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# Synthesis, structural characterization and $^{57}$Fe-Mössbauer spectra of ferrocenylhexasilanes

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**Abstract**

Linear and cyclic ferrocenylhexasilanes 1,6-Fc–$Si_6Me_{12}$–X [X = Me, –$C_6H_4CH{=}C(CN)_2$], 1,3- and 1,4-Fc–$Si_6Me_{10}$–X [X = Me, –$C_6H_4CH{=}C(CN)_2$], have been synthesized and their Mössbauer spectra have been measured. All compounds possess localized electronic structures on the Mössbauer timescale and partial Fe(III) character of the iron atom due to Cp → ($Si_n$) electron transfer. The Mössbauer data obtained, furthermore, indicate considerable aryl–ferrocenyl interaction via the hexasilane moiety. The single crystal X-ray structures of 1,3- and 1,4-Fc–$Si_6Me_{10}$–$C_6H_4CH{=}C(CN)_2$ exhibit the cyclohexasilane ring in chair conformation with the bulky Fc- and aryl substituents in equatorial positions. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Polysilanes; Ferrocene; Crystal structures; Mössbauer spectroscopy

## 1. Introduction

Quite recently organic and organometallic materials with second order nonlinear optical properties have been the subject of intense investigation what led to the development of certain structure/NLO property relationships [1]. Pertinent studies revealed that large second order nonlinearities are always associated with chromophores comprised of electron donors and acceptors linked by a conjugated π system. In the class of organometallic NLO compounds ferrocene based systems are prominent [1b,c], what is mainly due to attractive features like air- and thermal stability, photochemical stability and synthetic versatility combined with large optical nonlinearities.

Recently several reports appeared in the literature concerning the synthesis and characterization of dipolar silicon compounds showing an extended transparency range combined with nonlinear optical activities [2]. Silicon, however, was found to be only a weak charge transmitter when donor and acceptor phenyl–Si–phenyl moieties are connected by linear Si–Si-chains and the resulting optical nonlinearities are just moderate. Quite similar results independently have been obtained by Pannell et al. [3] and in our laboratories [4] for disilanes containing ferrocene as a donor and various organic acceptor groups. For the corresponding cyclohexasilane derivatives, however, we observed significantly increased values of the quadratic hyperpolarizabilities β and noticeable electron transmission effects via the cyclohexasilane ring [5].

In cyclic polysilanes delocalization of σ(Si–Si) electrons over the ring silicon atoms gives these molecules a variety of properties resembling those of aromatic hydrocarbons [6]. So far the chemistry and the properties of cyclopolysilanes have been explored mainly by the groups of Hengge [7] and West [8]. Here we report the detailed synthesis, characterization and crystal structures of the donor/acceptor substituted cyclohexasilanes 1-ferrocenyl-4-[(2,2-dicyanoethenyl)phenyl]decamethylcyclohexasilane (**3**) and 1-ferrocenyl-3-[(2,2-dicyanoethenyl)phenyl]decamethylcyclohexasilane (**4**). For comparison we have also synthesized ferrocenylundecamethylcyclohexasilane (**6**) and the open chained compounds 1-ferrocenyl-2-[(2,2-dicyanoethenyl)phenyl]disilane (**1**), 1-ferrocenyl-6-[(2,2-dicyanoethenyl)phenyl]-

