Preliminary communication

$^1J(^{57}Fe—^{13}C)$ SPIN COUPLING CONSTANTS AND ^{57}Fe CHEMICAL SHIFTS IN FERROCENES. THE STRUCTURE OF METALLOCENYLCARBENIUM IONS

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Summary

The $^1J(^{57}Fe—^{13}C)$ constants and ^{57}Fe chemical shifts in ferrocene derivatives were measured. The structure of metallocenylcarbenium ions is discussed.

The unusual stability of metallocenylcarbenium ions [1] has been drawn to the attention of chemists for a number of years. Two principal viewpoints on the role of the metal atom in stabilizing such ions are known: on one hand there is strong interaction between the metal atom and exocyclic carbon (C_{exo}) in structure I [1, 2], on the other hand [3, 4] structure II or resonant model II↔III are preferable. Cais [5] and Gleiter [6] have proposed the structures IV and V, respectively, with the nonplanar substituted ligand (recently this has been discussed as fulvenic one [7]). In spite of the use of a variety of physical and chemical methods and even X-ray analysis [8, 9] the role of the iron atom in stabilizing the ferrocenylcarbenium ions is not known.

(I)   (II)   (III)

(IV)   (V)
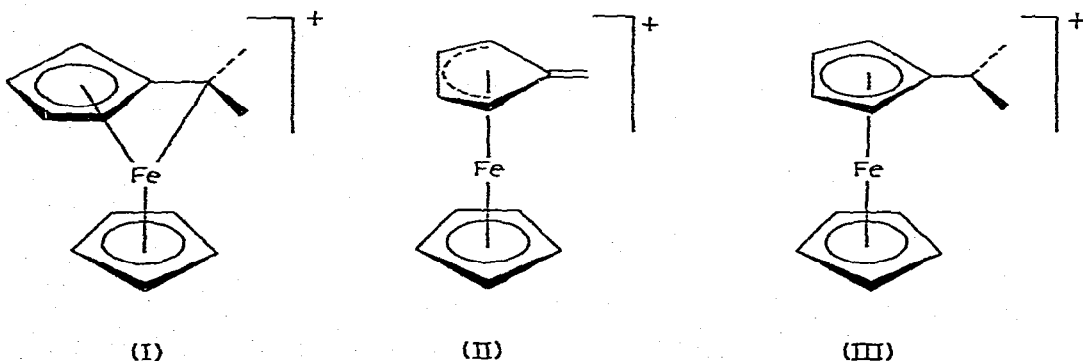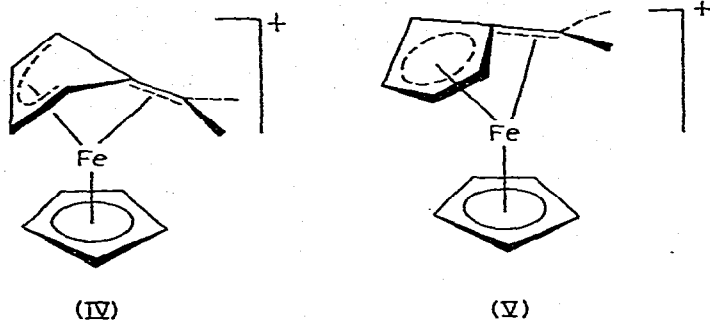
. We assumed that valuable information on the structure of these ions in solution may be obtained from the $^{13}C-\{^1H\}$ NMR spectra of the cations enriched with ^{57}Fe isotope (nuclear spin ½). Apart from this study there were no measured $J(^{57}Fe-^{13}C)$ spin coupling constants except Mann's paper on the respective satellites in the ^{13}C NMR spectra of enriched $Fe(CO)_5$ (natural ^{57}Fe abundance 2.245%) and its phosphine derivatives [10].

Ferrocene with up to 82% of ^{57}Fe isotope was prepared from enriched iron, converted into $^{57}FeCl_2 \cdot 4 H_2O$ and treated with potassium cyclopentadienyl. From this ferrocene sample acetyl-, ethyl-ferrocene and 1-ferrocenylethanol were obtained. The latter compound was dissolved in concentrated H_2SO_4 to generate 1-ferrocenylethyl cation.

The $^{13}C-\{^1H\}$NMR spectrum of enriched ferrocene shows an intensive doublet with $^1J(^{57}Fe-^{13}C) = 4.88 \pm 0.12$ Hz, and a weak singlet due to $^{56}Fe-(C_5H_5)_2$ at $\delta^C = 67.7$ ppm in the methylene chloride solution. The parameters of $^{13}C-\{^1H\}$ NMR spectra of ferrocene derivatives and the cation are shown in Table 1. The α- and β-carbon signals in the substituted five-membered rings of these systems were assigned with the use of a deuterium label [11].

The most remarkable observations are the following.

The carbon signals in the cyclopentadienyl rings of the compounds investigated split owing to spin coupling with ^{57}Fe while no such splitting was detected in the case of exocyclic carbons. It should be noted that we failed to attain such high resolution in the cation spectrum as in the acetylferrocene. However, a comparison of line widths of the ring and *exo* carbons in the cation does not manifest broadening of the latter owing to spin coupling with ^{57}Fe.

$^1J(^{57}Fe-^{13}C)$ constant depends essentially on the position of the carbon atom in the substituted ring and the character of the substituent, it is more sensitive to the electronic changes with respect to $^1J(^{13}C-^1H)$ constants in these systems [12]. We observed the absence of correlation in the change of δ^C and $^1J(^{57}Fe-^{13}C)$ for the same type of carbons, on going from one compound to the other which is probably due to a rehybridization of the iron orbitals in the presence of the substituent.

