

1,2-*N,N*-dimethylaminomethylferrocenyl as a ligand towards silicon

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Abstract

The reinvestigation of reactions of [2-(dimethylaminomethyl)ferrocenyl]lithium (**1**), (FcN)Li, with silicon tetrachloride respectively, chlorotrimethylsilane delivers new analytical data for (FcN)SiCl₃ (**2**) and (FcN)SiMe₃ (**3**), especially the structure of **2** has been subjected to X-ray structure analyses. The reaction of **2** with sodiumisopropylate yields the novel (FcN)Si(O-ⁱC₃H₇)₃ (**4**) which was subjected to X-ray diffraction analysis by its hydrochloride (FcN)Si(O-ⁱC₃H₇)₃ × HCl (**5**). The reaction of **1** with 1,6-dichlorododecamethylhexasilane yields the novel (FcN)(SiMe₂)₆(FcN) (**6**). © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

The ligand 1,2-*N,N*-dimethylaminomethylferrocenyl (FcN) has been used with several transition-metal ions [1]. In contrast to this well-investigated compound class the homologous complexes modified by a formal substitution of the transition metal by SiR₃ could attract only scarce attention so far. During the past several years various FcN-silanes have been prepared [2]. Up to now, to the best of our knowledge, none X-ray structure analyses has been reported for this class of compounds. On the other hand in former works important spectroscopic data (²⁹Si- and ¹³C-NMR) of FcN-silicon compounds are missing also [3] and there are no publications about (FcN)Si-compounds with coordination number of silicon greater than four. For this reason it seemed interesting to reinvestigate this field of chemistry. Besides that, there has been considerable interest in the chemistry of three-dimensional metal

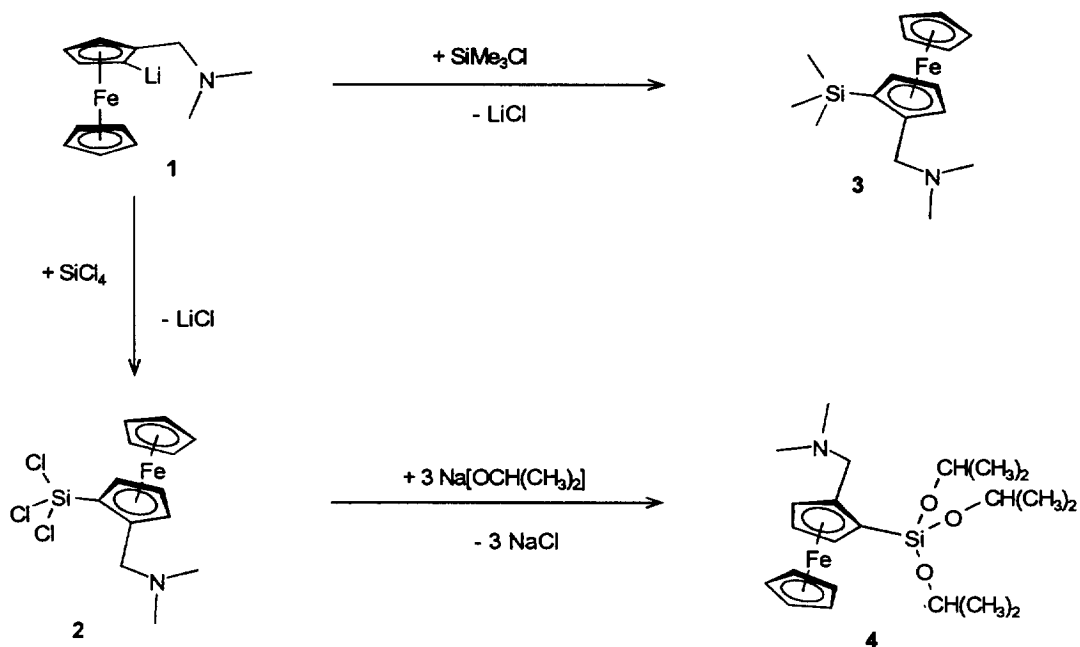
containing siloxanes [4]. Halogenosilane complexes are interesting as synthons for metal containing polysilanes and silanoles. For that purpose reactive halide groups are highly recommended.

In order to enrich this class of compounds with new results and new compounds we report here the preparations and characterizations of (FcN)SiCl₃ (**2**) and (FcN)Si(O-ⁱC₃H₇)₃ × HCl (**5**), for which structural data also have been obtained. Furthermore, we also demonstrate that it is even possible to prepare (FcN)Si-derivatives including a longer silicon chain.