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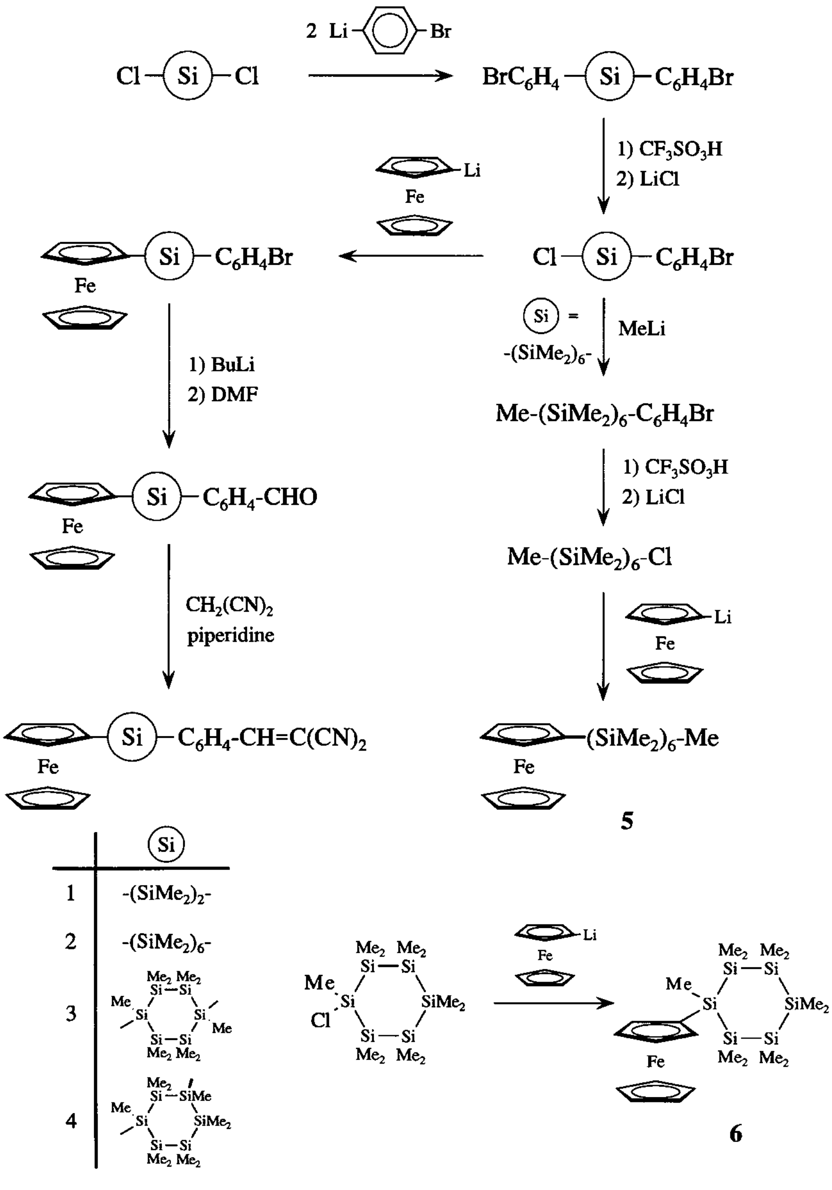
dodecamethylhexasilane (**2**) and 1-ferrocenyltridecamethylhexasilane (**5**). Detailed $^{57}$Fe-Mössbauer studies have been performed on these compounds in order to assess intramolecular donor/acceptor interactions.

## 2. Results and discussion

### 2.1. Synthesis

The hexasilane derivatives **2**–**6** addressed in this paper were prepared employing standard organometallic reactions (Scheme 1).

Attempts to react 1,3- or 1,4-dichlorodecamethylcyclohexasilane with one equivalent of *p*-BrPhLi only resulted in the formation of mixtures of the corresponding mono- and bis-(*p*-bromophenyl)permethylcyclohexasilane. Similar results were obtained starting from 1,6-dichlorododecamethylhexasilane. When both chlorines, however, are replaced by *p*-bromophenyl groups using two equivalents of *p*-BrPhLi in a primary step, one of the Si–aryl bonds can be rechlorinated selectively with triflic acid/LiCl and the desired (*p*-bromophenyl)chloropermethylhexasilanes are formed. At this stage the ferrocene moiety easily can be attached to the hexasilane skeleton with monolithioferrocene. Finally the 2,2-dicyanoethylene group can be generated by derivatization of the aryl–Br linkage with *n*-BuLi/DMF followed by Knoevenagel condensation of the resulting aromatic aldehyde with malononitrile. After column chromatography **2**, **3** and **4** are obtained as red air stable solids.



Scheme 1. Synthesis of compounds **1**–**6**.

Table 1
$^1$H- and $^{29}$Si-NMR chemical shifts and assignment for compounds **2**, **3** and **4**[a]

