

STRUCTURE AND FLUXIONAL BEHAVIOUR OF HEPTALENEIRONTRICARBONYL  
AND HEPTALENEBIS(IRONTRICARBONYL)

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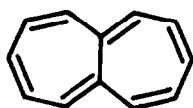
**Abstract** - The synthesis of heptaleneirontricarbonyl (**4**) is described. The structures of **4** and of the closely related heptalenebis(irontricarbonyl) (**3**) are elucidated by NMR spectroscopy (<sup>1</sup>H and <sup>13</sup>C) and by X-ray crystallography. Compounds **3** and **4** are shown by dynamic NMR to undergo an isodynamic 1,2-migration of the Fe(CO)<sub>3</sub>-groups as well as a carbonyl scrambling. The relevant kinetic data allow for a mechanistic discussion of the dynamics and a comparison with other irontricarbonyl complexes.

### Introduction

The bicyclic 12π-system heptalene (**1**)<sup>1,2</sup> has long been the subject of both theoretical and spectroscopic studies. The points of issue are (i) whether or not the molecule possesses π-bond fixation in its ground state,<sup>2,3</sup> (ii) what is the energy difference between π-bond delocalized and π-bond localized structures,<sup>4</sup> and (iii) what is the conformation of the π-system.<sup>5</sup>

Making use of <sup>13</sup>C NMR spectroscopy we succeeded in establishing the C<sub>2v</sub>-symmetry of the molecule which thus must exist as a π-bond localized species.<sup>2,4</sup> The measurements had to be performed at temperatures below -150 °C, since at higher temperatures a rapid π-bond shift occurs. The dynamic process, if rapid within the NMR-time scale, renders a C<sub>2v</sub> symmetry to the molecule and obscures the verification of a double-minimum potential. The very low activation barrier of the π-bond shift process (≈ 4 kcal/mol) characterizes **1** as being subject to a Pseudo-Jahn-Teller-distortion.<sup>3</sup>

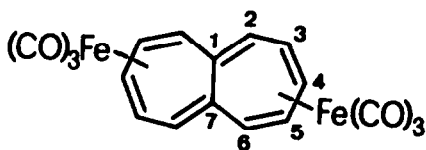
Simple MO arguments point out that the bicyclic molecule heptalene can be treated as a perturbed [12]annulene.<sup>6</sup> It is therefore not surprising that the properties of **1** reveal a close analogy both with the "true" [12]annulenes and with the lower annulene homologue cyclooctatetraene (**2**). Heptalene, in close similarity to **2**,<sup>7</sup> can be reduced electrochemically at rather low potentials to yield a radical anion<sup>8</sup> and a dianion.<sup>9</sup> The ions are characterized via convincing ESR and NMR spectroscopic evidence as π-bond delocalized species with essentially planar



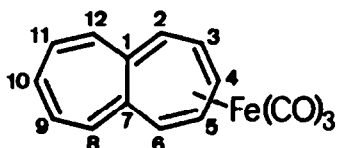
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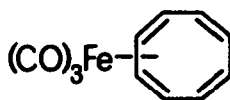
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3



4



5

$\pi$ -perimeters. The profound structural changes that can be brought about by these electron transfer processes are also documented by the high thermal stability of the heptalene dianion in contrast to the low persistence of the neutral compound.

In dealing with the outstanding properties of ionic heptalene species we have been looking for alternative modes of modifying, and perhaps stabilizing the heptalene  $\pi$ -system. Guided again by experience from the cyclooctatetraene field, namely the interesting static and dynamic properties of cyclooctatetraene-irontricarbonyl (5),<sup>10-13</sup> we considered analogous complexes containing heptalene as ligand. In a preliminary paper we reported the synthesis of heptalenebis(irontricarbonyl) (3).<sup>14</sup> When analyzing the structure of (3) an inclusion of the heptaleneirontricarbonyl (4) appeared promising. The successful synthesis of the latter enabled us to comparatively study the structure and the fluxional behaviour of both title complexes 3 and 4. It appears from our <sup>13</sup>C and <sup>1</sup>H NMR spectroscopic work that the information on the heptalene complexes is obtained in a much more straightforward manner than in the cyclooctatetraene case.

While the crystal structure of 3 has already been described in the literature<sup>15</sup> we report herein the outcome of our X-ray crystallographic studies of 4. The structural description of the molecules both in solution and in the crystalline state provides essentially analogous results.

### Experimental Section

**Syntheses.** Compound 3 has been prepared using the method described earlier.<sup>14</sup> The synthesis of 4 went as follows:

In a Schlenk tube fitted with magnetic stirrer and cooled in an ice bath, a solution of 650 mg (1.5 mmol) heptalenebis(irontricarbonyl) and 830 mg (7.5 mmol) trimethylamine-N-oxide dihydrate in 100 ml acetone were stirred under argon. After 48 hours, 10 g of alumina was added and the solvent removed *in vacuo* (rotary evaporator). Column chromatography (Woelm neutral alumina, activity grade 3 / pentane), collection of the olive green band and removal of the solvent (rotary evaporator) gave 159 mg (36 % based on starting complex) of an essentially pure olive green solid. Collection of the red band and removal of the solvent (rotary evaporator) gave 200 mg recovered crystalline heptalenebis(irontricarbonyl).

