144. Carbonyliron Complexation and Carbonyl Insertion of Allenic Ketones

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(14.VII.92)

The allenic α-ketones **5a–f** give, on irradiation in the presence of [Fe(CO)$_5$], the bis(tricarbonyliron) complexes **6a–f**. In the case of ketone **5e**, a minor bis(tricarbonyliron) complex with the proposed unique structure **8** is also obtained. Ketones **5a–d**, which are disubstituted at C(4), under the same conditions, afford also the lactones **7a–d** in moderate yields. The latter reaction is a new carbonyliron-mediated carbonyl insertion. The structure of the binuclear complexes **1a** and **6e** were established by X-ray crystallography.

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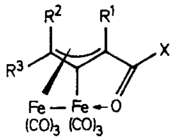
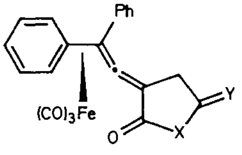
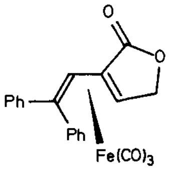
1. Introduction. – In recent years, attention was drawn to the iron-carbonyl complexation of allenic esters [1–3], lactones [2], acids, amides, and imides [3]. A binuclear complex of type **1** was reported to be the main product from the reaction with the esters [2] and the amides [3], while the lactones and the imides gave, besides **1**, substantial amounts of the complex of type **2** with participation of the Ph ring at C(4) in the complexation. Also the mononuclear complexes **3** and **4** were formed [2] [3].



1 X = RO, R$_2$N, RCON(Ph)



2 X = O, Y = H$_2$
X = PhN, Y = O



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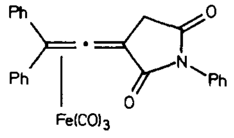

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In the meantime, the structure of the amide complex **1a** (X = Et$_2$N, R^1 = H, R^2 = R^3 = Ph) was established by X-ray crystallography (*Fig. 1* and *Chapt. 3*).

In the present paper the behaviour of α-allenic ketones on irradiation in the presence of [Fe(CO)$_5$] is described.

2. Results and Discussion. – Irradiation of α-allenic ketones **5a** [4], **5b** [5], and **5d** in the presence of an excess of [Fe(CO)$_5$] in hexane with a high-pressure Hg-lamp (*Solidex* filter) gave a mixture of red and yellow products which were chromatographically separated.

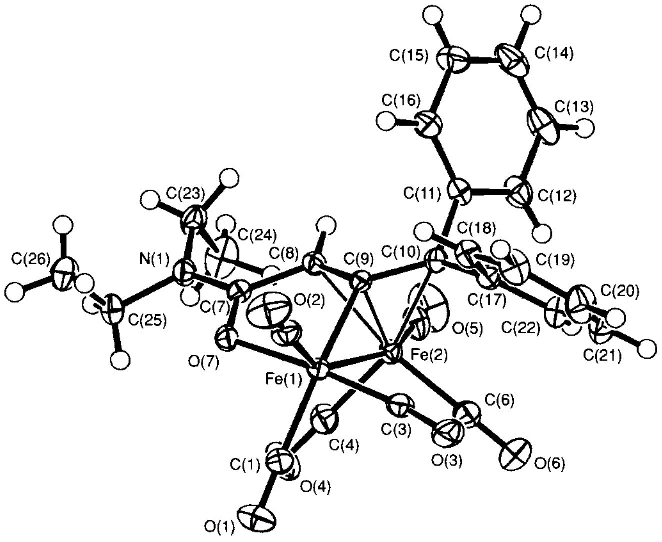
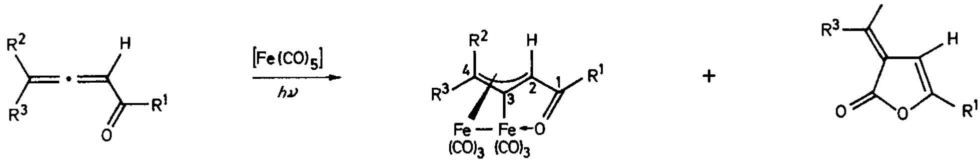


Fig. 1. *ORTEP plot with 50% probability ellipsoids of the molecular structure of μ-(*N,N-*diethyl-4,4-diphenylbuta-2,3-dienamide)bis(tricarbonyliron)-(*Fe–Fe*) (**1a**, X = Et$_2$N, R^1 = H, R^2 = R^3 = Ph)

The red crystalline products were shown to be the corresponding binuclear complexes **6a**, **6b**, (*E*)- and (*Z*)-**6d**, which are of type **1** (*Scheme 1*)[1]).