| | δ($^1$H) (ppm)[a] | | δ($^{29}$Si) (ppm)[a] | |
|---|---|---|---|---|
| **2** | 7.34, 7.31, 7.24, 7.21 (s, 1H) | Phenyl | −16.60(1)[b] | **Si**Me$_2$Ph |
| | 4.20 (t, 2H), 4.07 (s, 5H), 4.00 (t, 2H) | Ferrocene | −17.69(1) | **Si**Me$_2$Fc |
| | 0.43 (s, 6H), 0.31 (s, 6H), 0.21 (s, 6H), | –Si(**CH**$_3$) | −38.61(1) | |
| | 0.20 (s, 6H), 0.17 (s, 6H), 0.15 (s, 6H) | | −39.01(1) | **Si**Me$_2$ |
| | | | −42.65(1) | |
| | | | −43.24(1) | |
| *trans*-**3** | 7.35 (s, 2H, 7.15 (s, 2H) | Phenyl | −39.94(1) | (Si4)[c] |
| | 6.56 (s, 1H) | –**H**C=C(CN)$_2$ | −40.68(2) | (Si2/Si3) |
| | 4.21 (t, 2H), 4.11 (s, 5H), 4.0 (t, 2H) | Ferrocene | −41.00(2) | (Si1) |
| | 0.52 (s, 3H), 0.40 (s, 3H), 0.33 (s, 6H), | –Si(**CH**$_3$) | −41.64(1) | |
| | 0.27 (s, 6H) 0.26 (s, 6H), 0.12 (s, 6H) | | | |
| *cis*-**3** | 7.31 (s, 2H), 7.15 (s, 2H) | Phenyl | −39.45(1) | (Si4) |
| | 6.51 (s, 1H) | –**H**C=C(CN)$_2$ | −41.44(2) | |
| | 4.22 (t, 2H), 4.11 (s, 5H), 4.0 (t, 2H) | Ferrocene | −41.76(2) | (Si2/Si3) |
| | 0.53 (s, 3H), 0.43 (s, 3H), 0.30 (s, 6H), | –Si(**CH**$_3$) | −41.92(1) | (Si1) |
| | 0.29 (s, 6H), 0.15 (s, 6H), 0.13 (s, 6H) | | | |
| *cis*-**4** | 7.35 (s, 2H), 7.15 (s, 2H) | Phenyl | −38.93(1) | (Si3) |
| | 6.56 (s, 1H) | –**H**C=C(CN)$_2$ | −40.99(1) | |
| | 4.21 (t, 2H), 4.11 (s, 5H), 4.01 (t, 2H) | Ferrocene | −41.08(2) | (Si2/Si4/Si5/Si6) |
| | 0.53 (s, 3H), 0.45 (s, 3H), 0.35 (s, 3H), | | −41.19(1) | |
| | 0.34 (s, 3H), 0.27 (s, 3H), 0.22 (s, 3H), | –Si(**CH**$_3$) | −41.81(1) | (Si1) |
| | 0.21 (s, 3H), 0.19 (s, 6H), 0.16 (s, 3H) | | | |
| *trans*-**4** | 7.35–7.25 (m, 4H) | Phenyl | −39.09(1) | (Si3) |
| | 6.54 (s, 1H) | –**H**C=C(CN)$_2$ | −41.43(1) | |
| | 4.20 (m, 2H), 4.06 (s, 5H), | Ferrocene | −41.46(1) | (Si2/Si4/Si5/Si6) |
| | 4.03–3.95 (m, 2H) | | −41.53(1) | |
| | | | −41.61(1) | |
| | 0.50, 0.36, 0.32, 0.29, 0.26, 0.24, 0.22,<br>0.17, 0.15, 0.11 (s, 3H) | –Si(**CH**$_3$) | −42.24(1) | (Si1) |

[a] Versus ext. Me$_4$Si; hydrocarbon solution.
[b] Number of Si-atoms in brackets.
[c] Atom numbering according to Figs. 1 and 2.

Since the substituents can be attached to the cyclohexasilane ring either *cis* or *trans* relative to each other, isomeric mixtures of the disubstituted permethylcyclohexasilanes **3** and **4** are obtained containing nearly equal amounts of the *cis*- and *trans*-isomers. Separation of the isomers easily can be achieved by recrystallization. As confirmed by X-ray crystallography (compare the following section) the stereoisomer with both bulky substituents in equatorial positions (*trans* in the case of **3** and *cis* in the case of **4**) crystallizes selectively from hexane solutions of **3** and **4** at −80°C. The second isomer can be enriched in the filtrate up to 85% by removing the less soluble isomer by repeated crystallization from hexane at −80°C.

The proposed structures are consistent with MS and NMR data and with the results of C, H, N elemental analyses. $^{29}$Si- and $^1$H-NMR data are given in Table 1. Only weak electronic effects of the substituents on the ring silicon atoms are apparent in the $^{29}$Si-NMR spectra. Introduction of the electron withdrawing –CH=C(CN)$_2$ group into the phenyl ring, for instance, causes a slight downfield shift of the α-Si resonances in **3** and **4** ($\Delta\delta = 0.8$ and 1.4 ppm) relative to PhSi$_6$Me$_{11}$ [9]. While the NMR spectra of the open chained hexasilanes **2** and **5** can be interpreted rather straightforward, complicated NMR patterns are observed for the cyclic compounds **3** and **4**. Substitution of two of the methyls in Si$_6$Me$_{12}$ with different groups R and R′ produces four nonequivalent silicons in the case of **3** and six nonequivalent silicons in the case of **4**. The stereoisomers of **3** and **4** additionally exhibit different $^{29}$Si chemical shift values. The methyl groups, furthermore, can be either *cis* or *trans* to the substituents what leads to 6 nonequivalent methyls for each isomer of **3** (intensity ratio 1:2:2:2:2:1) and to ten nonequivalent methyls for each isomer of **4**. The resulting number of resonance lines actually appears in the experimental $^1$H- and $^{29}$Si-NMR spectra, though some are to close to each other to be completely resolved.

### 2.2. X-ray Structures of 3 and 4

Drawings of the molecular structures of **3** and **4** with atom labeling are depicted in Figs. 1 and 2. Selected bond lengths and angles are summarized in Table 2.

