62. Synthesis and Structure of Carbonyliron Complexes of Allenecarboxylates and Allenic Lactones

by **Latchezar S. Trifonov** and **Alexander S. Orahovats***

Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

and **Roland Prewo** and **Heinz Heimgartner***

Organisch-chemisches Institut der Universität Zürich, Winterthurerstrasse 190, CH–8057 Zürich

(7.III.88)

On irradiation in the presence of $Fe(CO)_5$, the allenecarboxylates **1** afforded binuclear carbonyliron complexes **6** *(Scheme 3)*, whereas the allenic lactone **7** under similar conditions gave a mixture of one binuclear and two mononuclear carbonyliron complexes (**9, 8,** and **10**; *Scheme 4*). The structure of the complexes has been elucidated by X-ray crystallography. The structure of the binuclear complex **9** corresponds to that of **6**, while **8** has been shown to be a 1,3-butadiene(tricarbonyl)iron complex. The unique structure of **10** represents a new type of allenic complex. A stepwise formation of the complexes *via* intermediate allene(tetracarbonyl)iron complexes of type **11** and **13** is suggested. Treatment of the binuclear complex **6b** with $FeCl_3$ led to the formation of the free ligand and a mixture of mononuclear complexes **13** and **14** *(Scheme 5)*. On heating, the 1,3-diene complex **8** yielded the free ligand **15**, the product of a (1,3) H shift in the allene **7**; the complex **10** on the other hand liberates **7** on treatment with ethylenetetracarbonitrile (TCNE) *(Scheme 6)*.

1. Introduction. – In [1], we have reported on octacarbonyldicobalt-induced (1,3) H shifts in 1-methylallenecarboxylates and allenic lactones of type **1** leading to 1,3-buta-dienes **2** *(Scheme 1)*. In the former case, the butadiene-2-carboxylates of type **2** dimerize under the reaction conditions (benzene, 90°) in a *Diels-Alder* fashion.

Scheme 1

$$\textbf{a} \quad R^2 = H, R^3 = CH_3, CH_3CH_2 \qquad\qquad \textbf{b} \quad R^2 - R^3 = CH_2$$
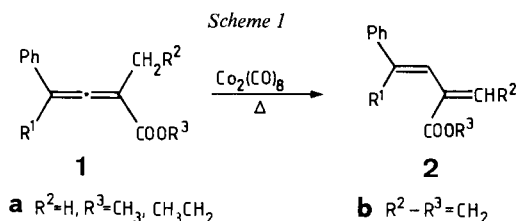
Similar (1,3) H shifts in carbonyliron complexes of allenes have already been reported [2–5]. Thus, treatment of tetramethylallene (**3**) with $Fe_2(CO)_9$ yields two carbonyliron complexes, **4** and **5** [2] *(Scheme 2)*. It has been shown that complex **4** is predominantly formed, but upon prolonged heating or with excess $Fe_2(CO)_9$, **4** is converted to the more stable **5**[1]).

---

[1]) The transformation of allene complexes of type **4** into butadiene complexes **5** has been achieved also in a two-step reaction *via* intermediate allyl-tetracarbonyliron cations [3].

Scheme 2
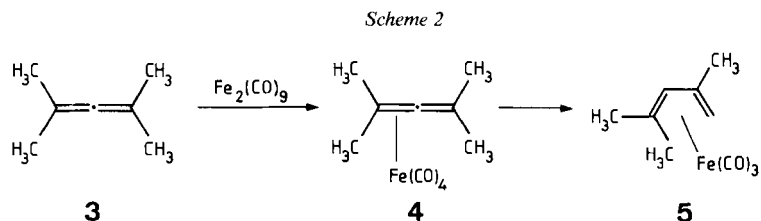
Allenes are also known to form binuclear carbonyliron complexes [4–7] (see also [8]). The structures of two of these complexes, obtained from the reaction between nonacarbonyldiiron (Fe$_2$(CO)$_9$) and ethyl 2-methyl-2,3-butadienoate [4] and allene [7] have been established by X-ray crystallography. Treatment of allene with Fe$_2$(CO)$_9$ at 50° yielded, besides the heptacarbonyldiiron complex, a bis(π-allylene)-Fe$_2$(CO)$_9$ complex *via* dimerization of the allene ligand [6]. Similar binuclear complexes were described as products of the reactions between Fe$_2$(CO)$_9$ and 1,2-cyclononadiene [9] or phenylallene [10], and also between Fe$_3$(CO)$_{12}$ and allene [11] or 1,2,6,7-cyclodecatetraene [12].

In the present paper, we report on the photochemical formation of carbonyliron complexes of allenecarboxylates and allenic lactones.

2. Photochemical Formation of Allenecarbonyliron Complexes. – Irradiation of allenecarboxylates **1a–c** *(Scheme 3)* in the presence of excess Fe(CO)$_5$ in hexane with a Hg high-pressure lamp yields crystalline, red hexacarbonyldiiron complexes **6a–c** in good yields (56, 50, and 65%, respectively)[2]) which are stable in the crystalline state but decompose slowly in solution.

The ^{1}H-NMR spectra of **6a** and **6b** exhibited two one-proton *doublets* at low field (7.79 and 7.49 ppm for **6a**, and 8.04 and 7.62 ppm for **6b**), suggesting that one Ph ring might be involved in the complexation [13]. A single-crystal X-ray analysis of **6a** (see *Chapt. 3*), however, proved the structure shown in *Scheme 3*, which is essentially the same as the structure of hexacarbonyldiiron complex of an allenecarboxylate not bearing a substituent at C(4) [4]. The lack of absorption of the ester CO group in the usual region in

Scheme 3

1a-c   **6a-c**

a R = R' = CH$_3$
b R = CH$_3$, R' = CH$_3$CH$_2$
c R = Ph, R' = CH$_3$CH$_2$

---
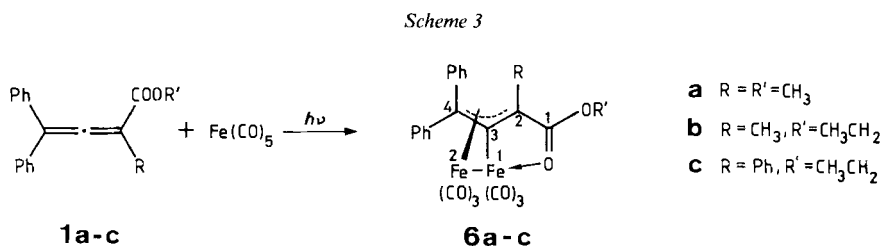
[2])   Yellow complexes with the proposed structure **i** (as evidenced from the strong bands at 2050 and 1980 cm^{-1} in the IR spectra (*cf.* [5]) and the ^{1}H-NMR spectra with absorptions at *ca.* 1.3, 1.6, and 4.5 ppm for the olefinic protons) were also detected but not isolated in pure form on irradiation of **1a,b** in the presence of Fe(CO)$_5$.
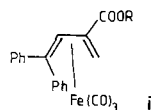
the IR spectra of **6a–c** is in accordance with the complexation of the CO group (see also [4]).