The splitting of the signal due to the key atom in the cation, $^1J(^{57}Fe-^{13}C_K) = 3.3 \pm 0.4$ Hz allows us to exclude structure II with sixteen electrons at the iron atom which has been already criticized [2]. We disagree with Traylor's opinion [4] that contribution of a canonical form II to the resonance hybride II↔III is essential.

TABLE 1

THE ^{13}C—{^{1}H} NMR PARAMETERS OF FERROCENE DERIVATIVES

Compound[a]	Solvent	Chemical shift δ (ppm)/constant $J(^{57}Fe-^{13}C)$ (Hz)					
		C_K	C_α	C_β	C_5H_5	C_{exo}	CH_3
Fc—C(CH₃)=O	CH₂Cl₂	79.1/5.13 ± 0.03	69.1/4.33 ± 0.03	71.8/4.70 ± 0.03	69.4/4.58 ± 0.03	200.3	26.9
	CS₂	80.2/6.0 ± 0.4	72.5/4.5 ± 0.1	72.5/4.0 ± 0.1	70.4/4.7 ± 0.1	198.2	27.4
Fc—CHCH₃ OH	CS₂	95.4/5.25 ± 0.03	66.8/4.76 ± 0.06 66.7/4.70 ± 0.06	68.5/4.82 ± 0.20 68.4/4.76 ± 0.20	69.0/4.64 ± 0.04	65.7	24.6
Fc—CH₂CH₃	CS₂	90.9/4.82 ± 0.06	68.1/4.89 ± 0.02	67.7/4.76 ± 0.02	69.1/4.73 ± 0.03	23.2	15.6
Fc—C⁺(H)CH₃	H₂SO₄	104.7/3.3 ± 0.4	80.9/4.5 ± 0.2 80.0/4.1 ± 0.2	93.3/2.1 ± 0.2 93.0/2.0 ± 0.2	81.5/4.30 ± 0.06	117.3	19.0

[a] Fc = ferrocenyl.

The absence of C_{exo} splitting in the cation demonstrates that it has no major coupling with the iron which would be expected on the basis of structures I, IV and V. Richards et al. have suggested [2] the shift of $Fe(C_5H_5)$ fragment towards the C_{exo} atom in the cation is due to the greater shielding of α-protons with respect to the β-protons of the substituted ring (as a result of such shift the α-carbon positive charge density should decrease somewhat and an anisotropic α-carbon shielding with the iron atom should increase as well). Such discussion is based on the commonly accepted opinion (generally on the ^{1}H NMR spectra) [13] that unlike β-positions the α-positions in ferrocenes with electron-attracting substituents (e.g. acylferrocenes) are more sensitive to the electron-withdrawing substituent effect. However, recently the β-carbons of acylferrocenes were found to be less shielded with respect to the α-carbons [11]. Inconsistency in the effect of acyl substituents from the ^{1}H and ^{13}C NMR spectra is obviously explained by the carbonyl magnetic anisotropy causing a deshielding of α-protons.

One could have expected that if, in agreement with Gleiter [6], if the deviation of an exocyclic bond from the ring plane to the Fe atom in the cation was 40° (the strong $Fe-C_{exo}$ bonding) it would render the $^1J(^{57}Fe-{}^{13}C_{exo})$ constant. The charges reported in [6] (0.033 and 0.022 for α- and β-carbons) contradict relative shielding of α- and β-nuclei in the ferrocenylcarbenium ions as is evident from the ^{13}C NMR spectra with the use of a deuterium label. The absence of significant iron—C_{exo} coupling indicates a small barrier to rotation about the exocyclic bond ("weak double bonding") observed by Turbitt and Watts [14] and with the constant $J(^{13}C_{exo}-{}^1H) = 163$ Hz manifesting the sp^2 C_{exo} hybridization [12, 15].

The data available enable us to assume structure III for ferrocenylcarbenium ions without essential change of the ferrocene nucleus symmetry. However, our results do not exclude certain participation of the metal in direct stabilization of the cationic center. Such a possibility should be enhanced in the ruthenocenyl- [14, 16] and osmocenyl-carbenium ions [16]. Thus the stability of metallocenyl-carbenium ions is determined predominantly by an effective positive charge delocalization over the entire metallocenyl unit.

Determination of the $^1J(^{57}Fe-{}^{13}C)$ constant allowed measurement, for the first time, of the ^{57}Fe chemical shift by means of the high resolution NMR technique with triple heteronuclear resonance, $^{13}C-{}^1H$ noise decoupling and monochromatic irradiation at the ^{57}Fe resonant frequency on a Bruker HX-90 spectrometer (at ^{13}C operating frequency 22.635 MHz). The ^{57}Fe resonance of the CS_2 ferrocene solution is observed upon sample irradiation at 2 918 505 Hz (^2D frequency in D_2O in stabilization channel was equal to 13 811 113 Hz). The ^{57}Fe chemical shifts in 1-ferrocenylethanol, ethyl- and acetyl-ferrocene are 0.00, 36.6 and 215.55 ppm, respectively (from ferrocene signal, CS_2, 30°). The ^{57}Fe chemical shift of protonated ferrocene ($\delta^C = 78$ ppm) in $BF_3 \cdot H_2O$ medium is shifted upfield from the ferrocene signal, $\delta^{Fe} = -1098.85$ ppm.

The measurement of ^{57}Fe chemical shift and the $^1J(^{57}Fe-{}^{13}C)$ spin coupling constant opens new fields in the study of a great variety of iron complexes.

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