The cyclohexasilane rings in **3** and **4** adopt slightly distorted chair conformations. The bulky substituents in the 1,3 or 1,4-positions, respectively, occupy equatorial sites in order to minimize non-bonding interactions. The aromatic rings are arranged roughly perpendicular to one of the adjacent Si–Si bonds as shown by the torsional angles in Table 2. Deviations from perpendicularity are larger for compound **4** and amount to about 15°. The tilt between the phenyl and the cyclopentadienyl ring is 62° for compound **3** and 89° for compound **4**. Both compounds possess nearly eclipsed ferrocenyl geometry with almost coplanar cyclopentadienyl rings. The average Si–Si distances of 2.349 Å in **3** and 2.344 in **4** are close to that in elemental silicon, 2.352 Å [10], 1,4-$Ph_2Si_6Me_{10}$, 2.350 Å [11] and $Si_6Me_{12}$, 2.338 Å [12]. These distances agree well with the Si–Si covalent bond length of 2.34 Å. The average Si–Si–Si bond angles [110.8(3)° for **3** and 110.7(5)° for **4**] and the average Si–Si–Si–Si torsion angles [56.0(9)° for **3** and 56.6(7) for **4**] are close to the respective angles found in other cyclohexasilane structures studies so far [11–13]. **3** and **4** crystallize in centrosymmetric point groups, where the unit cell contains two, respectively four symmetry equivalent molecules (compare Fig. 3). The molecules

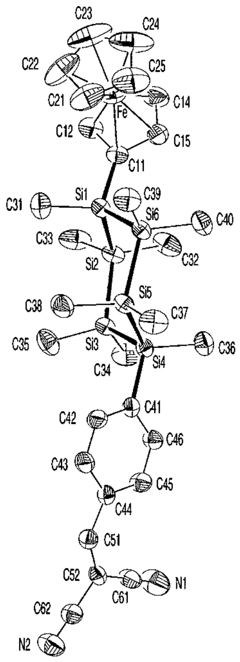


Fig. 1. ORTEP plot of the molecular structure of **3** (hydrogens are omitted for clarity).

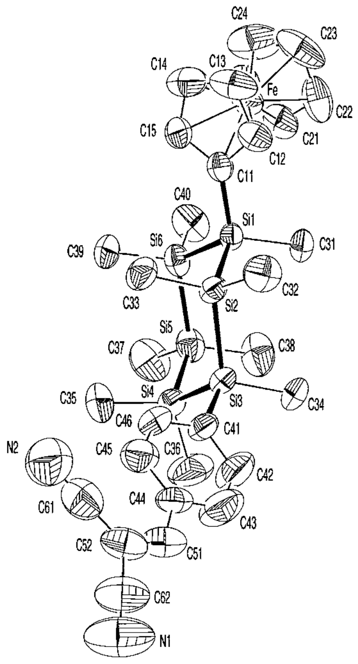


Fig. 2. ORTEP plot of the molecular structure of **4** (hydrogens are omitted for clarity).

Table 2
Selected bond lengths, angles and torsion angles for **3** and **4**

| | **3** | **4** |
|---|---|---|
| *Bond lengths* | | |
| Si(1)–Si(2) | 2.353(4) | 2.351(6) |
| Si(2)–Si(3) | 2.351(4) | 2.342(7) |
| Si(3)–Si(4) | 2.343(4) | 2.356(6) |
| Si(4)–Si(5) | 2.354(4) | 2.341(7) |
| Si(5)–Si(6) | 2.347(4) | 2.321(7) |
| Si(6)–Si(1) | 2.351(4) | 2.353(6) |
| Si(1)–C(11) | 1.879(9) | 1.866(9) |
| Si(3)–C(41) | | 1.898(10) |
| Si(4)–C(41) | 1.901(9) | |
| Si–C(methyl) mean | 1.890 | 1.884 |
| *Bond angles* | | |
| Si(1)–Si(2)–Si(3) | 116.31(13) | 110.2(2) |
| Si(2)–Si(3)–Si(4) | 110.20(13) | 110.6(2) |
| Si(3)–Si(4)–Si(5) | 108.50(14) | 112.9(2) |
| Si(4)–Si(5)–Si(6) | 111.68(13) | 108.9(2) |
| Si(5)–Si(6)–Si(1) | 108.19(13) | 112.9(2) |
| Si(6)–Si(1)–Si(2) | 110.10(14) | 108.9(2) |
| Si(1)–Si(2)–C(11) | 103.7(3) | 105.3(3) |
| Si(6)–Si(1)–C(11) | 113.5(3) | 112.2(3) |
| Si(2)–Si(3)–C(41) | | 109.9(3) |
| Si(3)–Si(4)–C(41) | 107.2(3) | 108.8(3) |
| Si(4)–Si(5)–C(41) | 110.5(3) | |
| C–Si–C mean | 108.0 | 108.1 |
| C(cp)–C(cp) mean | 108.1 | 108.0 |
| C(ph)–C(ph) mean | 119.9 | 120.0 |
| N(1)–C(61)–C(52) | 178.7(11) | 177.3(14) |
| N(2)–C(62)–C(52) | 179.3(11) | 178.0(12) |
| *Dihedral angles* | | |
| Si(2)–Si(1)–C(11)–C(15) | −90.2(9) | −107.4(7) |
| Si(2)–Si(1)–C(11)–C(12) | 84.5(8) | 72.2(6) |
| Si(3)–Si(4)–C(41)–C(46) | 87.0(8) | |
| Si(3)–Si(4)–C(41)–C(42) | −91.3(8) | |
| Si(4)–Si(3)–C(41)–C(46) | | −75.7(7) |
| Si(4)–Si(3)–C(41)–C(42) | | 101.6(8) |
| C(44)–C(51)–C(52)–C(61) | 1.5(17) | −2.4(16) |
| C(45)–C(44)–C(51)–C(52) | −5.6(17) | −11.5(15) |
| C(42)–C(43)–C(44)–C(51) | −175.0(9) | −177.4(10) |

