

⁵⁷Fe NMR Spectroscopy of Some Sila-[1]ferrocenophanes and a Phospha-[1]ferrocenophane

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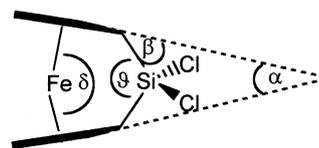
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Ferrocene, [1]Ferrocenophanes, ⁵⁷Fe NMR

⁵⁷Fe NMR spectra (11.66 MHz) of the 1,1-diorganosila-[1]ferrocenophanes, [Fe(C₅H₄)₂]-SiR¹R² (**1**) (R¹ = R² = Me) and (**2**) (R¹ = Me, R² = Ph), the 1-chloro-1-organosila-[1]ferrocenophanes [Fe(C₅H₄)₂Si(Cl)R¹ **3** (R¹ = Me) and **4** (R¹ = Ph), and of 1,1-dichlorosila-[1]ferrocenophane, [Fe(C₅H₄)₂SiCl₂ **5**, were measured. All ⁵⁷Fe resonance signals are shifted to lower frequencies with respect to ferrocene, the largest shift being observed for **5** (–147.7 ppm). The influence of chloro substituents at silicon in comparison to organo groups is much more pronounced in the ferrocenophanes than in non-cyclic 1-silyl- or 1,1'-di(silyl)-ferrocene derivatives. In the case of 2,2,6,6-tetramethylpiperidin-1-yl-phospha-[1]ferrocenophane, [Fe(C₅H₄)₂]P(tmp) **6**, the ⁵⁷Fe nucleus is deshielded (129.8 ppm) with respect to ferrocene, and the coupling constant ²J(⁵⁷Fe, ³¹P) = 3.4 Hz was measured for the first time.

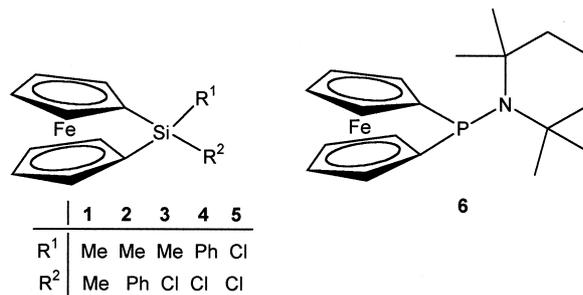
Introduction

Among the huge number of ferrocene derivatives [1]ferrocenophanes are particularly attractive, considering the distortion of the sandwich structure (Scheme 1) and the concomitant reactivity of such complexes [1]. Aspects of structure and reactivity of [m]ferrocenophanes may be reflected by chemical shifts $\delta^{57}\text{Fe}$ [2], although ⁵⁷Fe NMR spectroscopy has been rarely applied owing to the overall unfavorable NMR properties of ⁵⁷Fe (I = 1/2; natural abundance: 2.2%; receptivity with respect to ¹³C: 4.19 · 10⁻³). So far, chemical shifts $\delta^{57}\text{Fe}$ of a few [m]ferrocenophanes (mainly for m = 3) have been determined in most cases indirectly by heteronuclear ¹³C{¹H, ⁵⁷Fe} triple resonance experiments of ⁵⁷Fe labeled [3]ferrocenophanes [3], and a more systematic study of such ring systems by ⁵⁷Fe NMR is still missing. Our current interest in ferrocene derivatives containing heteroelements [4] has already prompted us to obtain $\delta^{57}\text{Fe}$ data of some representative examples, including one sila-[1]- and one disila-[2]ferrocenophane [5]. In the present work we have studied some sila-[1]ferrocenophanes and one phospha-[1]ferrocenophane by ⁵⁷Fe NMR spectroscopy (Scheme 2). NMR spectra of other nuclei predict that the molecular structures



- α : tilt angle of the cyclopentadienyl rings (19.2(4)°)
- β : deviation of the C(ring)-Si vector from the cyclopentadienyl ring plane (40.7(5)°)
- δ : deformation angle at Fe between the midpoints of the cyclopentadienyl rings (166.5(2)°)
- φ : angle C-Si-C (110.9(2)°)

Scheme 1. Distortion of the sandwich structure in 1-sila-[1]ferrocenophanes, shown for **5** [6c].



