabuta-1,3-diene Tricarbonyliron Transfer Reagents**

| transfer reagent | reaction conditions | **28**, yield [%] | ref |
|---|---|---|---|
| **22** (1.2 equiv) | toluene, 110 °C, 6 h | 71 | 87 |
| **22** (4.0 equiv) | toluene, 90 °C, 24 h | 69 | 88 |
| **30** (4.0 equiv) | toluene, 90 °C, 16 h | 64 | 88 |
| **30** (4.0 equiv) | toluene, 60 °C, 48 h | 66 | 88 |

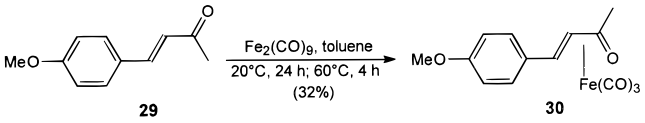
of ergosteryl acetate **(27)** in toluene under reflux for 6 h with 1.2 equiv of (bda)Fe(CO)$_3$ **(22)** provided the tricarbonyliron−diene complex **28** in 71% yield (Scheme 14, Table 5).[87] Barton obtained a similar

**Scheme 14**




yield by reaction at lower temperatures for a prolonged period of time, however, using a considerably larger excess of the reagent.[88] The same group also described the complexation of the more electron-rich 4-methoxybenzylideneacetone **(29)** to tricarbonyl($\eta^4$-4-methoxybenzylideneacetone)iron **(30)** (Scheme 15),

**Scheme 15**



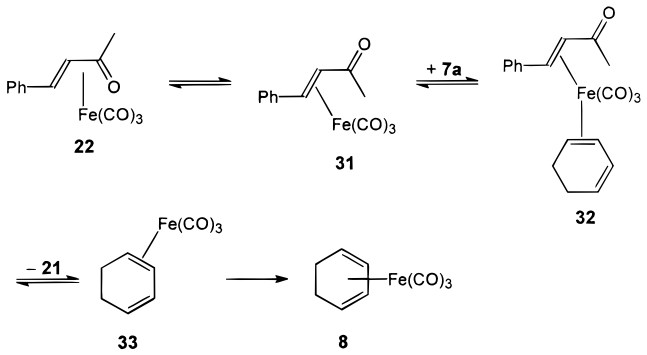

which was reported to be more reactive in transfer reactions than the parent complex **22**. Therefore, the transfer of the metal fragment using complex **30** occurs under milder reaction conditions and provides yields of **28** which are in the same range (Table 5).[88] The higher reactivity of complex **30** was confirmed for the transfer of the tricarbonyliron fragment to cyclohexa-1,3-diene **(7a)**, which on heating in tetrahydrofuran under reflux provided complex **8** in 85% yield after 20 min.[46,47] An in situ generation of the transfer reagent **30** by reaction of the free ligand **29** and nonacarbonyldiiron in the presence of ergosteryl benzoate was also reported.[88] However, the catalytic effect of the free ligand **29**, which was claimed for the complexation of ergosteryl benzoate with nonacarbonyldiiron,[88] could not be confirmed.[46]

Further applications of (bda)Fe(CO)$_3$ **(22)** include, for example, the transfer of the tricarbonyliron fragment to several heptafulvenes,[78] a series of acyclic and cyclic 1,3-dienes,[80,84] bicyclo[4.2.0]octadiene

derivatives,[82,83,89−91] and substituted phospholes.[92] The diastereoselective complexation of (*R*)-(−)-α-phellandrene[93] and of chiral 1-oxabuta-1,3-diene ligands was also achieved with (bda)$Fe(CO)_3$.[94,95] Moreover, the transfer reactions of metal fragments using the benzylideneacetone ligand were extended to the $[Fe(CO)_2PPh_3]$ and the $[Fe(CO)_2P(OPh)_3]$ moieties.[96] The electronic and steric effects in the bonding of the transfer reagents (bda)$Fe(CO)_2L$ (with L = CO, $PPh_3$, $P(OR)_3$) were studied by molecular orbital calculations.[97]

On the basis of kinetic studies obtained for the reaction with cyclooctatriene and cyclohexa-1,3-diene, Brookhart proposed a mechanism for the transfer of the tricarbonyliron fragment from ($\eta^4$-benzylideneacetone)tricarbonyliron **(22)** to 1,3-dienes, which is shown for the case of cyclohexa-1,3-diene **(7a)** in Scheme 16.[83,84] At slightly elevated temperature,

**Scheme 16**

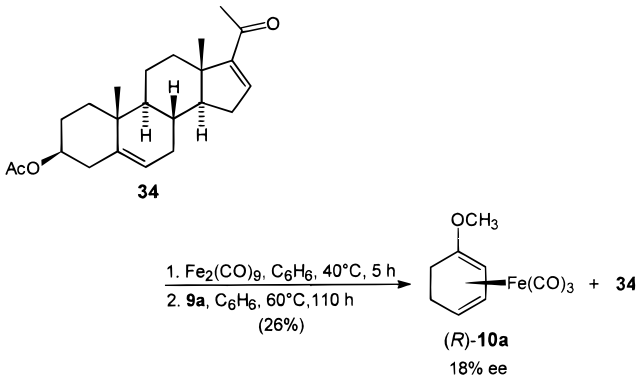



complex **22** undergoes a haptotropic migration ($\eta^4$ to $\eta^2$) to ($\eta^2$-benzylideneacetone)tricarbonyliron **(31)**, which represents a coordinatively unsaturated 16-electron complex. Coordination of one double bond of cyclohexa-1,3-diene **(7a)** to the iron atom forms ($\eta^2$-benzylideneacetone)tricarbonyl($\eta^2$-cyclohexa-1,3-diene)-iron **(32)**. Although being an 18-electron complex, **32** is not very stable and generates by loss of benzylideneacetone **(21)** the 16-electron-complex tricarbonyl-($\eta^2$-cyclohexa-1,3-diene)iron **(33)**. Finally, an irreversible haptotropic migration ($\eta^2$ to $\eta^4$) of the metal fragment transforms complex **33** into tricarbonyl($\eta^4$-cyclohexa-1,3-diene)iron **(8)**.

The reversibility of the steps leading from complex **22** to the intermediate **33** derives support by the fact that several nonplanar cyclic dienes (e.g., cyclohexa-1,4-diene **(7b)**, cycloocta-1,5-diene **(15a)**, and cycloocta-1,3-diene **(15b)**) fail to react with (bda)$Fe(CO)_3$ **(22)**.[84] The mechanism described in Scheme 16 involves an initial cleavage of the iron−ketone coordination leading to the 16-electron complex **31**. This dissociative pathway was additionally supported by extensive kinetic studies of ligand exchange reactions at ($\eta^4$-enone)iron complexes either with triphenylphosphine, triphenylarsine, and triphenylantimony by Cardaci[98−100] or with 1,3-dienes by Howell.[101−103] However, in both cases, a competing associative pathway, which by reaction of (bda)$Fe(CO)_3$ **(22)** with **7a** would lead directly to complex **32**, can also be involved.[98−103] The ligand exchange reaction of (bda)-$Fe(CO)_3$ with phosphines was used to prepare complexes of the type $(PR_3)_2Fe(CO)_3$.[104−105]

Birch and co-workers could show that the complexation of prochiral 1,3-dienes using chiral tricarbonyl-($\eta^4$-1-oxabuta-1,3-diene)iron complexes proceeds with moderate asymmetric induction.[106,107] The chiral transfer reagents were prepared in situ and used without isolation for the ligand exchange reaction with the prochiral 1,3-diene. Thus, heating (−)-3$\beta$-(acetyloxy)pregna-5,16-dien-20-one **(34)** with nonacarbonyldiiron in benzene at 40 °C for 5 h and subsequent transfer of the tricarbonyliron fragment to 1-methoxycyclohexa-1,3-diene **(9a)** provided complex **10a** in 26% yield with 18% ee of the *R* enantiomer (Scheme 17).[107] The absolute configuration of the

**Scheme 17**




tricarbonyliron complex (*R*)-**10a** was determined by chemical correlation.[108]

This result demonstrated for the first time that enantioenriched planar chiral tricarbonyl($\eta^4$-1,3-diene)iron complexes are available by complexation of prochiral 1,3-dienes with chiral transfer reagents. The observed asymmetric induction using a chiral transfer reagent supports an intermediate like complex **32** for the transfer reaction, in which both the prochiral 1,3-diene and the chiral 1-oxabuta-1,3-diene are bonded to the tricarbonyliron fragment at the same time (compare Scheme 16).

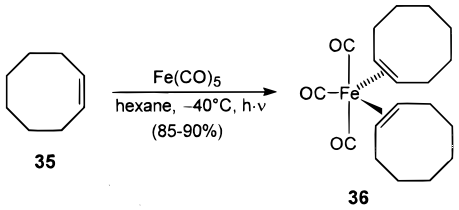
Enantiomerically enriched planar chiral tricarbonyl($\eta^4$-1-oxabuta-1,3-diene)iron complexes were obtained via the reversible thermal displacement of a carbon monoxide ligand with (+)-neomenthyldiphenylphosphine and separation of the intermediate diastereoisomers.[109,110] An alternative route which provides enantioenriched planar chiral ($\eta^4$-benzylideneacetone)$Fe(CO)_2(L)$ complexes (L = phosphine or phosphite ligand) involves kinetic resolution of the corresponding racemic ($\eta^2$-benzylideneacetone)Fe-$(CO)_3(L)$ complexes using brucine *N*-oxide as decarbonylating agent.[111] However, these planar chiral 1-oxabutadiene complexes are not appropriate reagents for efficient enantioselective complexations of prochiral 1,3-dienes because they show racemization under the conditions required for the transfer reaction.[109−111]

## 2. Tricarbonylbis($\eta^2$-*cis*-cyclooctene)iron

A further tricarbonyliron transfer reagent was described by Grevels in 1984. The photolysis of pentacarbonyliron with an excess of *cis*-cyclooctene **(35)** in hexane at −40 °C provided tricarbonylbis($\eta^2$-

*cis*-cyclooctene)iron (Grevels' reagent) **(36)**, which was isolated in 85−90% yield (Scheme 18).[112] The

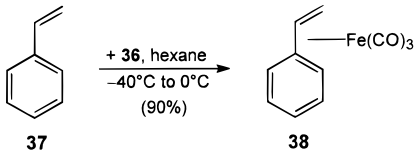
**Scheme 18**




initial product of this reaction is tetracarbonyl($\eta^2$-*cis*-cyclooctene)iron, which is subsequently transformed to complex **36** on extended irradiation. The crystals of compound **36** can be handled at room temperature, but in solution, complex **36** is labile and decomposes at temperatures above −35 °C. Grevels' reagent **(36)** represents a convenient source for the tricarbonyliron fragment and has the advantage compared to (bda)-$Fe(CO)_3$ **(22)** that the tricarbonyliron transfer reaction with 1,3-dienes occurs at temperatures below 0 °C.

