Evidence for a 1,3-Sigmatropic Shift in a Fluxional Organometallic System, *trans,trans*-1,4-Bis(dicarbonyl-π-cyclopentadienyliron)buta-1,3-diene: Nuclear Magnetic Resonance Study

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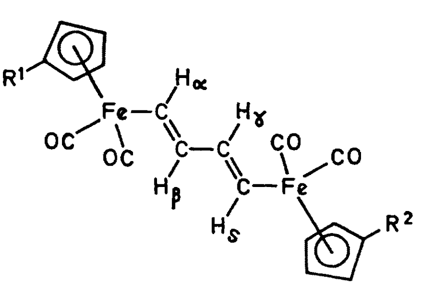
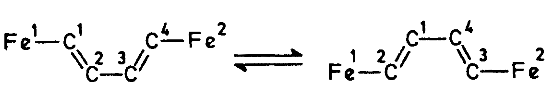
Summary The structure of the ^{13}C satellite lines in the ^{1}H n.m.r. spectrum of *trans,trans*-1,4-bis(dicarbonyl-π-cyclopentadienyliron)buta-1,3-diene (I) and the dimethyl derivative (II) indicates that the fluxional process in these molecules involves mainly 1,3-shifts of the metal–carbon bonds: the n.m.r. spectrum of the monomethyl derivative (III) supports this conclusion.

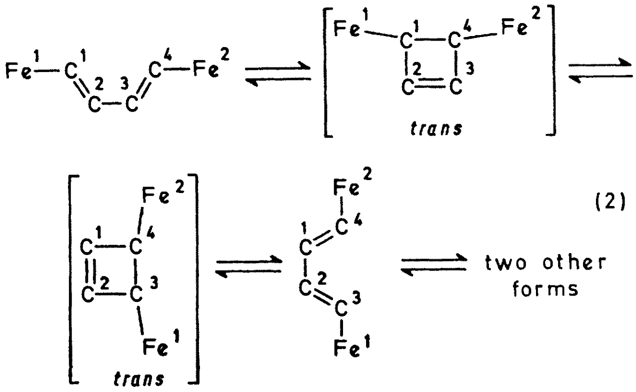
THERE has recently been considerable interest in the mechanisms of the fluxional processes occurring in certain organometallic systems, whereby a transition-metal atom σ-bonded to an unsaturated organic group rapidly changes its point of attachment.[1] We have presented evidence for a 1,2-shift mechanism in some systems of this kind but no definite example has hitherto been known of a 1,3-shift in this type of process. Here we report that a 1,3-shift does occur in *trans,trans*-1,4-bis(dicarbonyl-π-cyclopentadienyliron)buta-1,3-diene (I).



(I) $R^1 = R^2 = H$
(II) $R^1 = R^2 = Me$
(III) $R^1 = Me, R^2 = H$



(1)



(2)

Churchill and his co-workers[2] reported the apparent equivalence of all four protons in the diene fragment indicated by the n.m.r. spectrum and suggested that this may be due to rapid concerted 1,2-shifts of both metal atoms (reaction 1). We reject this mechanism in favour of single 1,3-shifts, perhaps involving a cyclobutene intermediate (reaction 2), on the basis of a study of the ^{13}C satellite lines in the n.m.r. spectra of compounds (I) and (II).

A proton bound to a ^{13}C atom in the diene fragment will give rise to two satellite lines further split by essentially first-order coupling to each of the other three protons. The effective H–H coupling constants which should be observed under fast-exchange conditions are obtained by averaging over the two structures shown in (1) or the four structures in (2). Thus if the concerted 1,2-shift mechanism is correct the proton bound to ^{13}C is coupled to the other three protons with coupling constants $J_{\alpha\beta}$, $J_{\alpha\gamma}$ and $\frac{1}{2}(J_{\alpha\delta} + J_{\beta\gamma})$, but if 1,3-shifts predominate the coupling constants are $\frac{1}{4}(2J_{\alpha\beta} + J_{\alpha\delta} + J_{\beta\gamma})$ (twice) and $J_{\alpha\gamma}$. Assuming reasonable values for the coupling constants under slow-exchange conditions (the exact values chosen are not critical to the argument) and assuming that $J_{\alpha\gamma}$ is not resolvable we conclude that the fine-structure of the ^{13}C satellites will show successive splittings of 14 and 6 Hz in the first case and a binomial triplet with a splitting of 10 Hz in the second. The low solubility of compound (I) made observation of the ^{13}C satellites difficult, but with the more soluble derivative (II) the low-field satellite could be observed after spectrum accumulation over 64 scans to be a triplet with a splitting of *ca.* 10 Hz, J(C–H) 158 Hz (in 2-methyltetrahydrofuran). The high-field satellite was obscured by the cyclopentadienyl resonance.

Confirmation of this result was provided by the ^{1}H n.m.r. spectrum of the monomethyl derivative (III). In both the mechanisms suggested each iron atom visits only two carbon atoms, so when the iron atoms are not equivalent the diene protons should have two different environments even under fast-exchange conditions. The averaged spectrum for each mechanism can be predicted as before: the 1,3-shift mechanism would give an A_2B_2 spectrum with J_{AB} *ca.* 10 Hz and the concerted 1,2-shifts an AA′BB′ spectrum with approximate coupling constants J_{AB} 6, $J_{AA'} = J_{BB'}$ 14, $J_{AB'}$ 1 Hz. The observed spectrum, although not fully resolved, can be analysed as an A_2B_2 system with J_{AB} 10 Hz, $\delta = 0{\cdot}16$ (in acetone at −50°) and does not resemble spectra calculated with the coupling constants predicted for the 1,2-shift mechanism. We conclude that the fluxional process in this system involves mainly 1,3-shifts and that the concerted 1,2-shift process does not occur at a significant rate on the n.m.r. time-scale even at room temperature since the simultaneous operation of both mechanisms would make all four diene protons in compound (III) appear equivalent.

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[1] C. H. Campbell and M. L. H. Green, *J. Chem. Soc.* (*A*), 1970, 1318, and references therein.

[2] M. R. Churchill, J. Wormald, W. P. Giering, and G. F. Emerson, *Chem. Comm.*, 1968, 1217.