Synthesis, Structure and Conformation of *cis*- and *trans*-(μ-1,6-Dimethylheptalene)bis(tricarbonyliron)

Felix W. Grimm, Klaus Hafner*, and Hans J. Lindner

Institut für Organische Chemie der Technischen Hochschule Darmstadt,
Petersenstr. 22, D-64287 Darmstadt, Germany
Telefax: (internat.) +49(0)6151/163574

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The reaction of 1,6-dimethylheptalene (2) with $Fe_2(CO)_9$ affords two binuclear iron complexes **4a** and **4b**, each bearing two tricarbonyliron moieties, in *trans* and *cis* orientation, respectively. The reaction leads additionally to the formation of the monocomplexed compound **3**. NMR studies indicate that the heptalene moiety of the new compounds is a π-bond isomer of **2**, and this is clearly attributable to steric factors. Single-crystal X-ray structure analyses of the metal complexes **4a** and **4b** confirm that the $Fe(CO)_3$ fragments adopt *trans* and *cis* geometries, respectively, with respect to the plane of the carbocycle. The ring systems of the two isomers adopt different conformations in the solid state. In the case of **4a**, a hitherto unknown chair-like conformation is determined, whereas in complex **4b** the ring system shows a twisted double boat conformation.

Tricarbonyliron complexes are versatile and widely used transition metal π-complexes by virtue of their potential in stabilizing sensitive organic compounds; frequently they facilitate reactions which cannot be achieved with the uncomplexed frameworks[1]. Heptalenes continue to be of theoretical and preparative interest, and extensive investigations have been made into bond shifting, ring inversion and the related transition states in order to determine the nature of the 12-π-electron system of these bicyclic annulenes[2]. However, little is known of heptalenes as ligands in metal complexes, despite the fact that they can be assumed to be strong and versatile twofold η^4-ligands on account of their extensive π-electron system. To date, only a small number of literature reports have dealt with such species. In 1977, Vogel et al. published the synthesis of tricarbonyl(heptalene)chromium[2a] and tricarbonyl(heptalene)iron[3], and furthermore described the preparation of bis(tricarbonyliron)heptalene[2b] (**1**). X-ray structure analysis[4] of the latter revealed a *cis* orientation of the two $Fe(CO)_3$ moieties with respect to the seven-membered rings of the heptalene. However, both cyclooctatetraene[5] and 1,3,5,7-tetramethylcyclooctatetraene[6], are known to form *cis* as well as *trans* dimetal complexes, a phenomenon which would also be expected to be observed with heptalenes. In this context we have resumed study of the metal complexation of heptalenes and in this paper we report on the synthesis, characterization and X-ray structure analysis of both *cis*- and *trans*-diiron complexes of the readily accessible 1,6-dimethylheptalene (**2**)[7].

Results and Discussion

The reaction of **2** with an excess of enneacarbonyldiiron $[Fe_2(CO)_9]$ in dry acetone affords a mixture of the metal complexes **3** and **4a, b** (Scheme I, Table 1), which can be separated by column chromatography in a ratio of 4:2:1 in yields up to 63%. Compounds **4a** and **4b** were isolated after recrystallization as deep orange and deep violet needles, respectively. The resulting monotricarbonyliron complex **3** was obtained as a violet microcrystalline solid. The iron complexes were characterized by elemental analysis as well as by mass, IR, UV and NMR spectral data.