The low-field proton signals mentioned above are probably due to restricted rotation of one Ph ring situated near the bulky $Fe(CO)_3$ groups. The molecular asymmetry of the complexes **6a–c** is reflected in the CH_2O signals in the ^1H-NMR spectra of **6b** and **6c** which appear as two diastereotopic *doublets of quartets*. The signals in the ^{13}C-NMR spectra of C(2) (at 68.3, 68.8, and 77.2 ppm), of C(3) (at 123.6, 123.1, and 119.7 ppm), and of C(4) (at 77.2, 76.4, and 80.7 ppm, respectively) of **6a,b**, and **c** are characteristic for allenehexacarbonyldiiron complexes of this type.

The allenecarboxylates **1a–c**, when treated with $Fe_2(CO)_9$ at room temperature (similar to [4]), gave also the complexes **6a–c**, but in low yield.

The allenic lactone **7** gave, on short irradiation in the presence of excess $Fe(CO)_5$, three air-stable crystalline complexes, one yellow and two red[3]). Their structures **8, 9**, and **10** *(Scheme 4)* were established by means of single-crystal X-ray analysis (see *Chapt. 3*).

The yellow mononuclear iron complex **8** *(Scheme 4)* showed the expected spectral data of a non-complexed CO group (absorption at 1760 cm^{-1} in the IR spectrum and at 174.0 ppm in the ^{13}C-NMR spectrum). The complexation of the 1,3-butadiene fragment led to a strong high-field shift of the H–C(3) signal (at 2.25 ppm) and also of the ^{13}C-NMR signals of C(2), C(3), C(1'), and C(2') (see *Exper. Part*)[4]).

The less polar, red hexacarbonyldiiron complex **9** *(Scheme 4)* was shown to have a structure analogous to the structure of **6a–c**. The complexation of the CO group explains the lack of CO absorption in the IR spectrum and also the low-field shift of the CO signal in the ^{13}C-NMR spectrum (lower field than 184 ppm). The presence of low-field aromatic signals in the ^1H-NMR spectrum (see *Exper. Part*) is an evidence for restricted Ph rotation as in the case of **6a–c**. Interestingly, one of the protons at C(3) gives a very high-field shifted signal (at 0.47 ppm), which is obviously due to a situation near to the η^3-hapto coordinated Fe(2)-atom. The ^{13}C-NMR signals of C(2) (at 69.1 ppm), C(1') (at 124.1 ppm), and C(2') (at 77.2 ppm) of **9** are well comparable with the corresponding signals of the ester complexes **6a–c** (see above).

Scheme 4

7   8   9   10

---
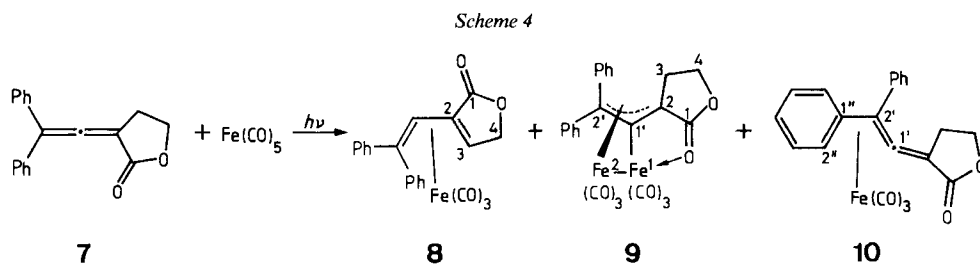
[3])   The same complexes were formed, however, in low yields, when 7 was treated with $Fe_2(CO)_9$ in benzene at r.t. for 2 days.

[4])   The yellow complex isolated directly after chromatography (without recrystallization) showed spectral data (IR and MS) which suggest the structure of a tetracarbonyliron complex of type **11** (*cf.* [2] [3]).

11
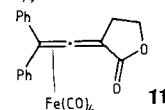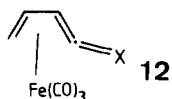
The more polar, red complex was shown by X-ray crystallography to have the unique structure **10** *(Scheme 4)*. It could be considered as the first representative of complexes of types **12** with X = CR$_2$[5]).

The complexation of the Ph ring leads to a high-field shift of the signal of H—C(2″) (at 3.85 ppm) in the ¹H-NMR spectrum and also of the C-atoms taking part in the complexation in the ¹³C-NMR spectrum[6]) (72.5 ppm for C(2″), 178.7 or 172.9 ppm for C(1′), 79.7 ppm for C(2′), and 109.0 or 113.1 ppm for C(1″)). The lack of signals for the Fe—CO groups in the ¹³C-NMR of **10** at r.t. might be attributed to the fluxional behaviour of these groups. At −45°, however, three signals appear (at 212.1, 210.4, and 202.9 ppm).
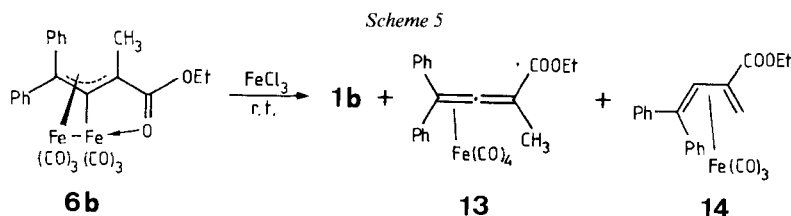
Scheme 5

The binuclear complex **6b**, on oxidation with FeCl$_3$, afforded the free allene **1b** and a mixture of two yellow, mononuclear complexes which was not amenable to chromatographic separation *(Scheme 5)*[7]). The composition LFe(CO)$_4$ and LFe(CO)$_3$, was proposed for these complexes on the basis of IR and MS. For the main complex, structure **14** is evidenced by the IR spectrum (strong absorptions at 2050, 1980, and 1695 cm⁻¹) and the ¹H-NMR spectrum, which showed the characteristic signals for olefinic protons in a Fe(CO)$_3$(diene) complex at 1.3, 1.6, and 4.5 ppm, respectively *(cf. Footnote 2*; [3] [13] [16–19]). The less intense IR absorptions at 2085, 2015, and 1935 cm⁻¹ *(cf.* [14]) as well as the CH$_3$ *singlet* in the ¹H-NMR (2.0 ppm) can be ascribed to **13**.

