

## Mechanism of the Fluxional Behaviour in (1—5- $\eta$ -Cycloheptadienyl)-(1—5- $\eta$ -cycloheptatrienyl)iron

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Evidence for a 1,2-shift mechanism of the 1—5- $\eta$ -cycloheptatrienyl moiety with respect to the central iron atom of the title compound is presented together with absolute assignments of the  $^{13}\text{C}$  n.m.r. chemical shifts of the  $\text{C}_7\text{H}_7$  ring. A low-temperature rocking motion of both rings can be frozen out at  $-70^\circ\text{C}$ .

THE previously reported<sup>1</sup> compound  $[\text{Fe}(\eta^5\text{-C}_7\text{H}_7)(\eta^5\text{-C}_7\text{H}_9)]$  (1) exhibits two distinct types of fluxional motion over two discrete temperature ranges. It is the purpose of this paper to describe these processes, principally from evidence obtained from variable-temperature  $^{13}\text{C}$  n.m.r. studies but also with reference to the X-ray structure of the compound and its  $^1\text{H}$  n.m.r. spectra.

assigned by comparison with the  $^1\text{H}$  spectrum of the isoelectronic Ru compound<sup>2</sup> and by proton-proton double-resonance experiments (Table 2). Increasing the temperature from  $-70$  to  $-10^\circ\text{C}$  caused 12 of the 14 carbon-13 signals to coalesce pairwise whilst two remain unaltered (Figure 2). The explanation of this behaviour might be analogous to the description of similar effects

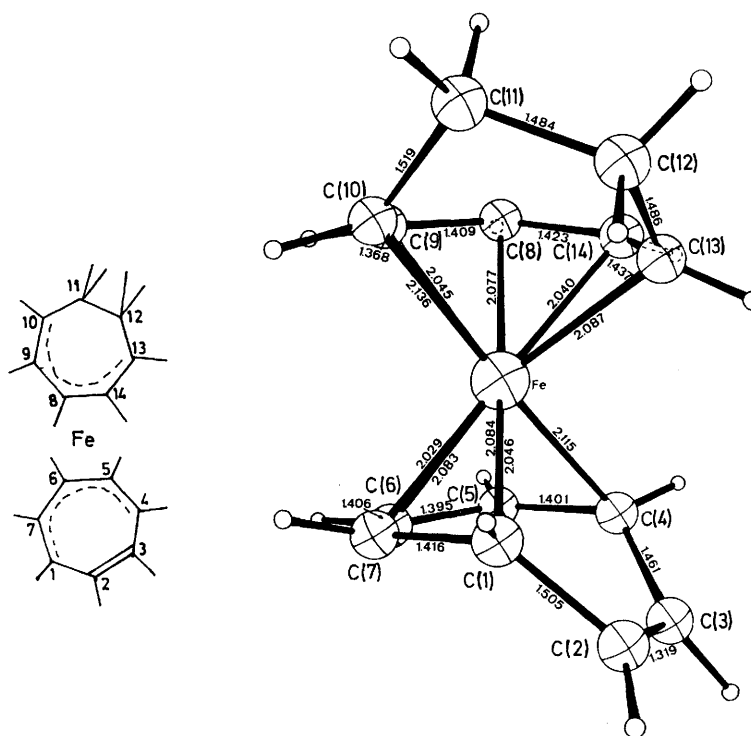


FIGURE 1 Side view of X-ray structure of molecule 1

### RESULTS AND DISCUSSION

The solid-state structure of (1) is illustrated in Figure 1. It contains 14 carbon and 16 hydrogen atoms which are all spatially inequivalent. It is particularly interesting that the 'open' non-bonded faces of both rings are skewed at *ca.*  $50^\circ$  to each other. In agreement with this the n.m.r. spectra of (1) in solution ( $\text{CDCl}_3$  or  $\text{C}_6\text{D}_5\text{CD}_3$ ) showed 14 inequivalent carbon-13 signals and 16 partly overlapping inequivalent proton signals at low temperatures (Tables 1 and 2). Proton resonances were

<sup>1</sup> J. R. Blackborow, K. Hildenbrand, E. Koerner von Gustorf, C. Krüger, A. Scrivanti, C. R. Eady, and D. Entholt, *J.C.S. Chem. Comm.*, 1976, 16.

