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Preparation, characterization and properties of dipolar 1,2-*N*,*N*-dimethylaminomethylferrocenylsilanes

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Abstract

A series of substituted 1,2-*N*,*N*-dimethylaminomethylferrocenyl compounds were synthesized and characterized by ^{1}H-NMR, ^{13}C-NMR, ^{29}Si-NMR, ES–MS, IR, UV–vis and ^{57}Fe-Mössbauer spectroscopy. The new (*R*,*S*)-2-(*N*,*N*-dimethylaminomethyl)ferrocenyl-(aryl)silanes (*R*,*S*)-FcNSiMe$_n$(C$_6$H$_4$X)$_m$ ($n = 2–0$, $m = 1$, X = *p*-F (**5**); $m = 2$, X = *p*-F (**6**); $m = 3$, X = *p*-F (**7**) and $m = 1$, X = *p*-Br (**14**) were formed by the reaction of 2-dimethylaminomethylferrocenyllithium FcNLi (**1**) with chloroarylsilanes ClSi(Me)$_n$(C$_6$H$_4$X)$_m$ ($n = 2–0$, $m = 1$, X = *p*-F (**2**); $m = 2$, X = *p*-F (**3**); $m = 3$, X = *p*-F (**4**) and $m = 1$, X = *p*-Br (**13**)). The treatment of **5**, **6** and **14** with gaseous hydrogen chloride or picric acid resulted in the formation of the hydrochloride complexes **9**, **10**, **15** and the picrates **11**, **12** and **16**. The treatment of **14** with LiR or Mg and DMF resulted in the formation of (*R*,*S*)-2-(*N*,*N*-dimethylaminomethyl)ferrocenyl(4-formylphenyl)dimethylsilane (**18**). The crystal structures of **7**, **12** and **15** were determined by single crystal X-ray analyses. ^{57}Fe-Mössbauer spectroscopy gives evidence of a significant electronic coupling between the ferrocenyl unit and the organic acceptor moiety of the molecules in the ground state.

Keywords: 1,2-*N*,*N*-Dimethylaminomethylferrocenyl; Ferrocene; Mössbauer spectroscopy; Crystal structures; Silicon

1. Introduction

Due to the outstanding stability and the unique redox-behavior the ferrocenyl unit is used in a vast variety of synthesis [1]. Compared with organic non-linear optics, the field of organometallic compounds with non-linear optical properties is relatively young and unexplored [2–4]. Dipolar ferrocene compounds are investigated as compounds with potential non-linear optical properties. Some ferrocenyl derivatives with strong SHG-activity have already been reported [5–9].

The ability to functionalize both the ferrocene and the silanyl moiety in ferrocenylsilanes permits the physical properties to be tailored. Potential applications of such compounds in non-linear optics have spurred research in this area [10–13].

Very recently, functionalized ferrocene moieties like the 1,2-*N*,*N*-dimethylaminomethylferrocenyl entity (FcN) have become attractive units for the construction of novel organometallic silane molecules [14]. Thus, the treatment of chlorosilanes with 2-dimethylaminomethylferrocenyl lithium (FCNLi) (**1**) produces optically isomeric molecules such as, for example, (*R*,*S*)-(FcN)$_2$SiMe$_2$. Optical activity (Scheme 1) and an interesting redox behavior are the prominent features of such FcN-substituted silanes.

With this in mind, we proceeded to synthesize and characterize the new dipolar 2-(*N*,*N*-dimethylaminomethyl)ferrocenyl-(4-aryl)silanes. Molecules of this type permit different functional substituents to be introduced at the silicon, especially acceptor groups, e.g. the fluorophenyl entity. Some donor quality towards the silicon atom may originate from the *N*,*N*-dimethylaminomethyl substituent at the cyclopentadienyl ring

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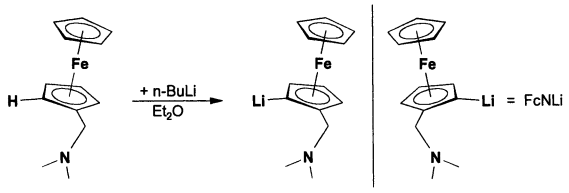


Scheme 1.

[15]. Furthermore, protonation of the nitrogen atom seems to provide an additional option for arriving at well-crystallized compounds.

The expected mixed-valence behavior of iron was investigated by means of Mössbauer spectroscopy.

2. Results and discussion

2.1. Synthesis and properties

The 2-(*N*,*N*-dimethylaminomethyl)ferrocenyl(4-fluorophenyl)silanes (**5**), (**6**) and (**7**) were synthesized in a two-step procedure starting from (4-fluorphenyl)magnesiumbromide. The treatment of the chloro(4-fluorophenyl)silanes (**2**), (**3**) and (**4**) with 2-dimethylaminomethylferrocenyllithium [16] (FcNLi) (**1**) in THF resulted in the formation of the silanes (**5**), (**6**) and (**7**) (Scheme 2).

The compounds **5** and **6** are brown liquids and **7** is a yellow solid. All three compounds possess single resonance signals in the ^{29}Si-NMR spectrum at −7.8 (**5**), −11.0 (**6**) and −14.4 ppm (**7**), respectively. Compound **7** is highly soluble in organic solvents and stable in air.

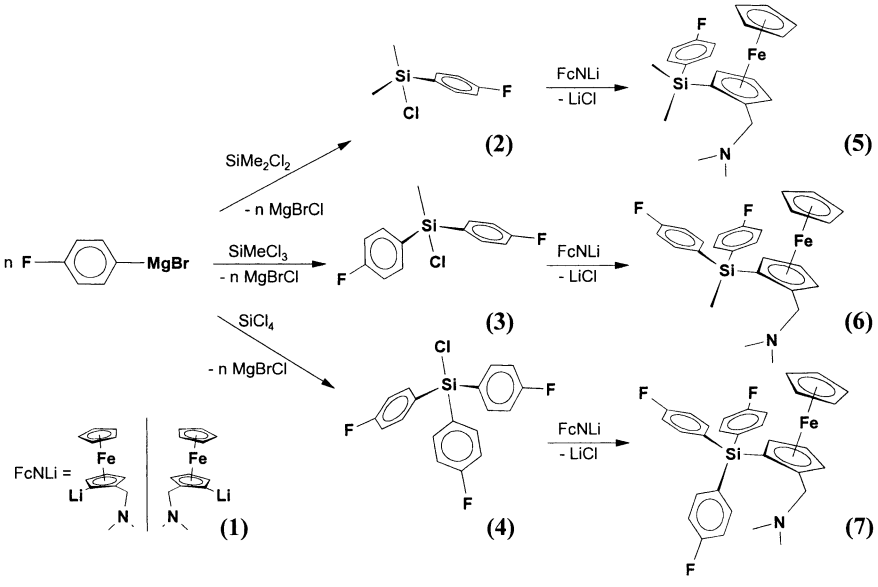
Its crystallization from toluene resulted in the formation of yellow crystals suitable for an X-ray crystallographic study (Fig. 1). Clear homogeneous crystals of up to 10 mm in size were grown.

Since our goal was to synthesize crystalline compounds, we were looking for useful ways to prepare derivatives of liquids **5** and **6**. Thus, to exploit the *N*,*N*-dimethylamino group at the ferrocenyl moiety, both compounds were reacted with hydrogen chloride, L-(+)-tartaric acid and picric acid. Hydrogen chloride with **5** and **6** in *n*-pentane at 0 °C (after 30 min treatment) gave fine yellow precipitates of the hydrogen chloride adducts (**9**) and (**10**) (Scheme 3).

The solids **9** and **10** do not crystallize very well. Both compounds are moisture- sensitive and have to be handled under anaerobic conditions. Single crystals of sufficient quality could be isolated only from compound **10**. The X-ray structure analysis delivered crystallographic data with final *R*-values of 12%.

Treatment of **5** and **6** with chiral tartaric acid should enable diastereomeric products to be formed which would be highly desirable, but till now all of our trials have failed. We are planning further experiments to obtain ammonium salts with other chiral acids. The reaction of **5** and **6** with the stronger picric acid engendered the compounds **11** and **12** (Scheme 4). Both of the ammonium picrates are stable in air and well-crystallized. The molecular structure of **12** was identified via X-ray structure analysis Figs. 6 and 8.

The *p*-bromophenyl substituent should be regarded as an alternative to the fluorophenyl moiety for the preparation of dipolar ferrocenylsilanes. A useful synthetic sequence was found starting from (*p*-bromophenyl)chlorodimethylsilane (**13**) [17]. The reaction of this compound with FcNLi (**1**) in THF yielded the oily brown (*R*,*S*)-2-(*N*,*N*-dimethylaminomethyl)ferrocenyl(*p*-bromophenyl)dimethylsilane (**14**) (Scheme 5). De-



Scheme 2.

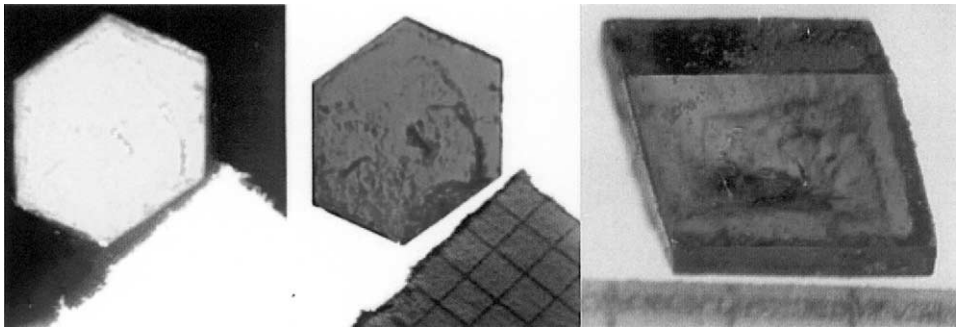
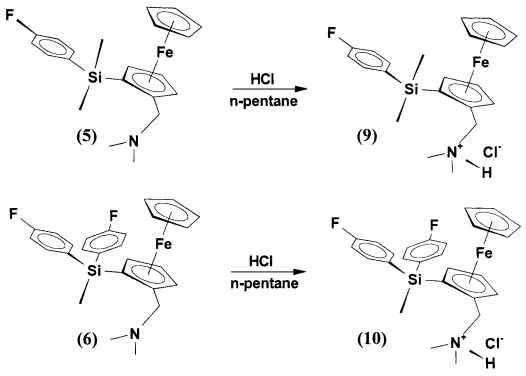
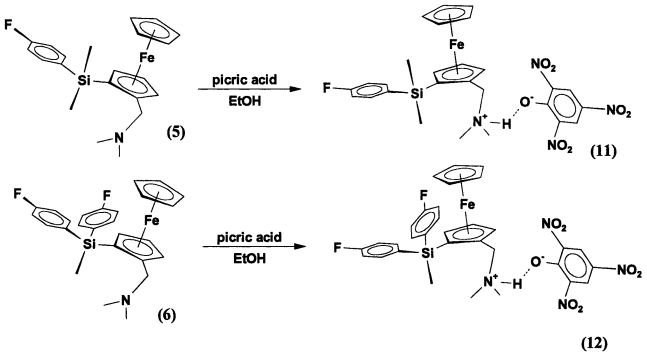


Fig. 1. View of two crystals of (*R*,*S*)-FcNSi(C_6H_4F)$_3$ (**7**). Left and middle: polarized light; right: transparent prism.

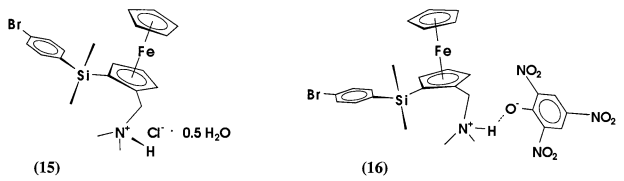


Scheme 3.



Scheme 4.