The mononuclear 1,3-butadiene complex **8**, on heating at 100°, gave the free ligand **15** *(Scheme 6)*. Thus, the sequence **7→8→15** represents an alternative method for the isomerization of allenic lactones to 2-vinylbutenolids (see [1]).

The loss of aromaticity arising from the complexation of the C(1″)=C(2″) bond of **10**, as seen from ¹³C-NMR spectral data, led us to attempt to trap with ethylenetetracarbonitrile (TCNE) the remaining 'diene' system of the complexed Ph ring. At room temperature, however, the expected *Diels-Alder* adduct was not formed, but the allene **7** was isolated[8]).

---

[5])   Fe(CO)$_3$ complexes of type **12** with X = O and NR have been prepared previously. However, the equally imaginable ones with X = CR$_2$ have not (see [14]). Recently, the formation of Co(cyclopentadienyl) complexes of vinylallenes similar to **12** have been reported [15].

[6])   For a detailed discussion of ¹³C-NMR data of Fe(CO)$_3$(1,3-diene) complexes, see [16].

[7])   On irradiation (N$_2$, Hg high-pressure lamp, *Vycor*), **6a,b** gave mainly **1a,b**, respectively.

[8])   The complex **10** gave, on irradiation in the presence of excess Fe(CO)$_5$ (N$_2$, Hg high-pressure lamp, quartz, 1 h), a mixture of **8** and **9**, accompanied by two other complexes. Under the same conditions, in the absence of Fe(CO)$_5$, however, **10** afforded the free allene **7** as the main product; in this manner it was shown that **10** is not a precursor of **8** and **9**.

Scheme 6

8   **15**

10   **7**
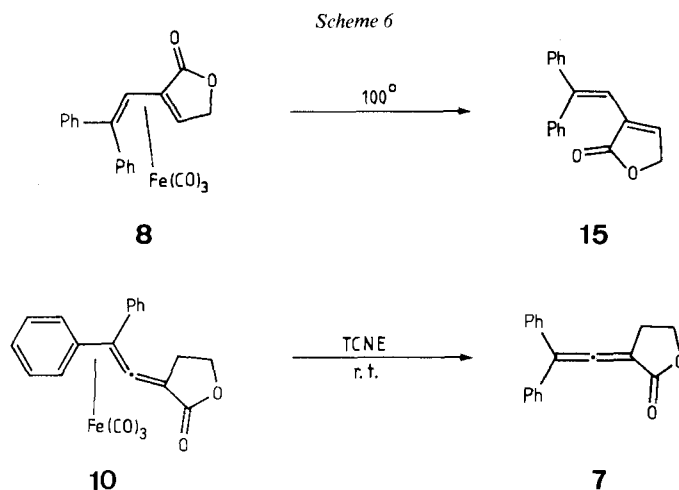
3. Crystal Structure Determination of the Carbonyliron Complexes 6a, 8, 9, and 10. –

Crystals of **6a**, **8**, **9**, and **10**, obtained from hexane/Et$_2$O, were used for X-ray structure determination[9]). The intensities were collected on a *Nicolet-R3* diffractometer in the ω-scan mode using MoK_α radiation, and the usual corrections except for absorption were applied. The structures were solved by *Patterson* methods and refined by blocked cascade refinements (on *F*) with *ca*. 100 variables per block using the program system SHELXTL 5.1 [20]. The H-atoms were located in difference *Fourier* maps after anisotropic refinement of the other atoms and were refined with individual isotropic temperature factors. No attempt was made to determine the absolute structure in the crystal selected for the diffraction analysis of **10**.

Crystallographic data are given in the *Table*. Molecular drawings of **6a**, **8**, **9**, and **10** (arbitrary radii for the H-atoms, 50% probability ellipsoids for the others) are presented in *Figs. 1–4*, and schematic diagrams with atom labels and bond lengths are given in *Fig. 5*. Complexes **6a** and **9** have two, **8** and **10** one Fe-atom. Each Fe-atom obeys to the 18-electrons rule and is bound to three CO ligands.
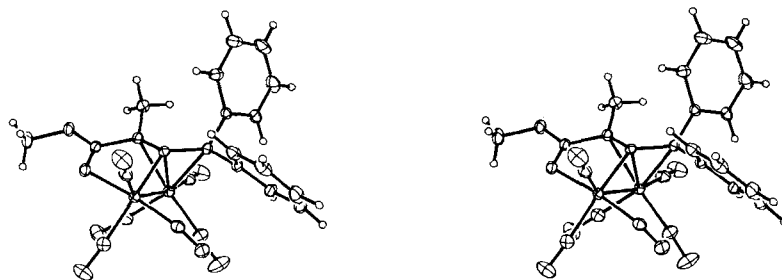
Fig. 1. *Crystal structure of hexacarbonyldiiron complex* **6a**

Table. *Crystallographic Data of Carbonyliron Complexes* **6a**, **8**, **9**, *and* **10**

	6a	8	9	10
Crystallized from	hexane/Et$_2$O	hexane/Et$_2$O	hexane/Et$_2$O	hexane/Et$_2$O
Colour	red	yellow	red	red
Crystal temp. (*ca.*) [K]	130	130	130	130
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P2_12_12_1$
Atoms in the asymmetric unit	C$_{24}$H$_{16}$Fe$_2$O$_8$	2× (C$_{21}$H$_{14}$FeO$_5$)	C$_{24}$H$_{14}$Fe$_2$O$_8$	C$_{21}$H$_{14}$FeO$_5$
Cell parameters[a])				
a [Å]	8.974(1)	9.444(1)	9.588(1)	9.663(2)
b [Å]	10.969(2)	9.885(1)	10.518(1)	9.733(2)
c [Å]	11.845(2)	38.993(5)	11.629(1)	18.751(4)
α [°]	77.28(1)	90	79.56(1)	90
β [°]	88.17(2)	100.52(3)	74.33(1)	90
γ [°]	82.23(1)	90	87.86(1)	90
V [Å^3]	1126.9	3579.0	1110.4	1763.6
2θ (max)	67°	55°	60°	55°
Symmetry independent reflections	8831	8237	6470	2324
Reflections used in the refinement ($F > \sigma(F)$)	7804	7361	5966	2255
Variables	371	599	363	300
R	0.053	0.055	0.038	0.052
R_w	0.041	0.057	0.043	0.064
Rec. weighting scheme[b]) $1/w$	$\dfrac{\sigma^2(F) + 0.0001F^2}{1 - e^{-4s^2}}$	$\sigma^2(F) + 0.0008F^2$	$\sigma^2(F) + 0.0004F^2$	$\sigma^2(F) + 0.001F^2$
$\sigma(d_{(C-C)})$ [Å]	0.002–0.004	0.004–0.005	0.002–0.004	0.006–0.007

[a]) The cell dimensions were obtained from 72, 56, 52, and 7 accurately centered reflections with $35° < |2\theta| \leqslant 43°$, $31° < |2\theta| < 35°$, $38° < |2\theta| < 45°$, and $38° < 2\theta < 43°$, respectively.

