Journal of Organometallic Chemistry, 243 (1983) 315–321
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

HYDROGEN-1 AND PHOSPHORUS-31 NMR SPECTRA OF ONE OF THE C_{2v} ISOMERS OF $Fe_2(CO)_6(\mu\text{-}PHMe)_2$

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(Received August 30th, 1982)

Summary

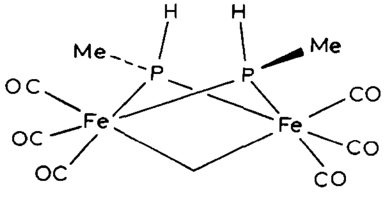
The more symmetric (C_{2v}) isomer of $Fe_2(CO)_6(PHMe)_2$, was obtained free of a second (C_s) isomer by fractional crystallization and ^1H and ^{31}P NMR spectra were recorded. Chemical shift and coupling constants were obtained for this $Y_3XAA'X'Y'_3$ heteronuclear spin system using a modification of the NUMARIT program.

In 1972 our group described the syntheses of $Fe_2(CO)_6(PHMe)_2$ and $Fe_2(CO)_6(PHPh)_2$ from $Fe(CO)_4(PH_2Me)$ and $Fe(CO)_4(PH_2Ph)$, respectively (eq. 1) [1].

$$Fe(CO)_4(PH_2R) \rightarrow Fe_2(CO)_6(PHR)_2 + 2CO\ (+H_2) \qquad (1)$$
$$(R = Me, Ph)$$

These conversions could be accomplished either thermally or photolytically. The dinuclear products are yellow to orange crystalline solids with properties similar to many other known $Fe_2(CO)_6(X)_2$ compounds [2].

The Fe_2P_2 framework in compounds of this general formula is not planar due to an iron–iron bond [2]. Because of this, the two positions occupied by substituent groups on each bridging phosphorus group are dissimilar and three isomers should be possible. Two isomers, I and II below, have C_{2v} symmetry; the third (III) has C_s symmetry. Evidence for the existence of two isomers of the compound $Fe_2(CO)_6(PHPh)_2$ has recently been obtained by ^{31}P NMR spectroscopy [3].



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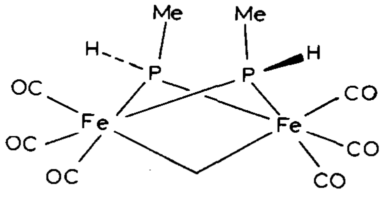

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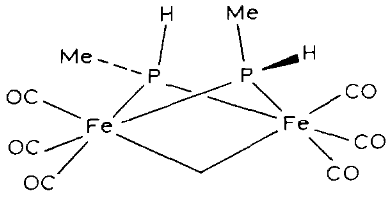

III

In our earlier work [1], two isomers of $Fe_2(CO)_6(PHMe)_2$ were detected by an ^1H NMR experiment. There was a predominant product having a single methyl proton environment which gave an eight line multiplet and a second product in which two methyl environments could be identified by two distinct NMR multiplet patterns. No resonance for the phosphine-hydrogen was detected in these early experiments, a result for which no obvious explanation could be offered.

In the intervening years since our earlier work there have been a number of developments concerning this project. We succeeded in getting crystals of the predominant isomer of the compound $Fe_2(CO)_6(PHMe)_2$ and its structure was determined to be I by single crystal X-ray diffraction techniques [4]. In addition, the acquisition of more sophisticated NMR equipment in this department permitted us to look further into the NMR spectra of both compounds. This paper reports these NMR studies.

Experimental

Samples of $Fe_2(CO)_6(PHMe)_2$ were available from our earlier studies on these compounds [1]. This compound crystallized by slow evaporation of a heptane solution at 4°C, giving bright yellow crystals. Careful fractional crystallization of

TABLE 1

NMR PARAMETERS FOR $Fe_2(CO)_6(PHMe)_2$

Compound	Chemical shifts (ppm) [a]		Coupling constants (Hz)	
$Fe_2(CO)_6(PHMe)_2$	δ(H)	2.74	J(P–H)	365.7
(C_{2v} form)	$\delta(CH_3)$	1.83	J(P–P′)	−150.8
			J(P–H′)	28.7
	δ(P)	−60.7	J(H–H′)	−1.9
			J(H–Me)	5.5
			J(H–Me′)	−0.3
			J(P–Me)	−12.99
			J(P–Me′)	−1.21
			J(Me–Me′)	0
$Fe_2(CO)_6(PHMe)_2$	δ(P)	−59.7,	J(P–P′)	168.0
(C_s form)		−52.8		

[a] Proton chemical shifts in ppm downfield from internal TMS; ^{31}P chemical shifts relative to 85% H_3PO_4 (external standard).

