

N-Ferrocenyl Amines Bearing Boryl and Silyl Substituents at the Nitrogen Atom, Studied by ^{57}Fe NMR Spectroscopy

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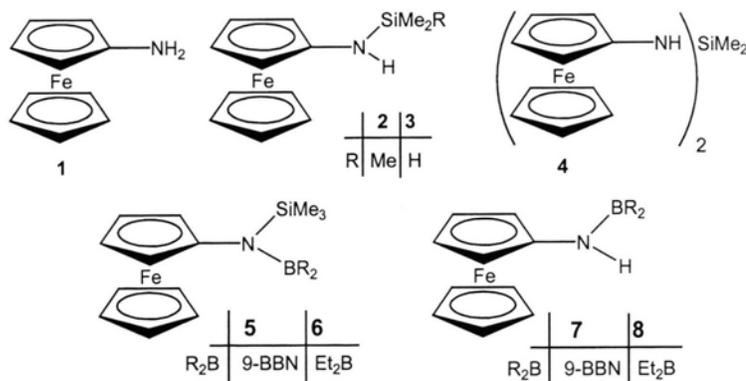
Ferrocenes, Aminosilanes, Aminoboranes

A series of ferrocene sandwich compounds such as N-ferrocenyl amine, Fc-NH_2 (**1**), the N-silylated derivatives Fc-NH-SiMe_3 (**2**), $\text{Fc-NH-SiMe}_2\text{H}$ (**3**), $(\text{Fc-NH})_2\text{SiMe}_2$ (**4**), the N-silyl-N-boryl derivatives $\text{Fc-N}(\text{SiMe}_3)(9\text{-BBN})$ (**5**) (9-BBN = 9-borabicyclo[3.3.1]nonyl) and $\text{Fc-N}(\text{SiMe}_3)\text{BEt}_2$ (**6**), and the N-borylated derivatives Fc-NH-(9-BBN) (**7**) and Fc-NH-BEt_2 (**8**) were studied by ^{57}Fe NMR spectroscopy. The $\delta^{57}\text{Fe}$ data reveal that $\text{C}_{\text{Fc}}\text{N}(\text{pp})\pi$ interactions lead to ^{57}Fe nuclear magnetic deshielding (with respect to ferrocene) which is attenuated if competing $\text{BN}(\text{pp})\pi$ bonding becomes efficient (**7, 8**).

boryl amines, all of which have been investigated by numerous physical methods. In the case of aminoboranes, the competition between different π acceptors for $(\text{pp})\pi$ interactions has been noted for example in N-aryl- and N-silyl-aminoboranes [1, 2]. In this context, ferrocenyl amine (**1**) and its N-silyl (**2–4**), N-silyl-N-boryl (**5, 6**), and N-boryl derivatives (**7, 8**) are of interest (Scheme 1). Ferrocenyl amine has been known for a long time [3], whereas various N-silyl and N-boryl derivatives have been prepared only recently [4]. The ^{11}B , ^{13}C , $^{15/14}\text{N}$ and ^{29}Si NMR data indicate analogies to other N-silyl- and N-boryl amines [4]. Another sensitive probe in this chemistry should be ^{57}Fe NMR spectroscopy [5], although it is rarely used owing to the insensitivity of the method. We have found [6] however, that in the case of ferrocenes the situation is not as bad as one might expect, taking into account literature reports [5,7,8]. In the present work, we have measured for the first time the ^{57}Fe chemical shifts ($\delta^{57}\text{Fe}$) of ferrocenyl amine **1** and its derivatives **2–8**.

The $\delta^{57}\text{Fe}$ values for **1–8** are given in Table 1, together with $\delta^{11}\text{B}$, $\delta^{15/14}\text{N}$ and $\delta^{29}\text{Si}$ data from the literature [4]. ^{57}Fe NMR spectra could be obtained after 1 to 6 h of spectrometer time (see Fig. 1). In general, there is no problem in identifying the sharp ^{57}Fe NMR signals on the rolling baseline. The ^{57}Fe NMR spectrum shown in Fig. 1 is a typical example, and no cosmetic treatment was applied in order to suppress fully or partially the rolling baseline. In ferrocenes, relaxation times $T_1(^{57}\text{Fe})$ are fairly short [6,9], allowing for short repetition times, if the measurements are carried out at high field strengths B_0 . Under these conditions, spin-lattice energy exchange due to the

Due to its high electronegativity, the nitrogen atom is a strong σ acceptor in amines but can also act as a strong π donor because of its lone pair of electrons. The latter property is for example of particular interest in aryl amines, N-silyl- and N-



Scheme 1.

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Table 1. ^{11}B , $^{15/14}\text{N}$, ^{29}Si and ^{57}Fe NMR spectroscopic data^a of **1** to **8**.

	$\delta^{15}\text{N}$ [$^1J(^{29}\text{Si},^{15}\text{N})$] ($^1J(^{15}\text{N},^1\text{H})$)	$\delta^{11}\text{B}$	$\delta^{29}\text{Si}$	$\delta^{57}\text{Fe}^b$
1	-345.7 (72.5)	-	-	+1639.2
2	-340.0 [17.0] (78.5)	-	+3.2	+1683.5
3	-344.3 [17.3] (78.2)	-	-12.6	+1663.4
4	-333.6 [21.0] (78.1)	-	-11.0	+1658.2
5	-284 ± 2 (^{14}N)	+58.5	+8.3	+1709.4
6	-285 ± 2 (^{14}N)	+55.7	+8.4	+1701.7
7	-280.4 (81.0)	+51.4	-	+1601.4
8	-275.7 (81.0)	+49.2	-	+1593.2

^a The compounds **1** and **2** were dissolved in CDCl_3 ; compounds **4–8** in $[\text{D}_8]\text{toluene}$ or C_6D_6 (there were no appreciable shift differences for these solvents); coupling constants $^1J(^{29}\text{Si},^{15}\text{N})$ [± 0.1 Hz] are given in brackets and $^1J(^{15}\text{N},^1\text{H})$ (± 0.5 Hz) are given in parentheses; $^{15/14}\text{N}$, ^{11}B and ^{29}Si NMR [4]; ^{57}Fe NMR this work; ^b $\delta^{57}\text{Fe}$ (ferrocene) = +1541.7 (CDCl_3) [6].

chemical shift anisotropy, depending on B_0^2 , becomes the dominant relaxation mechanism.

