# 157. Carbonyliron Complexes of Allenic Acids, Esters, Amides, and Imides

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On irradiation in the presence of $Fe(CO)_5$, the allenic amides and imides showed a similar course of complexation to that of esters and lactones, respectively, *e.g.* the amides of type **10** led to diiron complexes of type **11** (*Scheme 3*), whereas the imide **12** yielded a mixture of a dinuclear and two mononuclear complexes (**13**–**15**, *Scheme 4*). The racemic ester **6** also gave mononuclear (**7a**, **7b**, and **9**) and dinuclear complexes (**8a** and **8b**; *Scheme 2*). In case of the allenic acid **4**, only complexation of type **5** was observed (*Scheme 1*).

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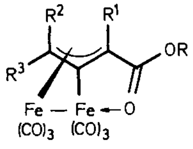
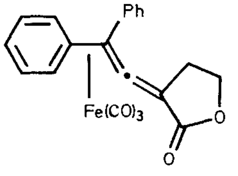
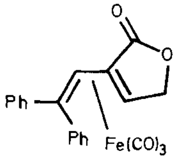
**1. Introduction.** – The complexation of allenecarboxylates and allenic lactones with ironcarbonyls under thermal and photochemical conditions was recently investigated [1] [2]. The main ester complex was shown to be the diiron complex **1**, while the allenic lactone gave, besides a diiron complex of type **1**, a monoiron complex **2**, with participation of the aromatic ring at C(4), and also a complex **3**, derived from the isomerized starting lactone [2]. Allenecarboxylates and allenic lactones have also been found to undergo a thermal Co-induced H migration to 1,3-dienes [3].



**1**



**2**

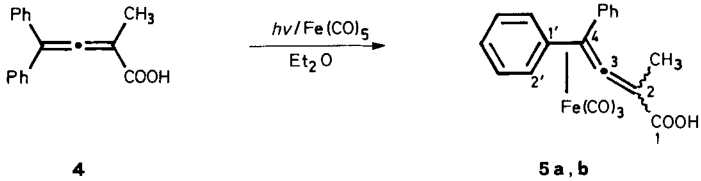


**3**

We now report on the photochemical complexation, in the presence of $Fe(CO)_5$, of some allenecarboxylic-acid derivatives, *i.e.* acids, esters with two different substituents at C(4), amides, and imides.

**2. Results and Discussion.** – The allenecarboxylic acid **4** gave on irradiation in the presence of an excess of $Fe(CO)_5$ two red complexes in trace amounts. The strong absorption at *ca.* 2050 $cm^{-1}$ and at *ca.* 1990 $cm^{-1}$ in the IR spectra of these compounds is a strong evidence for complexes of type $[Fe(CO)_3L]$ [2] [4]. The presence of a broad 1-H *singlet* at 3.90 ppm and at 3.62 ppm, besides the normal Me *singlet* in the $^1H$-NMR

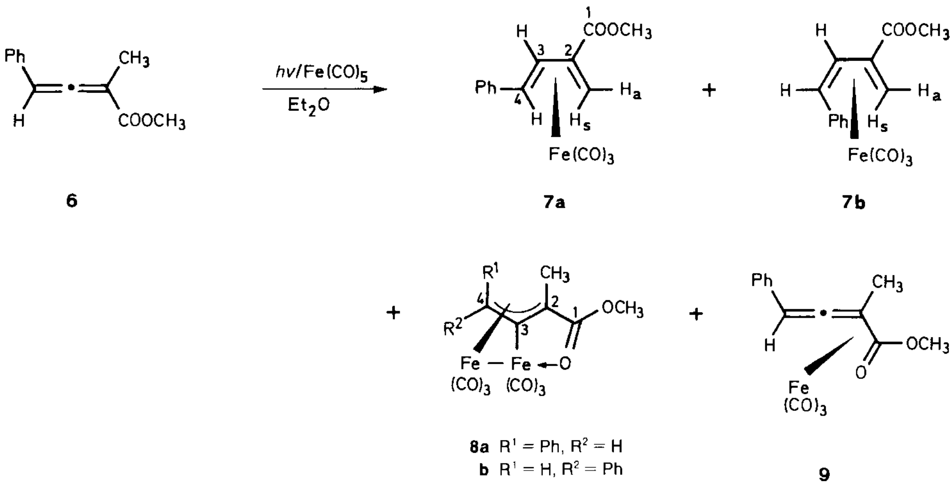
Scheme 1



spectra, suggests complexation of one of the Ph rings. Accordingly, structures **5a** and **5b**, differing in the geometry at C(2), are suggested for these complexes (*Scheme 1*).

Under similar reaction conditions, the racemic ester **6**[1]) afforded a mixture of complexes which, after chromatography, gave a red and a yellow fraction. Recrystallization of the latter led to a pure yellow complex to which structure **7a** (*Scheme 2*) was ascribed on the basis of the IR, mass, and mainly of the $^1$H-NMR spectrum (see *Exper. Part*). The

Scheme 2



(*E*)-configuration of the complexed C(3)=C(4) bond was assigned making use of the coupling constant $^3J(H,H) = 10.0$ Hz, which is of diagnostic value for (*E*)-olefinic protons in [Fe(buta-1,3-diene)$(CO)_3$] complexes [6]. The $^1$H-NMR analysis of the mother liquor of **7a** revealed the presence of the (*Z*)-isomer **7b**, possessing the characteristic $^3J(H,H) = 7.5$ Hz [6][2]).