<sup>2</sup> J. Müller, C. G. Kreiter, B. Mertschenck, and S. Schmidt, *Chem. Ber.*, 1975, **108**, 273.

in the  $^1\text{H}$  n.m.r. spectra of bis(cyclohexadienyl)iron compounds:<sup>3,4</sup> we can assume the coexistence of two enantiomeric forms of (1) in solution, one of which is described by the solid-state structure and schematically depicted in Figure 3. It is evident that by an internal rotation of the two rings relative to each other by an angle of *ca.*  $2 \times 50^\circ = 100^\circ$  these structures are interconverted (Figure 3). Warming increases the rate of this rocking motion and apparent planes of symmetry are induced in both rings on the n.m.r. time scale. The two unchanged  $^{13}\text{C}$  signals can then be assigned to  $\text{C}^6$  and

<sup>3</sup> J. F. Helling and D. M. Braitsch, *J. Amer. Chem. Soc.*, 1970, **92**, 7209.

<sup>4</sup> L. M. Jackman and F. A. Cotton, 'Dynamic Nuclear Magnetic Resonance Spectroscopy,' Academic Press, New York, 1975.

$C^8$  atoms through which the apparent symmetry planes must pass. A similar coalescence process was observed in the proton spectrum (Table 2). The difference in the overall position of the coalesced proton signals with respect to their components is attributed to the different magnetic shielding experienced by the protons due to a

small temperature-dependent amplitude change of the arc described by the free double bond as the rings rock with respect to each other.

Further increase in temperature from  $-10$  to  $+70$  °C caused the partial collapse of four of the eight  $^{13}C$  n.m.r. signals (Figure 4) in a way which can be best assigned to

