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STEREOCHEMICALLY NONRIGID ORGANOMETALLIC MOLECULES

XXXIII.* CARBON-13 NUCLEAR MAGNETIC RESONANCE OF $(h^5\text{-}C_5H_5)(CO)_2Fe(h^1\text{-}C_5H_5)$ from +52 to −88° **

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SUMMARY

The carbon-13 nuclear magnetic resonance spectrum of $(h^5\text{-}C_5H_5)(CO)_2\text{-}Fe(h^1\text{-}C_5H_5)$ has been recorded over the temperature range +52 to −88°. The results add further support to the view that the rearrangement pathway for the $h^1\text{-}C_5H_5$ ring is a sequence of 1,2 shifts. Assignment of resonances was made by comparison with the chemical shifts of the allyl group in $(h^5\text{-}C_5H_5)(CO)_2Fe\text{–}CH_2CH\text{=}CH_2$, the spectrum of which was also recorded, as well as by consideration of relative intensities and the multiplets due to proton splitting. The Arrhenius activation parameters, which are considered to be more accurate than those previously derived from PMR spectra, were evaluated as: $E_a = 10.7 \pm 0.5$ kcal/mol and $\log A = 12.6 \pm 0.5$.

INTRODUCTION

Molecules which are fluxional due to the rapid rearrangement of $M\text{–}(h^1\text{-}C_5H_5)$ groups have been extensively studied since this type of stereochemical non-rigidity was first observed by Wilkinson and Piper[1]. In the first variable-temperature PMR study of the phenomenon[2], in $(h^5\text{-}C_5H_5)(CO)_2Fe(h^1\text{-}C_5H_5)$, it was concluded that the rearrangement pathway was a sequence of 1,2 shifts of the Fe–C σ bond. This conclusion rested on the correctness of the assignment of the α- and β-proton resonances of the $h^1\text{-}C_5H_5$ ring and there have been a number of subsequent studies[3–9] intended to check this assignment, or to verify 1,2 shifts in some other, indirect, way[10,11]. In several of these studies[4,6] the activation parameters have been estimated from the temperature dependence of the PMR spectra. All of the data and interpretations thereof which are presently in the literature support the original[2] proposal that 1,2 shifts constitute the main, if not the sole rearrangement pathway for $M\text{–}(h^1\text{-}C_5H_5)$ moieties.

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Carbon-13 NMR spectroscopy has some inherent advantages in the study of stereochemically nonrigid organic or organometallic molecules, but because of several well-known difficulties (*e.g.*, low intrinsic sensitivity, low natural abundance, saturation due to long relaxation times) no such investigation appears yet to have been reported. By means of the pulsed Fourier transform mode of measurement the difficulties can be circumvented. When such instrumentation became available to us we chose for the first subject of study by ^{13}C NMR spectroscopy the same molecule which had also, in this laboratory, been the first fluxional organometallic molecule studied by ^{1}H NMR spectroscopy, namely, $(h^5\text{-}C_5H_5)(CO)_2Fe(h^1\text{-}C_5H_5)$, (I). The results are reported here.

EXPERIMENTAL

A 1.5 *M* solution of (I) in CS_2/toluene (3/1) was used for low temperature spectra, a 1.5 *M* solution in toluene for high temperatures ($>25°$). No solvent shift from CS_2/toluene to pure toluene was noticed. Fourier transform carbon-13 NMR spectra were recorded on a Bruker HFX-90 spectrometer at 22.625 MHz. A 10-mm sample tube fitted with a coaxial capillary containing either CF_2BrCF_2Br ($< 25°$) or C_6F_6 ($>25°$) for ^{19}F field/frequency stabilization was used. By collecting the Fourier transform resulting from 1000 to 1500 repetitive R.F. pulses of 45 μs duration (corresponding to a 45° tilt angle) at intervals of 0.8 seconds, spectra with reasonable (60/1 on the $h^5\text{-}C_5H_5$) signal to noise were obtained. Spectra were collected at 3° intervals from -88 to $-49°$, at $+25$ and $+52°$. Temperature calibration was made by comparing the reading of an (alcohol) thermometer immersed in a toluene-filled sample tube and inserted into the magnet gap against the thermocouple of the machine (located just below the sample tube); the two readings differed by less than 2° over the entire temperature range. By fitting the observed linewidths to those obtained from an NMR line-shape program EXCHSYS*, data points in the temperature range $+52$ to $-66°$ were obtained and plotted to give ΔE.