Recrystallization from hexane of the olive green solid in a double Schlenk tube (argon!) gave 140 mg (32 % based on starting complex, 46 % on complex consumed) of moderately air stable (decomposition noticeable after two days in air) black needles; m.p. 96-97 °C (dec.). <sup>1</sup>H NMR and <sup>13</sup>C NMR see Table 1; MS (70 ev): m/z 294 (M<sup>+</sup>, 6 %), 266 (M<sup>+</sup>-CO, 20), 238 (M<sup>+</sup>-2CO, 11), 210 (M<sup>+</sup>-3CO, 40), 154 (M<sup>+</sup>-Fe(CO)<sub>3</sub>, 15), 128 (M<sup>+</sup>-Fe(CO)<sub>3</sub>-C<sub>2</sub>H<sub>2</sub>, 70), 56 (Fe<sup>+</sup>, 100); IR (CsI): 3030, 2035, 1993, 1550

$\text{cm}^{-1}$ ; UV/VIS (cyclohexane)  $\lambda_{\text{max}} = 245 \text{ nm}$  ( $\epsilon = 18300$ ) sh, 296 (21800), 460 (3000) sh. Anal. Calcd for  $\text{C}_{15}\text{H}_{10}\text{FeO}_3$ : C, 61.26; H, 3.43. Found: C, 61.40; H, 3.71.

NMR measurements. The  $^1\text{H}$  NMR spectra were recorded on a Varian EM390-spectrometer (CW-mode) (in particular for high-temperature measurements of 3) and on a Bruker WP60-spectrometer (FT-mode). In the former case the temperatures were measured both with a thermocouple and by using the calibrated resonances of an ethylene glycol test tube. The temperatures determined by each method were in agreement and constant within  $\pm 1^\circ\text{C}$ .

Table 1  $^1\text{H}$  ( $\delta_{\text{H}}$ ) and  $^{13}\text{C}$  ( $\delta_{\text{C}}$ ) NMR chemical shifts, and H,H-coupling constants [Hz] of 3 and 4 <sup>a)</sup>

	<u>3</u>	<u>4</u>		<u>3</u>	<u>4</u>
$\delta$ (H-2)	6.04	5.47	$J_{2,3}$	8.42	8.76
$\delta$ (H-3)	2.98	3.47	$J_{2,4}$	0.15	0.17
$\delta$ (H-4)	5.56	4.95	$J_{2,5}$	0.00	0.03
$\delta$ (H-5)	5.31	4.95	$J_{2,6}$	0.16	0.45
$\delta$ (H-6)	3.38	4.05	$J_{3,4}$	7.26	7.60
$\delta$ (H-8-H-12)		$\approx 5.9$	$J_{3,5}$	1.46	1.42
			$J_{3,6}$	-0.01	-0.02
			$J_{4,5}$	4.54	4.77
			$J_{4,6}$	1.35	1.37
			$J_{5,6}$	7.85	7.85

	<u>3</u>	<u>4</u>
$\delta$ (C-1)	132.4	146.2
$\delta$ (C-2)	133.0	124.1
$\delta$ (C-3)	57.1	60.7
$\delta$ (C-4)	92.4	90.9
$\delta$ (C-5)	86.3	87.2
$\delta$ (C-6)	67.6	71.4
$\delta$ (C-carbonyl)	210.5, 210.7, 215.2	213.4, 213.8, 214.6
$\delta$ (C-7)		134.0
$\delta$ (C-10)		131.1
$\delta$ (C-8, C-12)		142.3, 130.8
$\delta$ (C-9, C-11)		129.4, 124.9

a)  $\delta_{\text{H}}$ : 60 MHz; tetramethylsilane as internal reference; 0.05 molar in  $\text{CD}_2\text{Cl}_2/\text{CF}_2\text{Br}_2$  (1:1);  $0^\circ\text{C}$  for 3,  $-75^\circ\text{C}$  for 4.  $\delta_{\text{C}}$ : 20 MHz;  $[\text{D}_8]$ -THF;  $-70^\circ\text{C}$ , ( $-120^\circ\text{C}$  for C-carbonyl) for 3 and 4. Details are given in the Experimental Section.

The  $^{13}\text{C}$  NMR spectra were taken on a Varian CFT20-spectrometer at 20 MHz. The detection of the carbonyl resonances at low field required a spectral width of 6000 Hz. During the low-temperature experiments for 4, tip angles between  $15^\circ$  and  $20^\circ$  were applied and ca. 6000 transients were accumulated. The  $^{13}\text{C}$  NMR measurements for 3 required a much greater number of scans. Signal assignments were obtained by selective  $^1\text{H}$ -decoupling experiments except for the non-complexed unit of 4 where the  $^1\text{H}$  NMR resonances strongly overlap.

The  $^{13}\text{C}$  NMR spectra of 4 ( $-110^\circ\text{C}$  to  $+60^\circ\text{C}$ ) were recorded for degassed solutions in  $[\text{D}_8]$ -tetrahydrofuran (THF) (sealed 8 mm-tubes), those ones of 3 ( $+30$

$^{\circ}\text{C}$  to  $+90\text{ }^{\circ}\text{C}$ ) in  $[\text{D}_8]$ -THF and  $[\text{D}_8]$ -toluene, respectively. At elevated temperatures rapid decomposition of 3 occurred in halogenated solvents. The  $^1\text{H}$  NMR measurements of 3 at elevated temperatures were performed as two separate series either in  $[\text{D}_{14}]$ -diglyme or in molten  $[\text{D}_8]$ -naphthalene using a  $[\text{D}_6]$ -benzene lock. In the latter case the solvent crystallized before the slow exchange domain was obtained. In order to determine "static" spectral data for simulation purposes,  $[\text{D}_6]$ -benzene was added to the  $[\text{D}_8]$ -naphthalene system which allowed measurements at room temperature. On benzene addition the signal of H-6 was shifted downfield while the other resonances remained unaffected. No significant temperature dependence of the chemical shifts could be observed so that in the simulation of exchange-broadened spectra the "static" resonance frequencies were kept constant. The temperature-dependent  $^{13}\text{C}$  NMR chemical shifts of 4 were determined for temperatures below  $-75\text{ }^{\circ}\text{C}$  (slow-exchange domain) and "corrected" resonance frequencies within the exchange domain were obtained via extrapolation. When matching the  $^{13}\text{C}$  NMR lineshapes of 4 the natural line widths for the particular temperatures could simply be determined from those signals (C-4, C-10, see below) not being affected by dynamic broadening.