The $^1$H-NMR analysis of the red crude mixture showed the presence of two isomeric diiron complexes **8a** and **8b**, and of one monoiron complex **9** in a ratio of 2:2:1. The structures of **8a** and **8b**, obtained in *ca.* 90% purity after recrystallization from hexane/$Et_2O$, were assumed on the basis of the shielding effect of the Ph ring on the Me group at

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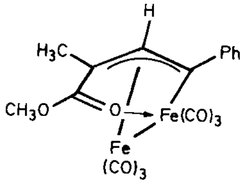
[1]) Prepared *via* $CH_2N_2$ methylation of the corresponding acid [5].

[2]) A similar mononuclear complex has been assumed in the case of the 4,4-diphenyl-allenecarboxylate [2].



**8c**

C(2) (absorbing at 1.09 and at 1.35 ppm, respectively) and on the deshielding effect of the Fe atom at C(3) on *H*–C(4) (absorbing at 6.43 and 6.33 ppm, respectively) in the $^1$H-NMR spectra and on the absence of the ester C=O absorption in the IR spectra of the two isomers [1] [2].

Repeated recrystallization of **8a** and **8b** from hexane/$Et_2O$ led, in low yield, to dark-red crystals suitable for an X-ray analysis. The molecular structure of the crystals of both batches, *i.e.* the diiron complex **8c**, has been shown to be identical. Obviously, an

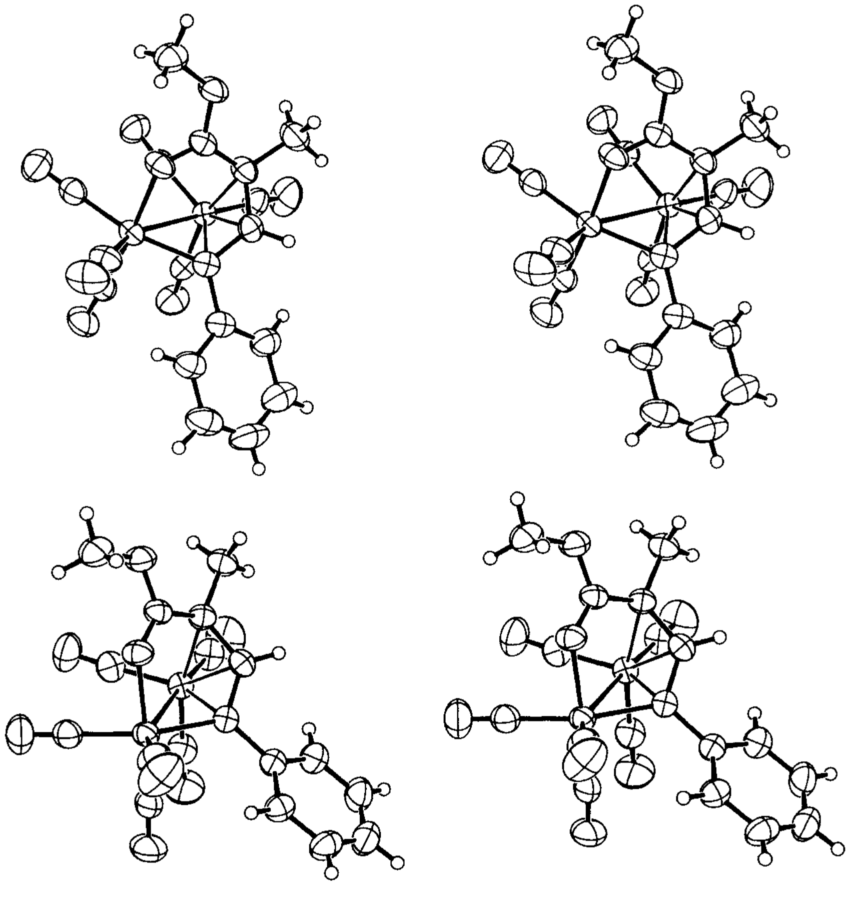
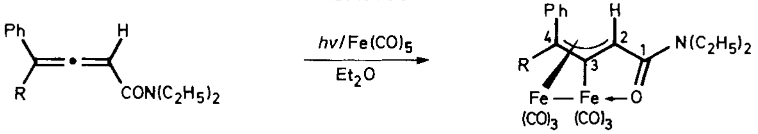


Fig. *Stereoscopic view of the two unique molecules in the crystal structure of* **8c** isomerization of **8a** and **8b** *via* 1,2-shift of *H*–C(4) to C(3) occurred during the recrystallization. Stereoscopic views of the two unique molecules in the asymmetric unit of the crystals of **8c** are shown in the *Figure*. Several dinuclear ironcarbonyl complexes of similar structure are already known (*cf.* [7]).

The structure **9** of the monoiron complex, which was not isolated in pure form, is supported by the $^1$H-NMR spectrum. Thus, the complexation of the C(2)=C(3) bond is evidenced by the small shift of the *H*–C(4) signal upon complexation ($\Delta\delta$ = 0.53 ppm), since complexation of the C(3)=C(4) bond should result in a $\Delta\delta$ of *ca.* 3 ppm [8] [9]. This structure is also corroborated by the absence of the ester C=O absorption in the IR spectrum.