[b]) $s = (\sin\theta)/\lambda$.
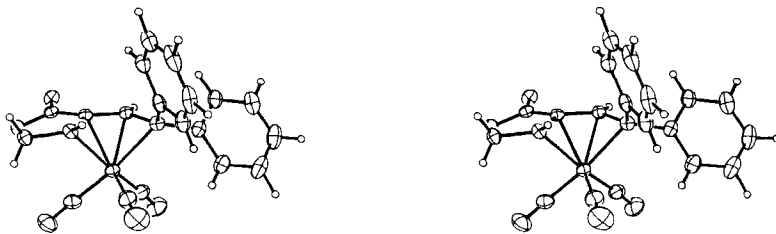
Fig. 2. *Crystal structure of tricarbonyliron complex* **8**

The asymmetric unit in the crystals of **8** contains two molecules with only minor differences. The largest ones concern the bonds Fe—C(3) with 0.022 Å, C(7)—C(8) with 0.019 Å, and Fe—C(19) with 0.015 Å, while the other differences range from 0 to 0.010 Å. In most of those bond angles which exhibit the largest differences (up to 3.8°), C(19) is involved. The other differences are smaller than 2.2°, except for Fe—C(6)—C(13) and Fe—C(21)—O(21) which differ by 3.0 and 2.8°, respectively. In **8**, a rather planar s-*cis*-1,3-diene subsystem forms an η^4 complex with the Fe-atom. As usual in such complexes, the distances from the Fe-atom to both outer C-atoms of the diene moiety, C(3) and C(6), are longer than those to the other two, C(4) and C(5). Also, the length of the C(2)—C(5) bond is not larger than that of the C(2)—C(3) and the relatively long C(5)—C(6) bond. There is
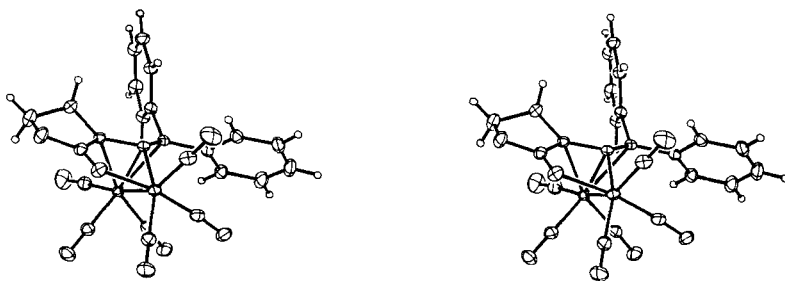
Fig. 3. *Crystal structure of hexacarbonyldiiron complex* **9**

a remarkable deviation of the *cis*-bonded Ph group from the diene plane, the torsion angle C(2)—C(5)—C(6)—C(13) measures −54.0 or −49.0°. It is, thus, comparable to that for *cis*-bonded Me groups in other 1,3-diene complexes [16]. The opposite torsion angle H(3)—C(3)—C(2)—C(5), 45 or 43°, is only a little smaller.

Compound **10** also contains an s-*cis*-1,3-diene subsystem. However, it differs from that of **8** by cumulated double bonds at C(5) in the free ligand. Another difference results from the fact that one double bond of the diene also belongs to an aromatic system. Therefore, the Fe—C(5) bond is shorter than usual in Fe(diene) complexes which probably results from a higher s character of the orbital at C(5) involved. Accordingly, the angle C(2)—C(5)—C(6) amounts to 134.5° as compared to the expected 180° in the free ligand. The sum of the bond angles at C(5) is 358.4°, the difference of the torsion angles C(2)—C(5)—C(6)—C(7), (137.2°), and Fe—C(5)—C(6)—C(7), (−54.3°), is 191.5°, thus, indicating a roughly planar arrangement of C(5) and its neighbour atoms. In a completely planar arrangement, these values are 360 and 180°, respectively. The other three Fe—C bonds are longer than usual. The bonds C(5)—C(6) and C(6)—C(7) are also somewhat longer. The bond lengths in the Ph ring involved in the complexation indicate that both atoms bound to the Fe-atom, C(7) and C(8), are no longer completely integrated in the aromatic π system (*cf.* NMR spectra). The bonds C(9)—C(10) and C(11)—C(12) are significantly shortened, the others somewhat elongated; C(2)—C(5) has the usual length for isolated double bonds. In a free allene, the plane spanned by C(1), C(2), and C(3) should be perpendicular to that of C(7), C(6), and C(13). Here, the angle between the planes measures 50.5°. The *cis*-situated atom at the end of the diene subsystem deviates from plane C(6), C(7), C(8) to the side opposed to the Fe-atom. The torsion angle is −36°.
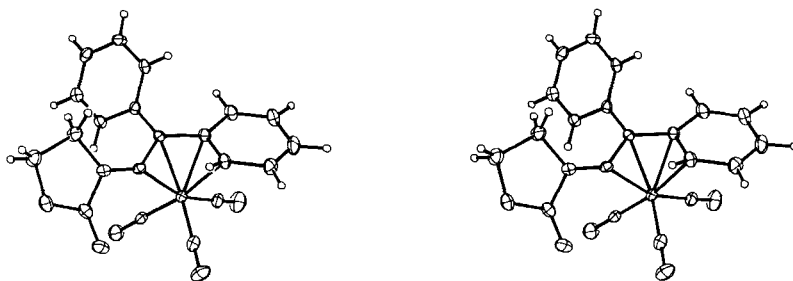
Fig. 4. *Crystal structure of tricarbonyliron complex* **10**