The lineshape analyses were performed with the aid of the computer program DNMRIT<sup>16</sup> which has been written and kindly made available by J. Heinzer. DNMRIT is applicable to the strongly coupled spin system of 4. In the case of 4 the subspectra stemming from the complexed and uncomplexed  $\pi$ -fragment have been dealt with separately.

The kinetic parameters obtained from an Arrhenius-plot are given in Table 2. The errors quoted were calculated assuming rate constant errors of  $\pm 20\%$  3 and  $\pm 10\%$  4, and temperature errors of  $\pm 1\text{ }^{\circ}\text{C}$ .

The  $^1\text{H}$  NMR data of 3 and 4 presented in Table 1 were obtained from an exact analysis with the aid of the simulation program ITRCAL (Bruker, BNC 28). RMS errors are  $0.20\text{ Hz}$  3 and  $0.14\text{ Hz}$  4.

Crystallographic measurements.<sup>35)</sup> The intensity data were collected on an Enraf-Nonius CAD-4 four cycle diffractometer by the  $\omega$ -2 $\theta$  scan mode, with MoK $\alpha$ -radiation and graphite monochromator. Unit cell parameters were precisely determined by least squares refinement of 25 reflections. The non-hydrogen atoms were located by using the direct method and refined by full-matrix least squares technique with anisotropic thermal parameters. Hydrogen atoms were obtained from a difference Fourier map. All calculations were performed on a PDP 11/23 minicomputer with the use of the SDP system of Enraf-Nonius.

#### The Structure of 3 and 4.

The  $^{13}\text{C}$  NMR spectrum of 3 at room temperature exhibits 7 signals (see Table 1). Apart from the resonance at  $\delta$  212, which can easily be assigned to the (equivalent) carbonyl carbons, there is a distinct shift difference between 4 high-field signals and 2 signals in the olefinic part of the spectrum. It is clear from ample  $^{13}\text{C}$  NMR spectroscopic experience, namely from a comparison with cyclooctatetraeneirontricarbonyl (5),<sup>17</sup> that the complex is of a (1-4) tetrahapto type. Moreover, one easily concludes from the number of signals that the complex having heptalene attached to two  $\text{Fe}(\text{CO})_3$ -groups maintains a  $\text{C}_2$  axis within the hydrocarbon framework. Structures without symmetry can safely be excluded. Off-resonance- $^1\text{H}$ -decoupling experiments indicate the quaternary carbons C-1 (C-7) to resonate essentially in the olefinic region and thus not to be involved in a complexed diene moiety. Consequently, one is left with 3 as only acceptable structure.

Both findings,  $\text{C}_2$ -symmetry and  $\eta^4$ -complexation, are also borne out by an analysis of the (room temperature)  $^1\text{H}$  NMR spectrum (Table 1) of 3. It shows 5 well

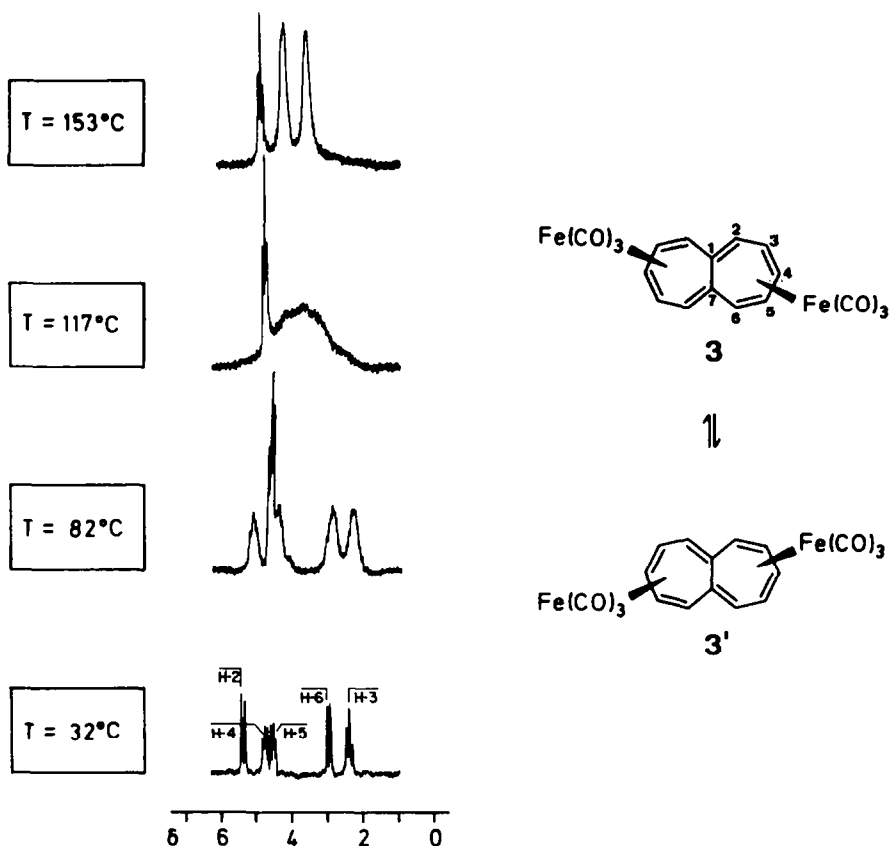


Figure 1.  $^1\text{H}$  NMR spectra of **3** (90 MHz,  $[\text{D}_8]$ -naphthalene/ $[\text{D}_6]$ -benzene) at different temperatures.