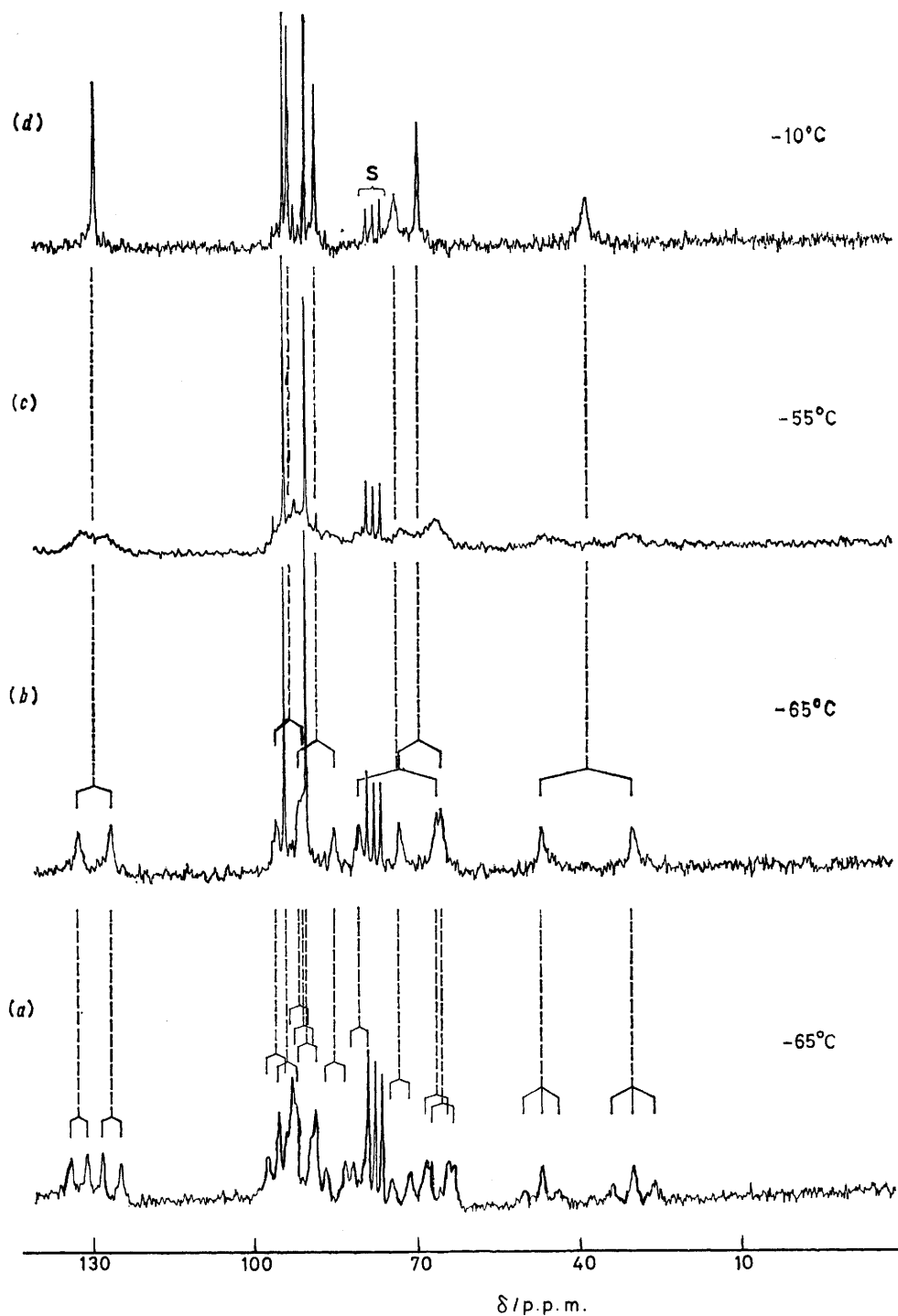


FIGURE 2 Low-temperature  $^{13}C$  spectra of  $[Fe(\eta^5-C_7H_7)(\eta^5-C_7H_9)]$  in  $CDCl_3$ ; (a)  $-65$  °C;  $^1H$  off-resonance decoupling; thirty peaks (twelve doublets, two triplets); (b)  $-65$  °C;  $^1H$  noise-decoupling; fourteen peaks; (c)  $-55$  °C and (d)  $-10$  °C;  $^1H$  noise-decoupling; coalescence from fourteen signals to eight (twelve pairwise coalescences, two remaining unaltered). Spectral assignment and chemical shifts can be obtained from Table 1. Pulse sequence 0.6 s, pulse angle  $30^\circ$ , 5 000 scans

TABLE I

Carbon-13 n.m.r. spectra of  $[\text{Fe}(\eta^5\text{-C}_7\text{H}_7)(\eta^5\text{-C}_7\text{H}_9)]$  in  $[\text{}^2\text{H}_8]$ toluene with  $^1\text{H}$  noise decoupling. Chemical shifts are with respect to  $\text{SiMe}_4$  ( $\delta = 0$ )

-65 °C		-10 °C		80 °C	
Number of $\delta$ carbons	Assignment	Number of $\delta$ carbons		Number of $\delta$ carbons	
25.0 <sup>a</sup>	1 — C <sup>11</sup> (C <sup>12</sup> )	34.3	2	34.3	2
43.2	1 — C <sup>12</sup> (C <sup>11</sup> )				
63.4	1 — C <sup>1</sup> (C <sup>4</sup> )	68.3 <sup>b</sup>	2		
64.5	1 — C <sup>10</sup> (C <sup>13</sup> )				
71.8	1 — C <sup>4</sup> (C <sup>1</sup> )	72.9	2	72.9	2
80.0	1 — C <sup>13</sup> (C <sup>10</sup> )				
84.9	1 — C <sup>14</sup> (C <sup>9</sup> )	89.0	2	89.0	2
91.0	1 — C <sup>8</sup>				
91.3	1 — C <sup>7</sup> (C <sup>5</sup> )	91.0	1	91.0	1
91.9	1 — C <sup>9</sup> (C <sup>14</sup> )				
95.1	1 — C <sup>6</sup>	94.2 <sup>b</sup>	2		
96.6	1 — C <sup>5</sup> (C <sup>7</sup> )	95.1 <sup>b</sup>	1		
129.7	1 — C <sup>3</sup> (C <sup>2</sup> )				
136.4	1 — C <sup>2</sup> (C <sup>3</sup> )	133.2 <sup>b</sup>	2		