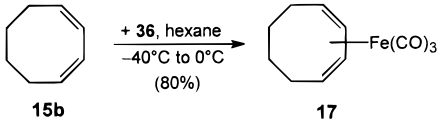
The ligand exchange reaction of complex **36** occurs with a range of acyclic and cyclic dienes and can be monitored by infrared spectroscopy. A complete transfer of the metal fragment is usually achieved with a 2-fold excess of the 1,3-diene and affords the corresponding tricarbonyl($\eta^4$-1,3-diene)iron complexes in many cases almost quantitatively.[112] This tricarbonyliron transfer reaction was also successfully applied to a series of vinyl-substituted aromatic compounds. Thus, starting from styrene **(37)**, the parent complex tricarbonyl($\eta^4$-styrene)iron **(38)** was available in 90% yield (Scheme 19).

**Scheme 19**



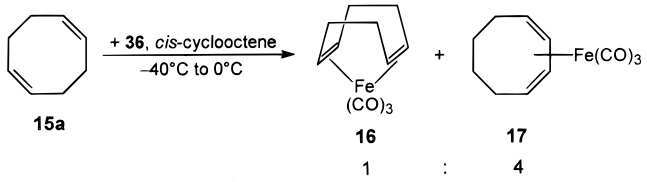

The nonplanar cycloocta-1,3-diene **(15b)** does not undergo a ligand exchange reaction with (bda)Fe-$(CO)_3$.[84] The direct complexation of **15b** by photolysis with pentacarbonyliron afforded the thermally unstable complex **17** in only 25% yield.[60] Using Grevels' reagent, the complexation of cycloocta-1,3-diene **(15b)** provided complex **17** in 80% yield because of the extremely mild conditions required for the tricarbonyliron transfer reaction.

**Scheme 20**



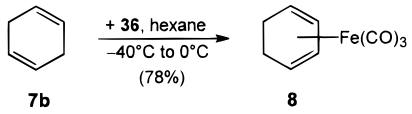

It was also shown that (bda)$Fe(CO)_3$ does not transfer the tricarbonyliron fragment to nonconjugated dienes.[84] In contrast, the reaction of complex **36** with cycloocta-1,5-diene (**15a**) led to a 1:4 mixture of tricarbonyl($\eta^4$-cycloocta-1,5-diene)iron **(16)** and tricarbonyl($\eta^4$-cycloocta-1,3-diene)iron **(17)**, which is the result of double bond isomerization (Scheme 21).

**Scheme 21**




The transfer of the tricarbonyliron fragment from Grevels' reagent to cyclohexa-1,4-diene **(7b)** also takes place with concomitant migration of the double bond and provides tricarbonyl($\eta^4$-cyclohexa-1,3-diene)iron **(8)** in 78% yield.[112]

**Scheme 22**




In a ligand exchange reaction with *trans*-cyclooctene, the labile complex **36** was applied to the synthesis of the corresponding stable complex tricarbonylbis($\eta^2$-*trans*-cyclooctene)iron.[113,114] Franck-Neumann used Grevels' reagent **(36)** for the quantitative complexation of 2-trialkylstannylbuta-1,3-dienes to the corresponding tricarbonyliron complexes.[115] An in situ preparation of Grevels' reagent and subsequent transfer of the tricarbonyliron fragment to dienes without isolation has also been described.[116,117]

## 3. ($\eta^4$-1-Azabuta-1,3-diene)tricarbonyliron Complexes

The ($\eta^4$-1-azabuta-1,3-diene)tricarbonyliron complexes were first described by Otsuka[118] and Lewis[119] three decades ago but found only a few applications in synthesis.[120−126] More recently, the ($\eta^4$-1-azabuta-1,3-diene)tricarbonyliron complexes were shown to represent a novel and very useful class of tricarbonyliron transfer reagents.[127−130] They can be prepared either by condensation of amines with tetracarbonyl(3−4-$\eta$-1-oxabuta-1,3-diene)iron complexes,[118,123] by thermal reaction of 1-azabuta-1,3-dienes with nonacarbonyldiiron,[118,122] or by an aza-Wittig reaction with tetracarbonyl(3−4-$\eta$-1-oxabuta-1,3-diene)iron complexes.[131] Since the tetracarbonyl(3−4-$\eta$-1-oxabuta-1,3-diene)iron complexes are very labile,[77,81,132] the 1-azabuta-1,3-dienes are the more appropriate starting materials. The most convenient way for the synthesis of the ($\eta^4$-1-azabuta-1,3-diene)-tricarbonyliron complexes is shown in Scheme 23.

The imine condensation of cinnamaldehyde **(39)** with the amines **40** provided the 1-azabuta-1,3-dienes **41**. Reaction of the 1-azabuta-1,3-dienes **41** with nonacarbonyldiiron in tetrahydrofuran at room temperature afforded the ($\eta^4$-1-azabuta-1,3-diene)tricarbonyliron complexes **42** (Scheme 23, Table 6).[129,130] The ultrasound-promoted complexation, previously applied by Ley and co-workers to buta-1,3-dienes,[38,39] was found to be superior to the thermally induced

**Scheme 23**

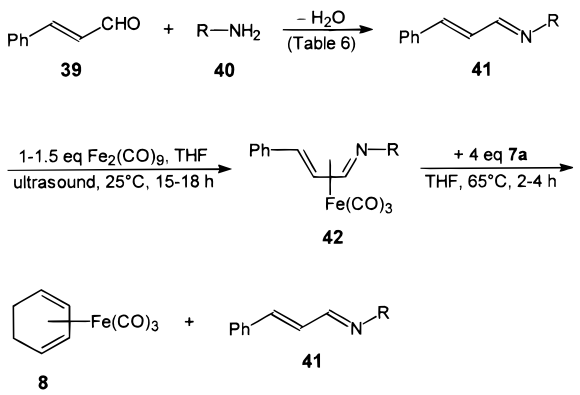



**Table 6. Synthesis of the ($\eta^4$-1-Azabuta-1,3-diene)tricarbonyliron Complexes 42 and Transfer Reaction to Cyclohexa-1,3-diene (7a)**

| | R | **41**, yield [%] | **42**, yield [%] | **8**, yield [%] | ref |
|---|---|---|---|---|---|
| **a** | $C_6H_5$ | 82 | 82 | 88 | 129 |
| **b** | 4-$MeOC_6H_4$ | 100 | 88 | 95 | 129 |
| **c** | 2-$MeOC_6H_4$ | 87 | 80 | 74 | 129 |
| **d** | 2,4-$(MeO)_2C_6H_3$ | 81 | 43 | 80 | 129 |
| **e** | $C_6H_5CH_2$ | 80 | 76 | 73 | 130 |
| **f** | (*S*)-$C_6H_5(Me)CH$ | 92 | 80 | 70 | 130 |

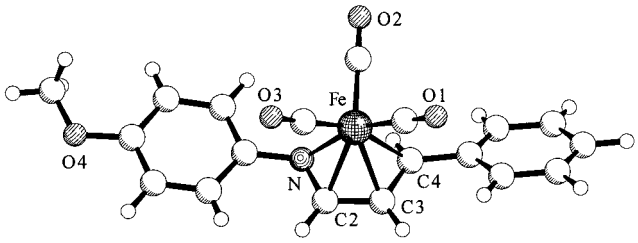



**Figure 1.** Molecular structure of the ($\eta^4$-1-azabuta-1,3-diene)tricarbonyliron complex **42b** in the crystal (SCHAKAL representation; arbitrary numbering). Selected bond lengths [Å]: Fe−N 2.075(3), Fe−C2 2.074(4), Fe−C3 2.068(4), Fe−C4 2.167(4).

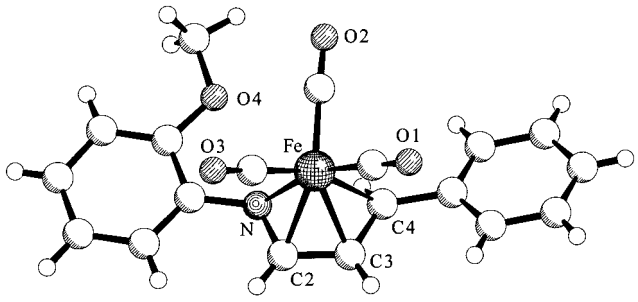



**Figure 2.** Molecular structure of the ($\eta^4$-1-azabuta-1,3-diene)tricarbonyliron complex **42c** in the crystal (SCHAKAL representation; arbitrary numbering). Selected bond lengths [Å]: Fe−N 2.074(2), Fe−C2 2.064(2), Fe−C3 2.050(2), Fe−C4 2.132(3).

complexation of the 1-azabuta-1,3-dienes **41**. An X-ray crystal structure determination of the tricarbonyliron transfer reagents **42b** and **42c** confirmed the $\eta^4$-bonding mode and the tetragonal-pyramidal coordination of the iron atom (Figures 1 and 2).[129]

The transfer of the tricarbonyliron fragment from the ($\eta^4$-1-azabuta-1,3-diene)tricarbonyliron complexes **42** to cyclohexa-1,3-diene **(7a)** generally takes place within a few hours in tetrahydrofuran at reflux and provides complex **8** in high yield (Scheme 23, Table 6).[129,130] An excess of the cyclohexa-1,3-diene **(7a)** (4 equiv) is applied for the transfer reaction, and thus, the yields are based on the complexes **42** as the more valuable component. The best overall result was obtained using complex **42b** as transfer reagent. Moreover, the free ligand **41b** was recovered after the transfer reaction in more than 95% yield simply by crystallization.

The ($\eta^4$-1-azabuta-1,3-diene)tricarbonyliron complexes **42** have several advantages over the two former tricarbonyliron transfer reagents. They can be synthesized in high yield under mild reaction conditions (ultrasound, room temperature), and the red crystalline complexes are stable in the air for months. Not only Grevels' reagent, but also the tricarbonyl($\eta^4$-1-oxabuta-1,3-diene)iron complexes are in general more labile, and this is reflected by their higher reactivity for the transfer of the tricarbonyliron fragment to 1,3-dienes. Some information on the relative reactivities of different tricarbonyliron transfer reagents was obtained from competition experiments in which different 1-heterobuta-1,3-dienes were allowed to compete for a tricarbonyliron fragment. The reaction of tricarbonyl($\eta^4$-4-methoxybenzylideneacetone)iron **(30)** with the 1-azadiene **41b** in benzene under reflux led to a complete transfer of the metal fragment within 20 min and afforded exclusively 4-methoxybenzylideneacetone **(29)** and the tricarbonyliron complex **42b**. On the other hand, a transfer of the tricarbonyliron fragment from complex **42b** to 4-methoxybenzylideneacetone **(29)** did not occur.[129] Similarly, a direct comparison of different ($\eta^4$-1-azabuta-1,3-diene)tricarbonyliron complexes **42** in their reactivity for the tricarbonyliron transfer reaction was given by heating of the complexes **42** with free 1-azadienes **41**. The competition reactions between either **41a** or **41e** and the complex **42b** led to an equilibrium containing an excess of the free 1-azadiene **41b** and complexes **42a** or **42e**, respectively.[129,130] These results thus confirmed the higher reactivity of complex **42b** for the transfer of the tricarbonyliron fragment, which was already found in the reaction with cyclohexa-1,3-diene **(7a)** (Table 6).