separated, equally intense signals of which three (at  $\delta$  6.04, 5.56, and 5.31) appear at much lower field than the remaining ones ( $\delta$  2.98 and 3.38). Within a simple first-order treatment signal assignments can be deduced from decoupling experiments; irradiating the triplet-signal at  $\delta$  5.56 modifies the triplet at  $\delta$  2.98 to a doublet, leaving the doublet resonance at  $\delta$  3.38 unchanged. On irradiation with the resonance frequency of the signal at  $\delta$  5.31 the doublet at  $\delta$  3.38 collapses to a singlet. Finally, irradiating the triplet resonance at  $\delta$  2.98 causes the triplet at  $\delta$  5.56 to appear as a doublet and the doublet at  $\delta$  6.04 as a singlet. The resulting  $^1\text{H}$ -signal assignments nicely support the conclusions obtained from other  $\eta^4$ -complexes: complexation moves upfield the relevant  $^1\text{H}$  NMR signals whereby the "terminal" protons within the complexed diene moiety (H-3, H-6) resonate at significantly higher field than the "inner" ones (H-4, H-5).

An exact analysis of the  $^1\text{H}$  NMR spectrum provides the H,H-coupling constants which are also reported in Table 1. The lowering of the vicinal coupling constants within the diene ligand is completely analogous to the situation known for butadieneirontricarbonyl.<sup>18</sup> It also appears characteristic that consecutive coupling constants significantly alternate in magnitude.

Having identified the individual  $^1\text{H}$  NMR signals one can achieve the  $^{13}\text{C}$ -signal assignments via selective  $^1\text{H}$ -decoupling experiments. The results are in agreement with the well established fact that on complexation of the diene  $\pi$ -system the carbon resonances experience a significant upfield shift which is higher for the terminal carbons.

What cannot be deduced from the spectroscopic data outlined above is whether or not the two  $\text{Fe}(\text{CO})_3$ -groups are localized on one side of the  $\pi$ -system. On the other hand, since our structural description of **3** in solution is in complete accord with the results of an X-ray analysis<sup>15</sup>, we can assume that the

Table 2 Activation parameters for the 1,2-Fe(CO)<sub>3</sub>-migration in 3 and 4

	$E_a \left[ \frac{\text{kcal}}{\text{mol}} \right]$	$\Delta H^\ddagger \left[ \frac{\text{kcal}}{\text{mol}} \right]$	$\Delta S^\ddagger \left[ \frac{\text{cal}}{\text{grad.mol}} \right]$	$\Delta G^\ddagger \left[ \frac{\text{kcal}}{\text{mol}} \right]$	$\theta \text{ } ^\circ\text{C}$
<u>3</u> <sup>a)</sup>	24.3 ± 0.6	24.0 ± 0.6	15.1 ± 1.6	19.8 ± 0.1	
<u>3</u> <sup>b)</sup>	18.9 ± 0.8	18.1 ± 1.0	0.7 ± 1.0	17.8 ± 0.1	
<u>4</u> <sup>c)</sup>	10.8 ± 0.2	10.3 ± 0.2	-4.2 ± 0.6	11.4 ± 0.1	

a) <sup>1</sup>H NMR in [D<sub>10</sub>]-naphthalene; b) <sup>1</sup>H NMR in [D<sub>14</sub>]-diglyme; c) <sup>13</sup>C NMR in [D<sub>8</sub>]-THF. Details are given in the Experimental Section.

irontricarbonyl-units are positioned on the same side of the heptalene framework. The crystal structure of 3 possesses a C<sub>2</sub> symmetry of the hydrocarbon and the two iron atoms with a maximal deviation of 0.01 Å. A double-boat structure is formed in which the two complexed butadiene units are twisted with respect to a rather flat internal (non-complexed) region (see below).

A NMR spectroscopic study of the "mono-complex" heptaleneirontricarbonyl (4) is complicated by the fact that the room-temperature spectra exhibit severe line-broadening as a consequence of some fluxional behaviour. While these effects will be dealt with later we mention here that the structural elucidation relies on spectra taken below -70 °C, i.e. within the slow-exchange limit of the dynamic process.

There are 13 <sup>13</sup>C NMR signals, one for the carbonyl resonance and one for any heptalene carbon: here again the resonances of 4 proton-bearing carbons (see Figure 2 and Table 1) at much higher field than the remaining ones are only compatible with structure 4.

Among the four multiplet signals observed within the <sup>1</sup>H NMR spectrum (see Figure 3) the high-field resonances at δ 3.47 and δ 4.05 can safely be assigned to H-3 and H-6, respectively. Decoupling experiments indicate that H-4 and H-5 both absorb at δ 4.95. The signal of the "olefinic" proton H-2 can be found (via irradiation at the H-3 resonance) at δ 5.47.

An exact analysis was performed for the subspectrum of the 5-spin system within the complexed ring. Although spin-spin couplings between protons of different rings have been neglected the parameters given in Table 1 allow for a satisfactory simulation of the experimental spectrum. The vicinal coupling constants appear to be quite similar to those in 3. This result indicates, again, that the structure of the complexed seven-membered ring is quite similar in both 3 and 4. Within the complexed diene unit of 4 the inner protons resonate downfield from the terminal ones, and all nuclei are significantly more shielded than those of the uncomplexed part. Inspection of Table 1 reveals that both effects are much more pronounced in 3. Analogous findings hold for a comparison of the <sup>13</sup>C NMR chemical shifts.

