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Ferrocene Derivatives, Part 67[1]
^{57}Fe-NMR Spectroscopy of Ferrocenes**

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^{57}Fe NMR-spectra of 28 mono and disubstituted ferrocenes with a natural abundance of ^{57}Fe have been measured relative to internal ferrocene. Most of the resonances appear at the high frequency side. The shielding influence of the various substituents is discussed qualitatively. ^{57}Fe shifts are very sensitive to ring tilting as occurring in [3]ferrocenophanes.

(Keywords: ^{57}Fe *Shifts; Hybridization influence on chemical shifts; Ring tilting)*

^{57}Fe-*Kernresonanzspektren von Ferrocenderivaten. Ferrocenderivate 67*

^{57}Fe-NMR-Signale von 28 mono- und disubstituierten Ferrocenen mit natürlicher Häufigkeit an ^{57}Fe wurden gegen Ferrocen als innerem Standard gemessen. Die meisten Resonanzen sind zu höherer Frequenz verschoben. Die ^{57}Fe-Verschiebung reagiert sehr empfindlich auf Ringneigung, wie an [3]Ferrocenophanen gezeigt wurde. Substituenteneinflüsse auf die Verschiebung werden qualitativ diskutiert.

Introduction

The detection of NMR-signals of ^{57}Fe is very difficult because of its low gyromagnetic ratio, low natural abundance (2.3%) and long spin lattice relaxation time. However, with regard to the wide distribution of iron in biological complexes and catalytic active organometallic compounds NMR studies of the ^{57}Fe nucleus should provide valuable structural informations.

** For a preliminary communication see Ref.[2]. Parts of this work were presented at the "NMR-Diskussionstagung" in Dortmund in January 1982 (by *E. H.*) and at "GERM VI" in Pont à Mousson in March 1982 (by *W. R.*).

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Up to now only a few NMR-studies of ^{57}Fe have appeared in the literature: Some shifts have been obtained by indirect methods using ^{57}Fe enriched material[3]. The first direct observation of ^{57}Fe-NMR signals has been achieved by a steady state pulse technique and several complexes of the type $Fe(CO)_3$ (diene) have been measured using this method[4]. With now commercially available high field supercon spectrometers a direct detection of ^{57}Fe NMR signals is possible[2] and in favourable cases *J* polarisation transfer experiments can greatly enhance the sensitivity[5].

Materials and Methods

All ferrocene derivatives used in this work (see Table 1) were prepared and purified by methods described in the literature[6]. The resonances were obtained at 8.1 MHz on a Bruker WM-250 spectrometer on samples with a natural abundance of ^{57}Fe with the conventional pulse-FT-technique in NMR tubes of 15 mm diameter. The deuterium resonance of the solvent ($CDCl_3$) provided the field frequency lock. Typical parameters are: SW = 4 000 Hz, AQ = 2 s, PW = 60 μs, NS = 20 000–40 000, concentration: 1–1.5 *M*, internal standard: ferrocene.

Results and Discussion

The chemical shift data presented in Table 1 and compiled in Fig. 1 span a range of about 800 ppm. 1,1'-Di-pivaloyl-ferrocen (**23**) ($\delta = 526.1$ ppm) exhibits the ^{57}Fe signal with the highest frequency within the ferrocene derivatives. The highest frequency detected so far was found for *Cp*$Fe(CO)_2Br$[8] [$\delta = 2\,545$ ppm, $Fe(CO)_5$].

Monosubstituted Ferrocenes

There is a clearly defined resonance region for these ferrocenes with sp^3-substituents from −3 to + 45 ppm. Alkyl substituted ferrocenes (*R* = methyl, ethyl, *i*-propyl and *t*-butyl; **2, 3, 5** and **6**) appear in an even narrower range from 30–45 ppm. Electronegative substituents in β-position cause shielding of the ^{57}Fe nucleus (see Fig. **1**).

The resonances of ferrocenes with substituents containing sp or sp^2 hybridized carbon atoms appear at significantly higher frequency, where resonance effects seem to deshield the iron nucleus: e.g. for phenylferrocene (**10**, 188.1 ppm) and vinylferrocene (**7**, 165.8 ppm). Electronegative substituents in β-position have a shielding effect, quite similar to that described earlier, e.g. ethinylferrocene (**8**, 141.9 ppm) vs. cyanoferrocene (**9**, 121.3 ppm) or acetylferrocene (**19**, 234.2 ppm) vs. methyl ferrocenecarboxylate (**21**, 194.7 ppm) (see Fig. 1).