8
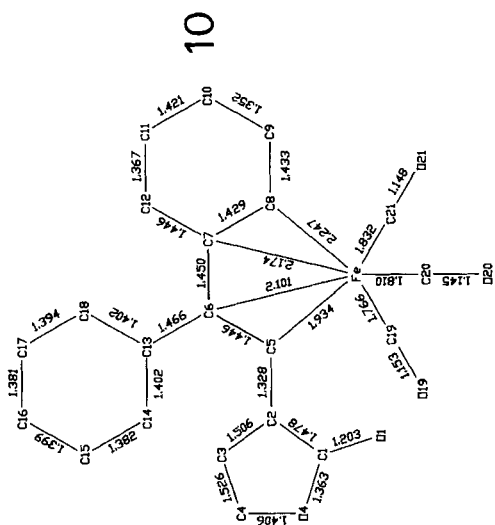
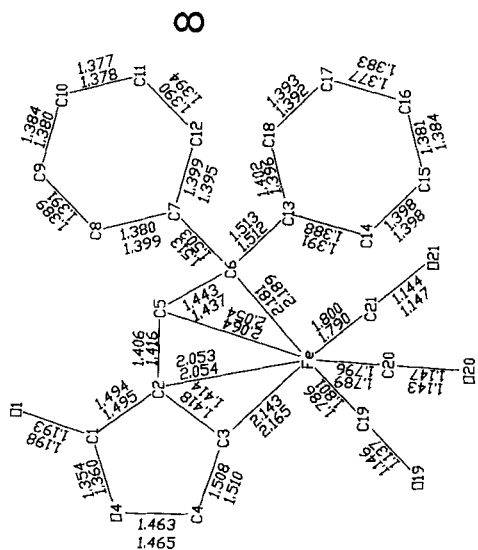10

6a

9
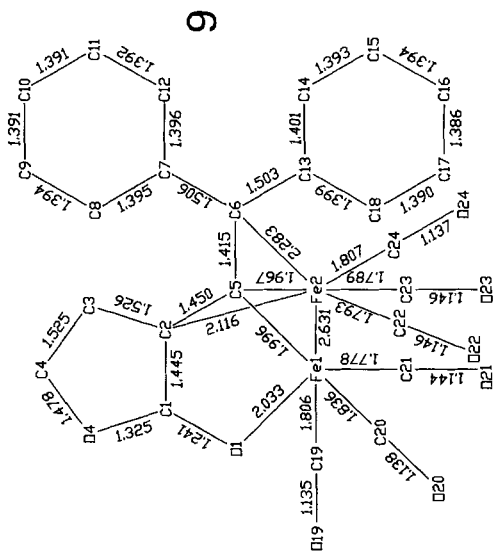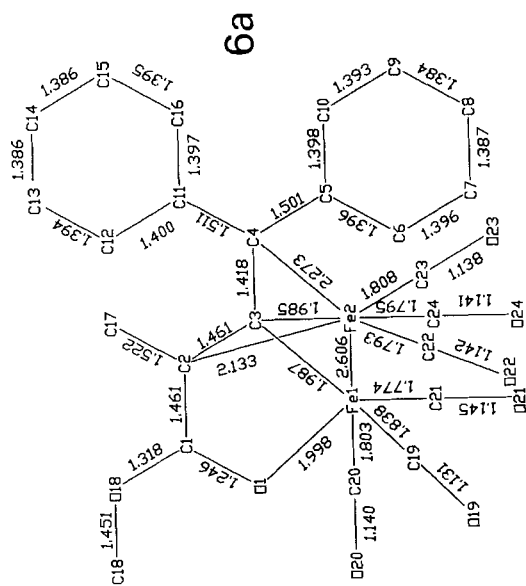
Both binuclear complexes, **6a** and **9**, only differ by the butanolide ring of **9** which is cleaved in **6a** by a formal hydrogenolysis. Therefore, comparable bond lengths are very similar. The largest difference shows the Fe(1)–O(1) bond which, in **9**, is 0.035 Å longer than in **6a**, and in the Fe(1)–Fe(2) bond which, in **9**, is 0.025 Å longer. This may be declared by the butanolide ring in **9** pulling O(1) away from Fe(1), and that Fe(1) partially follows this motion. The differences in the C(1)–C(2) and in the Fe(2)–C(2) bonds are also relatively large, 0.016 and 0.017 Å, respectively, while those of the other bonds range from 0.000 to 0.010 Å. The Fe–C distances to the CO ligands range from 1.774 to 1.838 Å, but the differences between equivalent distances in both structures are remarkably low with a maximum of 0.006 Å.

In the free ligand, atoms C(2), C(3), C(4) in **6a**, and C(2), C(5), C(6) in **9** build up an allene subsystem. In the complex, they form an angle of 119.0 and 118.2°, respectively. In a projection perpendicular to the plane C(2), C(3), C(4) in **6a**, and C(2), C(5), C(6) in **9**, Fe(2) lies on the line connecting C(2) and C(4), or C(2) and C(6). Its distance to the plane is 1.818 and 1.820 Å, respectively. Fe(1) is not coplanar to these C-atoms but the middle atom, C(3) or C(5) is only 0.256 or 0.255 Å, respectively, apart from the plane set up by its neighbour atoms Fe(1), C(2), and C(4) or C(6). This deviation from planarity may be declared by the bonding of all four atoms to Fe(2). Fe(1) also binds to the carbonyl O-atom (O(1)) of the butanolide ring, while the distances to C(1) and C(2) are longer than 2.65 Å. The five-membered ring Fe(1), O(1), C(1), C(2), and C(3) or C(5) takes on the envelope conformation, in which C(3) or C(5) lies outside the plane. The butanolide ring of **9** also forms an envelope, here with C(3) outside the plane. The angle between the planes C(1), C(2), and C(17) or C(3), and C(4), C(5), C(11) or C(6), C(7), C(13), for which one may assume an angle of 90° in the free ligand, is only 25.2 or 21.7°. The 'cis' torsion angles set up by the former 'allene' atoms C(2), C(3), and C(4) in **6a**, or C(2), C(5), and C(6) in **9**, and their next neighbour atoms range from 30.1 to 38.8°, while the 'trans' angles differ by less than 6° from 180°.

4. Conclusion. – The allenecarboxylates **1** and allenic lactone **7** afforded, on irradiation in the presence of Fe(CO)₅, binuclear carbonyliron complexes **6** and **9** and mononuclear complexes **8** and **10**, the latter representing a new type of allene-carbonyliron complexation. The presence of an α-CO group attached to the allene moiety appears, therefore, to disfavour the dimerization of the allene (no bis(η-allylene) complexes were observed). Of the newly isolated complexes, only **8** was found to liberate a 2-vinyl-butenolide, which makes this method for (1,3) H shifts less convenient in comparison with the method utilizing Co₂(CO)₈ (see [1]).