The crystal structure of 4 (see Figure 4 and Table 3) determined in this work, fully supports the NMR analysis and also reveals the analogy with 3. The non-complexed π-system of 4 does not deviate significantly from coplanarity, and the bond length alternation within the trans-butadiene unit C-2, C-1, C-7, C-8

(1.35, 1.48 Å) corresponds to that of butadiene itself (1.34, 1.47 Å).<sup>19</sup> The bond lengths and bond angles within the complexed butadiene moiety (see Table 3)<sup>35</sup> are rather similar to those found in related complexes.<sup>15,19-22</sup> The threefold symmetry of the Fe(CO)<sub>3</sub>-group is severely perturbed: while one bond angle formed between the carbonyl carbons and the iron is reduced to about 92°, the other ones are increased to 101°.

Table 3 a) Bond distances [Å] and b) bond angles [degrees] of 4.<sup>a)</sup>

a)											
C1	C2	1.345(5)	C5	C6	1.419(5)	FE	C13	1.788(4)			
C1	C12	1.453(5)	C6	C7	1.473(5)	FE	C14	1.781(4)			
C1	C7	1.475(5)	C7	C8	1.351(5)	FE	C15	1.798(4)			
C2	C3	1.442(5)	C8	C9	1.437(6)	C13	O1	1.137(5)			
C3	C4	1.412(5)	C9	C10	1.329(7)	C14	O2	1.149(5)			
C4	C5	1.384(6)	C10	C11	1.392(7)	C15	O3	1.136(5)			
			C11	C12	1.326(6)						
b)											
C7	C1	C12	122.5(3)	C8	C7	C1	125.3(3)	C13	FE	C14	101.2(2)
C7	C1	C2	121.1(3)	C8	C7	C6	114.1(3)	C13	FE	C15	101.2(2)
C12	C1	C2	116.2(4)	C1	C7	C6	120.6(3)	C14	FE	C15	91.7(2)
C1	C2	C3	132.0(3)	C7	C8	C9	132.8(4)	FE	C13	O1	176.2(3)
C2	C3	C4	127.0(4)	C8	C9	C10	129.2(5)	FE	C14	O2	179.4(4)
C3	C4	C5	119.3(3)	C9	C10	C11	126.8(4)	FE	C15	O3	177.6(4)
C4	C5	C6	120.7(3)	C10	C11	C12	129.2(4)				
C7	C6	C5	130.7(3)	C11	C12	C1	134.0(4)				

a)Numbers in parentheses are estimated standard deviations in the least significant digits.

#### The Dynamic Behaviour of 3 and 4.

A monocyclic  $\pi$ -system consisting of  $z$  conjugated double bonds, part of which are complexed with a metal atom, allows for  $z$  equivalent arrangements of the metal. A rapid motion of the metal between these positions may cause an exchange of the magnetic sites of the nuclei involved and thus induce line-broadening effects within the NMR spectra. This is indeed the case for cyclooctatetraeneirontricarbonyl (5) one of the earliest fluxional organometallic species investigated by DNMR.<sup>10-13,17,23-26</sup> Similar "ring whizzing"<sup>24,27</sup> is also expected for the heptalene case. In the following chapter we evaluate the nature of the dynamic process occurring in the title compounds.

Up to a temperature of ca. 80 °C the <sup>13</sup>C NMR spectra of 3 remain essentially unchanged. On raising the temperature above +85 °C, however, the signals of C-2, C-3, C-5, and C-6 broaden progressively while those of C-1 and C-4 remain sharp. Even at +170 °C one does not obtain the fast-exchange limit of the dynamic process. The observation of line-broadening only for particular signals is significant for the exclusion of some random exchange. The <sup>1</sup>H NMR spectra (with smaller shift differences of related signals) provide additional information since one approaches the limit of fast exchange. The <sup>1</sup>H NMR spectrum recorded at +82 °C exhibits significant broadening of the resonances of H-2, H-3, H-5, and H-6. Coalescence of exchange-broadened resonances (H-2, H-6 and H-3, H-5) is obtained at ca. 108 °C. Even at 153 °C there is some remaining line broadening which gives

rise to unresolved singlet signals. The signal of H-4 also loses some of its fine structure; it exhibits a triplet structure, but remains in the same position throughout the whole temperature variation. One concludes that the broadening of the signal of H-4 is induced by an averaging of the respective H,H-coupling constants and not by a change of its chemical shift. Accordingly, the process responsible for the line-broadening effects exchanges the magnetic sites of nuclei 2 and 6, and also of nuclei 3 and 5, respectively, while not influencing the sites of nuclei 1 and 4.