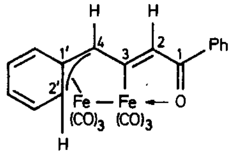
Scheme 1



5a R^1 = Me, R^2 = R^3 = Ph
b R^1 = R^2 = R^3 = Ph
c R^1 = Ph,
R^2–R^3 = biphenyl-2,2'-diyl
d R^1 = R^3 = Ph, R^2 = Me
e R^1 = R^2 = Ph, R^3 = H
f R^1 = Me, R^2 = Ph, R^3 = H

6a R^1 = Me, R^2 = R^3 = Ph
b R^1 = R^2 = R^3 = Ph
c R^1 = Ph, R^2–R^3 = biphenyl-2,2'-diyl [a])
(*E*)-**6d** R^1 = R^2 = Ph, R^3 = Me [1])
(*Z*)-**6d** R^1 = R^3 = Ph, R^2 = Me [1])
6e R^1 = R^3 = Ph, R^2 = H
(*E*)-**6f** R^1 = Me, R^2 = Ph, R^3 = H [c]) [1])
(*Z*)-**6f** R^1 = Me, R^2 = H, R^3 = Ph [c]) [1])

7a R^1 = Me, R^2 = R^3 = Ph
b R^1 = R^2 = R^3 = Ph
c R^1 = Ph,
R^2–R^3 = biphenyl-2,2'-diyl
d R^1 = R^2 = Ph, R^3 = Me
e [b])
f [b])



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[a]) Attempts to isolate pure compounds were unsuccessful.
[b]) Lactones could not be isolated from intractable mixtures.
[c]) Attempts to separate the complexes on TLC were unsuccessful.

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[1]) (*E*) and (*Z*) refer to the relation of Ph–C(4) and Fe–C(3).

The signal of H–C(2) in the ^{1}H-NMR spectra of **6a**, **6b**, (*E*)- and (*Z*)-**6d** appears at 3.22, 3.93, 3.76, and 4.19 ppm, respectively. Characteristic for structure **6** are also the signals of C(2) (at *ca.* 67 ppm), of C(4) (*ca.* 118 ppm), and of C(1) and C(3) (210–196 ppm) in the ^{13}C-NMR spectra (see [2] and *Exper. Part*). The lack of a ketone carbonyl absorption and the presence of 5 strong bands for the Fe–CO groups in the IR spectra, similarly to the case of the esters [2], also support structure **6**.

The assignment of the (*E*)- and (*Z*)-configuration at the C(3), C(4) bond of complexes **6d**²) is based on the shielding effect of the Ph–C(4) ring on H–C(2), absorbing at 3.76 ppm for (*E*)-**6d**, while for (*Z*)-**6d** it absorbs at 4.19 ppm. On the other hand, Me–C(4) of (*E*)-**6d** and C_{ipso} of Ph–C(4) of (*Z*)-**6d** are shifted slightly downfield by the neighboring Fe-atom (δ(Me) at 32.6 ppm in (*E*)-**6d** and 30.4 ppm in (*Z*)-**6d**; $\delta(C_{ipso})$ at 147.7 ppm in (*E*)-**6d** and 149.8 ppm in (*Z*)-**6d**).

The yellow products isolated on irradiation of **5a**, **5b**, and **5d** were identified as the lactones **7a**, **7b**, and **7d**, respectively. Interestingly, only one of the two feasible isomeric lactones, namely **7d**, was detected and isolated on irradiation of ketone **5d**. The allenic ketone **5c** afforded, under the same reaction conditions, a dark brown-red complex, presumably **6c**, which was not isolated in pure form, and the known lactone **7c** (see [6] and *Exper. Part*).

The MS of lactones **7a**, **7b**, and **7d** show clearly an addition of CO onto the starting ketone. The CO absorption at *ca.* 1760 cm^{-1} is typical for an unsaturated 5-ring lactone. In the ^{1}H-NMR spectra, H–C(3) appears as a *s* at 5.95, 6.57, and 6.59 ppm, respectively. The absorptions of C(1), C(3), and C(4) in the ^{13}C-NMR spectra also are characteristic for structure **7** (**7a**: 167.0, 104.9, and 155.1 or 150.9 ppm; **7b**: 166.4, 103.4, and 154.1 or 152.8 ppm; **7d**: 165.8, 101.1, and 153.4 or 151.3 ppm).

To the structure of **7d**, the (*E*)-configuration at the exocyclic double bond is ascribed on the basis of the very low-field signal of the Me group in the ^{1}H-NMR spectrum (at 2.43 ppm), obviously due to the deshielding effect of the lactone-CO group [7].

