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A ^{13}C NMR STUDY OF SOME DERIVATIVES OBTAINED FROM IRON CARBONYLS AND DIPHENYLACETYLENE

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Summary

The molecule $Fe_2(CO)_7(PhC_2Ph)_2$ has been studied by ^{13}C NMR and is static at —40°C with a spectrum which is consistent with the known structure observed in the crystals. In the range —40 to +41°C the three carbonyl resonance coalesce possibly by a single carbonyl averaging process. At room temperature violet $Fe_3(CO)_8(PhC_2Ph)_2$ is found to be static by ^{13}C NMR having a spectrum consistent with the known solid state structure. Dark green $Fe_3(CO)_8(PhC_2Ph)_2$ is static via ^{13}C NMR at —62°C with a spectrum consistent with the known solid state structure. Between —62 and +96°C a fluxional process occurs which scrambles the bridge carbonyls and four of the six terminal carbonyl groups. In this process the bridging carbonyls appear to be preferentially moving toward the iron atoms with which they have the shortest iron—carbon bond as observed in the solid state structure.

Introduction

Some years ago Reppe and Vetter reported that an alkaline solution of iron carbonyl hydride and acetylenes at moderate temperatures gave hydroquinones [1]. Since that time a large variety of iron carbonyl-acetylene intermediates, cyclopentadienones, quinones, tropones and substituted benzene derivatives have been isolated from the reactions of iron carbonyls with acetylenes in chemically inert organic solvents [2]. In the following scheme are given some of the intermediate compounds that have been isolated by reaction of $Fe(CO)_5$, $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ with disubstituted acetylenes (Scheme 1). The proposed

SCHEME 1

$$\begin{tikzcd}
\mathrm{Fe_3(CO)_{12}} + \mathrm{RC{\equiv}CR} \arrow[r] \arrow[d] & \mathrm{Fe_3(CO)_9(RC_2R)} \arrow[d] \\
\mathrm{Fe(CO)_4(RC_2R)} \arrow[d] & \begin{array}{l}\mathrm{Fe_3(CO)_8(RC_2R)_2}\\ \text{(II) (violet isomer)}\end{array} \arrow[d] \\
\mathrm{Fe_2(CO)_7(RC_2R)} \arrow[d, "\mathrm{RC{\equiv}CR}"] & \begin{array}{l}\mathrm{Fe_3(CO)_8(RC_2R)_2}\\ \text{(III) (dark green isomer)}\end{array} \arrow[d] \\
\begin{array}{c}\mathrm{Fe_2(CO)_7(RC_2R)_2}\\ \text{(I)}\end{array} & \mathrm{Fe_2(CO)_6(RC_2R)_2}
\end{tikzcd}$$

pathways of interconversion were suggested by Hübel from his extensive study of the chemistry of certain of the organometallic intermediates [2]. In recent years single crystal X-ray methods have been used to determine the solid state structure of several of these iron carbonyl-acetylene intermediates. In solution at room temperature or higher many of these complexes may exhibit fluxional properties. A determination of these properties will add a new dimension to their molecular structure. A ^{13}C NMR study of the molecules I-III in Scheme 1 is the subject of this report.

Experimental

Instrumentation and ^{13}C NMR procedures

The ^{13}C NMR spectra were obtained with a Varian XL-100-15 spectrometer operating in the pulsed Fourier transform mode at 25.1 MHz. The instrument is equipped with a Transform Technology, Inc. pulse unit which delivers a 90° pulse in 15 μsec and 36K Nicholet 1089 Computer system with disc. The ^{13}C chemical shifts were measured relative to an internal standard peak and reported relative to tetramethylsilane. The conversion factors used are $\delta(\mathrm{TMS}) = \delta(\mathrm{CH_2Cl_2}) + 53.89$ ppm and $\delta(\mathrm{TMS}) = \delta(\mathrm{dioxane}) + 67.38$ ppm. To aid in the relaxation of carbonyl carbon nuclei tris(acetylacetonato)chromium(III) (about 0.05 *M* concentration) was added to each NMR sample [3].

