# 127. Synthesis and $^1H$-, $^{13}C$-, and $^{57}Fe$-NMR Spectra of Mono- and Bis[tricarbonyl($\eta^4$-diene)iron], and ($\eta^3$-Allyl)tetracarbonyliron Trifluoroborate Complexes[1])

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(14.III.88)

A variety of mono- and bis[$Fe(CO)_3(\eta^4$-diene)] complexes with alkyl, $CH_2OH$, CHO, $COCH_3$, COOR, and CN substituents on the 1,3-diene system have been synthesized. Dienes with a (*Z*)-configurated terminal Me group show steric inhibition of metal complexation resulting in lower yields and formation of tetracarbonyl($\eta^2$-diene) and tricarbonyl($\eta^4$-heterodiene) complexes as additional products. Regioselective attack by C-nucleophiles at the carbonyl C-atom of the functional group with or without concomitant 1,3 migration of the $Fe(CO)_3$ group was used to synthesize polyenes and isoprenoid building blocks as mono- or dinuclear $Fe(CO)_3$ complexes. *Wittig-Horner*-type reactions of $Fe(CO)_3$-complexed synthons result in stereospecific formation of (*E*)-configurated olefins. The $^1H$-, $^{13}C$-, and $^{57}Fe$-NMR spectra of 73 olefinic and allylic organoiron complexes are reported. H,H, C,H, and C,C coupling constants have been evaluated and are analyzed in terms of the geometry of the coordinated diene. The results are corroborated by the crystal structure of tricarbonyl[3–6-$\eta$-((*E*)-6-methyl-3,5-heptadiene-2-one)]iron (**34**) which shows an unusual distortion of the $(CH_3)_2C=$ group. The $^{57}Fe$-NMR chemical shifts extend over the ranges of 0–600 ppm for [$Fe(CO)_3(\eta^4$-diene)] complexes, 780–1710 ppm for [$Fe(CO)_4(\eta^3$-allyl)] [$BF_4$] and [$FeX(CO)_3(\eta^3$-allyl)] complexes, and 1270–1690 ppm for [$Fe(CO)_3(\eta^4$-enone)] complexes, relative to $Fe(CO)_5$.

**1. Introduction.** – Coordination of 1,3-dienes to a $Fe(CO)_3$ group provides a means of moderating the reactivity of the unsaturated system to catalytic hydrogenation, hydroboration, and electrophilic and *Diels-Alder* reactions [2]. It also influences the reactivity of functional groups attached to the diene system in terms of chemo- and stereoselectivity [3]. Furthermore, steric interactions of the $Fe(CO)_3$ group with the diene substituents provide a source for considerable geometric distortions of the diene system as shown by X-ray crystallography [3d] [4] and NMR spectroscopy [5].

A general use of tricarbonyliron-complexed synthons in organic synthesis requires a more than qualitative understanding of these effects, and for this reason, we have synthesized several series of substituted-diene complexes and investigated their structural properties and chemical reactivity. Similar studies have already been reported for [$Rh(C_5H_5)$(diene)], [$Co(C_5H_5)$(diene)], and [Co(indenyl)(diene)] complexes with 1,3- and 1,4-dienes and have revealed a decreased shielding of the $^{103}Rh$- and $^{59}Co$-NMR resonances with increasing ring size or distortion of the complexed diene ligand [6]. This in turn correlates with a decrease in thermal stability and an increase in catalytic activity in the case of the cobalt complexes [6a] [7]. Therefore, the NMR spectroscopic properties of

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[1]) Transition-Metal NMR Spectroscopy, Part XI. Part X: [1].

transition-metal diene complexes provide a sensitive probe into the structure and reactivity of such compounds.

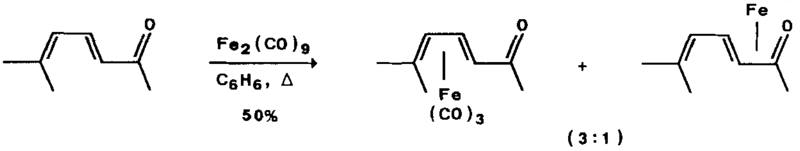
**2. Synthetic Methods.** – 2.1. *Functionalized Butadiene Complexes.* A variety of methods for the preparation of ironcarbonyl complexes of dienes are described in the literature. Many of these are restricted to special substrates, *e.g.* metal-vapour synthesis [8], rearrangement of ligands [9], reaction of ironcarbonyls with halogen compounds [10], or ligand exchange reactions [2] [11]. The most convenient way for the synthesis of [$Fe(CO)_3$(diene)] complexes is the interaction of the ligand with either $Fe(CO)_5$ or $Fe_2(CO)_9$ from which carbonyl ligands are displaced on heating or irradiation [12].

The $Fe(CO)_5$/UV method is especially useful for preparing [$Fe(CO)_3$(diene)] complexes of dienes without substituents containing hetero atoms (yields usually 65–85%). However, isomerizations and side reactions occurred, with ligands containing a carbonyl function. In this case, the use of $Fe_2(CO)_9$ at elevated temperature provided better results, although yields were somewhat lower (45–80%). In some cases, this limitation was overcome by the addition of an excess of $Fe_2(CO)_9$ after *ca.* half of the reaction time *(cf. Exper. 4, Exper. Part)*. The heterodiene complexes **64–66**, **69**, and **70** were synthesized by the $Fe(CO)_5/h\nu$ method *(cf. Exper. 5, Exper. Part)* in 60–80% yield.

The yield of the complexation reaction appeared to be mainly controlled by two effects, electron density and steric hindrances in the s-*cis*-1,3-diene ligand. Dienes with a terminal substituent with a (*Z*)-arrangement relative to the central C–C bond have to undergo considerable conformational rearrangement on complexation (see below). On the other hand, a CN group attached to the diene dramatically reduces the reactivity of the ligand, even if no steric strain is present. As a general rule, yields decrease as the (–*M*)-effect of the substituent increases.

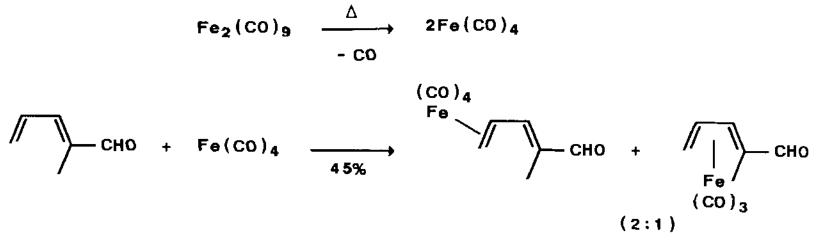
In some cases, the tendency to avoid steric strain on complexation resulted in the formation of unexpected products. Thus, the complexation of (*E*)-6-methyl-3,5-heptadien-2-one is presumably hindered by the interference of the $CH_3$(8) group with the

*Scheme 1*



**34** **35**

*Scheme 2*



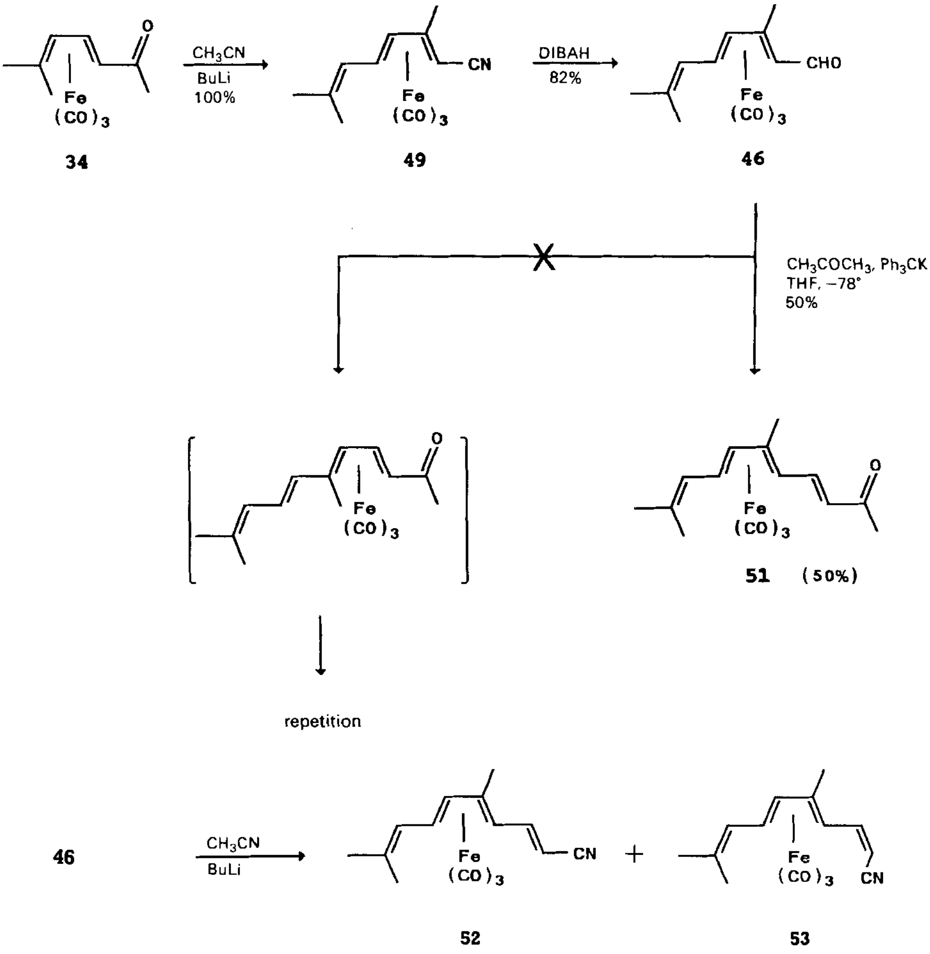
**36** **37**

$Fe(CO)_3$ moiety: in addition to **34**, a considerable amount of the unstable dark-red enone complex **35** was formed (identification by NMR spectroscopy²), *Scheme 1*).

In the synthesis of **37**, the same type of steric interaction led to a $[Fe(CO)_4(\eta^2\text{-diene})]$ complex **36** as the major product³) *(Scheme 2)*. This is in accordance with the proposed mechanism for the formation of $[Fe(CO)_3(\eta^4\text{-diene})]$ complexes *via* the $\eta^2$-stage [13].

2.2. *Isoprenoid Complexes.* 2.2.1. *Reactions of Isoprenoid Synthons.* It has been shown that aldol condensations and similar reactions of functionalized $[Fe(CO)_3(\text{diene})]$ complexes can be used for the synthesis of polyene chains [3a]. One of the aims of the present

*Scheme 3*



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²) Indicative for the enone mode of complexation are the $^1H$- and $^{13}C$-NMR signals for an uncomplexed double bond as well as the low-frequency shift of the $^{13}C$ resonance of C(2).

³) As in the case of **35**, the signals of an uncomplexed bond (C(2)=C(3)) are observed in the $^1H$- and $^{13}C$-NMR spectra.

investigation was the adaptation of this method to the formation of polyisoprene units. The reaction sequence necessary for the achievement of this goal is shown in *Scheme 3*.

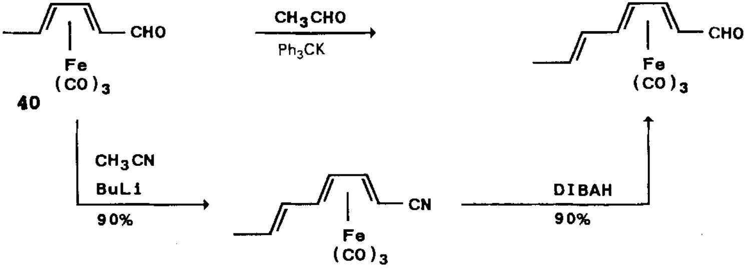
For several reasons, **34** was chosen as starting material: its ligand can be prepared easily from commercially available compounds, and **34** is stable to air and can be handled without excessive precautions[4]).

The action of BuLi and MeCN on **34** at low temperature gave **49** in quantitative yield whereas the corresponding reaction using the 2,4-hexadienal complex **40** as starting material is described to provide 90% of the nitrile **47** *(cf. Scheme 4)* [3a]. The improved yield in the former case is probably due to the migration of the $Fe(CO)_3$ group from a sterically crowded 3–6-$\eta$ coordination in **34** to a sterically relaxed 2–5-$\eta$ coordination in **49**. The reduction **49**→**46** proceeded as expected using diisobutylaluminum hydride (DIBAH).

Condensation of the aldehyde **46** with the enolate ion of acetone would provide the acetylated terpenoid complex which in turn could have been used as starting material for a repetition of the whole sequence *(Scheme 3)*. For the deprotonation of acetone, $Ph_3CK$ was used because of its low tendency to attack C=O bonds and its deep red colour which allows titration of the substrate. However, on reaction with **46**, no migration of the $Fe(CO)_3$, residue to the newly formed double bond occurred, but complex **51** was formed in poor yield. Some modifications including variation of the stoichiometry and inverse addition of the reagent *(cf. Exper. Part)* led to slightly increased yields of **51**, but again no 3–6-$\eta$-bonded product could be isolated. The same substrate **46** was subjected to condensation with MeCN/BuLi in order to verify that the unusual behaviour of **46** with respect to nucleophilic attack is not a consequence of the applied base. As in the formation of **51**, no migration could be observed and a mixture of the corresponding nitriles **52** and **53** was isolated in high yields. On the other hand, treatment of the 2,4-hexadienal complex **40** with the system $CH_3CHO/Ph_3CK$ provided 50% of [$Fe(CO)_3$(2–5-$\eta$-(2,4,6-octatrien-1-al))] [3a]. This condensation combines the reaction of **40** with MeCN/BuLi and subsequent treatment of the product with DIBAH [3a] into one step *(Scheme 4)*.

From these facts, including the quantitative yield in the step **34**→**49**, we conclude that the reason for the unexpected behaviour of **46** can be attributed to the Me group at C(3). On migration of the metal atom, this substituent would be forced to change from a sterically unhindered to a hindered position. The resulting unfavourable configuration is

*Scheme 4*



**40**

**47**

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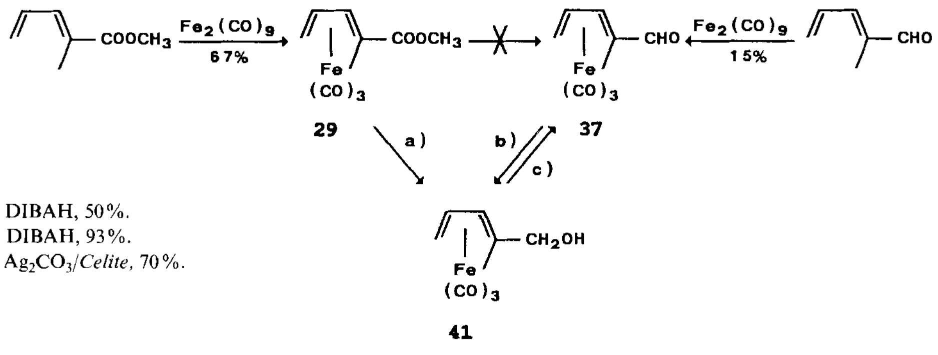
[4]) Attempts to synthesize **34** by *Friedel-Crafts* acetylation of the tricarbonyliron complex **11** of 2-methyl-2,4-pentadiene failed. We ascribe this fact to steric hindrance caused by one of the Me group at C(2) which interferes with the Ac group in the (*Z*)-isomer of **34** which is initially formed on acetylation [14].

rejected, and the reaction terminates with the formation of **51**, rendering a repetition of the sequence according to *Scheme 3* impossible. This evidence agrees with the dependance of the yield of complexation on the different constitution of the diene ligand as discussed in *2.1* and illustrates the importance of steric effects in the chemistry of [Fe(CO)$_3$(diene)] complexes.