$Fe_2(CO)_6(PHMe)_2$ gave a pure sample of the more abundant, (and less soluble) C_{2v} isomer I. Later fractions were enriched in the C_s isomer but this was never obtained completely free of the first isomer. There was no evidence that the third isomer was present. Three isomers of $Fe_2(CO)_6(PHPh)_2$ had been identified in the earlier work, in the ratio 50/45/5 [3].

NMR spectra (^{31}P and ^1H) were obtained on samples dissolved in $CDCl_3$ at 37°C using a Varian XL-100 spectrometer operating in the FT mode (100.1 MHz for ^1H NMR spectra and 40.49 MHz for ^{31}P spectra). The spectra were analyzed and computer simulated spectra obtained using a modified version of the NUMARIT program written by K.M. Worvill, University of East Anglia, and J.S. Martin, University of Alberta, in 1975 [5].

Experimental and simulated ^1H and ^{31}P NMR spectra for $Fe_2(CO)_6(PHMe)_2$ are given in Figs. 1 and 2 respectively. Decoupled $^1H\{^{31}P\}$ and $^{31}P\{^1H\}$ spectra are shown in Figs. 3 and 4. Chemical shift and coupling constant data are given in Table 1.

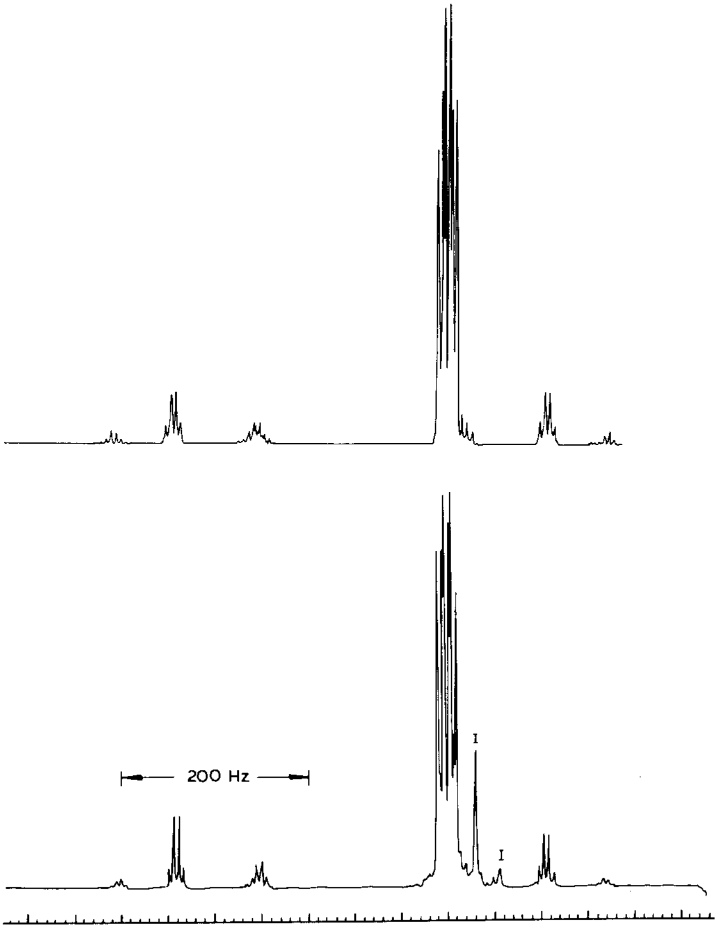

Fig. 1. Calculated (top) and observed (bottom) ^1H NMR spectra of the C_{2v} isomer (I) of $Fe_2(CO)_6(PHMe)_2$.

Discussion

Preliminary ^{1}H NMR data had indicated that two isomers of $Fe_2(CO)_6(PHMe)_2$ were present in samples of this compound. By careful fractional crystallization one isomer could be obtained. This isomer, one of the C_{2v} forms now known to be I, had a lesser solubility in heptane than did the second lower symmetry (C_s) isomer.

