

^{57}Fe NMR of Ferrocenes by ^1H – ^{57}Fe INEPT Techniques

Bernd Wrackmeyer,* Oleg L. Tok, and Max Herberhold*

Laboratorium für Anorganische Chemie der Universität Bayreuth,
D-95440 Bayreuth, Germany

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Summary: ^{57}Fe NMR spectra (11.66 MHz) of the sandwich complexes ferrocene (**1**), butylferrocene (**2**), and acetylferrocene (**3**) were measured at natural abundance of ^{57}Fe by application of the polarization transfer technique (INEPT; ^1H – ^{57}Fe). In contrast to previous assumptions this technique works very well, although it has to be based on rather small (~ 0.3 – 0.7 Hz) long-range scalar ^{57}Fe – ^1H couplings across two bonds. Thus, the ^{57}Fe NMR signal of ferrocene (~ 150 mg in 2 mL of $\text{CDCl}_3/\text{hexane}$ (1:1)) was observed already after 4 transients, and after 400 transients (70 min of spectrometer time) the ^{13}C satellites ($^1J(^{57}\text{Fe}, ^{13}\text{C}) = 4.7$ Hz) were detected, allowing us to determine the isotope-induced chemical shift $^1\Delta^{12/13}\text{C}(^{57}\text{Fe}) = -440$ ppb at natural abundance of the isotopes.

After 50 years of intensive research, there is a huge family of complexes derived from ferrocene, FeCp_2 , and the attraction of ferrocene chemistry has even increased in recent years, considering the role of ferrocenes in materials science.¹ Although the principal structural features of ferrocene derivatives are well-known, in particular in the solid state from X-ray structural analysis and in solution from ^1H , ^{13}C , and ^{31}P NMR (if appropriate) spectroscopy, more precise information on their electronic structures is still desirable. In this context, ^{57}Fe NMR spectroscopy² can provide useful data, as has been shown for ferrocene derivatives,^{2–5} for CpFe half-sandwich compounds,^{6–9} and for η^4 -diene iron complexes.^{10,11} There is also increasing interest in applying ^{57}Fe NMR to the study of biologically relevant iron-containing systems.^{12,13} Recently we have shown⁵

that improvements in measuring ^{57}Fe NMR signals of ferrocenes directly by single-pulse techniques at natural abundance promise a brighter future of ^{57}Fe NMR as compared with the gloomy picture drawn originally.^{2–4,6–10} These improvements can be traced to better NMR instrumentation (e.g., higher field strengths, B_0 , and improved hardware such as frequency generation, amplifiers, and probe head design) and also to optimized experimental parameters.⁵ Here we report on the application of polarization transfer (PT) techniques (^1H – ^{57}Fe) to ferrocenes (**1–3**).

The inherently unfavorable NMR properties of the ^{57}Fe nucleus ($I = 1/2$; natural abundance 2.2%; receptivity with respect to ^{13}C 4.19×10^{-3}) clearly indicate that direct observation of ^{57}Fe NMR signals by single-pulse techniques will never be easy, even under the best experimental conditions. It had been shown already in the 1970s that ^{57}Fe -enriched complexes can be studied by heteronuclear $^{13}\text{C}\{^{57}\text{Fe}\}$ double-resonance experiments.^{2,14} At natural abundance of ^{57}Fe , indirect detection via ^1H or ^{31}P ^{2,8,9} appears to be now the most attractive alternative, which, however, requires a sizeable scalar coupling between ^{57}Fe and ^1H or ^{31}P , present only in complexes containing an Fe–H or Fe–P bond. In contrast, it appears that the inverse detection also works for $(\text{Cp})\text{Fe}(\text{CO})_2\text{R}$ with $^2,3J(^{57}\text{Fe}, ^1\text{H}_R) \approx 1$ – 2 Hz.⁹ Another alternative would be the application of polarization transfer (PT) techniques (^1H – ^{57}Fe) such as INEPT¹⁵ or DEPT,¹⁶ leading to an improvement of the signal-to-noise ratio by a factor of ~ 30 with respect to single pulse detection. However, it has been pointed out² that the application of PT techniques may not be feasible in the absence of Fe–H bonds, owing to the small magnitude of the coupling constants $^nJ(^{57}\text{Fe}, ^1\text{H})$

* To whom correspondence should be addressed. Tel.: +49-921-552542. Fax: +49-921-552157. E-mail: B.W., b.wrack@uni-bayreuth.de; M.H., max.herberhold@uni-bayreuth.de.