The possibility of **6a** being an intermediate in the formation of **7a** was ruled out, because, on irradiation of the former under the same reaction conditions, only traces (*ca.* 1%) of **7a** were detected along with **5a** (13%). Again no lactone **7a** was observed on heating of **6a**. On treatment with $AgOCOCF_3$ in CH_2Cl_2, **6a** gave **5a** (36%) and **7a** (11%), while on oxidation with $FeCl_3$ it afforded **5a** as main product and only traces of **7a**.

On irradiation of the monosubstituted ketones **5e** and **5f** in the presence of an excess of [$Fe(CO)_5$] in hexane with a high-pressure Hg-lamp through a *Solidex* filter, also red and yellow products were formed, however, in very low yields³). No pure products could be obtained from the complex yellow fraction. The red fraction obtained from **5f** most likely contained the binuclear complexes (*E*)- and (*Z*)-**6f**⁴), in analogy to (*E*)- and (*Z*)-**6d** (*vide supra*). Careful TLC separation of the red products obtained from **5e** gave two red substances, a crystalline one and the other one as a red oil. The more polar complex has structure **6e** with (*Z*)-configuration, as established by X-ray crystallography (*Fig. 2* and *Chapt. 3*). The less polar oily complex turned out to have the unique structure **8** and is not the anticipated (*E*)-isomer of **6e**, as in the case of **5d**.

The tentative structure **8** is supported by the presence of three 1-H *s*'s in the ^{1}H-NMR spectrum at 6.73, 6.54, and 4.71 ppm, suggesting involvement of Ph–C(4) in the complexation. This is also in accordance with the 3 *d*'s in the ^{13}C-NMR spectrum at 107.1, 91.3, and 69.2 ppm. The lack of a ketone-CO band in the IR spectrum indicates the coordination of the ketone O-atom with the Fe-atom. The presence of six strong bands in the region of 2070–1955 cm^{-1} in the IR spectrum together with the MS corroborate the constitution [$Fe_2(CO)_6L$].

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²) The crude reaction mixture contained (*E*)-**6d** and (*Z*)-**6d** in a ratio of 2:1.

³) This is mainly the result of the low-yield preparation of the starting allenic ketones, which were not isolated in pure form, because of their rapid dimerization.

⁴) The products could not be separated by TLC.

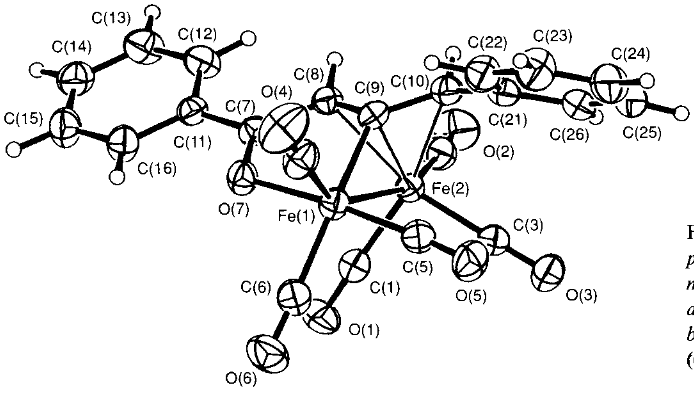
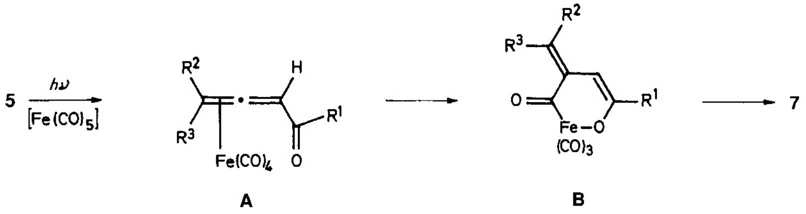


Fig. 2. *ORTEP plot with 30% probability ellipsoids of the molecular structure of μ-(1,4-diphenylbuta-2,3-dien-1-one)-bis(tricarbonyliron)(* Fe–Fe*)* **(6e)**

In conclusion, allenic ketones of type **5** afforded, on irradiation in the presence of $Fe(CO)_5$, binuclear carbonyliron complexes of type **6**. In case of ketones **5a–d** with disubstitution on C(3) of the allenic unit, but-3-en-4-olides **7** were formed in addition to **6**. The structure of the binuclear complexes **6** are analogous to the previously described complexes with allenecarboxylates [2] [3], allenic lactones [2], allenic amides [3], and allenic imides [3]. A different type of dinuclear complex, with the proposed structure **8**, was isolated from the reaction of the 3-monosubstituted **5e**.

The formation of the but-3-en-4-olides **7** is a new iron-carbonyl-mediated CO insertion. Likely intermediates in the reaction are the tetracarbonyliron complex **A** and the metallocycle **B** (*Scheme 2*).