*Scheme 3*



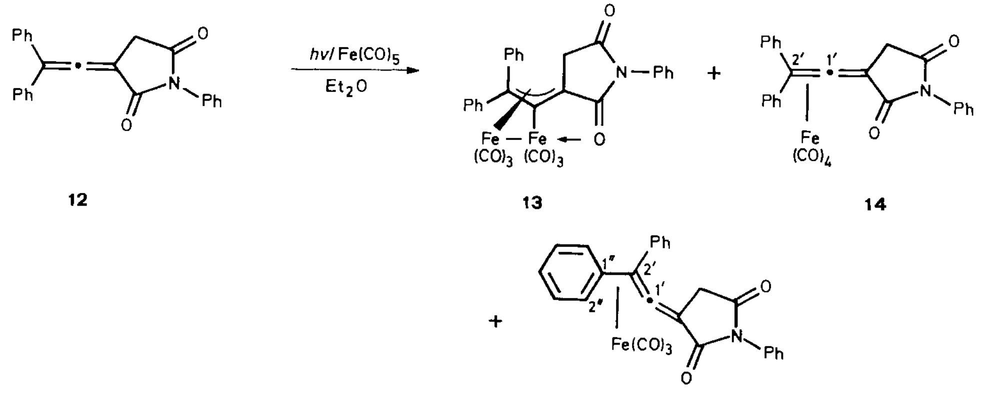
**10 a** R = $CH_3$
**b** R = Ph

**11 a** R = $CH_3$
**b** R = Ph

The allenic amides **10a** and **10b** gave, on similar treatment, the red diiron complexes **11a** and **11b** (*Scheme 3*), respectively, as sole products in good yields, with spectral data analogous to those of the corresponding ester complexes. Interestingly, **10a** afforded only one of the two feasible isomeric complexes, to which structure **11a** with (*Z*)-oriented Me–C(4) and Fe–C(3) was ascribed, on the basis of the high-field shift of the *H*–C(2) signal in the $^1$H-NMR spectrum (at 2.89 ppm) which is due to the '*syn*'-oriented Ph ring. Similar chemical shifts have been observed in allenic ketone complexes in which both isomers were obtained [10].

The allenic *N*-phenyl imide **12** gave a resolvable mixture of the diiron complex **13**, and the monoiron complexes **14** and **15** (*Scheme 4*). The spectral data of **13** were analogous to

*Scheme 4*



**12**

**13**

**14**

**15**

those of the other presently discussed diiron complexes (*vide supra*). The [Fe(CO)$_4$L]-type of complexation in **14** was evidenced by the mass and the IR spectra (strong absorptions at 2105, 2050, 2030, and 2015 cm$^{-1}$), while the complexation of the C(1')=C(2') bond was supported by the presence of only one 2-H *singlet* in the $^1$H-NMR spectrum for C*H*$_2$(4)[3]. The structure of the orange complex **15** was assigned on the basis of the very close similarity of the spectral data to those of the corresponding lactone analogue **2** (see *Exper. Part* and [2]).

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## Experimental Part

*General.* See [11]. Prep. TLC on silica gel (*Kieselgel 60 PF$_{254}$; Merck*) on 20 × 20 cm plates (10 g silica gel per plate). Column chromatography (CC) on silica gel (*Kieselgel 60*, 0.040–0.063 mm; *Merck*). M.p.: on *Kofler* apparatus; not corrected. UV spectra: on a *Specord M 40* (*Carl Zeiss*, Jena) spectrophotometer. IR spectra: on a *UR-20* (*Carl Zeiss*, Jena) spectrometer. $^1$H- and $^{13}$C-NMR spectra: *Bruker WM-250* spectrometer at 250 MHz and 62.9 MHz, respectively; chemical shifts ($\delta$) in ppm (internal standard TMS = 0 ppm). MS: *JEOL JMS D-300* instrument.

**1. Syntheses of Starting Materials.** Allenic acid **4** was obtained according to [12], methyl ester **6** *via* CH$_2$N$_2$ methylation of the corresponding acid [5]. Amides **10a** and **10b** were prepared following the procedure given in [13], starting with 2-phenylpropionyl chloride (hydratropic-acid chloride) or diphenylacetyl chloride and [(*N,N*-diethylcarbamoyl)methylidene]triphenylphosphorane [14]. The crude reaction mixture in the first case was subjected to prep. TLC separation using petroleum ether/Et$_2$O 2:1 to afford pure **10a** (73%) as a colorless oil; in the latter case the reaction mixture was filtered through a short silica gel column using the same eluent to give pure **10b** (61%) as colorless prisms (crystallisation from hexane/Et$_2$O). Allenic imide **12** was obtained by the same procedure starting from triphenyl(*N*-phenyl-2,5-dioxopyrrolidin-3-ylidene)phosphorane [15]. The mixture was chromatographed on a silica-gel column with petroleum ether/Et$_2$O 3:2 and the crude product was crystallized from hexane/(i-Pr)$_2$O to afford pure **12** (36%) as colorless crystals.

**2. Irradiation in the Presence of Pentacarbonyliron (Fe(CO)$_5$).** *General Procedure.* A soln. of 1 mmol of the allene derivative and 3 ml of Fe(CO)$_5$ in Et$_2$O/hexane 2:1 (for **4**), in hexane (for **6**), in hexane/Et$_2$O 2:1 (for **10a** and **10b**) or in Et$_2$O/hexane 4:1 (for **12**, 250 ml in each case) was irradiated with an 80-W *Hanovia* high-pressure Hg lamp through *Solidex* filter at r.t. under Ar for 1 h (for **4**, **10a**, **10b**, and **12**) or 4 h (for **6**). The solvent was removed under vacuum and the residue subjected to CC on silica gel using petroleum ether/Et$_2$O/acetone 3:3:1 (for **4**), petroleum ether/Et$_2$O 10:1 (for **6**), petroleum ether/Et$_2$O 5:1 (for **10a** and **10b**), or to prep. TLC separation with petroleum ether/AcOEt/actone 10:1:1 (for **12**).

