

¹³C AND ¹H NMR SPECTRA OF MONOSUBSTITUTED FERROCENES CONTAINING A CHIRAL CENTRE IN THE SUBSTITUENT

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(Received September 9th, 1973)

Summary

The ¹³C-¹H and ¹H NMR spectra of ferrocenyl chalcones (β -benzoylvinylferrocene and cinnamoylferrocene) and their iron carbonyl complexes were recorded. Splitting of the resonances of both α - and β -substituted cyclopentadienyl ring atoms was found in ¹³C-¹H NMR spectra of all complexes. In ¹H NMR spectra splitting of the resonances of the substituted cyclopentadienyl ring α -protons was detected only in the case of (cinnamoylferrocene)iron tricarbonyl. The splitting effect mentioned can be due to the anisochronism (magnetic nonequivalence) of all carbon and hydrogen nuclei because of the iron carbonyl fragment coordination causes the substituent to become the chiral group. The coordination of iron carbonyl group results in a reduction of the conjugation in the α, β -unsaturated ketone system. This phenomenon is discussed on the basis of ¹³C-¹H and ¹H NMR data.

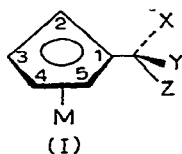
Introduction

We have previously studied the ¹³C NMR spectra of monosubstituted ferrocenes [1,2]. Various problems on structure and properties of the ferrocene derivatives in an unreactive state, especially the electron density distribution in the substituted π -cyclopentadienyl ligand, have been discussed in terms of the ¹³C NMR data. In addition, it was detected [2] that, when a cyclopentadienyl ligand was attached directly to classical tetrahedral asymmetric carbon atom (structure I, $M = \pi\text{-C}_5\text{H}_5\text{Fe}$; $X = \text{H}$, $Y = \text{OH}$, $Z = \text{CH}_3$ or C_6H_5), carbon atoms in α -position, C(2) and C(5), became spectroscopically discernible. The splitting of β -nuclei, C(3) and C(4), resonances was found to be analogous to those detected for C(2) and C(5) but less pronounced.

Recently it was shown [3] that in the ¹H NMR spectra of cymantrene derivatives containing an asymmetric α -carbon atom in the substituent (structure I, $M = \text{Mn}(\text{CO})_3$; $X = \text{H}$, $Y = \text{OH}$, $Z = \text{CF}_3$ or C_6H_5), α -protons of the cyclopentadienyl

TABLE I
 ^{13}C - $\{^1\text{H}\}$ NMR DATA FOR $\pi\text{-C}_5\text{H}_5\text{Fe}\pi\text{-C}_5\text{H}_5\text{R}$ COMPOUNDS (δ ppm, $\delta(\text{TMS}) = 0$)

No.	R	Solvent	Temperature ($^\circ\text{C}$)	π -cyclopentadienyl rings				phenyl rings				
				C(1)	C(2,5)	C(3,4)	C(6)	C(7), C(8)	C(9)	Fe-C \equiv O	C(10)	C(11), C(12)
II	$\text{CH}=\text{CHCO}_2\text{C}_6\text{H}_5$	CH_2Cl_2	10	79.2	69.2	71.4	69.9	119.0 147.5	210.2	138.6	128.6	132.4
IV	$\text{CH}=\text{CHCO}_2\text{C}_6\text{H}_5$ $\text{Fe}(\text{CO})_4$	CH_2Cl_2	10	89.0	62.4 68.0	70.0 70.4	69.6	50.0 59.0	194.4	208.3	128.1	132.7
III	$\text{COCH}=\text{CHC}_6\text{H}_5$	CH_2Cl_2	20	80.8	69.7	72.9	70.2	123.3 140.4	192.3	135.3	128.3 128.9	130.1
		acetone	25	69.1	69.1	72.0	69.3	123.1 139.3			127.8 129.3	129.4
V	$\text{COCH}=\text{CHC}_6\text{H}_5$ $\text{Fe}(\text{CO})_4$	CH_2Cl_2	20	68.7	68.7	72.5	70.1	57.2	207.7	142.8	126.2 129.0	126.6
		acetone	27	80.3	69.1 71.2	72.6 72.9	70.5	51.1 58.3	198.7	208.5	143.5	127.0
		CH_3NO_2	20	80.7	69.8 71.8	73.2 73.6	71.0	51.1 58.0	200.0	208.9	143.9	129.4
IV	$\text{COCH}=\text{CHC}_6\text{H}_5$ $\text{Fe}(\text{CO})_3$	CH_2Cl_2	15	76.0	67.8 71.2	71.5 72.8	70.0	61.2 67.7		145.2	126.6 128.9	126.8