Scheme 2



3. **Crystal-Structure Determinations**[5]. – Crystals of **1a** and **6e** were obtained from hexane/Et_2O. The intensities were collected on a *Nicolet-R3* diffractometer in the *Wyckoff* ω-scan mode using graphite monochromated MoK_α radiation ($\lambda = 0.71069$ Å) at 193 and 294 K, respectively. Data collection and refinement parameters are listed in the *Table*. The intensities were corrected for *Lorentz* and polarization effects, and absorption corrections were applied using DIFABS [8]. Structure solution was performed using the *Patterson* function routine of SHELXS86 [9], and full-matrix least-squares refinement on F was performed with SHELX76 [10] (for **6e**) and with the TEXSAN program package [11] (for **1a**). For each structure, the positions of the Fe-atoms were determined from a *Patterson* function synthesis. This solution was expanded by *Fourier* techniques to yield the positions of all non-H-atoms. 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 temperature factors. A secondary extinction coefficient was included in the refinement of **1a**. The final difference *Fourier* maps were featureless.

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[5] Atomic coordinates, bond lengths, and angles were deposited with the *Cambridge Crystallographic Data Center*, 12 Union Road, Cambridge CB2 1EZ, England.

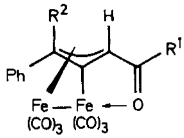
Table. *Crystallographic Data of Bridged Bis(tricarbonyliron) Complexes* **1a** *and* **6e**

	1a	**6e**
Crystallized from	hexane/Et_2O	hexane/Et_2O
Color	dark red	red
Crystal temp. (*ca.*) [K]	193	294
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$
Z	4	2
Molecular formula	$C_{26}H_{21}Fe_2NO_7$	$C_{22}H_{12}Fe_2O_7$
Formula weight	571.13	500.03
Cell parameters[a]) a [Å]	10.378(1)	9.874(10)
b [Å]	17.224(2)	12.480(13)
c [Å]	14.154(2)	9.410(9)
α [°]	90	107.13(8)
β [°]	99.49(1)	102.55(8)
γ [°]	90	82.15(9)
V [Å^3]	2495.3(6)	1069(2)
D_x [g cm^{-3}]	1.520	1.554
Linear absorption coeff. [cm^{-1}]	12.1	14.0
2θ(max)	60°	60°
Total reflections measured	8364	7996
Symmetry-independent reflections	7287	6169
Reflections used in refinement ($I > 3\sigma(I)$)	5380	3836
Variables	410	328
Final R	0.0314	0.0354
R_w[b])	0.0334	0.0393
Goodness of fit s	1.670	1.346
Weighting factor g ($w = [\sigma^2(F) + gF^2]^{-1}$)	0.0001	0.00262
$\sigma(d(C-C))$ [Å]	0.002–0.003	0.004–0.006

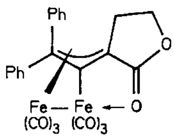
[a]) The cell dimensions were obtained from 25 accurately centered reflections with $32° < 2\theta < 34°$ (**1a**) and $20° < 2\theta < 28°$ (**6e**).

[b]) Function minimised $\Sigma w(|F_o| - |F_c|)^2$.

The structures of the binuclear complexes **1a** and **6e** are very similar to each other and to the previously described structures **9** and **10** [2]. Bond lengths and angles differ only slightly in the four structures, and the bond lengths within the coordination spheres of the Fe-atoms are almost identical for **1a**, **6e**, and **9**. In the ketone complex **6e**, the Fe-atom not coordinated with O is at the centre of a distorted capped octahedron (C(9) caps the C(8)–C(10)–Fe(1) face) and the O-coordinated Fe-atom is enclosed in a distorted octahedron. The Fe(1)–C(9) and Fe(2)–C(9) distances are almost equal. As is usual, the Fe(2)–C(8) and Fe(2)–C(10) distances are 0.18–0.26 Å longer than the Fe(2)–C(9) distance.



1a R^1 = Et$_2$N, R^2 = Ph
6e R1 = Ph, R^2 = H
9 R^1 = MeO, R^2 = Ph [2]



10 [2]

Our thanks are due to the analytical services of our Institutes. Financial support by the *Swiss National Science Foundation* and by *F. Hoffmann-La Roche AG,* Basel, is gratefully acknowledged.

Experimental Part

General. See [3]. If not otherwise stated, IR spectra were taken in $CHCl_3$, ^1H- and ^{13}C-NMR spectra in $CDCl_3$ at 250 and 62.9 MHz, respectively.