A partial separation of the red complexes derived from the ester **6** was achieved, using petroleum ether/Et$_2$O 100:1. The eluate from the red zone was collected into two equal fractions: the first one was shown, by $^1$H-NMR, to contain **8a**, **8b**, and **9** in a ratio of 10:2:1, while the second one was shown to contain **8b** and **9** in a ratio of 2:1. Recrystallization of the crude products (*vide infra*) afforded **8a** and **8b** in *ca.* 90% purity.

**3. Reaction with 2-Methyl-4,4-diphenylbuta-2,3-dienoic Acid (4).** – *Tricarbonyl(2-methyl-4,4-diphenylbuta-2,3-dienoic acid)iron* (**5a, b**). *Data of* **5a**: Yield 6%. Red crystals (Et$_2$O/hexane). The compound does not melt up to 350°. IR (CHCl$_3$): 3515*w*, 3200–2750*m* (br.), 2060v*s*, 1990v*s* (br.), 1675*s* (sh), 1650*s*, 1605*w*. $^1$H-NMR (250 MHz, CDCl$_3$): 7.85–7.75 (*m*, 1 arom. H); 7.62 (*d*, *J* = 7.0, 2 arom. H); 7.5–7.2 (*m*, 6 arom. H); 3.90 (br. *d*, *J* = 4.5, H–C(2')); 1.65 (*s*, CH$_3$). MS: 250 (12, [$M$ – Fe(CO)$_3$]$^+$), 221 (25), 207 (29), 178 (56), 105 (100), 77 (96).

*Data of* **5b**: Yield 6%. Red crystals (Et$_2$O). Decomposes at *ca.* 150° without melting. IR (CHCl$_3$): 3515*w*, 3200–2750*m* (br.), 2050v*s*, 1985v*s* (br.), 1685*s* (sh), 1665*s*, 1605*w*. $^1$H-NMR (250 MHz, CDCl$_3$): 7.73 (*d*, *J* = 9.8,

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[3] The complexation of the C(3)=C(1') bond would result in the presence of two signals for the C*H*$_2$(4) protons, one '*syn*'- and one '*anti*'-oriented with respect to the Fe-atom.

1 arom. H); 7.59 (*d, J* = 6.8, 2 arom. H); 7.45–7.1 (*m*, 6 arom. H); 3.61 (br. *d, J* ≈ 3, H–C(2′)); 2.23 (*s*, $CH_3$). MS: 392 (0.3), 364 (0.5). 362 (0.3, $[M - CO]^+$), 336 (0.5), 334 (0.4, $[M - 2\,CO]^+$), 308 (1), 306 (0.4, $[M - 3\,CO]^+$), 278 (4), 250 (62, $[M - Fe(CO)_3]^+$), 145 (100), 117 (40), 105 (62).

**4. Reaction with Methyl 2-Methyl-4-phenylbuta-2,3-dienoate (6).** – *Data of* **6**: Colorless oil. IR ($CHCl_3$): 3000*w*, 2950*w*, 1950*w*, 1715*s*, 1605*w*. $^1H$-NMR (250 MHz, $CDCl_3$): 7.35–7.2 (*m*, 5 arom. H); 6.46 (*q, J* = 3.0, H–C(4)); 3.73 (*s*, $CH_3O$); 2.01 (*d, J* = 3.0, $CH_3$). $^{13}C$-NMR (62.9 MHz, $CDCl_3$): 212.3 (*s*, C(3)); 167.3 (*s*, C(1)); 132.3 (*s*, arom. C); 128.7, 127.6, 127.3 (3*d*, arom. CH); 99.0 (*s*, C(2)); 97.2 (*d*, C(4)); 52.1 (*q*, $CH_3O$); 15.0 (*q*, $CH_3$). MS: 189 (15), 188 (100, $M^{+\cdot}$), 173 (20, $[M - CH_3]^+$), 157 (10, $[M - CH_3O]^+$), 145 (29), 129 (82, $[M - COOCH_3]^+$), 128 (71), 127 (30), 105 (20), 77 (21), 51 (18).

*Tricarbonyl[methyl (3*E*)-2-methylidene-4-phenylbut-3-enoate]iron* (**7a**). Yield 10%. Yellow needles (hexane). M.p. 99.0–103.0°. IR ($CHCl_3$): 2950*m*, 2925*w*, 2915*w*, 2055*vs*, 1985*vs* (br.), 1715*s*, 1595*w*. $^1H$-NMR (250 MHz, $CDCl_3$): 7.4–7.1 (*m*, 5 arom. H); 6.76 (br. *d, J* = 10.0, H–C(3)); 3.90 (*s*, $CH_3$); 2.51 (*dd, J* = 3.0, 1.2, $H_a$–C(1′)); 2.19 (*d, J* = 10.0, H–C(4)); 0.60 (*d, J* = 3.0, $H_s$–C(1′)). $^{13}C$-NMR (62.9 MHz, $CDCl_3$): 209.5 (*s*, Fe–CO); 170.7 (*s*, $COOCH_3$), 138.3 (*s*, arom. C); 128.8, 127.3, 126.4 (3*d*, arom. CH)); 86.5 (*d*, C(3)); 82.0 (*s*, C(2)); 64.2 (*d*, C(4)); 52.5 (*q*, $CH_3$); 38.5 (*t*, C(1′)). MS: 328 (4, $M^{+\cdot}$), 300 (38, $[M - CO]^+$), 272 (92, $[M - 2\,CO]^+$), 244 (100, $[M - 3\,CO]^+$), 216 (8), 184 (96), 128 (75).