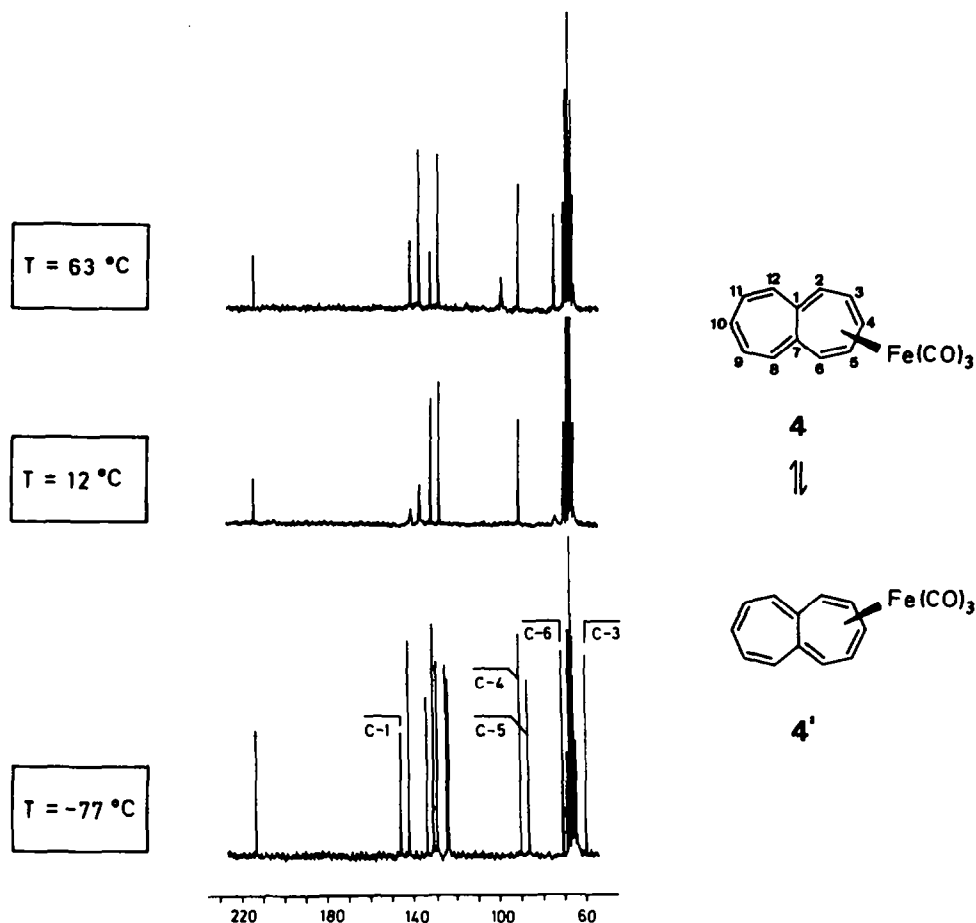
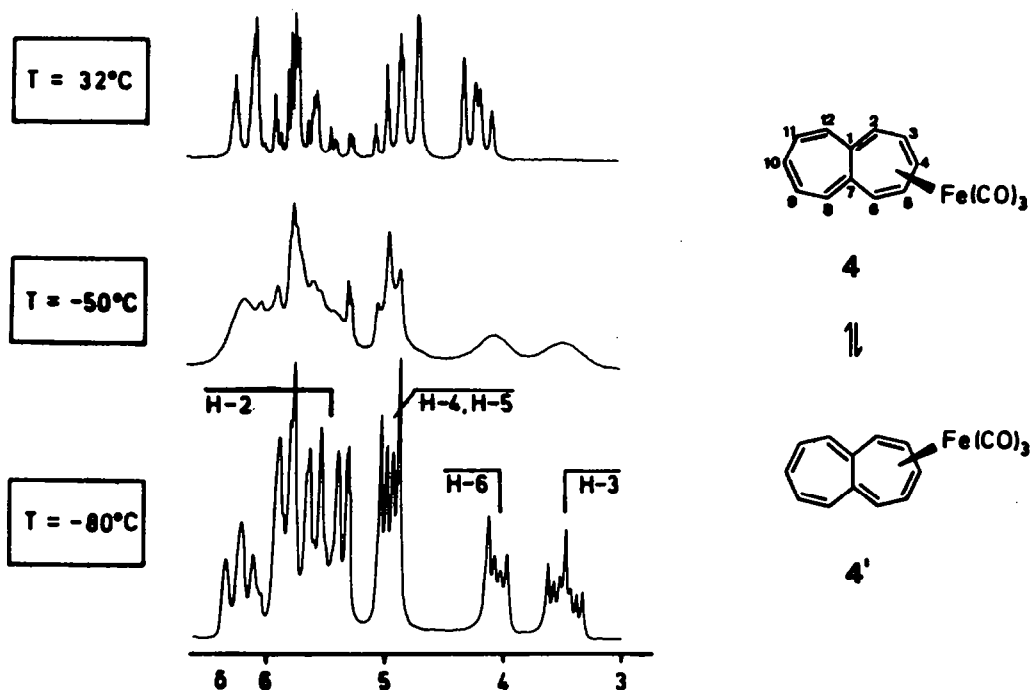


Figure 2.  $^{13}\text{C}$  NMR spectra of 4 (20 MHz,  $(\text{D}_2\text{O})$ -THF) at different temperatures.

From the structural analogy between 3 and its mono-complex 4 one might have anticipated the occurrence of a similar fluxionality. While a closer investigation of 4 will indeed support this view, a striking difference can be found in the respective temperature domains: line-broadening effects in the  $^{13}\text{C}$  NMR spectra of 4 can indeed be seen above  $-70^\circ\text{C}$ , coalescence of signals occurs at ca.  $-30^\circ\text{C}$ , and the fast-exchange limit is attained at ca.  $50^\circ\text{C}$ . In the case of 4 we restrict ourselves to the  $^{13}\text{C}$  NMR technique since its time domain allows for full coverage of the limits of fast and slow exchange and the inherent spectral simplicity renders an analysis more straightforward than in the case of  $^1\text{H}$  NMR. The positions of the coalescing signals indicate a mutual exchange between equally populated sites. Furthermore, since detailed signal assignments have been achieved for the carbons of the complexed seven-membered ring, one can now readily identify the average resonance positions for H-2 and H-6, H-3 and H-5, H-8 and H-12, as well as H-9 and H-11, respectively. An inspection of formula 4 makes clear that, in contrast to 3, C-1 and C-7 now also exchange their magnetic sites. Two signals do not undergo line broadening. The one at  $\delta$  90 is known to be due to C-4. From what



will be said below the other resonance has to be assigned to C-10. One concludes that the same type of exchange process, namely a 1,2-shift of the  $\text{Fe}(\text{CO})_3$ -group, occurs in both 3 and 4. For the latter the migration of  $\text{Fe}(\text{CO})_3$  interchanges structures 4 and 4'.