2. Results and discussion

The compounds **2** and **3** were prepared as parts of other investigations ([2,3]b) (Scheme 1). The treatment of an excess of SiCl₄ with a solution of (FcN)Li (**1**) in DME results (FcN)SiCl₃ (**2**) as orange-red solid (Scheme 1). Our result is contrary to former works where **2** was reported as red liquid [2]. Recrystallization

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from pentane at -20°C gave analytically pure orange-red crystals of **2** suitable for an X-ray crystallographic study (Fig. 1.). The $^1\text{H-NMR}$ spectrum exhibits the typical signals for the FcN ligand at 2.09 (s, $-\text{N}(\text{CH}_3)_2$), 2.94, 2.91, 3.77, 3.74 (AB, CH_2-N), 4.00 (s, C_5H_5) and 4.40, 4.43, 4.46 ppm as multiplets for the protons of the substituted cyclopentadienyl ring. $^{13}\text{C-NMR}$ data of **2** are in agreement with the proposed structure (Table 5). The $^{29}\text{Si-NMR}$ signal for the SiCl_3 group appears at -4.95 ppm. The UV measurement shows the $^1\text{A}_{1g} \rightarrow ^1\text{E}_{1g}$ transition signal at 443 nm. It is

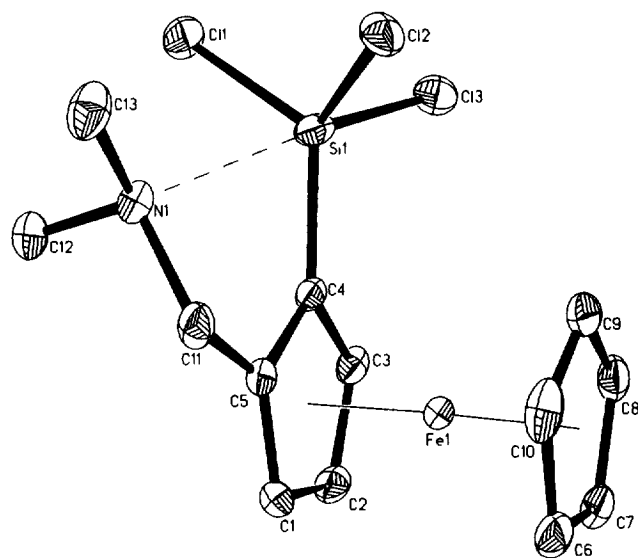


Fig. 1. Molecular structure of **2** with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity.

displaced hypsochromically by 5.2 nm compared to FcNH (437.8 nm) ([1]b).

A single crystal X-ray diffraction study of **2** was carried out. The Fe1 atom is coordinated by both five-membered ring systems (Fig. 1), thus, a nearly linear $\text{Cg}(1)-\text{Fe}(1)-\text{Cg}(2)$ angle of $177.9(1)^{\circ}$ is formed. This fragment adopts an eclipsed conformation. The $\text{Cg}(1)-\text{Fe}(1)$ and $\text{Cg}(2)-\text{Fe}(1)$ distances were determined to be 1.650(2) and 1.657(2) Å, respectively. A particularly interesting feature of the structure is the distance between Si(1) and N(1) of 2.682(2) Å being much shorter than expected from the sum of van der Waals radii (3.5 Å [5]) but considerably longer than the dative $\text{Si} \leftarrow \text{N}$ bond in phenyl-(2,2',2''-nitritriethoxy)silane, 2.193(5) Å [6]. Thus, a substantial bonding interaction $\text{Si}(1) \cdots \text{N}(1)$ may be assumed. In addition, some evidence for this may be gathered from the coordination geometry of the silicon atom tending from tetrahedral towards trigonal bipyramidal. The axial positions of the bipyramid are occupied by N(1) and Cl(3). In effect, the $\text{Si}(1)-\text{Cl}(3)$ distance, 2.098(1) Å, is significantly longer than those observed for the equatorial $\text{Si}(1)-\text{Cl}$ bonds, 2.052(1) and 2.042(1) Å. The Si(1) atom is shifted towards Cl(3) and lies 0.381(1) Å above the plane defined by the three equatorial substituents. In result, the angles formed by Cl(3), Si(1) and any equatorial substituent of Si(1) range from $100.1(1)$ to $102.3(1)^{\circ}$ and differ considerably from ideal values of both the ideal trigonal bipyramidal coordination and the ideal tetrahedral coordination. The corresponding angles with N(1) instead of Cl(3) are in the range of $73.0(1)$ to $82.3(1)^{\circ}$. Bond distances and angles of **2** are given in Table 2.

Table 1
Crystallographic data and experimental parameters for compounds **2** and **5**

Compound	(FcN)SiCl ₃ 2	(FcN) Si(O- ⁱ C ₃ H ₇) ₃ × HCl 5
Empirical formula	C ₁₃ H ₁₆ Cl ₃ FeNSi	C ₂₂ H ₃₈ ClFeNOSi
Formula weight (g mol ⁻¹)	376.6	483.9
Crystal	Platelet, red-orange	Prism, yellow
Crystal size [mm]	0.40 × 0.30	0.60 × 0.50 × 0.40
Crystal system	Monoclinic	Monoclinic
Space group; Z	<i>P</i> 2 ₁ / <i>c</i> ; 4	<i>P</i> 2 ₁ / <i>c</i> ; 4
<i>a</i> (Å)	9.119(2)	16.379(1)
<i>b</i> (Å)	12.307(3)	16.411(1)
<i>c</i> (Å)	14.166(3)	9.585(2)
β (°)	102.90(3)	93.52 (1)
Volume (Å ³)	1549.6(5)	2572(2)
ρ_{calc} (g cm ⁻³)	1.614	1.250
Absorption coefficient (mm ⁻¹)	1.552	0.758
θ range for data collection (°)	2.22–26.29	1.25–24.00
Reflections/ <i>R</i> _{int}	7063/0.021	9978/0.041
Data/parameters	2812/233	3835/346
GOF on <i>F</i> ²	1.005	1.100
<i>R</i> ₁ / <i>wR</i> ₂ (<i>I</i> > 2 σ (<i>I</i>))	0.022/0.060	0.054/0.091
<i>R</i> ₁ / <i>wR</i> ² (all data)	0.024/0.062	0.086/0.102
Largest diff. peak and hole (e Å ⁻³)	0.298/−0.279	0.522/−0.228