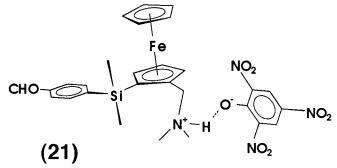
rivatives of **14** with hydrogen chloride and picric acid were prepared in the same manner used for the *p*-fluorophenyl compounds. The hydrochloride (**15**) and the picrate (**16**) are yellow crystalline products. An X-ray structure analysis was done with a single crystal of **16**. The structure was refined to an *R*-value of 10% due to the disorder of the nitro groups at the picrate anion.



Further preparative efforts were directed towards the synthesis of the aldehyde (**18**). We are interested in using this compound as an educt for the synthesis of dicyanovinylidene derivatives. Three different procedures (a–c in Scheme 5) were performed to transform the bromo-phenyl group into the phenyl-aldehyde. While such a transformation appears simple to achieve, the task was more difficult than expected. The reaction of **14** was performed with *t*-butyllithium in THF (method a) as well as with magnesium in THF (method b), followed by nucleophilic substitution of the carbanionic intermediate with dimethylformamide (DMF) and finally a working up of the products mixture with ammonium chloride in water. Both reaction sequences gave a mixture of the desired aldehyde (**18**) and (*R*,*S*)-FcNSiMe$_2$C$_6$H$_5$ (**19**). The portion of **19** was below 10% with both methods. The reaction with *n*-butyllithium in THF–*n*-hexane (route c) followed by treatment with DMF and ammonium chloride in water led to a mixture of three reaction products: the aldehyde (**18**), the phenyl silane (**19**) and the carbonic acid (**20**). We were able to separate these products with an elegant procedure. The carbonic acid (**20**) is insoluble in ether, whereas the other two products dissolve easily. The preparation of a bisulfite adduct [18,19] of the aldehyde (**18**) enabled us to separate **18** from **19**. The aldehyde (**18**) was regenerated from its bisulfite adduct by treating it with a diluted solution of Na_2CO_3. We were able to isolate all three reaction products (**18**), (**19**) and (**20**) as pure compounds.

The transformation of **18** into its bisulfite adduct is an effective method to separate the aldehyde from the product mixture. Thereby, we were able to avoid the chromatographic separation procedure and to reduce the preparative efforts necessary to isolate these products. We will report in a forthcoming contribution about the transformation into the 1,1-dicyanoethylene-2-phenyl derivative.

The reaction of **18** with picric acid in methanol gave the well-crystallized picrate (**21**). It was characterized with X-ray structure analysis.



(21)

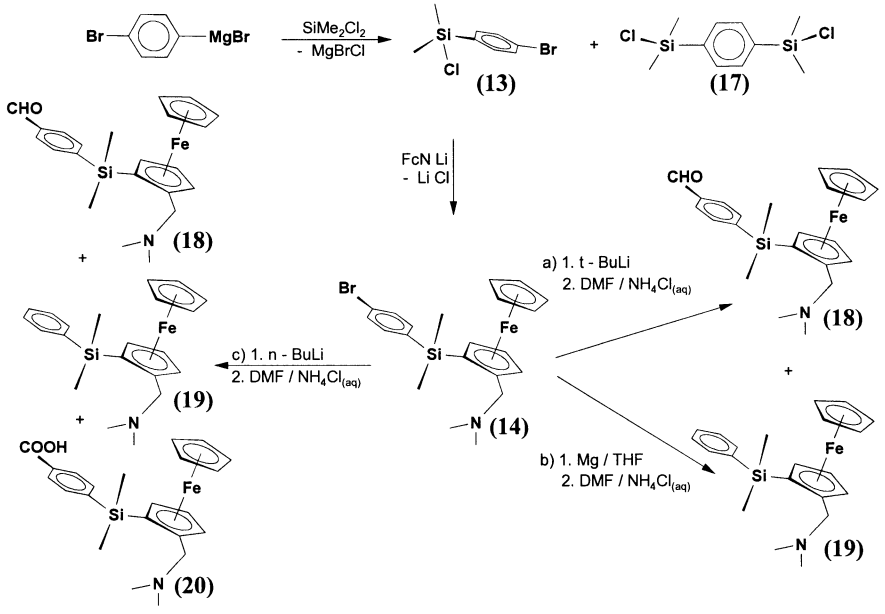
3. Spectroscopic properties and solid state properties

3.1. NMR spectroscopy

The (*R*,*S*)-2-(*N*,*N*-dimethylaminomethyl)ferrocenyl(aryl)silanes (*R*,*S*)-FcNSiMe$_n$(C$_6$H$_4$X)$_m$ ($n = 2$–0, $m = 1$) have some common spectroscopic features. Fig. 2 shows the ^{1}H-NMR spectrum of compound **12** as a typical example. The ^{1}H-NMR spectra are dominated by an intensive singulet at 4.0–4.2 ppm that is caused by the unsubstituted C$_5$H$_5$-ring. The three protons at the 1,2-substituted Cp-rings give rise to three signals between 4.0 and 5.2 ppm with the intensity ratio 1:1:1. The signals appear mainly as multiplets due to $^3J(^1\mathrm{H},^1\mathrm{H})$- and $^4J(^1\mathrm{H},^1\mathrm{H})$-coupling of the ring protons. From the protons of the phenyl groups arise multiplets between 7.0 and 7.8 ppm. The resonances of the protons of the dimethylamino groups occur at 1.7–2.0 ppm. The signal pattern of the dimethylaminomethyl group changes significantly when this group is protonated. The resonance frequency shifts towards lower field and the signal is split up into a doublet due to the coupling with the additional attached proton at the nitrogen in the **H**NMe$_2^+$-group. The methylene group of the –C**H$_2$**–NMe$_2$ unit is also affected by protonation. The methylene protons of the 2-(*N*,*N*-dimethylaminomethyl)ferrocenyl compounds give rise to two signals that appear as doublets due to geminal $^2J(^1\mathrm{H},^1\mathrm{H})$-coupling at about 12 Hz. If the 2-(*N*,*N*-dimethylaminomethyl)ferrocenyl compound is protonated, an additional coupling occurs with the vicinal proton of the **H**NMe$_2^+$-group. These coupling constants are in the range of 4–8 Hz. The value of this vicinal coupling depends on the torsion angle **H**–NMe$_2^+$–C–**H** [20]. The 2-(*N*,*N*-dimethylaminomethyl)ferrocenyl(aryl)dimethylsilanes FcNSiMe$_2$(C$_6$H$_4$X) exhibit two signals arising from the methyl groups bound to the silicon atom between 0.5 and 1 ppm. Only one signal emerges for the 2-(*N*,*N*-dimethylaminomethyl)ferrocenyl(diaryl)-methylsilanes FcNSiMe(C$_6$H$_4$X)$_2$.

The ^{13}C-NMR spectra prove that pure compounds were formed. All signals listed in the experimental part were properly assigned. The presence of the *para*-fluoro substituent in the compounds **5**, **6**, **7**, **9**, **10**, **11**, and **12** provides the ^{13}C–^{19}F-coupling constants as additional analytic tool to assign the signals of the phenyl carbon atoms. The coupling constants decrease as the line of bonds increases between fluorine and the carbon atoms in the following order: $^1J(^{13}\mathrm{C},^{19}\mathrm{F}) = 247$–250 Hz (*ipso*-C), $^2J(^{13}\mathrm{C},^{19}\mathrm{F}) = 19$–20 Hz (*ortho*-C), $^3J(^{13}\mathrm{C},^{19}\mathrm{F}) = 7$–8 Hz (*meta*-C), $^4J(^{13}\mathrm{C},^{19}\mathrm{F}) = 3$ Hz (*para*-C).

The ^{29}Si-NMR spectra show one singulet at −7 to −11 ppm for the *N*,*N*-dimethylaminomethylferrocenylsilanes. Mass spectra and elemental analyses complete the characterization of the compounds.



Scheme 5.

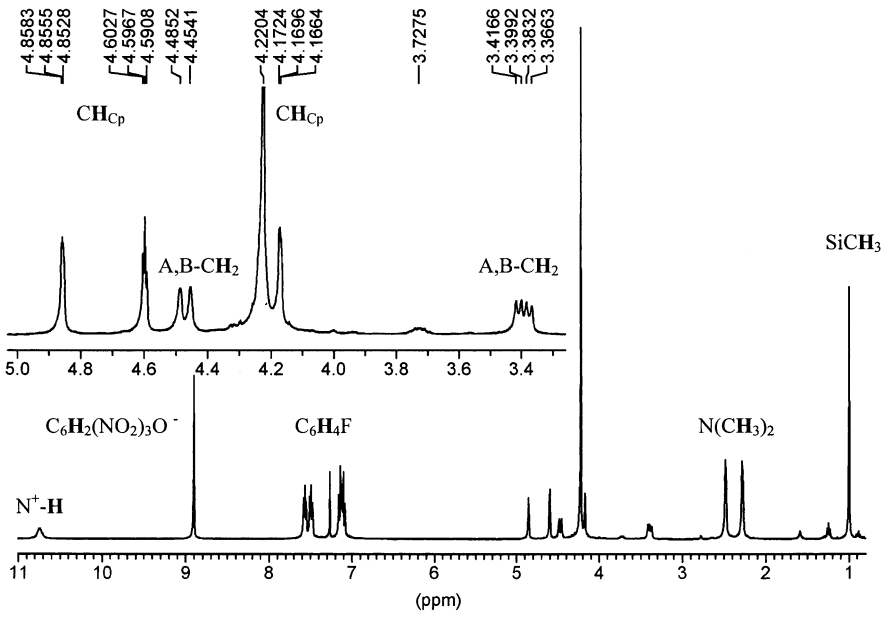


Fig. 2. ^{1}H-NMR ($CDCl_3$) of compound (*R*,*S*)-FcNSiMe(C_6H_4F)$_2^+$ picrate$^-$ (**12**).

3.2. Mössbauer spectroscopy

Mössbauer spectroscopy is an excellent method for investigating electronic charge transfer. By means of this method, the electronic configuration of iron in ferrocene derivatives was found to be $3d^{5.44}\ 4s^{0.74}\ 4p^{1.41}$ (Fe^{II}) [21]. The substitution of one hydrogen atom at the cyclopentadienyl ring with electron acceptors should result in a reduced electron density at the iron atom. This means that the ferricinium ion (Fe^{III}) is formed with the electronic configuration $3d^5$ 4s.

Table 1 demonstrates the results of the ^{57}Fe-Mössbauer spectra fit. The Mössbauer spectra recorded at different temperatures of compound **16** are shown in Fig. 3. The isomer shifts of the spectra that were observed correspond to the common values of Fe^{II} and Fe^{III}. All spectra display two doublets. The doublet with large quadrupole splitting was created by the iron in the ferrocene skeleton (Fe^{II}), the one with small quadrupole splitting indicates ferricinium (Fe^{III}). The appearance of the Fe(III) signal in the spectra clearly indicates the electron accepting character of the organosilanyl group attached to the ferrocene. Electron transfer in the direction Cp→Si removes electron density from the cyclopentadienyl ring, what is compensated by the partial oxidation Fe(II)→Fe(III). The observed charge transfer is a temperature dependent intramolecular donor–acceptor interaction [12,21]. This type of interactions show an Arrhenius behavior. At 80 K the activation energy of the charge transfer hinders a differentiation in the degree of oxidation of the different moieties. Since all measurement results obtained are reversible when the temperature is raised and lowered, a partial oxidation in air could be excluded.