1. *Starting Materials.* The allenic ketones **5a**, **5b**, **5d–f** were obtained from the corresponding acyl chlorides, using a known procedure [12]. The crude products were not isolated in pure form because of their rapid dimerization at r.t. Consequently, they were characterized mainly by their IR spectra. Only for the newly prepared ketones **5c** and **5d**, ^1H- and ^{13}C-NMR spectra of the crude products were taken.

For the synthesis of ketone **5c**, the diphenyleneketene [13] was reacted with (benzoylmethylidene)triphenylphosphorane [14] in CH_2Cl_2 at r.t. for 30 min. The mixture was filtered through a short SiO_2 column with petroleum ether/Et_2O 10:1 and the eluate, containing **5c**, was used directly for the reaction.

3-(Fluoren-9-ylidene)-1-phenylpropen-1-one (**5c**). Oil. IR: 1930*m*, 1650*s*, 1595*m*, 1580*m*. ^1H-NMR: 7.96 (*dd, J* = 8.0, 1.5, 2 arom. H); 7.72 (*dd, J* = 7.5, 1.0, 2 arom. H); 7.58 (*d, J* = 7.0, 2 arom. H); 7.5–7.2 (*m*, 7 arom. H); 7.08 (*s*, H–C(2)). ^{13}C-NMR: 212.5 (*s*, C(3)); 204.5 (*s*, C(1)); 139.2–120.0 (arom. C, CH); 108.7 (*s*, C(4)); 100.8 (*d*, C(2)).

1,4-Diphenylpenta-2,3-dien-1-one (**5d**). Oil. IR: 3050*w*, 2985*w*, 2915*w*, 1930*m*, 1635*s*, 1590*m*. ^1H-NMR: 7.88 (*dd, J* = 8.5, 1.0, 2 arom. H); 7.5–7.05 (*m*, 8 arom. H); 6.60 (*q, J* = 3.1, H–C(2)); 2.17 (*d, J* = 3.1, Me). ^{13}C-NMR: 215.1 (*s*, C(3)); 191.3 (*s*, C(1)); 137.6–126.0 (arom. C, CH); 104.6 (*s*, C(4)); 95.6 (*d*, C(2)); 16.0 (*q*, Me).

2. *Irradiation in the Presence of Pentacarbonyliron* ([$Fe(CO)_5$]). 2.1. *General Procedure.* Solns. of the allenic ketones **1a–f** (4 mmol) and $Fe(CO)_5$ (3 ml) in 250 ml of hexane (for **5b** and **5f**) or in hexane/Et_2O 10:1 (for all other ketones) were irradiated with a 50-W *Hanovia* high pressure Hg-lamp (*Solidex* filter) at r.t. under Ar for 1 h. The solvent was evaporated and the residue subjected to column chromatography (silica gel, petroleum ether/Et_2O 6:1; for **5b**) or to prep. TLC (SiO_2, petroleum ether/Et_2O 10:1; for all other cases). The solvent from the red fractions or from the red-zone eluates was evaporated, and the residue was recrystallized from hexane/Et_2O to afford the pure dinuclear complexes **6**. The crude mixture of (*E*)- and (*Z*)-**6d** was recrystallized from hexane to give pure (*E*)-**6d**, and the mother liquor was subjected to prep. TLC with petroleum ether/Et_2O 100:1 (3 × development) to give, after elution of the red zone with $CHCl_3$, evaporation, and recrystallization from hexane, pure (*E*)-**6d** (larger R_f) and (*Z*)-**6d** (smaller R_f). The yellow fractions or eluates from the yellow zones were evaporated and the residue recrystallized from benzene/hexane (for **7d**), from hexane/Et_2O (for **7c**), and from hexane (for **7a** and **7b**) to afford the pure lactones.

2.2. *Bis(tricarbonyliron) Complexes* **6**. *μ-(5,5-Diphenylpenta-3,4-dien-2-one)bis(tricarbonyliron)(*Fe–Fe*)* (**6a**). Red crystals (27%) which decompose at *ca.* 180–190° without melting. IR: 2065v*s*, 2020v*s*, 1990v*s*, 1980v*s*, 1965v*s*, 1585*w*. ^1H-NMR: 7.79 (*d, J* = 7.2, 2 arom. H); 7.49 (*d, J* = 7.3, 2 arom H); 7.3–7.05 (*m*, 6 arom H); 3.22 (*s*, H–C(3)); 2.09 (*s*, Me). ^{13}C-NMR: 212.6 (br.), 209.6, 207.8, 207.0, 200.0 (5*s*, Fe–CO, C(2), C(4)); 148.8, 147.6 (2*s*, arom. C); 130.2, 129.7, 128.2, 127.9, 127.1, 126.6 (6*d*, arom. CH); 121.7 (*s*, C(5)); 69.9 (*d*, C(3)); 25.8 (*q*, Me). MS: 514 (5, $M^{+\cdot}$), 486 (8, $[M - CO]^+$), 458 (63, $[M - 2CO]^+$), 430 (9, $[M - 3CO]^+$), 402 (100, $[M - 4CO]^+$), 374 (65, $[M - 5CO]^+$ or $[M - Fe(CO)_3]^+$), 346 (77, $[M - 6CO]^+$ or $[M - Fe(CO)_3 - CO]^+$), 318 (42, $[M - Fe(CO)_3 - 2CO]^+$), 191 (58), 189 (42), 165 (38).