It should be pointed out that the main reaction pathway with the esters **1a,b** and lactone **7** is the one leading to the binuclear complexes **6a,b**, and **9**, respectively, and not the (1,3) H migration. This is a differentiation from the case of the formation of **5** from **3** *(Scheme 2)* and the results obtained with Co₂(CO)₈ [1].

Experimental Part

General. See [21].

Irradiation of **1a–c** *and* **7** *in the Presence of Fe(CO)$_5$.* A soln. of **1a–c** (4 mmol) in hexane (250 ml) or of **7** (3 mmol) in hexane/Et$_2$O 1:2 (250 ml) and Fe(CO)$_5$ (3 ml) was irradiated with a Hg high-pressure lamp (50 W, *Hanovia*) through quartz under N$_2$ at r.t. for 10 h in the case of **1a–c** and for 1 h in the case of **7**. The solvent was removed under reduced pressure at r.t., and the residue was chromatographed on a SiO$_2$ column with petroleum ether/Et$_2$O 15:1 in the case of **1a–c** and with petroleum ether/Et$_2$O 4:1 in the case of **7**. The red or yellow fractions were evaporated to dryness at r.t. under vacuum, and the residue was recrystallized from hexane/Et$_2$O to give pure **6a–c**, **8**, **9**, and **10**, respectively.

Hexacarbonyl(methyl 2-methyl-4,4-diphenyl-2,3-butadienoate)diiron (**6a**). Yield 56%. M.p. 161.0–164.0° (dec.). IR (nujol): 2070vs, 2020vs, 1995vs (sh), 1985vs, 1965vs, 1685w, 1575m. ^{1}H-NMR (250 MHz, CCl$_4$): 7.79 (*d*, *J* = 7.6, 1 arom. H); 7.49 (*d*, *J* = 7.6, 1 arom. H); 7.39 (*d*, *J* = 7.2, 2 arom. H); 7.3–6.95 (*m*, 6 arom. H); 3.79 (*s*, CH$_3$OCO); 0.72 (*s*, CH$_3$–C(2)). ^{13}C-NMR (50.4 MHz, CDCl$_3$): 212.9, 210.8, 207.4, 207.0, 193.4, 191.0 (6*s*, Fe–CO, C(1)); 151.2, 149.0 (2*s*, 2 arom. C); 131.0, 129.7, 128.3, 128.0, 127.8, 126.6, 126.3 (7*d*, arom. C); 123.6 (*s*, C(3)); 77.2 (*s*, C(4)); 68.3 (*s*, C(2)); 54.6 (*q*, CH$_3$O); 21.6 (*q*, CH$_3$–C(2)). MS (70 eV): 545 (2, $M^+ + 1$), 517 (1, $[M^{+\cdot} + 1] - $ CO), 489 (3, $[M^+ + 1] - 2$ CO), 488 (2), 461 (1, $[M^+ + 1] - 3$ CO), 433 (3, $[M^+ + 1] - 4$ CO), 432 (2), 405 (3, $[M^{+\cdot} + 1] - 5$ CO), 349 (10), 265 (100, $[M^{+\cdot} + 1] - $ Fe$_2$(CO)$_6$), 205 (20, Ph$_2$C$_4$H$_3^+$).

Hexacarbonyl(ethyl 2-methyl-4,4-diphenyl-2,3-butadienoate)diiron (**6b**). Yield 50%. M.p. 155.0–160.0° (dec.). IR (CsI): 2066vs, 2018vs, 1994vs, 1988vs, 1969vs, 1960vs, 1618w, 1595w, 1577m. ^{1}H-NMR (250 MHz, C$_6$H$_6$): 8.04 (*d*, *J* = 7.6, 1 arom. H); 7.62 (*d*, *J* = 7.6, 1 arom. H); 7.31 (*d*, *J* = 7.0, 2 arom. H); 7.2–6.8 (*m*, 6 arom. H); 3.59 (*dq*, *J* = 10.5, 7.1, 1 H, CH$_3$CH$_2$O); 3.43 (*dq*, *J* = 10.5, 7.1, 1 H, CH$_3$CH$_2$O); 0.82 (*s*, CH$_3$–C(2)); 0.65 (*t*, *J* = 7.1, CH$_3$CH$_2$O). ^{13}C-NMR (50.4 MHz, CDCl$_3$): 210.8, 207.4, 207.1, 193.6, 190.7 (5*s*, Fe–CO, C(1)); 151.3, 149.1 (2*s*, 2 arom. C); 131.0, 129.6, 128.2, 127.9, 127.8, 126.5, 126.2 (7*d*, arom. C); 123.1 (*s*, C(3)); 76.4 (*s*, C(4)); 68.8 (*s*, C(2)); 64.3 (*t*, CH$_3$CH$_2$O); 21.7 (*q*, CH$_3$–C(2)); 14.2 (*q*, CH$_3$CH$_2$O). MS (70 eV): 559 (0.5, $M^+ + 1$), 503 (1, $[M^+ + 1] - 2$ CO), 502 (0.5), 447 (1, $[M^+ + 1] - 4$ CO), 446 (1), 419 (2, $[M^+ + 1] - 5$ CO), 363 (2), 279 (100, $[M^+ + 1] - $ Fe$_2$(CO)$_6$), 205 (44, Ph$_2$C$_4$H$_3^+$). Anal. calc. for C$_{25}$H$_{18}$Fe$_2$O$_8$ (557.97): C 53.80, H 3.25, Fe 20.01; found: C 53.92, H 3.91, Fe 20.03.