The ¹H-NMR data of the SiMe₃ analog (**3**) are in agreement with former investigations [3](b). Additional we report the ²⁹Si-NMR and ¹³C-NMR resonances in Table 5. The UV spectrum (recorded in pentane) shows a signal at 439 nm (¹A_{1g} → ¹E_{1g} transition), it is a little displaced compared to FcNH [1](b). The reaction of (FcN)SiCl₃ (**2**) with three equivalents of Na[O-ⁱC₃H₇] in diethylether yields (FcN)Si(O-ⁱC₃H₇)₃ (**4**) as red-brown oil (Scheme 1).

Structure of **4** is clearly established by spectroscopic data (see Table 5). The FcN-system is indicated by the ¹H-NMR spectrum which exhibits a multiplet at 4.24 ppm and one singlet at 2.25 ppm (−N(CH₃)₂). The resonances of the isopropylate group are found at δ = 1.12 and 4.10 ppm. The assigned structure is proofed by the ¹³C-NMR spectrum (Table 5). Unfortunately we were not able to crystallize complex **4**. But its ammonium salt crystallizes very well. The reaction of **4** with HCl yields the hydrochloride complex **5** as yellow crystals (Scheme 2).

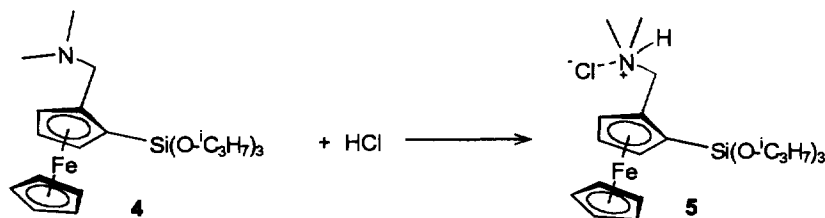
In the ²⁹Si-NMR spectrum, one signal in the typical region at −58.16 ppm is observed. The ¹H- and ¹³C-NMR spectra of **5** show the non-equivalence of methyl groups of −N(CH₃)₂, for example the methyl protons of

the two CH₃ groups appear as separate signals (see Table 5). The protonation of nitrogen was confirmed by the downfield shift of the two methyl groups attached to it, observed at 2.75 and 2.54 ppm in the spectrum of complex **5** (2.25 ppm in the HCl-free compound **4**). The protonated amino group gives rise to an additional broad peak at 12 ppm.

The molecule structure of **5** (Fig. 2) shows a coordination geometry of the iron atom similar to that found in **2**. The Cg(1)–Fe(1)–Cg(2) angle was determined to be 170.4 (2)°, while the Cg(1)–Fe(1) and Cg(2)–Fe(1) distances are 1.635(5) and 1.678(5) Å, respectively. Short intermolecular contacts between the chloride ion and the nitrogen bonded H atom were observed. The N(1)–H(1)⋯Cl(1) distance was found to be 2.19 Å. This value differs strongly from the sum of van der Waals radii (H⋯Cl = 2.95 Å [7]) and indicates the presence of a N–H⋯Cl hydrogen bond [8]. The corresponding N(1)–H(1)⋯Cl(1) angle is 168°. An additional stabilization of this structure is caused by weak intramolecular C(11)–H(11a)⋯O(1) interactions in the range of 2.40 Å. For comparison, the sum of van der Waals radii for H⋯O is 2.72 Å [5]. The character of similar weaker interactions that might be considered as being analogous to very weak hydrogen bonds has been the subject of much discussion [9]. As expected, the Si⋯N(1) distance of 4.341(4) Å shows only a van der Waals type interaction. This behavior is due to the protonation of nitrogen and contrasts with the features of structure **2** as discussed above. Further, the tetrahedron about Si(1) is only slightly distorted. Selected bond lengths and angles of **5** are listed in Table 3.