<sup>a</sup> Horizontal lines indicate observed coalescence processes.

<sup>b</sup> Broadened by exchange above -10 °C and unobservable at 80 °C.

a fluxional revolution of the  $\eta^5\text{-C}_7\text{H}_7$  ring with respect to the iron atom. The collapse of the four  $^{13}\text{C}$  signals was

motion in four different ways: as a 1,2; 1,3; 1,4; or random shift of the uncomplexed double bond with

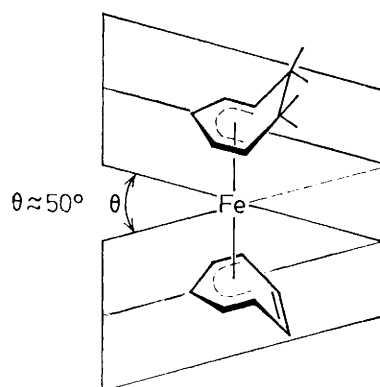


FIGURE 3 Scheme of one of the two interconverting forms of (1) in solution. Note that the planes do not imply symmetry of the electronic environments of the carbon nuclei

respect to some particular direction about which the cycloheptadienyliron moiety is fixed.<sup>4-6</sup> We first established that during this motion both rings remained  $\eta^5$ -bonded. This can be seen by inspection of the  $^{13}\text{C}$  n.m.r. signals of the 1-5- $\eta$ -cycloheptadienyl residue which remain unchanged throughout. We then simulated the four distinct mechanisms together with a fifth (an equal mixture of the first four) on a computer, using the formalism developed by Kubo<sup>7a</sup> and by Sack<sup>7b</sup> for  $n$ -site exchange. The lineshapes of the  $^{13}\text{C}$  resonances of the (1-5- $\eta$ - $\text{C}_7\text{H}_7$ ) moiety can be described by a  $4 \times 4$  matrix<sup>8</sup> in the temperature region where the shift mechanism is observed.

Because of intensity problems the temperature-dependent spectra were obtained from proton-noise-decoupled  $^{13}\text{C}$  n.m.r. spectra. In general this is bad practice, since the Overhauser effects must be assumed to be of the same magnitude for each signal. However, the distinction between the proposed mechanism and the

TABLE 2  
Hydrogen-1 n.m.r. ( $\tau$ ) of (1) in  $[\text{}^2\text{H}_8]$ toluene