The new NMR data for this pure isomer were of considerable interest. First the P–H resonance, which had previously not been observed, was found in this spectrum. It appears that a combination of two factors, low solubility of the compound and the high multiplicity of this resonance had been responsible for the failure to locate this resonance. With the higher sensitivity using the spectrometer in the FT mode, this resonance was easily distinguished (Fig. 1). It consisted of six sets of multiplets in a symmetric pattern characteristic of a XAAX′ spin system, with X and A representing H and P atoms respectively. A simple analysis of this pattern gave coupling constants *J*(P–H) 360, *J*(P–P) ~ 150, and *J*(H–H) ~ 0 Hz. These numbers are approximately the values anticipated. However the further coupling of this hydrogen with methyl group protons was complex, and further coupling constants were not easily defined. Neither was the origin of eight line multiplet pattern for the methyl proton obvious. Thus we turned to the NUMARIT program to determine these further parameters. Using this program we were able to define a complete set of coupling constants and chemical shifts (Table 1). The accuracy of the fit of these

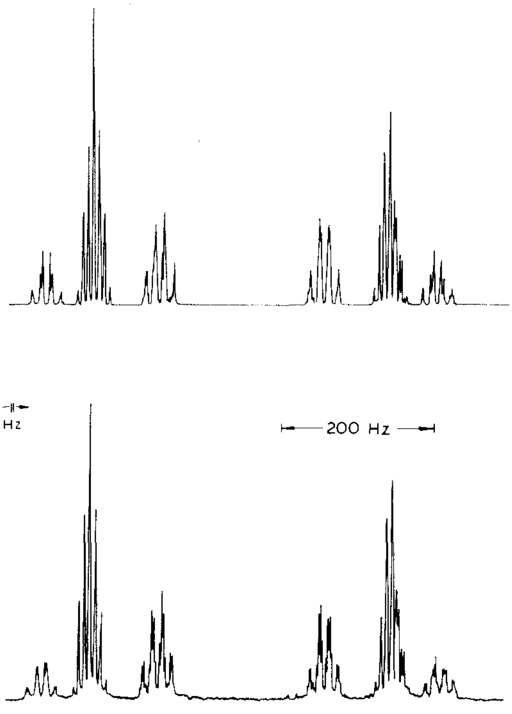

Fig. 2. Calculated (top) and observed (bottom) ^{31}P NMR spectra of the the C_{2v} isomer (I) of $Fe_2(CO)_6(PHMe)_2$.

data with experiment can be seen visually in a comparison of experimental and calculated spectra for this compound.

It is noted that the original assumption of $J(\mathrm{H-H'}) = 0$ Hz was used initially since this leads to a six line pattern for an XAA′X′ systems; if $J(\mathrm{H-H'}) \neq 0$ Hz (and all other coupling constants are non-zero values) then a 10 line pattern would arise [6]. However, in the final analysis it became necessary to assign a small value to $J(\mathrm{H-H})$, 1.2 Hz. This was necessary when we looked at the $\mathrm{CH_3}$ proton resonances in the $^1\mathrm{H}\{^{31}\mathrm{P}\}$ spectrum (Fig. 3). These resonances collapse to two patterns which look like asymmetric triplets. With $^{31}\mathrm{P}$ decoupling, these resonances are most easily interpreted as a $\mathrm{Y_3XX'Y_3}$ spin system. As with the previously observed XAA′X′ system, six lines are seen for $\mathrm{Y_3}$ if all coupling constants except $J(\mathrm{Y_3-Y_3'})$ are finite. A small value of $J(\mathrm{H-H'})$ is thus required. Including this value did not alter the calculated undecoupled $^1\mathrm{H}$ NMR spectrum. The intensities of the satellite lines in the full 10 line spectrum are dependent on relative values of the various coupling constants and we can assume therefore that the additional lines expected are of too low intensity to be detected.