Materials

The compounds $Fe_3(CO)_8(PhC_2Ph)_2$, violet and dark green isomers, were prepared from $Fe_3(CO)_{12}$ and diphenylacetylene by the method of Hübel and Braye [4].

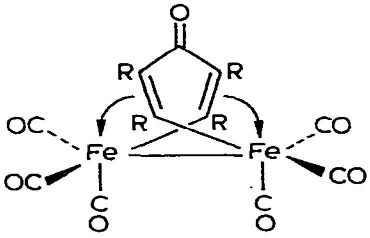
$Fe_2(CO)_7(PhC_2Ph)_2$

Two grams (0.009 mole) of $Fe_2(CO)_9$ and 3.25 g (0.018 mol) of diphenylacetylene were stirred under nitrogen in 50 ml 30-60° petroleum ether for 24 h. The solution was evaporated to dryness under vacuum and the solid mixture was placed on an acid alumina (Woelm, activity 1) column. Diphenylacetylene was eluted with hexane, and $Fe_2(CO)_6(PhC_2Ph)_2$ was eluted with 10% benzene in hexane. The red $Fe_2(CO)_7(PhC_2Ph)_2$ was eluted from the column with benzene. The red fraction was evaporated to dryness and the solid was crystallized from benzene/pentane solution at —78°C as red needles, 3.5 g (60% yield based on $Fe_2(CO)_9$) m.p. 154-155°C (dec.).

Results and discussion

$Fe_2(CO)_7(PhC_2Ph)_2$ (I)

Treatment of $Fe_2(CO)_9$ with diphenylacetylene in petroleum ether for 24 h at room temperature forms I in moderate yield. The ^{57}Fe Mössbauer spectrum of this compound suggested that the two iron atoms were structurally equivalent [5]. An X-ray structure study of the closely related compound $Fe_2(CO)_7$-$(CH_3C_2CH_3)_2$ yielded a structure of type A [6]. The ^{13}C NMR spectrum of the carbonyl carbon region of I at various temperatures is presented in Fig. 1. At —30°C three carbonyl carbon resonances in a 1/1/1 ratio are observed which is consistent with the solid state structure. At about +10°C the two upfield signals at 205.8 and 205.4 ppm coalesce. Finally at a higher temperature (+41°C), the peak of area two at 209.0 ppm and the peak of area four at about 205 ppm coalesce.



(A)

Line shape analysis suggests that the two coalescence points for the carbonyl resonances may well be due to a single carbonyl averaging process. From the coalescence temperatures of averaging signals we estimate rates of 24.6 sec^{-1} at 283 K and 275 sec^{-1} at 314 K. From the rates, assuming a frequency factor of $10^{13.3}$ ($\Delta S^{\neq} = 0$) in the Arrhenius equation, the activation energy is estimated to be about 13.4 ± 1.0 kcal mol^{-1}. If more than one process is involved in the permutation of the carbonyl groups, it can not be distinguished by this NMR study.

The movements of the dienone ligand during the fluxional process are of considerable interest but can not be determined from the present data.

The ring carbon resonances were pinpointed by preparing I with diphenylacetylene which was ^{13}C-enriched in the acetylene carbons. The ring carbon assignments are presented in Table 1. We suggest that the signal at 192.3 ppm is probably due to the ring carbon atoms that are nearest to the iron atoms.