-65 °C		-10 °C		80 °C	
Position	Integral [Assignment] <sup>a</sup>	Position	Integral [Assignment]	Position	Integral [Assignment]
10.0	1 [ $\text{H}^{11}$ ( $\text{H}^{12}$ )] <sup>b</sup>				
8.8	1 [ $\text{H}^{12}$ ( $\text{H}^{11}$ )] <sup>c</sup>				
8.4	2 [ $\text{H}^{11}$ , $\text{H}^{12}$ ] <sup>b,c</sup>	8.6	2 [ $\text{H}^{11}$ , $\text{H}^{12}$ ] <sup>b</sup>	8.6	2 [ $\text{H}^{11}$ , $\text{H}^{12}$ ] <sup>b</sup>
7.1	1 [ $\text{H}^9$ ( $\text{H}^{14}$ )]	7.5	2 [ $\text{H}^{11}$ , $\text{H}^{12}$ ] <sup>c</sup>	7.6	2 [ $\text{H}^{11}$ , $\text{H}^{12}$ ] <sup>c</sup>
6.4	1 [ $\text{H}^{14}$ ( $\text{H}^9$ )]	6.8	2 [ $\text{H}^1$ , $\text{H}^4$ ]		
5-5.7	7 [ $\text{H}^1$ , $\text{H}^2$ ( $\text{H}^3$ ), $\text{H}^4$ , $\text{H}^5$ ( $\text{H}^7$ ), $\text{H}^6$ , $\text{H}^{10}$ , $\text{H}^{13}$ ] <sup>d</sup>	5.5-	7 [ $\text{H}^5$ , $\text{H}^6$ , $\text{H}^7$ , $\text{H}^9$ , $\text{H}^{14}$ ]	5.65	5 [ $\text{H}^8$ - $^{10}$ , $\text{H}^{13}$ , $\text{H}^{14}$ ]
4.4	2 [ $\text{H}^3$ ( $\text{H}^2$ ), $\text{H}^8$ ] <sup>d</sup>	6.07	$\text{H}^{10}$ , $\text{H}^{13}$ ]		
3.3	1 [ $\text{H}^7$ ( $\text{H}^5$ )] <sup>d</sup>	5.0	2 [ $\text{H}^2$ , $\text{H}^3$ ]	5.6	7 [ $\text{H}^1$ - $^7$ ]
		4.2	1 [ $\text{H}^8$ ]		

<sup>a</sup> See Figure 1. <sup>b</sup> endo to iron. <sup>c</sup> exo to iron. <sup>d</sup> Not unambiguously assigned.

not complete before the compound decomposed, but was, however, reversible up to 90 °C.

It is possible analytically to describe such a fluxional

<sup>5</sup> F. A. Cotton and D. L. Hunter, *J. Amer. Chem. Soc.*, 1976, **98**, 1413.

<sup>6</sup> F. A. Cotton, D. L. Hunter, and P. Lahuerta, *J. Amer. Chem. Soc.*, 1974, **96**, 7926.

other possibilities was clear enough for us to disregard slight changes in intensity due to Overhauser effects. Figure 5 shows the difference between the five distinct

<sup>7</sup> (a) R. Kubo, *Nuovo Cimento Suppl.*, 1957, **6**, 1063; (b) R. A. Sack, *Mol. Phys.*, 1958, **1**, 163.

<sup>8</sup> See e.g. G. M. Whitesides and J. S. Fleming, *J. Amer. Chem. Soc.*, 1967, **89**, 2855.

mechanisms when one particular assignment for the  $^{13}\text{C}$  signals of the  $\text{C}_7\text{H}_7$  ring was taken. (By inspection the  $\text{C}^6$  and  $\text{C}^2, \text{C}^3$  signals can easily be assigned; however,  $\text{C}^1, \text{C}^4$  and  $\text{C}^5, \text{C}^7$  can be interchanged.) The lower part of Figure 5 shows the effect of the interchange of  $\text{C}^5, \text{C}^7$  and  $\text{C}^1, \text{C}^4$  for the 1,2-shift mechanism; the two cases are quite distinct. We therefore simulated five different mechanisms (1,2; 1,3; 1,4; random; and mixed)