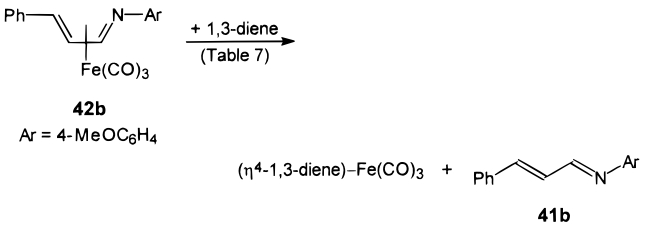
Using complex **42b** as tricarbonyliron transfer reagent, a range of cycloalka-1,3-dienes and substituted buta-1,3-dienes were transformed to the corresponding tricarbonyl($\eta^4$-1,3-diene)iron complexes in high yields (Scheme 24, Table 7).[130] In some cases, higher temperatures for the transfer reaction were chosen in order to come to reasonable reaction times. Reaction of complex **42b** with an excess of 1-methoxycyclohexa-1,3-diene **(9a)** provided a 1:1 mixture of tricarbonyl($\eta^4$-1-methoxycyclohexa-1,3-diene)iron **(10a)** and tricarbonyl($\eta^4$-2-methoxycyclohexa-1,3-diene)iron **(10b)**. However, an attempted transfer of the metal fragment from complex **42b** to cyclohexa-1,4-diene **(7b)** led, even under more drastic reaction conditions (toluene, 110 °C, 24 h), only to reisolation of the transfer reagent. Thus, as previously described for $(bda)Fe(CO)_3$,[84] the azadiene complex **42b** cannot be used for the complexation of 1,4-dienes with concomitant conjugation of the double bonds. In

**Table 7. Complexation of 1,3-Dienes by the Tricarbonyliron Fragment Using the ($\eta^4$-1-Azabuta-1,3-diene)tricarbonyliron Complex 42b as Transfer Reagent**

| 1,3-diene | reaction conditions | yield [%][a] |
|---|---|---|
| cyclohexa-1,3-diene **(7a)** | THF, 65 °C, 2 h | 95, **8** |
| cyclohexa-1,4-diene **(7b)** | toluene, 110 °C, 24 h | – |
| 1-methoxycyclohexa-1,3-diene **(9a)** | benzene, 80 °C, 4 h | 64, **10a**/**10b** |
| cyclohepta-1,3-diene **(13)** | benzene, 80 °C, 4.5 h | 84, **14** |
| 2,3-dimethylbuta-1,3-diene | benzene, 80 °C, 25 h | 71 |
| sorbic aldehyde **(25)** | toluene, 110 °C, 1 h | 69, **26** |

[a] Yield of the corresponding ($\eta^4$-1,3-diene)-$Fe(CO)_3$ complex.

**Scheme 24**

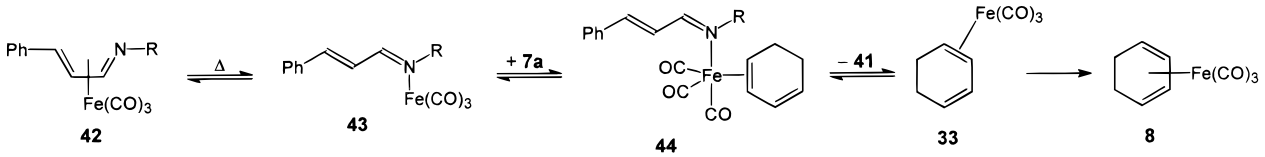



contrast, this transformation could be achieved using the much more reactive Grevels' reagent.[112]

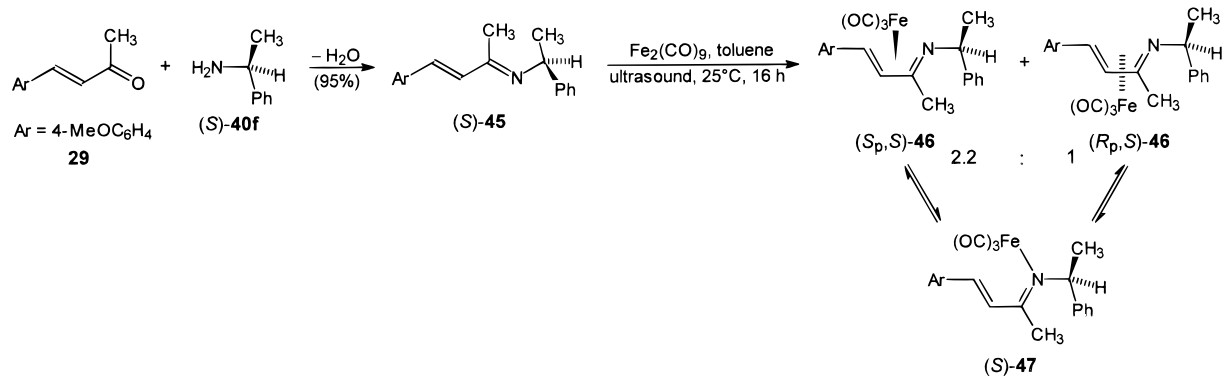
On the basis of the early kinetic studies by Cardaci and co-workers[133−135] on ligand exchange reactions of complexes **42a** and **42b** with triphenylphosphine and additional mechanistic investigations,[128,136] the following mechanism was proposed for the transfer of the tricarbonyliron fragment from an ($\eta^4$-1-azabuta-1,3-diene)tricarbonyliron complex **42** to cyclohexa-1,3-diene **(7a)** (Scheme 25).[127,129] A thermally induced haptotropic migration ($\eta^4$ to $\eta^1$) transforms complex **42** to the (1-$\eta$-1-azabuta-1,3-diene)tricarbonyliron complex **43**, which represents a coordinatively unsaturated 16-electron complex. The vacant coordination site of complex **43** is filled by $\eta^2$-coordination to cyclohexa-1,3-diene **(7a)**. The intermediate 18-electron complex **44**, which could not be isolated, was proposed to have a trigonal-bipyramidal structure with the $\eta^1$-coordinated $\alpha,\beta$-unsaturated imine in axial and the $\eta^2$-coordinated 1,3-diene in equatorial position. Loss of the 1-azabuta-1,3-diene **41** generates complex **33**, which on haptotropic migration ($\eta^2$ to $\eta^4$) of the metal fragment affords tricarbonyl($\eta^4$-cyclohexa-1,3-diene)iron **(8)**.

Support for this mechanism derived from the investigation of the thermal epimerization of the tricarbonyliron complexes of chiral 1-azabuta-1,3-dienes (Scheme 26).[136] Condensation of 4-methoxybenzylideneacetone **(29)** with (*S*)-1-phenylethylamine ((*S*)-**40f**) provided the chiral 1-azabuta-1,3-diene (*S*)-**45**. The ultrasound-promoted complexation of (*S*)-**45** with nonacarbonyldiiron afforded the two enantiopure diastereoisomeric complexes ($S_p$,*S*)-**46** and ($R_p$,*S*)-**46** in a ratio of 2.2:1. The two diastereoisomers could be separated by chromatography on silica gel at −30 to −45 °C. At temperatures above 0 °C, an epimerization of the separated diastereoisomers occurred, which afforded again the thermodynamic mixture of 2.2:1 in favor of ($S_p$,*S*)-**46**. The kinetics of the epimerization of the major diastereoisomer ($S_p$,*S*)-**46** to the minor diastereoisomer ($R_p$,*S*)-**46** were followed, and the activation energy for this process was determined: $E_A = 22.4 \pm 1$ kcal/mol.[136] From the kinetic data it was concluded that the epimerization of the diastereoisomeric complexes **46** is a reversible reaction of pseudo-first order and thus should proceed by an intramolecular mechanism. In agreement with this interpretation is an epimerization via the 16-electron imine complex (*S*)-**47**. Compound (*S*)-**47** corresponds to complex **43** (Scheme 25), which is the coordinatively unsaturated intermediate for the tri-

**Scheme 25**




**Scheme 26**



carbonyliron transfer reaction. The matrix photolysis of ($\eta^4$-1-azabuta-1,3-diene)tricarbonyliron complexes at 10 K afforded (1-$\eta$-1-azabuta-1,3-diene)tricarbonyliron complexes similar to **43** which were assigned based on IR spectroscopy.[137]

## *IV. Catalytic Complexation of Dienes with Nonacarbonyldiiron or Pentacarbonyliron*

The complexation of the 1-azabuta-1,3-dienes **41** can be achieved with nonacarbonyldiiron under thermal conditions at temperatures[118,122] which are also used for the transfer of the metal fragment.[129,130] Therefore, an in situ preparation of the ($\eta^4$-1-azabuta-1,3-diene)tricarbonyliron complexes **42** even in the presence of the diene and subsequent transfer of the metal fragment is feasible. Moreover, the free 1-azabuta-1,3-dienes **41** are regenerated and can be reisolated almost quantitatively after the transfer reaction. The major advantage of the complexes **42** compared to the two former reagents is that substoichiometric amounts of the corresponding free ligands **41** can be employed to induce the complexation of dienes with nonacarbonyldiiron. This observation was the starting point to develop a highly efficient catalytic complexation of dienes by the tricarbonyliron fragment.[127,130,138]

The 1-azabuta-1,3-diene **41b** was selected as the catalyst because the corresponding complex **42b** represents the most efficient transfer reagent. The best results for the catalytic complexation with nonacarbonyldiiron as the tricarbonyliron source were obtained using a slight excess of the 1,3-diene (1.2−1.5 equiv) and 12.5−25 mol % of **41b** in 1,2-dimethoxyethane under reflux for 16−17 h. The equivalents of 1,3-diene and catalyst as well as the yields of the resulting tricarbonyl($\eta^4$-1,3-diene)iron complexes are based on the tricarbonyliron equivalents.