*μ-(1,4,4-Triphenylbuta-2,3-dien-1-one)bis(tricarbonyliron)(*Fe–Fe*)* (**6b**). Dark-red crystals (8%) which decompose at *ca.* 185–190° without melting. IR: 2060v*s*, 2020v*s*, 1990v*s*, 1980v*s*, 1965v*s* (sh), 1585*m*. ^1H-NMR: 7.84 (*d, J* = 7.1, 2 arom. H); 7.63 (*d, J* = 7.2, 2 arom. H); 7.55 (*t, J* = 6.9, 2 arom. H); 7.38 (*t, J* = 7.7, 2 arom. H); 7.3–7.1 (*m*, 7 arom. H); 3.93 (*s*, H–C(2)). ^{13}C-NMR: 214.5, 212.4, 209.6, 207.9, 207.1, 200.5 (6*s*, Fe–CO, C(1), C(3)); 148.9, 147.0, 133.8 (3*s*, arom. C); 130.2, 129.7, 128.9, 128.3, 128.0, 127.0, 126.6 (7*d*, arom. CH); 121.4 (*s*, C(4)); 67.3 (*d*, C(2)). MS: 576 (3, $M^{+\cdot}$), 548 (2, $[M - CO]^+$), 520 (25, $[M - 2CO]^+$), 492 (1, $[M - 3CO]^+$), 464 (83, $[M - 4CO]^+$), 436 (54, $[M - 5CO]^+$ or $[M - Fe(CO)_3]^+$), 408 (56, $[M - 6CO]^+$ or $[M - Fe(CO)_3 - CO]^+$), 380 (20), 324 (25), 246 (20), 204 (33), 105 (100, $PhCO^+$).

*μ-[(2*Z*,3*E*)-1,4-Diphenylpenta-2,3-dien-1-one]bis(tricarbonyliron)(*Fe–Fe*)* ((*E*)-**6d**). Red crystals (16%). M.p. 131.0–132.0°. IR: 2065v*s*, 2025v*s*, 2000v*s*, 1985v*s*, 1950*s*, 1600*m*. ^1H-NMR: 7.9–7.1 (*m*, 10 arom. H); 3.76 (*s*, H–C(2)); 2.43 (*s*, Me). ^{13}C-NMR: 214.3, 209.8, 196.9 (3*s*, Fe–CO, C(1), C(3)); 147.7 (*s*, arom. *C*–C(4)); 133.8 (*s*, arom. *C*–C(1)); 133.6, 129.2, 128.9, 128.1, 128.0, 126.9 (6*d*, arom. CH); 118.4 (*s*, C(4)); 65.4 (*d*, C(2)); 32.6 (*q*, Me). MS: 514 (6, $M^{+\cdot}$), 486 (8, $[M - CO]^+$), 458 (46, $[M - 2CO]^+$), 430 (9, $[M - 3CO]^+$), 402 (77, $[M - 4CO]^+$), 374 (48,

[M – 5CO]$^+$ or [M – Fe(CO)$_3$]$^+$), 246 (100, [M – 6CO]$^+$ or [M – Fe(CO)$_3$ – CO]$^+$), 318 (17), 290 (13), 262 (20), 240 (23), 184 (42).

*μ-[(2Z,3Z)-1,4-Diphenylpenta-2,3-dien-1-one]bis(tricarbonyliron)(*Fe–Fe*)* ((*Z*)-**6d**). Red amorphous solid (5%). IR: 2065*vs*, 2025*vs*, 1995*vs*, 1980*vs* (sh), 1950*s*, 1600*m*. ^{1}H-NMR: 7.9–7.1 (*m*, 10 arom. H); 4.19 (*s*, H–C(2)); 2.13 (*s*, Me). ^{13}C-NMR: 214.4, 212.3, 210.3, 208.4, 207.2, 196.8 (6*s*, Fe–CO, C(1), C(3)); 149.8 (*s*, arom. *C*–C(4)); 134.1 (*s*, arom *C*–C(1)); 133.6, 128.9, 128.2, 127.9, 127.3 (5*d*, arom. CH); 115.3 (*s*, C(4)); 65.0 (*d*, C(2)); 30.4 (*q*, Me). MS: 514 (4, $M^{+\cdot}$), 486 (5, [M – CO]$^+$), 458 (52, [M – 2CO]$^+$), 430 (8, [M – 3CO]$^+$), 402 (81, [M – 4CO]$^+$), 374 (50, [M – 5CO]$^+$ or [M – Fe(CO)$_3$]$^+$), 346 (100, [M – 6CO]$^+$ or [M – Fe(CO)$_3$ – CO]$^+$), 318 (9), 290 (11), 262 (17), 240 (16), 184 (38), 105 (62, PhCO$^+$).