RESULTS

At a probe temperature of 27° the proton-decoupled ^{13}C spectrum of (I) consists of a sharp resonance due to the *pentahapto* ring, a broad resonance ($\Delta\nu_{\frac{1}{2}} \approx 94$ Hz) due to the *monohapto* ring and a resonance due to the two carbonyl groups**.

As a solution of (I) (1.5 *M* in 3/1 CS_2/toluene solvent) was cooled to $-78°$ the broad signal collapsed completely and was supplanted by three signals, in the intensity ratio 2/2/1, which gradually sharpened. The chemical shifts of all resonances due to (I) at $-78°$ are given in Fig. 1a. Of singular importance is the observation that *the signal at* 47.5 *ppm sharpened more slowly with decreasing temperature than that at* 71.2 *ppm.*

The weighted average of the chemical shifts of the three resonances at low temperature is 80.4 ppm, while the chemical shift of the single line at 52° is 80.8 ppm. The discrepancy is at the threshold of error.

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* Line-shape analysis and Arrhenius plots were carried out using the program EXCHSYS, written by J. K. Krieger and G. M. Whitesides, Massachusetts Institute of Technology, 1971.

** The room temperature spectrum of (I) has also been measured in another laboratory[12].

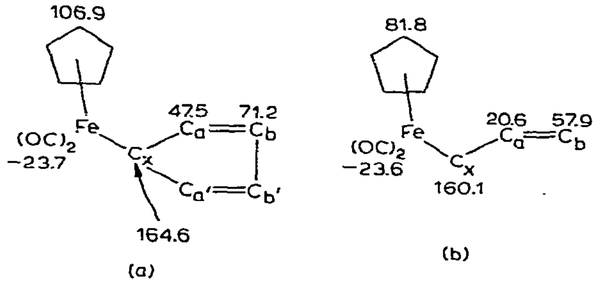

Fig. 1. Carbon-13 chemical shifts in ppm relative to internal CS_2.

For comparison, the chemical shifts for the ^{13}C signals of (II), $(h^5\text{-}C_5H_5)(CO)_2\text{-}Fe\text{-}CH_2CH{=}CH_2$, are given in Fig. 1b. The assignments for (II) are entirely unequivocal on the basis of relative intensities, proton splitting and the known[13] high positive chemical shift expected for an aliphatic carbon atom bound to the metal atom.

The assignment of the C_a and C_b signals in (I) is based on two lines of argument. First, by comparison with the chemical shifts in (II), the C_a resonance is expected at lower field than the C_b resonance. Exact correspondence between the C_a and C_b shifts in the two compounds would not be expected since (*a*) rotation about the C_x–C_a bond is possible in (II) but not in (I), and (*b*) rotational conformational preferences about the Fe–C_x bond will probably differ in the two compounds. Thus diamagnetic anisotropy effects stemming from the π electron distributions in the h^5-C_5H_5 and CO groups would be expected to differ somewhat in their influence on C_a and C_b in the two cases. Also, the presence of another double bond across the ring in (I) but not in (II) might be expected to alter the absolute values, but probably not the difference of the C_a and C_b chemical shifts in (I) as compared with (II). Nevertheless, an inversion of the order by as much as 61 ppm seems extremely unlikely. We therefore conclude that since $\delta(C_a) < \delta(C_b)$ holds in (II) then $\delta(C_a) < \delta(C_b)$ will also hold in (I).

The close similarity of the $\delta(C_x)$ values in (I) and (II) is expected and provides further assurance that the assignments of C_x and C_b [which in (II) both have triplet structure resulting from proton splitting] have been correctly assigned in (II).

A second line of support for the assignment shown in Fig. 1 derives from the observation that from −78 to −88° the signal at 47.5 ppm in (I) begins to broaden again. Similar broadening of H_a resonances has previously been observed[13,14]. This effect can be ascribed to hindered rotation about the Fe–C_x bond. It leads to freezing out of conformations in which H_a and H'_a (or C_a and C'_a) have slightly different environments relative to the other ligands. It is much more noticeable for H_a and C_a than for H_b and C_b because the former are much closer to the other ligands. This effect thus serves to distinguish between H_a (or C_a) and H_b (or C_b).

