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^{57}Fe-NMR spectroscopy revisited: ferrocene derivatives containing heterosubstituents

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Abstract

^{57}Fe-NMR spectra (16.1 MHz; natural abundance) of mono- and 1,1′-disubstituted ferrocene derivatives (**1**–**15**), including two ferrocenophanes (**14**, **15**), could be measured in a much shorter time than expected according to previous reports (500 MHz spectrometer, standard equipment; solutions in 5-mm tubes). Substituents were ^{t}Bu, alkynyl, silyl, germyl, stannyl and boryl groups, and the bridges in the ferrocenophanes were $SiMe_2$ (**14**) and $Me_2SiSiMe_2$ units (**15**). The δ^{57}Fe values cover a fairly large range of > 450 ppm. There is a large difference (365 ppm) in ^{57}Fe nuclear shielding for the two ferrocenophanes, with the higher ^{57}Fe shielding in the [1]ferrocenophane **14**. Parallel trends were observed between δ^{57}Fe of ferrocene derivatives and δ^{55}Mn of comparable sandwich complexes derived from $[(\eta^5\text{-}C_5H_5)Mn(\eta^6\text{-}C_6H_6)]$. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The importance of ferrocene chemistry [1] has called for the systematic application of numerous physical methods. However, ^{57}Fe-NMR spectroscopy [2a] which should in principle serve as a highly diagnostic tool, did not receive much attention. This can be ascribed to literature reports [2–4] which have pointed out that special probeheads are necessary to accommodate large sample volumes (e.g. ≥ 7 ml in 15 mm or 20 mm (o.d.) tubes) containing > 1 g of the ferrocene derivative. Even then, apparently 12–24 h of spectrometer time had been required to record meaningful ^{57}Fe-NMR signals by direct single pulse NMR [5]. Thus, the unfavourable experimental circumstances owing to the inherent extremely low ^{57}Fe-NMR receptivity (^{57}Fe: $I = 1/2$; natural abundance 2.2%; receptivity with respect to ^{13}C: 4.19×10^{-3}) have discouraged widespread application of ^{57}Fe-NMR spectroscopy at natural abundance [6]. We report here that this rather gloomy picture of ^{57}Fe-NMR can be substituted for a much brighter outlook.

2. Results and discussion

2.1. ^{57}Fe-NMR measurements

We have used optimized experimental conditions for measuring 16.1 MHz ^{57}Fe-NMR spectra of ferrocene derivatives at natural abundance of ^{57}Fe in 5-mm tubes (sample volume 0.5 ml) with a standard probehead for low-frequency nuclei. The ^{57}Fe-NMR signal of a 0.8 M solution of ferrocene (ca. 75 mg in 0.5 ml of $CDCl_3$) could be observed already after 30 min of spectrometer time (S/N ca. 2.5:1). This improvement with respect to previous attempts [2–4] can be traced at least in part to the higher field strength B_0: the increase in the sensitivity of the NMR experiment is accompanied by shorter relaxation times $T_1(^{57}\text{Fe})$, since in the case of ferrocenes, the chemical-shift-anisotropy (CSA) relaxation mechanism is dominating [7], and this interaction depends on B_0^2. The relaxation time $T_1(^{57}\text{Fe})$ of ferrocene in $CDCl_3$ or C_6D_6 at 20 °C for $B_0 = 11.5$ T is in the range of 2.5–3.5 s. One can assume an additional advantage in comparison with previous ^{57}Fe-NMR

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measurements considering improvements in the performance of the NMR hardware in the last 10–15 years.

2.2. Trends in δ^{57}Fe of ferrocenes and comparison with δ^{55}Mn of comparable manganese sandwich complexes

Since the previous ^{57}Fe-NMR studies of ferrocenes did not include derivatives with heteroelement substituents (except for iodine), we have measured the ^{57}Fe chemical shifts (δ^{57}Fe) of silyl, germyl, stannyl and boryl substituted ferrocenes for the first time. In addition to monosubstituted ferrocenes (**2**–**6**), several 1,1′-disubstituted ferrocenes (**7**–**13**) and two ferrocenophanes (**14**, **15**) were included in this study (Table 1). In both the ferrocenyl (**2**–**6**) and the ferrocenediyl complexes (**7**–**13**), the parallel cyclopentadienyl ligands undergo unrestricted rotation about the main axis of the molecules running through the central Fe and the two centres of the respective cyclopentadienyl rings (angle Z–Fe–Z′180°). In the ferrocenophanes **14** and **15**, the cyclopentadienyl rings are held in fixed positions, bent by an inclination angle α towards the bridging silicon atom(s) (fc[SiMe$_2$] (**14**): $\alpha = 20.8(5)°$; $\delta = 164.78(8)°$ [8]; fc[(SiMe$_2$)$_2$] (**15**): $\alpha = 4.19(2)°$; $\delta = 176.48(3)°$ [8]) in the solid state.