Scheme 1

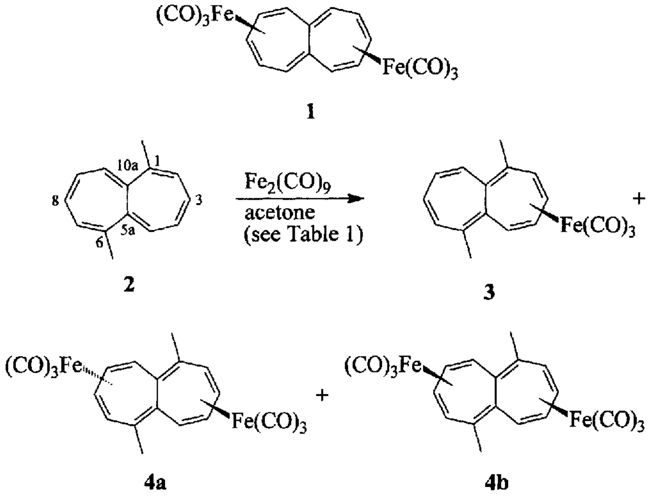

Table 1. Reaction parameters for the synthesis of **3** and **4a, b** from **2**

entry	ratio $Fe_2(CO)_9$: **2**	reaction period	**2**	**3**	*trans*-**4a**	*cis*-**4b**
1	8:1	4d	63%	-	9%	3%
2	8:1	7d	40%	-	19%	6%
3	12:1	7d	23%	40%	15%	8%
4	16:1	7d	10%	9%	15%	2%

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Due to the π-bond fixation of heptalenes in the ground state[2a–e] two nonequivalent bond shift isomers of **2** should exist. However, at room temperature, only the isomer **2**[8] depicted in Scheme 1 is observed; this was established by NMR on the basis of $^1H-^1H$ coupling constants[7]. Examination of models indicates that a smaller steric interaction between the substituents at the *peri*-positions may be the reason why only this bond shift isomer is observed. Detailed analysis of the NMR spectra of the iron complexes **3** and **4a**, **b** confirms their heptalene ligands to be the π-bond isomer of **2**. NMR resonances of tricarbonyliron complexed nuclei are found to be significantly shifted upfield compared with those of the uncomplexed compounds, the terminal nuclei of the complexed unit being more shielded than the internal. The NMR data of the complexes **3** and **4a**, **b** are typical for such systems. In the case of **4a** two doublets are observed, at $\delta = 3.02$ and $\delta = 3.65$, which are due to the terminal ring protons (2,5-H, 7,10-H). These are strongly shifted to higher magnetic field, compared to the corresponding protons of the free ligand **2** ($\Delta\delta = -2.63$ and $\Delta\delta = -2.35$). The signals of the internal ring protons (3,4-H, 8,9-H) result in a multiplet at $\delta = 5.40$ and show the expected lower upfield shift ($\Delta\delta = -0.7$ to -1.0). However, the ^1H-NMR spectrum of **4b** shows four separate ring proton signals. The terminal ring protons of **4b**, as well as those of the methyl groups, are, in contrast to some of the internal protons, more strongly shielded ($\delta = 2.81$ and $\delta = 3.39$) than those in **4a**. One resonance of the internal protons is found at $\delta = 5.60$, attributable to a less shielded internal proton, while another resonance at $\delta = 5.27$ represents a more strongly shielded internal proton than those in **4a**. This observation indicates a less symmetrical arrangement of the $Fe(CO)_3$ groups with respect to the butadiene moieties in **4b** as compared to those of **4a**. On the basis of ^1H-NMR data, no statement can be made with regard to the positions of the double bonds. The ^{13}C-NMR spectra of **3** and **4a**, **b** show four signals shifted upfield as compared to those of the free ligand **2**, which correspond to metal complexed carbon atoms. Polarization transfer experiments (DEPT) of the metal complexes reveal that only proton-coupled carbon nuclei are shielded. The signals of C-1 and C-5a as well as C-6 and C-10a show no upfield shift, which is only compatible with the structures **3** and **4a**, **b**. These structures should be preferred on steric grounds, as a π-bond shift of **2** may give rise to a larger distance between the $Fe(CO)_3$ moieties and the methyl groups.