*Tricarbonyl[methyl (3*Z*)-2-methylidene-4-phenylbut-3-enoate]iron* (**7b**). Yield *ca.* 10% (mixture with **7a**). $^1H$-NMR (250 MHz, $CDCl_3$; after subtracting the signals of **7a**): 7.4–6.9 (*m*, 5 arom. H); 6.22 (br. *d, J* = 7.5, H–C(3)); 4.24 (*d, J* = 7.5, H–C(4)); 3.89 (*s*, $CH_3$); 2.70 (*dd, J* = 2.6, 1.5, $H_a$–C(1′)); 0.88 (*d, J* = 2.6, $H_s$–C(1′)).

*Hexacarbonyl[methyl (*E*/*Z*)-2-methyl-4-phenylbuta-2,3-dienoate]diiron* (**8a, b**). *Data of* **8a**: Yield *ca.* 12% (containing *ca.* 10% of **8b**). Orange-red microcrystals (hexane/$Et_2O$). $^1H$-NMR (300 MHz, $CDCl_3$): 7.45–7.35, 7.35–7.15 (2*m*, 5 arom. H); 6.43 (*s*, H–C(4)); 3.75 (*s*, $CH_3O$); 1.09 (*s*, $CH_3$–C(2)). $^{13}C$-NMR (100.8 MHz, $CDCl_3$); 193.2, 189.5 (2*s*, Fe–CO, C(1)); 143.7 (*s*, arom. C); 130.2, 127.7, 126.6 (3*d*, 5 arom. CH); 128.0 (*s*, C(3)); 93.5 (*d*, C(4)); 73.4 (*s*, C(2)); 54.6 (*q*, $CH_3O$); 22.0 (*q*, $CH_3$–C(2)).

*Data of* **8b**: Yield *ca.* 15% (containing *ca.* 10% of **8a**). Red crystals. $^1H$-NMR (300 MHz, $CDCl_3$): 7.65–7.55, 7.35–7.15 (2*m*, 5 arom. H); 6.33 (*s*, H–C(4)); 3.79 (*s*, $CH_3O$); 1.35 (*s*, $CH_3$–C(2)). $^{13}C$-NMR (100.8 MHz, $CDCl_3$): 212.4, 193.3 (2*s*, Fe–CO, C(1)); 142.8 (*s*, arom. C); 130.9, 128.0, 127.0 (3*d*, 5 arom. CH); 128.1 (*s*, C(3)); 90.6 (*d*, C(4)); 68.2 (*s*, C(2)); 54.6 (*q*, $CH_3O$); 16.5 (*q*, $CH_3$–C(2)).

*Tricarbonyl(methyl 2-methyl-4-phenylbuta-2,3-dienoate)iron* (**9**). Yield *ca.* 4% (1:2 mixture with **8b**): IR ($CHCl_3$): 2075*vs*, 2030*vs*, 2005*vs*, 1990*vs*, 1980*s*, 1600*w*, 1580*m*. $^1H$-NMR (300 MHz, $CDCl_3$): 7.75–7.55, 7.45–7.15 (2*m*, arom. H); 5.93 (*s*, H–C(4)); 3.58 (*s*, $CH_3O$); 1.68 (*s*, $CH_3$–C(2)).

**5. Reaction with *N,N*-Diethyl-4-phenylpenta-2,3-dienamide (10a).** – *Data of* **10a**: Yield 73%. Colorless oil. IR ($CHCl_3$): 2980*m*, 2930*w*, 1945*m*, 1615*s*. $^1H$-NMR (250 MHz, $CDCl_3$): 7.45–7.2 (*m*, 5 arom. H); 6.16 (*q, J* = 3.0, H–C(2)); 3.42 (*q, J* = 7.1, 2 $CH_2$); 2.18 (*d, J* = 3.0, $CH_3$–C(4)); 1.16, 1.15 (2*t, J* = 7.1, 7.0, 2 $CH_3CH_2$). $^{13}C$-NMR (62.9 MHz, $CDCl_3$): 209.9 (*s*, C(3)); 164.1 (*s*, C(1)); 135.0 (*s*, arom. C); 128.3, 127.3, 125.9 (3*d*, 5 arom. CH); 104.1 (*s*, C(4)); 89.9 (*d*, C(2)); 42.8, 40.7 (2*t*, 2 $CH_2$); 16.2 (*q*, $CH_3$–C(4)); 14.4, 12.8 (2*q*, 2 $CH_3CH_2$). MS: 230 (45), 229 (76, $M^{+\cdot}$), 214 (13), 200 (14), 186 (6), 158 (22), 129 (22), 128 (20), 100 (100, $CON(C_2H_5)_2^+$), 72 (84, $N(C_2H_5)_2^+$).