Table 2
Selected bond lengths and angles for **2**

Bond lengths (Å)			
Cl(1)–Si(1)	2.052(1)	Fe(1)–C(6)	2.038(2)
Cl(2)–Si(1)	2.042(1)	Fe(1)–C(7)	2.046(2)
Cl(3)–Si(1)	2.098(1)	Fe(1)–C(8)	2.048(2)
Si(1)–C(4)	1.824(2)	Fe(1)–C(9)	2.054(2)
Fe(1)–C(1)	2.065(2)	Fe(1)–C(10)	2.044(2)
Fe(1)–C(2)	2.049(2)	N(1)–C(11)	1.475(2)
Fe(1)–C(3)	2.033(2)	N(1)–C(12)	1.472(2)
Fe(1)–C(4)	2.046(2)	N(1)–C(13)	1.468(2)
Fe(1)–C(5)	2.055(2)	Si(1)⋯N(1)	2.682(2)
Bond angles (°)			
C(4)–Si(1)–Cl(2)	119.1(1)	C(12)–N(1)–C(11)	109.9(2)
C(4)–Si(1)–Cl(1)	119.7(1)	C(2)–C(1)–C(5)	108.1(2)
Cl(2)–Si(1)–Cl(1)	110.1(1)	C(3)–C(2)–C(1)	108.8(2)
C(4)–Si(1)–Cl(3)	102.3(1)	C(2)–C(3)–C(4)	107.7(2)
Cl(2)–Si(1)–Cl(3)	101.0(1)	C(5)–C(4)–C(3)	107.3(1)
Cl(1)–Si(1)–Cl(3)	100.1(1)	C(5)–C(4)–Si(1)	123.8(1)
C(4)–Si(1)⋯N(1)	73.0(1)	C(3)–C(4)–Si(1)	128.8(1)
Cl(2)–Si(1)⋯N(1)	82.3(1)	C(1)–C(5)–C(4)	108.0(2)
Cl(1)–Si(1)⋯N(1)	81.8(1)	C(1)–C(5)–C(11)	131.5(2)
C(13)–N(1)⋯N(1)	175.2(1)	C(4)–C(5)–C(11)	120.3(2)
C(13)–N(1)–C(12)	108.9(2)	C(7)–C(6)–C(10)	107.7(2)
C(13)–N(1)–C(11)	111.0(2)		



Scheme 2.

The same synthesis route leads to a compound containing a longer silicon chain. The reaction of two equivalents of (FcN)Li (1) with Cl(SiMe₂)₆Cl in THF/pentane at -78°C results (FcN)(SiMe₂)₆(FcN) (6, Scheme 3).

The ¹H- and ¹³C-NMR spectra for the complex 6 are quite similar. Each one contains the typical resonances of the 1,2-*N,N*-dimethylaminomethylferrocenyl ligand (see Table 5). In the case of compound 6 we observed chemical shift differences between the methylene group protons again. The recorded non-equivalence of methylene group protons in 1,2-disubstituted ferrocenes agrees with results given in previous papers [10]. The ¹H-NMR resonances for the methyl groups bonded to silicon appear in a typical range at δ values nearly zero, but the number of six signals is suspicious, because the ²⁹Si-NMR spectrum of 6 indicates only three resonances (Table 5). The silicon chain is bonded to an asymmetric carbon atom. For this reason the methyl groups should be diastereotop.

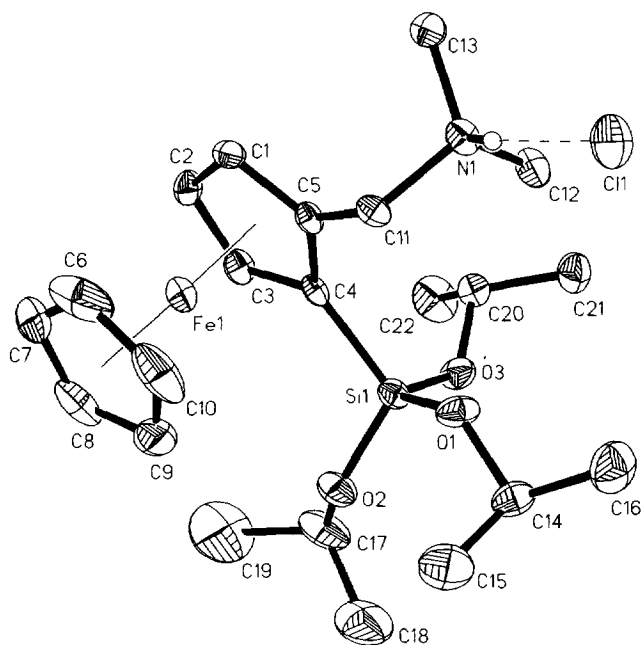


Fig. 2. Molecular structure of 5 with thermal ellipsoids at the 30% probability level. Hydrogen atoms (other than N-H...Cl) are omitted for clarity.

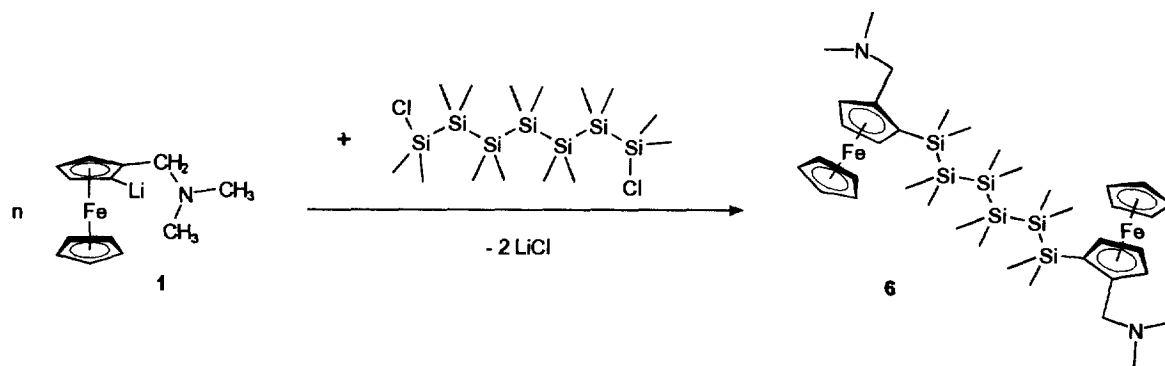
3. Mössbauer spectroscopy

The Mössbauer spectra were recorded at 100 K absorber temperature. Table 4 contains the results of these measurements. All these spectra show the same pattern (Fig. 3).