X-ray Structural Analyses of 4a and 4b

The molecular structures of triclinic **4a** and monoclinic **4b** are depicted in Figures 1 and 2. In both cases the carbocycle is twofold η^4-ligated to separate $Fe(CO_3)$ groups and the iron atoms are present in a tetragonal pyramidal environment. The X-ray structure analyses confirm the location of the double bonds derived from the NMR data as described above. In compound **4a** the $Fe(CO)_3$ fragments are positioned on opposite sides of the ring plane, complexing the two terminal butadiene moieties. Between the complexed units the remaining *s-trans*-2,4-hexadiene system, together with C6, C6a, C9 and C9a, forms a slightly twisted internal region with a maximal deviation from the best plane of 0.122(2) Å for C9 and C9a. This plane and the planes formed by the complexed units enclose interplanar angles of 139.7(1)° and −139.7(1)°, respectively. In this way, **4a** displays an unusual chair-like conformation which has not previously been observed for the heptalene system. The C−C bond distances in the carbocycle **4a** are found to range between 1.391(4) Å and 1.484(4) Å (except for C7−C10 = 1.512(4) Å) and are in very good agreement with those in **1**[3]. The length of the C4−C5 bond is 1.391(4) Å and represents the shortest C−C bond in the bicyclic compound. The corresponding value in **1** amounts to 1.393 Å.

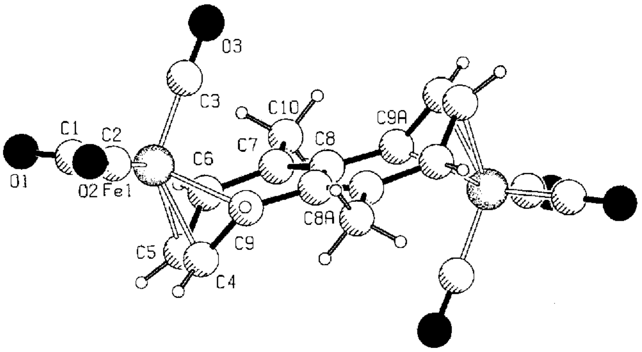

Figure 1. Crystal structure of *trans*-**4a**. The numbering of the atoms does not correspond to the nomenclature. Selected bond lengths [Å]: Fe−Fe 6.545(1), Fe−C1 1.803(3), Fe−C2 1.791(3), Fe−C3 1.784(3), Fe−C4 2.052(3), Fe−C5 2.049(3), Fe−C6 2.113(3), Fe−C9a 2.134(3), C8-C8a 1.474(5), C8a−C9 1.484(4), C9-C4 1.431(4), C4−C5 1.391(4), C5−C6 1.428(4), C6−C7 1.476(4), C7−C8 1.357(4). − Selccted bond angles [°]: C1−Fe−C2 91.18(13), C1−Fe−C3 100.83(13), C2−Fe−C3 100.83(14), C8a−C9a−C4 127.5(2), C9a−C4−C5 118.2(3), C4−C5−C6 118.7(3), C5−C6−C7 129.6(2), C6−C7−C8 126.5(2), C7−C8−C8a 122.6(3), C8−C8a−C9a 120.9(3)