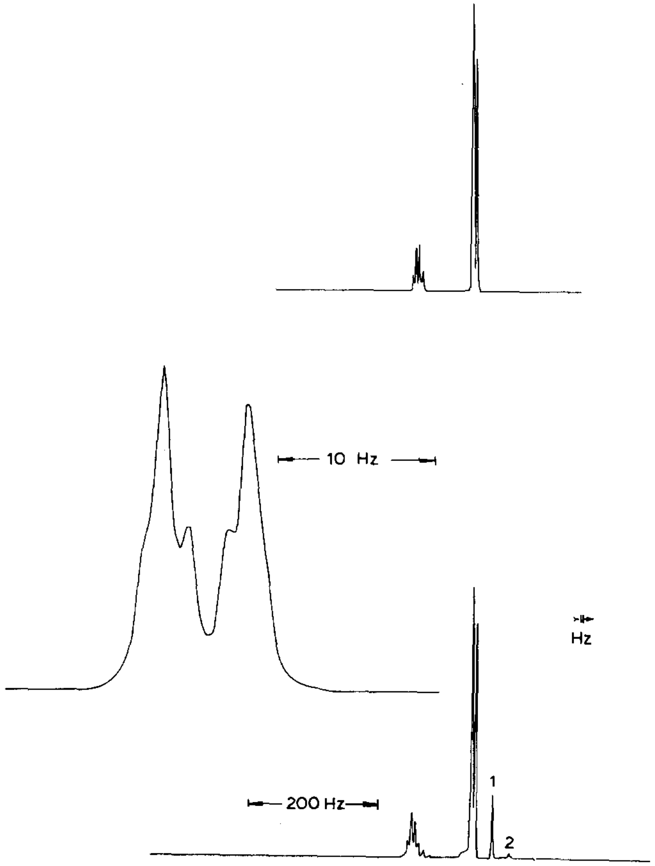

Fig. 3. Calculated (top) and observed (bottom) $^1\mathrm{H}\{^{31}\mathrm{P}\}$ spectrum of the C_{2v} isomer (I) of $\mathrm{Fe_2(CO)_6(PHMe)_2}$. Resonances labeled 1 and 2 are due to impurities. The insert (middle) shows a scale expansion of the methyl proton region.

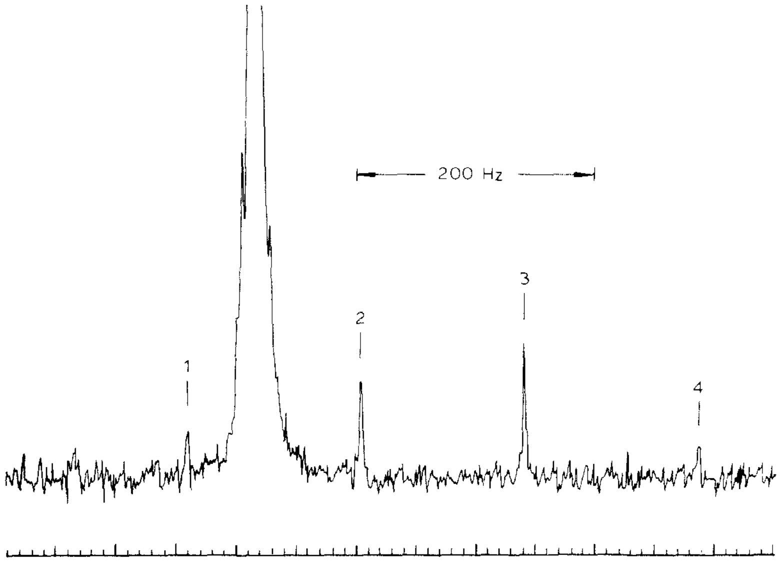

Fig. 4. $^{31}P\{^1H\}$ spectrum of the C_{2v} isomer (I) of $Fe_2(CO)_6(PHMe)_2$. The low intensity lines 1–4 are due to presence of the C_s isomer as an impurity in this sample.

The ^{31}P NMR spectrum for this compound was also recorded (Fig. 2). The basic six line pattern for this resonance was, of course, the same as was seen for the ^1H nucleus; however the multiplicities of each resonance arising from $J(P-CH_3)$ were different. Experimental and calculated spectra are shown.

We were confronted with a small surprise in the $^{31}P\{^1H\}$ decoupled spectrum for this compound. The primary resonance is, of course a singlet. However at maximum resolution four additional resonances, an AB pattern, were just visible in the noise (Fig. 4). These peaks are associated with the C_s isomer of this compound, present as a trace component of this sample. The chemical shifts and coupling constant data for this compound are similar to data for the analogous isomer of $Fe_2(CO)_6(PHPh)_2$ [3].

Acknowledgement

We thank Dr. R.C. Cavell and Dr. J.S. Martin of the University of Alberta for providing a copy of the NUMARIT program. Our department NMR facilities were purchased with partial financial assistance of NSF.

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4 J.R. Huntsman, Ph.D. Thesis, Univ. of Wisconsin, (1973); see Diss. Abst., 34 (1974) 4897B.
5 The NUMARIT program, obtained by us from the University of Alberta, utilizes the magnetic equivalence method and twofold symmetry factoring making it practical for large spin systems. The

magnetic equivalence method [6,7] allows a magnetically equivalent group to be treated as a single nucleus whose spin is the sum of the individual spins. Here the methyl group protons were treated in this fashion. This reduces the matrix size and also simplifies the structure of the matrix. The conditions for magnetic equivalence require the quantum mechanical spin operator F^2 to commute with Hamiltonian and transition operators. This forces the off diagonal elements of the matrix to be zero and forbids transition between states which would change the group's F value. The Hamiltonian matrix then factors into submatrices which can be solved independent of each other. The twofold symmetry factoring allows further simplification. When two submatrices are related by a twofold symmetry operation they are degenerate, requiring energy levels and transitions to be calculated for only one submatrix. Because NUMARIT is a homonuclear program, it was neccessary to assign the ^{31}P chemical shift an arbitrarily large value to separate it from the hydrogen region. Other minor program changes were incorporated to allow use of this program on our Harris/7 minicomputer.

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