Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

NOTE

STEREOCHEMICALLY NONRIGID ORGANOMETALLIC MOLECULES XXV*. THE LOW-TEMPERATURE PMR SPECTRUM OF *cis*-(1,2,6-*trihapto*:-3,4,5-*trihapto*-1,3,5-CYCLOOCTATRIENE)HEXACARBONYLDIIRON

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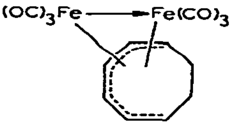
(Received June 2nd, 1969)

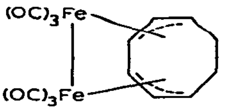
INTRODUCTION

The existence of the compound $C_8H_{10}Fe_2(CO)_6$, obtained by reaction of 1,3,5-cyclooctatriene with $Fe_3(CO)_{12}$ was reported by King[2], who suggested the structure (I) for it. Shortly after this, Emerson *et al.*[3] concluded from a Mössbauer study that the compound *in the solid state* has chemically equivalent iron atoms. Therefore, they rejected structure (I) and proposed structure (II). It has recently been shown[4], however, that the correct structure *in the solid state* is the dissymmetric structure shown as (III).

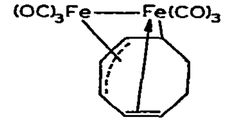
There still remains the problem of the structure of the $C_8H_{10}Fe_2(CO)_6$ molecule in solution. The PMR spectrum at ambient temperature cannot be reconciled with the time-invariant structure (III), but appears instead to require a structure having a plane of symmetry which divides the protons into three pairs of bound-olefin protons and two equivalent pairs of non-equivalent methylene protons. Structures (I) and (II) each satisfy this prescription.



(I)



(II)



(III)

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* For Part XXIV see ref. 1.

Three ways of reconciling the room-temperature PMR data with the known structure of the molecule in the solid state may be considered.(1). There is a rearrangement to structure (I) when the substance dissolves. (2). There is a rearrangement to structure (II) when the substance dissolves. (3). Structure (III) persists as the instantaneous structure in solution, but at room temperature, there is a rapid interconversion of the two enantiomorphous structures of type (III), presumably passing through (I) as a transition state or fleeting intermediate. An analogous situation arose in the case of $C_8H_8Ru_2(CO)_6$ and it has been shown that an explanation of type (3) applies in that case[1]. We report here the PMR spectra of $C_8H_{10}Fe_2(CO)_6$ at various low temperatures down to −107° which indicate that (3) is the correct interpretation in the present case.

RESULTS AND DISCUSSION

The compound was dissolved in a mixture of dichlorodifluoromethane and perdeuterotoluene, $C_6D_5CD_3$ (*ca.* 1/1 by volume) and spectra recorded on a Varian Associates A60 spectrometer. Temperature calibration was achieved with a calibrated copper constantum thermocouple in a manner previously described[1]. Ten spectra through the temperature range +28° to −107° are shown in Fig. 1.

The spectrum at +28° is essentially identical to that previously reported by King[2]. It consists of five multiplets, each of the same relative intensity. These are *marked* A, B, C, D, E. Fig. 2 shows a sketch of the dissymmetric structure with the protons numbered. From a comparison with the spectrum of $C_8H_8Ru_2(CO)_6$, which has already been assigned[1], the following assignment would be proposed, on the assumption that explanation (3) is correct:

A, B: 2, 3, 4, 5
C: 1, 6
D, E: 7, 8, 9, 10

A spin decoupling experiment, carried out on a Varian Associates HA100 spectrometer, allowed a more detailed assignment of the A and B multiplets [which are badly overlapped in the $C_8H_8Ru_2(CO)_6$ case]. Upon irradiation of multiplet C, there were only slight changes in D and E and essentially no change in A, but B was reduced to a narrow multiplet, comparable in width to A, though without resolved fine structure. This shows that, in more detail, the assignment should be:

A: 3, 4
B: 2, 5

We will now examine the changes which take place upon lowering the temperature and show that they are consistent with the assignments just proposed and the postulated oscillatory rearrangement.

Multiplet C is already conspicuously broadened at −15°. The collapse continues until at −57° it is too broad to be seen. While the complexity of the overall changes in the spectrum is too great to permit an entirely unambiguous observation of the growth of separate peaks for the 1 and 6 protons at still lower temperatures, the observations are compatible with the notion that these separate peaks arise at the approximate positions τ 7 and τ 9, as in the case of $C_8H_8Ru_2(CO)_6$.