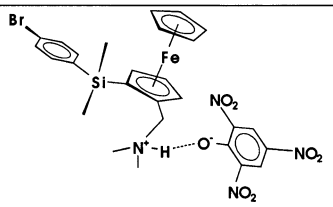
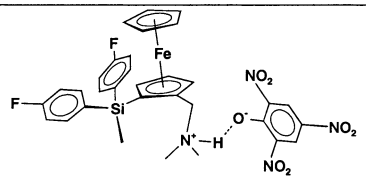
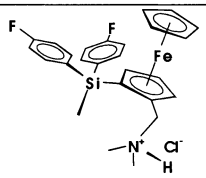
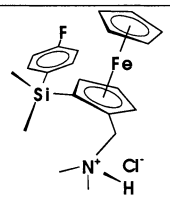
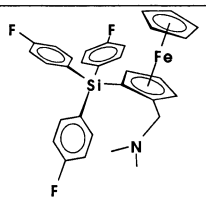
3.3. Solid-state structures

X-ray structure analyses of the compounds **7**, **12** and **15** were performed in order to confirm the structure of the prepared compounds. Crystal data and data collection parameters are given in Table 3, and a selection of bond distances and angles are provided by Table 2. ORTEP diagrams of the structures are shown in Figs. 4–8. From the fact that the compounds crystallize in centrosymmetric space groups it is concluded that, both isomers (*R* and *S*) are present in the structures. The structures turn out to be very similar with respect to the ferrocenyl unit. The distances between the iron atom and the cyclopentadienyl carbon atoms are in the range of 2.01–2.06 Å. In all structures, the 1,2-substituted ferrocenyl moiety adopts a nearly eclipsed conformation of the cyclopentadienyl ring (see Fig. 4). This conformation is caused by the substituents at the cyclopentadienyl ring, which force the neighboring ring into an eclipsed position through steric interaction with the hydrogen atoms at this ring.

The silicon atoms are tetrahedral coordinated in all four molecules. Obviously, there is a slight distortion of the tetrahedral angles due to steric interaction of the phenyl groups and the ferrocenyl unit at the silicon atom. Bonding interactions between silicon and nitrogen in dimethylaminomethylferrocenylsilanes have been discussed for FcN–$SiCl_3$ with a distance of 2.682 Å [15]. The distance Si···N in **7** is 3.748 Å, which is longer than the sum of the van der Waals radii (3.5 Å). That means there is no interaction between silicon and nitrogen in **7** in the solid state.

There is a significant hydrogen bridge in the (*R*,*S*)-FcNSiMe(C_6H_4F)$_2$ picrate (**12**) linking the hydrogen

Table 1
Mössbauer spectroscopic data

Number	Formula	Temperature in K	DT[a]
(16)		80	10
		175	45
		295	55
(12)		80	9
		175	17
		295	24
(10)		80	13
		175	23
		295	not resolved
(9)		80	5
(7)		80	11

[a] Degree of transformation $Fe^{II} \rightarrow Fe^{III}$ in %

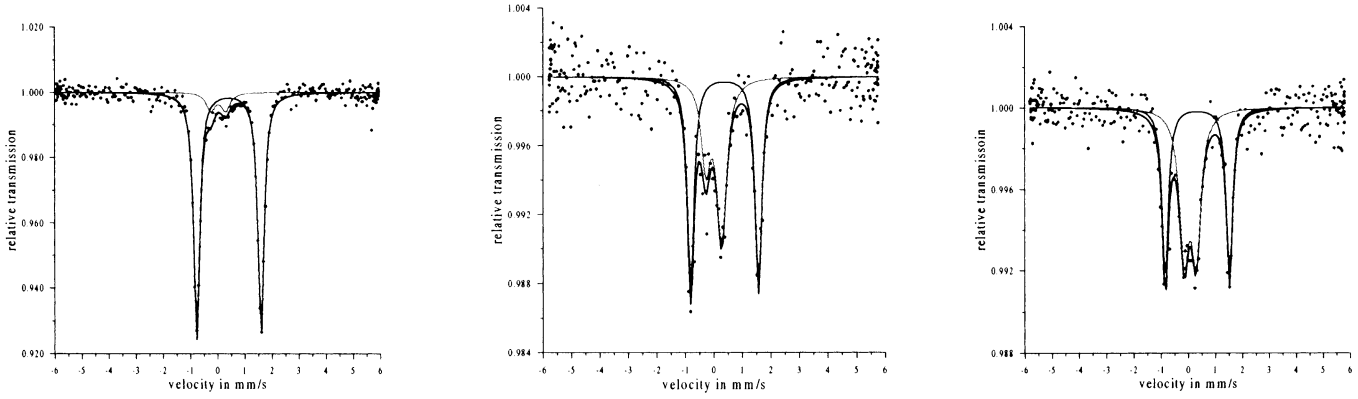


Fig. 3. ^{57}Fe-Mössbauer spectra of **16** at different temperatures (left 80 K, middle 175 K, right 298 K).

Table 2
Selected bond lengths (Å) and bond angles (°)

Bond lengths		*Bond angles*	
(*R*,*S*)-*FcNSi*(C_6H_4F)$_3$ (**7**)			
Si–C(2)	1.858(4)	C(2)–Si–C(14)	106.1(2)
Si–C(14)	1.872(4)	C(2)–Si–C(20)	113.1(2)
Si–C(20)	1.875(4)	C(2)–Si–C(26)	111.1(2)
Si–C(26)	1.868(4)	C(26)–Si–C(14)	107.9(2)
C(17)–F(1)	1.355(4)	C(26)–Si–C(20)	109.5(2)
C(23)–F(2)	1.370(4)	C(14)–Si–C(20)	108.8(2)
C(29)–F(3)	1.359(5)		
(*R*,*S*)-*FcNSiMe*(C_6H_4F)$_2^+$ *picrate*$^-$ (**12**)			
Si(1)–C(2)	1.867(3)	C(2)–Si(1)–C(15)	108.8(2)
Si(1)–C(14)	1.857(4)	C(2)–Si(1)–C(21)	107.6(2)
Si(1)–C(15)	1.876(3)	C(14)–Si(1)–C(2)	114.0(2)
Si(1)–C(21)	1.870(3)	C(14)–Si(1)–C(21)	109.9(2)
C(18)–F(1)	1.360(4)	C(14)–Si(1)–C(15)	110.5(2)
C(24)–F(2)	1.373(4)	C(21)–Si(1)–C(15)	105.6(2)
N(1)–H(1)	0.93(2)		
H(1)....O(1)	1.83(3)		
(*R*,*S*)-*FcNSiMe*$_2$(C_6H_4Br)$^+$ *Cl*$^-$·0.5H_2O (**15**)			
Si(1)–C(2)	1.856(6)	C(2)–Si(1)–C(15)	109.3(4)
Si(1)–C(14)	1.868(8)	C(2)–Si(1)–C(14)	113.9(3)
Si(1)–C(15)	1.864(7)	C(2)–Si(1)–C(16)	108.7(3)
Si(1)–C(16)	1.889(7)	C(14)–Si(1)–C(16)	109.5(3)
		C(15)–Si(1)–C(16)	105.2(3)
Br(1)–C(19)	1.890(8)	C(15)–Si(1)–C(14)	109.8(4)
N(1)–H(1)	1.03(2)		
H(1)···Cl(1)	2.09(3)		

atom of the dimethlyammonium group with the oxygen atom of the picrate ion (H(1)···O(1) = 1.83 Å).

A hydrogen bridge was also found in the structure of **15** between the dimethlyammonium group and the chloride ion (H(1)···Cl(1) = 2.09 Å). The compound **15** crystallizes as a semi-hydrate with 0.5 mol water per mol of dimethylamoniummethyl-ferrocenyl chloride; therefore, the exact formula is given as: (*R*,*S*)-FcNSiMe$_2$(C_6H_4Br)$^+$ Cl$^-$·0.5H_2O. Because it was not possible to localize the hydrogen atoms of the water molecule from the X-ray data, Fig. 7 shows one isolated oxygen atom (O(1)). The elemental analyses of **15** agree with the proposed structure.

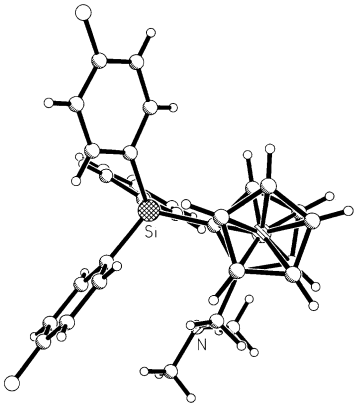


Fig. 4. ORTEP diagram of **7**, showing the conformation of the cyclopentadienyl rings.

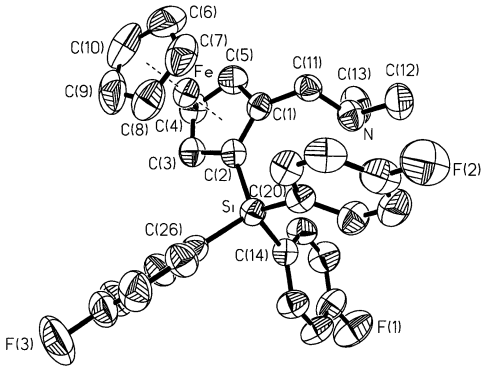


Fig. 5. ORTEP diagram of **7**, 50% probability thermal ellipsoids, hydrogen atoms omitted for clarity.

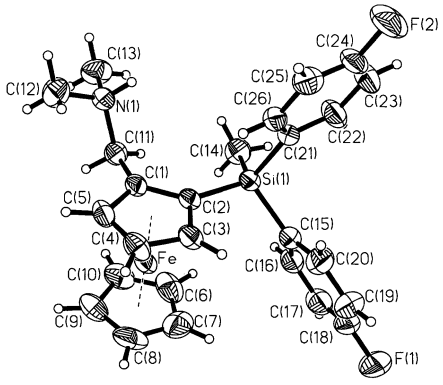


Fig. 6. ORTEP diagram of the cation of **12**, 50% probability thermal ellipsoids.

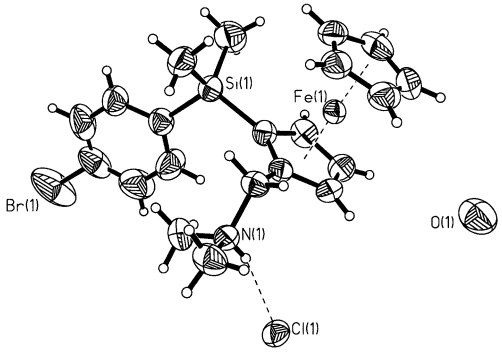


Fig. 7. ORTEP diagram of **15**·0.5 H_2O, 50% probability thermal ellipsoids.

Due to thermal motion and/or disorder of the nitro groups of the picrate anion, the picrate anion in **12** exhibits large atomic displacement parameters for the oxygen atoms (see Fig. 8). X-ray structure analyses of the compounds **10** and **16** revealed that the picrate anions in both structures are heavily disordered leading to final *R*-values of 13 and 10%, respectively. Because of insufficient results, these structures will not discussed

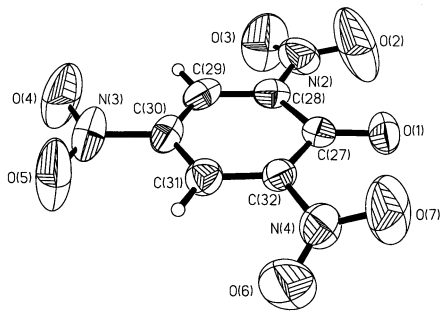


Fig. 8. ORTEP diagram of the picrate anion in **12**, 50% probability thermal ellipsoids.

here in more detail. Both structures are included in the Cambridge Crystallographic Database.

Intermolecular distances between the fluorine atom and hydrogen atoms are in the range of 2.66–2.9 Å, which means they are above the sum of van der Waals radii (1.2 + 1.35 = 2.55 Å). These distances could signify weak hydrogen bonds [22], but it seems less likely that these contacts have a substantial influence on the solid-state structure types.