**Figure 3.**  $^1\text{H}$  NMR spectra of 4 (60 MHz,  $\text{CD}_2\text{Cl}_2/\text{CF}_2\text{Br}_2$ , 1:1) at different temperatures.

Having characterized the dynamic processes occurring in 3 and 4 as isodynamic 1,2-shifts, we could perform lineshape analyses to evaluate the relevant activation parameters. In the case of 4 the mutual exchange can simply be dealt with since one has to simulate the  $^{13}\text{C}$  singlet signals. Program DNMRIT is also suited to treat the strongly coupled spin system giving rise to the  $^1\text{H}$  NMR spectrum of 3.

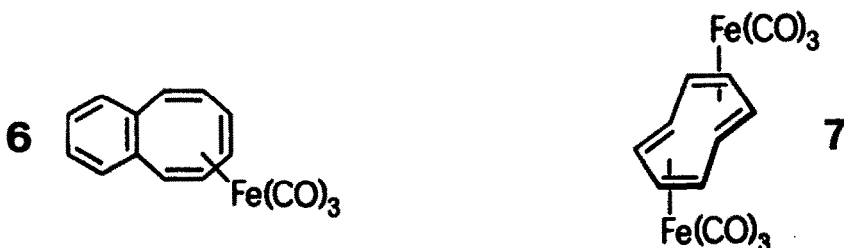
In the whole temperature range covered, the  $^{13}\text{C}$  NMR spectra of both 3 and 4 exhibit one sharp carbonyl resonance at very low field. Inspection of formulas makes clear that any carbonyl carbon atom can exist in three non-identical sites (see below); the above results are compatible with either a fortuitous shift equivalence or with some time-averaged equivalence produced by an exchange process. For compound 4 evidence in favour of some fluxional behaviour has been obtained from spectra taken below  $-90^\circ\text{C}$ . While at ca.  $-95^\circ\text{C}$  the resonance at  $\delta$  212 broadens significantly, it is split at lower temperatures into three lines of equal intensity. This finding provides experimental support for a CO-scrambling. The analogous experiments for 3 show one signal for each of the 6 carbonyl carbons down to a temperature of ca.  $-60^\circ\text{C}$ . On cooling, one also observes broadening, and finally splitting into three equally intense signals. It should be mentioned that the observed shift difference is significantly greater than that in 3.

### Discussion

It is important for an analysis of the observed dynamic behaviour that the exchange process broadens particular resonances while leaving others unchanged. A  $\text{Fe}(\text{CO})_3$ -entity within a monocyclic,  $\eta^4$ -complexed  $\pi$ -system will not affect the magnetic environment of an "inner" carbon atom in the course of one single 1,2-shift. This is no longer true for the analogous 1,3-migration. On the other hand,

when there is a sequence of successive 1,2-shifts, every carbon will undergo a change of its environment; nevertheless one will expect that some resonances broaden faster than others since the mean residence time of nuclei in the particular sites is different. In fact, if assignments of individual signals have been achieved the observation of differential broadening within the slow-exchange domain of cyclooctatetraeneirontricarbonyl (5) can be used to discriminate a 1,2-shift from the 1,3-mechanism.<sup>18</sup> Moreover, any 1,z-shift within 5 exchanges isoenergetic structures which has to be contrasted with the structural features of 3 and 4. The dynamic process occurring in 3 exchanges the magnetic sites of nuclei 2 (8) and 6 (12) as well as of nuclei 3 (9) and 5 (11), but does not affect those of nuclei 1 (7) and 4 (10). The only process giving rise to such an exchange behaviour, is a simultaneous, uni-directional 1,2-shift of both  $\text{Fe}(\text{CO})_3$ -groups. This mechanism interconverts the isoenergetic structures 3 and 3'. The qualitative arguments proposed here readily exclude other mechanisms: if 3 transforms into structures with lower symmetry, e.g. via a 1,3-shift or via another non-isodynamic 1,2-shift, the magnetic sites of nuclei 1 (7) and 4 (10) would not be invariant. The same is true for mechanisms involving different types of motion of the  $\text{Fe}(\text{CO})_3$ -fragments, processes by which the complex would lose its symmetry.

When evaluating the steric and electronic terms relevant for the 1,2-shift of the  $\text{Fe}(\text{CO})_3$ -moieties, one will compare the behaviour of 3 and 4 with those of reference compounds such as 5, 6,<sup>28</sup> or 7.<sup>29</sup>



In accordance with formula 4 a 1,2-shift of the  $\text{Fe}(\text{CO})_3$ -moiety in the complexed ring implies a  $\pi$ -bond migration in the uncomplexed  $\pi$ -unit. The latter process is analogous to the  $\pi$ -bond shift proceeding in the periphery of the parent compound 1.<sup>2</sup> Within a rather naive approach the occurrence of such an extremely rapid valence isomerization in 1 can be explained by the fact that both the "delocalization" energy and the additional steric strain produced by some conformational change are small.

The situation prevailing in 4 differs markedly from the one in both 3 and in benzocyclooctatetraeneirontricarbonyl (6).<sup>28</sup> In compound 6 the 1,2-shift of the  $\text{Fe}(\text{CO})_3$ -group is severely inhibited by the existence of the fused benzene ring whose stability poses an additional barrier to the  $\pi$ -bond migration within the eight-membered ring. In a related fashion the dynamic behaviour of the heptalenebis(irontricarbonyl) (3) involves a superposition of two more or less synchronous 1,2-shifts. The immediate expectation that the relevant energy barrier is roughly twice as high that as in the example of the mono-complex 4 is nicely borne out by the kinetic data presented in Table 2.