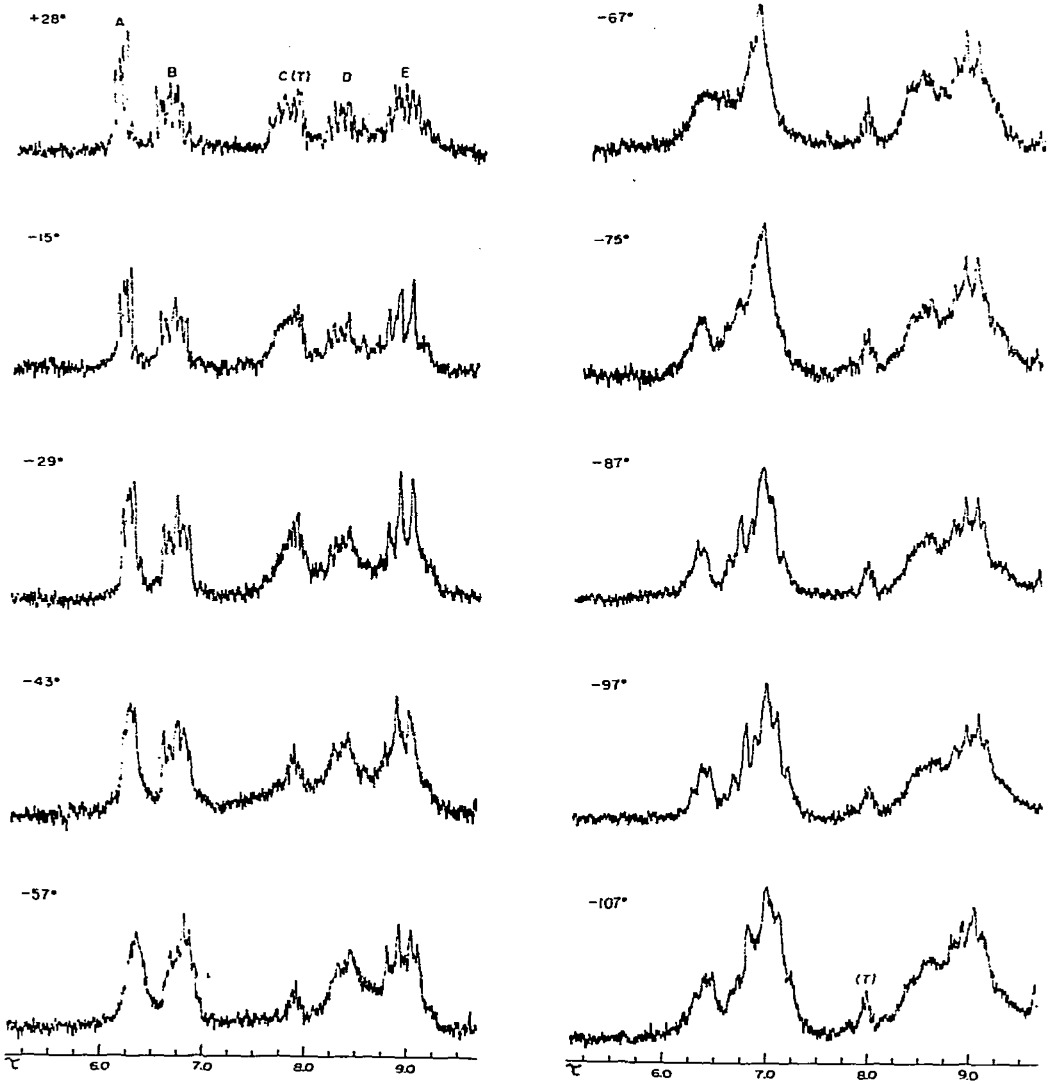

Fig. 1. The PMR spectra of *cis*-(1,2,6-*trihapto*:3,4,5-*trihapto*-1,3,5-cyclooctatriene)hexacarbonyldiiron at ten temperatures from −107° to +28°. Spectra were recorded using a 1/1 mixture of $C_6D_5CD_3/CF_2Cl_2$ as solvent. The variations of certain chemical shifts by several tenths of a τ unit with temperature are real. The peak marked (T) is due to a trace of $C_6D_5CD_2H$.

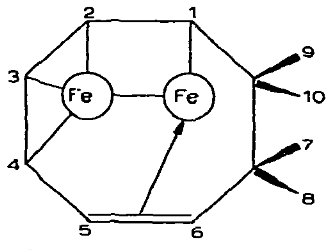

Fig. 2. A schematic representation of the molecular structure showing a numbering scheme for the protons.

Multiplet A collapses less readily. Fine structure largely disappears between −29° and −43° and severe broadening of the multiplet as a whole occurs between −57° and −67°. It appears that it definitely separates into two discrete peaks between −67° and −75°. The peak at higher field lies partly within the envelope of multiplet B, which by then also encompasses the intensity due to proton 6, while also suffering collapse of its original (high temperature) fine structure.

The changes in the region of the aliphatic protons, 7, 8, 9 and 10 are not susceptible to any detailed analysis. Evidently the chemical shift differences between 7 and 9 and between 8 and 10 are small. Thus no gross collapse of peaks would be expected, and none is observed.

In summary, the results presented here demonstrate the following main points. (1). The dissymmetric structure found for *cis*-(1,2,6-*trihapto* : 3,4,5-*trihapto*-1,3,5-cyclooctatriene)hexacarbonyldiiron in the crystalline state continues to be the preferred structure in solution, as in the related case of *cis*-(1,2,6-*trihapto* : 3,4,5-*trihapto*cyclooctatetraene)hexacarbonyldiruthenium. (2). The molecule in solution undergoes an oscillatory intramolecular rearrangement by which the two mirror images of the molecule are interconverted*. This occurs rapidly enough at ambient temperature to give a PMR spectrum which indicates that there is a time-average plane of symmetry in the molecule. (3). Once again, the molecular structure found in the crystalline compound and the instantaneous structure found in solution are qualitatively the same. This has been true of all fluxional molecules studied so far.

ACKNOWLEDGEMENTS

We thank Prof. R. B. King for supplying the sample of $C_8H_{10}Fe_2(CO)_6$ and Dr. John Fleming for assistance in the decoupling experiment. This work was supported, in part, by the National Science Foundation under Grant No. 7034X. During the course of this work T. J. Marks was a predoctoral fellow of the National Science Foundation.

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* For the sake of rigor, it should be noted that the possibility of complete rotation of the $(OC)_3FeFe(CO)_3$ group about an axis perpendicular to the Fe–Fe line and to the mean plane of the carbon atoms 1–6, thereby passing through structure (II), is not ruled out by the observed spectra. We have not considered this a likely occurrence however, for various reasons, one of which is that such a motion was positively ruled out by the data for $C_8H_8Ru_2(CO)_6$.