4. Conclusions

New dipolar *N*,*N*-dimethylaminomethylferrocenylsilanes with organic acceptor groups were synthesized. The final products are stable in air. Compound **7** with three phenyl groups at silicon crystallizes well. X-ray structure analyses of compounds with two or one phenyl groups are not so easily accessible, therefore crystalline derivatives were obtained by using hydrogen chloride or picric acid. ^{57}Fe-Mössbauer spectroscopy gives evidence of a significant electronic coupling between the ferrocenyl unit and the organic acceptor moiety of the molecules in the ground state. Such compounds should have some special optical qualities. Therefore, NLO-measurements with these molecules are planned to find evidence of this behavior. We are currently synthesizing compounds with other organic acceptor groups. Furthermore, we are extending our strategy of derivatization of the *N*,*N*-dimethylaminomethylferrocenylsilanes with chiral acids, with the aim of separating the diastereomers.

5. Experimental

5.1. General remarks

All the samples were prepared and handled under Argon using dry glassware and dry solvents. Dry THF, ether, *n*-pentane, *n*-hexane and toluene were repeatedly distilled from fresh sodium–benzophenone until no effervescence was observed. The solvents were distilled once more and then stored in a sealed schlenk tube prior to use. *N*,*N*-Dimethylformamide (DMF) was allowed to stand on 4 Å molecular sieves and distilled from CaH_2 under reduced pressure prior to use. 1,4-Dibromobenzene, 1-bromo-4-fluorobenzene and picric acid were purchased from Fluka Chemie AG and used without further purification. Synthesis of FcNLi (**1**) was done according to the usual procedure [16].

NMR spectra were recorded on Bruker DPX 400 with $SiMe_4$ (TMS) $CDCl_3$ or CD_3CN as internal standard at 25 °C with 400.13 MHz for ^{1}H-NMR, 100.62 MHz for ^{13}C-NMR and 79.49 MHz for ^{29}Si-NMR. Signals are noted as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet, doublet) and br (broad). Elemental analyses were performed on a CHN-O-RAPID (Hanau). Lower carbon content values than real were measured due to the formation of silicon carbide. Infrared spectra were recorded with a Carl Zeiss Jena Specord M82 IR instrument in the range 4000–400 cm^{-1} using the KBr disc method (additionally in CH_2Cl_2 solution). Electronic spectra were obtained with a M40-Zeiss UV–vis spectrometer. GC–MS spectra were obtained on a 70 eV Hewlett–Packard 5890 Series II/5971 Series GC–MS system. ES–MS (ESI, MeOH solution, positive ion detection mode) were recorded on a 59987 A Series/5989-B-MS Hewlett–Packard/Palo Alto, USA system.

The ^{57}Fe Mössbauer spectra were recorded with a WISSEL instrument in transmission geometry at temperatures of 80, 175, 298 K for **10**, **12** and **16**; at 80 and 295 K for **7** and **9**. The γ-ray source is ^{57}Co–Rh in a rhodium matrix, 1.8 GBq. The spectra were fitted by assuming Lorentz-profiles. Fit parameter: isomer shift (δ) relative to α-iron, quadrupole splitting (ε), line width (Γ) and intensity (I), velocity calibration with α-iron. The intensities (I) of the partial spectra are the result of the calculated area-parts of the sum spectra. Assuming the same Debye–Waller factor within a substance, the calculated area-parts correspond to the quantity of the phase portion in the sample. Due to the strong temperature dependence of the Debye–Waller factor in the investigated samples, the quality of the 298 K spectra of **7** and **9** are insufficient and no satisfactory interpretation is possible.

5.1.1. Representative example synthesis of (4-fluorophenyl)chlorodimethylsilane (2)

The synthetic procedures used to prepare compounds **2**–**4** and **5**–**7** are similar. A solution of 1-bromo-4-fluorobenzene (0.2 mol, 21.79 ml) in THF (100 ml) was added slowly (1 h) to a suspension of magnesium (0.21 mol, 5.1 g) in THF (about 100 ml) activated by a crystal of iodine. The mixture was stirred for 2 h and subsequently refluxed for 2 h. The solution was stirred at room temperature (r.t.) overnight and the excess mag-

nesium was removed. This Grignard reagent was added slowly (1 h) to the solution of $SiMe_2Cl_2$ (0.29 mol, 35.0 ml) in THF (100 ml). The mixture was heated at reflux for 5 h. The solvent was removed under vacuum and *n*-hexane was added. The solution was filtered and washed three times with *n*-hexane. The combined *n*-hexane solutions were concentrated under vacuum. The residue was distilled under reduced pressure and a colorless oil was obtained (61–73 °C/6 Torr, isolated yield 19.6 g, 52%). Spectroscopic data for **2**: ^{1}H-NMR ($CDCl_3$–TMS): 0.66 (s, $SiMe_2$, 6H, $^2J(^1H, ^{29}Si,) = 6.9$ Hz), 7.60, 7.08 (AA′XX′, Ar-H, 2·2H), impurities: 0.46 (< 1%) ppm; ^{13}C-NMR ($CDCl_3$–TMS): 2.2 (s, $SiMe_2$, $^1J(^{13}C, ^{29}Si,) = 59.9$ Hz), 115.3 (d, C_2 *ortho*, $^2J(^{13}C,^{19}F) = 20$ Hz), 131.9 (d, C_4 *para*, $^4J(^{13}C,^{19}F) = 3.2$ Hz), 135.3 (d, C_3 *meta*, $^3J(^{13}C,^{19}F) = 8.0$ Hz), 164.3 (d, C_1 *ipso*, $^1J(^{13}C,^{19}F) = 250$ Hz) ppm; ^{29}Si-NMR: ($CDCl_3$–TMS) 20.2 (s, $SiMe_2$, $^1J(^{29}Si,^{13}C) = 59.8$ Hz), impurities: 14.3 (ca. 1%) ppm; IR: $\nu_{C-H} = 3036$ (w), 2961 (m) 2912 (w) cm^{-1}, $\nu_{C=C} = 1592$ (s), 1501 (s) cm^{-1}, $\delta_{C-H} = 1406$ (w), 1388 (m), 1255 (s), 1236 (s) cm^{-1}, $\nu_{C-F} = 1165$ (s), 1111 (s) cm^{-1}, ν_{C-H} (*para*) = 844 (s), 824 (s), 808 (s), 790 (s) cm^{-1}, $\nu_{Si-Cl} = 515$ (s), 487 (s) cm^{-1}; MS (EI, 70 eV): *m/e* = 188 $[M]^+$, 173 $[ClSiMeC_6H_4F]^+$, 153 $[SiMe_2C_6H_4F]^+$, 137 $[SiMeC_6H_4F]^+$, 122 $[SiC_6H_4F]^+$, 110 $[MeC_6H_4F]^+$, 91 $[MeC_6H_4]^+$; purity by GC 98%.

5.1.2. Representative example synthesis of (R,S)-$FcNSiMe_2C_6H_4F$ (5)

A suspension of FcNLi (**1**) (4.5 g, 18 mmol) and THF (70 ml) was added slowly drop-wise to a stirred solution of **2** (3.6 g, 19 mmol) in 40 ml of *n*-pentane at −78 °C. The mixture was warmed up slowly to ambient temperature and was stirred over night at r.t. Subsequently the solvent and unreacted **2** was stripped off, and the dark viscous product was dissolved with *n*-pentane and filtered. The solvent was removed under reduced pressure, and a brown oil **5** was obtained. Spectroscopic data for **5**: ^{1}H-NMR ($CDCl_3$–TMS): 0.54 (s, SiMe, 3H), 0.61 (s, SiMe, 3H), 1.96 (s, NMe_2, 6H), 2.89 (d, NCH_2, 1H, $^2J(^1H,^1H) = 12.4$ Hz), 3.39 (d, NCH_2, 1H, $^2J(^1H,^1H) = 12.4$ Hz), 4.00 (s, Cp, 1H), 4.07 (s, Cp, 5H), 4.25 (t, Cp, 1H, $^3J(^1H,^1H) = 2.3$ Hz), 4.31 (s, Cp, 1H), 7.0, 7.56 (AA′XX′, Ar-H, 2·2H) ppm; ^{13}C-NMR ($CDCl_3$–TMS): −1.26 (s, SiMe), −0.96 (s, SiMe), 44.7 (s, NMe_2), 59.4 (NCH_2), 68.8 (Cp), 69.8 (CH, Cp), 70.0 (C, Cp), 73.8 (CH, Cp), 74.8 (CH, Cp), 90.2 (C, Cp), 114.4 (d, C_2 *ortho*, $^2J(^{13}C,^{19}F) = 19.2$ Hz), 135.5 (d, C_4 *para*, $^4J(^{13}C,^{19}F) = 3.2$ Hz), 135.7 (d, C_3 *meta*, $^3J(^{13}C,^{19}F) = 7.2$ Hz), 163.6 (d, C_1 *ipso*, $^1J(^{13}C,^{19}F) = 247.7$ Hz) ppm; ^{29}Si-NMR: ($CDCl_3$–TMS) −7.8 (s, $SiMe_2$) ppm; IR (CH_2Cl_2): $\nu_{C-H} = 3062$ (w), 2995 (w) 2928 (w) cm^{-1}, $\nu_{C=C} = 1587$ (w), 1500 (w) cm^{-1}, $\delta_{C-H} = 1421$ (w), 1264 (s), $\nu_{C-F} = 1167$ (w), 1102 (s) cm^{-1}, ν_{C-H} (*para*) = 742 (s), 706 cm^{-1}; GC–MS (EI, 70 eV): *m/e* = 395 $[M]^+$, 351 $[FcCH_2SiMe_2C_6H_4F]^+$, 338 $[FcSiMe_2C_6H_4F]^+$, 284 $[FcNSiMe]^+$, 242 $[FcN]^+$, 242 $[FcSiMe_2]^+$, 227 $[FcSiMe]^+$, 213 $[FcSi]^+$, 199 $[FcCH_2]^+$, 121 $[FeCp]^+$, 56 $[Fe]^+$.

5.1.3. Synthesis of (bis-(4-fluorophenyl))chloromethylsilane (3)

Based on the procedure that used for the synthesis of **2**, compound **3** was prepared with 40 ml (0.367 mol) of 1-bromo-4-fluorobenzene, 9.72 g (0.4 mol) magnesium and 200 ml THF. This Grignard reagent was added slowly (1 h) to a solution of $SiMeCl_3$ (0.19 mol, 22.4 ml) in THF (200 ml) at −78 °C. The resulting colorless oil was distilled under reduced pressure (111–117 °C/4 Torr, isolated yield 24 g, 49%). This purification lead to colorless oil (**3**). Spectroscopic data for **3**: ^{1}H-NMR ($CDCl_3$–TMS): 0.91 (s, SiMe, 3H, $^2J(^1H,^{29}Si) = 6.8$ Hz,), 7.09, 7.59 (m, AA′XX′, Ar-H, 2·2H), impurities: 1.05 (< 1%) ppm; ^{13}C-NMR ($CDCl_3$–TMS): 1.1 (s, SiMe, $^1J(^{13}C, ^{29}Si) = 61.5$ Hz), 115.5 (d, C_2 *ortho*, $^2J(^{13}C,^{19}F) = 20.8$ Hz), 130.0 (d, C_4 *para*, $^4J(^{13}C,^{19}F) = 3.2$ Hz), 136.3 (d, C_3 *meta*, $^3J(^{13}C,^{19}F) = 8.0$ Hz), 164.6 (d, C_1 *ipso*, $^1J(^{13}C,^{19}F) = 251.7$ Hz) ppm; ^{29}Si-NMR: ($CDCl_3$–TMS) 10.0 (s, SiMe), impurities: 7.4 (< 1%) ppm; MS (EI, 70 eV): *m/e* = 268 $[M]^+$, 253 $[ClSi(C_6H_4F)_2]^+$, 234 $[ClSi(C_6H_4F)C_6H_4]^+$, 233 $[SiMe(C_6H_4F)_2]^+$, 218 $[Si(C_6H_4F)_2]^+$, 190 $[(C_6H_4F)_2]^+$, 173 $[ClSiMeC_6H_4F]^+$, , 151 $[(C_6H_4)_2]^+$, 123 $[SiC_6H_4F]^+$, 110 $[MeC_6H_4F]^+$, 91 $[MeC_6H_4]^+$, 75 $[C_6H_4]^+$; purity by GC 98.8%.