The observation of two doublets points to the presence of Fe^{II} and Fe^{III}. The doublet D₁, is created by the iron (II) in the ferrocene skeleton (Fe^{II}) and the doublet D₂ indicates a ferricinium (Fe^{III}). But the intramolecular electron transfer should be slow on the time scale of Mössbauer experiment, mixed valence case [11]. The small Fe^{III} (D₂) contribution in compound 2 should be caused by the electron acceptor property of the SiCl₃-group which reduces the electron density at the iron atom via the cyclopentadienyl ring. A similar electron density reduction at the iron atom we find for compound 3. In this case the SiMe₃-group causes the charge transfer. Normally the acceptor character of the SiCl₃-group should be stronger than that one of the SiMe₃-group. The found reverse behaviour shown in the Mössbauer spectra could be explained by the interaction of the SiCl₃-group with the electron lone pair at

Table 3
Selected bond lengths and angles for 5

Bond lengths (Å)			
Si(1)–O(1)	1.615(3)	Fe(1)–C(9)	2.033(3)
Si(1)–O(2)	1.617(3)	Fe(1)–C(3)	2.035(4)
Si(1)–O(3)	1.621(3)	Fe(1)–C(2)	2.047(4)
Si(1)–C(4)	1.839(4)	Fe(1)–C(4)	2.050(4)
Fe(1)–C(6)	2.019(5)	O(1)–C(14)	1.429(3)
Fe(1)–C(10)	2.020(3)	O(2)–C(17)	1.422(5)
Fe(1)–C(5)	2.023(3)	O(3)–C(20)	1.435(4)
Fe(1)–C(1)	2.029(4)	N(1)–C(12)	1.476(4)
Fe(1)–C(7)	2.030(6)	N(1)–C(13)	1.478(4)
Fe(1)–C(8)	2.030(4)	N(1)–C(11)	1.512(4)
Bond angles (°)			
O(1)–Si(1)–O(2)	108.1(2)	O(1)–C(14)–C(16)	108.1(3)
O(1)–Si(1)–O(3)	113.0(2)	O(1)–C(14)–C(15)	108.8(2)
O(2)–Si(1)–O(3)	106.1(2)	C(16)–C(14)–C(15)	113.2(3)
O(1)–Si(1)–C(4)	105.7(2)	O(2)–C(17)–C(18)	109.3(6)
O(2)–Si(1)–C(4)	113.7(2)	O(2)–C(17)–C(19)	105.5(5)
O(3)–Si(1)–C(4)	110.4(2)	C(18)–C(17)–C(19)	111.0(7)
C(12)–N(1)–C(13)	112.8(2)	O(3)–C(20)–C(21)	109.0(4)
C(12)–N(1)–C(11)	113.4(2)	O(3)–C(20)–C(22)	108.8(4)
C(13)–N(1)–C(11)	112.9(3)	C(21)–C(20)–C(22)	111.8(5)



Scheme 3.

the nitrogen atom of the ligand as exhibited in the crystal structure. The hydrochloride-complex **5** gave the same of the Mössbauer pattern as the compounds **2** and **3**. Probably protonation of the nitrogen atom and the weak interaction of the C(11) proton with the oxygen atom of the isopropylate group give rise to electron density reduction at the iron atom. The Mössbauer spectrum of compound **6** (at 100 K) exhibits clearly as well Fe^{II} as Fe^{III} signal. Peaks have nearly the same intensity. We assume an intervalence electron transfer between the iron atoms in both ferrocenyl systems of compound **6**. Appearance of doublets only of an expected singlet presumably results from the fact that this charge transfer is too slow at 100 K in relation to the time constant of the Mössbauer window ($K = 10^8 \text{ s}^{-1}$) [11]. The UV-absorption band suffers shift in different solvents. The possibility, that two spinstates are in thermal equilibrium could not be found out by measuring the Mössbauer spectra in the temperature region 77–296 K.

4. Experimental section

4.1. General

All manipulations involving air- and moisture-sensitive organometallic compounds were carried out by the use of the standard Schlenk and glove-box techniques under an argon atmosphere. All solvents were freshly

Table 4
Mössbauer data of the derivatives **2,3,5** and **6**

Compound	D ₁				D ₂			
	δ (mm s ⁻¹)	ϵ (mm s ⁻¹)	Γ (mm s ⁻¹)	I (%)	δ (mm s ⁻¹)	ϵ (mm s ⁻¹)	Γ (mm s ⁻¹)	I (%)
2	0.511(1)	2.300(2)	0.267(3)	94(1)	0.16(3)	0.46(3)	0.36(8)	6(2)
3	0.514(9)	2.384(3)	0.234(8)	84(2)	0.19(4)	0.48(6)	0.38(9)	16(2)
5	0.504(3)	2.315(1)	0.218(1)	64(2)	0.19(2)	0.49(2)	0.42(4)	36(2)
6	0.514(6)	2.35(1)	0.26(2)	61(3)	0.19(2)	0.50(3)	0.39(5)	39(3)

δ , isomer shift (rel.aFe); ϵ , quadrupole splitting; Γ , line width; I, line area.

distilled, degassed and dried prior to use. Syntheses of (FcN)Li [12] and Cl(SiMe₂)₆Cl [13] were carried out according to known procedures. All other reagents were commercial products and were used without further purification.