Table 1
Chemical shifts δ^{57}Fe of the ferrocene derivatives **1**–**15**

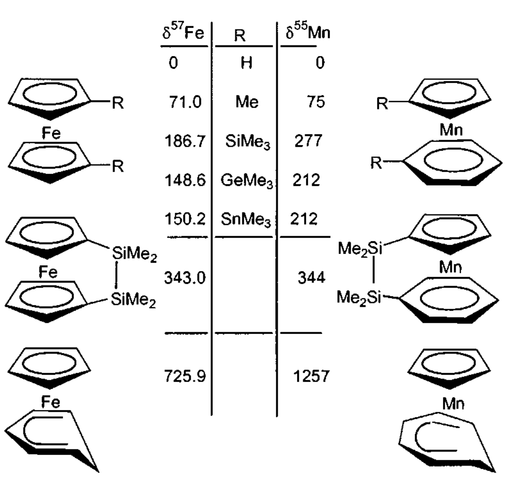
No.	Compound	δ^{57}Fe	No.	Compound	δ^{57}Fe
1	Fc–H	0 [a]	**7**	fc(tBu)$_2$	79.3 [b]
2	Fc–C≡CH	142.1 [c]	**8**	fc(C≡CSiMe$_3$)$_2$	309.5
3	Fc–SiMe$_3$	83.8	**9**	fc(SiMe$_3$)$_2$	186.7
4	Fc–SiMe$_2$Cl	71.1	**10**	fc(SiMe$_2$H)$_2$	170.3
5	Fc–SiCl$_3$	73.8	**11**	fc(GeMe$_3$)$_2$	148.6
6	Fc–SnMe$_3$	68.8	**12**	fc(SnMe$_3$)$_2$	150.2
			13	fc(BBr$_2$)$_2$	436.6 438.5 [b]
			14	fc[SiMe$_2$]	−21.9
			15	fc[(SiMe$_2$)$_2$]	343.0

In CDCl$_3$ at 20 ± 1 °C (ca. 0.6–1 M solutions) if not stated otherwise. Decoupling of ^{1}H did not affect the ^{57}Fe line widths and was not used. Line widths $h_{1/2}$ of ^{57}Fe-NMR signals were in the order of 1–2 Hz, mainly determined by experimental conditions (digital resolution, applied exponential line broadening). Abbreviations: Fc = ferrocenyl, (η^5-C$_5$H$_5$)Fe(η^5-C$_5$H$_4$-); fc = 1,1′-ferrocenediyl, Fe(η^5-C$_5$H$_4$−)$_2$.

[a] δ^{57}Fe of ferrocene (Fc-H) = +1541.7 relative to δ^{57}Fe of Fe(CO)$_5$ with $\Xi(^{57}\text{Fe}) = 3.237798$ MHz.

[b] In C$_6$D$_6$ (2 M).

[c] In exact agreement with Refs. [2b] and [2c].



Scheme 1. Comparison of chemical shifts δ^{57}Fe and δ^{55}Mn of sandwich complexes (δ^{55}Mn data from Ref. [11]; δ^{57}Fe data for fc(Me)$_2$ from Ref. [7], and for the half-open ferrocene from Ref. [4]).

Similar to the effect of alkyl groups [2–4], the effect of organoelement substituents on δ^{57}Fe is almost additive as shown for the 1,1′-disubstituted ferrocenes **8**, **9** and **12**. The largest deshielding effect in the present series is caused by BBr$_2$ groups in fc(BBr$_2$)$_2$ (**13**). In the series of silicon-substituted ferrocene derivatives, the ^{57}Fe nuclear shielding varies over a range of 365 ppm (Table 1), the δ^{57}Fe values for the two ferrocenophanes being at the extreme ends of this range. This demonstrates the high sensitivity of δ^{57}Fe to structural changes, and further application of ^{57}Fe-NMR to the chemistry of ferrocenophanes [8–10] appears to become particularly promising.

In the case of Group 14 substituents, the comparison with δ^{55}Mn of analogously substituted manganese sandwich complexes, derived from [(η^5-C$_5$H$_5$)Mn(η^6-C$_6$H$_6$)] [11], is attractive, since it allows comparison of the electronic structures of the manganese and iron sandwich complexes. As shown in Scheme 1, the trends in the chemical shifts δ^{57}Fe and δ^{55}Mn are strikingly similar.

The growing availability of experimental chemical shifts δ^{57}Fe is a challenge for quantum mechanical calculations of this NMR parameter. So far, the ^{57}Fe nuclear shielding of ferrocene could not be reproduced very well [12], and the weaknesses of present exchange-correlation (XC) functionals have been pointed out [13].

3. Conclusions

Our results indicate that δ^{57}Fe data for ferrocenes can be obtained in a much shorter time and with much smaller sample volumes (reduced by about 90%), than had been reported previously [2–4]. Therefore, we expect that ^{57}Fe-NMR will be used more often in ferrocene chemistry. The comparison of δ^{57}Fe with δ^{55}Mn is a first interesting aspect, and future work will establish links to δ^{59}Co of analogous cobaltocenium ions, and to both redox potentials and ^{57}Fe Mössbauer spectra of ferrocenes [14].

4. Experimental

All ferrocene derivatives **1**–**15** [15] were prepared following established literature procedures, and the solvents as well as the samples for NMR measurements were handled with care to exclude moisture and traces of oxygen.

^{57}Fe-NMR spectra (see Table 1 for further details) were recorded using a Bruker DRX 500 instrument. The length of the 90° pulse (80 μs) was calibrated by measuring the ^{73}Ge-NMR signal of $GeCl_4$ in $CDCl_3$ at 17.5 MHz, assuming that the value would be similar for ^{57}Fe (16.1 MHz). Careful tuning of the probehead was repeated for each sample, and best homogeneity of B_0 was adjusted by optimizing the ^{1}H-NMR signals. Typically, more than 5000 transients with acquisition times of 0.4–0.5 s and a 30° pulse angle were used to cover a spectral window of 10 kHz (621 ppm). In order to reduce the base line distortion due to acoustic ringing, the delay between end of pulse and beginning of acquisition (dead time) was increased to 200 μs. The $T_1(^{57}\mathrm{Fe})$ value for ferrocene was obtained by the inversion-recovery method.

Acknowledgements

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