show a stacking behavior parallel to the silica rings along the *a* axis in the case of **3** and along the *b* axis in the case of **4**.

### 2.3. Mössbauer spectra

$^{57}$Fe-Mössbauer spectra of the ferrocenyl oligosilanes **1**–**6** were obtained in order to probe the nature of the iron sites. The Mössbauer effect spectral parameters are presented in Table 3.

As shown in Fig. 4 each spectrum displays a doublet and a broad singlet with isomer shift ($\delta$) and quadrupole splitting ($\varepsilon$) values characteristic of Fe(II) and Fe(III) sites, what implies, that **1**–**6** have localized electronic structures on the Mössbauer time scale ($10^{-7}$ s) [14,15]. The singlet can be interpreted as a doublet with small quadrupole splitting as well without any significant impact on the results. In general, ferrocenyl groups (Fe(II)) give spectra with large quadrupole splitting in the range of 2.0 to 2.2 mm s$^{-1}$, while the spectra

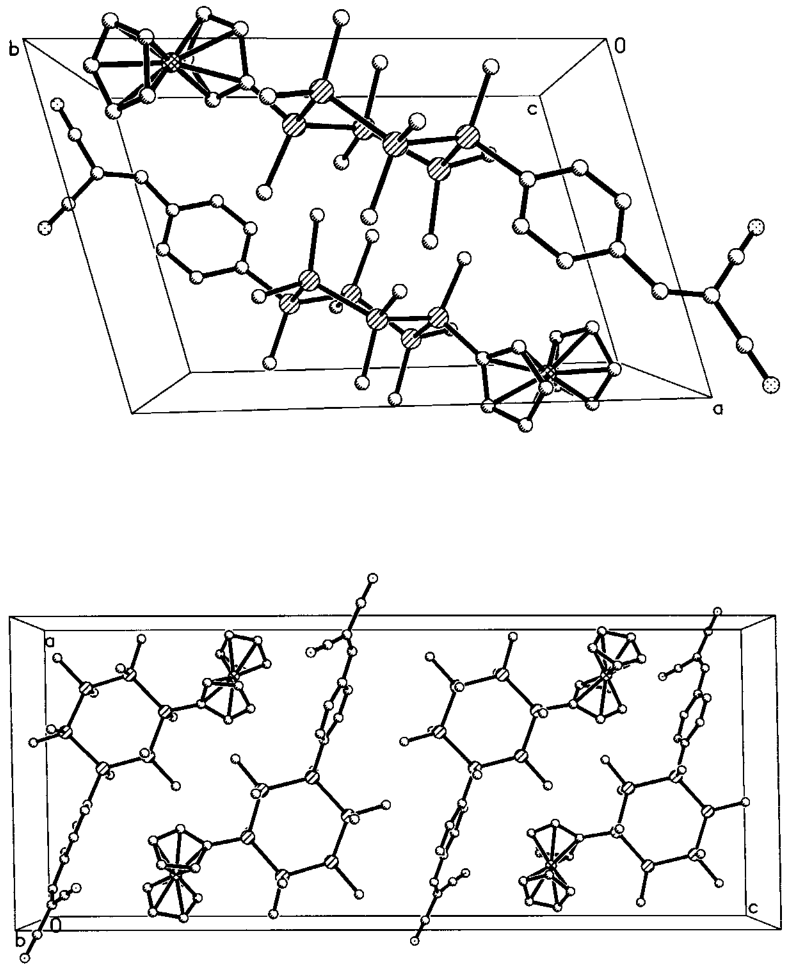


Fig. 3. Stereo view of the unit cells of compounds **3** (top) and **4** (bottom).