NMR spectra were recorded on Bruker MSL 200 and Varian Gemini XL-300. W spectra were measured on Specord M40 instrument. Mass spectra were measured on a Sector-Field-Mass-Spectrometer AMD 402. Mössbauer spectra were recorded on WISSEL system at 100 K, using a 1.8 GBq ⁵⁷Co source in a rhodium matrix (isomer shift relative α Fe).

4.2. Synthesis of complexes **2, 4–6**

4.2.1. Preparation of (FcN)SiCl₃ (**2**)

[2-(dimethylaminomethyl)ferrocenyl]-lithium (60 mmol, 14.9 g) was dissolved in DME and added slowly, over a period of 4 h, to an excess of SiCl₄ (240 mmol, 27.5 ml). The reaction mixture was allowed to stir for additional 3 h before the solvent and unreacted SiCl₄ were removed under vacuum. The resulting orange solid was recrystallized from pentane to remove LiCl. This purification leads to orange-red crystals. Yield: 18 g (80%), m.p.: 86–88°C; anal. found: C, 41.21; H, 4.05; N, 3.65; Cl, 27.95. C₁₃H₁₆Cl₃FeNSi (376.5) calc.: C, 41.47; H, 4.25; N, 3.71; Cl, 28.27. UV: pentane 443 nm. MS (70 eV) $m/e = 376$ (55%, M⁺), 331 (68%, [CH₂(Fc)SiCl₃]⁺), 297 (13%, [CH₂(Fc)SiCl₂]⁺), 242 (100%, [(FcN)H]⁺), 205 (15%, [(Fc)Si]), 184 (30%,

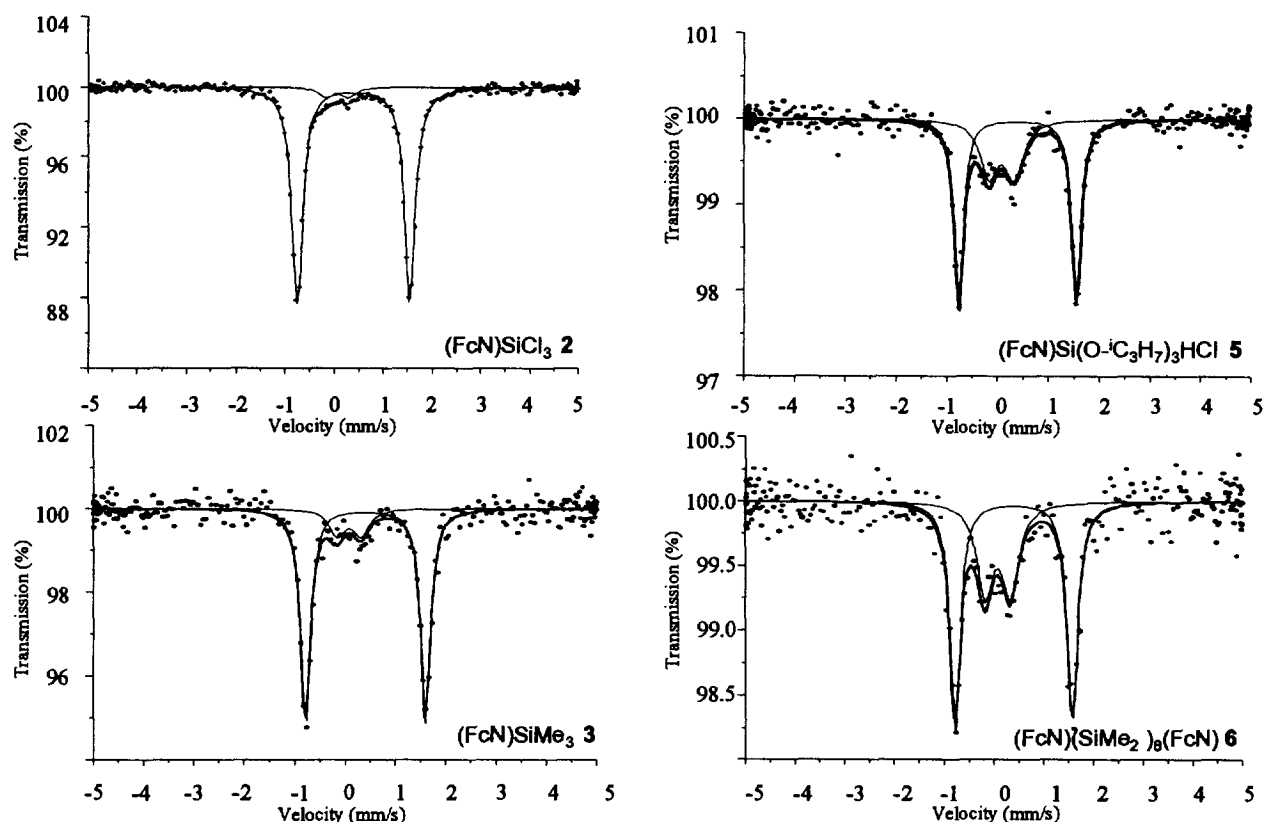


Fig. 3. Mössbauer spectra of compounds 2, 3, 5 and 6.

