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## Stereochemical Non-rigidity of Tricarbonyl(cyclo-octatetraene)iron as shown by Fourier Transform Carbon-13 Nuclear Magnetic Resonance

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**Summary** The fluxional behaviour of  $C_8H_8Fe(CO)_3$  was investigated by  $^{13}C$ -n.m.r. spectroscopy; the results obtained by  $^1H$ -n.m.r. were confirmed and a new kind of non rigidity was discovered in the carbonyl part of the molecule.

in  $CHFCl_2:CF_2Cl_2$  (2:1 v/v) at temperatures ranging from  $-20^\circ$  to  $4-10^\circ$ , with a Varian XL-100-15 spectrometer.

At  $-20^\circ$  the  $^{13}C$  signals are a narrow doublet ( $J \approx 158$  Hz) centred at 92.6 p.p.m. with respect to  $CS_2$  and a narrow singlet at  $-19.3$  p.p.m. The high-field doublet is due to the averaged ring carbons split by the attached proton, the low-field singlet is obviously due to the averaged carbonyl carbons.

THE cyclo-octatetraene ring in  $C_8H_8Fe(CO)_3$  (I) is known to be linked to the metal through only four of its eight carbon atoms and the overall geometry of the molecule is well known.<sup>1</sup> The temperature dependence of the  $^1H$  n.m.r. spectrum of (I) has shown that the molecule is 'fluxional' in the sense that the bonding of the ring rearranges through a sequence of (1, 2) shifts.<sup>2,3</sup>

Unlike the analogous case of  $C_8H_8Ru(CO)_3$ ,<sup>4</sup> the fluxionality of (I) is very fast. The spectrum of (I) obtained at the lowest temperature ( $-155^\circ$ ) is that published by Grubbs and his co-workers.<sup>5</sup> These authors, in agreement with Winstein and his co-workers<sup>2</sup> believed that the spectrum at  $-155^\circ$  was indeed the limiting spectrum giving the correct proton chemical shifts but some uncertainty still remained (see also ref. 6).

We now report new evidence on this valency tautomerism obtained from  $^{13}C$ -n.m.r. spectra. In  $^{13}C$ -n.m.r. the time scale is more favourable to the detection of the slow motion limiting spectrum owing to the much larger expected chemical shifts so that it is possible to reach a true limit at accessible temperatures.

We have taken the Fourier transform  $^{13}C$ -n.m.r. spectrum of (I), prepared according to Reihlen,<sup>7</sup> as a 0.12 M solution

At temperatures lower than  $-120^\circ$ , the high-field doublet splits into four well separated doublets (the  $J$  values remaining constant within experimental error) centered at 63.7, 72.3, 103.6, and 130.8 p.p.m., while the low-field signal splits into two signals at  $-20.0$  and  $-17.9$  p.p.m. with intensity ratio 2:1.

The low-temperature spectrum is in perfect agreement with the rigid structure of the molecule. The splitting of the carbonyl signal provides evidence that also in the  $(CO)_3$  part of the molecule, exchange does not take place in solution (on the n.m.r. time scale) at low temperature but an averaging process takes place at higher temperatures. Spectra at intermediate temperatures were obtained only in the neighbourhood of the high-temperature and of the low-temperature limits owing to sensitivity difficulties in the intermediate regions. These observations were however sufficient for a comparison of the averaging processes as deduced from  $^1H$  and  $^{13}C$  spectra by comparison with the spectra obtained by a CDC 6600 computer with the DNMR program written by Binsch.<sup>8</sup> Proton spectra were repeated with a Bruker Spectrometer operating at 90 MHz in order to obtain an Arrhenius plot for the proton exchange process. The limiting spectra agreed with the data of

Grubbs and Breslow.<sup>5</sup> The high- and low-temperature spectra of ring carbons were found to agree with simulated spectra which used rate data obtained from the proton Arrhenius plot. On the other hand the simulation of the carbonyl signals leads to significantly lower rate constants.

We conclude that the carbonyl exchange process rate is independent of the ring-atom exchange process.

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