2.2.2. *Interconversion of Hydroxymethyl and Carbonyl Groups in the Complexes.* As mentioned earlier, sterically hindered aldehydes give poor yields on complexation with $Fe_2(CO)_9$, whereas the corresponding esters usually exhibit a much better reactivity. On the other hand, the complexation of hydroxymethyl-substituted dienes, which proceeds in good yields, is often accompanied by side reactions and rearrangements which make isolation procedures tedious and time-consuming. Moreover, such ligands are difficult to prepare and handle because of their tendency to form polymers and their sensibility to oxidation. It seems, therefore, desirable to find a convenient way for the interconversion of ester, aldehyde, and hydroxymethyl substituents in the metal complexes. Both the tricarbonyliron complexes of the aldehydes and of the alcohols are of potential interest: the former with respect to chain elongation by aldol-type reactions, and the latter for the preparation of tricarbonyliron-complexed pentadienylium salts [15].

None of the published procedures [16] for the conversion of esters to aldehydes could be adapted to proceed reasonably on the corresponding tricarbonyliron complexes. However, the tricarbonyliron moiety being more or less inert with respect to reagents of the DIBAH type (*cf.* preparation of **46**), the ester function in the complex was reduced to the $CH_2OH$ substituent with moderate to good yields and the latter oxidized to the aldehyde using $Ag_2CO_3$ on *Celite* (*Fetizon* reagent) in benzene (yields *ca.* 70%), the $Fe(CO)_3$ moiety being again unaffected (see **29**→**41**→**37**, *Scheme 5*). Sometimes, better yields of the complexed alcohol were obtained on DIBAH reduction of the complexed aldehyde instead of the ester (see **37**→**41**).

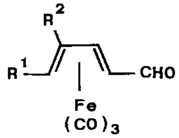
*Scheme 5*

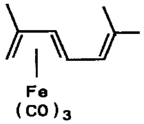


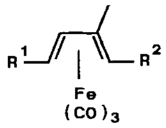
a) DIBAH, 50%.
b) DIBAH, 93%.
c) $Ag_2CO_3$/*Celite*, 70%.

Analogous transformations were performed in the bis-complexed $C_{14}$-series *(cf. 2.2.4)*.

2.2.3. *Bifunctionalized Diene Complexes.* Functionalized [Fe(CO)$_3$(diene)] complexes such as **39** or **40** can be used in *Wittig*-type olefinations [17]. For example, the reaction of **39** with isopropylphosphonium bromide/$NaNH_2$ [18] in THF at −78° proceeds smoothly to yield 88% of the $\eta^4$-complexed triene **44**. Furthermore, stereospecific formation (*E*) of







**39** $R^1 = H$, $R^2 = CH_3$
**40** $R^1 = CH_3$, $R^2 = H$

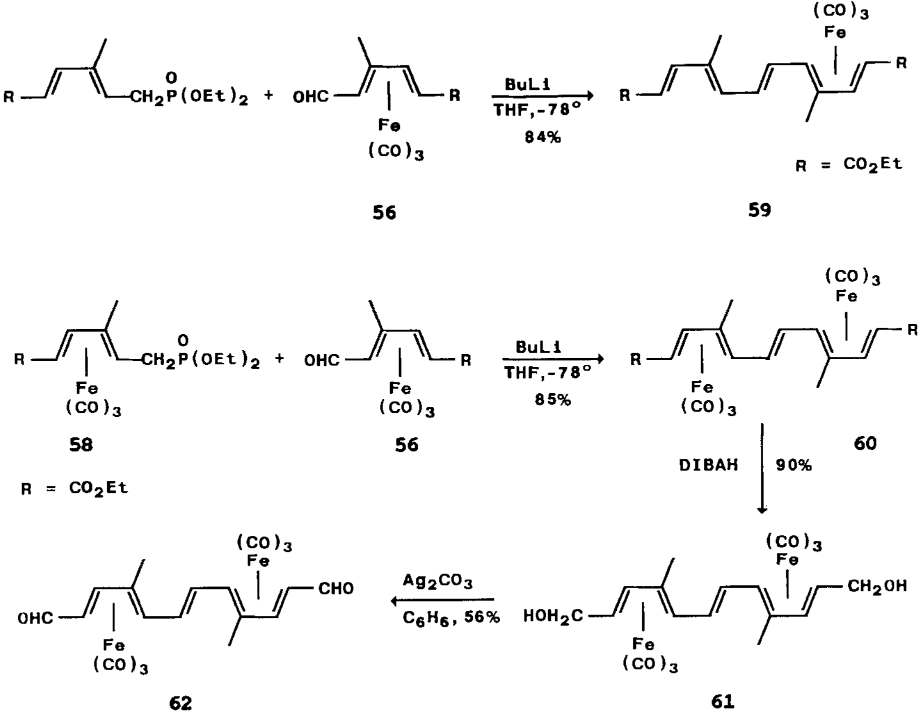
**44**

**54** $R^1 = R^2 = COOEt$
**55** $R^1 = CHO$, $R^2 = COOEt$
**56** $R^1 = COOEt$, $R^2 = CHO$
**57** $R^1 = COOEt$, $R^2 = CH_2OAc$

the new double bond can be achieved using the *Wittig-Horner* method [17] [5e]. To determine the scope of these reactions in polyene natural product synthesis, we prepared and complexed a number of bifunctionalized isoprene derivatives. Their complexation was accomplished by refluxing in $Et_2O$ with 1.5 equiv. of $Fe_2(CO)_9$, giving, *e.g.*, **54–57** in 65–85% yield. As in the case of the monofunctionalized diolefins, the yield depended on the diene substituents showing the following trends: COOR > CHO > $CH_2OAc \gg CN$. Again, nitriles gave poor yields in complexation reactions.

2.2.4. *Mono- and Bis-complexed $C_{14}$-Synthons.* Addition of tertiary phosphanes and phosphites to cationic iron complexes give metal-coordinated phosphonium salts and phosphonates which have been used in *Wittig* and *Wittig-Horner* reactions [17] [19]. For the preparation of mono- and bis-complexed $C_{14}$-synthons, we reacted complexed aldehydes first with uncomplexed and then with complexed ylides.

*Scheme 6*



To achieve the stereoselective coupling of two diene synthons in a *Wittig-Horner* reaction, ethyl 6-(diethoxyphosphoryl)-4-methyl-2,4-hexadienoate [20] was added to the complexed $C_7$-aldehyde **56** *(Scheme 6)*, giving the mono-complexed $C_{14}$-diester **59** in 84% yield. The $^1$H-NMR coupling constant between H–C(6) and H–C(7) (15.6 Hz) suggested (*E*)-configuration for the newly formed double bond.

The reaction of complexed $C_7$-aldehyde **56** with complexed $C_7$-phosphonate **58** proceeded smoothly to give the bis-complexed $C_{14}$-diester **60** in 85% yield *(Scheme 5)*. The (*E*)-configuration of the central C=C bond was again confirmed by the $^1$H-NMR: analysis of H–C(5), H–C(8), H–C(6), H–C(7) (*AA'XX'* spin system) including spectral simulation which gave a value of 14.6 Hz for $^3J$(H–C(6), H–C(7)). Reduction of the diester **60** gave the dinuclear $C_{14}$-diol **61** in 90% yield and subsequent oxidation the $C_{14}$-dialdehyde **62** (56%), which can be regarded as a building block for the synthesis of isoprenoid natural products.

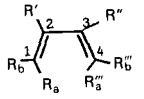
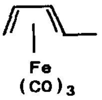
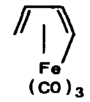
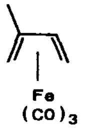
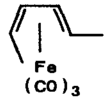
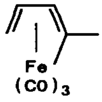
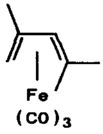
The relative position of the two $Fe(CO)_3$ groups in **60**–**62** was not determined. The two protecting groups could be attached to the same face (chiral form) or to opposite faces of the polyene (*meso*-form). In the case of a similar (*E*)-$C_{12}$-polyene complex, the X-ray crystal structure has shown that the $Fe(CO)_3$ groups are coordinated to opposite sides of the polyene [17].

These results show that the application of $[Fe(CO)_3(diene)]$ synthons in polyene synthesis allows the stereospecific formation of (*E*)-double bonds. This high selectivity suggests that steric interactions between the $Fe(CO)_3$ group of **56** and the approaching ylide result in the formation of the *trans*-oxaphosphetane intermediate. The successful application of the described reactions to polyene synthesis requires efficient decomplexation methods. A number of mild oxidation reactions have been described [21]. In our experience, best results were achieved with $Ce[(NH_4)_2(NO_3)_6]$ in the two-phase solvent MeCN/pentane. Complexed nitriles, ketones, and aldehydes have been decomplexed to give the free polyenes in yields of 85–95% [3a].

**3. $^1$H- and $^{13}$C-NMR Spectra.** – 3.1. *Methyl-Substituted [Fe(CO)$_3$(diene)] Complexes.* The $^1$H- and $^{13}$C-NMR chemical shifts of $Fe(CO)_3$-complexed methyl-substituted butadienes have been investigated by several authors in comparison to the free dienes and in terms of substituent effects [5b] [22]. However, no direct information on the conformation of complexed diene systems can be gained from chemical-shift data *(Table 1)*. Therefore, we have determined the H,H and C,H coupling constants (*Tables 2* and *3*) of selected compounds, *i.e.* **2**–**4**, **9**, **11**, and **12**, in order to reveal geometric distortions imposed on the dienes on complexation. The values obtained for the parent compound of the series, $[Fe(CO)_3(butadiene)]$ (**1**) [5a], are used as a reference.

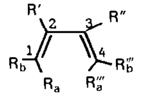
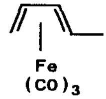
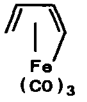
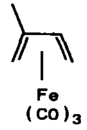
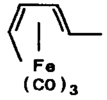
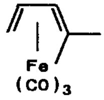
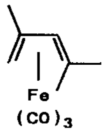
Compared to the free dienes, the vicinal coupling constants $^3J$(H,H) are reduced in tricarbonyliron complexes. In $[Fe(CO)_3(butadiene)]$ (**1**), the reduction amounts to 32% for the *cis* coupling ($^3J_c$) and to 45% for the corresponding *trans* interaction ($^3J_t$). On substitution of one or both of the terminal protons $H_a$ and $H_b$ by Me groups, a similar decrease of $^3J$(C,H) compared to the free dienes is observed. However, $^3J_t$(C,H) decreases to a larger extent (54–57%) than would be expected by comparison with the value for $^3J_t$(H,H) in **1**, whereas the reduction of $^3J_c$(H,H) by *ca.* 30% is in accordance with the expected range *(Table 4)*. As a consequence of this behaviour, the $^3J_t$(C,H) values of the terminal Me groups of complexed substituted butadienes are *smaller* than the respective

Table 1. *$^1$H-*a) *and $^{13}$C-NMR Chemical Shifts*b) (δ [ppm]) *of Complexes* **2–4**, **9**, **11**, *and* **12**

|  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|
| R,R',R'',R''' = H or Me | **2** | **3** | **4** | **9** | **11** | **12** |
| H$_a$–C(1) | –0.10 | 1.51 | 0.35 | – | 1.23 | 1.34 |
| H$_b$–C(1) | 1.30 | 1.86 | 1.88 | 2.47 | 1.38 | 1.51 |
| H–C(2) | 4.58 | 5.44 | – | 4.66 | 4.62 | – |
| H–C(3) | 4.54 | 5.32 | 4.24 | 4.74 | 4.52 | 4.60 |
| H$_a$–C(4) | 0.66 | – | 0.08 | 2.15 | – | – |
| H$_b$–C(4) | – | 2.73 | 1.53 | – | – | – |
| Me$_a$–C(1) | – | – | – | 0.88 | – | – |
| Me–C(2) | – | – | 2.40 | – | – | 1.72 |
| Me$_a$–C(4) | – | 1.07 | – | – | 0.79 | 1.27 |
| Me$_b$–C(4) | 1.04 | – | – | 1.24 | 1.21 | 0.84 |
| C(1) | 39.5 | 40.9 | 43.8 | 52.9 | 41.1 | 43.4 |
| C(2) | 89.3 | 90.5 | 103.1 | 93.7 | 92.2 | 102.5 |
| C(3) | 80.8 | 88.3 | 84.8 | 83.3 | 85.5 | 92.6 |
| C(4) | 58.4 | 53.9 | 37.9 | 57.4 | 71.5 | 66.6 |
| *Me*$_a$–C(1) | – | – | – | 14.1 | – | – |
| Me–C(2) | – | – | 22.8 | – | – | 24.5 |
| *Me*$_a$–C(4) | – | 13.6 | – | – | 33.3 | 33.2 |
| *Me*$_b$–C(4) | 19.2 | – | – | 20.2 | 20.5 | 20.3 |

a) In $CDCl_3$, **3**, **4**, and **12**; in $C_6D_6$, **2**, **9**, and **11**.
b) In $CDCl_3$, **2**, **4**, and **9**; in $C_6D_6$, **3**, **11**, and **12**.

Table 2. *H,H Coupling Constants* J [Hz] *of Complexes* **2–4**, **9**, **11**, *and* **12**a)b)

|  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|
| *J*(H,H) | **2** | **3** | **4** | **9** | **11** | **12** |
| *J*(1a,1b) | –2.4 | –2.9 | –2.4 | – | –3.3 | –3.1 |
| *J*(4a,4b) | – | – | –2.4 | – | – | – |
| *J*(1a,2) | 9.0 | 9.7 | – | – | 9.6 | – |
| *J*(1b,2) | 7.1 | 7.6 | – | 7.9 | 7.9 |  |
| *J*(2,3) | 5.2 | 5.0 | – | 4.9 | 5.0 | – |
| *J*(3,4a) | 8.6 | 7.7 | 9.0 | 9.2 | – | – |
| *J*(3,4b) | – | – | 6.8 | – | – | – |
| *J*(1a,3) | –1.0 | –1.0 | –1.0 | – | – | 0.8 |
| *J*(1b,3) | 1.0 | 1.2 | 1.5 | 1.6 | 1.0 | 1.5 |
| *J*(2,4a) | 0.7 | – | – | 1.0 | – | – |
| *J*(2,4b) | – | 1.6 | – | – | – | – |

a) Relative signs were attributed according to complex **1** [5a] unless obtained from spectral analysis.
b) In addition, the following coupling constants were determined: **2**: $^5J(1a,4a) = -0.4$, $^3J(CH_3,4a) = 6.2$; **3**: $^5J(1a,4b) = -0.2$, $^3J(CH_3,4b) = 7.2$; **9**: $^3J(CH_3,1b) = 7.1$, $^3J(CH_3,4a) = 6.2$ Hz.