$Fe_3(CO)_8(PhC_2Ph)_2$ isomers

Heating $Fe_3(CO)_{12}$ and diphenylacetylene in methanol for a short time formed the violet complex $Fe_3(CO)_8(PhC_2Ph)_2$(II) [4]. When this compound was heated to 80°C an isomerization occurred to form the dark green complex III [4]. The single crystal X-ray structures of these two isomers have been determined [7] and these are illustrated in Figs. 2 and 3. At room temperature, the

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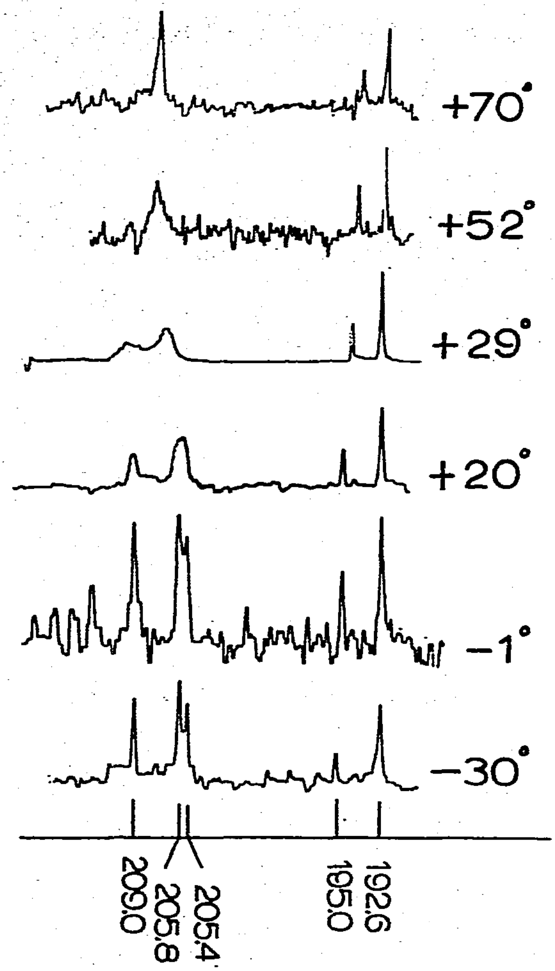
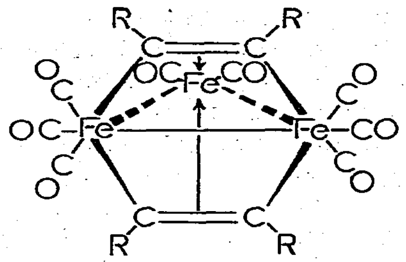


Fig. 1. The ^{13}C NMR spectra of $Fe_2(CO)_7(PhC_2Ph)_2$ in the CO region at various temperatures. The two peaks at highest field at 195.0 and 192.6 ppm are due to the organic carbonyl and one of the ring carbon atoms respectively. Spectra at 29°C and lower were recorded in dichloromethane solvent and those above 29°C in dioxane solvent.

TABLE 1

^{13}C NMR DATA OF IRON CARBONYL-DIPHENYLACETYLENE DERIVATIVES

Compound	Temp. (°C)	δc (ppm) [relative area]	Assignment
$Fe_2(CO)_7(PhC_2Ph)_2$ (I)	−68	209.0[2], 205.8[2], 205.4[2]	carbonyl carbons
		195.7	organic carbonyl carbon
		192.3	ring carbons nearest iron atoms
		93.8	ring carbons nearest organic carbonyl
$Fe_3(CO)_8(PhC_2Ph)_2$ (II) (violet isomer)	+30	210.0[4]	carbonyl carbons
		207.0[2]	carbonyl carbons
		201.0[4]	acetylene carbons
		198.5[2]	carbonyl carbons
$Fe_3(CO)_8(PhC_2Ph)_2$ (III) (dark green isomer)	+96	221.2[6], 203.7[2]	carbonyl carbons
		120.5, 119.0	acetylene carbons
	−32	253.7[2], 204.6[4], 203.0[2]	carbonyl carbons
		118.4, 117.6	acetylene carbons



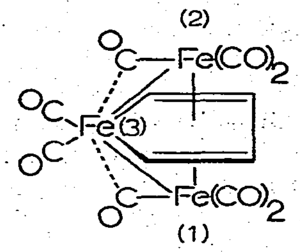


Fig. 2. The structure of the violet isomer of the formula $Fe_3(CO)_8(PhC_2Ph)_2$.