*Hexacarbonyl(*N,N*-diethyl-4-phenylpenta-2,3-dienamide)diiron* (**11a**). Yield 35%. Dark red crystals (hexane). M.p. 98.0–105.0°. IR ($CHCl_3$): 2970*w*, 2925*w*, 2065*vs*, 2020*vs*, 1985*vs*, 1970*vs*, 1945*s*, 1560*s*. $^1H$-NMR (250 MHz, $CDCl_3$): 7.4–7.15 (*m*, 5 arom. H); 3.5–3.3 (*m*, 1 H of $CH_2$); 3.2–2.9 (*m*, 3 H of $CH_2$); 2.89 (*s*, H–C(2)); 2.37 (*s*, $CH_3$–C(4)); 1.1–1.0 (*m*, 2 $CH_3CH_2$). $^{13}C$-NMR (62.9 MHz, $CDCl_3$): *ca.* 213 (very br., Fe–CO); 210.3 (*s*, Fe–CO); 189.3, 184.5 (2*s*, C(1), C(3)); 148.1 (*s*, arom. C); 129.0, 127.6, 126.4 (3*d*, 5 arom. CH); 115.0 (*s*, C(4)); 55.6 (*d*, C(2)); 45.3, 41.8 (2*t*, 2 $CH_2$); 32.1 (*q*, $CH_3$–C(4)); 13.7, 13.2 (2*q*, 2 $CH_3CH_2$). MS: 509 (1, $M^{+\cdot}$), 481 (5, $[M - CO]^+$), 453 (26, $[M - 2\,CO]^+$), 425 (8, $[M - 3\,CO]^+$), 397 (43, $[M - 4\,CO]^+$), 369 (44, $[M - 5\,CO]^+$ or $[M - Fe(CO)_3]^+$), 341 (100, $[M - 6\,CO]^+$ or $[M - Fe(CO)_3 - CO]^+$), 285 (12), 184 (15), 100 (14).

**6. Reaction with *N,N*-Diethyl-4,4-diphenylbuta-2,3-dienamide (10b).** – *Data of* **10b**: Yield 61%. Colorless crystals ($Et_2O$/hexane). M.p. 103.0–105.0°. IR ($CHCl_3$): 2980*m*, 2930*w*, 1940*m*, 1615*s*. $^1H$-NMR (250 MHz, $CDCl_3$): 7.5–7.2 (*m*, 10 arom. H); 6.38 (*s*, H–C(2)); 3.42, 3.35 (2*q, J* = 7.1, 2 $CH_3CH_2$); 1.15, 1.10 (2*t, J* = 7.1, 2 $CH_3CH_2$). $^{13}C$-NMR (62.9 MHz, $CDCl_3$): 211.0 (*s*, C(3)); 163.7 (*s*, C(1)); 134.9 (*s*, 2 arom. C); 128.6, 128.4, 127.8 (3*d*, 10 arom. CH); 113.3 (*s*, C(4)); 90.8 (*d*, C(2)); 42.8, 40.7 (2*t*, 2 $CH_3CH_2$); 14.5, 12.9 (2*q*, 2 $CH_3CH_2$). MS: 292 (17), 291 (70, $M^{+\cdot}$), 276 (5), 262 (13, $[M - C_2H_5]^+$), 220 (40), 191 (20), 189 (27), 100 (100, $OCN(C_2H_5)_2^+$), 72 (78, $N(C_2H_5)_2^+$).

*Hexacarbonyl(*N,N*-diethyl-4,4-diphenylbuta-2,3-dienamide)diiron* (**11b**). Yield 64%. Dark red crystals ($Et_2O$/hexane). M.p. 158.0–160.0°. IR ($CHCl_3$): 2980*w*, 2930*w*, 2070*vs*, 2025*vs*, 1995*vs*, 1980*vs*, 1960*s*, 1560*s*. $^1H$-NMR (250 MHz, $CDCl_3$): 7.78 (*d, J* = 7.3, 1 arom. H); 7.46 (*d, J* = 7.2, 1 arom. H); 7.3–7.0 (*m*, 8 arom. H); 3.5–3.3 (*m*, 1 H, 2 $CH_3CH_2$); 3.25–3.0 (*m*, 3 H, 2 $CH_3CH_2$); 3.02 (*s*, H–C(2)); 1.15–1.0 (*m*, 2 $CH_3CH_2$). $^{13}$C-NMR (62.9 MHz, $CDCl_3$): 213.5 (br. *s*, Fe–CO); 210.5, 208.5, 207.6, 192.5, 184.4 (5*s*, Fe–CO, C(1), C(3)); 149.2, 147.6 (2*s*, 2 arom. C); 130.4, 129.7, 128.0, 127.6, 126.6, 126.2 (6*d*, 10 arom. CH); 118.7 (*s*, C(4)); 57.8 (*d*, C(2)); 45.5, 41.9 (2*t*, 2 $CH_3CH_2$); 13.7, 13.3 (2*q*, 2 $CH_3CH_2$). MS: 571 (1, $M^{+\cdot}$), 515 (5, $[M-2\ CO]^+$), 459 (10, $[M-4\ CO]^+$), 431 (14, $[M-5\ CO]^+$ or $[M-Fe(CO_3]^+$), 403 (8, $[M-6\ CO]^+$ or $[M-Fe(CO)_3-CO]^+$), 347 (4), 293 (25), 115 (25), 100 (100, $OCN(C_2H_5)_2^+$), 72 (46, $N(C_2H_5)_2^+$).