Hexacarbonyl(ethyl 2,4,4-triphenyl-2,3-butadienoate)diiron (**6c**). Yield 65%. M.p. 135–140° (dec., with partial melting at 90–100°). IR (nujol): 2065vs, 2020vs, 2000vs, 1985vs, 1955vs, 1685w, 1590w. ^{1}H-NMR (250 MHz, C$_6$H$_6$): 7.99 (br. *d*, *J* = 6.3, 2 arom. H); 7.34 (*d*, *J* = 7.6, 2 arom. H); 7.3–6.95 (*m*, 11 arom. H); 3.50 (*dq*, *J* = 11.0, 7.1, 1 H, CH$_3$CH$_2$O); 3.28 (*dq*, *J* = 11.0, 7.1, 1 H, CH$_3$CH$_2$O); 0.62 (*t*, *J* = 7.1, CH$_3$CH$_2$O). ^{13}C-NMR (200 MHz, CDCl$_3$): 216.8, 212.2 (br.), 205.7, 204.7, 189.7, 183.8 (6*s*, Fe–CO, C(1)); 146.8, 145.7, 142.0 (3*s*, 3 arom. C); 129.2, 128.4, 128.2, 128.0, 127.7, 125.3 (6*d*, arom. C); 119.7 (*s*, C(3)); 80.7 (*s*, C(4)); 77.2 (*s*, C(2)); 64.6 (*t*, CH$_3$CH$_2$O); 14.2 (*q*, CH$_3$CH$_2$O). MS (70 eV): 621 (0.5, $M^+ + 1$), 593 (0.3, $[M^+ + 1] - $ CO), 592 (0.3), 565 (0.5, $[M^+ + 1] - 2$ CO), 537 (0.2, $[M^+ + 1] - 3$ CO), 536 (0.2), 535 (0.3), 509 (0.3, $[M^{+\cdot} + 1] - 4$ CO), 481 (0.4, $[M^{+\cdot} + 1] - 5$ CO), 425 (0.6), 343 (58), 342 (30), 341 (100, $[M^+ + 1] - $ Fe$_2$(CO)$_6$), 269 (13), 267 (10).

Tricarbonyl[2-(2,2-diphenylvinyl)-2-buten-4-olide]iron (**8**). Yield 23%. M.p. 140.0–144.0° (dec.). IR (CHCl$_3$): 2060vs, 1995vs (br.), 1778s. ^{1}H-NMR (200 MHz, CDCl$_3$): 7.9–6.5 (*m* with *s* at 6.75, 10 arom. H, H–C(1′)); 4.60 (*dd*, *J* = 14.5, 3.0, H–C(4)); 4.09 (*d*, *J* = 14.5, H–C(4)); 2.25 (*d*-like, *J* ≈ 3, H–C(3)). ^{13}C-NMR (200 MHz, CDCl$_3$, 40°)[10]: 208.8 (*s*, Fe–CO); 174.0 (*s*, C(1)); 145.4, 138.9 (2*s*, 2 arom. C); 132–126 (arom. C); 87.8, 84.1 (2*s*, C(2), C(2′)); 80.7 (*d*, C(1′)); 72.3 (*t*, C(4)); 66.2 (*d*, C(3)). MS (70 eV): 402 (0.5, $M^{+\cdot}$), 374 (1, $M^{+\cdot} - $ CO), 346 (8, $M^{+\cdot} - 2$ CO), 319 (23), 318 (100, $M^{+\cdot} - 3$ CO), 274 (7), 262 (50, $M^{+\cdot} - $ Fe(CO)$_3$), 261 (11), 260 (50), 234 (24), 233 (75), 218 (20), 217 (15), 215 (18), 205 (38), 204 (34), 203 (33), 202 (30). Molecular weight (osmom., C$_6$H$_6$): found 469.

Hexacarbonyl[2-(2,2-diphenylvinylidene)-4-butanolide]diiron (**9**). Yield 14%; decomposes above 160° without melting. IR (nujol): 2070vs, 2020vs, 2005vs, 1980vs, 1965vs, 1630m, 755s. ^{1}H-NMR (200 MHz, CDCl$_3$): 7.90, 7.63 (2*s*, 2 arom. H); 7.47 (br. *s*, 2 arom. H); 7.3–7.0 (*m*, 6 arom. H); 4.61 (*t*-like, *J* ≈ 8, H–C(4)); 4.36 (*q*-like, *J* ≈ 8, H–C(4)); 2.25 (*q*-like, *J* ≈ 12, H–C(3)); 0.47 (*dd*-like, *J* ≈ 12, 6, H–C(3)). ^{13}C-NMR (62.9 MHz, CDCl$_3$): 209.4, 207.1, 206.9, 195.7, 184.5 (5*s*, Fe–CO, C(1)); 148.9, 147.3 (2*s*, 2 arom. C); 130.8, 130.0, 128.3, 127.9, 127.1, 126.1 (6*d*, arom. C); 124.1 (*s*, C(1′)); 77.2 (*s*, C(2′)); 69.1 (*s*, C(2)); 60.7 (*t*, C(4)); 32.9 (*t*, C(3)). MS (70 eV): 542 (0.3, $M^{+\cdot}$), 514 (0.2, $M^{+\cdot} - $ CO), 486 (45, $M^{+\cdot} - 2$ CO), 458 (24, $M^{+\cdot} - 3$ CO), 431 (21), 430 (72, $M^{+\cdot} - 4$ CO), 403 (26), 402 (100, $M^{+\cdot} - 5$ CO or $M^{+\cdot} - $ Fe(CO)$_3$), 374 (47, $M^{+\cdot} - $ Fe(CO)$_4$), 346 (15), 330 (10), 318 (69), 274 (18), 264 (23), 262 (43, $M^{+\cdot} - $ Fe$_2$(CO)$_6$), 260 (42), 205 (23), 204 (24), 203 (22), 202 (30), 189 (24), 165 (20), 105 (43). Molecular weight (osmom., C$_6$H$_6$): found 560.

---

[10]   At 25°, the Fe(CO)$_3$ group appears as a broad signal.

Tricarbonyl[2-(2,2-diphenylvinylidene)-4-butanolide]iron (**10**). Yield 15%. M.p. 133.0–137.0° (dec.). IR (CHCl$_3$): 2063vs, 2000vs (br.), 1743s, 1678s. ^{1}H-NMR (400 MHz, CDCl$_3$): 7.64, 7.56, 7.47, 7.25 (4s, 9 arom. H); 4.19 (s, CH$_2$(4)); 3.85 (s, H–C(2″)); 2.59 (s, CH$_2$(3)). ^{13}C-NMR (200 MHz, CDCl$_3$, –45°)[10]): 212.1, 210.4, 202.9 (3s, Fe–CO); 178.7, 172.9 (2s, C(1), C(1′)); 136.0 (d, 1 arom. C); 133.7 (s, 1 arom. C); 130.9, 130.0, 128.9, 128.1, 127.1, 125.0 (6d, 8 arom. C); 113.1, 109.0 (2s, C(2), 1 arom. C); 79.7 (s, C(2′)); 72.5 (d, 1 arom. C); 64.9 (t, C(4)); 29.0 (t, C(3)). CI-MS: 403 (15, M^+ + 1), 347 (15), 336 (50), 263 (100, C$_{18}$H$_{14}$O$_2^+$ + 1). Molecular weight (osmom., C$_6$H$_6$): found 414. Anal. calc. for C$_{21}$H$_{14}$FeO$_5$ (402.14): C 62.72, H 3.51, Fe 13.89; found: C 62.50, H 3.70, Fe 14.37.