Scheme 2. [1]Ferrocenophanes studied by ⁵⁷Fe NMR spectroscopy.

Compound	$\delta^{57}\text{Fe}$	$\delta^{57}\text{Fe}$ Compound
$[\text{Fe}(\text{C}_5\text{H}_4)_2]\text{SiMe}_2\text{SiMe}_2$ ^[b]	+1884.7	$\text{Fe}(\text{C}_5\text{H}_5)_2$ ^[b]
1 $[\text{Fe}(\text{C}_5\text{H}_4)_2]\text{SiMe}_2$ ^[b]	+1519.8	$\text{Fe}(\text{C}_5\text{H}_4\text{-SiMe}_3)_2$ ^[b]
2 $[\text{Fe}(\text{C}_5\text{H}_4)_2]\text{Si}(\text{Ph})\text{Me}$ ^[d]	+1518.6	$\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_4\text{-SiMe}_3)$ ^[b]
3 $[\text{Fe}(\text{C}_5\text{H}_4)_2]\text{Si}(\text{Cl})\text{Me}$ ^[d]	+1462.2	$\text{Fe}(\text{C}_5\text{H}_4\text{-SiMe}_2\text{Cl})_2$ ^[c]
		$^2J(^{57}\text{Fe}, ^{29}\text{Si}) = 2.7 \text{ Hz}$
4 $[\text{Fe}(\text{C}_5\text{H}_4)_2]\text{Si}(\text{Cl})\text{Ph}$ ^[d]	+1454.7	$\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_4\text{-SiMe}_2\text{Cl})$ ^[b]
5 $[\text{Fe}(\text{C}_5\text{H}_4)_2]\text{SiCl}_2$ ^[d]	+1394.0	$\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_4\text{-SiCl}_3)$ ^[b]
6 $[\text{Fe}(\text{C}_5\text{H}_4)_2]\text{P}(\text{tmp})$ ^[e]	+1671.5	
		$^2J(^{57}\text{Fe}, ^{31}\text{P}) = 3.4 \text{ Hz}$

Table 1. ^{57}Fe NMR data ^[a] of sila-[1]ferrocenophanes (**1** - **5**), phospho-[1]ferrocenophane (**6**), ferrocene and some silyl-substituted derivatives for comparison.

^[a] At 23 ± 1 °C; $\delta^{57}\text{Fe}$ values ± 0.05 ppm; coupling constants ± 0.2 Hz; ^[b] ref. [5], in CDCl_3 ; ^[c] this work, in CDCl_3 ; ^[d] this work, in CHCl_3 with 5% C_6D_6 ; ^[e] this work, in CH_2Cl_2 with 5% C_6D_6 ; tmp = 2,2,6,6-tetramethylpiperidin-1-yl.

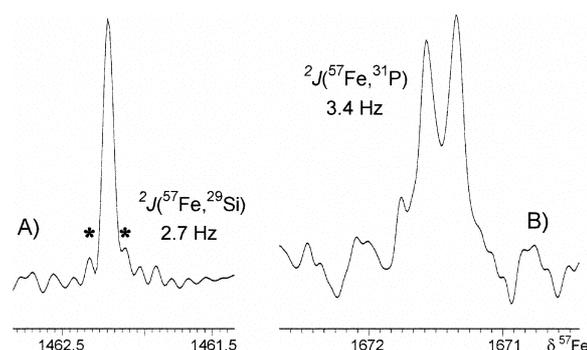


Fig. 1. 11.66 MHz $^{57}\text{Fe}\{^1\text{H}\}$ NMR spectra of A) $[\text{Fe}(\text{C}_5\text{H}_4)_2]\text{Si}(\text{Cl})\text{Me}$ (**3**) [0.7 g in 2.5 ml of CH_2Cl_2 / C_6D_6 (5%); result of 45000 transients; acquisition time 1.2 s; ca. 15 h of spectrometer time; ^{29}Si satellites are marked by asterisks], and B) $[\text{Fe}(\text{C}_5\text{H}_4)_2]\text{P}(\text{tmp})$ (**6**) [0.3 g in 2.5 ml of CH_2Cl_2 / C_6D_6 (5%); result of 15000 transients, acquisition time 1.2 s; ca. 5 h of spectrometer time].

of these distorted sandwich complexes as determined for the crystalline state [6, 7] are essentially retained in solution; for example the $^{13}\text{C}(1)$ resonances are shifted markedly to low frequencies [6a] with respect to ferrocene, and are indicative of the strained structure of [1]ferrocenophanes.