Table 3
Mössbauer data for compounds **1**–**6**

| | Doublet | | | | Singlet | | |
|---|---|---|---|---|---|---|---|
| | $\delta$ (mm s$^{-1}$) | $\varepsilon$ (mm s$^{-1}$) | $I$ (%) | $\Gamma$ (mm s$^{-1}$) | $\delta$ (mm s$^{-1}$) | $I$ (%) | $\Gamma$ (mm s$^{-1}$) |
| **1** | 0.528(1) | 2.323(3) | 89(1) | 0.306(4) | 0.32(1) | 11(1) | 0.46(5) |
| **2** | 0.53(4) | 2.313(8) | 67(2) | 0.30(1) | 0.31(2) | 33(3) | 0.65(8) |
| **3** | 0.544(6) | 2.36(1) | 67(3) | 0.252(2) | 0.28(3) | 33(4) | 0.72(8) |
| **4** | 0.532(4) | 2.332(9) | 60(3) | 0.251(8) | 0.30(2) | 40(3) | 0.80(6) |
| **5** | 0.526(1) | 2.320(2) | 89(1) | 0.267(3) | 0.29(2) | 11(1) | 0.57(6) |
| **6** | 0.529(3) | 2.335(2) | 90(1) | 0.275(3) | 0.27(3) | 10(1) | 0.75(1) |

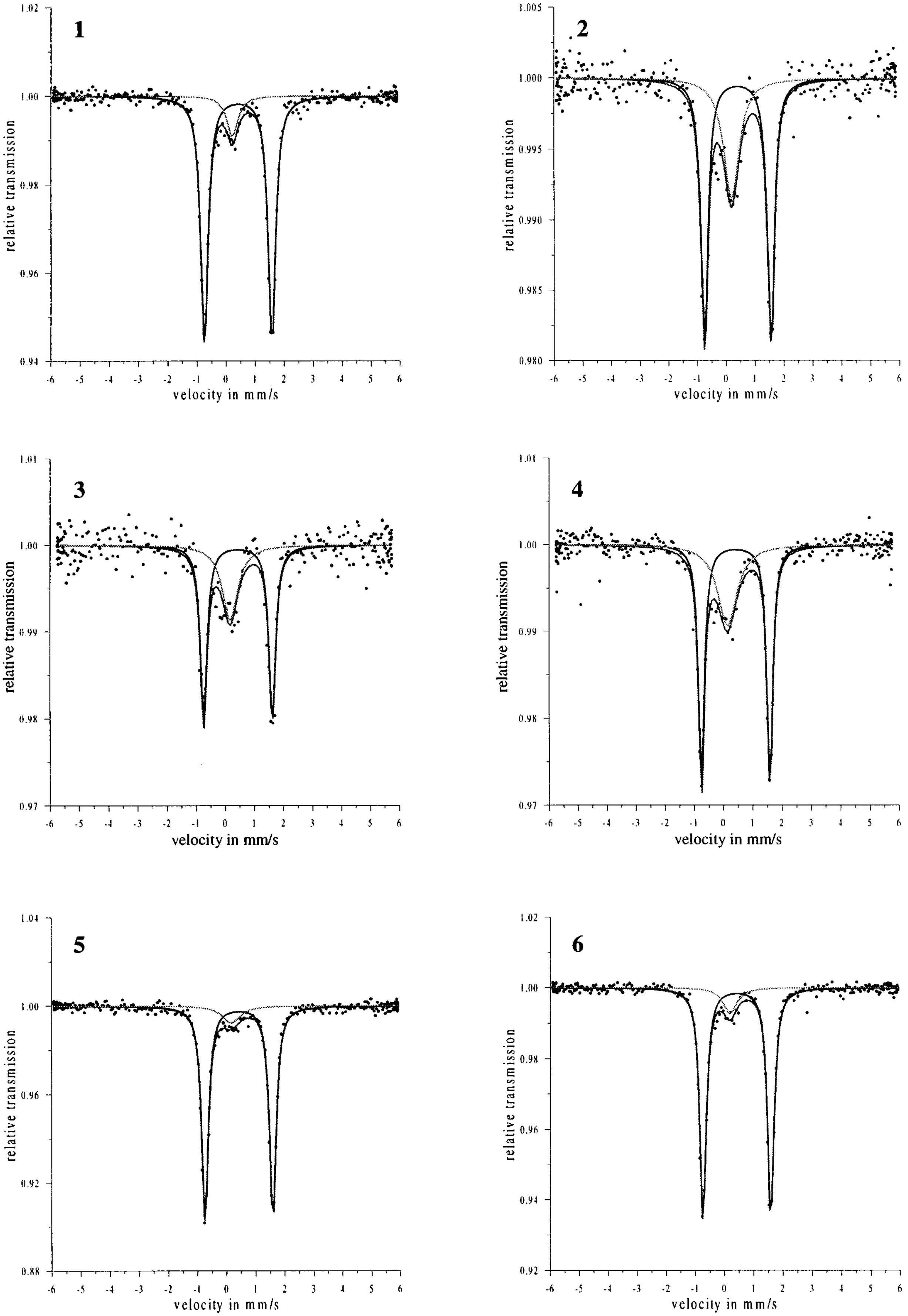


Fig. 4. Mössbauer spectra of compounds **1**–**6**.

of ferricinium cations (Fe(III)) are characterized by small or vanishing quadrupole splitting [16].