Table 3. *C,H Coupling Constants* J [Hz] *of Complexes* **2–4**, **9**, **11**, *and* **12**

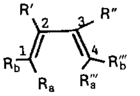
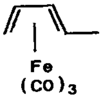
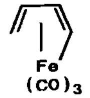
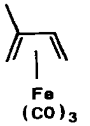
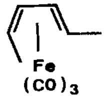
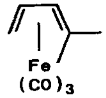
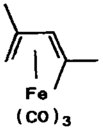
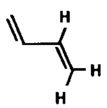
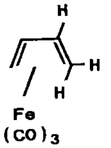
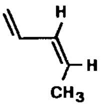
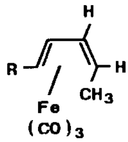
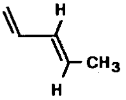
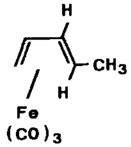
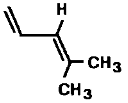
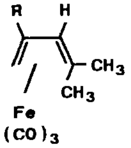
|  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|
| $J$(C,H) | **2** | **3** | **4** | **9** | **11** | **12** |
| $J$(C(1),1a) | 161.1 | 163.7 | 160.8 | – | 163.6 | 163.0 |
| $J$(C(1),1b) | 157.9 | 155.8 | 155.8 | 150.7 | 155.3 | 153.5 |
| $J$(C(2),2) | 169.5 | 166.2 | – | 167.5 | – | – |
| $J$(C(3),3) | 167.0 | 167.0 | 167.0 | 163.0 | – | – |
| $J$(C(4),4a) | 159.9 | – | 161.5 | 160.5 | – | – |
| $J$(C(4),4b) | – | 151.5 | 157.0 | – | – | – |
| $J$(C(1),2) | 3.3 | 2.4 | – | 3.1 | 2.3 | – |
| $J$(C(2),1a) | – | 0.3 | 0.9 | – | – | – |
| $J$(C(2),1b) | -1.1 | 1.6 | 1.0 | 0.4 | – | – |
| $J$(C(2),3) | 2.2 | 1.7 | 1.8 | 2.5 | – | – |
| $J$(C(3),2) | 2.2 | 2.4 | – | 2.8 | – | – |
| $J$(C(3),4a) | – | – | 0.3 | 0.5 | – | – |
| $J$(C(3),4b) | – | 1.0 | 1.0 | – | – | – |
| $J$(C(4),3) | 3.1 | 3.2 | 3.5 | 1.9 | – | – |
| $J$(C(1),3) | 7.8 | 9.2 | 7.0 | 9.2 | 9.1 | 8.0 |
| $J$(C(2),4a) | 3.7 | – | 3.6 | 4.6 | – | – |
| $J$(C(2),4b) | – | 9.4 | 8.6 | – | – | – |
| $J$(C(3),1a) | 3.7 | 4.6 | 3.4 | – | – | – |
| $J$(C(3),1b) | 11.0 | 9.1 | 8.2 | 11.8 | – | – |
| $J$(C(4),2) | 7.6 | 9.5 | – | 9.4 | – | – |
| $J$(*Me*–C(1),2) | – | – | – | 4.0 | – | – |
| $J$(*Me*–C(2),1a) | – | – | 4.5 | – | – | 5.0 |
| $J$(*Me*–C(2),1b) | – | – | 4.5 | – | – | 5.0 |
| $J$(*Me*–C(2),3) | – | – | 2.5 | – | – | 2.9 |
| $J$($Me_a$–C(4),3) | – | 4.0 | – | – | 3.8 | 3.8 |
| $J$($Me_b$–C(4),3) | 4.5 | – | – | 4.9 | 5.0 | 4.9 |

Table 4. *Vicinal H,H and C,H Coupling Constants* J [Hz] *in 1,3-Dienes and their Tricarbonyliron Complexes*

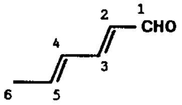
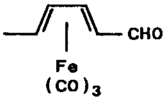
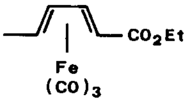
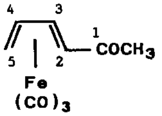
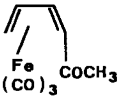
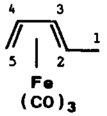
| |  |  | |  |  | |
|---|---|---|---|---|---|---|
| $^3J_t$(H,H) | 17.02 [23] | 9.33 [5a] | $^3J_t$(C,H) | 9.4 | 4.0 (R = H) | 4.0 (R = $CH_3$) |
| $^3J_c$(H,H) | 10.15 | 6.93 | $^3J_c$(H,H) | 10.81 [24] | 7.7 (R = H) | 7.9 (R = $CH_3$) |
| |  |  | |  |  | |
| $^3J_t$(H,H) | 15.06 [24] | 8.6 | $^3J_t$(C,H) | 8.2 | 3.8 (R = H) | 3.8 (R = $CH_3$) |
| $^3J_c$(C,H) | 6.5 | 4.5 | $^3J_c$(C,H) | 7.0 | 5.0 (R = H) | 4.9 (R = $CH_3$) |

$^{3}J_{c}$(C,H) data, a fact that has never been observed so far for olefinic compounds [25] and can only be explained by considerable geometric distortions of (*Z*)-substituted complexes. Me Substitution at one of the central C-atoms (*cf.* **4**), however, does not lead to an inversion of the $J_t/J_c$ ratio *(Table 3)*.

Further information can be gained from the study of $^{2}J$(H,H) *(Table 2)* and $^{1}J$(C,H) data *(Table 3)*. Both the decrease of $^{2}J$(H,H) to negative values (*cf.* free butadiene: +1.47 Hz) and the fact that the $^{1}J$(C,H) values for terminal C-atoms are smaller than those for the central C-atoms indicate a rehybridization of the terminal centers in a sense of increased sp$^{3}$ character. Similar effects were observed in the ruthenium and osmium analogues of **1**. The result of these variations in geometry and electron distribution are improved (p-d)-orbital overlap and coordination [5a] [5c].

Finally, we have tried to use $^{1}J$(C,C) data as a probe into relative C–C bond lengths in complexed dienes. A linear relationship is known to exist between the $^{1}J$(C,C) value and the bond length [26], which appears to hold also for organometallic compounds, provided only complexes of the same metal are compared [5c] [27]. The values of $^{1}J(2,3) = 43.3$, $^{1}J(3,4) = 43.5$, and $^{1}J(4,5) = 46.2$ Hz for the olefinic part of complex **2** [5c] *(Table 5)*

Table 5. *One-Bond C,C Coupling Constants* $^{1}$J [Hz] *in 2,4-Hexadienal and Tricarbonyliron Complexes of Functionalized 1,3-Dienes*a)

| Compound | $^{1}J$(1,2) | $^{1}J$(2,3) | $^{1}J$(3,4) | $^{1}J$(4,5) | $^{1}J$(5,6) |
|---|---|---|---|---|---|
|  | 54.6 | 67.2 | 54.8 | 69.6 | 42.4 |
| **40**  | 50.8 | 44.7 | 44.8 | 45.1 | 42.1 |
| **31**  | 73.6 | 45.9 | 44.3 | 45.2 | 41.5 |
| **32**  | b) | 45.9 | b) | 43.7 | – |
| **33**  | 51.2 | 43.4 | 44.0 | 42.8 | – |
| **2**  | 43.0 | 43.3 | 43.5 | 46.2c) | – |

a) Numbering of the C-atoms was unified to facilitate comparison of data.
b) Not obtained.
c) From [5c].

indicate a very similar bond order for the C–C bonds and, therefore, a delocalization of the $\pi$ system. This is in accordance with values obtained by X-ray analysis for similar compounds [28].

3.2. *Functionalized [Fe(CO)$_3$(diene)] Complexes.* Complexed butadienes bearing functional groups at the terminal C-atoms exhibit very similar $^1$H- and $^{13}$C-NMR properties compared to the Me-substituted compounds discussed above. However, some additional features seem worth discussing at a more detailed level.

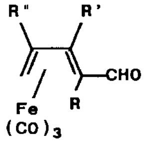
The influence of the functional group on the $^{13}$C-NMR chemical shift of the carbonyl C-atoms is shown in *Table 6*. Limiting values for this series have been reported for the complex of 2,4-hexadiene (see *Formula* **8**; 212.9 ppm) and hexadiene-1,6-dinitrile (205.3 ppm) [29]. The small but characteristic increments correlate with the mesomeric and inductive effects of the substituents. This is in accordance with earlier investigations on symmetrically substituted [Fe(CO)$_3$(diene)] complexes where $\delta$(CO) has been discussed in terms of the *Hammett* constants of the functional group [29]. The electron density of the diene system is, therefore, reflected in the chemical shift of the carbonyl resonance which in turn can be used as an at least qualitative measure for the amount of Fe→CO back donation [30].

Table 6. *$^{13}$C-NMR Chemical Shifts* ($\delta$ [ppm], CDCl$_3$) *of Tricarbonyliron Groups in Functionalized 1,3-Diene Complexes*

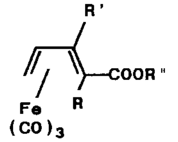
| R–C(1) | Compound | $\delta$(Fe–*CO*) |
|---|---|---|
| Me | **7, 11** | 211.9; 212.0 |
| H | **10** | 211.4 |
| CH$_2$OH | **41, 42, 43** | 211.0; 211.0; 211.0 |
| CH=CH–CN | **52, 53** | 210.2; 210.4 |
| COOR | **29, 30** | 209.2; 209.2 |
| CHO | **37, 38, 39** | 208.8; 208.3; 208.6 |
| CN | **49** | 208.6 |

As in the case of Me-substituted Fe(CO)$_3$ complexes, bond lengths of selected compounds have been probed by measuring one-bond C,C coupling constants. It is known that $^1J$(C,C) values are sensitive to polarization effects and are influenced by electronegative substituents in uncomplexed compounds, especially if the electron-withdrawing residue is directly connected to the coupled C-atoms [31]. The observed coupling constants of the diene C-atoms, however, are very similar for the compounds taken into consideration *(Table 5)*. This rather surprising result indicates a delocalized $\pi$ system as well as a more or less complete loss of conjugation of the diene system with the functional group. This is in excellent agreement with the observed reactivity of the complexed functionalized dienes with respect to nucleophilic attack as described in [3a].

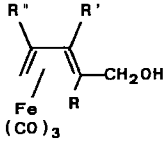
A further interesting effect can be found by comparing compounds of the same type but with varying position of the Me substituent, *e.g.* the series **37**/**38**/**39**, **29**/**30**, or **41**/**42**/**43** *(cf. Exper. Part)*. Whenever the terminal H$_a$-atom is opposed by a Me group at the C-atom adjacent to the functional group, it experiences a downfield shift of *ca.* 0.5–1.5 ppm in the $^1$H-NMR spectrum. This effect, obviously due to the steric strain exerted on the ligand by the Me group, can be a helpful tool for the assignment of $^1$H resonances.



**37** R = Me, R′ = R″ = H
**38** R′ = Me, R = R″ = H
**39** R″ = Me, R = R′ = H



**29** R = R″ = Me, R′ = H
**30** R′ = Me, R″ = Et, R = H

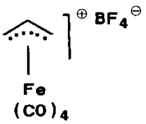


**41** R = Me, R′ = R″ = H
**42** R′ = Me, R = R″ = H
**43** R″ = Me, R = R′ = H

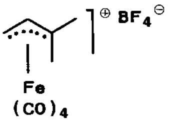
Finally, we have investigated compound **34** with respect to coupling constants. Both $^3J$(H,H) and $^3J$(C,H) values correspond to results from similar Me-substituted compounds, *e.g.* **11** (*Tables 2* and *3*). In particular, the same inversion of the values of $^3J_t$(C,H) (4.2 Hz) and $^3J_c$(C,H) (4.9 Hz) is observed as for the Me-substituted butadiene series, thus indicating the same steric implications for the Me group irrespective of the functionalization. As will be shown in *Chapt. 5*, the NMR spectroscopic features of **34** in solution correspond to its structure in the solid state as determined by X-ray crystallography.

**4. $^{57}$Fe-NMR Chemical Shifts.** – The structural changes in the coordinated diene ligand are also reflected in the $^{57}$Fe shielding constants, and the effects may be divided into three major types, *i.e.* stereoelectronic effects due to direct metal-C coordination, electron-withdrawing effects of substituents on the diene system, and effects associated with a change in the formal charge of the metal complex. The magnitude of the effects increases in the given order.