The ^{57}Fe nuclear magnetic shielding in ferrocene derivatives are dominated by changes in the paramagnetic term related to the HOMO-LUMO energy gap of iron-centred orbitals [10]. If the principal features of the sandwich structure remain unchanged, almost all substituents in ferrocenes studied so far [5–9] exert a deshielding effect. This is also true for the NH_2 group in **1** ($\Delta^{57}\text{Fe} \approx +100$ ppm with respect to ferrocene), and even more so for N-silylamino groups as in **2–4**. The $\delta^{13}\text{C}(2,5)$ values of **2–4** [4] indicate stronger $\text{C}_{\text{Fc}}\text{N}(\text{pp})\pi$ interactions than in **1**. This is in agreement with the nitrogen NMR data which

suggest a pyramidal surrounding of the nitrogen atom in **1** as compared to a trigonal planar arrangement in **2–4**. The replacement of the hydrogen atom in **2** by a dialkylboryl group induces a small shift of the ^{57}Fe resonance signal to higher frequency, a minor change, considering $\text{BN}(\text{pp})\pi$ bonding (indicated by the deshielding of nitrogen nuclei) and the reduced $\text{C}_{\text{Fc}}\text{N}(\text{pp})\pi$ interactions (indicated by deshielding of the $^{13}\text{C}(2,5)$ nuclei). However, in the absence of the N–SiMe_3 group as in **7** and **8**, the ^{57}Fe resonance signals are shifted considerably to low frequencies with respect to **5** and **6**, and even with respect to **1**. Again, all other NMR data indicate strong $\text{BN}(\text{pp})\pi$ bonding (e.g. hindered rotation about the BN bond) and reduced $\text{C}_{\text{Fc}}\text{N}(\text{pp})\pi$ interactions. It is concluded that the ^{57}Fe nuclear magnetic shielding in N-ferrocenyl amines increases if the nitrogen atom bears substituents which compete efficiently with the ferrocenyl group for π interactions with the lone pair of electrons at the nitrogen atom. Work is now in progress to apply ^{57}Fe NMR spectroscopy to other ferrocene derivatives with nitrogen-containing substituents such as $\text{NHC}(\text{O})\text{R}$, NC , NSO , N_3 , etc. as well as to corresponding 1,1'-disubstituted ferrocenes.

Experimental Section

All compounds were prepared following the reported procedures (**1** [11], **2** [12], **3–8** [4]), and the samples were handled under argon, using dry glassware and carefully dried solvents. ^{57}Fe NMR measurements were performed using a Bruker DRX 500 instrument equipped with a low-fre-

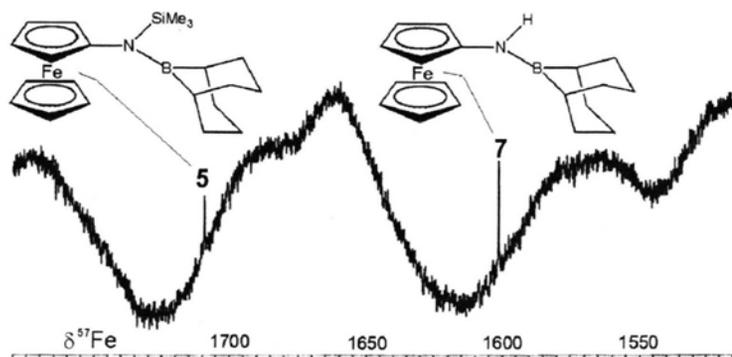


Fig. 1. 16.2 MHz $^{57}\text{Fe}\{^1\text{H}\}$ NMR spectrum of a solution obtained from the reaction of **2** with 9-BBN [4] which leads to a mixture of the two N-ferrocenyl-aminoboranes **7** and **5** (60:40; total weight 100 mg in 0.6 ml of C_6D_6 ; acquisition time 0.4 s; pulse duration 25 μs corresponding to a 30° pulse; 32000 transients; repetition time 10 ms; spectral width 24300 Hz, zero-filling to 32 K data points; line broadening 1 Hz; 4 h of spectrometer time). The rolling baseline owing to acoustic ringing is a typical feature of NMR spectra when low- γ nuclei are measured without using special pulse sequences [13].

quency probehead (tuning range from ^{187}Os to ^{13}C , also tuneable to ^{31}P). The duration of the 90° pulse $\pi/2(^{57}\text{Fe}) \approx 90 \mu\text{s}$ was determined from ^{73}Ge NMR of GeCl_4 , assuming that the quality of tuning of the probehead is comparable for both frequencies [$\nu(^{73}\text{Ge}) \approx 17.5 \text{ MHz}$ as compared to $\nu(^{57}\text{Fe}) = 16.2 \text{ MHz}$]. Chemical shifts $\delta^{57}\text{Fe}$ are

given with respect to neat $\text{Fe}(\text{CO})_5$ as an external reference [$\delta^{57}\text{Fe} = 0$ for $\Xi(^{57}\text{Fe}) = 3.237798 \text{ MHz}$].

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