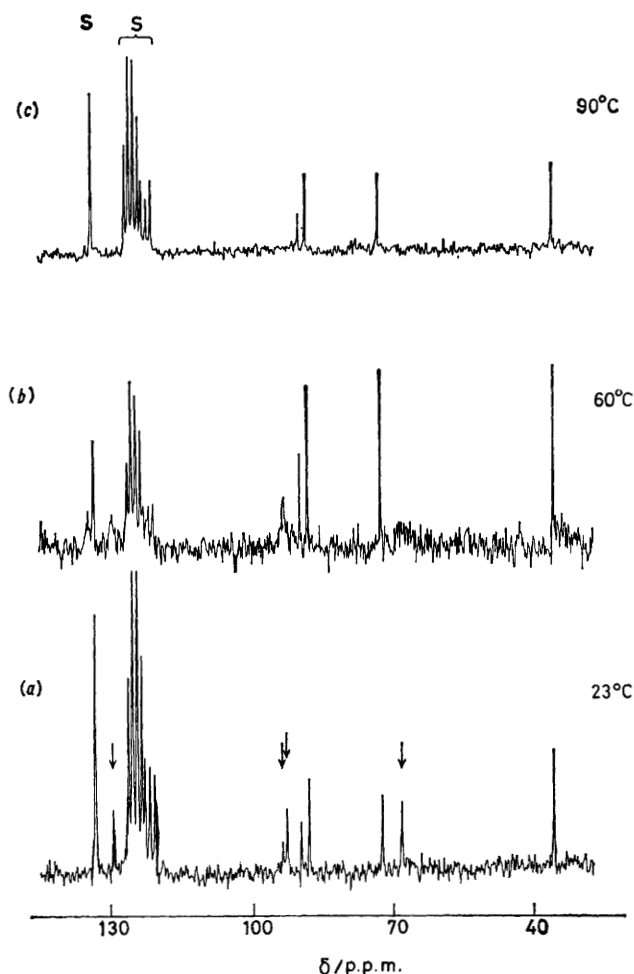


FIGURE 4 High-temperature  $^{13}\text{C}$  spectra of  $[\text{Fe}(\eta^5\text{-C}_7\text{H}_7)(\eta^5\text{-C}_7\text{H}_9)]$  in  $[\text{D}_6]\text{toluene}$ ; (a) 23 °C; (b) 60 °C; and (c) 90 °C.  $^1\text{H}$  noise-decoupling; fluxional collapse of  $^{13}\text{C}$  signals of the  $(\eta^5\text{-C}_7\text{H}_7)$ -ring (indicated by arrows). Spectral assignment and chemical shifts can be obtained from Table 1. Pulse sequence 0.6 s, pulse angle 30°, 5 000 scans; S = solvent

with the two possible  $^{13}\text{C}$  shift assignments. The only 'close fit' from the 10 possible was obtained with a 1,2-shift mechanism with the  $^{13}\text{C}$  assignments given in Table 4. Figure 6 illustrates two representative spectra and spectral simulations using this mechanism. The clear point of distinction is that the left-hand signal broadens more slowly than the right-hand signal, and that the middle signals eventually become less broadened than either of the others. Using the 1,2-shift mechanism with the other possible  $^{13}\text{C}$  assignment, the middle signal becomes eventually less broadened than the right

but more broadened than the left-hand signal. In all the other possible mechanisms the left-hand signal is

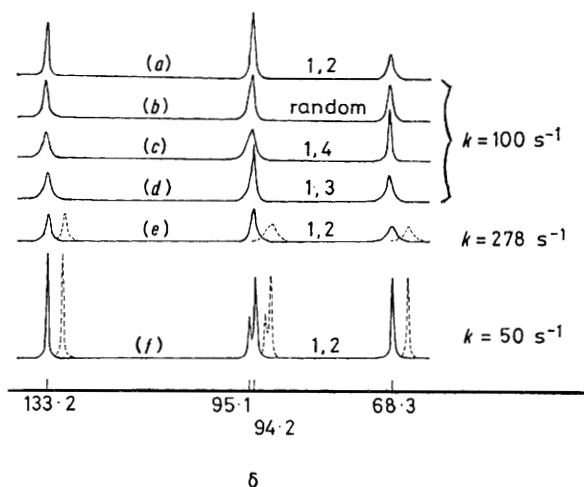


FIGURE 5 A comparison of the simulations of the possible mechanisms of exchange. (a) 1,2 shift, (b) random shift, (c) 1,4 shift, and (d) 1,3 shift. (e) and (f) represent the 1,2 shift mechanism at two different exchange rates. The simulation using the correct chemical-shift assignment of  $\text{C}^4, \text{C}^1$  and  $\text{C}^5, \text{C}^7$  (full line) is compared with the simulation using the false assignment (dotted line); the dotted-line spectrum has been off-set to the right for purposes of clarity. Note that the 1,2 shift mechanism is the only one with the low-field peak less broadened than the high-field peak