Fig. 3. The structure of the dark green isomer of the formula $Fe_3(CO)_8(PhC_2Ph)_2$.

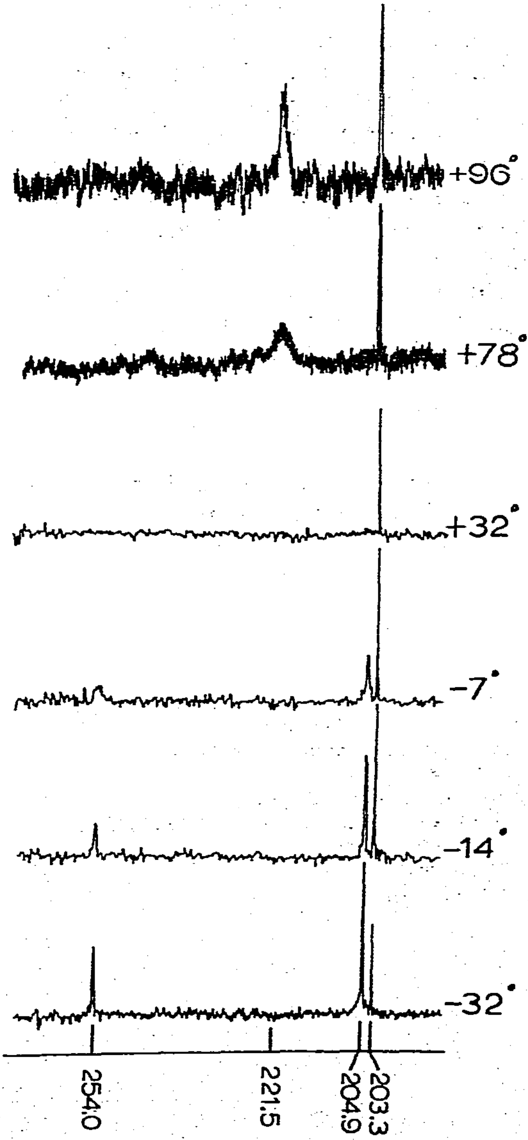


Fig. 4. The ^{13}C NMR spectra of $Fe_3(CO)_8(PhC_2Ph)_2$, dark green isomer, in the CO region at various temperatures. Spectra at 32° C and lower were recorded in dichloromethane solvent and those above 32° C in dioxane solvent.

^{13}C NMR spectrum of II exhibited four resonances in the 210 to 198 ppm region with a 2/4/2/4 area ratio. We attribute these signals to the carbonyl carbon atoms as well as the acetylene carbon atoms of the two equivalent diphenylacetylene ligands. This pattern of signals is consistent with that expected for a static configuration based on the solid state structure. A high temperature NMR study of II was precluded due to the facile and irreversible isomerization of II to a dark green compound III under these conditions.

The variable temperature ^{13}C NMR spectra of the carbonyl region of III are presented in Fig. 4. At —32°C and lower temperatures three carbonyl carbon signals are observed in a 2/4/2 ratio. One of the area two resonances is at a very low field position (254.0 ppm) and is attributed to bridging carbonyl groups based on previous studies [8]. This low temperature pattern is consistent with the solid state structure of this molecule. As the temperature is increased to +96°C the two carbonyl signals at 254.0 ppm and 204.9 ppm first broaden and then coalesce. It appears then that the bridging carbonyl and the terminal carbonyl groups on Fe(1) and Fe(2) are scrambling. In the X-ray structure of III the bridging carbonyl carbon-to-Fe(1) distance (1.84 Å) is significantly shorter than the bridging carbonyl carbon-to-Fe(3) distance (1.99 Å). This type of carbonyl group is moderately unsymmetrical and may fit into the semibridging carbonyl class [9]. In this scrambling process the bridging carbonyls appear to be preferentially moving towards the iron atoms with which they have the shortest bonds. The acetylene carbon signals given in Table 1 were pinpointed by preparing III employing ^{13}C-enriched diphenylacetylene.

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