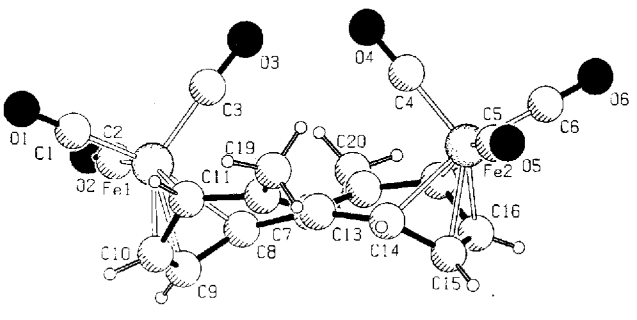

Figure 2. Crystal structure of *cis*-**4b**. The numbering of the atoms does not correspond to the nomenclature. Selected bond lengths [Å]: Fe1−Fc2 6.167(1), Fe1−C1 1.789(4), Fe1−C2 1.791(3), Fe1−C3 1.787(3), Fe2−C14 2.131(3), Fe2−C15 2.060(3), Fe2−C16 2.042(3), Fe2−C17 2.144(3), C7−C8 1.475(4), C8−C9 1.430(5), C9−C10 1.362(5), C10−C11 1.426(5), C11−C12 1.475(4), C12−C13 1.347(5), C13−C7 1.471(4). − Selected bond angles [°]: C1−Fe−C2 90.0(2), C1−Fe−C2 102.6(2), C2−Fe−C3 101.0(2), C7−C8−C9 129.1(3), C8−C9−C10 121.5(3), C9−C10−C11 119.1(3), C10−C11−C12 124.4(3), C11−C12−C13 126.9(3), C12−C13−C7 121.4(2), C13−C7−C8 120.4(3)

The structure of **4b** shows great resemblance to that established earlier for **1**. The $Fe(CO)_3$ groups proved both to be on the same side of the carbocycle. In marked contrast to **4a**, the structure of **4b** reveals a C_2 symmetry of the doubly complexed bicycle with two annelated seven-membered rings in a boat conformation. The two complexed butadiene units are orientated almost perpendicularly towards each other [dihedral angle: 87.4(1)°], whereas those of **4a** are coplanar. The carbon atoms of the central *s-trans*-2,4-hexadiene system are not in a plane, but a dihedral angle C18−C7−C13−C12 of −142.9(3)° is found. The C−C bond lengths are comparable to those in **1** and **4a**. However, the shortest C−C bonds, the central bonds of the complexed units, amount to 1.362(5) Å and 1.388(5) Å and are therefore remarkably shorter than those observed in **1** and **4a**. The iron−iron distance in **4b** [6.167(1) Å] resembles that encountered in **1** [6.21(1) Å] and differs from that in **4a** [6.545(1) Å].

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Experimental

Solvents were distilled from appropriate drying agents before use. Enneacarbonyldiiron[9] and **2**[7] were prepared according to literature procedures. – IR: Perkin Elmer FT-IR Paragon 1000PC. – UV: Beckman DK-2A, UV 5240. – Elemental analyses: Perkin Elmer CHN 240 B. – NMR: Bruker WM 300, AC 300, ARX 300 (300 MHz and 75.47 MHz for ^{1}H and ^{13}C, respectively) ^{1}H- and ^{13}C NMR spectra were recorded in $CDCl_3$ with TMS as internal standard. – MS: Finnigan MAT 311-A/100 MS. – Column chromatography: basic alumina [activity BII−III (Brockmann) ICN Biomedicals]. – Melting points: Kofler apparatus (Reichert, Vienna, Austria).

Preparation of Complexes **3** *and* **4a, b**: Solid $Fe_2(CO)_9$ (8.0 g, 22 mmol) was added under dry nitrogen to a solution of 500 mg (2.75 mmol) 1,6-dimethylheptalene (**2**) in 200 ml acetone. After the reaction mixture had been stirred for 4 d at room temp., an additional 4.0 g (11 mmol) $Fe_2(CO)_9$ was added. After further stirring for 3 d, the mixture was filtered through alumina, using *n*-hexane as eluent. The volatile components were evaporated in vacuo at 25 °C and to the red-brown residue 20 ml *n*-hexane was added. The orange-red precipitate was separated by filtration, washed twice with 5 ml *n*-hexane and dried in vacuo to give 65 mg (5%) of **4a** (identical with band 3 of the chromatography described below). The filtrate, together with the mother liquor, was evaporated and the residue was submitted to column chromatography with *n*-hexane on alumina. A yellow band was eluted first to give 113 mg (23%) of unreacted **2**. Then **3** was eluted, followed by *trans*-**4a** and finally *cis*-**4b**.