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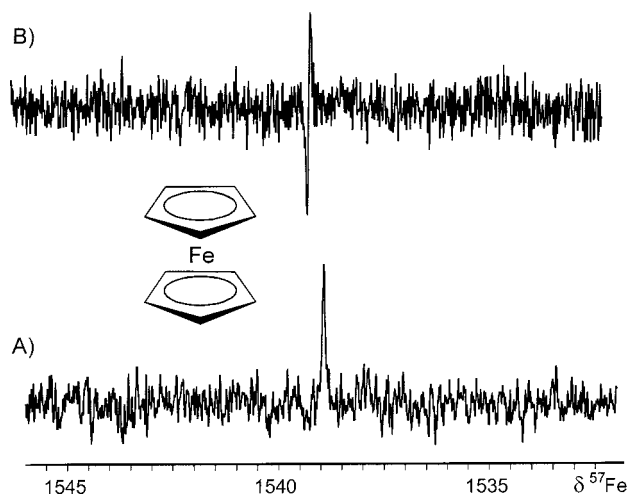


Figure 1. 11.66 MHz ^{57}Fe NMR spectra (INEPT;¹² based on delays according to ${}^2J(^{57}\text{Fe},^1\text{H}) = 0.5$ Hz; measured at 23 ± 1 °C (assumed accuracy of temperature inside of the sample, controlled to 23 ± 0.2 °C outside of the sample)) of ferrocene, Cp_2Fe (saturated solution (~ 150 mg) in $\text{CDCl}_3/\text{hexane}$ ($\sim 1:1$)). The delays in the INEPT pulse sequence were adjusted to ${}^2J(^{57}\text{Fe},^1\text{H}) = 0.5$ Hz (instead of the experimental value 0.4 ± 0.1 Hz) in order to compensate for pulse durations and dead times due to the hardware. Part A (refocused with optimized low-power ^1H composite pulse decoupling): acquisition time 3 s; repetition time 11 s; line broadening 0.2 Hz; 8 transients. The reduced intensity of the ^{57}Fe NMR signal when compared with the spectrum in (B) indicates that some ^{57}Fe magnetization is lost during the refocusing periods (0.22 s). Part B (basic pulse sequence; ^1H nondecoupled): acquisition time 3 s; repetition time 8 s; line broadening 0.2 Hz; 8 transients.

($n > 1$) and the concomitant loss of ^1H and ^{57}Fe magnetization during the pulse sequence.

We show now for ferrocene (**1**: $\delta(^{57}\text{Fe})$ 1538.4, in CDCl_3 without hexane $\delta(^{57}\text{Fe}) = +1541.7$ ⁵), butylferrocene (**2**; $\delta(^{57}\text{Fe})$ 1570.8), and acetylferrocene (**3**; $\delta(^{57}\text{Fe})$ 1774.4) that this assumption was misleading. It has already been shown for $\text{CpFe}(\text{CO})_2\text{R}$ that small coupling constants, in these particular cases ${}^{2,3}J(^{57}\text{Fe},^1\text{H}_R)$, can be used for indirect detection of the ^{57}Fe resonance via ^1H NMR.⁹ Polarization transfer appears to work well for many ferrocene derivatives, and meaningful spectra can be acquired within a very short time (see Figures 1 and 2). Thus, the ^{57}Fe NMR signal of ferrocene (~ 150 mg in 2 mL of $\text{CDCl}_3/\text{hexane}$ (1:1)) can easily be observed already after four or eight transients (spectrometer time < 100 s). The same signal, complete with its ^{13}C satellites, was measured after 70 min (Figure 2), allowing us to determine ${}^1J(^{57}\text{Fe},^{13}\text{C}) = 4.7$ Hz, in agreement with data from the ^{13}C NMR spectra of ^{57}Fe -enriched ferrocene,¹⁴ and the previously unknown isotope-induced chemical shift ${}^1\Delta(^{12/13}\text{C}(^{57}\text{Fe})) = -440$ ppb at natural abundance of both isotopes. Considering the different nature of the Fe–C bonds in ferrocene and of the Fe– C_{Me} bond in $(\text{Cp})\text{Fe}(\text{CO})_2\text{Me}$, it is interesting to note that in the latter a similar value, ${}^1\Delta(^{12/13}\text{C}_{\text{Me}}(^{57}\text{Fe})) = -471$ ppb, has been measured for the η^1 -linked methyl group.⁹ The magnitude of the coupling constants ${}^2J(^{57}\text{Fe},^1\text{H})$ used for the calculation of the delays in the pulse sequences was assumed to be on the order of 0.3–0.7 Hz (best results were obtained for **1** with 0.5 Hz, for **2** with 0.3 Hz, and for **3**