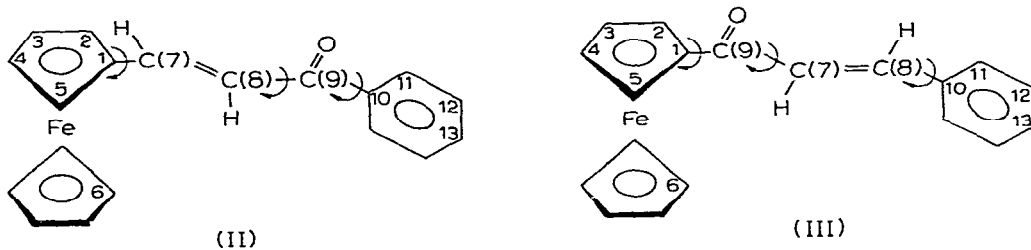


ring (H_2 and H_5) gave rise to two different signals. In some cases ($X = CH_3$, $Y = OH$, $Z = PO(OAlk)_2$) it was possible to observe the splitting of both the α - and β -protons resonances.

The present paper is devoted to the investigation of ^{13}C and 1H NMR spectra of some new monosubstituted ferrocenes. The effect of more complicated chiral groups in the substituents upon the spectra of the respective derivatives was examined. Some other details of the spectra of ferrocenyl chalcones and their iron carbonyl complexes will be discussed.

Results and discussion

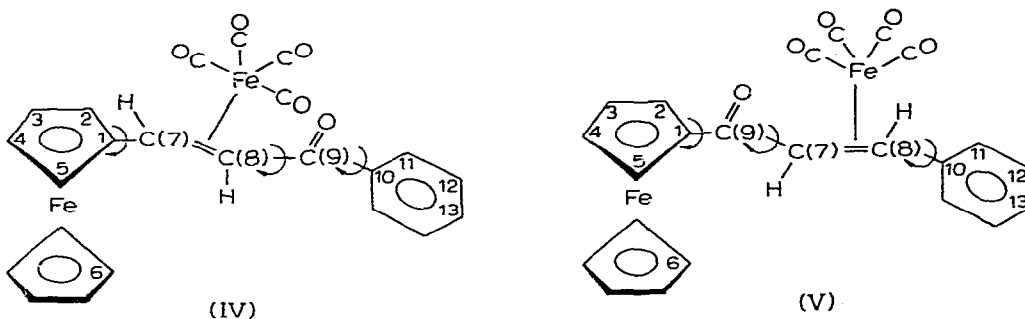
We have taken the ^{13}C - $\{^1H\}$ and 1H NMR spectra of ferrocenyl chalcones [β -benzoylvinylferrocene(II) and cinnamoylferrocene(III)] as well as the spectra of olefinic-iron tetracarbonyl (IV and V) and -iron tricarbonyl (VI) π -complexes. These complexes have been prepared on the basis of starting compounds II and III.