The optimal conditions for the catalytic complexation of cyclohexa-1,3-diene **(7a)** with nonacarbonyldiiron were found by variation of the concentration of catalyst **41b** (Figure 3). Using an amount of

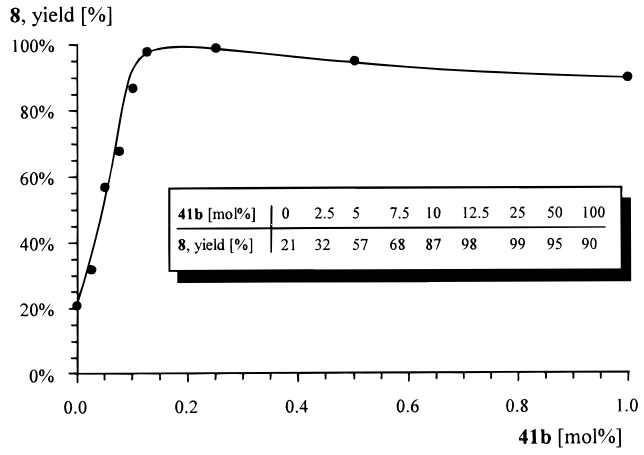
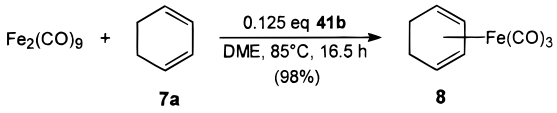



**Figure 3.** Variation of the amount of catalyst **41b** for the catalytic complexation of cyclohexa-1,3-diene **(7a)** with nonacarbonyldiiron (reaction conditions: 0.5 equiv of $Fe_2(CO)_9$, 1.5 equiv of **7a**, DME, 85 °C, 16 h); equivalents and yields based on iron.

catalyst **41b** in the range of 12.5−25 mol % provided the highest yields of complex **8**. A further increase of the amount of catalyst up to 1 equiv led even to a slight decrease of the yield of complex **8**. With large amounts of catalyst **41b**, the transfer of the tricarbonyliron fragment to the free 1-azabuta-1,3-diene **41b** generating complex **42b** predominates toward the end of the reaction, because at this point the concentration of the substrate **7a** is low compared to the concentration of **41b**. Therefore, the complexation of **7a** does not come to completion with stoichiometric amounts of catalyst. Under the optimized conditions, the catalytic complexation of cyclohexa-1,3-diene **(7a)** with nonacarbonyldiiron (10.0 g) and 12.5 mol % of **41b** provided tricarbonyl($\eta^4$-cyclohexa-1,3-diene)iron **(8)** (11.9 g) in 98% yield (Scheme 27).[138]

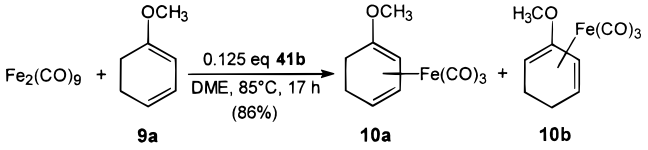
**Scheme 27**




This result demonstrated the feasibility to transfer both tricarbonyliron fragments of nonacarbonyldiiron in a complexation reaction quantitatively to a 1,3-diene. Therefore, no pyrophoric iron or pentacarbonyliron is formed in this process. For comparison, the uncatalyzed complexation of **7a** using identical conditions otherwise provided complex **8** in 21% yield (Table 2). Linkage of the 1-aryl ring of the 1-azabuta-1,3-diene **41** to the Merrifield resin provided a polymer-bound catalyst which can be recycled more easily after the reaction. Application of this solid-phase catalyst to a heterogeneous catalytic complexation of **7a** with nonacarbonyldiiron afforded complex **8** in 83% yield.[127]

The catalytic complexation of 1-methoxycyclohexa-1,3-diene **(9a)** with nonacarbonyldiiron and 12.5 mol % of catalyst **41b** under the optimized conditions described above afforded the mixture of the regioisomeric complexes tricarbonyl($\eta^4$-1-methoxycyclohexa-1,3-diene)iron **(10a)** and tricarbonyl($\eta^4$-2-methoxycyclohexa-1,3-diene)iron **(10b)** in 86% yield based on the tricarbonyliron equivalents (Scheme 28).[130] A

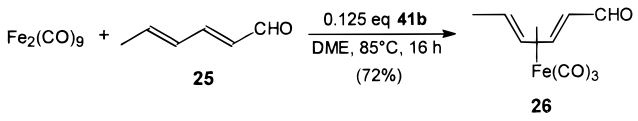
**Scheme 28**




comparison with the yields of the conventional thermally induced uncatalyzed complexation using nonacarbonyldiiron (24−32%, Table 3) shows again the remarkable improvement.

Substituted acyclic 1,3-dienes can be used as substrates for the catalytic complexation. Thus, the complexation of sorbic aldehyde **(25)** with nonacarbonyldiiron using **41b** as the catalyst under the same set of reaction conditions afforded the tricarbonyliron complex **26** in 72% yield (Scheme 29).[130] The efficiency of the catalysis by using 12.5 mol % of **41b** for the complexation with nonacarbonyldiiron is

**Scheme 29**




**Scheme 30**

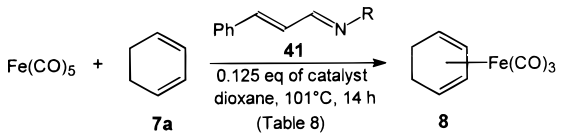



**Table 8. Catalytic Complexation of Cyclohexa-1,3-diene (7a) with Pentacarbonyliron—Variation of the Catalyst at a Constant Reaction Time of 14 h**

| catalyst | R | **8**, yield [%] | rel. acticity |
|---|---|---|---|
| | | 0.7 | |
| **29** | | 4.2 | 0.10 |
| **41a** | $C_6H_5$ | 41 | 1.00 |
| **41b** | 4-$MeOC_6H_4$ | 50 | 1.22 |
| **41c** | 2-$MeOC_6H_4$ | 83 | 2.02 |
| **41d** | 2,4-$(MeO)_2C_6H_3$ | 90 | 2.20 |
| **41e** | $C_6H_5CH_2$ | 47 | 1.15 |
| (*S*)-**41f** | (*S*)-$C_6H_5$(Me)CH | 41 | 1.00 |

emphasized by the fact that the yields of the tricarbonyl($\eta^4$-1,3-diene)iron complexes compared to the stoichiometric reaction by using the complex **42b** as transfer reagent are in the same range or in some cases even better (see Table 7).

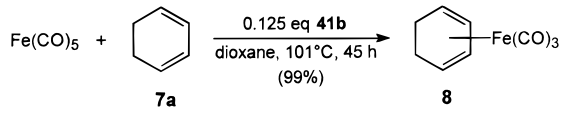
Pentacarbonyliron is much cheaper than nonacarbonyldiiron or dodecacarbonyltriiron and, therefore, represents the much more attractive starting material for the synthesis of carbonyliron complexes.[139] It is well-known, however, that in the conventional thermally induced complexation of dienes with pentacarbonyliron, much higher reaction temperatures are required (compare Tables 2 and 3). In fact, a highly efficient catalytic complexation of dienes with pentacarbonyliron using 1-azabuta-1,3-dienes **41** as catalysts could be developed by increasing the temperature and reaction time of the catalytic complexation with nonacarbonyldiiron. Thus, for the complexation of cyclohexa-1,3-diene **(7a)** (1.5 equiv) with pentacarbonyliron (1 equiv) in dioxane under reflux, various catalysts (12.5 mol %) were compared at a constant reaction time of 14 h (Scheme 30, Table 8).[128,138,140]

The blank experiment (reaction without catalyst) gave complex **8** in only 0.7% yield. In the presence of 12.5 mol % 4-methoxybenzylideneacetone **(29)** complex **8** was obtained in 4.2% yield. This increase of the yield was ascribed to an in situ complexation of the 1-oxabuta-1,3-diene **29** followed by transfer of the metal fragment to **7a** but is clearly not based on a catalytic effect.[130,138] On the other hand, application of 12.5 mol % of the 1-azabuta-1,3-dienes **41** as catalysts led to a significant increase of the yield. The result which was obtained for the catalytic complexation of **7a** using the 1,4-diphenyl-1-azabuta-1,3-diene **(41a)** as catalyst (41% yield of complex **8**) was taken as a standard, and the relative activity of this catalyst was defined as 1.00. It was found that the electron density at the imine nitrogen atom of the 1-azabuta-1,3-dienes **41** correlates with their activity for catalytic complexation.[129,138] Thus, the higher activity of catalyst **41b** (1.22) can be explained by the inductive effect of the *para*-methoxy group in the 1-aryl ring. An even more significant increase of the catalytic activity is caused by an *ortho*-methoxy group in the 1-aryl ring as observed for **41c** (2.02). This strong effect of the *ortho*-methoxy group is rationalized by an internal (associative) displacement of a carbon monoxide ligand and subsequent stabilization of the intermediate 16-electron spezies via coordination to the oxygen (chelate formation). Thus, the "*ortho*-methoxy effect" described above can be considered as a chelate effect. The high relative catalytic activity of **41d** (2.20) demonstrates that both the inductive and the chelate effect are additive. The catalysts **41e** and (*S*)-**41f** have a relative activity which is in the same range as that observed for **41b** and **41a**.[130] However, the lower stability of the 1-azabuta-1,3-dienes **41e** and (*S*)-**41f** and of their corresponding complexes, **42e** and (*S*)-**42f**, leads to decomposition under the reaction conditions, and therefore, the recovery of these catalysts is very poor.

The 1-azabuta-1,3-diene **41b** was chosen as the standard catalyst for further optimization and applications, although it is not the most reactive catalyst. However, the corresponding amine, *p*-anisidine **(40b)**, is very cheap and the 1-azabuta-1,3-diene **41b** is readily crystallizing. Therefore, compound **41b** can be isolated quantitatively from the condensation with cinnamaldehyde **(39)** by crystallization, and it is recovered after the catalytic complexation by simple crystallization.

In an optimized procedure, the catalytic complexation of 1.5 equiv of cyclohexa-1,3-diene **(7a)** with 2 g of pentacarbonyliron in the presence of 12.5 mol % of catalyst **41b** was performed in dioxane under reflux for 45 h and provided tricarbonyl($\eta^4$-cyclohexa-1,3-diene)iron **(8)** in 99% yield based on pentacarbonyliron (Scheme 31).[138] A successful upscaling of

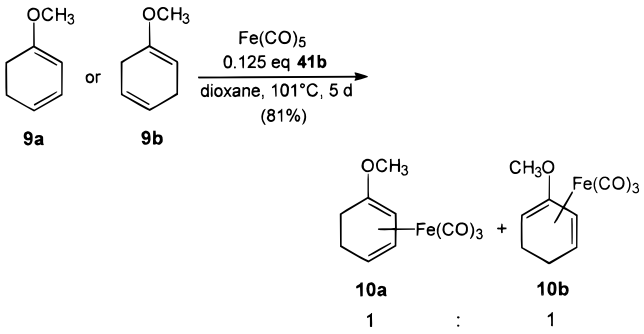
**Scheme 31**




this reaction for the production of large quantities of the tricarbonyliron complex **8** was reported. The catalytic complexation of an excess of **7a** with 50.0 g of pentacarbonyliron provided 50.2 g of complex **8** (89% yield).[138] A similar optimized procedure was developed for the catalytic complexation of the dihydroanisoles **9a** and **9b** on a large scale (Scheme 32).[130]

The catalytic complexation of an excess of either 1-methoxycyclohexa-1,3-diene **(9a)** or 1-methoxycyclohexa-1,4-diene **(9b)** with pentacarbonyliron (15 g scale) using catalyst **41b** in dioxane under reflux for 5 days afforded a 1:1 mixture of the two regioisomeric complexes **10a** and **10b** in 81% yield. Moreover, this result demonstrated that, in contrast to the stoichiometric reaction with the azadiene complexes **42**, the catalytic complexation of 1,4-dienes

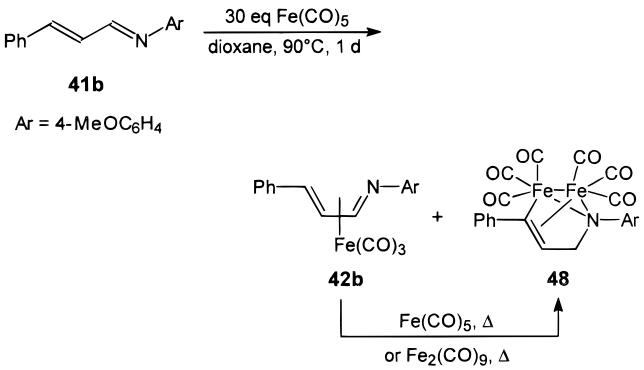
**Scheme 32**




with pentacarbonyliron using the azadienes **41** affords by a concomitant isomerization of the diene the tricarbonyl($\eta^4$-1,3-diene)iron complexes.