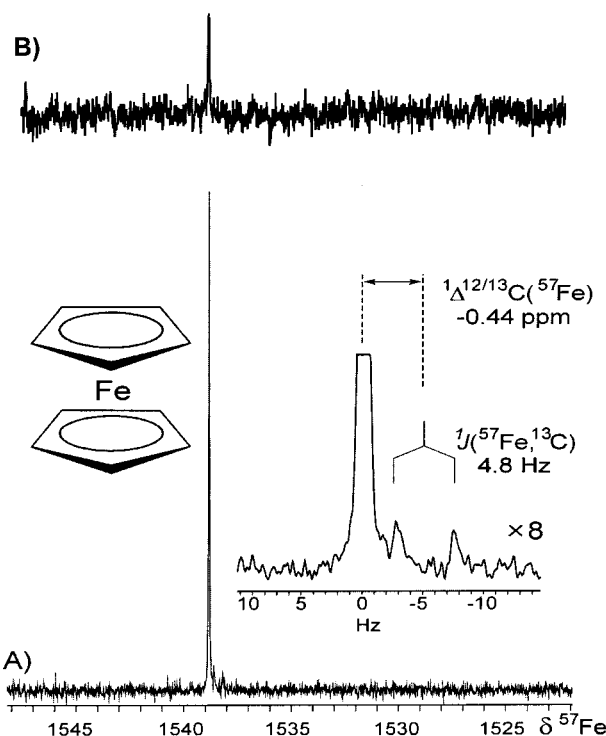


Figure 2. 11.66 MHz ^{57}Fe NMR spectra (INEPT,¹² refocused and ^1H decoupled; based on ${}^2J(^{57}\text{Fe},^1\text{H}) = 0.5$ Hz; 23 ± 1 °C (see legend of Figure 1)), measured for observation of ^{13}C satellites and determination of the isotope-induced chemical shift ${}^1\Delta(^{12/13}\text{C}(^{57}\text{Fe}))$ (the same sample as used for spectra shown in Figure 1; result of 400 transients; ~ 70 min of spectrometer time). For comparison, the $^{57}\text{Fe}\{^1\text{H}\}$ single-pulse spectrum is shown on top, where the same time (acquisition time 1.5 s; 2800 transients, 30° pulses) has been used as for the INEPT spectrum.

with 0.7 Hz). The nondecoupled spectrum of ferrocene (**1**) recorded by INEPT (see Figure 1B) indicates that $|{}^2J(^{57}\text{Fe},^1\text{H})| \approx 0.4 \pm 0.1$ Hz. The expected 10-line pattern (the central line is canceled as the result of the pulse sequence) is not resolved; the separation of the nonresolved anti-phase multiplets is ~ 1 Hz, and the magnitude of ${}^2J(^{57}\text{Fe},^1\text{H})$ should be slightly less than half of this value. The application of the DEPT pulse sequences¹⁵ (^1H decoupled or nondecoupled) was not successful. This could be the consequence of longer evolution times by a factor of ≥ 2 as compared to those of INEPT, which may cause serious loss of ^1H and ^{57}Fe magnetization. Attempts to measure the ^{57}Fe NMR signal of bis(pentamethylcyclopentadienyl)iron, $\text{FeCp}^*\text{}_2$ (**4**), by INEPT experiments within a short time, on the basis of ${}^3J(^{57}\text{Fe},^1\text{H})$, failed. It must be concluded that the magnitude of ${}^3J(^{57}\text{Fe},^1\text{H})$ is less than 0.25 Hz (this means a sum of delays of ≥ 2 s in the basic INEPT pulse sequence) and that loss of ^1H magnetization prevents efficient polarization transfer. ^{57}Fe NMR spectra of numerous other ferrocene derivatives, studied already by single-pulse techniques,^{3,5} have been remeasured successfully, using ^1H – ^{57}Fe techniques.

Chemical shifts $\delta(^{57}\text{Fe})$ of many ferrocene derivatives can be determined relatively quickly by INEPT experiments. Considering that an instrument with only moderate field strength ($B_0 = 8.46$ T) was used, the studies can certainly be extended to less concentrated samples, even to reaction solutions, by using higher field strengths

B_0 (up to 21 T) which have become increasingly available nowadays. The successful extension of the INEPT experiments to ^{187}Os NMR can be envisaged, opening the access to an even less developed area² when compared with ^{57}Fe NMR. The measurements of ^{57}Fe NMR data may help to develop further concepts regarding structure and reactivity,¹⁷ to understand other data coming, for example, from electrochemistry or ^{57}Fe Mössbauer spectroscopy of ferrocenes,¹⁸ and to stimulate theoretical work on optimizing the geometry of transition-metal complexes and the calculation of metal nuclear magnetic shieldings.¹⁹