The appearance of the Fe(III) signal in all spectra clearly indicates the electron accepting character of the polysilanyl groups attached to ferrocene. Electron transfer in the direction $Cp \rightarrow (Si_n)$ removes electron density from the cyclopentadienyl ring, what is compensated by the partial oxidation $Fe(II) \rightarrow Fe(III)$. The relative intensities of the Fe(II) and Fe(III) signals deserve particular attention, because the intensity of the Fe(III) singlet in the spectra of the dipolar hexasilanes **2**, **3** and **4** turns out to by significantly enhanced as compared to the other compounds investigated in this study. Two important conclusions may be drawn from this observation: (i) When the dicyanoethylphenyl acceptor group is attached to the $(Si_6)$ moiety in **5** and **6**, $Cp \rightarrow (Si_n)$ electron transfer is more pronounced, what is a clear indication for the transmission of the electron accepting properties of the $-Ph-CH=C(CN)_2$ group via the hexasilane framework. (ii) The magnitude of $Cp \rightarrow (Si_n)$ electron transfer is increased when going from disilane **1** to the more extended Si–Si-skeletons in **2**, **3** and **4**, what may be related to the higher polarizability of the larger hexasilane frameworks. Both findings are consistent with recent cyclovoltammetric studies and NLO measurements [5] also showing increased transparency for electronic effects in particular for the cyclohexasilane moiety.

In conclusion, the Mössbauer analysis performed in this study further substantiates the assumption, that especially the cyclohexasilane framework is able to act as a good mediator for electronic effects.

## 3. Experimental

### 3.1. General procedures

All reactions and other manipulations were carried out using standard Schlenk techniques under an inert atmosphere of nitrogen. All solvents were dried and distilled under nitrogen prior to use. Malononitrile, triflic acid and 1,4-dibromobenzene were used as purchased without further purification. *N*,*N*-Dimethylformamide was allowed to stand on 4 Å molecular sieve and distilled from $CaH_2$. Ferrocenyllithium [17], 4-bromophenyllithium [18], 1-ferrocenyl-2-[(2,2-dicyanoethenyl)phenyl]disilane (**1**) [3], ferrocenylundecamethylcyclohexasilane (**6**) [5] and the starting silicon compounds 1,6-dichlorododecamethylhexasilane [19], 1,3-dichlorodecamethylcyclohexasilane and 1,4-dichlorodecamethylcyclohexasilane [20,21] were synthesized as previously reported. NMR spectra were recorded on a Bruker 300-MSL spectrometer; $^{1}$H-NMR (300.13 MHz): $C_6D_6$ solution, ext. standard $Me_4Si$; $^{29}$Si-NMR (59.62 MHz): toluene solution, ext. lock $D_2O$, ext. standard TMS. Mass spectra were run either on a HP 5971/A/5890-II GC/MS coupling (HP 1 capillary column, length 25 m, diameter 0.2 mm, 0.33 μm polydimethylsiloxane) or on a Kratos Profile mass spectrometer equipped with a solids probe inlet. Elemental analyses were carried out on a Hanau Vario Elementar EL apparatus. Mössbauer spectra were obtained at a temperature of 80 K in transmission geometry using a WISSEL system. The source material was $^{57}$Co/Rh with an activity of 10 mCi. The spectrometer was calibrated with α-Fe. All isomer shifts are relative to α-Fe. All spectra were fit assuming Lorentz profiles.

### 3.2. Ferrocenyllithium

75 mmoles of *tert*-butyllithium in hexane were added slowly to a solution of 21 g (113 mmol) of ferrocene in 150 ml of THF at 0°C. Subsequently ferrocenyllithium was crystallized by cooling the solution to −30°C overnight, filtered and washed with cold THF in order to remove excess ferrocene and unreacted *tert*-butyllithium. Further purification of the reaction product can be achieved by recrystallization from THF at −30°C.

### 3.3. 1-Ferrocenyl-6-[(2,2-dicyanoethenyl)phenyl]-dodecamethylhexasilane (**2**)

#### 3.3.1. 1,6-bis-(4-Bromophenyl)dodecamethylcyclohexasilane

To a solution of 37.7 g (89.8 mmol) of 1,6-dichlorododecamethylhexasilane in 100 ml diethylether, a −70°C cold solution of 184 mmol of 4-bromophenyllithium in 150 ml of diethylether was added dropwise. The mixture was stirred for 2 h at room temperature and subsequently refluxed for 1 h. After aqueous workup with 50 ml of saturated $NH_4Cl$ solution the combined organic layers were dried over $Na_2SO_4$ and the solvent was stripped off in vacuum. Recrystallization of the crude product from 1-propanol affords pure white crystals of 1,6-bis-(4-bromophenyl)dodecamethylhexasilane in 75% yield. $^{29}$Si-NMR (Toluol/$D_2O$, ext. $Me_4Si$, ppm): −16.80; −38.34; −42.55.