Tricarbonyl(1,6-dimethylheptalene)iron (**3**): Violet solid, yield 350 mg (40%), m.p. 30−31 °C (dec.). – IR ($CHCl_3$): $\tilde{\nu}$ = 2045 cm^{-1} (s), 1985 (s), 1601 (w). – UV (CH_2Cl_2): λ_{max} (lg ε) = 281 nm (4.12), 331 (4.00). – ^{1}H NMR ($CDCl_3$): δ = 1.81 (s, 3H, 1-CH_3), 2.04 (s, 3H, 6-CH_3), 3.15 (br. s, 1H, 2-H), 3.89 (br. s, 1H, 5-H), 5.07 (br. s, 1H, 3- or 4-H), 5.58 (br. s, 1H, 3- or 4-H), 5.79 (br. s, 1H, 10-H), 6.05 (br. dd, ^3J = 11.25 Hz, ^3J = 11.1 Hz, 2H, 8- and 9-H), 6.24 (br. s, 1H, 7-H). – ^{13}C NMR ($CDCl_3$): δ = 23.0 (1-CH_3), 23.7 (6-CH_3), 57.7 (C-2), 65.2 (C-5), 86.9 (C-3 or C-4), 88.3 (C-3 or C-4), 123.8 (C_{quat}), 125.3 (C-8 or C-9), 126.3 (C-8 or C-9), 128.2 (C_{quat}), 129.8 (C-10), 136.2 (C-7), 211.4 (CO). – MS (70 eV); *m/z* (%): 322 (6) [M$^+$], 294 (24) [M$^+$ − CO], 266 (20) [M$^+$ − 2 CO], 238 (100) [M$^+$ − 3 CO], 210 (18) [M$^+$ − $Fe(CO)_2$], 182 (9) [M$^+$ − $Fe(CO)_3$]. – $C_{17}H_{14}FeO_3$ (322.1): calcd. C 63.38, H 4.38; found C 63.79, H 4.84.

trans-(μ-1,6-Dimethylheptalene)bis(tricarbonyliron) (**4a**): Deep orange crystals, yield 190 mg (15%), m.p. 179−180 °C (dec.) (benzene). – IR (KBr): $\tilde{\nu}$ = 2036 cm^{-1} (s), 1973 (s), 1948 (s), 1213 (w), 868 (w), 606 (s), 576 (m), 559 (m). – UV (CH_2Cl_2): λ_{max} (lg ε) = 285 nm (4.21), 330 (4.21), 442 (3.98). – ^{1}H NMR ($CDCl_3$): δ = 1.96 (s, 6H, CH_3), 3.02 (dm$_c$, ^3J = 6 Hz, 2H, 2- and 7-H), 3.65 (dm$_c$, ^3J = 6 Hz, 2H, 5- and 10-H), 5.40 (m$_c$, 4H, 3-, 4-, 8-, and 9-H). – ^{13}C NMR ($CDCl_3$): δ = 26.6 (CH_3), 62.5 (C-5 and C-10), 65.5 (C-2 and C-7), 87.9 (C-3 and C-8 or C-4 and C-9), 91.44 (C-3 and C-8 or C-4 and C-9), 126.3 (C_{quat}), 134.7 (C_{quat}), 211.8 (CO). – MS (70 eV); *m/z* (%): 434 (43) [M$^+$ − CO], 406 (6) [M$^+$ − 2 CO], 378 (30) [M$^+$ − 3 CO], 350 (57) [M$^+$ − 4 CO], 322 (52) [M$^+$ − 5 CO], 294 (100) [M$^+$ − 6 CO]. – $C_{20}H_{14}Fe_2O_6$ (462.0): calcd. C 51.99, H 3.05; found C 51.84, H 3.09.