If the assignment we have made for the resonances of (I) is accepted, then the fact that the 47.5 ppm resonance sharpens more slowly than the 71.2 ppm resonance as the temperature is lowered demonstrates, qualitatively, that 1,2 shifts are the predominant mode of site exchange, according to arguments previously presented[2,6].

A distinct advantage of carbon-13 NMR at the natural abundance level becomes apparent when spectra in the exchanging region are analyzed. The fluxional process can be described by one spin exchanging between three sites (a, b, x) with the proper degeneracies. Not only can we conclude *qualitatively* that 1,2 shifts are at the very least predominant. Quantitative treatment of the carbon-13 spectra observed between −49 and −78° requires the fluxionality to be described as a 1,2 and *only* a 1,2 shift, since the exchanging linewidths (linewidths after natural linewidths have been subtracted) strictly reflect the 2/2/1 (a/b/x) ratio predicted for a 1,2 shift mechanism[4].

In contrast to the proton line-shape analysis of (I) where only spectra near the high-temperature limit (0 to +35°) were used[4] because of the complications of spin–spin coupling at low temperatures, kinetic data can be extracted from the carbon-13 spectra of (I) over the entire range from +52 to −69° (corresponding to exchange rates of 10^5 to 10 sec^{-1}). Line shape analysis based on a one spin–three site model and the corresponding Arrhenius plots give $E_a = 10.7 \pm 0.5$ kcal/mol and $\log A = 12.6 \pm 0.5$. E_a is a little higher than values previously obtained from proton spectra (8.5 ± 0.8 kcal/mol[4] and 9.8 ± 0.1 kcal/mol[6]). It was expedient in the proton line-shape analysis to use the h^5-C_5H_5 resonance as a measure of the natural linewidth, assuming the *monohapto* ring protons to have similar nonexchange linewidths. The present work suggests that this may not be a reliable assumption. At −88° (below the temperature needed to stop exchange), the linewidths at half-height are 5.1 Hz for C_b and C_x, 6.1 Hz for C_a, *but only* 3.5 Hz for the carbon atoms of h^5-C_5H_5. Proton rate studies will probably tend to overestimate the exchange rate, since it is not possible to separate rigorously the observed linewidths into contributions from spin–spin coupling, natural linewidth variations and exchange-broadening. Because the exchange rate is overestimated, low values of E_a are then calculated. For this reason, and because carbon-13 data could be employed over a much wider temperature range, the present activation data are considered to be more reliable than those previously derived from PMR studies.

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REFERENCES

1 G. Wilkinson and T. S. Piper, *J. Inorg. Nucl. Chem.*, 2 (1956) 32; T. S. Piper and G. Wilkinson, *ibid.*, 3 (1956) 104.
2 M. J. Bennett, F. A. Cotton, A. Davison, J. W. Faller, S. J. Lippard and S. M. Morehouse, *J. Amer. Chem. Soc.*, 88 (1966) 4371.
3 F. A. Cotton and T. J. Marks, *J. Amer. Chem. Soc.*, 91 (1969) 3178.
4 C. H. Campbell and M. L. H. Green, *J. Chem. Soc. A*, (1970) 1318.
5 F. A. Cotton and T. J. Marks, *Inorg. Chem.*, 9 (1970) 2802.
6 F. A. Cotton and T. J. Marks, *J. Amer. Chem. Soc.*, 91 (1969) 7523.
7 P. West, M. C. Woodville and M. D. Rausch, *J. Amer. Chem. Soc.*, 91 (1969) 5649.
8 A. Davison and P. E. Rakita, *Inorg. Chem.*, 9 (1970) 289.
9 N. M. Sergeyev, G. I. Avramenko and Yu. A. Ustynyuk, *Inorg. Chem.*, 10 (1971) 2364.
10 F. A. Cotton, A. Musco and G. Yagupsky, *J. Amer. Chem. Soc.*, 89 (1967) 6136.
11 D. J. Ciappenelli and F. A. Cotton, *Syn. Inorg. Metal-Org. Chem.*, in press.
12 Yu. K. Grishin, N. M. Sergeyev and Yu. A. Ustynyuk, *J. Organometal. Chem.*, 34 (1972) 116.
13 F. A. Cotton and P. Legzdens, *J. Amer. Chem. Soc.*, 90 (1968) 6232.
14 Yu. A. Ustynyuk and A. V. Kisin, *J. Organometal. Chem.*, 33 (1971) C61.