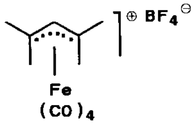
The stereoelectronic effects can be most clearly recognized in the Me-substituted [Fe(CO)$_3$(diene)] complexes **2–12** as well as in the cationic Me-substituted [Fe(CO)$_4$(allyl)][BF$_4$] complexes **13–25**. The $^{57}$Fe-NMR chemical shifts are collected in *Tables 7* and *8* (see also [6a]). Me-Substitution on the parent complex **1** always leads to a deshielding of the $^{57}$Fe nucleus, and there are characteristic increments $\Delta\delta$ depending on the position of the Me group: Me$_{trans}$–C(1) +30 ppm, Me$_{cis}$–C(1) +105 ppm, CH$_3$–C(2) +35 ppm, (CH$_3$)$_2$C(1) +180 ppm. The very large deshielding caused by *cis* configuration of the terminal Me group and C(2)–C(3) appears to be a direct consequence of the geometric distortion (rehybridization) at the terminal diene C-atom caused by steric interaction between the CH$_3$, =C–H$_a$ and Fe(CO)$_3$ groups. Increased s-contribution in the C(1,4)-Fe bonding corresponds to an increased back-bonding or decrease in the HOMO-LUMO gap with an increase of the paramagnetic shielding term [7c]. Similar deshielding effects of the $^{59}$Co resonance have already been described for [Co($\eta^5$-indenyl)(diene)] complexes with a *cis*-configurated Me group at C(1) [6a]. The Me substituent



**13**



**20**



**25**

$\delta$(Fe) [ppm]: 796 896 998

Table 7. *$^{57}$Fe-NMR Chemical Shifts* ($\delta$ [ppm]) *of Me-Substituted [Fe(CO)$_3$(1,3-butadiene)] Complexes*

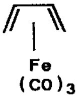
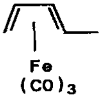
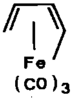
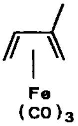
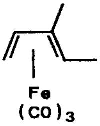
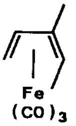
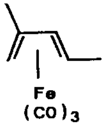
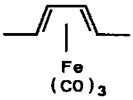
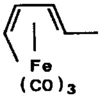
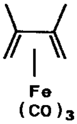
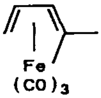
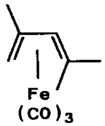
| Compound | Solvent | Conc. [M] | $\delta$(Fe) | $T_1/T_2$ |
|---|---|---|---|---|
| **1**  | $C_6D_6$ | 4.4 | 4.3 ± 0.3 | 2.07 ± 0.04 |
| | $C_6D_6$ | 2.9 | 0.4 ± 1.0$^{a}$) | – |
| | $C_6D_6$ | 2.9 | 0.0 ± 0.4$^{b}$) | – |
| | $C_6H_{14}$ | 3.6 | 16.9 ± 0.3 | 1.3 ± 0.1 |
| | neat | – | 5.5 ± 0.3 | 1.90 ± 0.03 |
| **2**  | $C_6D_6$ | 3.8 | 33.2 ± 1.0$^{a}$) | – |
| | $C_6D_6$ | 3.8 | 34.7 ± 0.3 | 2.70 ± 0.07 |
| **3**  | $C_6D_6$ | 3.4 | 105.2 ± 0.4$^{c}$) | 1.43 ± 0.04 |
| | $C_6D_6$ | 3.4 | 104.8 ± 1.0$^{a}$) | |
| | $C_6H_{14}$ | 1.8 | 119.2 ± 0.8 | 2.5 ± 0.1 |
| **4**  | $C_6D_6$ | 2.7 | 36.8 ± 0.3$^{c}$) | 1.61 ± 0.07 |
| | $C_6D_6$ | 2.7 | 37.5 ± 1.0$^{a}$) | – |
| | $C_6H_{14}$ | 4.4 | 54.4 ± 0.2 | 1.8 ± 0.1 |
| | neat | – | 47.7 ± 0.3 | 5.3 ± 0.4 |
| **5**  | $C_6D_6$ | 3.0 | 51.2 ± 1.0$^{a}$) | – |
| **6**  | $C_6D_6$ | 0.6 | 129.9 ± 1.0$^{a}$) | – |
| **7**  | $C_6D_6$ | 0.5 | 65.4 ± 1.0$^{a}$) | – |
| **8**  | $C_6H_{14}$ | 1.6 | 86.4 ± 0.8 | 2.0 ± 0.2 |
| **9**  | $C_6H_{14}$ | 2.1 | 165.3 ± 0.5 | 2.5 ± 0.4 |
| **10**  | $C_6H_{14}$ | 1.1 | 68.5 ± 0.5 | 1.6 ± 0.1 |
| **11**  | $C_6D_6$ | 2.6 | 179.4 ± 1.0$^{a}$) | – |

*Table 7* (cont.)

| Compound | | Solvent | Conc. [M] | δ(Fe) | $T_1/T_2$ |
|---|---|---|---|---|---|
| **12** |  | $C_6D_6$ | 2.7 | 216.0 ± 1.0[a]) | – |

a) Determined at 12.9 MHz and (296 ± 1) K; all other data at 2.9 MHz and (300 ± 1) K.
b) From [5d].
c) Determined at 2.9 MHz and 295 K.

Table 8. *$^{57}$Fe-NMR Chemical Shifts* (δ [ppm]), *of Alkyl-Substituted [Fe(CO)$_4$(allyl)][BF$_4$] Complexes* (in $CF_3COOH$) *and [FeX(CO)$_3$(allyl)] Complexes* (in $C_6D_6$)[a])

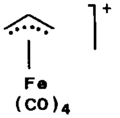
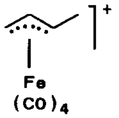
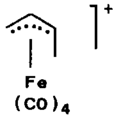
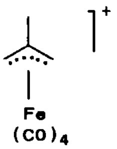
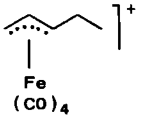
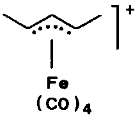
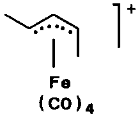
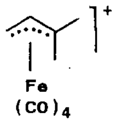
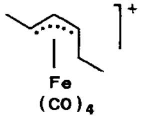
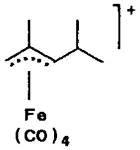
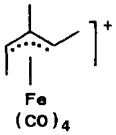
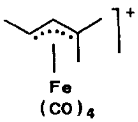
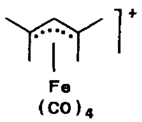
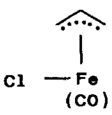
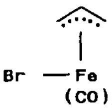
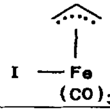
| Compound | | Conc. [M] | δ(Fe) | $T_1/T_2$ |
|---|---|---|---|---|
| **13** |  | 1.5 | 796.0 ± 0.6 | 1.8 ± 0.1 |
| **14** |  | 0.4 | 806.7 ± 1.7 | b) |
| **15** |  | 0.2 | 837.4 ± 2.6 | b) |
| **16** |  | 0.7 | 867.7 ± 0.7 | 1.3 ± 0.1 |
| **17** |  | 0.75 | 785.1 ± 0.7 | 6.9 ± 0.3 |
| **18** |  | 0.3 | 802.6 ± 2.6 | 1.2 ± 0.3 |
| **19** |  | 0.3 | 847.4 ± 2.1 | 1.0 ± 0.2 |

*Table 8* (cont.)

| Compound | | Conc. [M] | $\delta$(Fe) | $T_1/T_2$ |
|---|---|---|---|---|
| **20** |  | 0.3 | 895.6 ± 0.8 | 2.1 ± 0.1 |
| **21** |  | 0.2 | 834.9 ± 2.3 | [b] |
| **22** |  | 0.3 | 860.8 ± 1.8 | 2.0 ± 0.7 |
| **23** |  | 0.75 | 884.0 ± 1.4 | 2.7 ± 0.1 |
| **24** |  | 0.4 | 862.5 ± 6.6 | [b] |
| **25** |  | 0.25 | 997.7 ± 4.7 | [b] |
| **26** |  | 0.3 | 1708.0 ± 3.0 | [b] |
| **27** |  | 0.55 | 1528.0 ± 3.0[c] | [b] |
| **28** |  | 0.7 | 1234.9 ± 3.0[d]<br>1355.7 ± 3.0 | [b] |

---

[a] Determined at 2.9 MHz and (300 ± 1) K; **26** and **28** at 12.9 MHz and (296 ± 1) K.

[b] Decomposition of sample during measurement did not permit determination.

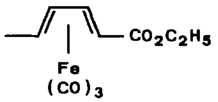
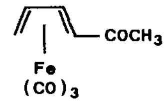
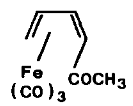
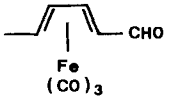
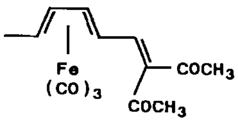
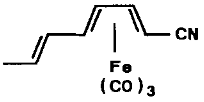
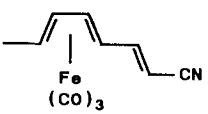
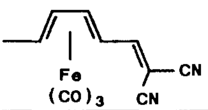
[c] From [5d].

[d] For assignment of stereoisomers, see *Fig. 1* and [32].

effects are additive which is most clearly demonstrated in the series of substituted $[Fe(CO)_4(\eta^3\text{-allyl})][BF_4]$ complexes (see **13**, **20**, and **25**; *cf. Table 8*). In this series of cationic complexes, also inductive effects of Me groups can be observed leading to a shielding of the $^{57}Fe$ nucleus, *e.g.* in **23** as compared to **20** ($\Delta\delta(Fe) = -11.6$ ppm).

The effect of electron-withdrawing substituents on the diene system is associated with a strong deshielding of the $^{57}Fe$ resonance as shown by the data given in *Table 9*. The high-frequency shift increases in the series COOR < $COCH_3$ < CHO < CN, which correlates qualitatively with the electron-withdrawing power of the substituent. The largest effects are observed when the substituent X is directly attached to the Fe-atom, *i.e.* in the series of $[FeX(CO)_3(\eta^3\text{-allyl})]$ complexes given in *Fig. 1* (see *Table 8*). We learn from these data that $^{57}Fe$ shielding decreases with increasing electronegativity of the halogen atom in

Table 9. *$^{57}Fe$-NMR Chemical Shifts* ($\delta$ [ppm]) *of Functionalized* $[Fe(CO)_3(diene)]$ *Complexes*

| Compound | | Solvent | Conc. [M] | $\delta$(Fe) | $T_1/T_2$ |
|---|---|---|---|---|---|
| 31 |  | acetone | 3.6 | 312.3 ± 0.6 | 2.0 ± 0.1 |
| 32 |  | $Et_2O$ | 0.9 | 334.6 ± 0.9 | 1.7 ± 0.1 |
| 33 |  | $Et_2O$ | 1.0 | 359.4 ± 0.9 | 2.1 ± 0.3 |
| 40 |  | $Et_2O$ | 0.5 | 377.9 ± 2.4 | 1.7 ± 0.4 |
| 45 |  | acetone | 0.5 | 373.6 ± 3.3 | 1.0 ± 0.3 |
| 47 |  | $CDCl_3$ | 0.3 | 527.4 ± 1.0[a]) | – |
| 48 |  | $CDCl_3$ | 0.3 | 359.0 ± 1.0[a]) | – |
| 50 |  | $CH_2Cl_2$ | 0.3 | 588.7 ± 1.3 | 1.7 ± 0.3 |

[a]) Determined at 12.9 MHz and (296 ± 1) K; all other data at 2.9 MHz and (300 ± 1) K.

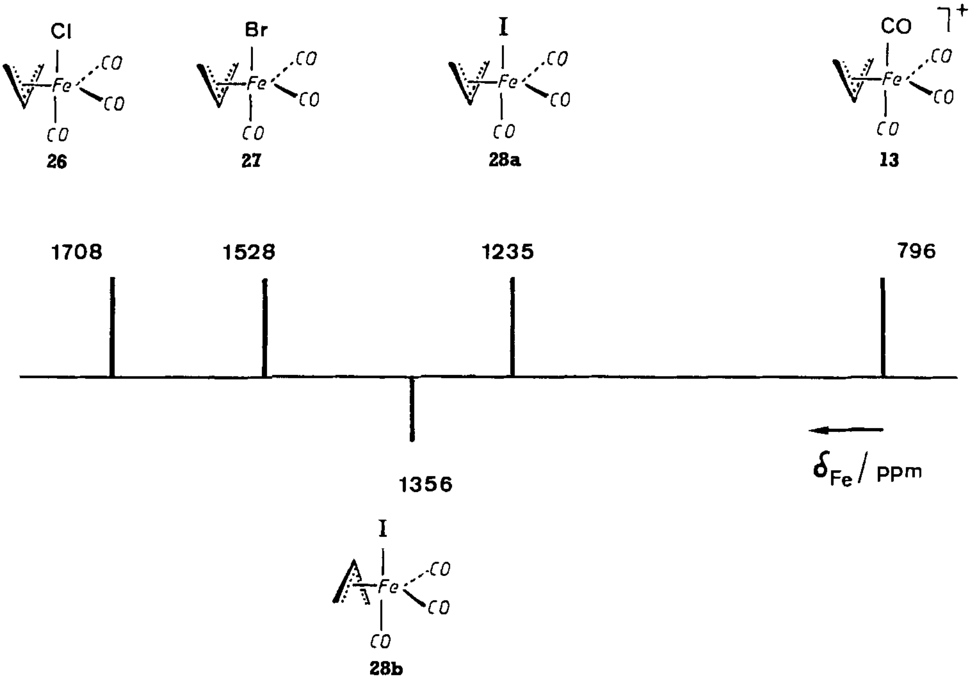
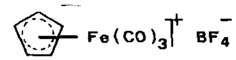
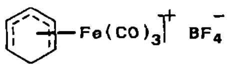
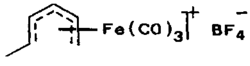
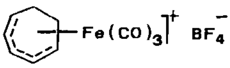
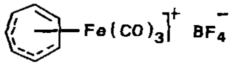


Fig. 1. *Schematic* $^{57}$*Fe-NMR spectra of* $[FeX(CO)_3(\eta^3\text{-allyl})]$ *complexes and* $[Fe(CO)_4(C_3H_5)][BF_4]$

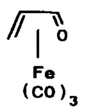
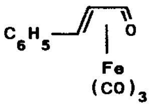
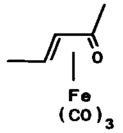
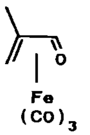
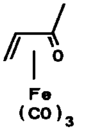
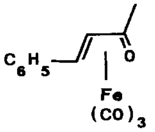
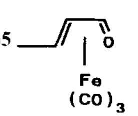
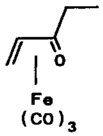
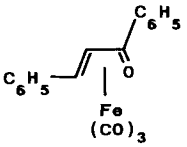
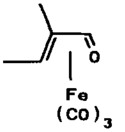
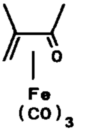
a semiquantitative manner. In addition, for the iodo complex **28**, the two stereoisomers, known to be in a slow exchange on the NMR time scale [32], show different chemical shifts ($\Delta\nu = 1.56$ kHz at 12.9 MHz). The very large deshielding effects in **26**–**28** are certainly due, at least in part, to an increase in the effective positive charge at the Fe-atom. Other cationic dienyl- and trienyliron complexes also measured in $CF_3COOH$ appear in the same resonance range, *i.e.* 680–1440 ppm *(Table 10)*.

Table 10. $^{57}$*Fe-NMR Chemical Shifts* ($\delta$ [ppm], $CF_3COOH$, 300 K) *of Cationic Dienyl- and Trienyliron Complexes*

| Compound | Conc. [M] | $\delta$(Fe) | $T_1/T_2$ | Ref. |
|---|---|---|---|---|
|  | 1.8 | 686.3 ± 1.0 | – | [33] [6a] |
|  | 1.2 | 1124.9 ± 0.9 | 1.8 ± 0.2 | [33] |
|  | 0.4 | 1017.9 ± 1.3 | 2.4 ± 0.4 | [33] [6a] |
|  | 0.8 | 925.6 ± 0.7[a]) | – | [33] [5d] |
|  | 0.85 | 1435.3 ± 2.5 | 1.6 ± 0.5 | [33] [6a] |

[a]) Measured at 273 K.