**7. Reaction with 3-(2,2-Diphenylethenylidene)-*N*-phenylpyrrolidine-2,5-dione (12).** – *Data of* **12**. Yield 36%. Colorless crystals ($(i\text{-}Pr)_2O$/hexane). M.p. 169.0–172.0°. IR ($CHCl_3$): 3050*w*, 3000*w*, 1945*m*, 1760*m*, 1705*s*, 1590*w*. $^1$H-NMR (250 MHz, $CDCl_3$): 7.55–7.3 (*m*, 15 arom. H); 3.76 (*s*, $CH_2$). $^{13}$C-NMR (62.9 MHz, $CDCl_3$): 207.3 (*s*, C(1′)); 172.1, 167.3 (2*s*, C(2), C(5)); 134.0, 132.1 (2*s*, 3 arom. C); 128.9, 128.7, 128.5, 126.4 (4*d*, 15 arom. CH); 118.7 (*s*, C(2′)); 96.2 (*s*, C(3)); 33.3 (*t*, $CH_2$). MS: 352 (18), 351 (74, $M^{+\cdot}$), 323 (46), 322 (38), 231 (26), 204 (100), 203 (71), 202 (80), 105 (24), 77 (20).

*Hexacarbonyl[3-(2,2-diphenylethenylidene)-*N*-phenylpyrrolidine-2,5-dione]diiron* (**13**). Yield 9%. Amorphous red solid; decomposes at 100–105°. IR ($CHCl_3$): 3050*w*, 2920*w*, 2120vs, 2020vs, 2000vs, 1985vs, 1970*s*, 1760*m*, 1610*s*. $^1$H-NMR (250 MHz, $CDCl_3$): 7.89 (*d*, $J = 6.1$, 1 arom. H); 7.6–7.0 (*m*, 14 arom. H); 2.85 (*d*, $J = 21.3$, $H_a$–C(4)); 1.64 (*d*, $J = 21.3$, $H_s$–C(4)). $^{13}$C-NMR (62.9 MHz, $CDCl_3$): 212.8 (br. *s*, Fe–CO); 209.6, 206.7, 193.3, 187.2 (4*s*, Fe–CO, C(2), C(1′)); 175.7 (*s*, C(5)); 149.2, 146.9 (2*s*, 2 arom. C); 130.8 (*s*, arom. C–N); 129.3, 128.9, 128.2, 127.2, 125.6 (5*d*, 15 arom. CH); 126.0 (*s*, C(2′)); 67.9 (*s*, C(3)); 41.5 (*t*, C(4)). MS: 353 (51), 206 (100), 205 (29), 191 (26), 167 (17), 165 (27), 128 (38), 91 (50).

*Tetracarbonyl[3-(2,2-diphenylethenylidene)-*N*-phenylpyrrolidine-2,5-dione]iron* (**14**). Yield 35%. Yellow crystals ($Et_2O$/hexane). M.p. 136.0–138.0. IR ($CHCl_3$): 3075*w*, 3055*w*, 2985*w*, 2105vs, 2050vs, 2030vs, 2015vs, 1760*m*, 1690*s*, 1595*w*. $^1$H-NMR (250 MHz, $CDCl_3$): 7.6–7.1 (*m*, 15 arom. H); 3.07 (*s*, $CH_2$). $^{13}$C-NMR (62.9 MHz, $CDCl_3$): 205.3 (*s*, Fe–CO); 178.9, 173.3 (2*s*, C(2), C(5)); 156.2 (*s*, C(1′)); 142.6, 140.9, 140.3 (3*s*, 2 arom. C, C(3)); 132.6 (*s*, arom. C–N); 129.2, 129.0, 128.7, 128.6, 127.6, 127.5, 127.2, 126.6, 126.5 (9*d*, 15 arom. CH); 39.8 (*t*, C(4)); 35.8 (*s*, C(2′)). MS: 353 (50), 351 (24), 206 (48), 168 (65), 167 (69), 93 (100), 91 (40).

*Tricarbonyl[3-(2,2-diphenylethenylidene)-*N*-phenylpyrrolidine-2,5-dione]iron* (**15**). Yield 41%. Orange crystals ($C_6H_6$/hexane). M.p. 141.0–144.0° (dec.). UV (Cyclohexane): 336 (11700), *ca.* 460 (sh, 1100). IR ($CHCl_3$): 2960*w*, 2930*w*, 2065vs, 2000vs, 1755*m*, 1705*s*, 1655*m*, 1595*w*. $^1$H-NMR (250 MHz, $CDCl_3$): 7.7–7.3 (*m*, 14 arom. H); 3.98 (br. *s*, H–C(2″)); 3.07 (*s*, $CH_2$). $^{13}$C-NMR (62.9 MHz, $CDCl_3$, *ca.* 30°): 179.5, 173.1 (2*s*, C(2), C(5)); 169.6 (*s*, C(1′)); 134.1 (*s*, arom. C); 132.7 (*s*, arom. C–N); 136.0, 131.3, 130.4, 129.3, 128.9, 128.6, 128.0, 127.6, 126.5, 125.6 (10*d*, 10 arom. CH, CH(3″–6″); 113.9, 110.3 (2*s*, C(3), C(1″)); 80.3 (*s*, C(2′)); 73.4 (*d*, C(2″)); 35.4 (*t*, C(4)). $^{13}$C-NMR (100.8 MHz, $CDCl_3$, – 50°): 211.5, 210.2, 202.6 (3*s*, Fe–CO); 180.7, 174.0, 169.9 (3*s*, C(2), C(5), C(1′)); 133.3, 131.7 (2*s*, arom. C, arom. C–N); 136.0, 131.3, 130.1, 129.1, 128.5, 128.3, 128.0, 127.8, 126.2, 125.2 (10*d*, 10 arom. CH, CH(3″–6″)); 113.1, 109.6 (2*s*, C(3), C(1″)); 80.0 (*s*, C(2′)); 72.8 (*d*, C(2″)); 34.8 (*t*, C(4)). MS: 435 (5, $[M-2\ CO]^+$), 407 (30, $[M-3\ CO]^+$), 353 (52), 351 (34, $[M-Fe(CO)_3]^+$), 260 (17), 206 (100), 91 (46).