more broadened than the right-hand signal. Kinetic parameters of the two fluxional processes and the assignments of the  $^{13}\text{C}$  resonances of the  $\text{C}_7\text{H}_7$ -ring are presented in Tables 3 and 4.

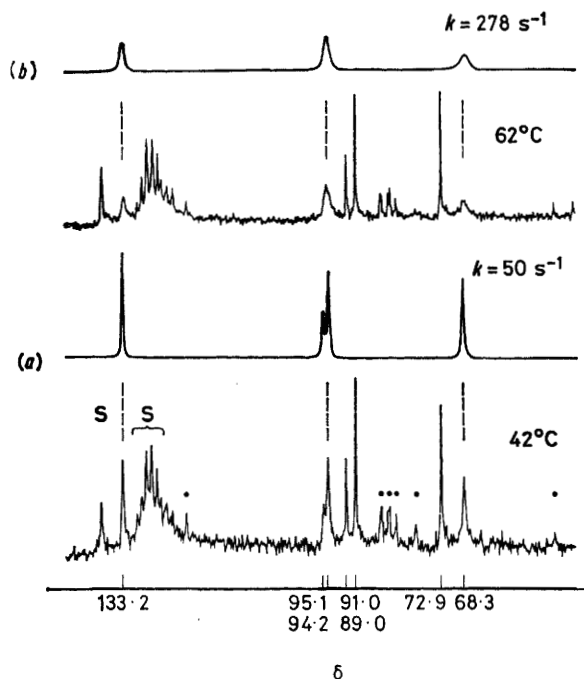


FIGURE 6 Actual and simulated  $^{13}\text{C}$  spectra using the 1,2 mechanism with chemical-shift assignments given in Table 1; (a) 42 °C and (b) 62 °C; pulse sequence 0.6 s; pulse angle 30°; 5 000 scans; S = solvent ( $[\text{D}_6]\text{toluene}$ ); ● = impurities

So far only three other  $\eta^5$ -cycloheptatrienylmetal complexes have been described, namely  $[\text{Ru}(\text{1-5-}\eta\text{-C}_7\text{H}_7)(\text{1-5-}\eta\text{-C}_7\text{H}_9)]$ ,<sup>2</sup>  $[\text{Fe}(\text{1-5-}\eta\text{-C}_7\text{H}_7)(\text{CO})_3]^+$ ,<sup>9,10</sup> and  $[\text{Mn}(\text{1-5-}\eta\text{-C}_7\text{H}_7)(\text{CO})_3]$ .<sup>10</sup> The n.m.r. spectra of these species are strongly temperature dependent but no

TABLE 3

Kinetic parameters of the exchange processes of  $[\text{Fe}(\eta^5\text{-C}_7\text{H}_7)(\eta^5\text{-C}_7\text{H}_9)]$

'Rocking' motion †	$E^\ddagger = 40 \text{ kJ mol}^{-1}$ <sup>a</sup> $\log A = 12.5$
'1,2-Shift' motion	$E^\ddagger = 71 \text{ kJ mol}^{-1}$ <sup>b</sup> $\log A = 13.1$

† This is a simple two-site exchange problem.

<sup>a</sup> Error  $\pm 6 \text{ kJ mol}^{-1}$ . <sup>b</sup> Error  $\pm 10 \text{ kJ mol}^{-1}$ .