5.1.4. Synthesis of (R,S)-$FcNSiMe(C_6H_4F)_2$ (6)

The procedure followed was that used for the synthesis of compound **5**. A suspension of FcNLi (**1**) (4.3 g, 17.2 mmol) and THF (50 ml) was added slowly drop-wise to a stirred solution of (**3**) (4.85 g, 18 mmol) in 30 ml of *n*-pentane at −78 °C. The solvent was removed under reduced pressure and a brown oil (**6**) was obtained. Spectroscopic data for **6**: ^{1}H-NMR ($CDCl_3$–TMS): 0.90 (s, SiMe, 3H, $^2J(^1H,^{29}Si) = 6.6$ Hz,), 1.89 (s, NMe_2, 6H), 2.79 (d, NCH_2, 1H, $^2J(^1H,^1H) = 12.4$ Hz), 3.20 (d, NCH_2, 1H, $^2J(^1H,^1H) = 12.6$ Hz), 3.93 (dd, Cp, 1H), 4.03 (s, Cp, 5H), 4.30 (t, Cp, 1H, $^3J(^1H,^1H) = 2.4$ Hz), 4.38 (dd, Cp, 1H), 7.02, 7.54 (m, AA′XX′, Ar-H, 2·2H) ppm; ^{13}C-NMR ($CDCl_3$–TMS): −2.2 (s, SiMe, $^1J(^{13}C, ^{29}Si) = 56.7$ Hz), 44.7 (s, NMe_2), 59.2 (NCH_2), 68.5 (C, Cp), 70.0 (Cp), 70.2 (CH, Cp), 74.2 (CH, Cp), 75.7 (CH, Cp), 90.5 (C, Cp), 114.5 (d, C_2 *ortho*, $^2J(^{13}C,^{19}F) = 20$ Hz), 114.6 (d, C_2' *ortho*, $^2J(^{13}C,^{19}F) = 20.0$ Hz), 133.2 (d, C_4 *para*, $^4J(^{13}C,^{19}F) = 3.2$ Hz), 133.4 (d, C_4' *para*, $^4J(^{13}C,^{19}F) = 4.0$ Hz), 137.0 (d, C_3 *meta*, $^3J(^{13}C,^{19}F) = 8.0$ Hz), 137.1 (d, C_3' *meta*, $^3J(^{13}C,^{19}F) = 8.0$ Hz), 163.7 (d, C_1 *ipso*, $^1J(^{13}C,^{19}F) = 248.5$ Hz), 163.7 (d, C_1' *ipso*, $^1J(^{13}C,^{19}F) = 247.7$ Hz) ppm; ^{29}Si-NMR: ($CDCl_3$–TMS) −11.0 (s, SiMe) ppm.

5.1.5. Synthesis of (Tris-(4-fluorophenyl))chlorosilane (4)

The synthesis procedure of **4** was based on that one used for the synthesis of compound (4-fluorophenyl)chlorodimethylsilane (**2**) with 60 ml (0.55 mol) of 1-bromo-4-fluorobenzene, 19 g (0.78 mol) magnesium and 200 ml THF. This Grignard reagent was added slowly (1 h) to a solution of $SiCl_4$ (0.195 mol, 22.4 ml) in THF (200 ml) at −78 °C. The resulting colorless oil was distilled under reduced pressure (192–194 °C/2 Torr). This purification lead to white crystals (**4**) (isolated yield 38 g, 59%). Spectroscopic data for **4**: ^{1}H-NMR ($CDCl_3$–TMS): 7.10, 7.59 (m, AA′XX′, Ar-H, 2·2H), ppm; ^{13}C-NMR ($CDCl_3$–TMS): 115.7 (d, C_2 *ortho*, $^2J(^{13}C,^{19}F) = 20.8$ Hz), 128.2 (d, C_4 *para*, $^4J(^{13}C,^{19}F) = 4.0$ Hz), 137.4 (d, C_3 *meta*, $^3J(^{13}C,^{19}F) = 8.0$ Hz), 164.8 (d, C_1 *ipso*, $^1J(^{13}C,^{19}F) =$ 252.5 Hz) impurities: 29.3, 31.0, 63.0 (< 3%) ppm; ^{29}Si-NMR: ($CDCl_3$–TMS) 1.0 (s, SiPhF), impurities: −13.5, 13.7 (< 3%) ppm.

The first fraction of the distillation under vacuum was identified as 4,4′-difluorobiphenyl (**8**). Spectroscopic data for **8**: ^{1}H-NMR ($CDCl_3$–TMS): 7.11, 7.48 (m, AA′XX′, Ar-H, 2·4H), ppm; ^{13}C-NMR ($CDCl_3$–TMS): 115.7 (d, C_2,C_2' *ortho*, $^2J(^{13}C,^{19}F) = 21.5$ Hz), 128.6 (d, C_3, C_3' *meta*, $^3J(^{13}C,^{19}F) = 8.0$ Hz), 136.4 (d, C_4, C_4' *para*, $^4J(^{13}C,^{19}F) = 3.2$ Hz), 162.4 (d, C_1, C_1' *ipso*, $^1J(^{13}C,^{19}F) = 246.1$ Hz) ppm.

5.1.6. Synthesis of (R,S)-FcNSi(C_6H_4F)$_3$ (7)

Compound **7** was synthesized analogously to the procedure used for the synthesis for (*R*,*S*)-FcNSi-$Me_2C_6H_4F$ (**5**). A suspension of FcNLi (**1**) (5.97 g, 23.95 mmol) and THF (50 ml) was added slowly dropwise to a stirred solution of **4** (8.348 g, 20 mmol) in 30 ml of *n*-pentane at 0 °C. The solvent was removed under reduced pressure. Finally a yellow solid (**7**) remained. The product was recrystallized from PhMe to yellow crystals of **7.** Spectroscopic data for **7**: ^{1}H-NMR ($CDCl_3$–TMS): 1.76 (s, NMe_2, 6H), 2.70 (d, NCH_2, H, $^2J(^1H,^1H) = 12.4$ Hz), 2.95 (d, NCH_2, H, $^2J(^1H,^1H) = 12.4$ Hz), 4.02 (Cp, 5H), 4.05 (s, Cp, 1H), 4.38 (s, Cp, 1H), 4.44 (s, Cp, 1H), 7.08, 7.61 (m, AA′XX′, Ar-H, 2·2H) ppm; ^{13}C-NMR ($CDCl_3$–TMS): 44.7 (s, NMe_2), 58.8 (NCH_2), 65.9 (C, Cp), 69.3 (Cp), 70.6 (CH, Cp), 74.4 (CH, Cp), 76.5 (CH, Cp), 90.9 (C, Cp), 114.8 (d, C_2 *ortho*, $^2J(^{13}C,^{19}F) = 19.2$ Hz), 131.1 (d, C_4 *para*, $^4J(^{13}C,^{19}F) = 4.0$ Hz), 138.2 (d, C_3 *meta*, $^3J(^{13}C,^{19}F) = 7.2$ Hz), 163.9 (d, C_1 *ipso*, $^1J(^{13}C,^{19}F) = 249.3$ Hz) ppm; ^{29}Si-NMR: ($CDCl_3$–TMS) −14.4 (s, SiPhF) ppm; Anal. Calc. for $C_{31}H_{28}F_3FeNSi$: C, 67.02; H, 5.08; N, 2.52. Found: C, 66.62; H, 5.31; N, 2.62%.

5.1.7. Synthesis of (4-bromophenyl)chlorodimethylsilane (13)

Synthesis of **13** was performed according to that one used for the synthesis of **2** with 35 g (0.148 mol) of 1,4-dibromobenzene, 4.1 g (0.168 mol) magnesium and 200 ml THF. This Grignard reagent was added slowly (1 h) to a solution of $SiMe_2Cl_2$ (0.228 mol, 27.45 ml) in THF (200 ml) at 0 °C. The resulting colorless oil was distilled under reduced pressure (70–76 °C/1–2 Torr, isolated yield 11.1 g, 30%). This purification gave a colorless oil (**13**). Spectroscopic data for **13**: ^{1}H-NMR ($CDCl_3$–TMS): 0.66 (s, $SiMe_2$, 6H), 7.503 (AA′XX′, Ar-H, 2·2H, $^3J(^1H,^1H) = 8.40$ Hz), impurities: 0.811, 0.461, 0.308 (< 1%) ppm; ^{13}C-NMR ($CDCl_3$–TMS): 2.0 (s, $SiMe_2$), 125.3 (s, C_4 *para*), 131.3 (s, C_2 *ortho*), 134.7 (s, C_3 *meta*), 135.0 (s, C_1 *ipso*), impurities:133.1 (1,4-dibromobenzene), 160.0, 62.2, 33.5, 30.5, 29.2 ppm; ^{29}Si-NMR: ($CDCl_3$–TMS) 20.5 (s, $SiMe_2$), impurities: 14.3, −0.6 (ca. 2%) ppm.

The third fraction of the distillation under vacuum was identified as 1,4-bis(dimethylchlorosilyl)benzene (**17**). Spectroscopic data for **17:** ^{1}H-NMR (C_6D_6–TMS): 0.42 (s, $SiMe_2$, 6H), 7.50 (AA′XX′, Ar-H, 2·2H), impurities: 0.31, 0.35, 0.56 (< 2%) ppm; ^{13}C-NMR (C_6D_6–TMS): 1.8 (s, $SiMe_2$, $^1J(^{13}C,\ ^{29}Si) = 59.4$ Hz)), 131.5, 132.9, 135.0, 138.7, impurities: 133.0 (1,4-dibromobenzene), 0.9, 2.6 ppm; ^{29}Si-NMR: (C_6D_6–TMS) 20.3 (s, $SiMe_2$, $^1J(^{13}C,\ ^{29}Si) = 59.3$ Hz)), impurities: 16.8, −0.5 ppm; MS (EI, 70 eV): $m/e = 262$ $[M]^+$, 247 $[ClSiMe_2(C_6H_4)SiMeCl]^+$, 227 $[ClSiMe_2(C_6H_4)$-$SiMe_2]^+$, 211 $[ClSiMe_2(C_6H_4)SiMe]^+$, 197 $[ClSiMe_2$-$(C_6H_4)Si]^+$, 181 $[ClSiMe(C_6H_4)Si]^+$, 175 $[SiMe_2$-$(C_6H_4)SiMe]^+$, 153 $[ClSiMe(C_6H_4)]^+$, 133 $[SiMe_2$-$(C_6H_4)]^+$, 119 $[SiMe(C_6H_4)]^+$, 105 $[Me_2(C_6H_4)]^+$, 91 $[MeC_6H_4]^+$.