The catalytic complexations of dienes with pentacarbonyliron generate several intermediate carbonyliron complexes of the 1-azabuta-1,3-diene catalyst **41b**. In an attempt to isolate some of these reaction intermediates, the catalyst **41b** was treated with an excess of pentacarbonyliron using conditions which resemble those for the catalytic complexation but without the diene (Scheme 33).[138]

**Scheme 33**




As expected, the major product (47% yield) was the ($\eta^4$-1-azabuta-1,3-diene)tricarbonyliron complex **42b**, which represents the tricarbonyliron transfer reagent known from the stoichiometric reaction (see section III. 3). The labile hexacarbonyldiiron complex **48** was isolated as a byproduct (5% yield). Previously, related hexacarbonyldiiron complexes were obtained only from aryl and heteroaryl aldehyde imines.[141−148] The hexacarbonyldiiron complex **48** has a novel structural feature, because it represents the first example of such an organometallic compound which derives from a cinnamaldehyde imine. Therefore, the molecular structure of the cluster **48** was confirmed by an X-ray analysis (Figure 4).[138] The structure determination confirmed the 1,3-hydrogen shift from the 4-position of the 1-azabuta-1,3-diene to the 2-position. For the benzaldehyde imines, it was shown that the 1,3-hydrogen shift proceeds by an intramolecular pathway.[143,147] In contrast to previous reports,[144,146,147] the formation of hexacarbonyldiiron complexes by 1,3-hydrogen shift occurs also with cinnamaldehyde imines. This observation is of importance for the catalytic complexation.

It could be shown that the dinuclear iron complex **48** is formed by reaction of the mononuclear complex

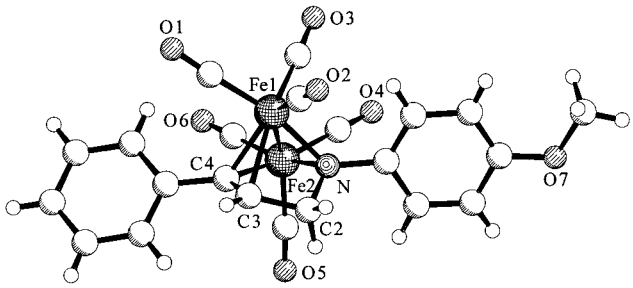



**Figure 4.** Molecular structure of the hexacarbonyldiiron complex **48** in the crystal (SCHAKAL representation; arbitrary numbering). Selected bond lengths [Å]: Fe1−Fe2 2.4704(6), Fe1−N 1.979(2), Fe1−C3 2.169(2), Fe1−C4 2.132(2), Fe2−N 1.971(2), Fe2−C4 1.975(2).

**42b** with either pentacarbonyliron or nonacarbonyldiiron under thermal conditions (6−8% yield).[138] Using the same reaction conditions given above, the tricarbonyliron transfer reagent **42b** can also be used as a catalyst for the catalytic complexation of cyclohexa-1,3-diene **(7a)** with pentacarbonyliron. However, the hexacarbonyldiiron complex **48** exhibits no catalytic activity for this complexation. At elevated temperatures (80 °C), the dinuclear complex **48** serves as a stoichiometric transfer reagent and transfers only one tricarbonyliron fragment to **7a** with decomposition of the residual organometallic fragment. Thus, it was concluded that the formation of the dinuclear complex **48** occurs via the mononuclear complex **42b** at high concentrations of pentacarbonyliron relative to the catalyst **41b** and leads to an irreversible loss of catalyst.[138]

A more detailed discussion of the mechanism of the catalytic complexation is provided in section V. 2.

## *V. Asymmetric Catalytic Complexation of Prochiral Cyclohexa-1,3-dienes*

Asymmetric catalysis offers the most efficient access to enantiomerically pure compounds as starting materials for enantioselective organic synthesis because the chiral auxiliary is applied only in catalytic amounts.[149] This methodology has been used for the asymmetric catalytic hydrogenation, cyclopropanation, epoxidation, dihydroxylation, and other reactions at prochiral double bonds to generate compounds with central chirality at carbon. In recent years it was shown that by using chiral 1-azabuta-1,3-dienes an asymmetric catalytic complexation of prochiral dienes by the tricarbonyliron fragment can be realized also. This reaction represents a novel type of asymmetric catalysis since it constitutes the first example which generates planar chiral transition metal $\pi$-complexes starting from the corresponding prochiral substrates.

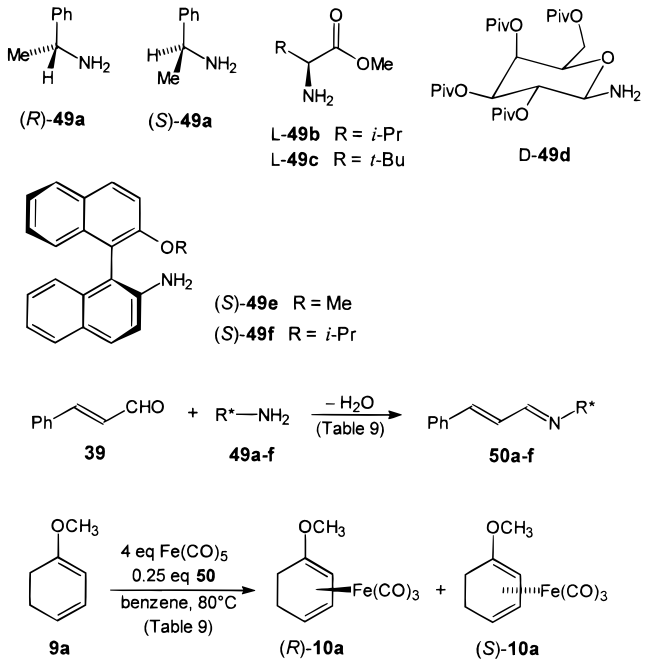
### 1. Catalysts from Cinnamaldehyde and a Chiral Amine

A few points have to be considered for the choice of the reaction conditions of an asymmetric catalytic complexation using chiral 1-azabuta-1,3-dienes. The catalytic complexation of the prochiral ligand 1-methoxycyclohexa-1,3-diene **(9a)** using the achiral catalyst **41b** with either nonacarbonyldiiron (Scheme 28) or

pentacarbonyliron (Scheme 32) afforded the planar chiral complex **10a**, of course as a racemic mixture, together with the regioisomer **10b**. Using nonacarbonyldiiron as the tricarbonyliron source, the uncatalyzed complexation of **9a** takes place at the same temperature as the catalytic complexation.[130] The uncatalyzed complexation, however, provides the planar chiral complex as a racemic mixture. To avoid the uncatalyzed complexation, the following standard reaction conditions were developed for the asymmetric catalytic complexation of prochiral 1,3-dienes: 1 equiv of the 1,3-diene, 4 equiv of pentacarbonyliron, 25 mol % of the chiral catalyst, benzene, reflux. Also, the isomerization of the 1,3-diene **9a** during complexation by the tricarbonyliron fragment, providing complex **10b**, was not observed under these conditions. A simple analytical probe for the fast and accurate determination of the enantiomeric excess of planar chiral tricarbonyl($\eta^4$-1,3-diene)iron complexes was provided by the HPLC separation on commercial $\beta$-cyclodextrin columns.[150]

The condensation of cinnamaldehyde **(39)** with the chiral amines **49**, analogous to the synthesis of the achiral catalysts **41** (Scheme 23), offered a simple and direct access to the chiral 1-azabuta-1,3-dienes **50**. The chiral catalysts **50** were applied to the asymmetric catalytic complexation of 1-methoxycyclohexa-1,3-diene **(9a)** using the standard reaction conditions (Scheme 34, Table 9).[151−153]

**Scheme 34**




The blank experiment (reaction without catalyst) for 9 days under the standard conditions afforded complex **10a** in only 2% yield.[152] This result confirmed that under the standard reaction conditions described above, the uncatalyzed complexation of **9a**, which provides the racemic product, does not contribute significantly to the formation of complex **10a**. Application of the 1-phenylethylamine-derived catalysts (*R*)- and (*S*)-**50a** to the complexation of **9a** provided complex **10a** with 6% ee of the *S* and the *R* enantiomer, respectively.[151] Although the degree of asymmetric induction in this example was very low, it demonstrated for the first time that an asymmetric catalytic complexation of prochiral dienes with transition metal fragments is feasible. Using the amino acid-derived 1-azabuta-1,3-dienes L-**50b** (from l-valine methyl ester (L-**49b**)) and L-**50c** (from L-*tert*-leucine methyl ester (L-**49c**)) for the catalytic complexation of **9a** the asymmetric induction was only slightly higher (12% ee and 15% ee of the *R* enantiomer).[152] The 2,3,4,6-tetra-*O*-pivaloyl-$\beta$-D-galactopyranosylamine D-**49d** developed by Kunz and coworkers represents a well-established efficient chiral auxiliary.[154−156] In fact, the asymmetric induction in the catalytic complexation of **9a** using the corresponding 1-pyranosyl-1-azabuta-1,3-diene D-**50d** was higher (28% ee of (*R*)-**10a**).[153] However, the catalytic activity of D-**50d** for the complexation was significantly lower. The 1,4-diaryl-1-azabuta-1,3-dienes exhibited the highest catalytic activity in the catalytic complexation of cyclohexa-1,3-diene using achiral 1-azabuta-1,3-dienes.[130] Therefore, axially chiral binaphthylamines were used for the synthesis of chiral 1-azabuta-1,3-dienes from cinnamaldehyde **(39)**. Catalytic complexation of **9a** with the catalyst (*S*)-**50e**, obtained from the known (*S*)-2-amino-2′-methoxy-1,1′-binaphthyl ((*S*)-**49e**),[157−159] afforded complex **10a** in 87% yield and with 25% ee of the *R* enantiomer.[151] Application of the corresponding isopropyl derivative (*S*)-**50f** as catalyst provided 32% ee of the *R* enantiomer.[153] These results led to the conclusion that in fact chiral 1-aryl-substituted 1-azabuta-1,3-dienes exhibit a higher catalytic activity, as previously found for the achiral 1-azabuta-1,3-diene catalysts. Moreover, an increase of the steric demand of substituents close to the nitrogen atom of the 1-azabuta-1,3-diene improves the asymmetric induction (see the ee values obtained with L-**50b**, L-**50c** and (*S*)-**50e**, (*S*)-**50f**, Table 9). This observation indicated a close proximity of the imine nitrogen and the tricarbonyliron fragment at the stage of the two diastereotopic complexes which are involved in the rate-determining step of enantioface selection at the prochiral diene.