cis-(μ-1,6-Dimethylheptalene)bis(tricarbonyliron) (**4b**): Deep violet crystals, yield 100 mg (8%), m.p. 164−166 °C (dec.) (*n*-hexane/CH_2Cl_2). – IR (KBr): $\tilde{\nu}$ = 2050 cm^{-1} (s), 2025 (s), 2004 (s), 1950 (s), 864 (w), 637 (w), 607 (m), 552 (m). – UV (CH_2Cl_2): λ_{max} (lg ε) = 289 nm (4.17), 348 (4.35), 451 (3.86). – ^{1}H NMR ($CDCl_3$): δ = 1.83 (s, 6H, CH_3), 2.81 (dd, ^3J = 7.2 Hz, ^4J = 1.1 Hz, 2H, 2- and 7-H), 3.39 (d, ^3J = 7.8 Hz, 2H, 5- and 10-H), 5.27 (ddd, ^3J = 7.5 Hz, ^3J = 4.5 Hz, ^4J = 1.1 Hz, 2H, 4- and 9-H), 5.60 (dd, ^3J = 6.6 Hz, ^3J = 4.7 Hz, 2H, 3- and 8-H). – ^{13}C NMR ($CDCl_3$): δ = 24.9 (CH_3), 59.6 (C-2 and C-7), 60.6 (C-5 and C-10), 87.1 (C-4 and C-9), 88.7 (C-3 and C-8), 129.5 (C_{quat}), 136.3 (C_{quat}), 210.4 (CO). – MS (70 eV); *m/z* (%): 462 (6) [M$^+$], 434 (16) [M$^+$ − CO], 406 (16) [M$^+$ − 2 CO], 378 (16) [M$^+$ − 3 CO], 350 (44) [M$^+$ − 4 CO], 322 (88) [M$^+$ − 5 CO], 294 (100) [M$^+$ − 6 CO]. – $C_{20}H_{14}Fe_2O_6$ (462.0): calcd. C 51.99, H 3.05; found C 52.07, H 2.99.

X-ray Crystallographic Studies[10]: Crystal data are presented in Table 2. Orange-red crystals of **4a** suitable for X-ray diffraction were grown from a concentrated solution of **4a** in benzene at room temp.; violet needles of **4b** were crystallized from an *n*-hexane/dichloromethane solution at room temp. The intensity data were

Table 2. Crystallographic data

compound	**4a**	**4b**
Formula	$C_{20}H_{14}Fe_2O_6$	$C_{20}H_{14}Fe_2O_6$
M [g mol^{-1}]	462.04	462.04
Space group	P -1	P21/n
Crystal system	triclinic	monoclinic
Crystal size, [mm]	1.25 x 0.5 x 0.35	0.5 x 0.3 x 0.1
a [Å]	6.6648 (7)	9.163 (2)
b [Å]	6.721 (2)	10.277 (2)
c [Å]	10.738 (1)	20.122 (4)
α [°]	93.30 (2)	90
β [°]	103.00 (1)	98.37 (2)
γ [°]	102.40 (2)	90
V [Å^3]	454.9 (2)	1874.7 (7)
Z	1	4
$D_{calcd.}$ [Mg m^{-3}]	1.687	1.637
F(000)	234	936
μ [mm^{-1}]	1.65	1.65
Measurement range	$1.96 < \Theta < 22.97$	$2.05 < \Theta < 22.98$
No. of rflns. measured	2073	5185
No. of indpt. rflns.	1270	2595
R_{int}	0.0368	0.0948
R1	0.0357	0.0441
wR2	0.1001	0.0729
no. of parameters	155	277
largest diff. peak	0.560	0.671
and hole [eÅ^{-3}]	- 0.605	- 1.174

collected with a Enraf-Nonius CAD4 diffractometer (Mo-K_α radiation, graphite monochromator). The structures were solved by direct methods using the SHELXS-86[11] and subjected to full-matrix least-squares refinement techniques based on F^2 (SHELXL-93)[12]. All hydrogens were found by difference Fourier synthesis, with the exception of 19-H and 20-H of **4b**, which are positioned in ideal geometry.

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