Table 11. *$^{57}$Fe-NMR Chemical Shifts* ($\delta$ ($\pm$ 1) [ppm], $C_6D_6$, 12.9 MHz) *of Substituted [Fe(CO)$_3$(enone)] Complexes*

| Compound | | $\delta$(Fe) | Compound | | $\delta$(Fe) | Compound | | $\delta$(Fe) |
|---|---|---|---|---|---|---|---|---|
| **63** |  | 1274 | **67** |  | 1504 | **71** |  | 1335 |
| **64** |  | 1279 | **68** |  | 1325 | **72** |  | 1559 |
| **65** |  | 1279 | **69** |  | 1318 | **73** |  | 1688 |
| **66** |  | 1277 | **70** |  | 1349 | | | |

Finally, the coordination of a carbonyl O-atom to the Fe-atom, exemplified in the [Fe(CO)$_3$($\eta^4$-enone)] complexes **63–73** results in large deshielding effects of 1200–1700 ppm relative to [Fe(CO)$_3$($\eta^4$-butadiene)] (**1**; *Table 11*). Heterodiene coordination to an Fe(CO)$_3$ moiety can, therefore, easily be detected by $^{13}$C-NMR *(cf. 2.1)* and $^{57}$Fe-NMR spectroscopy. A comparison of the propenal complex **63** with the butenone complex **68** again shows the deshielding effect of the Me group on the $^{57}$Fe nucleus (+49 ppm), but in general, Me substituent effects are small in this series ( $<$ 15 ppm).

Also reported in *Tables 7–9* are the ratios $T_1/T_2$ of the $^{57}$Fe spin-lattice and spin-spin relaxation times which were obtained in the field $B_0 = 2.114\ T$ from the dependence of the steady-state signal amplitudes on the flip angle [34]. In a recent detailed relaxation study [35], including compounds **1–4**, the experimental relaxation rates $T_1^{-1}$ determined at 2.9 MHz ($B_0 = 2.1\ T$) and 12.9 MHz ($B_0 = 9.4\ T$) were analyzed for contribution from different relaxation mechanisms. Spin-rotation (SR) and chemical-shift anisotropy (CSA) combined with molecular reorientation were pointed out to be the dominating mechanisms while contributions from all other relaxation mechanisms were negligible. Assuming SR and CSA to be the dominating mechanisms for the longitudinal relaxation of all compounds in *Tables 7–9*, a ratio $T_1/T_2 \approx 1$ points out that the transverse relaxation is exclusively due to the same mechanisms. A ratio $T_1/T_2 > 2$, however, is an indication for additional contributions to $T_2^{-1}$ arising from *e.g.* fluxionality of the complex or adsorption of the molecule to colloidal or visible paramagnetic particles in the sample.

**5. X-Ray Crystallographic Results for Compound 34.** – A plot of one of the two crystallographically independent molecules is shown in *Fig. 2;* the fractional atomic

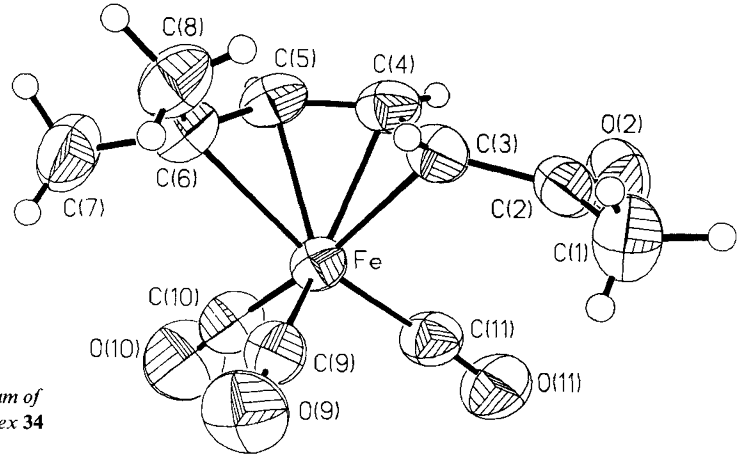


Fig. 2. *ORTEP diagram of the structure of complex* **34**

Table 12. *Atomic Coordinates* ($\cdot 10^4$) *and Temperature Factors* ($Å^2 \cdot 10^3$) *for* **34**

| Atom | x/a | y/b | z/c | $U_{eq}$ a) |
|---|---|---|---|---|
| Fe | 5517 (1) | 3025 (1) | 5886 (1) | 43 (1) |
| C(1) | 1782 (4) | 1102 (3) | 3938 (3) | 77 (1) |
| C(2) | 2696 (3) | 2294 (3) | 4060 (2) | 54 (1) |
| O(2) | 2096 (2) | 3135 (2) | 4050 (2) | 73 (1) |
| C(3) | 4348 (3) | 2407 (2) | 4224 (2) | 48 (1) |
| C(4) | 5265 (3) | 3534 (2) | 4307 (2) | 52 (1) |
| C(5) | 6789 (3) | 3752 (2) | 4722 (2) | 54 (1) |
| C(6) | 7545 (3) | 2856 (2) | 5025 (3) | 56 (1) |
| C(7) | 9048 (4) | 3237 (3) | 5761 (3) | 80 (1) |
| C(8) | 7501 (4) | 1730 (3) | 4228 (4) | 67 (1) |
| C(9) | 5490 (3) | 1614 (2) | 6292 (2) | 49 (1) |
| O(9) | 5478 (3) | 707 (2) | 6506 (2) | 77 (1) |
| C(10) | 6596 (3) | 3895 (3) | 7136 (3) | 62 (1) |
| O(10) | 7226 (3) | 4451 (2) | 7955 (2) | 100 (1) |
| C(11) | 3870 (3) | 3473 (2) | 6401 (2) | 54 (1) |
| O(11) | 2861 (3) | 3769 (2) | 6770 (2) | 82 (1) |
| Fe′ | 1468 (1) | 2101 (1) | -508 (1) | 45 (1) |
| C(1′) | -729 (4) | 3696 (3) | 2049 (4) | 85 (2) |
| C(2′) | -531 (3) | 2538 (3) | 1479 (2) | 57 (1) |
| O(2′) | -1585 (2) | 1715 (2) | 1283 (2) | 78 (1) |
| C(3′) | 999 (3) | 2407 (2) | 1216 (2) | 48 (1) |
| C(4′) | 1260 (3) | 1260 (2) | 887 (2) | 49 (1) |
| C(5′) | 2571 (3) | 1057 (2) | 407 (3) | 57 (1) |
| C(6′) | 3734 (3) | 1970 (3) | 260 (3) | 60 (1) |
| C(7′) | 4820 (4) | 1642 (4) | -571 (4) | 86 (2) |
| C(8′) | 4504 (3) | 2927 (3) | 1209 (3) | 75 (1) |
| C(9′) | 2222 (4) | 3592 (3) | -594 (3) | 66 (1) |
| O(9′) | 2736 (4) | 4531 (2) | -613 (2) | 106 (1) |
| C(10′) | 1737 (3) | 1408 (3) | -1886 (3) | 61 (1) |
| O(10′) | 1855 (3) | 971 (2) | -2786 (2) | 95 (1) |
| C(11′) | -472 (3) | 1930 (3) | -1049 (3) | 64 (1) |
| O(11′) | -1691 (3) | 1839 (3) | -1444 (2) | 102 (1) |

a) Equivalent isotropic $U$ defined as one third of the trace of the orthogonalized $U$ tensor.

coordinates are given in *Table 12*. As expected, **34** exhibits geometrical features similar to those observed in other [Fe(CO)$_3$(diene)] compounds [3d] [28]. Very similar distances C(3)–C(4), C(4)–C(5), and C(5)–C(6) indicate a more or less complete equilibration of bond orders in the diene subsystem. This is in agreement with the one-bond, C,C coupling constants $^1J$(C,C) obtained for related compounds in solution *(cf. Chapt. 3.2, Table 5)*. Further evidence for a delocalized $\pi$-system is provided by the planarity of the diene system, the largest distance of the C-atoms C(3) to C(6) from their mean plane being 0.016 Å.

The substituents at C(3) and C(6), however, do not occupy positions in the plane defined by the diene system. In particular, C(8) and H–C(3) are twisted out of the $\pi$-plane to a considerable extent *(Table 13)*. This effect has also been observed in other substituted [Fe(CO)$_3$(diene)] complexes investigated by X-ray crystallography [3d] [36] [37], irrespective of the nature of the substituent. We, therefore, conclude that the conformational distortion in **34** is mainly caused by steric interaction between H–C(3) and the *'syn'*-oriented Me–C(6), and by a similar interaction of this Me group and H–C(3), respectively, with the Fe-atom. The latter effect is reflected in the distances Fe–C(6) (2.213(3) Å) and Fe–C(3) (2.120(2) Å). This interpretation has recently been corroborated by force-field calculations [37].

Table 13. *Selected Torsional Angles* (°) *in the Two Independent Molecules* **a** *and* **b** *of* **34**

| Structure element | **a** | **b** |
|---|---|---|
| C(2)–C(3)–C(4)–C(5) | 164.8 | 167.3 |
| H–C(3)–C(4)–C(5) | –41 | –41 |
| C(4)–C(5)–C(6)–C(7) | –163.4 | –162.4 |
| C(4)–C(5)–C(6)–C(8) | 52.4 | 53.4 |

The large deviation from planarity of C(8) forces C(7) to adopt a position nearer to the Fe-atom. However, the out-of-plane distortion is considerably smaller than for C(8) *(Table 13)*. This in turn leads to torsional angles of 5° for H–C(5)–C(6)–C(7) and 140° for H–C(5)–C(6)–C(8), thus yielding an explanation for the unusual $^3J$(C,H) values of substituted [Fe(CO)$_3$(diene)] complexes reported in *Chapts. 3.1* and *3.2, i.e.*, $^3J_t < {}^3J_c$. With some restrictions, **34** can be described to exhibit a square-pyramidal geometry with one of the carbonyl groups of the Fe(CO)$_3$ moiety in the apical position and the Fe-atom in the center of the pyramid.

This work has been supported by the *Swiss National Science Foundation*, the *Dr. Helmut Legerlotz-Stiftung*, and *Fonds zur Förderung der wissenschaftlichen Forschung* in Österreich.

## Experimental Part

1. *Instrumental.* NMR spectra: $^1$H-NMR *Varian EM-390* (90 MHz), *XL-200* (200 MHz), and *Bruker AM-400* (400 MHz); $^{13}$C-NMR *Varian XL-100* (25.2 MHz), *XL-200* (50.4 MHz), and *Bruker AM-400* (100.6 MHz); $^{57}$Fe-NMR *Bruker AM-400* (12.9 MHz), and home-built spectrometer (2.9 MHz) described in [5d] [38]; $J$(H,H) and $J$(C,H) in *Tables 2* and *3* from complete analysis of the multi-spin systems including iterative computer simulation using the PANIC program *(Bruker)*; accuracy of $J$(H,H) and $J$(C,H), ±0.25 Hz, of $J$(C,C), ±0.5 Hz; $^1$H-NMR in 5-mm tubes, $^{13}$C-NMR in 10-mm tubes, and $^{57}$Fe-NMR spectra in 20-mm (12.9 MHz) or 22-mm tubes (2.9 MHz); $\delta$(Fe) relative to Fe(CO)$_5$ as an external standard, $\delta$(H) and $\delta$(C) relative to internal TMS; deuterated

solvents were degassed and stored over aluminium oxide, and the samples were prepared under $N_2$ and sealed; $J$(C,C)'s were determined with the $^{13}$C-isotope in natural abundance using the INADEQUATE pulse sequence [39] or by a combination of INADEQUATE and INEPT [40], in both cases at 50.3 MHz, or with a conventional FT technique at 25.2 MHz with double precision data acquisition; estimated errors smaller than ±0.5 Hz; ambiguous assignments of $^{1}$H- and $^{13}$C-NMR data are indicated by an asterisk. Mass spectra: *Varian MAT 711* at 70 eV.

2. *X-Ray Crystallographic Study. Tricarbonyl[3–6-η-((*E*)-6-methyl-3,5-heptadien-2-one)]iron* (**34**), $C_{11}H_{12}FeO_4$, mol. wt. 264.06, crystallized from hexane/$Et_2O$ 1:1 at −20° in orange-yellow triclinic crystals of space group $P1$ with two independent molecules in the asymmetric unit cell, $a = 9.083(1)$, $b = 11.791(1)$, $c = 11.856(1)$ Å; $\alpha = 97.83(1)$, $\beta = 95.36(1)$, $\gamma = 99.90(1)^{\circ}$5); $D_{\text{calc.}} = 1.43$ g/cm$^3$. The intensity of 4563 reflections within $\lambda^{-1} \cdot \sin\theta < 0.60$ Å$^{-1}$ were measured on a *Nicolet-R3* diffractometer in the ω-scan technique using graphite monochromatized Mo$K_\alpha$ radiation. They were averaged to 4334 symmetry-independent reflections after the usual corrections except for absorption were applied. Both structure solution (heavy-atom method) and refinement were performed using the SHELXTL program [41]. All H-atoms were localized using difference electron density calculations and varied with isotropic temperature factors while the other atoms were refined with anisotropic temperature factors. In the last blocked cascade refinement (with *ca.* 100 variables per block), the 3982 unique structure factors with $F > 1\sigma_F$ were used to bring the 385 variables to convergence at $R = 0.041$, $wR = 0.049$, $1/w = \sigma_F{}^2 + 0.001F^2$.

3. *Syntheses.* (Butadiene)tricarbonyliron was purchased from *Strem Chemicals* and used without further purification. The following compounds were synthesized according to procedures given in the literature: **2–5**, **7–12** [42]; **26–28** [43]; **31**, **40** [44]; **32**, **33** [45]; **45**, **47** **48**, **50** [3a]; **63**, **67**, **68**, **71–73** [46] [11]. All preparations were carried out under $N_2$ in dry, $O_2$-free solvents. The products were filtered over $Al_2O_3$ (aluminiumoxid *90*, stand., act. II–III, 70–230 mesh; *Merck AG*) prior to chromatography. Chromatographic separations were performed on silica gel *60* (70–230 mesh, *Merck AG*) under atmospheric pressure. Traces of solvents were removed at r.t./$10^{-3}$ Torr after purification. M. p.: *Kofler* apparatus, uncorrected.

4. *General Procedure for the Complexation of Functionalized Dienes.* A *Schlenk*-type flask is charged with 15 mmol (5.46 g) of $Fe_2(CO)_9$ [47]. $O_2$ is removed by alternating evacuation with a water-jet pump and refilling with $N_2$. Then, 50 ml of benzene (distilled from Na and made $O_2$-free by bubbling $N_2$ through the distillate for 10 min) and 10 mmol of the freshly distilled functionalized diene are added in a $N_2$ counter current. The mixture is gently refluxed under stirring in a weak stream of $N_2$ for 6–10 h (TLC control, silica gel, hexane/$Et_2O$ 2:1). Then, the mixture is allowed to cool to r.t. and evaporated. The crude complexes are worked up as indicated for the specific compounds.

In some cases, yields are increased by adding more $Fe_2(CO)_9$ after *ca.* half the reaction time. Using a larger amount of $Fe_2(CO)_9$ at the beginning of the reaction has no influence on the yields.