It is obvious from an inspection of Table 2 that the entropy of activation of the 1,2-migration in 3 is small for the diglyme solution but adopts a large positive value for the naphthalene solution. One might assume that 3 is tightly associated with the aromatic solvent molecules. This aggregation is destroyed in the transition state of the dynamic process.

In compounds 3 and 4 the angle between the mean planes of the complexed and non-complexed subunits is about  $40^\circ$ . That an appreciable orbital overlap between the complexed butadiene- $\pi$ -system and the neighbouring  $\pi$ -fragments is important

for the occurrence of a facile 1,2-motion along the  $\pi$ -periphery<sup>29</sup> becomes obvious from the lack of fluxionality in trans-C<sub>8</sub>H<sub>8</sub>(Fe(CO)<sub>3</sub>)<sub>2</sub> (7).<sup>30</sup> It has been shown that the latter possesses two nearly orthogonal, independent butadiene units.<sup>31</sup>

Remarkably enough the free enthalpy of activation in 4 ( $\Delta G^\ddagger \approx 11$  kcal/mole) is significantly higher than in the closely related compound 5 ( $\Delta G^\ddagger \approx 8$  kcal/mole).<sup>23</sup> It is worth mentioning in this context that the 1,2-shift in 5 proceeds much faster than the  $\pi$ -bond migration in the free ligand.<sup>2,32,33</sup> On the other hand, the  $\pi$ -bond migration in heptalene (1) is extremely rapid, much more rapid than the 1,2-shift in 4. These relations seem to indicate that steric factors, e.g. the attainment of a flattened transition state, are not responsible for the difference between 4 and 5.

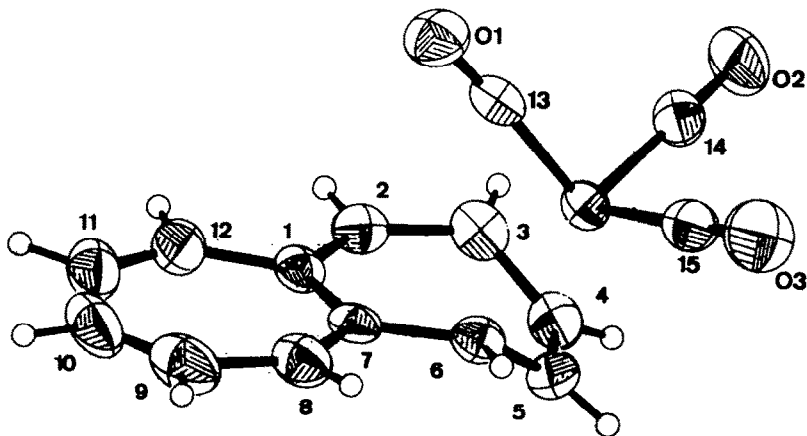


Figure 4. Molecular structure of 4 (see text).

We finally touch upon the CO-scrambling which is observed for both 3 and 4. A metaltricarbonyl-complexed butadiene moiety occupies two basal positions of a square pyramidal structure which should give rise to a single apical and two basal carbonyls. Accordingly, if the rotation of the diene with respect to the tricarbonyl fragment is slow within the NMR time scale, one expects two <sup>13</sup>C resonances in an intensity ratio of 1:2. In compounds 3 and 4 the two basal carbonyls are no longer equivalent. In the case of slow carbonyl scrambling one therefore expects three different carbonyl signals, and this is indeed borne out by the low-temperature measurements.

It is clear that a lineshape analysis of the CO-resonances is much less reliable than that one of the 1,2-shift, due to the smaller differences in the resonance frequencies and to the smaller temperature range involved in the former case. Nevertheless, one can arrive at reliable arguments helpful for clarifying some controversies in the literature. It has been discussed whether the "carbonyl exchange" is independent of the "ring-atom exchange".<sup>17,24,34</sup> A decision is not straightforward as long as the activation energies of both processes are rather similar. This is indeed the case for the mono-complexed species such as 4 ( $\Delta G^\ddagger = 8.9 \pm 0.3$  kcal/mole (-103 °C)) and 5. The free enthalpy of activation for the CO-scrambling in 3 ( $\Delta G^\ddagger = 9.7 \pm 0.3$  kcal/mole (-89 °C)) is slightly greater than that for 4, but significantly smaller than the one for the "ring-whizzing" in 3. Consequently, the CO-scrambling is expected to proceed independently, i.e. not induced by the exchange within the  $\pi$ -ligand.

## Conclusion

The present study reveals a close analogy between heptaleneirontricarbonyl and heptalene(bisirontricarbonyl) in both their "static" structure and in their

fluxional behaviour. A comparative kinetic description of the ring whizzing and CO-scrambling processes occurring in both compounds **3** and **4** proves to be much more straightforward than e.g. in cyclooctatetraeneirontricarbonyl and to be of general significance for diene irontricarbonyl complexes.

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- Crystal data for:  $C_{16}H_{10}O_3Fe$ ,  $M = 294.09$ . The Compound crystallizes in the monoclinic space group  $P2_1/n$  with cell dimensions of  $a = 10.412(2)$ ,  $b = 6.612(1)$ ,  $c = 18.576(4)$  Å,  $\beta = 91.77(2)^\circ$ ;  $V = 1278.2$  Å<sup>3</sup>,  $Z = 4$ ,  $D(\text{calcd}) = 1.528$  g cm<sup>-3</sup>,  $\mu(\text{MoK}\alpha) = 11.759$  cm<sup>-1</sup>. 1552 reflections with  $K > 2 \sigma(I)$  were taken as observed. Final  $R = 0.039$ . Further details of the crystal structure investigation may be obtained from the Cambridge Crystallographic Data Centre.