5.1.8. Synthesis of (R,S)-FcNSiMe$_2$C$_6$H$_4$Br (14)

Synthesis of **14** was done on the same pathway as in case of compound **5**. A suspension of FcNLi (**1**) (4.3 g, 17.2 mmol) and THF (50 ml) was added slowly dropwise to a stirred solution of **13** (4.85 g, 18 mmol) in 30 ml of *n*-pentane at −78 °C. The solvent was removed under reduced pressure and gave a brown oil (**14**). Spectroscopic data for **14**: ^{1}H-NMR ($CDCl_3$–TMS): 0.53 (s, SiMe, 3H, $^2J(^1H,^{29}Si) = 6.60$ Hz,), 0.60 (s, SiMe, 3H, $^2J(^1H,^{29}Si) = 6.58$ Hz,), 1.95 (s, NMe_2, 6H), 2.86 (d, NCH_2, 1H, $^2J(^1H,^1H) = 12.44$ Hz), 3.41 (d, NCH_2, 1H, $^2J(^1H,^1H) = 12.44$ Hz), 3.99 (dd, Cp, 1H), 4.07 (s, Cp, 5H) 4.25 (t, Cp, 1H, $^3J(^1H,^1H) = 2.0$ Hz), 4.30 (dd, Cp, 1H), 7.44, (m, AA′XX′, Ar-H, 2·2H) ppm; ^{13}C-NMR ($CDCl_3$–TMS): −1.5 (s, SiMe), −1.1 (s, SiMe), 44.7 (s, NMe_2), 59.4 (NCH_2), 68.8 (Cp), 69.5 (C, Cp), 69.8 (CH, Cp), 73.9 (CH, Cp), 74.8 (CH, Cp), 90.2 (C, Cp), 123.3 (s, C_4 *para*), 130.4 (s, C_2 *ortho*), 135.6 (s, C_3 *meta*), 139.0 (s, C_1 *ipso*) ppm; ^{29}Si-NMR: ($CDCl_3$–TMS) −7.3 (s, $SiMe_2$, $^1J(^{29}Si,^{13}C) = 61.23$ Hz), impurities: −0.63 (<

12%) ppm; ES–MS (EI, 70 eV, pos., MeCN–CH_3COOH): $m/e = 455$ ($[M]^+ - 1$, cation), 412 $[FcCH_2SiMe_2C_6H_4Br]^+$, 332 $[FcCH_2SiMe_2C_6H_4]^+$, 257 $[FcCH_2SiMe_2]^+$, 198 $[FcCH_2]^+$.

5.2. Synthesis of 1,2-N,N-dimethylaminomethylferrocenyl picrates

5.2.1. Synthesis of (R,S)-$FcNSiMe_2C_6H_4Br$ picrate (16)

An ethanolic solution of picric acid was added dropwise to a solution of **14** (1 g, 2.19 mmol) in EtOH (25 ml). The suspension was warmed up for 3 min and filtrated after ended precipitate formation. The resulting yellow precipitate was washed with cold EtOH and Et_2O. The yellow solid was dissolved in hot EtOH and filtrated. The product was recrystallized from EtOH–MeCN 1:1 to yellow crystals of **16**. Spectroscopic data for **16**: ^{1}H-NMR ($CDCl_3$–TMS): 0.53 (s, SiMe, 3H), 0.78 (s, SiMe, 3H), 2.28 (s, NMe, 3H), 2.48 (s, NMe, 3H), 3.66 (d, NCH_2, 1H, $^2J(^1H,^1H) = 13.4$ Hz), 4.45 (d, NCH_2, 1H, $^2J(^1H,^1H) = 13.0$ Hz), 4.25 (s, Cp, 5H), 4.33 (s, Cp, 1H), 4.58 (t, Cp, 1H), 4.74 (s, Cp, 1H), 7.35 (m, AA′XX′, Ar-H, 2·H, $^3J(^1H,^1H) = 8.0$ Hz), 7.48 (m, AA′XX′, Ar-H, 2·H, $^3J(^1H,^1H) = 8.0$ Hz), 8.90 (s, NO_2Ar-H, 2 H), 10.8 (br, H–N^+, 1 H) ppm; ^{13}C-NMR ($CDCl_3$–TMS): −1.3 (s, SiMe), −0.1 (s, SiMe), 40.8 (br, NMe_2), 43.3 (br, NMe_2), 58.0 (NCH_2), 69.7 (Cp), 70.6 (C, Cp), 73.6 (CH, Cp), 74.6 (CH, Cp), 76.5 (CH, Cp), 78.9 (C, Cp), 124.4 (s, C_4 *para*), 131.3 (s, C_2 *ortho*), 135.2 (s, C_3 *meta*), 137.5 (s, C_1 *ipso*) 126.6, 128.3, 141.7, 162.2 (6·C, NO_2Ar) ppm; ^{29}Si-NMR: ($CDCl_3$–TMS) −7.7 (s, $SiMe_2$) ppm; ES–MS (EI, 70 eV, pos., MeCN): $m/e = 457$ ($[M]^+$, cation), 411 $[FcCH_2SiMe_2C_6H_4Br]^+$, 332 $[FcCH_2SiMe_2C_6H_4]^+$, 273 $[FcNSi]^+$, 198 $[FcCH_2]^+$; Anal. Calc. for $C_{27}H_{29}BrFeN_4O_7Si$: C, 47.31; H, 4.26; N, 8.18. Found: C, 47.45; H, 4.38; N, 8.09%.

5.2.2. Synthesis of (R,S)-$FcNSiMe_2C_6H_4F$ picrate (11)

Synthesis of compound **16** was done based on that one of **16** with 1 g (2.53 mmol) of **5** in EtOH (25 ml). The product was recrystallized from hot acetone–*i*-propanol 1:3 to yellow crystals of **11**. Spectroscopic data for **11**: ^{1}H-NMR (CD_3CN–TMS): 0.54 (s, SiMe, 3H), 0.76 (s, SiMe, 3H), 2.40 (br, NMe_2, 6H), 3.66 (d, NCH_2, 1H, $^2J(^1H,^1H) = 13.6$ Hz), 4.37 (d, NCH_2, 1H, $^2J(^1H,^1H) = 13.7$ Hz), 4.25 (s, Cp, 5H), 4.35 (dd, Cp, 1H, $^3J(^1H,^1H) = 2.2$ Hz, $^4J(^1H,^1H) = 1.1$ Hz), 4.56 (t, Cp, 1H, $^3J(^1H,^1H) = 2.4$ Hz), 4.71 (dd, Cp, 1H, $^3J(^1H,^1H) = 2.5$ Hz, $^4J(^1H,^1H) = 1.1$ Hz), 7.08, 7.58 (m, AA′XX′, Ar-H, 2·2H), 8.68 (s, NO_2Ar-H, 2 H), 10.67 (br, H–N^+, 1 H) ppm; ^{13}C-NMR (CD_3CN–TMS): −1.1 (s, SiMe), 0.1 (s, SiMe), 42.9 (s, br, NMe), 43.5 (s, NMe_2), 58.9 (NCH_2), 70.6 (Cp), 72.1 (C, Cp), 74.1 (CH, Cp), 75.5 (CH, Cp), 77.5 (CH, Cp), 80.7 (C, Cp), 115.9 (d, C_2 *ortho*, $^2J(^{13}C,^{19}F) = 19.6$ Hz), 136.0 (d, C_4 *para*, $^4J(^{13}C,^{19}F) = 3.2$ Hz), 137.1 (d, C_3 *meta*, $^3J(^{13}C,^{19}F) = 7.6$ Hz), 164.7 (d, C_1 *ipso*, $^1J(^{13}C,^{19}F) = 246.5$ Hz), 126.7, 127.6, 143.1, 162.7 (6·C, NO_2Ar) ppm; ^{29}Si-NMR: (CD_3CN–TMS) −8.1 (s, $SiMe_2$) ppm; ES–MS (EI, 70 eV, pos., MeCN): $m/e = 395$ ($[M]^+ - 1$, cation), 350 $[FcCH_2SiMe_2C_6H_4F]^+$, 299 $[FcNSiMe_2]^+$, 198 $[FcCH_2]^+$; Anal. Calc. for $C_{27}H_{29}FFeN_4O_7Si$: C, 51.92; H, 4.68; N, 8.97. Found: C, 51.77; H, 4.91; N, 8.85%.

5.2.3. Synthesis of (R,S)-$FcNSiMe(C_6H_4F)_2$ picrate (12)

Synthesis of compound **12** was done analogously to that one of **16** with 1 g (2.10 mmol) of **6** in EtOH (25 ml). Spectroscopic data for yellow crystals of **12**: ^{1}H-NMR ($CDCl_3$–TMS): 1.0 (s, SiMe, 3H), 2.28 (d, br, NMe, 3H, $^3J(^1H,^1H) = 4.4$ Hz,), 2.48 (d, br, NMe, 3H, $^3J(^1H,^1H) = 4.0$ Hz,), 3.39 (dd, br, NCH_2, 1H, $^2J(^1H,^1H) = 13.3$ Hz, $^3J(^1H,^1H) = 6.9$ Hz), 4.47 (d, br, NCH_2, 1H, $^2J(^1H,^1H) = 12.4$ Hz), 4.17 (dd, Cp, 1H, $^3J(^1H,^1H) = 2.4$ Hz, $^4J(^1H,^1H) = 1.1$ Hz), 4.22 (s, Cp, 5H), 4.60 (t, Cp, 1H, $^3J(^1H,^1H) = 2.4$ Hz), 4.85 (dd, Cp, 1H, $^3J(^1H,^1H) = 2.2$ Hz, $^4J(^1H,^1H) = 1.1$ Hz), 7.12, 7.47–7.58 (m, AA′XX′, Ar-H, 2·2H), 8.90 (s, NO_2Ar-H, 2 H), 10.73 (br, H–N^+, 1 H) ppm; ^{13}C-NMR ($CDCl_3$–TMS): −1.0 (s, br, SiMe), 40.7 (s, NMe), 43.8 (s, NMe), 57.8 (NCH_2), 69.3 (C, Cp), 69.9 (Cp), 73.9 (CH, Cp), 74.7 (CH, Cp), 77.3 (CH, Cp), 79.4 (C, Cp), 115.4 (d, C_2 *ortho*, $^2J(^{13}C,^{19}F) = 20.0$ Hz), 115.8 (d, C_2' *ortho*, $^2J(^{13}C,^{19}F) = 20.0$ Hz), 131.2 (d, C_4 *para*, $^4J(^{13}C,^{19}F) = 3.2$ Hz), 131.7 (d, C_4' *para*, $^4J(^{13}C,^{19}F) = 3.2$ Hz), 136.9 (d, C_3 *meta*, $^3J(^{13}C,^{19}F) = 8.0$ Hz), 137.0 (d, C_3' *meta*, $^3J(^{13}C,^{19}F) = 7.2$ Hz), 164.1 (d, C_1 *ipso*, $^1J(^{13}C,^{19}F) = 250.9$ Hz), 164.2 (d, C_1' *ipso*, $^1J(^{13}C,^{19}F) = 251.7$ Hz), 126.6, 128.4, 141.8, 162.1 (6·C, NO_2Ar) ppm; ^{29}Si-NMR: ($CDCl_3$–TMS) −11.6 (s, $SiMe_2$) ppm; ES–MS (EI, 70 eV, pos., MeCN): $m/e = 475$ ($[M]^+ - 1$, cation), 431 $[FcCH_2SiMe_2C_6H_4F]^+$, 335 $[FcCH_2SiMe_2]^+$, 199 $[FcCH_2]^+$, 122 $[FeCp]^+$; Anal. Calc. for $C_{32}H_{30}F_2FeN_4O_7Si$: C, 54.55; H, 4.29; N, 7.95. Found: C, 54.67; H, 4.38; N, 7.99%.