**Table 9. Synthesis of the Chiral Catalysts 50 from Cinnamaldehyde and Asymmetric Catalytic Complexation of 1-Methoxycyclohexa-1,3-diene (9a) with Pentacarbonyliron**

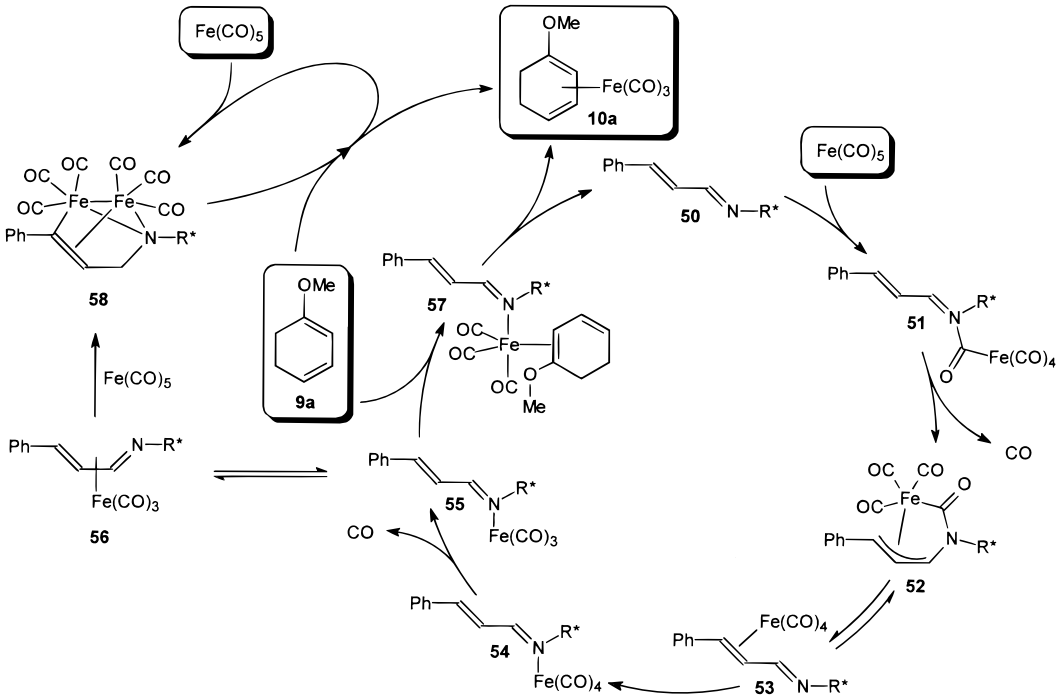
| **50**, yield [%] | reaction time | **10a**, yield [%] | ee [%][a] | ref |
|---|---|---|---|---|
| | 9 d | 2 | 0 | 152 |
| (*R*)-**50a**, 92 | 45 h | 68 | 6 (*S*) | 151 |
| (*S*)-**50a**, 92 | 45 h | 69 | 6 (*R*) | 151 |
| L-**50b**, 99 | 88 h | 91 | 12 (*R*) | 152 |
| L-**50c**, 97 | 67 h | 61 | 15 (*R*) | 152 |
| D-**50d**, 53 | 48 h | 38 | 28 (*R*) | 153 |
| (*S*)-**50e**, 90 | 42 h | 87 | 25 (*R*) | 151 |
| (*S*)-**50f**, 46 | 48 h | 81 | 32 (*R*) | 153 |

[a] Enantiomeric excess determined by chiral HPLC (absolute configuration of the excess enantiomer).

## 2. Mechanistic Considerations

On the basis of the results for the catalytic complexations described above, mechanistic studies on ligand exchange reactions at ($\eta^4$-1-azabuta-1,3-diene)-tricarbonyliron complexes,[133−135,137] previous work on

**Scheme 35**




tetracarbonyl($\eta^2$-1-oxabuta-1,3-diene)iron complexes,[160−162] and our own mechanistic studies,[128,136,138,163] the following mechanism was proposed for the asymmetric catalytic complexation of prochiral cyclohexa-1,3-dienes (e.g., **9a**) with pentacarbonyliron using chiral 1-azabuta-1,3-dienes **50** as catalysts (Scheme 35).[153]

The nucleophilic attack at a carbonyl ligand of pentacarbonyliron by the imine nitrogen of the chiral 1-azabuta-1,3-diene **50** generates the ($\sigma$-carbamoyl)-tetracarbonyliron complex **51**, which is transformed to the ($\eta^3$-allyl)($\sigma$-carbamoyl)tricarbonyliron complex **52** by a subsequent intramolecular ligand displacement. Isomerization by two consecutive haptotropic migrations convert complex **52** via the intermediate [(3−4-$\eta$)-1-azabuta-1,3-diene]tetracarbonyliron complex **53** to the [(1-$\eta$)-1-azabuta-1,3-diene]tetracarbonyliron complex **54**. At this stage, loss of a second carbon monoxide ligand provides the [(1-$\eta$)-1-azabuta-1,3-diene]tricarbonyliron complex **55**. This 16-electron complex represents the reactive intermediate of the catalytic cycle. The coordinatively unsaturated species **55** can be stabilized in a reversible intramolecular process by haptotropic migration ($\eta^1$ to $\eta^4$) of the tricarbonyliron fragment to afford the [(1−4-$\eta$)-1-azabuta-1,3-diene]tricarbonyliron complex **56**. Alternatively, the vacant coordination site at the iron atom of complex **55** can be occupied externally by a double bond of the diene system. In the case of 1-methoxycyclohexa-1,3-diene **(9a),** the coordination presumably occurs to the methoxy-substituted and thus more electron-rich double bond. The resulting 18-electron intermediate **57** was proposed to have a trigonal-bipyramidal structure with the 1-$\eta$-coordinated 1-azabuta-1,3-diene ligand in axial and the (1−2-$\eta$)-1-methoxycyclohexa-1,3-diene ligand in an equatorial position. At this stage of the catalytic complexation the enantioselection is achieved. The coordination of the prochiral diene **9a** at the metal center of the chiral 16-electron complex **55** can occur from either one of the two enantiotopic faces, which leads to diastereoisomeric complexes. The approach of the metal to the prochiral diene from the face providing the diastereoisomer which is lower in energy predominates, and thus, the formation of the resulting enantiomer is favored. Loss of the $\eta^1$-coordinated 1-azabuta-1,3-diene ligand from complex **57** regenerates the chiral catalyst **50**. The metal remains coordinated to the same enantiotopic face of the prochiral ligand during the haptotropic migration ($\eta^2$ to $\eta^4$) of the tricarbonyliron fragment. Therefore, the final isomerization of the intermediate 16-electron complex tricarbonyl[(1−2-$\eta$)-1-methoxycyclohexa-1,3-diene]iron to tricarbonyl[(1−4-$\eta$)-1-methoxycyclohexa-1,3-diene]iron **(10a)** takes place with retention of configuration and **10a** is obtained in enantioenriched form.

Besides this first, "mononuclear" catalytic cycle, there exists also a second, "dinuclear" catalytic cycle for the complexation of the diene **9a** with pentacarbonyliron (Scheme 35). The ($\eta^4$-1-azabuta-1,3-diene)-tricarbonyliron complex **56** is known as a stable tricarbonyliron transfer reagent from the stoichiometric reactions described in section III.3 and can be reversibly formed from the 16-electron intermediate **55** (compare Scheme 26).[136] Complex **56** can be transformed to the hexacarbonyldiiron complex **58** with an excess of pentacarbonyliron, as shown above for the formation of the hexacarbonyldiiron complex **48** from the standard catalyst **41b** (Scheme 33).[138] The dinuclear complex **48** was shown to be able to transfer one of the two tricarbonyliron fragments to a 1,3-diene at elevated temperatures. After the transfer of the metal fragment from **48**, decomposition of the residual organometallic complex occurs under the reaction conditions of this stoichiometric process. Therefore, complex **48** does not show a catalytic activity for the complexation of dienes. In

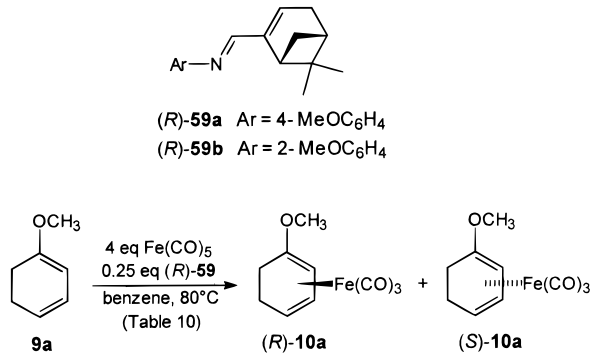
contrast to the reactivity of complex **48**, some other dinuclear iron complexes are capable of catalyzing the complexation of 1,3-dienes with pentacarbonyliron. The feasibility of the dinuclear iron complexes for a catalytic activity in the complexation is dependent on the structure of their ligands as shown in more recent investigations (see below).[153,163] In the dinuclear catalytic cycle, the hexacarbonyldiiron complex **58** transfers one tricarbonyliron fragment to the diene **9a** forming complex **10a** and complex **58** is regenerated by further reaction with pentacarbonyliron.

## 3. Chiral Catalysts from Terpenes and Steroids—Photolytic Induction of Asymmetric Catalysis

The chiral catalysts **50**, obtained simply by imine condensation of cinnamaldehyde and a chiral amine (Scheme 34), provided complex **10a** in 81% yield with 32% ee as the best result for the asymmetric catalytic complexation of the prochiral diene **9a** with pentacarbonyliron (Table 9). In view of the proposed mechanism described above (Scheme 35), the reaction conditions were systematically optimized and structurally different chiral catalysts were synthesized starting from terpenes and steroids. Their characteristic structural feature is a cyclic system annulated at the 2,3- or at the 3,4-position of the 1-azabuta-1,3-diene core. This carbocyclic ring contains the stereogenic centers which are responsible for the asymmetric induction.

Condensation of (1*R*)-(−)-myrtenal with *p*-anisidine and *o*-anisidine provided the chiral catalysts (*R*)-**59a** (62% yield) and (*R*)-**59b** (75% yield). Both catalysts have an identical chiral auxiliary and led, obviously, by the same mode of asymmetric induction to the same enantiomeric excess for the *R* enantiomer of complex **10a** on catalytic complexation of **9a** with pentacarbonyliron (Scheme 36, Table 10).[151] At a

**Scheme 36**




reaction time of 38 h, catalyst (*R*)-**59b** provided complex **10a** in 67% yield while catalyst (*R*)-**59a** gave only a yield of 29%. The beneficial effect of an *ortho*-methoxy group in the 1-aryl ring on the catalytic activity of 1-azabuta-1,3-dienes was reported previously for the achiral catalysts.[128,138] On the basis of the mechanism presented in Scheme 35, the increased catalytic activity of 1-(*o*-anisyl)-substituted 1-azabuta-1,3-dienes such as (*R*)-**59b** is ascribed to a displacement of the carbon monoxide ligand at the stage of the intermediate **54** which is facilitated by

**Table 10. Asymmetric Catalytic Complexation of 1-Methoxycyclohexa-1,3-diene (9a )with Pentacarbonyliron Using the (1*R*)-(−)-Myrtenal-Derived Catalysts (*R*)-59**

| catalyst | reaction time [h] | **10a**, yield [%] | ee [%][a] | ref |
|---|---|---|---|---|
| (*R*)-**59a** | 38 | 29 | 33 (*R*) | 151 |
| (*R*)-**59b** | 38 | 67 | 33 (*R*) | 151 |
| (*R*)-**59b** | 72 | 95 | 33 (*R*) | 153 |
| (*R*)-**59c** | 48 | 47 | 11 (*R*) | 153 |

[a] Enantiomeric excess determined by chiral HPLC (absolute configuration of the excess enantiomer).