5. *General Procedure for the Synthesis of [Fe(CO)₃(heterodiene)] Complexes.* At 40–45°, 50 mmol of the heterodiene and 55–60 mmol of $Fe(CO)_5$ were irradiated overnight with a high-pressure mercury lamp (*Philips HPK, 125 W*). By TLC, 2 products could be detected, the [$Fe(CO)_4(\eta^2$-heterodiene)] and the [$Fe(CO)_3(\eta^4$-heterodiene)] complex. The benzene soln. was filtered through *Celite* to remove any decomposed material and then refluxed to convert the ene complex into the enone complex. Removal of the solvent and chromatography on silica gel yielded the pure compounds in 60–80% yield.

6. *Butadiene Complexes. Tricarbonyl[1–4-η-((*Z*)-3-methyl-1,3-pentadiene)]iron* (**6**) was prepared according to *Exper. 4* and the general procedures in [5e]. $^{57}$Fe-NMR: *Table 7.* $^{13}$C-NMR (25.2 MHz, $CDCl_3$): 105.2 (C(3)); 89.9 (C(2)); 56.0 (C(4)); 37.3 (C(3)); 25.1 (Me–C(3)); 13.5 ($Me_a$–C(4)).

*Tricarbonyl[2–5-η-(methyl (*E*)-2-methyl-2,4-pentadienoate)]iron* (**29**). According to *Exper. 4*, 0.92 g (7.3 mmol) of *methyl (*E*)-2-methyl-2,4-pentadienoate* [48] are treated with an excess of $Fe_2(CO)_9$. When no more starting material can be detected by TLC ($Et_2O$/hexane 1:19), most of the solvent is removed and the resulting slurry transferred to a column of $Al_2O_3$. Apolar impurities are removed by elution with hexane. Rinsing the column with $Et_2O$ and evaporation of the solvent yield 1.28 g (67%) of **29** as an orange oil. $^{1}$H-NMR (90 MHz, $CDCl_3$): 6.16 (*d*, H–C(3)); 5.49 (*ddd*, H–C(4)); 3.70 (*s*, COOMe); 2.00 (*d*, $H_b$–C(5)); 1.89 (*d*, $H_a$–C(5)); 1.10 (*s*, Me–C(2)). $^{13}$C-NMR (25.2 MHz, $CDCl_3$): 209.2 ($Fe(CO)_3$); 175.2 (C(1)); 91.6, 88.6 (C(3),C(4)*); 56.4 (C(2)); 51.6 (COO*Me*); 41.7 (C(5)); 14.2 (*Me*–C(2)). MS: 266 (2, $M^+$), 238 (11), 210 (22), 182 (57), 127 (100), 56 (46).

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5) Calculated from $2\theta$ values of 64 automatically centered reflection positions of a hemisphere with $40° < |2\theta| < 46°$.

*Tricarbonyl[2–5-η-(ethyl (*E*)-3-methyl-2,4-pentadienoate)]iron* (**30**). According to *Exper. 4*, 1.4 g (10 mmol) of *ethyl (*E*)-3-methyl-2,4-pentadienoate*[6] are reacted with $Fe_2(CO)_9$ in benzene. After 2 h, 2.5 g of additional $Fe_2(CO)_9$ are added. After all starting material has disappeared (TLC, $Et_2O$/hexane 1:19), the solvent is evaporated and the crude product dissolved in $Et_2O$ and filtered over $Al_2O_3$. Chromatography of the filtrate on silica gel with $Et_2O$/hexane 1:19 yields 2.30 g (82%) of **30** as a yellow oil. $^1$H-NMR (90 MHz, $CDCl_3$): 5.18 (*dd*, H–C(4)); 4.10 (*q*, $COOC\mathit{H}_2CH_3$); 2.54 (*s*, Me–C(3)); 1.80 (*dd*, $H_b$–C(5)); 1.26 (*t*, $COOCH_2C\mathit{H}_3$); 0.28 (*s*, H–C(2)); 0.49 (*dd*, $H_a$–C(5)). $^{13}$C-NMR (25.2 MHz, $CDCl_3$): 209.2 ($Fe(CO)_3$); 171.4 (C(1)); 104.3 (C(3)); 85.7 (C(4)); 59.9 ($COO\mathit{C}H_2CH_3$); 48.6 (C(2)); 38.2 (C(5)); 18.6 (*Me*–C(3)); 14.1 ($COOCH_2\mathit{C}H_3$). MS: 280 (5, $M^+$), 252 (14), 224 (21), 196 (49), 124 (100), 56 (24).

*Tricarbonyl[3–6-η-((*E*)-6-methyl-3,5-heptadien-2-one)]iron* (**34**). According to *Exper. 4*, 2.48 g (20 mmol) of *(*E*)-6-methyl-3,5-heptadien-2-one* [50] are complexed. The crude produt is filtered over a short column of $Al_2O_3$ and chromatographed twice on silica gel. In the 1st run using hexane/$Et_2O$ 1:1, a deep red fraction ($R_f$ 0.50) is collected and identified as *tricarbonyl[O–4-η-((*E*)-6-methyl-3,5-heptadien-2-one)]iron* (**35**) by NMR *(cf. Chapt. 2.1)*. The yellow band at $R_f$ 0.30 consists of **34** and unreacted starting material and has to be separated in a 2nd run with $CH_2Cl_2$. Recrystallization of the yellow fraction from pentane at –78° yields 2.16 g (41%) of **34**. M.p. 53°. $^1$H-NMR (400 MHz, $C_6D_6$): 5.69 (*dd*, H–C(4)); 4.42 (*d*, H–C(5)); 2.17 (*d*, H–C(3)); 1.76 (*s*, Me–C(2)); 1.13 (*s*, $Me_b$–C(6)); 0.82 (*s*, $Me_a$–C(6)); $^3J$(H–C(3), H–C(4)) = 8.7; $^3J$(H–C(4), H–C(5)) = 5.5; $^4J$(H–C(3), H–C(5)) = 0.1. $^{13}$C-NMR (100.8 MHz, $C_6D_6$): 208.1 ($Fe(CO)_3$); 199.0 (C(2)); 92.1 (C(5)); 86.8 (C(4)); 74.9 (C(6)); 57.0 (C(3)); 36.0 ($\mathit{Me}_b$–C(6)); 32.4 (C(1)); 25.0 ($\mathit{Me}_a$–C(6)); $^3J$($\mathit{Me}_a$–C(6), H–C(5)) = 4.2; $^3J$($\mathit{Me}_b$–C(6), H–C(5)) = 4.9. MS: 236 (4, $M^+$), 208 (6), 180 (17), 140 (10), 124 (18), 109 (100), 81 (46), 43 (56). Anal. calc. for $C_{11}H_{12}FeO_4$: C 50.00, H 4.55; found: C 50.30, H 4.80.

*Tricarbonyl[2–5-η-((*E*)-2-methyl-2,4-pentadienal)]iron* (**37**). According to *Exper. 4*, 1.92 g (20 mmol) of *(*E*)-2-methyl-2,4-pentadienal* [51] are treated with $Fe_2(CO)_9$ in benzene. The crude complex is filtered over $Al_2O_3$ ($Et_2O$) and chromatographed on silica gel ($Et_2O$/hexane 1:1). The yellow band at $R_f$ 0.35 is collected and the solvent is removed. Recrystallization from pentane at –78° yields 0.70 g (15%) of **37**. M.p. 30°. $^1$H-NMR (90 MHz, $CDCl_3$): 8.91 (*s*, H–C(1)); 5.34–5.67 (*m*, H–C(3), H–C(4)); 1.88–2.32 (*m*, $H_b$–C(5)); 1.30–1.60 (*m*, $H_a$–C(5)); 1.60 (*s*, Me). $^{13}$C-NMR (25.2 MHz, $CDCl_3$): 208.8 ($Fe(CO)_3$); 193.0 (C(1)); 92.0, 88.8 (C(3), C(4)*); 71.7 (C(2)); 43.6 (C(5)); 21.8 (Me). MS: 208 (3, $M^+$ – CO), 180 (8), 152 (16), 96 (23), 67 (65), 56 (52), 39 (100). Anal. calc. for $C_9H_8FeO_4$: C 45.76, H 3.39; found: C 45.61, H 3.13.

*Tricarbonyl[2–5-η-((*E*)-3-methyl-2,4-pentadienal)]iron* (**38**). Under $N_2$, 4.6 g of $Ag_2CO_3$ on *Celite* (1 mmol $Ag_2CO_3$/0.57 g, 8 mmol) [52] are suspended in 40 ml of abs. benzene. Residual moisture is removed by azeotropic distillation of *ca.* 10 ml of the solvent. After cooling to r.t., 180 mg (0.8 mmol) of **42** in 10 ml of abs. benzene are added, and the mixture is refluxed until all **42** has disappeared (*ca.* 30 min; TLC, $Et_2O$/hexane 1:2). The mixture is filtered, the solvent evaporated, and the raw product chromatographed on a short column of silica gel ($Et_2O$/hexane 1:2): 130 mg (70%) of yellow oil. $^1$H-NMR (90 MHz, $CDCl_3$): 9.57 (*d*, H–C(1)); 5.28 (*dd*, H–C(4)); 2.53 (*s*, Me); 2.00 (*dd*, $H_b$–C(5)); 1.10 (*d*, H–C(2)); 0.90 (*dd*, $\mathit{H}_a$–C(5)). $^{13}$C-NMR (25.2 MHz, $CDCl_3$): 208.3 ($Fe(CO)_3$); 195.5 (C(1)); 103.7 (C(3)); 86.9 (C(4)); 58.4 (C(2)); 39.4 (C(5)); 19.2 (Me). MS: 236 (5, $M^+$), 208 (8), 180 (40), 152 (72), 56 (100).

*Tricarbonyl[2–5-η-((*E*)-4-methyl-2,4-pentadienal)]iron* (**39**). According to *Exper. 4*, 0.8 g (8.3 mmol) of *(*E*)-4-methyl-2,4-pentadienal* [51] are reacted with 4.55 g (12.5 mmol) of $Fe_2(CO)_9$ in 50 ml of benzene. The raw mixture is dissolved in $Et_2O$ and filtered over a short column of $Al_2O_3$ to remove polar impurities und unreacted $Fe_2(CO)_9$. After evaporation, the residue is chromatographed on silica gel with $Et_2O$/hexane 1:3 ($R_f$ 0.20). Evaporation yielded 1.0 g (51%) of **39** as a red oil which solidified on standing and was recrystallized from pentane at –78°. M.p. 34°. $^1$H-NMR (90 MHz, $CDCl_3$): 9.35 (*d*, H–C(1)); 5.81 (*d*, H–C(3)); 2.22 (*s*, Me); 2.12 (*s*, $\mathit{H}_b$–C(5)); 1.11 (*dd*, H–C(2)); 0.89 (*s*, $H_a$–C(5)). $^{13}$C-NMR (25.2 MHz, $CDCl_3$): 208.6 ($Fe(CO)_3$); 196.0 (C(1)); 103.8 (C(4)); 84.4 (C(3)); 53.5 (C(2)); 44.8 (C(5)); 22.4 (Me). MS: 236 (10, $M^+$), 208 (21), 180 (64), 152 (75), 134 (59), 96 (29), 56 (100). Anal. calc. for $C_9H_8FeO_4$: C 45.76, H 3.39; found: C 45.90, H 3.64.

*Tricarbonyl[2–5-η-((*E*)-2-methyl-2,4-pentadien-1-ol)]iron* (**41**). Using the procedure described for the synthesis of **43**, **41** is prepared from 0.53 g (2 mmol) of **29**. Chromatography on silica gel ($Et_2O$/hexane 1:1) of the product obtained from the $Al_2O_3$-filtration step yields 240 mg (50%) of **41**. $^1$H-NMR (90 MHz, $CDCl_3$): 5.35 (*s*,

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[6] The pure (*E*)-isomer was prepared by the reaction of 35.8 g (0.1 mol) of methyltriphenylphosphonium bromide, 62.5 ml (0.1 mol) of BuLi (1.6N in hexane) and 13.6 ml (0.1 mol) of ethyl 3-methyl-4-oxocrotonate *(Fluka AG)*, according to the general procedure for *Wittig* olefinations, in 33% yield. The spectroscopic data are in agreement with published values, see *e.g.* [49].

H–C(3),H–C(4)); 3.63 (*d*, H–C(1)); 2.20 (*t*, OH); 1.5–2.0 (*m*, $H_a$–C(5), $H_b$–C(5)); 1.20 (*s*, Me). $^{13}$C-NMR (25.2 MHz, $CDCl_3$): 211.0 ($Fe(CO)_3$); 91.1, 86.4 (C(3),C(4)*); 73.2 (C(1)); 41.5 (C(5)); 15.7 (Me). MS: 210 (2, $M^+$ – CO), 182 (4), 154 (5), 56 (40), 40 (100).

*Tricarbonyl[2–5-η-((*E*)-3-methyl-2,4-pentadien-1-ol)]iron* (**42**). Using the procedure described for the synthesis of **43**, **42** is prepared from 0.56 g (2 mmol) of **30**. Chromatography of the product obtained from the $Al_2O_3$-filtration step on silica gel ($Et_2O$/hexane 1:1) yields 230 mg (48%) of **42**. $^1$H-NMR (90 MHz, $CDCl_3$): 5.16 (*dd*, H–C(4)); 3.80 (*d*, H–C(1)); 2.22 (*s*, Me); 2.00 (br. *s*, OH); 1.62 (*dd*, $H_b$–C(5)); 0.92 (*t*, H–C(2)); 0.50 (*dd*, $H_a$–C(5)). $^{13}$C-NMR (25.2 MHz, $CDCl_3$): 211.0 ($Fe(CO)_3$); 102.5 (C(3)); 83.5 (C(4)); 61.7 (C(1)); 61.7 (C(2)); 37.5 (C(5)); 18.1 (Me). MS: 238 (31, $M^+$), 210 (42), 182 (39), 154 (67), 136 (100), 56 (67).

*Tricarbonyl[2–5-η-((*E*)-4-methyl-2,4-pentadien-1-ol)]iron* (**43**). To 300 mg (1.27 mmol) of **39** in 20 ml of $Et_2O$ at –78° under $N_2$ (septum), 3.0 ml (3 mmol) of 1N DIBAH in hexane is added dropwise under stirring. After the addition is complete, the mixture is allowed to warm up to r.t. The workup procedure is identical to that for **46**. However, chromatography is not necessary since filtration over $Al_2O_3$ yields 280 mg (93%) of pure **43**. $^1$H-NMR (90 MHz, $CDCl_3$): 5.28 (*d*, H–C(3)); 3.70 (*d*, H–C(1)); 2.19 (*s*, Me); 2.19 (*s*, OH); 1.78 (*s*, $H_b$–C(5)); 0.92 (*dt*, H–C(2)); 0.50 (*s*, $H_a$–C(5)). $^{13}$C-NMR (25.2 MHz, $CDCl_3$): 211.0 ($Fe(CO)_3$); 100.5 (C(4)); 86.6 (C(3)); 64.7 (C(1)); 58.7 (C(2)); 43.7 (C(5)); 22.7 (Me). MS: 238 (2, $M^+$), 210 (7), 182 (9), 154 (17), 134 (58), 81 (85), 79 (97), 42 (100), 41 (99).