Experimental Section

The model compounds studied were commercially available and were used without further purification. The sample quality plays an important role in all polarization transfer (PT) experiments. Therefore, the line widths in the ^1H NMR spectra should be checked; highly resolved ^1H NMR spectra indicate that loss of ^1H magnetization during the initial steps of the PT pulse sequence may not be serious for PT efficiency. If there are broadened signals in the ^1H NMR spectra for those ^1H nuclei which will be used for PT, the great loss of ^1H magnetization causes seriously reduced PT efficiency. Samples were prepared in 10 mm (o.d.) tubes by filtration of hexane/ CDCl_3 or $\text{CHCl}_3/\text{CDCl}_3$ solutions through silica under an atmosphere of Ar in order to remove paramagnetic impurities.

^{57}Fe NMR spectra (see also Figures 1–3 for further details) were recorded at 23 ± 0.2 °C (control outside of the sample) using a Bruker Avance 360 instrument, equipped with a low-frequency probe head, tunable from 6.8 to 16.8 MHz, for which the ^1H (90°) pulse duration was $32 \mu\text{s}$. The duration of the 90° pulse for ^{57}Fe NMR ($\sim 40 \mu\text{s}$) was calibrated first by measuring the ^{73}Ge NMR signal of GeCl_4 in CDCl_3 at 12.56 MHz, assuming that the value of the ^{73}Ge 90° pulse would be similar for ^{57}Fe (11.66 MHz). The best homogeneity of B_0 was adjusted by optimizing the ^1H NMR signals for each sample. Chemical shifts $\delta(^{57}\text{Fe})$ are given relative to $\delta(^{57}\text{Fe}; \text{Fe}(\text{CO})_5, \text{neat})$ 0 with $\Xi(^{57}\text{Fe}) = 3.237\,798$ MHz.

A problem in measuring ^{57}Fe NMR spectra concerns the temperature dependence of the ^{57}Fe NMR signals. This is

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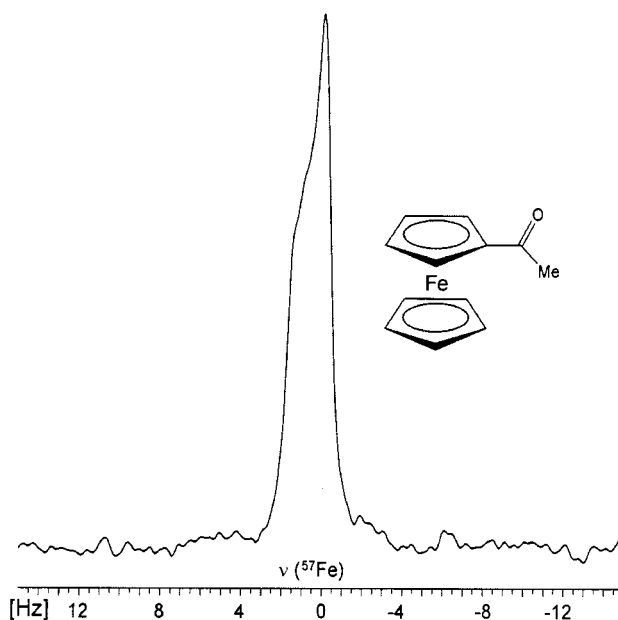


Figure 3. 11.66 MHz ^{57}Fe NMR spectrum (INEPT,¹² refocused with optimized low-power ^1H composite pulse decoupling; 23 ± 1 °C) of acetylferrocene, $\text{CpFe}(\text{C}_5\text{H}_4\text{C}(\text{O})\text{Me})$ (450 mg in 2 mL of $\text{CHCl}_3/\text{CDCl}_3$), after 20 h of measurement time. There are several overlapping ^{57}Fe NMR signals as a result of the temperature dependence of ^{57}Fe chemical shifts. The line width $h_{1/2}$ after 32 scans was ~ 0.5 Hz; the $\delta(^{57}\text{Fe})$ value was 1774.4.

shown in the case of acetylferrocene (**3**) for a spectrum recorded within 24 h (Figure 3). Even by using optimized low-power ^1H composite pulse decoupling (CPD), temperature gradients in the sample develop slowly and give rise to several overlapping ^{57}Fe NMR signals (the temperature control of the spectrometer is switched on to keep the temperature constant (± 0.2 K), outside of the sample). On the basis of the present results, it can be assumed that the observation of identical line widths of ^{57}Fe NMR signals of ferrocenes detected by single-pulse techniques with or without ^1H decoupling is due to temperature-induced chemical shifts which broaden the lines after long measurement times.

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