*μ-(1,4-Diphenylbuta-2,3-dien-1-one)bis(tricarbonyliron)(*Fe–Fe*)* (**6e**). Dark-red crystals (2%). IR: 2065*vs*, 2020*vs*, 1990*vs*, 1980*vs* (sh), 1965*vs*, 1950*s*, 1590*m*. ^{1}H-NMR: 7.76 (*d*, *J* = 7.5, 2 arom. H); 7.68 (*d*, *J* = 7.5, 2 arom. H); 7.60 (*t*, *J* = 7.5, 1 arom. H); 7.44 (*t*, *J* = 7.5, 2 arom. H); 7.33 (*t*, *J* = 7.5, 2 arom. H); 7.24 (*t*, *J* = 7.5, 1 arom. H); 6.28 (*s*, H–C(4)); 3.85 (*s*, H–C(2)). MS: 500 (9, $M^{+\cdot}$), 472 (8, [M – CO]$^+$), 444 (52, [M – 2CO]$^+$), 416 (8, [M – 3CO]$^+$), 388 (88, [M – 4CO]$^+$), 360 (100, [M – 5CO]$^+$ or [M – Fe(CO)$_3$]$^+$), 332 (75, [M – 6CO]$^+$ or [M – Fe(CO)$_3$ – CO]$^+$), 304 (46), 276 (8), 248 (12), 192 (15), 170 (16).

*μ-(1,4-Diphenylbuta-2,3-dien-1-one)bis(tricarbonyliron)(*Fe–Fe*)* (**8**). Dark-red oil (2%). IR: 2070*vs*, 2030*vs*, 2005*vs*, 1990*vs* (sh), 1980*vs* (sh), 1955*m*, 1670*w*, 1650*w*, 1600*m*. ^{1}H-NMR: 7.8–7.2 (*m*, 9 arom. H); 6.73, 6.54, 4.71 (3*s*, H–C(2), H–C(4), H–C(2′)). ^{13}C-NMR: 213.3, 211.6 (br.), 199.1 (3*s*, Fe–CO, C(1)); 153.4, 142.5 (2*s*, C(3), C(1′)); 133.8 (*s*, arom. C); 128.9, 128.6, 128.4, 128.3, 126.8, 123.7 (6*d*, arom. CH); 107.1, 91.3, 69.2 (3*d*, C(2), C(4), C(2′)). MS: 500 (9, $M^{+\cdot}$), 472 (8, [M – CO]$^+$), 444 (52, [M – 2CO]$^+$), 416 (8, [M – 3CO]$^+$), 388 (88, [M – 4CO]$^+$), 360 (100, [M – 5CO]$^+$ or [M – Fe(CO)$_3$]$^+$), 332 (75, [M – 6CO]$^+$ or [M – Fe(CO)$_3$ – CO]$^+$), 304 (46), 276 (8), 248 (12), 192 (15), 170 (16).

2.3. *But-3-en-4-olides* **7**. *2-(Diphenylmethylidene)-4-methylbut-3-en-4-olide* (**7a**). Yellow crystals (33%). M.p. 99.0–101.0°. UV (cyclohexane): 254 (13000), 359 (11850). IR: 3030*w*, 3000*w*, 1755*s*, 1635*m*. ^{1}H-NMR (60 MHz): 7.6–7.1 (*m*, 10 arom. H); 5.95 (br. *s*, H–C(3)); 2.11 (br. *s*, Me). ^{13}C-NMR: 167.0 (*s*, C(1)); 155.1, 150.9 (2*s*, C(4), C(1′)); 141.2, 138.3 (2*s*, arom. C); 130.4, 130.3, 129.1, 128.2, 127.9 (5*d*, arom. CH); 123.9 (*s*, C(2)); 104.9 (*d*, C(3)); 14.4 (*q*, Me). MS: 263 (25), 262 (100, $M^{+\cdot}$), 234 (47, [M – CO]$^+$), 192 (35), 191 (98), 190 (30), 189 (65), 165 (31).