$[\text{C}_5\text{H}_3\text{FeC}_5\text{H}_5]$, 163 (17%, $[\text{FeC}_5\text{H}_4\text{SiCl}_2]$, 121 (38%, $[\text{FeC}_5\text{H}_5]^+$), 66 (29%, $[\text{C}_5\text{H}_5]^+$).

4.2.2. Preparations of $(\text{FcN})\text{Si}(\text{O}-i\text{C}_3\text{H}_7)_3$ (**4**) and $(\text{FcN})\text{Si}(\text{O}-i\text{C}_3\text{H}_7)_3 \times \text{HCl}$ (**5**)

A solution of 11.9 g (147 mmol) of sodiumisopropylate in 100 ml diethyl ether was added to a mixture of 49 mmol (15.5 g) of $(\text{FcN})\text{SiCl}_3$ and 150 ml diethyl ether at -5°C . The reaction mixture was stirred for 12 h at ambient temperature. The solvent was removed in vacuo and the dark remaining viscous product was dissolved with pentane and filtered. The solvent was removed under reduced pressure and a brown oil (**4**) was obtained. MS (70 eV) $m/e = 446$ (100%, M^+), 431 (10%, $[\text{CH}_3\text{NCH}_2(\text{Fc})\text{Si}(\text{O}-i\text{C}_3\text{H}_7)_3]$), 401 (22%, $[\text{CH}_2(\text{Fc})\text{Si}(\text{OC}_3\text{H}_7)_3]^+$), 345 (35%, $[(\text{Fc})\text{Si}(\text{O})(\text{O}-i\text{C}_3\text{H}_7)_2]^+$), 303 (12%, $[(\text{Fc})\text{Si}(\text{O})_2\text{O}-i\text{C}_3\text{H}_7]$), 261 (20%, $[\text{FeSiO}_3]^+$), 242 (43%, $[(\text{FcN})\text{H}]^+$), 200 (21%, $[(\text{Fc})\text{CH}_2]^+$), 185 (30%, $[(\text{Fc})\text{H}]^+$), 149 (18%, $[\text{FeC}_5\text{H}_5\text{Si}]$).

A stream of gaseous hydrogen chloride was bubbled for 5 h through a solution of 3.1 g (10 mmol) of **4** in 100 ml of pentane. After all the unreacted HCl had been removed from the flask, the mixture was cooled at 0°C and compound **5** was crystallized as yellow crystals. Yield: 3.2 g (93%); anal. found: C, 53.94; H, 7.32;

N, 3.10. $\text{C}_{22}\text{H}_{38}\text{O}_3\text{ClFeNSi}$ (483.9) calc.: C, 54.54; H, 7.85; N, 2.89.

4.2.3. Preparation of $(\text{FcN})(\text{SiMe}_2)_6(\text{FcN})$ (**6**)

A solution of 1.5 g (3.57 mmol) of $\text{Cl}(\text{SiMe}_2)_6\text{Cl}$ in 20 ml of pentane was added dropwise within 1 h to a suspension of 1.78 g (7.14 mmol) $(\text{FcN})\text{Li}$ in about 50 ml of THF at -78°C (dry ice-EtOH bath). The mixture was stirred for another 8 h at room temperature. After solvent evaporation and extraction of the solid dark orange residue with 100 ml of *n*-hexane, the clear orange solution was cooled to -20°C overnight. The resulting fine yellow precipitate was washed with a little cold pentane, and the mother liquor was treated correspondingly again. The total yield was 2.45 g (82%) of fine yellow crystals. Anal. found: C, 54.25; H, 8.02; N, 3.56. $\text{C}_{38}\text{H}_{68}\text{Fe}_2\text{N}_2\text{Si}_6$ (833.18) calc.: C, 54.78; H, 8.22; N, 3.36. UV: pentane 454 nm, acetonitrile 446 nm.

4.3. X-ray crystal structure determination

Intensity data of **2** and **5** were measured by means of a Siemens Smart CCD-System using graphite monochromated $\text{Mo}-\text{K}_\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$; ω scan mode) at a temperature of 223 K. The structures were determined by direct methods using SHELXS [14]

Table 5
 ^1H , ^{13}C and ^{29}Si NMR data of the derivatives 2–6; at 25°C; data in ppm are relative to Me_4Si at 0.0 ppm