Results and Discussion

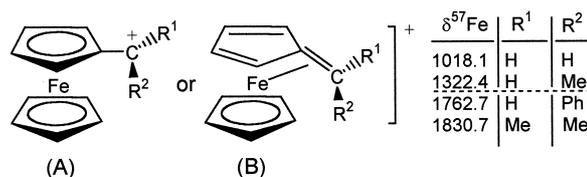
^{57}Fe NMR measurements

The known data set of ^{57}Fe chemical shifts ($\delta^{57}\text{Fe}$) clearly indicates that ^{57}Fe nuclear magnetic shielding in general is very sensitive towards small changes in the electronic structure of the iron compounds [2-4,8-11]. Improvements in instrumentation [5] and observation techniques [12] have facilitated solution-state ^{57}Fe NMR measurements, in particular of ferrocenes. Single pulse methods can be successfully applied, since relaxation times $T_1(^{57}\text{Fe})$ are fairly short (in general < 3 s for

$B_0 \geq 8.4$ T) as a result of the chemical-shift-anisotropy (CSA) relaxation mechanism. Polarization transfer (PT) can be based on small coupling constants $^2J(^{57}\text{Fe}, ^1\text{H})$ (0.5 ± 0.2 Hz) in favorable cases, allowing to measure $\delta^{57}\text{Fe}$ in very short time [12]. Furthermore, many ferrocene derivatives are stable, readily accessible, well soluble and can be easily separated from paramagnetic impurities (important for PT experiments [12]). The ^{57}Fe NMR data of the [1]ferrocenophanes together with some data for comparison are listed in Table 1. Typical ^{57}Fe NMR spectra for **3** and **6** are shown in Fig. 1.

Chemical shifts $\delta^{57}\text{Fe}$

The large difference (364.9 ppm) in the $\delta^{57}\text{Fe}$ values of 1,1,2,2-tetramethyl-1,2-disila-[2]ferrocenophane and 1,1-dimethyl-1-sila-[1]ferrocenophane **1** has been noted [5]. If the sandwich structure is not severely distorted, the substitution of one or both cyclopentadienyl rings with silyl groups generally leads to ^{57}Fe deshielding relative to $\text{Fe}(\text{C}_5\text{H}_5)_2$, and the contributions of the silyl groups are almost additive, similar to the influence of alkyl groups [8]. Substitution of the methyl groups at silicon by chloro ligands is accompanied by a small increase in ^{57}Fe nuclear shielding (< 20 ppm), as can be seen from the data on the right hand side of Table 1. The distortion of the sandwich structure (see Scheme 1) in the 1-sila-[1]ferrocenophanes leads to increased ^{57}Fe nuclear shielding. The influence of Si-methyl and Si-phenyl groups (**1**, **2**, **4**) appears to be very similar. Again, the presence of chloro ligands causes an increase of ^{57}Fe nuclear shielding. However, this effect is much more pronounced (e. g. $\delta^{57}\text{Fe} = +1519.8$ (**1**), $+1462.2$ (**3**), and $+1394.0$ (**5**)) than in the comparable non-cyclic compounds. A quantitative analysis of these effects would require precise knowledge of the electronic struc-



Scheme 3. Changes in ^{57}Fe nuclear shielding in α -ferrocenyl carbenium ions depending on π acceptor properties of the carbenium centre with the formal positive charge (A), or additional covalent Fe-C bonding (B) with $\text{R}^1 = \text{R}^2 = \text{H}$ and $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{Me}$ [9d].

ture of ferrocenes. Even in the case of ferrocene itself, it has been pointed out that the calculation of ^{57}Fe nuclear shielding is not straightforward [13]. However, a qualitative picture may be helpful. With respect to ^{57}Fe nuclear shielding the situation in [1]ferrocenophanes appears to be comparable to that in α -ferrocenyl carbenium ions (Scheme 3). Bending at the substituted carbon atom changes the bonding Fe-C interaction in a way which increases ^{57}Fe nuclear shielding. If substituents at the carbocationic center compete with these Fe-C interactions, deshielding effects become dominant. Chloro substituents at the silicon atom in 1-sila-[1]ferrocenophanes draw electron density towards the substituted carbon atom which is in a favorable position – due to the tilt of the cyclopentadienyl rings ($\alpha \approx 20^\circ$) – for additional Fe-C interactions.