5.3. Synthesis of 1,2-N,N-dimethylaminomethylferrocenyl hydrochlorides

5.3.1. Synthesis of (R,S)-$FcNSiMe_2C_6H_4Br \cdot HCl \cdot 0.5 H_2O$ (15)

A solution of 20% HCl was added slowly to a solution of 2.1 g (4.6 mmol) of **14** in 20 ml toluene for 30 min. The mixture was stirred for 2 days at r.t. The resulting fine yellow precipitate was washed with *n*-pentane and Et_2O. Then it was dissolved in hot MeCN and filtered. The clear yellow solution was cooled slowly at −20 °C. The product recrystallized to yellow crystals of **15**. Spectroscopic data for **15**: ^{1}H-NMR ($CDCl_3$–TMS):

0.53 (s, SiMe, 3H), 0.75 (s, SiMe, 3H), 2.14 (br, NMe, 3H), 2.42 (br, NMe, 3H), 3.54 (d, NCH_2, 1H, $^2J(^1H,^1H) = 13.16$ Hz), 4.36 (d, NCH_2, 1H, $^2J(^1H,^1H) = 13.92$ Hz), 4.22 (s, Cp, 5H), 4.31 (d, Cp, 1H), 4.37 (s, Cp, 1H), 4.61 (t, Cp, 1H, $^3J(^1H,^1H) = 2.2$ Hz), 7.34 (m, AA′XX′, Ar-H, 2·H, $^3J(^1H,^1H) = 8.0$ Hz), 7.47 (m, AA′XX′, Ar-H, 2·H, $^3J(^1H,^1H) = 8.0$ Hz), 11.96 (br, H–N^+, 1 H) ppm; ^{13}C-NMR ($CDCl_3$–TMS): −1.1 (s, SiMe), −0.1 (s, SiMe), 39.8 (br, NMe_2), 42.8 (br, NMe_2), 57.0 (NCH_2), 69.6 (Cp), 70.4 (C, Cp), 73.6 (CH, Cp), 75.6 (CH, Cp), 76.3 (CH, Cp), 78.8 (C, Cp), 124.4 (s, C_4 *para*), 131.3 (s, C_2 *ortho*), 135.2 (s, C_3 *meta*), 137.5 (s, C_1 *ipso*) ppm; ^{29}Si-NMR: ($CDCl_3$–TMS) −7.7 (s, $SiMe_2$, $^1J(^{29}Si,^{13}C) = 55.40$, Hz) ppm; ES–MS (EI, 70 eV, pos., MeOH): $m/e = 455$ ($[M]^+ - 2$, cation), 412 $[FcCH_2SiMe_2C_6H_4Br]^+$, 377 $[FcNSiMe_2C_6H_4]^+$, 304 $[FcNSiMe_2]^+$, 239 $[FcN]^+$, 948 $FcNSiMe_2C_6H_4Br$·HCl+cation $[M]^+$; Anal. Calc. for $C_{21}H_{28}BrClFeNO_{0.5}Si$: C, 50.27; H, 5.62; N, 2.79. Found: C, 50.03; H, 5.77; N, 2.88%.

5.3.2. Synthesis of (R,S)-FcNSiMe$_2$C$_6$H$_4$F·HCl (9)

A stream of dry gaseous hydrogen chloride was flushed slowly through the solution of 2.97 g (7.5 mmol) of **5** in 70 ml *n*-pentane at 0 °C for 30 min. The mixture was warmed up to ambient temperature and stirred over night at r.t. After that all the unreacted HCl was removed from the flask, and the precipitate was filtered off. The resulting fine yellow precipitate was washed with a little bit of *n*-pentane, dried in a stream of argon and under oil-pump vacuum to afford 3.1 g (95%) of **9** as a yellow solid. Spectroscopic data for **9**: ^{1}H-NMR ($CDCl_3$–TMS): 0.53 (s, SiMe, 3H), 0.76 (s, SiMe, 3H), 2.10 (d, NMe, 3H, $^3J(^1H,^1H) = 4.8$ Hz), 2.38 (d, NMe, 3H, $^3J(^1H,^1H) = 4.4$ Hz), 3.52 (dd, NCH_2, 1H, $^2J(^1H,^1H) = 13.2$ Hz), $^3J(^1H,^1H) = 6.14$ Hz), 4.30 (m, NCH_2), 4.22 (s, Cp, 5H), 4.33 (dd, Cp, 1H), 4.61 (t, Cp, 1H), 5.05 (dd, Cp, 1H), 7.04, 7.46 (AA′XX′, Ar-H, 2·2H) ppm; ^{13}C-NMR ($CDCl_3$–TMS): −0.92 (s, SiMe), −0.03 (s, SiMe), 39.7 (s, NMe_2), 42.8 (s, NMe_2), 57.0 (NCH_2), 69.6 (Cp), 70.9 (C, Cp), 73.6 (CH, Cp), 75.5 (CH, Cp), 76.3 (CH, Cp), 78.8 (C, Cp), 115.4 (d, C_2 *ortho*, $^2J(^{13}C,^{19}F) = 19.2$ Hz), 134.3 (d, C_4 *para*, $^4J(^{13}C,^{19}F) = 4.0$ Hz), 135.7 (d, C_3 *meta*, $^3J(^{13}C,^{19}F) = 8.0$ Hz), 163.8 (d, C_1 *ipso*, $^1J(^{13}C,^{19}F) = 250.1$ Hz) ppm; ^{29}Si-NMR: ($CDCl_3$–TMS) −8.2 (s, $SiMe_2$) ppm; IR (CH_2Cl_2): $\nu_{C-H} = 3056$ (w), 2990 (w) cm^{-1}, $\nu_{C=C} = 1590$ (w), 1498 (w) cm^{-1}, $\delta_{C-H} = 1420$ (w), 1266 (s), $\nu_{C-F} = 1165$ (w), 1107 (s) cm^{-1}, ν_{C-H} (*para*) = 739 (s), 705 cm^{-1}; ES–MS (EI, 70 eV, pos., MeOH): $m/e = 396$ ($[M]^+$, cation), 351 $[FcCH_2SiMe_2C_6H_4F]^+$, 332 $[FcCH_2SiMe_2C_6H_4]^+$, 199 $[FcCH_2]^+$, 826 $[FcNSiMe_2C_6H_4F·HCl+cation]^+$; Anal. Calc. for $C_{21}H_{27}ClFFeNSi$: C, 58.41; H, 6.30; N, 3.24, respectively, **9**·2 H_2O $C_{21}H_{31}ClFFeNO_2Si$: C, 53.91; H, 6.68; N, 2.99. Found: C, 54.25; H, 6.49; N, 3.13%.

5.3.3. Synthesis of (R,S)-FcNSiMe(C$_6$H$_4$F)$_2$·HCl (10)

The procedure to synthesize compound **10** was the same as used for **9** with 3.0 g (6.31 mmol) of **6** in 50 ml *n*-pentane. The product was recrystallized from hot EtOH–MeCN to yellow crystals of **10**. Spectroscopic data for **10**: ^{1}H-NMR (CD_3CN–TMS): 1.02 (s, SiMe, 3H, $^2J(^1H,^{29}Si) = 6.4$ Hz,), 1.98 (d, NMe, 3H, $^3J(^1H,^1H) = 5.12$ Hz), 2.42 (d, NMe, 3H, $^3J(^1H,^1H) = 4.96$ Hz), 3.30 (dd, NCH_2, 1H, $^2J(^1H,^1H) = 13.7$ Hz, $^3J(^1H,^1H) = 8.08$ Hz), 4.31 (dd, NCH_2, 1H, $^2J(^1H,^1H) = 13.8$ Hz, $^3J(^1H,^1H) = 3.0$ Hz), 4.11 (dd, Cp, 1H), 4.19 (s, Cp, 5H), 4.61 (t, Cp, 1H, $^3J(^1H,^1H) = 2.4$ Hz), 5.21 (dd, Cp, 1H), 7.16, 7.60 (m, AA′XX′, Ar-H, 2·2H) ppm; ^{13}C-NMR (CD_3CN–TMS): −1.3 (s, SiMe), 40.2 (s, NMe_2), 43.7 (s, NMe_2), 57.4 (NCH_2), 69.8 (C, Cp), 70.8 (Cp), 74.1 (CH, Cp), 76.6 (CH, Cp), 77.8 (CH, Cp), 81.6 (C, Cp), 115.9 (d, C_2 *ortho*, $^2J(^{13}C,^{19}F) = 19.9$ Hz), 116.2 (d, C_2' *ortho*, $^2J(^{13}C,^{19}F) = 20.0$ Hz), 133.4 (d, C_4 *para*, $^4J(^{13}C,^{19}F) = 3.2$ Hz), 133.5 (d, C_4' *para*, $^4J(^{13}C,^{19}F) = 4.0$ Hz), 138.3 (d, C_3 *meta*, $^3J(^{13}C,^{19}F) = 8.0$ Hz), 138.4 (d, C_3' *meta*, $^3J(^{13}C,^{19}F) = 7.6$ Hz), 164.9 (d, C_1 *ipso*, $^1J(^{13}C,^{19}F) = 247.3$ Hz), 165.1 (d, C_1' *ipso*, $^1J(^{13}C,^{19}F) = 247.7$ Hz) ppm; ^{29}Si-NMR: (CD_3CN–TMS) −11.3 (s, SiMe) ppm; ES–MS (EI, 70 eV, pos., MeOH): $m/e = 476$ ($[M]^+$, cation), 431 $[FcCH_2SiMe(C_6H_4F)_2]^+$, 334 $[FcCH_2SiMe(C_6H_4F)]^+$, 199 $[FcCH_2]^+$, 986 $[FcNSiMe(C_6H_4F)_2·HCl+cation]^+$; Anal. Calc. for $C_{26}H_{28}ClF_2FeNSi$: C, 61.00; H, 5.51; N, 2.74, respectively, **10**·H_2O $C_{26}H_{30}ClF_2FeNOSi$: C, 58.93; H, 5.66; N, 2.64. Found: C, 58.87; H, 5.82; N, 2.73%.

5.4. Synthesis of derivatives of 14

5.4.1. Synthesis of (R,S)-FcNSiMe$_2$C$_6$H$_4$CHO (18) (method a)

A solution of *t*-BuLi (15 ml, 22.5 mmol in *n*-pentane) was added slowly drop-wise to a stirred solution of **14** (4.91 g, 11 mmol) in 50 ml THF at −78 °C. The reaction mixture was stirred for 40 min at −78 °C. DMF (8.51 ml, 110 mmol) was added drop-wise and stirred for 60 min. The resulting mixture was hydrolyzed with ammonium chloride in water at 0 °C. The liquid layers were separated. The aqueous layer was extracted with *n*-pentane, the organic layer was combined with the extracts, and then dried over Na_2SO_4. Afterwards, the solvent was removed in vacuo. A brown oil (**18**) was obtained with compound **19** as impurity. The separation of **18** from **19** was achieved by preparing the bisulfit adduct of the aldehyde (**18**). The brown oil was dissolved in diethyl ether. Then $NaHSO_3$ was added in

excess. The yellow solid was separated by filtration and washed with hot diethyl ether. The solid was suspended in *n*-pentane. Na_2CO_3 in water at 0 °C was added slowly to this suspension over a period of 2 h. The organic layers was separated and dried over Na_2SO_4. The solvent was removed under reduced pressure and a brown oil (**18**) was obtained. Spectroscopic data for **18**: ^{1}H-NMR ($CDCl_3$–TMS): 0.57 (s, SiMe), 0.67 (s, SiMe), 1.92 (s, NMe_2, 6H), 2.87 (d, NCH_2, 1H, $^2J(^1H,^1H) = 12.44$ Hz), 3.44 (d, NCH_2, 1H, $^2J(^1H,^1H) = 12.44$ Hz), 4.04 (s, br, Cp, 1H), 4.10 (s, Cp, 5H) 4.28 (t, Cp, 1H, $^3J(^1H,^1H) = 2.2$ Hz), 4.30 (s, br, Cp, 1H), 7.77, (m, AA′XX′, Ar-H, 2·2H), 9.99 (CHO) ppm; ^{13}C-NMR ($CDCl_3$–TMS): −1.7 (s, SiMe), −1.2 (s, SiMe), 44.6 (s, NMe_2), 59.4 (NCH_2), 68.9 (Cp), 69.0 (C, Cp), 69.9 (CH, Cp), 74.0 (CH, Cp), 74.9 (CH, Cp), 90.4 (C, Cp), 128.2 (s, C_2 *ortho*), 134.5 (s, C_3 *meta*), 136.2 (s, C_4 *para*), 149.2 (s, C_1 *ipso*), 192.8 (CHO) ppm; ^{29}Si-NMR: ($CDCl_3$–TMS) −7.1 (s, $SiMe_2$) ppm; IR ($CHCl_3$): $\nu_{C-H} = 2942$ (w) cm^{-1}, $\nu_{C=O} = 1700$ (s) cm^{-1}, $\nu_{C=C} = 1591$ (w), 1521 (w) cm^{-1}, ν_{C-H} (*para*) = 780 (s), 740 (s) cm^{-1}; ES–MS (EI, 70 eV, pos., THF–$CDCl_3$): *m/e* = 406 ($[M]^+ + 1$, cation), 361 $[FcCH_2SiMe_2C_6H_4CHO]^+$, 333 $[FcCH_2SiMe_2C_6H_4]^+$, 199 $[FcCH_2]^+$.