**8. X-Ray Structure Determination of 8c** (s. *Fig.*)[4]. Data were collected on a *Nicolet-R3* diffractometer using the *Wyckoff* ω-scan mode and graphite monochromated Mo$K_\alpha$ radiation at 294 K ($\mu$(Mo$K_\alpha$) = 15.81 cm$^{-1}$). Data collection and refinement parameters are listed in the *Table*. Structure solution was performed using the *Patterson* function routine of SHELXS86 [16] and full-matrix least-squares refinement on *F* was performed with SHELX76 [17]. Empirical absorption corrections were applied using DIFABS [18]. The positions of the Fe-atoms were

Table. *Crystallographic Data of* **8c**

| | |
|---|---|
| Crystallized from | hexane/$Et_2O$ |
| Color | red |
| Crystal temp. (*ca.*) [K] | 297 |
| Space group | $P2_1/n$<br>monoclinic, centrosymmetric |
| *Z* | 8 |
| Molecular formula | $C_{18}H_{12}Fe_2O_8$ |
| Formula weight | 467.96 |

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[4] All crystallographic data are deposited with the *Cambridge Crystallographic Data Centre*, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW England.

*Table* (cont.)

| | |
|---|---|
| Cell parameters[a]) | |
| $a$ [Å] | 14.409 (1) |
| $b$ [Å] | 16.948 (2) |
| $c$ [Å] | 16.126(1) |
| $\beta$ [°] | 107.047 (7) |
| $V$ [Å$^3$] | 3765.2 (6) |
| Calc. density [Mg/m$^3$] | 1.651 |
| $2\theta$ (max) | 55° |
| Reflections measured | 9905 |
| Symmetry independent reflections | 8630 |
| Reflections used in the refinement ($I > 3\sigma(I)$) | 5430 |
| Variables | 601 |
| $R$ | 0.0348 |
| $R_w$ | 0.0345 |
| Weighting scheme $w$ | $(\sigma^2(F) + 0.000285\,F^2)^{-1}$ |

[a]) The cell dimensions were obtained from 25 accurately centered reflections with $32° < 2\theta < 34°$.

determined from a *Patterson* function synthesis; the positions of all remaining non-H-atoms were determined from subsequent *Fourier* syntheses. There are two independent molecules in the asymmetric unit, but there is no significant structural difference between them. All non-H-atoms were refined with anisotropic thermal parameters. All of the H-atoms were located in a difference *Fourier* map and their positions were allowed to refine with individual isotropic temp. factors. The final difference *Fourier* maps were featureless. Least-square plane calculations show that the angle between the plane of the Ph group and the three C-atoms of the allyl group is 37.8° for molecule *A* and 41.2° for molecule *B*. The angle between the planes of the ester function and the allyl group is 38.3° for molecule *A* and 40.1° for molecule *B*.

## REFERENCES

[1] D. Martina, F. Brion, A. De Cian, *Tetrahedron Lett.* **1982,** *23,* 857; *ibid.* **1982,** *23,* 861.

[2] L.S. Trifonov, A.S. Orahovats, R. Prewo, H. Heimgartner, *Helv. Chim. Acta* **1988,** *71,* 551.

[3] L.S. Trifonov, A.S. Orahovats, H. Heimgartner, *Helv. Chim. Acta* **1987,** *70,* 1070.

[4] K.K. Joshi, *J. Chem. Soc. (A)* **1966,** 594.

[5] W. Runge, G. Kresze, E. Ruch, *Liebigs. Ann. Chem.* **1975,** *759,* 1361.

[6] C.M. Adams, G. Cerioni, A. Hafner, W. von Philipsborn, R. Prewo, A. Schwenk, *Helv. Chim. Acta* **1988,** *71,* 1116.

[7] W.P. Fehlhammer, H. Stolzenberg, in 'Comprehensive Organometallic Chemistry', Eds. G. Wilkinson, F.G.A. Stone, and E.W. Abel, Pergamon Press, Oxford, 1982, Vol. 4, p. 566.

[8] L.V. Rybin, A.A. Pogrebuyak, M.T. Rubinskaya, D.A. Bochvar, E.G. Gal'pern, N.P. Gambaryan, *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1976,** *7,* 1596 (*CA:* **1976,** *85,* 160290c).

[9] 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. 386.

[10] L.S. Trifonov, A.S. Orahovats, H. Heimgartner, in preparation.

[11] L.S. Trifonov, A.S. Orahovats, *Helv. Chim. Acta* **1986,** *69,* 1585; *ibid.* **1987,** *70,* 262.

[12] H.-J. Bestmann, H. Hartung, *Chem. Ber.* **1966,** *99,* 1198.

[13] R.W. Lang, H.-J. Hansen, *Helv. Chim. Acta* **1980,** *63,* 438.

[14] P. Dalla Croce, *Ann. Chim. (Rome)* **1973,** *63,* 867 (*CA:* **1975,** *84,* 58138b).

[15] E. Hedaya, S. Theodoropulos, *Tetrahedron* **1968,** *24,* 2241.

[16] G.M. Sheldrick, SHELXS86, A program for crystal structure solution, University of Göttingen, FRG, 1986.

[17] G.M. Sheldrick, SHELX76, A program for crystal structure determination, Cambridge, 1976.

[18] N. Walker, D. Stuart, *Acta Crystallogr. Sect. A* **1983,** *39,* 158.