*Tricarbonyl[1–4-η-((*E*)-2,6-dimethyl-1,3,5-heptatriene)]iron* (**44**). At r.t. under $N_2$, 4.13 g of isopropylphosphonium bromide/$NaNH_2$ (9.5 mmol; 'instant-ylide', *Fluka AG*) are stirred in 40 ml of THF for 2 h. The mixture is chilled to –78°, and 2.24 g (9.5 mmol) of **39** in 10 ml of THF are added dropwise by means of a syringe. The cooling bath is removed and stirring continued at r.t. until almost all starting material has disappeared (*ca.* 3 h; TLC, $Et_2O$/hexane 1:3). The resulting black mixture is diluted with 30 ml of $H_2O$, acidified with 5 ml of conc. HCl/$H_2O$ 1:1, and the deep red org. layer is separated. The aq. layer is extracted 3 times with hexane, the org. layers are combined, and the solvent is evaporated. The residue is washed several times with small portions of hexane and filtered from the insoluble $Ph_3PO$. The combined washings (*ca.* 50 ml) are further purified by filtration over a column of $Al_2O_3$. Elution with hexane yields 2.19 g (88%) of **44** which can be recrystallized from pentane at –78°. M.p. 26–27°. $^1$H-NMR (90 MHz, $CDCl_3$): 5.24, 5.21 (2*d*, H–C(3),H–C(5)*); 2.17 (*s*, Me–C(2)); 1.80 (*dd*, H–C(4)); 1.80 (*d*, $H_b$–C(1)); 1.70 (*s*, 2 Me–C(6)); 0.50 (*d*, $H_a$–C(1)). $^{13}$C-NMR (25.2 MHz, $CDCl_3$): 211.9 ($Fe(CO)_3$); 134.8 (C(6)); 126.6 (C(5)); 98.5 (C(2)); 86.0 (C(3)); 58.1 (C(4)); 42.3 (C(1)); 26.0, 22.9, 18.4 (*Me*–C(2),2 *Me*–C(6)*). MS: 262 (2, $M^+$), 234 (7), 206 (7), 178 (23), 122 (11), 112 (18), 84 (52), 56 (100). Anal. calc. for $C_{12}H_{14}FeO_3$: C 54.96, H 5.34; found: C 56.37, H 5.48.

*Tricarbonyl[2–5-η-((2*E*,4*E*)-3,7-dimethyl-2,4,6-octatrienal)]iron* (**46**). To 2.80 g (9.76 mmol) of **49** in 25 ml of $Et_2O$ at –78° under $N_2$ (septum), 20 ml of DIBAH (1.0N in hexane 20 mmol) are added dropwise by syringe under stirring and keeping the temp. at –78°. When almost all **49** has dissappeared (TLC, $CH_2Cl_2$; $R_f$ (**49**) 0.61, $R_f$ (**46**) 0.49), the cooling bath is removed and the soln. stirred at r.t. for 15 min. Then, 1 ml of MeOH is added to destroy any excess of DIBAH. The resulting mixture is stirred for 20 min with 50 ml of sat. aq. $NH_4Cl$ soln. and afterwards treated with 20 ml of 10% $H_2SO_4$ soln. After separation of the org. layer, the aq. phase is diluted with *ca.* an equal volume of $H_2O$ and extracted 3 times with $CH_2Cl_2$. The org. layers are evaporated, and the residue is dissolved in $Et_2O$ and filtered over $Al_2O_3$. After evaporation, the crude product is chromatographed on silica gel with $CH_2Cl_2$. The yellow band at $R_f$ 0.50 is collected and yields 2.32 g (82%) of **46**. Traces of impurities can be removed by recrystallizing from pentane at –78°. M.p. 74°. $^1$H-NMR (90 MHz, $CDCl_3$): 9.50 (*d*, H–C(1)); 5.32, 5.22 (2*d*, H–C(4), H–C(6)*); 2.55 (*dd*, H–C(5)); 2.50 (*s*, Me–C(3)); 1.80, 1.74 (2*s*, 2 Me–C(7)); 1.33 (*d*, H–C(2)). $^{13}$C-NMR (25.2 MHz, $CDCl_3$): 209.1 ($Fe(CO)_3$); 195.3 (C(1)); 137.9 (C(7)); 125.2 (C(6)); 98.8 (C(3)); 87.5 (C(4)); 60.1, 57.1 (C(2), C(5)*); 26.1, 19.1, 18.5 (*Me*–C(3), 2 *Me*–C(7)*). MS: 290 (7, $M^+$), 262 (8), 234 (45), 206 (97), 162 (100), 56 (77). Anal. calc. for $C_{13}H_{14}FeO_4$: C 53.79, H 4.83; found: C 54.03, H 5.06.

*Tricarbonyl[2–5-η-((2*E*,4*E*)-3,7-dimethyl-2,4,6-octatrienenitrile)]iron* (**49**). At –78°, 1.58 ml (30 mmol) of MeCN (distilled from $P_2O_5$) in 30 ml of THF are stirred for 30 min. Through a septum, 18.75 ml (30 mmol) of 1.6N BuLi in hexane are added dropwise. The formation of the deprotonated MeCN is indicated by the appearance of a white precipitate. After 2.5 h of stirring at –78°, 2.64 g (10 mmol) of **34** in 10 ml of THF are added very slowly. The whole apparatus (including the cooling bath) is then insulated with Al foil and cotton, and the dark red mixture is stirred overnight. After removal of the thermal insulation, the clear soln. is stirred for 1 h at r.t. Then, *ca.* 10 ml of $H_2O$ are added, and the mixture is slightly acidified by the dropwise addition of dil. HCl soln. The org. layer is separated and the aq. layer extracted with 3 30-ml portions of $CH_2Cl_2$. The combined org. layers are evaporated, and the residue is filtered over a short column of $Al_2O_3$ using $Et_2O$: 2.84 g (99%) of **49**. M.p. 68–70°. $^1$H-NMR (90 MHz, $CDCl_3$): 5.29, 5.23 (2*d*, H–C(4),H–C(6)*); 2.41 (*s*, Me–C(3)); 2.12 (*dd*, H–C(5)); 1.79, 1.70 (2*s*, 2 Me–C(7)*); 0.66 (*s*, H–C(2)). $^{13}$C-NMR (25.2 MHz, $CDCl_3$): 208.6 ($Fe(CO)_3$); 137.8 (C(7)); 124.8 (C(6)); 122.0

(C(1)); 96.9 (C(3)); 86.3 (C(4)); 59.5 (C(5)); 26.3, 26.0, 20.0, 18.4 (C(2), *Me*–C(3), 2 *Me*–C(7)*). MS: 287 (3, $M^+$), 259 (5), 231 (56), 203 (100), 163 (41), 56 (40). Anal. calc. for $C_{13}H_{13}FeNO_3$: C 54.36, H 4.53, N 4.88; found: C 54.82, H 4.63, N 4.87.

*Tricarbonyl[5–8-η-((3*E*,5*E*,7*E*)-6,10-dimethyl-3,5,7,9-undecatetraen-2-one)]iron* (**51**). A soln. of 0.8 ml (1.1 mmol) of acetone (*Merck AG, p.a.*) in 15 ml of THF under $N_2$ is titrated with a soln. of triphenylmethylpotassium in dimethoxyethane [53] until the deep red colour of the reagent does not disappear any more. To destroy the excess of $Ph_3CK$, one more drop of acetone is added. The colourless soln. is cooled to −78° and stirred for 15 min. The soln. of the deprotonated acetone is then added dropwise by syringe to the stirred soln. of 0.29 g (1 mmol) of **46** in 15 ml of THF at −79°. After stirring for 1 h at −78°, the mixture is allowed to warm up to r.t. and quenched by the addition of $H_2O$. After acidifying with 1N HCl, the aq. layer is extracted several times with small amounts of $CH_2Cl_2$. The combined org. layer is evaporated and the residue dissolved in a small quantity of $Et_2O$ and filtered over $Al_2O_3$. Chromatography of the crude mixture on silica gel (hexane/$Et_2O$ 4:1) yields 100 mg of recovered **46** ($R_f$ 0.23) and 100 mg (50% referred to reacted **46**) of **51**. M.p. 62–70° (pentane, −78°). $^1$H-NMR (90 MHz, $CDCl_3$): 7.03 (*dd*, H–C(4)); 6.28 (*d*, H–C(3)); 5.29, 5.18 (2*d*, H–C(7), H–C(9)*); 2.38 (*dd*, H–C(8)); 2.34, 2.20 (2*s*, Me–C(2), Me–C(6)*); 1.80, 1.72 (2*s*, 2 Me–C(10)*); *ca.* 1.8 (*d*, H–C(5)). $^{13}$C-NMR (25.2 MHz, $CDCl_3$): 210.7 (CO); 197.2 (C(2)); 145.7 (C(4)); 136.6 (C(10)); 128.2 (C(3)); 125.9 (C(9)); 98.0 (C(6)); 85.5 (C(7)); 58.2, 57.6 (C(5), C(8)*); 27.4, 26.2, 19.4, 18.7 (C(1), *Me*–C(6), 2 *Me*–C(10)*). MS: 330 (4, $M^+$), 302 (3), 274 (15), 246 (99), 190 (52), 56 (99), 43 (100).

*Tricarbonyl[4–7-η-((2*E*,4*E*,6*E*)-5,9-dimethyl-2,4,6,8-decatetraenenitrile)]iron* (**52**) *and Tricarbonyl[4–7-η-((2*Z*,4*E*,6*E*)-5,9-dimethyl-2,4,6,8-decatetraenenitrile)]iron* (**53**). According to the procedure given for the preparation of **49**, 0.26 ml (5 mmol) of MeCN, 3.13 ml (5 mmol) of BuLi (1.6N in hexane), and 0.29 g (1 mmol) of **46** are reacted in 20 ml of THF. After filtration over $Al_2O_3$, 2 spots appear on TLC ($CH_2Cl_2$/hexane 1:1) with $R_f$ 0.54 and 0.47, resp. The fractions are separated by chromatography on silica gel ($CH_2Cl_2$/hexane 1:1) yielding first 94 mg (30%) of **53** and then 188 mg (60%) of **52**.

**52**: M.p. 110–114° (pentane, −78°). $^1$H-NMR (400 MHz, $CDCl_3$): 6.77 (*dd*, H–C(3)); 5.39 (*d*, H–C(2)); 5.22 (*d*, H–C(6)); 5.13 (*d*, H–C(8)); 2.30 (*dd*, H–C(7)); 2.26 (*s*, Me–C(5)); 1.74, 1.68 (2*s*, 2Me–C(9)*); 1.61 (*d*, H–C(4)). $^{13}$C-NMR (25.2 MHz, $CDCl_3$): 210.2 ($Fe(CO)_3$); 152.9 (C(3)); 137.0 (C(9)); 125.6 (C(8)); 118.2 (C(1)); 97.1 (C(5)); 95.4 (C(2)); 85.5 (C(6)); 58.6, 56.5 (C(4), C(7)*); 26.1, 19.2, 18.6 (Me–C(5), 2 Me–C(9)*). MS: 313 (6, $M^+$), 285 (12), 257 (72), 229 (88), 56 (100). Anal. calc. for $C_{15}H_{15}FeNO_3$: C 57.53, H 4.79, N 4.47; found: C 57.63, H 4.80, N 4.72.

**53**: M.p. 83–84° (pentane, −78°). $^1$H-NMR (400 MHz, $CDCl_3$): 6.60 (*dd*, H–C(3)); 5.24 (*d*, H–C(6)); 5.16 (*d*, H–C(8)); 5.12 (*d*, H–C(2)); 2.51 (*dd*, H–C(7)); 2.25 (*s*, Me–C(5)); 2.05 (*d*, H–C(4)); 1.78, 1.68 (2*s*, 2 Me–C(9)*). $^{13}$C-NMR (100.8 MHz, $CDCl_3$): 210.4 ($Fe(CO)_3$); 151.9 (C(3)); 137.6 (C(9)); 125.6 (C(8)); 116.8 (C(1)); 96.9 (C(5)); 94.1 (C(2)); 86.0 (C(6)); 58.9, 54.7 (C(4), C(7)*); 26.2, 19.3, 18.7 (Me–C(5), 2 *Me*–C(9)*). MS: 313 (3, $M^+$), 285 (4), 257 (29), 229 (100), 56 (80).

*Tricarbonyl[2–5-η-(diethyl (2*E*,4*E*)-3-methyl-2,4-hexadienedioate)]iron* (**54**). Complexation of diethyl 3-methyl-2,4-hexadienedioate [20] using $Fe_2(CO)_9$ (see *Exper. 4*) yields 86% of **54** as an orange oil which solidifies below 0°. $^1$H-NMR (400 MHz, $CDCl_3$): 5.77 (*d*, $J$ = 7.9, H–C(4)); 4.22–4.05 (*m*, 2 $OCH_2CH_3$); 2.54 (*s*, Me–C(3)); 1.26 (*m*, 2 $OCH_2CH_3$); 1.15 (*d*, $J$ = 7.9, H–C(5)); 0.99 (*s*, H–C(2)). $^{13}$C-NMR (50.4 MHz, $CDCl_3$): 171.9, 170.9 (C(1), C(6)); 103.7 (C(3)); 87.3 (C(4)); 60.4, 60.1 (2 $OCH_2CH_3$); 48.7, 44.8 (C(2), C(5)); 18.3 (C(7)); 13.9 (2 $OCH_2CH_3$). MS: 352 (4, $M^+$), 324 (13), 296 (6), 268 (100), 196 (93).

*Tricarbonyl[2–5-η-(ethyl (2*E*,4*E*)-3-methyl-6-oxo-2,4-hexadienoate)]iron* (**55**). Complexation of ethyl 3-methyl-6-oxo-2,4-hexadienoate [20] using $Fe_2(CO)_9$ (see *Exper. 4*) yields 80% of **55** as an orange oil. $^1$H-NMR (400 MHz, $CDCl_3$): 9.39 (*d*, $J$ = 3.3, H–C(6)); 5.74 (*d*, $J$ = 7.9, H–C(4)); 4.12 (*m*, $OCH_2CH_3$); 2.53 (*s*, Me–C(3)); 1.42 (*dd*, $J$ = 7.9, 3.2, H–C(5)); 1.24 (*t*, $OCH_2CH_3$); 1.19 (*s*, H–C(2)). $^{13}$C-NMR (25.2 MHz, $CDCl_3$): 195.9 (C(6)); 170.7 (C(1)); 85.3 (C(3)); 78.3 (C(4)); 60.5 ($OCH_2CH_3$); 52.7 (C(5)); 49.6 (C(2)); 18.6 (C(7)); 14.2 ($OCH_2CH_3$). MS: 308 (2, $M^+$), 280 (3), 252 (19), 224 (82), 178 (100), 152 (43).