2-(Diphenylmethylidene)-4-phenylbut-3-en-4-olide (**7b**). Lemon-yellow crystals (13%). M.p. 174.0–177.0°. UV (cyclohexane): 258 (8800), 396 (9000). IR: 3000*m* (br.), 1760*s*, 1610*m*, 1585*m*. ^{1}H-NMR: 7.67 (*dd*, *J* = 7.4, 2.6, 2 arom. H); 7.5–7.3 (*m*, 13 arom. H); 6.57 (*s*, H–C(3)). ^{13}C-NMR: 166.4 (*s*, C(1)); 154.1, 152.8 (2*s*, C(4), C(1′)); 141.2, 138.2 (2*s*, arom. C); 130.6, 129.8, 129.5, 128.7, 128.3, 127.9, 124.9 (7*d*, arom. CH); 124.2 (*s*, C(2)); 103.4 (*d*, C(3)). MS: 324 (26, $M^{+\cdot}$), 296 (2), 191 (6), 189 (8), 165 (4), 105 (100, PhCO$^+$), 77 (25).

2-(Fluoren-9-ylidene)-4-phenylbut-3-en-4-olide (**7c**). Dark-red crystals (24%). M.p. 220.0–222.0° ([7]: 217°). UV (cyclohexane): 248 (25500), 266 (25800), 278 (sh, 19900), 435 (26000), *ca.* 460 (sh, 23000). IR (KBr): 3050*w*, 3030*w*, 1761*s*, 1605*m*. ^{1}H-NMR: 9.22 (*d*, *J* = 7.0, H–C(1′)); 7.93 (*d*, *J* = 7.8, H–C(8′)); 7.9–7.8 (*m*, 2 arom. H); 7.63 (*t*, *J* = 7.5, 2 arom. H); 7.55–7.25 (*m*, 7 arom. H); 7.40 (*s*, H–C(3)). MS: 323 (25), 322 (100, $M^{+\cdot}$), 189 (20), 106 (12), 105 (98), 77 (69).

*(*E*)-2-(α-Methylbenzylidene)-4-phenylbut-3-en-4-olide* (**7d**). Lemon-yellow needles (22%). M.p. 135.0–138.0°. UV (cyclohexane): 245 (5730), 361 (7100). IR: 3060*w*, 3000*w*, 1765*s*, 1625*m*, 1595*m*. ^{1}H-NMR: 7.71 (*dd*, *J* = 7.5, 2.0, 2 arom. H); 7.5–7.35 (*m*, 8 arom. H); 6.59 (*s*, H–C(3)); 2.43 (*s*, Me). ^{13}C-NMR: 165.8 (*s*, C(1)); 153.4, 151.3 (2*s*, C(4), C(1′)); 139.2 (*s*, arom. C); 129.8, 128.9, 128.7, 128.0, 127.9, 124.9 (6*d*, arom. CH); 123.9 (*s*, C(2)); 101.1 (*d*, C(3)); 24.6 (*q*, Me). MS: 263 (7), 262 (30, $M^{+\cdot}$), 157 (4), 128 (8), 105 (100), 77 (41).

3. *Reactions with Dinuclear Complex* **6a**. 3.1. *Irradiation of* **6a**. A soln. of 257 mg (0.5 mmol) of **6a** in 275 ml of hexane/Et$_2$O 10:1 was irradiated with a 50-W *Hanovia* high-pressure Hg-lamp (*Solidex* filter) at r.t. under Ar for 1 h. The solvent was evaporated and the residue chromatographed on 5 prep. TLC plates (hexane/Et$_2$O 100:1 (2 ×), then hexane/Et$_2$O 50:1 (2 ×)). From the red zone, after elution with CHCl$_3$ and recrystallization of the crude product from hexane/Et$_2$O, 180 mg (70%) of **6a** were recovered. The colorless but UV(254 nm)-active zone afforded, after similar treatment, 13 mg (13%) of **5a**. The yellow zone gave a crude oily product (10 mg), which was shown to contain **7a** as a minor component (TLC, IR).

3.2. *Treatment of* **6a** *with AgOCOCF$_3$*. To a soln. of 103 mg (0.2 mmol) of **6a** in 4 ml of dry CH$_2$Cl$_2$, 60 mg (0.29 mmol) of AgOCOCF$_3$ were added, and the soln. was stirred at r.t. for 2 d. The mixture was chromatographed on 3 prep. TLC plates (petroleum ether/Et$_2$O 100:1 (2 ×), then petroleum ether/Et$_2$O 50:1 (3 ×)). The product from the yellow zone was eluted with CHCl$_3$ and the crude material recrystallized from hexane/Et$_2$O to give 5 mg (11%) of **7a** (TLC, IR, m.p.). Analogous workup of the colorless but UV(254 nm)-active zone gave 15 mg (36%) of **5a** (TLC, IR).

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