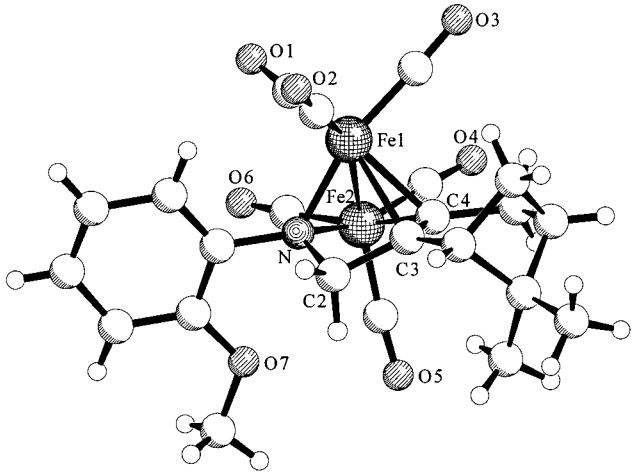
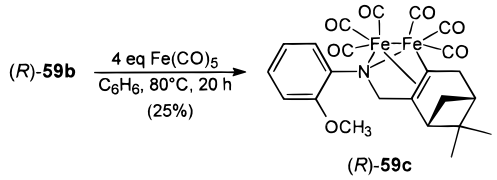



**Figure 5.** Molecular structure of the chiral hexacarbonyldiiron complex (*R*)-**59c** in the crystal (SCHAKAL representation; arbitrary numbering). Selected bond lengths [Å]: Fe1−Fe2 2.439(2), Fe1−N 1.970(8), Fe1−C3 2.255 (10), Fe1−C4 2.138(9), Fe2−N 1.970(7), Fe2−C4 1.958(8).

the *ortho*-methoxy group (associative mechanism). Moreover, the resulting 16-electron complex **55** may be stabilized by coordination of the oxygen to the iron atom (chelation). Extension of the reaction time to 3 days using catalyst (*R*)-**59b** afforded complex **10a** in 95% yield with the same asymmetric induction (33% ee of the *R* enantiomer).[153] The chiral hexacarbonyldiiron complex (*R*)-**59c** was isolated as a byproduct of this asymmetric catalytic complexation. Compound (*R*)-**59c** is structurally unique, because it represents the first example of a hexacarbonyldiiron complex which is formed by 1,3-hydrogen shift from a simple α,β-unsaturated imine. Previously this type of a dinuclear iron complex was obtained exclusively from the imines of aromatic aldehydes[141−148] and complex **48** (see above) represented the first example resulting from a vinylogous aromatic aldehyde. The structural assignment of the dinuclear iron complex (*R*)-**59c** was confirmed by an X-ray crystal structure determination (Figure 5).

Direct reaction of the 1-azadiene (*R*)-**59b** with pentacarbonyliron using similar conditions provided the dinuclear iron complex (*R*)-**59c** more conveniently (Scheme 37). It was demonstrated that the iron cluster (*R*)-**59c** represents a catalyst for the complexation of **9a** with pentacarbonyliron. However, with respect to catalytic activity and asymmetric induction, the 1-azadiene (*R*)-**59b** is superior to the iron cluster (*R*)-**59c**. Using (*R*)-**59c** as catalyst for the complexation of **9a** under the standard reaction

**Scheme 37**




conditions for 2 days provided complex **10a** in 47% yield with 11% ee of the *R* enantiomer (Table 10).[153] After the asymmetric complexation via the "dinuclear catalytic cycle", the hexacarbonyldiiron complex (*R*)-**59c** was reisolated (70% yield).

In contrast to the dinuclear iron complex **48**, the cluster (*R*)-**59c** shows a catalytic activity for the complexation of dienes with pentacarbonyliron which may result from the *ortho*-methoxy group of the 1-aryl ring. The reactive intermediate of the dinuclear catalytic cycle perhaps is formed by transfer of the tricarbonyliron fragment to the diene and stabilized by chelation via the oxygen. Because of the lability of the hexacarbonyldiiron complex, the turnover of the dinuclear catalytic cycle is lower. Moreover, the enantioselectivity which is obtained by transfer of the tricarbonyliron fragment from the dinuclear complex to the prochiral diene is considerably lower. From these results it was concluded that the reaction conditions for the catalysis should be modified to avoid a complexation via the dinuclear catalytic cycle.

In the mechanism shown in Scheme 35, a loss of a carbon monoxide ligand is proposed at the stage of the intermediates **51** and **54**. Decarbonylations of transition metal carbonyl complexes generally can be induced either thermally or photolytically. Therefore, it was speculated that the efficiency of the catalytic cycle perhaps could be increased by irradiation. The feasibility of a photolytic induction of the asymmetric catalytic complexation was demonstrated using the catalyst (*R*)-**60**, which was obtained from (1*R*)-(+)-camphor by aldol condensation of with 4-methoxybenzaldehyde and subsequent imine condensation with *p*-anisidine (69% overall yield).[151]

The complexation of the prochiral 1,3-diene **9a** with pentacarbonyliron using (*R*)-**60** as catalyst under the standard conditions described above but with the strict exclusion of light provided complex **10a** in only 14% yield after a reaction time of 14 days (Scheme 38, Table 11).[164] However, the asymmetric induction was much better and the *S* enantiomer was obtained in 56% ee. In a second set of experiments, the catalytic complexation was exposed to sunlight. The blank experiment afforded complex **10a** in 26% yield after 2 days and demonstrated that the uncatalyzed complexation, which leads to racemic product, is of importance under these conditions. A corresponding increase of the reaction rate for the catalytic complexation was confirmed. Using 25 mol % of (*R*)-**60** as catalyst, complex **10a** could be isolated in 66% yield after a reaction time of 2 days and quantitatively after 12 days. Surprisingly, despite the uncatalyzed pathway to racemic **10a**, the catalytic complexation of **9a** with pentacarbonyliron and catalyst (*R*)-**60** in the presence of daylight gave even a

**Scheme 38**

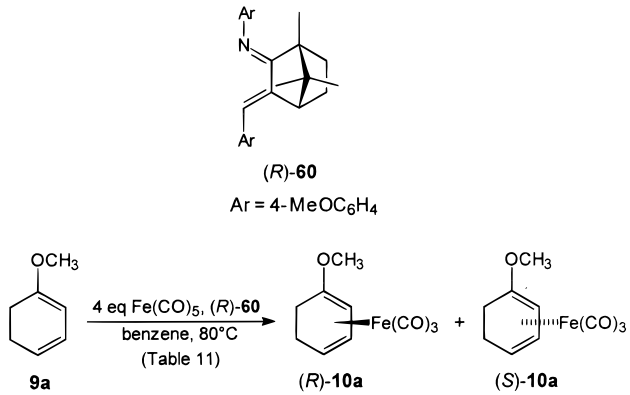



**Table 11. Influence of Light on the Asymmetric Catalytic Complexation of 1-Methoxycyclohexa-1,3-diene (9a) with Pentacarbonyliron Using the (1*R*)-(+)-Camphor-Derived Catalyst (*R*)-60**

| (*R*)-**60** [equiv] | reaction conditions | **10a**, yield [%] | ee [%][a] |
|---|---|---|---|
| 0.0 | dark, 9 d | 2 | |
| 0.25 | dark, 2 d | 3 | 53 (*S*) |
| 0.25 | dark, 14 d | 14 | 56 (*S*) |
| 0.0 | daylight, 2 d | 26 | |
| 0.25 | daylight, 2 d | 66 | 73 (*S*) |
| 0.25 | daylight, 12 d | 99 | 73 (*S*) |

[a] Enantiomeric excess determined by chiral HPLC (absolute configuration of the excess enantiomer).

higher asymmetric induction (73% ee of the *S* enantiomer) than the corresponding complexation in the dark.[164]

On the basis of these findings, a new set of standard reaction conditions for the photolytically and thermally induced asymmetric catalytic complexation was developed. The amount of pentacarbonyliron was reduced from 4 to 1.5 equiv to avoid the formation of hexacarbonyldiiron complexes and, thus, a participation of the dinuclear catalytic cycle. For a better reproducibility of the photolytic induction, a 10 W halogen lamp was used as the light source. All other reaction parameters (25 mol % of catalyst, benzene, reflux) were the same as those described previously.

Under the thermal conditions for the catalytic complexation of **9a** described above (Table 11, entry 3), the (1*R*)-(+)-camphor-derived catalyst (*R*)-**60** provided the highest asymmetric induction. This result was rationalized by the fact that the catalyst (*R*)-**60** has a fixed *s-cis* conformation of the 1-azabuta-1,3-diene moiety in contrast to the previous catalysts **50** and (*R*)-**59**. In the catalytic complexation with (*R*)-**60**, the extrusion of the first carbon monoxide from pentacarbonyliron by intramolecular ligand displacement is facilitated because a change of the conformation of the 1-azabuta-1,3-diene core is not required (cf. the conversion of **51** to **52** in Scheme 35). Thus, a series of chiral catalysts (**60**−**62**) was synthesized which have a fixed *s-cis* conformation of the 1-azabuta-1,3-diene moiety due to an annulated polycyclic terpenoid ring system at the 2,3-position. The simple two-step sequence aldol condensation with 4-methoxybenzaldehyde and condensation with *p*-anisidine

**Scheme 39**

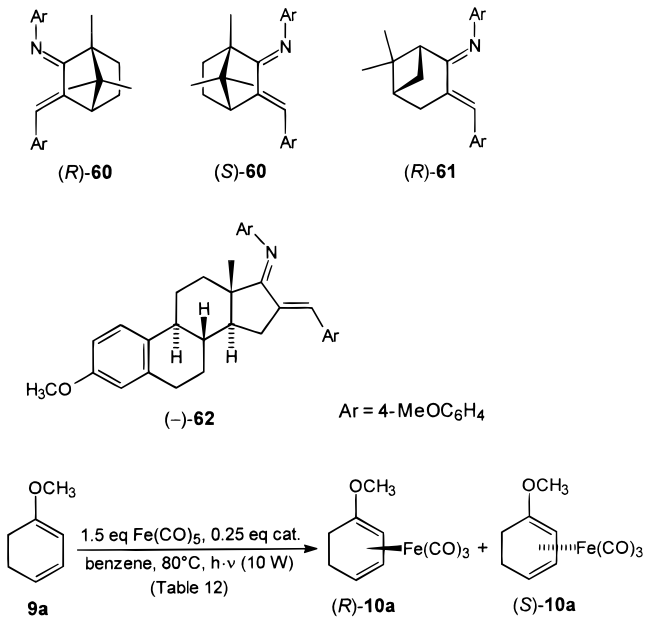



**Table 12. Photolytically Induced Asymmetric Catalytic Complexation of 1-Methoxycyclohexa-1,3-diene (9a) with Pentacarbonyliron Using Various Catalysts[a]**

| catalyst, yield [%] | *t* [d] | **10a**, yield [%] | ee [%][b] | $[\alpha]_D^{20}$ (*c*)[c] |
|---|---|---|---|---|
| | 1 | 20 | 0 | − |
| (*R*)-**59b**, 75 (1 step) | 2 | 98 | 39 (*R*) | −54.0 (1.02) |
| (*R*)-**60**, 69 (2 steps) | 1 | 97 | 86 (*S*) | +130.0 (1.09) |
| (*S*)-**60**, 65 (2 steps) | 1 | 99 | 85 (*R*) | −127.3 (1.00) |
| (*R*)-**61**, 76 (2 steps) | 5 | 92 | 59 (*S*) | +87.4 (0.96) |
| (−)-**62**, 94 (2 steps) | 2 | 94 | 57 (*R*) | −83.5 (0.97) |