Compound	δ ^1H		δ ^{13}C		δ ^{29}Si	
	FeN	Me-Si	Me-Si	FeN		
2 ^a	2.09 (s 6H); 4.00 (s 5H); 2.91, 2.94, 3.74, 3.77 (qAB $\text{CH}_2\text{-N}$); 4.40, 4.43, 4.46 (m 3H)				44.45, 57.78, 66.02, 70.48, 70.75, 73.49, 75.14, 91.95	–4.95
3 ^a	2.06 (s 6H); 4.03 (s 5H); 2.86, 2.90, 3.44, 3.48 (q AB $\text{CH}_2\text{-N}$); 4.12, 4.18, 4.24 (m 3H)	0.26	0.44		44.97, 59.69, 68.72, 69.43, 71.93, 73.53, 74.30, 90.09	–3.48
6 ^a	2.60 (s 6H); 4.17 (s 5H); 4.03, 4.26, 4.30, 4.37 (m)	0.44, 0.37, 0.11, 0.08, 0.04, 0.02	–0.82, –1.66, –4.18, –4.27, –4.86, –5.05		45.28, 59.77, 68.62, 69.18, 72.49, 73.45, 75.59, 90.03	–16.75, –38.54, –42.07
4 ^b	2.25 (s 6H), 4.24 (m, 11 H)	$\text{Si}(\text{O}-^i\text{C}_3\text{H}_7)_3$ 1.12 (t 18H), 4.10 (s 3H)	$\text{Si}(\text{O}-^i\text{C}_3\text{H}_7)_3$ 25.95, 65.72		58.22, 42.92, 42.00, 71.18, 73.38, 75.68, 78.37, 79.81	
5 ^a	2.54, 2.75 (d 6H); 4.19 (s 5H); 3.16, 3.06 ($\text{CH}_2\text{-N}$); 4.26, 4.36, 4.48 (m)	1.24 (m 18H); 4.14 (m 3H)	25.83, 65.88		40.50, 43.60, 56.91, 66.17, 70.09, 73.35, 75.48, 76.03, 78.43	–58.16

^a Recorded in CDCl_3 .

^b Recorded in C_6D_6 .

and full matrix least squares refinement based on F^2 (SHELXS-93 [15]). All hydrogen atoms, especially the nitrogen bonded H in 5, were located from difference Fourier maps. Their atomic positions were freely refined using isotropic displacement parameters Tables 6 and 7. Crystal data and details on data collection and refinement are collected in Table 1.

Table 6
 Atomic coordinates ($\cdot 10^4$) and equivalent isotropic parameters ($\text{\AA}^2 \cdot 10^3$) for 2

Atom	x	y	z	$U(\text{eq})^a$
Fe(1)	846(1)	1089(1)	8396(1)	25(1)
Cl(1)	3812(1)	–2032(1)	7036(1)	46(1)
Cl(2)	5214(1)	129(1)	8385(1)	39(1)
Cl(3)	3279(1)	–1692(1)	9162(1)	42(1)
Si(1)	3346(1)	–806(1)	7907(1)	33(1)
N(1)	3184(2)	356(1)	6285(1)	29(1)
C(1)	–378(2)	1074(2)	6981(1)	37(1)
C(2)	974(2)	317(2)	7552(1)	39(1)
C(3)	166(2)	–440(2)	7958(1)	31(1)
C(4)	1502(2)	–156(1)	7626(1)	25(1)
C(5)	1152(2)	791(1)	7025(1)	29(1)
C(11)	2307(2)	1273(1)	6542(1)	32(1)
C(12)	2296(2)	–220(2)	5437(1)	35(1)
C(13)	4591(2)	736(2)	6058(2)	42(1)
C(6)	582(3)	2605(2)	8912(1)	43(1)
C(7)	104(2)	1813(2)	9503(1)	39(1)
C(8)	1337(2)	1132(2)	9879(1)	38(1)
C(9)	2581(2)	1500(2)	9533(1)	41(1)
C(10)	2118(3)	2410(2)	8934(1)	44(1)

^a $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 7
 Atomic coordinates ($\cdot 10^4$) and equivalent isotropic parameters ($\text{\AA}^2 \cdot 10^3$) for 5

Atom	x	y	z	$U(\text{eq})^a$
Si(1)	2269(1)	5190(1)	–2144(1)	32(1)
Fe(1)	2412(1)	5213(1)	1457(1)	35(1)
Cl(1)	3958(1)	1706(1)	–1007(1)	55(1)
O(1)	2141(2)	4225(2)	–2399(3)	44(1)
O(2)	1377(2)	5611(2)	–2133(3)	47(1)
O(3)	2732(2)	5633(2)	–3384(3)	44(1)
N(1)	4097(2)	3480(2)	–460(4)	34(1)
C(1)	3644(2)	5067(2)	1632(4)	32(1)
C(2)	3450(2)	5911(2)	1543(4)	35(1)
C(3)	2988(2)	6040(2)	276(4)	36(1)
C(5)	3302(2)	4679(2)	405(4)	28(1)
C(4)	2879(2)	5281(2)	–475(4)	27(1)
C(6)	1980(4)	4617(6)	3100(8)	100(3)
C(7)	1815(4)	5440(6)	3210(7)	90(2)
C(8)	1333(3)	5663(3)	2055(7)	68(2)
C(9)	1192(2)	4987(2)	1204(3)	64(2)
C(10)	1594(2)	4339(2)	1880(3)	78(2)
C(11)	3326(1)	3769(1)	178(2)	32(1)
C(12)	4196(1)	3809(2)	–1873(2)	44(1)
C(13)	4836(2)	3586(2)	485(3)	42(1)
C(14)	1550(2)	3819(2)	–3310(3)	44(1)
C(15)	816(2)	3618(2)	–2507(3)	83(2)
C(16)	1949(5)	3080(4)	–3894(8)	71(2)
C(17)	1088(3)	6354(3)	–2746(7)	71(2)
C(19)	815(7)	6877(5)	–1523(10)	145(3)
C(18)	387(5)	6179(8)	–3767(9)	109(3)
C(20)	3563(2)	5909(2)	–3394(5)	38(1)
C(22)	3565(5)	6826(3)	–3551(9)	73(2)
C(21)	3967(4)	5497(4)	–4560(6)	57(1)

^a $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

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