Spending more spectrometer time on suitable samples (these are rare, since very sharp ^{57}Fe NMR signals are required) allows to observe ^{29}Si satellites (Fig. 1 A), and the coupling constant $^2J(^{57}\text{Fe}, ^{29}\text{Si}) = 2.7$ Hz could be determined for the first time in the case of **3**.

The phospho-[1]ferrocenophane **6** is the first complex of this type studied by ^{57}Fe NMR. The ^{57}Fe nucleus in **6** is less shielded when compared with sila-[1]ferrocenophanes, and the influence of substituents other than an amino group at phosphorus and / or differing phosphorus oxidation states have to be explored in forthcoming experiments. In the case of **6**, we note that another parameter becomes available for the first time, the scalar coupling constant $^2J(^{57}\text{Fe}, ^{31}\text{P})$ (Fig. 1 B). In general, this parameter cannot be determined straightforwardly from ^{31}P NMR spectra, since for most organophosphorus compounds the ^{57}Fe satellites would overlap

with the manifold of ^{13}C satellites. More sophisticated NMR experiments will have to be performed in order to find out whether the selection of ^{31}P - ^{57}Fe spin pairs is feasible in ^{31}P NMR spectra. In addition to chemical shifts $\delta^{57}\text{Fe}$, the data $J(^{57}\text{Fe}, ^{31}\text{P})$ and their structural dependence await further investigation.

Conclusions

^{57}Fe NMR spectroscopy is beginning to emerge as an attractive tool in ferrocene chemistry. There will be numerous applications since the sensitivity of $\delta^{57}\text{Fe}$ data to changes in the structure and to effects exerted by distant substituents is promising, as shown here in particular for sila-[1]ferrocenophanes. In the case of the phospho-[1]ferrocenophane **6**, the coupling constant $^2J(^{57}\text{Fe}, ^{31}\text{P})$, a new parameter in ferrocene derivatives containing phosphorus, was determined unequivocally by ^{57}Fe NMR for the first time.

Experimental Section

All compounds studied were prepared following procedures reported in the literature (**1** - **5** [6a, 6c, 14]; **6** [7b]). The purity of the samples was checked by ^1H , ^{13}C , ^{31}P and ^{29}Si NMR spectroscopy. For ^{57}Fe NMR measurements, the complexes (0.3 - 0.9 g) were dissolved in 2.5 - 3 ml of $\text{CHCl}_3 / \text{C}_6\text{D}_6$ (95 : 5 V/V) in 10 mm (o. d.) tubes under an atmosphere of argon. ^{57}Fe NMR spectra (by $^1\text{H} \rightarrow ^{57}\text{Fe}$ polarisation transfer [12] or single pulse techniques [5]; see also Figures 1 for further details) were recorded at $23 \pm 1^\circ\text{C}$ using a Bruker Avance 360 instrument (11.66 MHz for ^{57}Fe NMR), equipped with a low frequency probe head, tunable from 6.8 to 16.8 MHz, for which the $^1\text{H}(90^\circ)$ pulse was $32 \mu\text{s}$. The duration of the 90° pulse for ^{57}Fe NMR was $40 \mu\text{s}$ [12]. The homogeneity of B_0 was optimized by observing the ^1H NMR signals for each sample. Although the ^{57}Fe NMR signals are sharp in principle, temperature gradients in the sample tubes [12] cause some broadening which in most cases prevents observation of ^{29}Si satellites [see however Fig. 1 A)]. Chemical shifts $\delta^{57}\text{Fe}$ are given relative to $\delta^{57}\text{Fe}(\text{Fe}(\text{CO})_5, \text{neat}) = 0$ with $\Xi(^{57}\text{Fe}) = 3.237798$ MHz.

Acknowledgement

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