In the parent ferrocenyl chalcones II and III there is a symmetry plane which passes through the nucleus C(1) of substituted cyclopentadienyl ring, the substituent and ferrocenyl iron atom. Owing to this fact, the nuclei 1H and ^{13}C of substituted cyclopentadienyl ring within each of the two pairs (2-5 and 3-4) are connected by a symmetry plane and consequently are enantiotopic atoms. The 1H and ^{13}C - $\{^1H\}$ NMR spectra recorded in achiral solvents agree with this thesis. In the 1H NMR spectra of II and III the nuclei $H(2,5)$ and $H(3,4)$ give rise to triplet resonances, the chemical shifts and values of splitting of these signals being typical of compounds of this type [4,5]. In the ^{13}C - $\{^1H\}$ NMR spectra the single peaks correspond to both the nuclei C(2,5) and C(3,4) (Table 1).

The coordination of the iron carbonyl fragment with a double bond (or with a double bond and a carbonyl) causes the substituent to become the chiral group. Owing to this, the 1H and ^{13}C nuclei of the two pairs 2-5 and 3-4 of the substituted cyclopentadienyl ring are no longer connected by any symmetry operation and they become diastereotopic (and consequently anisochronic) atoms. According-

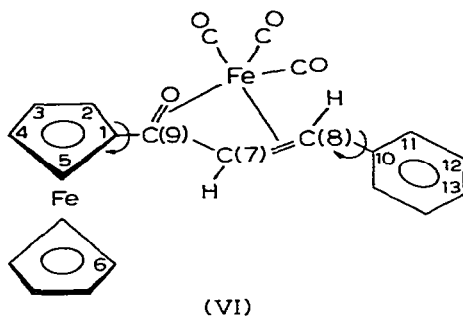
ly, in the ^1H and ^{13}C NMR spectra of complexes IV, V and VI one can expect the appropriate changes. Nevertheless, the capability of the ^1H NMR to detect the effect under discussion is restricted. Compounds of the type I ($M = \pi\text{-C}_5\text{H}_5\text{Fe}$; $X \neq Y \neq Z$) with a chiral centre in the ferrocene substituent were investigated by ^1H NMR repeatedly but no spectroscopic indication of diastereotopy (anisochronism) for atoms within pair (2-5) [as well as within pair (3-4)] was detected [6,7,8].



The ^1H NMR spectra of IV and V (in acetone) show no complication of the α - and β -triplet structures (Table 2). This result (which was obtained for a variety of substituted ferrocenes with different types of chiral centers in substituents) appears to be due to small intensity of the expected effect or to accidental coincidence of the shielding of nuclei H(2) and H(5) [as well as nuclei H(3) and H(4)], the shielding being averaged out of different conformational isomers. The magnetic nonequivalence of nuclei H(2) and H(5) was only found for VI in which the bulky chiral group is attached directly to ferrocenyl nucleus. There is the splitting of the H(2,5)-proton signal, but resonance of the H(3,4)-protons, which are situated far from the chiral substituent, is not split.

TABLE 2
 ^1H NMR DATA FOR $\pi\text{-C}_5\text{H}_5\text{Fe}\pi\text{-C}_5\text{H}_4\text{R}$ COMPOUNDS (δ ppm, $\delta(\text{TMS}) = 0$)

No.	R	Solvent	H(2,5)	H(3,4)	H(6)	H($\text{CH}^a = \text{CH}^b$)	H(C_6H_5)
II	$\text{CH}=\text{CHCOC}_6\text{H}_5$	acetone	4.80	4.54	4.23	7.35 7.81	7.38-7.75
IV	$\text{CH}=\text{CHCOC}_6\text{H}_5$ $\text{Fe}(\text{CO})_4$	acetone	4.71	4.50	4.21	5.25 5.45 $J(\text{ab})$ 16Hz	7.45-7.75 8.20-8.50
III	$\text{COCH}=\text{CHC}_6\text{H}_5$	acetone	5.03	4.64	4.26	7.25-8.00 $J(\text{ab})$ 13.5Hz	7.25-8.00
V	$\text{COCH}=\text{CHC}_6\text{H}_5$ $\text{Fe}(\text{CO})_4$	acetone	4.82	4.55	4.25	5.10 5.40	7.10-7.40
III	$\text{COCH}=\text{CHC}_6\text{H}_5$	CHCl_3	4.92	4.57	4.21	7.15 7.83	
VI	$\text{COCH}=\text{CHC}_6\text{H}_5$ $\text{Fe}(\text{CO})_3$	CHCl_3	4.64 4.99	4.51	4.21	3.52 6.23 $J(\text{ab})$ 16Hz $J(\text{ab})$ 9.5Hz	