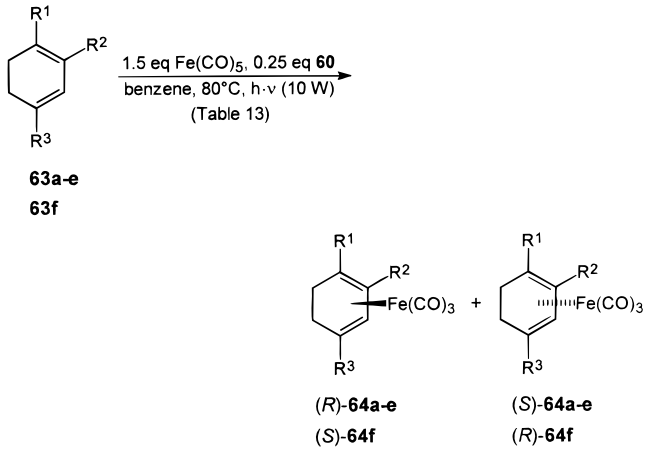
[a] Reaction using 1.5 equiv of $Fe(CO)_5$ and 0.25 equiv of catalyst in benzene at 80 °C with irradiation by a 10 W halogen lamp. [b] Enantiomeric excess determined by chiral HPLC (absolute configuration of the excess enantiomer). [c] Specific rotation in chloroform (concentration [g/100 mL]).

provided the catalysts (*S*)-**60** from (1*S*)-(−)-camphor, (*R*)-**61** from (1*R*)-(+)-nopinone, and (−)-**62** from (+)-estrone methyl ether.[153,164]

The blank experiment for the complexation of **9a** using the new set of standard reaction conditions without the presence of a catalyst provided by photolytic and thermal induction the racemic complex **10a** in 20% yield after a reaction time of 1 day. However, the catalytic complexation of **9a** with pentacarbonyliron proceeds much faster than the uncatalyzed complexation. Therefore, quantitative yields of complex **10a** and high asymmetric inductions of up to 86% ee were achieved by the photolytically induced asymmetric catalytic complexation using **60**−**62** as catalysts (Scheme 39, Table 12).[164] A comparison of the results for the asymmetric complexation with the catalysts (*R*)-**59b** and (*R*)-**60** by photolytic induction (Table 12) and the previous results, which were obtained by thermal induction only (Tables 10 and 11), emphasizes the superiority of the new procedure for the catalytic complexation. The yields are generally over 90%, the reaction times are considerably shorter, and the asymmetric inductions are higher. It was confirmed that the catalyst (*R*)-**59b**, which can adopt an *s-trans* conformation of the 1-azabuta-1,3-diene core, leads to a lower enantioselectivity than the catalysts **60**−**62** with a fixed *s-cis* conformation. The best catalysts for the asymmetric catalytic complexation of the diene **9a** with pentacarbonyliron are the camphor-derived catalysts **60**. Due to their high catalytic activity, the 1-azadienes **60** provide complex **10a** quantitatively within a reaction time of only 1 day. Moreover, camphor is commercially available in both enantiomeric forms, and thus, either enantiomer of complex **10a** can be obtained in high enantioselectivity (85−86% ee) by asymmetric catalytic complexation.

The photolytically induced asymmetric catalytic complexation with pentacarbonyliron and the camphor derivatives **60** as catalysts was applied to a range of prochiral cyclohexa-1,3-dienes **63a**−**f** (Scheme 40, Table 13).[164] By using either (*R*)-**60** or (*S*)-**60** as

**Scheme 40**




catalyst, an excess was achieved for both enantiomers of the resulting tricarbonyliron complexes **64a**−**f**. The examples which were reported demonstrate that prochiral cyclohexa-1,3-dienes with donor and acceptor substituents in various positions are useful as substrates. The best enantioselectivities of the asymmetric catalysis were achieved in the synthesis of the tricarbonyliron complexes **64a**−**c** and **64e** (72−86% ee). The asymmetric catalytic complexation of the prochiral cyclohexa-1,3-diene **63d** provided an enantiomeric excess of 50% for either enantiomer of the tricarbonyliron complex **64d**. The original synthesis of racemic **64d** was achieved by direct complexation of **63d** with a large excess of pentacarbonyliron at 142 °C (cf. Scheme 6).[56] Complex **64d** represents a versatile building block for the stereoselective synthesis of spirocyclic compounds.[165−168] The tricarbonyliron complex **64f** was obtained in only 42% ee for both enantiomers with the camphor derivatives **60** as catalysts. However, using the estrone derivative (−)-**62** as catalyst for the photolytically induced asymmetric complexation of **63f** provided complex **64f** after 2 days in 87% yield with 57% ee of the (+)-enantiomer.[164]

This final result indicates the right choice of the catalyst in each single case, and perhaps a further fine-tuning of the reaction conditions are required in order to achieve high asymmetric inductions in the

**Table 13. Photolytically Induced Asymmetric Catalytic Complexation of the Prochiral Cyclohexa-1,3-dienes 63 with Pentacarbonyliron Using the Camphor-Derived Catalysts 60**[a]

| | | | | | **64**, by cat. (*R*)-**60** | | **64**, by cat. (*S*)-**60** | |
|---|---|---|---|---|---|---|---|---|
| **63** | $R^1$ | $R^2$ | $R^3$ | *t* [d] | yield [%] | ee [%][a] | yield [%] | ee [%][b] |
| **a** | OMe | H | H | 1 | 97 | 86 (*S*) | 99 | 85 (*R*) |
| **b** | O*i*-Pr | H | H | 3 | 78 | 79 (+) | 82 | 81 (−) |
| **c** | OMe | H | Me | 2 | 86 | 72 (*S*) | 81 | 73 (*R*) |
| **d** | OMe | H | $CH_2COOMe$ | 2 | 93 | 50 (*S*) | 89 | 50 (*R*) |
| **e** | H | COOMe | H | 1 | 90 | 76 (−) | 87 | 74 (+) |
| **f** | COOMe | H | H | 1 | 81 | 42 (−) | 77 | 42 (+) |

[a] Reaction using 1.5 equiv of $Fe(CO)_5$ and 0.25 equiv of catalyst in benzene at 80 °C with irradiation by a 10 W halogen lamp. [b] Enantiomeric excess determined by chiral HPLC (absolute configuration or direction for rotation of the plane of polarized light).

asymmetric catalytic complexation of a broad range of structurally different prochiral dienes.

## VI. Conclusion

Using a labile tricarbonyliron complex for the transfer of the metal fragment to the diene, the complexation occurs under much milder reaction conditions than by direct reaction with pentacarbonyliron. Therefore, tricarbonyliron transfer reagents generally provide better yields for the synthesis of tricarbonyl($\eta^4$-1,3-diene)iron complexes from the corresponding dienes. A further drawback of the classical procedure is that very often a large excess of the binary carbonyliron complex (pentacarbonyliron, nonacarbonyldiiron, or dodecacarbonyltriiron) must be used. This is hazardous on workup, since residual pentacarbonyliron is in the reaction mixture and pyrophoric iron is formed. The tricarbonyl($\eta^4$-1-oxabuta-1,3-diene)iron complexes and tricarbonylbis($\eta^2$-*cis*-cyclooctene)iron are more reactive tricarbonyliron transfer reagents than the ($\eta^4$-1-azabuta-1,3-diene)-tricarbonyliron complexes. Only the free ligands corresponding to the latter reagents, the 1-azabuta-1,3-dienes, have the advantage that they catalyze the complexation of dienes by the tricarbonyliron fragment. With the azadiene-catalyzed complexation of cyclohexadienes, a quantitative exploitation of the tricarbonyliron fragments of pentacarbonyliron and nonacarbonyldiiron was achieved. This process is superior from the safety point of view especially on a large scale, because no residual pentacarbonyliron is left in the reaction mixture and no pyrophoric iron is formed.

The azadiene-catalyzed complexation of dienes has been applied to an asymmetric catalytic complexation of prochiral cyclohexa-1,3-dienes using chiral 1-azabuta-1,3-dienes as catalysts. Using the camphor-derived azadiene catalysts, asymmetric inductions of up to 86% ee and quantitative yields were obtained by simultaneous photolytic and thermal induction of the catalytic complexation. This method represents the first example of an asymmetric catalytic process which generates planar−chiral transition metal $\pi$-complexes by enantioselective complexation from the corresponding prochiral ligands. The scope of this methodology appears to be much broader. Related asymmetric catalytic complexations should provide planar−chiral ($\eta^4$-cyclohexa-1,3-diene)($\eta^5$-cyclopentadienyl)cobalt complexes from prochiral dienes and planar−chiral ($\eta^6$-arene)tricarbonylchromium complexes from prochiral arenes. Therefore, the asymmetric catalytic complexation of prochiral ligands with transition metal fragments should have a major impact on the future synthesis of enantiopure transition metal $\pi$-complexes as starting materials for organic synthesis.

## VII. Acknowledgements

I am indebted to my co-workers Peter Gonser, Michael Heininger, Holger Hermann, Daniela Herzberg, and Guy Rohde for their enthusiasm and excellent work as reflected in the scientific publications cited in the references. Additional support by Dr. Norbert Fotzik and Dr. Herbert Röttele with dynamic $^{13}C$ NMR measurements is gratefully acknowledged. I would like to thank Dr. Elke Baum, Gerhard Baum, and Dr. Helmut Goesmann (Institut für Anorganische Chemie der Universität Karlsruhe) and Professor Peter G. Jones (Institut für Anorganische und Analytische Chemie der Technischen Universität Braunschweig) for many X-ray crystal structure determinations. I am grateful to the Deutsche Forschungsmeinschaft, the Volkswagen Stiftung, and the Fonds der Chemischen Industrie for the financial support of our research projects. Moreover, I thank the BASF AG (Ludwigshafen) and the Schering AG (Berlin) for their support of our work with generous gifts of chemicals, Professor Horst Kunz (Institut für Organische Chemie der Universität Mainz) for 2,3,4,6-tetra-*O*-pivaloyl-$\beta$-D-galactopyranosylamine, and Professor Karlheinz Drauz (Degussa AG, Hanau) for L-*tert*-leucine.

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CR990267K