Tetracarbonyl[2-(2,2-diphenylvinylidene)-4-butanolide]iron (**11**). Yield *ca.* 25%, crude yellow-orange crystals. IR (nujol): 2075vs, 2005vs, 1980vs, 1970vs, 1760vs. MS (70 eV): 430 (0.6, M^+), 402 (0.4, M^+ – CO), 374 (0.7, M^+ – 2 CO), 346 (0.4, M^+ – 3 CO), 319 (7), 318 (100, M^+ – 4 CO), 274 (6), 262 (21, M^+ – Fe(CO)$_4$), 260 (41), 233 (14), 205 (10), 204 (17), 203 (12), 202 (10), 165 (7). Anal. calc. for C$_{22}$H$_{14}$FeO$_6$ (430.20): C 61.42, H 3.28; found: C 61.06, H 3.26.

Oxidation of **6b** *with FeCl$_3$*. A soln. of 298 mg (0.53 mmol) **6b** and 400 mg (1.49 mmol) FeCl$_3$·6 H$_2$O in 20 ml MeOH was stirred at r.t. for 24 h. The solvent was removed under vacuum, H$_2$O was added, and the org. material was extracted with Et$_2$O (2 × 25 ml). The solvent was evaporated, and the residue was subjected to prep. TLC separation on 3 plates with petroleum ether/Et$_2$O 9:1. The yellow zone was eluted with CHCl$_3$ and the solvent removed under vacuum to give a yellow oil (142 mg). The latter was dissolved in petroleum ether/Et$_2$O (3:1, 0.5 ml) and was kept at –15°, to deposit 56 mg (38%) **1b**. The mother liquor was evaporated *in vacuo* to dryness to give an orange oil. IR (CHCl$_3$): 2085w, 2050s, 2015m, 1980vs, 1935m, 1695s. MS (70 eV): 446 (0.5), 418 (0.5), 390 (2), 362 (1), 332 (80), 262 (100), 260 (80), 205 (33), 204 (38), 203 (28), 202 (20), 184 (30).

Treatment of **10** *with Ethylenetetracarbonitrile (TCNE)*. A soln. of 50 mg (0.25 mmol) **10** and 16 mg (0.25 mmol) TCNE in 1 ml of dry benzene was kept at r.t. for 28 h. The mixture was filtered through a short column with silica gel using petroleum ether/Et$_2$O 2:1. The filtrate was evaporated to dryness and the residue recrystallized from hexane to give 19.5 mg (61%) **7** identical with an authentic sample (m.p., TLC, IR) [1].

Heating of **10**. A soln. of 70 mg (0.35 mmol) **10** in 2 ml of dry benzene was heated in a sealed tube at 100° for 7 h. The mixture was subjected to prep. TLC (3 plates) with petroleum ether/Et$_2$O/EtOAc/2-butanone 70:15:8:7. The colourless but UV-active zone was eluted with CHCl$_3$, the solvent removed under vacuum, and the residue recrystallized from hexane to afford 26 mg (62%) **13** identical with an authentic sample (m.p., TLC, IR) [1].

REFERENCES

[1] L. S. Trifonov, A. S. Orahovats, H. Heimgartner, *Helv. Chim. Acta* **1987**, *70*, 1070.
[2] R. Ben-Shoshan, R. Pettit, *J. Am. Chem. Soc.* **1967**, *89*, 2231.
[3] D. H. Gibson, R. L. Vonnahme, J. E. McKiernan, *J. Chem. Soc., Chem. Commun.* **1971**, 720.
[4] D. Martina, F. Brion, A. De Cian, *Tetrahedron Lett.* **1982**, *23*, 857.
[5] F. Brion, D. Martina, *Tetrahedron Lett.* **1982**, *23*, 861.
[6] R. Ben-Shoshan, R. Pettit, *J. Chem. Soc., Chem. Commun.* **1968**, 247.
[7] R. E. Davis, *J. Chem. Soc., Chem. Commun.* **1968**, 248.
[8] T. L. Jacobs, in 'The Chemistry of Allenes', Ed. S. R. Landor, Academic Press, London, 1982, Vol. 2, p. 316.
[9] J. A. S. Howell, J. Lewis, T. W. Matheson, D. R. Russell, *J. Organomet. Chem.* **1975**, *99*, C55.
[10] S. Otsuka, A. Nakamura, K. Tani, *J. Chem. Soc. (A)* **1968**, 2248.
[11] A. Nakamura, *Bull. Chem. Soc. Jpn.* **1966**, *39*, 543.
[12] R. B. King, C. A. Harmon, *J. Organomet. Chem.* **1975**, *86*, 239.
[13] R. Victor, R. Ben-Shoshan, S. Sarel, *J. Chem. Soc., Chem. Commun.* **1971**, 1241.
[14] A. J. Deeming, in 'Comprehensive Organometallic Chemistry', Eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon Press, Oxford, 1982, Vol. 4, p. 457.
[15] T. C. C. Gartenmann, 'Gemischte Cycloadditionen zu Cyclopentadienoncobaltkomplexen und Reaktionen der Produkte', Dissertation, Universität Zürich, 1987.
[16] C. M. Adams, G. Cerioni, A. Hafner, H. Kalchhauser, W. von Philipsborn, R. Prewo, A. Schwenk, submitted to *Helv. Chim. Acta*.
[17] K. K. Joshi, *J. Chem. Soc. (A)* **1966**, 594.
[18] A. Hafner, 'Synthese, Reaktivität und NMR-Spektroskopische Untersuchungen von Eisencarbonylkomplexen acyclischer π-Kohlenwasserstoffe', Dissertation, Universität Zürich, 1986.
[19] C. M. Adams, 'Contributions to (Diene)Fe(CO)$_3$ Chemistry', Dissertation, Universität Zürich, 1987.
[20] G. M. Sheldrick, SHELXTL, an integrated system for solving, refining and displaying crystal structures from diffraction data, version 5.1, 1986.
[21] L. S. Trifonov, A. S. Orahovats, *Helv. Chim. Acta* **1986**, *69*, 1585; ibid. **1987**, *70*, 262.