As expected, in the $^{13}\text{C}\{-^1\text{H}\}$ NMR spectra of IV, V and VI, which contain chiral groups in their substituents, five signals correspond to the carbon nuclei C(1-5) of the substituted cyclopentadienyl ring. In the spectra of parent ferrocenyl chalcones II and III we have observed only three peaks for the five nuclei mentioned. Taking into account the data for a variety of different ferrocenes [2], it is not difficult to assign a peak to the knot nucleus C(1), which is attached directly to a substituent. The signal in the lowest field (of the range peculiar to the cyclopentadienyl carbon resonances) is due to this nucleus. In such a way we can obtain information for the chemical shifts of the nuclei C(2-5) (i.e. of the diastereotopic cyclopentadienyl carbon α - and β -atoms).

The comparison of asymmetric influence of chiral centers depending upon the structure of compounds and environment brought out the interesting regularities. In IV asymmetric centre is attached directly to ferrocenyl fragment and so the magnetic nonequivalence of the nuclei C(2,5) and C(3,4) can be detected in the spectra recorded in a solvent of low polarity, dichloromethane. In the case of V, in which the chiral group is separated from ferrocene by carbonyl, the

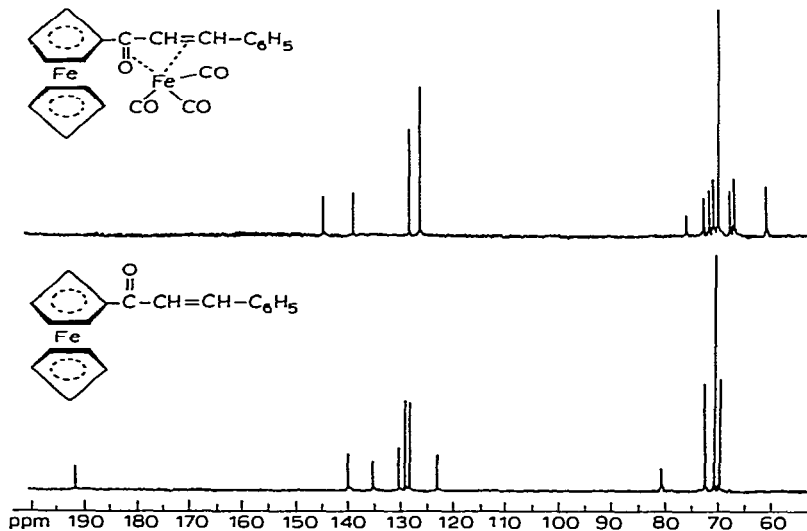


Fig. 1. ^{13}C NMR spectra of III and VI in CH_2Cl_2 (δ ppm, $\delta(\text{TMS}) = 0$).

splitting of the α - and β -carbon signals was not observed when CH_2Cl_2 was used. But in the more polar and strongly solvating acetone and nitromethane this effect became detectable. The bulky chiral group in VI favors the spectroscopic differentiation of diastereotopic nuclei C(2-5) in CH_2Cl_2 (Fig. 1).

Other details of the ^1H and ^{13}C NMR spectra of IV, V and VI are discussed below.

The ^1H NMR spectrum of iron tetracarbonyl complex IV in comparison with the spectrum of the parent ligand II shows an upfield shift of the vinyl proton resonances. Thus, signals in II superimpose on the multiplet of phenyl protons and in IV these vinyl protons give rise to two doublets at higher field. The signals of free cyclopentadienyl ring protons and β -protons of the substituted ring scarcely change the position when the iron carbonyl group coordinates with double bond of the substituent. However, α -proton resonances and phenyl group resonances are affected by concerted conjugation of the electron-donating ferrocenyl fragment and the electron-withdrawing benzoyl group in the parent ligand which is directed through the double bond. The coordination of the double bond of ligand II with $\text{Fe}(\text{CO})_4$ -group leads to breaking of the conjugation and consequently the electronic interaction between ferrocenyl and benzoyl groups must relax. Actually, when the iron carbonyl group coordinates, the triplet of the substituted ring α -protons undergoes a small upfield shift. This appears to be partly due to the decrease of the electron-withdrawing capacity of the substituent.