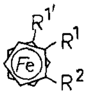

Table 1. ^{57}Fe *Chemical shifts of ferrocene derivatives in* $CDCl_3$ *(ferrocene as internal standard)*

Compound No.	*R*1	*R*1'	*R*2	δ (ppm)
1	H	H	H	0.0
2	CH_3	H	H	43.6
3	C_2H_5	H	H	34.0
4	C_2H_5	C_2H_5	H	69.2
5	$CH(CH_3)_2$	H	H	32.9
6	$C(CH_3)_3$	H	H	38.1
7	$CH=CH_2$	H	H	165.8
8	$C\equiv CH$	H	H	141.9
9	$C\equiv N$	H	H	121.3
10	C_6H_5	H	H	188.1
11	CH_2OH	H	H	—1.2
12	$CH(OH)CH_3$	H	H	7.0
13	CH_2OCH_3	H	H	—2.4
14	$CH_2C\equiv N$	H	H	—1.2
15	$CH_2N(CH_3)_2$	H	H	0.5
16	CH_2OCH_2—*Fc*	H	H	2.6
17	CHO	H	H	232.5
18	CHO	H	CHO	400.4
19	$COCH_3$	H	H	234.2
20	$COCH_3$	$COCH_3$	H	436.9
21	$COOCH_3$	H	H	194.7
22	$COOCH_3$	$COOCH_3$	H	379.8
23	$COC(CH_3)_2$	$COC(CH_3)_2$	H	526.1
24	COC_6H_5	H	H	289.1
25	CH_2OH	H	CHO	267.5
26	Cl	H	H	—1.2
27	Br	H	H	—14.4
28	$—CH_2CH_2CH_2—$		H	—259.3
29	$—CH_2CH_2CO—$		H	148.1

Disubstituted Ferrocenes

The shielding rules mentioned above apply also to these derivatives. Moreover the shielding effects appear to be additive. This can be demonstrated for instance by comparing ethyl-ferrocene (**3**, 34.0 ppm) with 1,1'-diethylferrocene (**4**, 69.2 ppm). An unexpected shielding is observed in [3]ferrocenophane-1-on (**29**, 148.1 ppm) and [3]ferroceno-

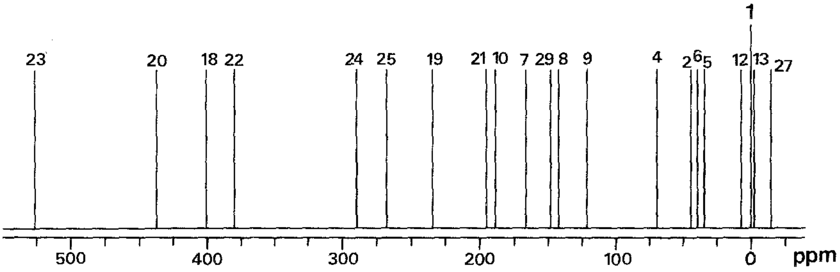

Fig. 1. ^{57}Fe shifts of selected ferrocene derivatives in $CDCl_3$ (see Table 1 for compounds)

phane (**28**, —259.3 ppm). Obviously the additivity rule is not valid in these cases. The ^{57}Fe-resonance of [3]ferrocenophane (**28**) is comparable to the resonance of the cations *Fc*CH_2^+ (—522.4 ppm), *Fc*-CH^+CH_3 (—212.3 ppm) and *Fc*H^+ (—1 100 ppm)[3]. X-ray studies of [3]ferrocenophane (**28**) show that the cyclopentadienylrings are tilted to some extent[7]; thus the iron shifts are very sensitive to rehybridisation which is induced by the ring distortion.

Similar arguments have been used to explain the unexpected shielding of the abovementioned cations (see also Refs.[3d] and [4c]). In contrast the ^{57}Fe resonance in *Fc*-CH^+-*Fc* appears at 740 ppm[3c]. Iron shielding seems therefore to be very sensitive to small variations in the electronic density of the cyclopentadienylrings and to the hybridization of the iron atom thus showing that some cationic species have more or less tilted cyclopentadienylrings.

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