*Tricarbonyl[2–5-η-(ethyl (2*E*,4*E*)-4-methyl-6-oxo-2,4-hexadienoate)]iron* (**56**). Complexation of ethyl 4-methyl-6-oxo-2,4-hexadienoate [20] using $Fe_2(CO)_9$ (see *Exper. 4*) yields 84% of **56** as an orange oil. $^1$H-NMR (400 MHz, $CDCl_3$): 9.55 (*d*, $J$ = 3.3, H–C(6)); 5.83 (*d*, $J$ = 8.0, H–C(3)); 4.16 (*m*, $OCH_2CH_3$); 2.54 (*s*, Me–C(4)); 1.42 (*d*, $J$ = 8.0, H–C(2)); 1.32 (*d*, $J$ = 5.3, H–C(5)); 1.27 (*t*, $OCH_2CH_3$). $^{13}$C-NMR (25.2 MHz, $CDCl_3$): 195.0 (C(6)); 171.5 (C(1)); 103.0 (C(4)); 88.3 (C(3)); 60.9 ($OCH_2CH_3$); 57.6 (C(5)); 45.8 (C(2)); 19.0 (C(7)); 14.2 ($OCH_2CH_3$). MS: 308 (6, $M^+$), 280 (2), 252 (16), 224 (78), 178 (100), 152 (33).

*Tricarbonyl[2–5-η-(ethyl (2*E*,4*E*)-6-acetoxy-4-methyl-2,4-hexadienoate)]iron* (**57**). Complexation of ethyl 6-acetoxy-4-methyl-2,4-hexadienoate [20] using $Fe_2(CO)_9$ (see *Exper. 4*) yields 65% of **57** as an oil. $^1$H-NMR (400 MHz, $CDCl_3$): 5.72 (*d*, $J$ = 7.9, H–C(3)); 4.29 (*dd*, $J$ = 7.0, 1.8, 2 H–C(6)); 4.11 (*m*, $OCH_2CH_3$); 2.26 (*s*, Me–C(4)); 2.08 (*s*, Ac); 1.24 (*t*, OCH$_2$C*H*$_3$); 1.21 (*t*, *J* = 7.0, hidden, H–C(5)); 1.01 (*d*, *J* = 7.9, H–C(2)). $^{13}$C-NMR (25.2 MHz, CDCl$_3$); 172.1 (*C*OCH$_3$); 170.3 (C(1)); 85.2 (C(4)); 79.1 (C(3)); 63.1 (C(6)); 60.5 (O*C*H$_2$CH$_3$); 56.8 (C(5)); 44.5 (C(2)); 20.7 (CO*C*H$_3$); 18.1 (C(7)); 14.2 (OCH$_2$*C*H$_3$). MS: 324 (2, $M^+$ – CO), 296 (6), 268 (48), 208 (43), 108 (62), 80 (100).

*Tricarbonyl[2–5-η-(ethyl (2*E*,4*E*)-6-(diethoxyphosphoryl)-4-methyl-2,4-hexadienoate)]iron* (**58**). Photolysis of ethyl 6-(diethoxyphosphoryl)-4-methyl-2,4-hexadienoate [20] using Fe(CO)$_5$ (see *Exper. 4*) yields 70% of **58** as a red oil. $^1$H-NMR (200 MHz, CDCl$_3$): 5.74 (*d*, *J* = 7.9, H–C(3)); 4.20–4.0 (*m*, 2 H–C(6), OC*H*$_2$CH$_3$, PO(OC*H*$_2$CH$_3$)$_2$); 2.24 (*t*, *J* = 5.6, H–C(5)); 2.22 (*s*, Me–C(4)); 1.35 (*td*, *J*(P,H) = 1,5, *J*(H,H) = 7.0, PO(OCH$_2$C*H*$_3$)$_2$); 1.25 (*t*, *J* = 7.1, OCH$_2$C*H*$_3$); 0.97 (*d*, *J* = 7.9, H–C(2)). $^{13}$C-NMR (50.4 MHz, CDCl$_3$): 209.3 (CO); 172.3 (C(1)); 101.8 (*d*, *J*(P,C) = 9.8, C(4)); 84.5 (C(3)); 61.8 (*d*, *J*(P,C) = 14.4, PO(O*C*H$_2$CH$_3$)$_2$); 60.4 (O*C*H$_2$CH$_3$); 53.0 (*d*, *J*(P,C) = 6.9, C(5)); 43.9 (C(2)); 28.5 (*d*, *J*(P,C) = 140.3, C(6)); 18.4 (C(7)); 16.3 (*d*, *J*(P,C) = 5.8, PO(OCH$_2$*C*H$_3$)$_2$); 14.1 (OCH$_2$*C*H$_3$).

*Tricarbonyl[2–5-η-(diethyl (2*E*,4*E*,6*E*,8*E*,10*E*)-4,9-dimethyl-2,4,6,8,10-dodecapentaenedioate)]iron* (**59**). A soln. of 580 mg (2 mmol) of ethyl (*E*)-6-(diethoxyphosphoryl)-4-methyl-2,4-hexadienoate [20] in 25 ml of dry THF is cooled to –78°, and 1.2 ml (1.92 mmol) of BuLi (1.6M in hexane) are slowly added. The dark red soln. containing the ylide is warmed to –50° and then re-cooled to –78°. At this temp., 540 mg (1.77 mmol) of **56** in 15 ml of THF are slowly added, the soln. is kept at –70° for 5 h and then allowed to warm overnight to 5°. Neutralization with 10% HCl soln. and extraction with CH$_2$Cl$_2$ give, after flash chromatography on silica gel (Et$_2$O/hexane 2:1), 0.66 g (84%) of **59**. $^1$H-NMR (200 MHz, CDCl$_3$): 7.35 (*d*, *J* = 15.6, H–C(10)); 6.71 (*dd*, *J* = 14.5, 11.6, H–C(7)); 6.37 (*d*, *J* = 11.6, H–C(8)); 6.15 (*dd*, *J* = 14.5, 10.8, H–C(6)); 5.93 (*d*, *J* = 15.6, H–C(11)); 5.73 (*d*, *J* = 8.4, H–C(3)); 4.23 (*q*, *J* = 7.2, C(12)OOC*H*$_2$CH$_3$)*; 4.14 (*m*, C(1)OOC*H*$_2$CH$_3$)*; 2.32 (*s*, Me–C(4)); 2.15 (*d*, *J* = 10.8, H–C(5)); 1.89 (*s*, Me–C(9)); 1.36–1.24 (2*t*, 1*d*, 2 COOCH$_2$C*H*$_3$, H–C(2)). $^{13}$C-NMR (50.4 MHz, CDCl$_3$): 209.1 (CO); 172.5 (C(1)); 166.9 (C(12)); 148.5 (C(10)); 137.2 (C(6)); 136.2 (C(8)); 133.6 (C(9)); 128.2 (C(7)); 117.1 (C(11)); 99.6 (C(4)); 84.6 (C(3)); 65.1 (C(5)); 60.6, 60.3 (COO*C*H$_2$CH$_3$); 43.9 (C(2)); 19.2 (*Me*–C(4)); 14.4, 14.3 (COOCH$_2$*C*H$_3$); 12.7 (*Me*–C(9)). MS: 444 (2, $M^+$), 416 (3), 388 (10), 360 (52), 240 (80) 128 (100).

7. *Bis(tricarbonyliron) Complexes. Hexacarbonyl[2–5-η:8–11-η-(diethyl (2*E*,4*E*,6*E*,8*E*,10*E*)-4,9-dimethyl-2,4,6,8,10-dodecapentaene-1,12-dioate)]diiron* (**60**). A soln. of 0.86 g (2 mmol) of **58** in 25 ml of dry THF is cooled to –78°, and 1.25 ml (1.92 mmol) of BuLi (1.6M in hexane) are slowly added. The dark red ylide soln. is warmed to –50° and then re-cooled to –78°. At –78°, 0.6 g (1.9 mmol) of **56** in 15 ml of THF are slowly added, and the soln. is kept at –70° for 5 h and then allowed to warm overnight to 5°. Neutralization with 10% HCl soln. and extraction with CH$_2$Cl$_2$ give, after flash chromatography on silica gel (Et$_2$O/hexane 2:1), 0.9 g (85%) of **60**. $^1$H-NMR (200 MHz, CDCl$_3$): 6.08 (*AA'* of *AA'XX'*, *J* = 14.4, 10.6, –0.81, H–C(6), H–C(7)); 5.69 (*d*, *J* = 7.8, H–C(3), H–C(10)); 4.13 (*m*, 2 OC*H*$_2$CH$_3$); 2.31 (*s*, Me–C(4), Me–C(9)); 2.04 (*XX'* of *AA'XX'*, *J* = 14.4, 10.6, –0.81, H–C(5), H–C(8)); 1.26 (*t*, 2 OCH$_2$C*H*$_3$); 1.19 (*d*, *J* = 7.8, H–C(2), H–C(11)). $^{13}$C-NMR (50.4 MHz, CDCl$_3$): 209.3 (CO); 172.4 (C(1), C(12)); 131.3 (C(6), C(7)); 99.1 (C(4), C(9)); 84.1 (C(3), C(10)); 65.2 (C(5), C(8)); 60.5 (O*C*H$_2$CH$_3$); 43.7 (C(2), C(11)); 19.0 (*Me*–C(4), *Me*–C(9)); 14.2 (OCH$_2$*C*H$_3$). MS: 584 (4, $M^+$), 556 (1), 528 (9), 500 (15), 472 (15), 444 (53), 416 (100).

*Hexacarbonyl[2–5-η:8–11-η-((2*E*,4*E*,6*E*,8*E*,10*E*)-4,9-dimethyl-2,4,6,8,10-dodecapentaene-1,12-diol)]diiron* (**61**). To a soln. of 0.4 g (0.7 mmol) of **60** in 25 ml of THF, cooled to –78°, 1.2 ml (1.2 mmol) of DIBAH (1M in hexane) are added dropwise. On completion of the reaction (TLC), 3 ml of MeOH are added to remove excess DIBAH. Subsequently, the mixture is hydrolyzed first with sat. NH$_4$Cl soln. and then with 10% H$_2$SO$_4$ soln. Extraction with CH$_2$Cl$_2$ and filtration over a short Al$_2$O$_3$ column give 315 mg (90%) of **61**. $^1$H-NMR (200 MHz, CDCl$_3$): 5.99 (*AA'* of *AA'XX'*, *J* = 14.4, 10.6, H–C(6), H–C(7)); 5.07 (*d*, *J* = 8.2, H–C(3), H–C(10)); 3.76–3.62 (2*m*, 2 H–C(1), 2 H–C(12)); 2.23 (*s*, Me–C(4), Me–C(9)); 1.85 (*XX'* of *AA'XX'*, *J* = 14.4, 10.6, H–C(5), H–C(8)); 1.23 (*td*, *J* = 8.2, 7.4, H–C(2), H–C(11)). $^{13}$C-NMR (50.4 MHz, (D$_6$)acetone): 212.7 (CO); 132.2 (C(6), C(7)); 97.8 (C(4), C(9)); 85.4 (C(3), C(10)); 66.3 (C(2), C(11) or C(5), C(8)); 64.5 (C(5), C(8) or C(2), C(11)); 60.5 (C(1), C(12)); 19.0 (*Me*–C(4), *Me*–C(9)). MS: 500 (4, $M^+$), 472 (2), 444 (6), 416 (15), 388 (2), 360 (3), 332 (26), 148 (100).

*Hexacarbonyl[2–5-η:8–11-η-((2*E*, 4*E*, 6*E*, 8*E*, 10*E*)-4, 9-dimethyl-2, 4, 6, 8, 10-dodecapentaenedial)]diiron* (**62**). A soln. of 0.1 g (0.2 mmol) of **61** in 5 ml of dry benzene is added to a slurry of Ag$_2$CO$_3$/*Celite* [52] in benzene. The mixture is refluxed for 3 h (→black; no **61** left). The mixture is then filtered through *Celite* and evaporated. Some decomposition products are removed by chromatography on silica gel (hexane/Et$_2$O 1:1) which yields 56 mg (56%) of **62**. $^1$H-NMR (200 MHz, CDCl$_3$): 9.32 (*d*, *J* = 4.3, H–C(1), H–C(12)); 6.18 (*AA'* of *AA'XX'*, *J* = 14.6, 10.8, –0.71, H–C(6), H–C(7)); 5.67 (*d*, *J* = 8.1, H–C(3), H–C(10)); 2.31 (*s*, Me–C(4), Me–C(9)); 2.30 (*XX'* of *AA'XX'*, *J* = 14.6, 10.8, –0.71, H–C(5), H–C(8)); 1.48 (*dd*, *J* = 8.1, 4.3, H–C(2), H–C(11)). $^{13}$C-NMR (50.4 MHz, (D$_6$)acetone): 196.5 (C(1), C(12)); 131.3 (C(6), C(7)); 100.4 (C(4), C(9)); 82.5 (C(3), C(10)); 65.7

(C(5), C(8)); 52.1 (C(2), C(11)); 19.1 (*Me*–C(4), *Me*–C(9)). MS: 496 (4, $M^+$), 440 (2), 412 (15), 384 (3), 356 (3), 328 (17), 182 (95), 68 (100).

8. *Heterodiene Complexes.* The following heterodiene complexes **64–66**, **69**, and **70** were prepared according to *Exper. 5* and characterized by $^{13}$C- and $^{57}$Fe-NMR data *(cf. Table 11).*

*Tricarbonyl[O–3-η-((*E*)-2-methylpropenal)]iron* (**64**). $^{13}$C-NMR (25.2 MHz, $C_6D_6$): 208.7 (CO); 123.8 (C(1)); 102.7 (C(2)); 45.7 (C(3)); 16.5 (*Me*–C(2)).

*[O–3-η-((*E*)-2-Butenal)]tricarbonyliron* (**65**). $^{13}$C-NMR (25.2 MHz, $C_6D_6$): 208.5 (CO); 123.1 (C(1)); 88.7 (C(2)); 59.8 (C(3)); 17.2 (C(4)).

*Tricarbonyl[O–3-η-((*E*)-2-methyl-2-butenal)]iron* (**66**). $^{13}$C-NMR (25.2 MHz, $C_6D_6$): 120.8 (C(1)); 103.3 (C(2)); 61.8 (C(3)); 14.2, 12.6 (C(4), *Me*–C(2)).

*Tricarbonyl[1–O-η-((*E*)-1-penten-3-one)]iron* (**69**). $^{13}$C-NMR (25.2 MHz, $C_6D_6$): 207.5 (CO); 150.9 (C(3)); 76.5 (C(2)); 38.6 (C(1)); 27.6 (C(4)); 11.2 (C(5)).

*Tricarbonyl[O–4-η-((*E*)-3-methyl-3-buten-2-one)]iron* (**70**). $^{13}$C-NMR (25.2 MHz, $C_6D_6$): 208.0 (CO); 143.3 (C(2)); 94.7 (C(3)); 45.0 (C(4)); 18.7, 17.8 (C(1), *Me*–C(3)).

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