In the ^1H NMR spectrum of iron tricarbonyl complex VI, in contrast to the spectrum of iron tetracarbonyl complex of cinnamoylferrocene, V, chemical shifts of the two olefinic protons are very dissimilar (δ 3.52 and 6.23 ppm).

In the ^{13}C NMR spectra in going from ferrocenyl chalcones to their iron tetracarbonyl complexes there is a great upfield shift ($\Delta\delta$ 70 - 90 ppm) of the vinyl carbon resonances. Shifts of the same order of magnitude can be detected in the ^{13}C NMR spectra when a double bond of an unsaturated compound coordinates with a rhodium atom ($\Delta\delta$ 60 - 100 ppm) [9] or in passing from butadiene to its iron tricarbonyl complexes ($\Delta\delta$ 50 - 70 ppm) [1,10,11]. The complexing of double bond with a silver atom is accompanied by much smaller shift ($\Delta\delta$ 4 ppm) [12,13].

Signals of ketonic carbonyl undergo a downfield shift of ca. 6 ppm when iron tetracarbonyl coordinates with the double bond of cinnamoylferrocene.

There is little variation in chemical shift of the carbon atoms of the free ferrocenyl nucleus when going from parent ferrocenes to their complexes. However, one can expect the substituted ring carbons of β -benzoylvinylferrocene and cinnamoylferrocene to respond to complexing in different ways. The coordination of iron tetracarbonyl with double bond relaxes the electron-withdrawing influence of benzoyl group upon cyclopentadienyl ring. This leads to a downfield shift (of 10 ppm) of the C(1)-resonance and induces a smaller upfield shift of the α - and β -carbon signals. It is known [2] that such shifts occur when electron-donating properties of substituents increase or, alternatively, when electron-withdrawing ability of the substituents decreases. Thus, the results obtained indicate that transfer (olefin) \rightarrow (olefin) $\text{Fe}(\text{CO})_4$ is succeeded by the decrease of electron-withdrawing effect of α,β -unsaturated ketone upon the ferrocenyl fragment. It appears to be due to the strong back donation metal \rightarrow

ligand which leads to the conjugation decrease in the $-\text{C}(\text{O})\text{CH}=\text{CH}$ system. Our data provided by electronic spectroscopy [14] are in agreement with this conclusion. The upfield shift on 3.5 ppm of *p*-carbon ^{13}C resonance in going from III to V also supports this suggestion. Recently, the postulate of electron density transfer from metal to ligand in π -complexing was also substantiated [1] in the appreciable upfield shift of olefinic carbon resonances.

The signals of cyclopentadienyl ring carbons are radically changed on π -complexing in the case of β -benzoylvinyl derivative but almost unaffected in the case of cynamoylferrocene. Phenyl carbons exhibit the opposite trend. Coordination of iron tetracarbonyl with the double bond relaxes the electron-withdrawing influence of the carbonyl group upon the phenyl ring, and leads to a downfield shift (of 7.5 ppm) of C(10)-carbon resonance in going from III to V.

Experimental

The $^{13}\text{C}\{-^1\text{H}\}$ NMR spectra were recorded on a Bruker HX-90 instrument at a frequency of 22.635 MHz. The ^1H NMR spectra were taken on a Perkin-Elmer R-12 spectrometer at a frequency of 60 MHz. The synthesis of all complexes will be described in another paper [14].

Acknowledgements

The authors wish to thank Prof. E.I. Fedin for his interest in this work and Mr. V.I. Robas for the help in recording of the ^{13}C NMR spectra.

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