TABLE 4

Assignment of the <sup>13</sup>C resonances of the C<sub>7</sub>H<sub>7</sub> ring

$\delta/\text{p.p.m.}$	Correct	Incorrect
133.2	C <sup>3</sup> , C <sup>2</sup>	C <sup>3</sup> , C <sup>2</sup>
68.3	C <sup>4</sup> , C <sup>1</sup>	C <sup>5</sup> , C <sup>7</sup>
94.2	C <sup>5</sup> , C <sup>7</sup>	C <sup>4</sup> , C <sup>1</sup>
95.1	C <sup>6</sup>	C <sup>6</sup>

detailed investigations of the mechanisms of rearrangements have been reported.\*

1,2-Shift mechanisms have been well established however in the  $\eta^4$ - and  $\eta^6$ -metal complexes  $[\text{M}(\text{1-4-}\eta\text{-C}_8\text{H}_8)(\text{CO})_3]$ <sup>5</sup> (M = Fe or Ru) (2) and  $[\text{M}(\text{1-6-}\eta\text{-tetramethyl-C}_8\text{H}_8)(\text{CO})_3]$ <sup>6</sup> (M = Cr, Mo, or W) (3), with activation energies of 34 kJ mol<sup>-1</sup> in [(2); M = Fe<sup>5</sup>] and 66 kJ mol<sup>-1</sup> in [(3); M = Cr].<sup>4</sup>

The latter value is of the same order of magnitude as the value we determined for the activation energy of the 1,2-shift in (1).

\* Note added in proof: while this paper was in preparation, a 1,2-shift mechanism has been established for the rearrangement of  $[\text{Mn}(\text{1-5-}\eta\text{-C}_7\text{H}_7)(\text{CO})_3]$  with an activation energy of about 63 kJ mole<sup>-1</sup> (T. H. Whitesides and R. A. Budnik, *Inorg. Chem.*, 1976, **15**, 874).

As the electronic structures of (1) and (2) or (3) are quite different and the structures of the transition states of this type of rearrangements are unknown, any explanation of the behaviour of the kinetic parameters is bound to be very speculative. So for further discussions we should like to refer to lit. cit. (33) in ref 5.

## EXPERIMENTAL

All the work-up procedures were carried out under argon (99.997%). Iron (2 g) was co-condensed with cycloheptatriene (40 cm<sup>3</sup>) on a hexane matrix at  $-196^\circ\text{C}$  over a period of 1 h in an apparatus described previously. The reaction mixture was allowed to warm to room temperature and hexane and cycloheptatriene were removed from the filtered solution *in vacuo* at  $0^\circ\text{C}$ . The resulting red solid was recrystallised from pentane at  $-80^\circ\text{C}$  (Found: C, 70.0; H, 6.65; Fe, 23.3. Calc. for C<sub>14</sub>H<sub>16</sub>Fe: C, 70.0; H, 6.70; Fe, 23.3%).

N.m.r. samples were run in [<sup>2</sup>H<sub>8</sub>]toluene in sealed evacuated 5- or 10-mm tubes on a Bruker W.H. 90 spectrometer. The temperature controller was calibrated with ethanol or ethylene glycol in the usual way. Operations were performed in the Fourier-transform mode at 90 MHz for hydrogen and 22.3 MHz for carbon, using solvent-deuterium locking. Samples of differing concentration (0.14, 0.2, and 0.3 mol dm<sup>-3</sup>) exhibited identical temperature dependences within experimental error. Errors in Table 3 for *E* were estimated graphically from a considered temperature error of  $\pm 2^\circ\text{C}$  and a rate error of  $\pm 6\%$ .

We thank Drs. Mark, Bausch, and Grevels at the Institut für Strahlenchemie for helpful discussions. One of us (R. H. G.) thanks the Alexander von Humboldt Stiftung for a research fellowship.

[6/1522 Received, 4th August, 1976]

<sup>9</sup> R. Pettit, *J. Amer. Chem. Soc.*, 1964, **86**, 2589.

<sup>10</sup> T. H. Whitesides and R. A. Budnik, *Chem. Comm.*, 1971, 1514.