5.4.2. Synthesis of (*R,S*)-$FcNSiMe_2C_6H_5$ (**19**)

The compound **19** was isolated as side product during purification of **18**. Spectroscopic data for brown oil (**19**).: ^{1}H-NMR ($CDCl_3$–TMS): 0.56 (s, SiMe), 0.61 (s, SiMe), 1.97 (s, NMe_2, 6H), 2.96 (d, NCH_2, 1H, $^2J(^1H,^1H) = 12.44$ Hz), 3.36 (d, NCH_2, 1H, $^2J(^1H,^1H) = 12.44$ Hz), 4.01 (s, br, Cp, 1H), 4.07 (s, Cp, 5H) 4.25 (t, Cp, 1H, $^3J(^1H,^1H) = 2.2$ Hz), 4.33 (s, Cp, 1H), 7.30, 7.59 (m, AA′XX′, Ar-H, 2·2H) ppm; ^{13}C-NMR ($CDCl_3$–TMS): −1.3 (s, SiMe), −1.0 (s, SiMe), 44.7 (s, NMe_2), 59.4 (NCH_2), 68.8 (Cp), 69.8 (CH, Cp), 70.2 (C, Cp), 73.7 (CH, Cp), 74.9 (CH, Cp), 90.1 (C, Cp), 127.4 (s, C_3), 128.6 (s, C_1),134.0 (s, C_2), 139.9 (s, C_4) ppm; ^{29}Si-NMR: ($CDCl_3$–TMS) −7.8 (s, $SiMe_2$), −7.1 (< 1%) impurities of **18** ppm; ES–MS (EI, 70 eV, pos., THF–$CDCl_3$): *m/e* = 378 ($[M]^+ + 1$, cation), 333 $[FcCH_2SiMe_2C_6H_4]^+$, 299 $[FcNSiMe_2]^+$, 272 $[FcNSi]^+$, 199 $[FcCH_2]^+$, impurities of **18**: 604 $[FcNSiMe_2C_6H_4CHO + FcCH_2]^+$, 407 $[FcNSiMe_2C_6H_4CHO]^+$.

5.4.3. Alternative syntheses of (*R,S*)-$FcNSiMe_2C_6H_4CHO$ (**18**) (method b and c): synthesis of (*R,S*)-$FcNSiMe_2C_6H_4COOH$ (**20**)

The synthetic procedures for preparing compound **18** according to method b and c were similar to the procedures used in method a. In method b, a solution of **14** (6.55 g, 14.3 mmol) in 60 ml THF with 1.00 g (41.1 mmol) magnesium was used. To this Grignard reagent a solution of DMF (143 mmol, 11.1 ml) at 0 °C was added slowly (1 h). Further purification was done using the procedure used in method a. In method c, a solution of *n*-BuLi (30.16 ml, 52.7 mmol) was added slowly dropwise to a stirred solution of **14** (12.02 g, 26.35 mmol) in 50 ml *n*-pentane at −78 °C. In this method, the phenyl silane (**19**) and the carboxylic acid (**20**) were obtained as by-products. The reaction mixture was treated with diethyl ether. Then, the resulting yellow solid was separated by filtration. Further purification was done according to the procedure used in method a. Spectroscopic data for **20**: ^{1}H-NMR ($CDCl_3$–TMS): 0.53 (s, SiMe), 0.76 (s, SiMe), 2.14 (s, NMe_2, 6H), 3.40 (d, NCH_2, 1H, $^2J(^1H,^1H) = 13.16$ Hz), 4.01 (d, NCH_2, 1H, $^2J(^1H,^1H) = 13.16$ Hz), 4.17 (s, Cp, 5H), 4.25 (s, br, Cp, 1H) 4.47 (s, br, Cp), 4.68 (s, br, Cp, 1H), 6.48 (COOH) 7.55, 7.98 (d, AA′XX′, Ar-H, 2·2H, $^3J(^1H,^1H) = 8.0$ Hz), impurities Et_2O:1.21, 3.49 ppm; ^{13}C-NMR ($CDCl_3$–TMS): −1.09 (s, SiMe), −0.33 (s, SiMe), 41.7 (s, NMe_2), 56.5 (NCH_2), 69.4 (Cp), 70.9 (C, Cp), 72.3 (CH, Cp), 74.6 (CH, Cp), 75.7 (CH, Cp), 82.5 (C, Cp), 128.8 (s, C_2 *ortho*), 133.5 (s, C_3 *meta*), 136.3 (s, C_4 *para*), 142.0 (s, C_1 *ipso*), 172.0 (COOH), impurities Et_2O: 15.3, 65.9; 69.2, 68.9: ppm; ^{29}Si-NMR: ($CDCl_3$–TMS) −8.0 (s, $SiMe_2$) ppm; ES–MS (EI, 70 eV, pos., MeCN–CH_3COOH): *m/e* = 421 ($[M]^+$, cation), 376 $[FcCH_2SiMe_2C_6H_4COOH]^+$, 332 $[FcCH_2SiMe_2C_6H_4]^+$, 299 $[FcNSiMe_2]^+$, 257 $[FcCH_2SiMe_2]^+$, 199 $[FcCH_2]^+$, impurities from previous injection of **14**: 457 $[FcNSiMe_2C_6H_4Br]^+$, 410 $[FcCH_2SiMe_2C_6H_4Br]^+$.

5.4.4. Synthesis of (*R,S*)-$FcNSiMe_2C_6H_4CHO$ picrate (**21**)

Compound **21** was synthesized analogously to synthesis of **16** with 1 g (2.47 mmol) of **18** in EtOH (25 ml). The product recrystallized from hot EtOH–MeCN 1:1 to yellow crystals of **21.** Spectroscopic data for (**21**): ^{1}H-NMR ($CDCl_3$–TMS): 0.59 (s, SiMe, 3H), 0.84 (s, SiMe, 3H), 2.37 (s, br, NMe, 3H), 3.72 (d, NCH_2, 1H, $^2J(^1H,^1H) = 13.2$ Hz), 4.44 (d, NCH_2, 1H, $^2J(^1H,^1H) = 13.2$ Hz), 4.26 (s, Cp, 5H), 4.38 (s, br, Cp, 1H), 4.62 (t, Cp, 1H, $^3J(^1H,^1H) = 5.12$ Hz), 4.76 (s, Cp, 1H), 7.68 (m, AA′XX′, Ar-H, 2·H, $^3J(^1H,^1H) = 8.0$ Hz), 7.82 (m, AA′XX′, Ar-H, 2·H, $^3J(^1H,^1H) = 8.0$ Hz), 8.87 (s, NO_2Ar-H, 2 H), 10.0 (CHO) ppm; ^{13}C-NMR (CD_3CN–TMS): −1.4 (s, SiMe), −0.1 (s, SiMe), 43.0 (br, NMe_2), 59.1 (NCH_2), 70.7 (Cp), 71.2 (C, Cp), 74.2 (CH, Cp), 75.7 (CH, Cp), 77.6 (CH, Cp), 81.0 (C, Cp), 129.4 (s, C_2 *ortho*), 135.4 (s, C_3 *meta*), 137.9 (s, C_4 *para*), 148.4 (s, C_1 *ipso*) 126.6, 127.3, 143.1, 162.7 (6*C, NO_2Ar), 193.8 (CHO) ppm; ^{29}Si-NMR: ($CDCl_3$–TMS) −7.0 (s, $SiMe_2$) ppm; ES–MS (EI, 70 eV, pos., MeCN): *m/e* = 405 ($[M]^+ - 1$, cation), 360 $[FcCH_2SiMe_2C_6H_4CHO]^+$, 198 $[Fc]^+$; Anal. Calc. for $C_{28}H_{30}FeN_4O_8Si$: C, 53.00; H, 4.76; N, 8.83. Found: C, 52.94; H, 4.91; N, 8.41%.

Table 3
Crystal data and structure refinement for solid state structures

Number	(**7**) FcN–Si(C_6H_4F)$_3$	(**12**) FcN–SiMe(C_6H_4F)$_2^+$ picrate$^-$	(**15**) FcN–SiMe$_2$(C_6H_4Br)$^+$ Cl^- with 0.5 H_2O
Empirical formula	$C_{31}H_{28}F_3FeNSi$	$C_{32}H_{30}F_2FeN_4O_7Si$	$C_{21}H_{27}BrClFeNO_{0.50}Si$
Formula weight (g mol^{-1})	555.48	704.54	500.74
Temperature (K)	293(2)	293(2)	293(2)
Wavelength (Å)	1.54178	1.54178	1.54178
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P-1$	$C2/c$	$P2/c$
Unit cell dimensions			
a (Å)	10.440(1)	22.061(3)	19.129(2)
b (Å)	11.364(1)	11.071(1)	7.282(1)
c (Å)	13.184(2)	27.762(3)	17.102(2)
α (°)	68.45(1)	90	90
β (°)	70.28(1)	110.74(1)	107.66(1)
γ(°)	84.72(1)	90	90
V (Å^3)	1368.6(3)	6341.1(11)	2270.0(5)
Z	2	8	4
D_{calc} (gm cm^{-3})	1.348	1.473	1.465
Absorption coefficient (mm^{-1})	5.179	4.744	9.029
F(000)	576	2912	1024
Crystal size (mm)	0.3 × 0.2 × 0.15	0.3 × 0.25 × 0.2	0.3 × 0.3 × 0.15
θ Range for data collection (°)	3.82–75.05	3.40–74.90	2.42–74.86
Index ranges	$-13 \le h \le 13$, $-14 \le k \le 14$, $-8 \le l \le 16$	$0 \le h \le 27$, $0 \le k \le 13$, $-34 \le l \le 32$	$-23 \le h \le 12$, $-5 \le k \le 9$, $-20 \le l \le 21$
Reflections collected	9606	6692	8491
Independent reflections	5643 [$R_{int} = 0.08$]	6520 [$R_{int} = 0.03$]	4666 [$R_{int} = 0.08$]
Completeness to θ (%)	(75.05°) 99.8	(74.90°) 99.6	(74.86°) 100.0
Absorption correction	Empirical	Empirical	None
Max/min transmission	0.9992, 0.5225	0.9997, 0.8506	
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5643/118/325	6520/50/431	4666/1/247
Goodness-of-fit on F^2	1.016	1.014	1.023
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0605$, $wR_2 = 0.1301$	$R_1 = 0.0546$, $wR_2 = 0.1204$	$R_1 = 0.0724$, $wR_2 = 0.1783$
R indices (all data)	$R_1 = 0.1143$, $wR_2 = 0.1570$	$R_1 = 0.1089$, $wR_2 = 0.1419$	$R_1 = 0.1273$, $wR_2 = 0.2167$
Largest difference peak and hole (e Å^{-3})	0.366 and −0.320	0.353 and −0.438	0.943 and −1.079

5.5. Experimental procedure for X-ray crystallography

Diffraction measurements were done on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Cu–K_α radiation with $\varpi-2\theta$ scans. The structures were solved with direct methods, non-hydrogen atoms were located by using difference Fourier synthesis and refined by full-matrix least-squares on F^2 with anisotropic thermal parameters. Hydrogen atoms were calculated and allowed to ride on their corresponding carbon atoms. Empirical absorption corrections were performed using psi-scans for **7** and **12**. Crystallographic data and the results of refinements are summarized in Table 3.

6. Supplementary material

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 142915 for compound **7**, 142916 for compound **12**, and 169198 for compound **15**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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