#### 3.3.2. 1-Chloro-6-(4-bromophenyl)dodecamethylhexasilane

A total of 5.9 ml (67.6 mmol) of triflic acid was added to a solution of 42.6 g (64.4 mmol) of 1,6-bis(4-bromophenyl)dodecamethylhexasilane in 1000 ml of toluene at −20°C over a period of 7 h. The mixture was stirred at room temperature (r.t.) overnight. Four hundred milliliters of toluene were removed in vacuum and replaced by diethylether. A total of 6.1 g (144.2 mmol) of anhydrous LiCl was added at 0°C and the mixture was stirred for another 12 h at r.t. After removal of the solvent in vacuum 200 ml of petroleum ether was added and the solution was filtered. Finally the solvent was stripped off again and the title compound was isolated from the resulting solid residue by Kugelrohr distillation at 160°C and $10^{-2}$ mbar followed by recrystallization from petroleum ether. Yield 73% of colorless crystals. $^{29}$Si-NMR (Toluol/$D_2O$, ext. $Me_4Si$, ppm): 25.70; −16.78; −38.42; −39.15; −40.53; −42.52. MS (70 eV) *m*/*e* (rel. int.): 540 [$M^+$, 9], 325 (6), 267 (100), 209 (33), 131 (15), 73 (47).

### 3.3.3. *1-Ferrocenyl-6-(4-bromophenyl)dodecamethylhexasilane*

A solution of ferrocenyllithium in 150 ml of THF [prepared from 21 g (112.9 mmol) of ferrocene and 75 mmol of *tert*-butyllithium] was added slowly to a stirred solution of 26.3 g (48.7 mmol) of 1-chloro-6-(4-bromophenyl)dodecamethylhexasilane in 10 ml of THF at r.t. The resulting mixture was refluxed overnight. Subsequently the solvent was stripped off and residual ferrocene was removed by sublimation at 50°C and $10^{-2}$ mbar. The resulting orange residue was dissolved in 150 ml of diethylether. After aqueous workup with saturated $NH_4Cl$ solution the combined organic layers were dried over $Na_2SO_4$ and concentrated. Chromatography on a silica gel column developed by a mixture of heptane + toluene (95:5) affords 9.7 g (30%) of the desired compound as an orange solid. $^{29}$Si-NMR (Toluol/$D_2O$, ext. $Me_4Si$, ppm): −16.73; −16.92; −38.40; −38.60; −42.65; −42.71. MS (EI, *m*/*z*, %): 690 [$M^+$, 2], 610 (7), 243 (100), 186 (11), 135 (15), 73 (20).

### 3.3.4. *1-Ferrocenyl-6-(4-formylphenyl)dodecamethylhexasilane*

To a solution of 9.0 g (13.1 mmol) of 1-ferrocenyl-6-(4-bromophenyl)dodecamethylhexasilane in 80 ml of THF at −78°C, a pentane solution of 26.1 mmol of *n*-butyllithium was added slowly. The mixture was stirred for another 5 min and 10.5 ml (135 mmol) of dry DMF was added. After stirring the mixture overnight at r.t. aqueous workup with saturated $NH_4Cl$ solution and recrystallization of the crude product from pentane affords orange crystals of the desired compound in 67% yield. $^{29}$Si-NMR (Toluol/$D_2O$, ext. $Me_4Si$, ppm): −16.32; −17.02; −38.17; −38.48; −42.26; −42.71 $^1$H-NMR ($C_6D_6$, ext. $Me_4Si$, ppm, rel. int.): 10.02 (s, 1H, CHO); 7.84–7.62 (4H, phenyl); 4.32 (t, 2H, ferrocene); 4.16 (s, 5H, ferrocene); 4.02 (t, 2H, ferrocene); 0.44–0.06 (36H, $Si(CH_3)$). MS (EI, *m*/*z*, %): 638 [$M^+$, 22], 243 (100), 186 (13), 73 (26).

### 3.3.5. *1-Ferrocenyl-6-[(2,2-dicyanoethenyl)phenyl]-dodecamethylhexasilane*

To a solution of 4.5 g (7.1 mmol) of 1-ferrocenyl-6-(4-formylphenyl)dodecamethylhexasilane dissolved in a mixture of 15 ml of THF and 80 ml of ethanol was added 0.51 g (7.8 mmol) of solid molononitrile and two drops of piperidine. The mixture was stirred for 45 min (DC monitoring recommended) and then the solvents were removed in vacuum. After column chromatography (silica gel) with toluene as the mobile phase and subsequent recrystallization from hexane orange–red crystals of the title compound were obtained in 62% yield. M.p.: 135–137°C. Anal. Found: C, 55.48; H, 7.26; N, 3.97. $C_{32}H_{50}FeN_2Si_6$ (687.12) Calc.: C, 55.94; H, 7.33; N, 4.07%. $^{29}$Si-NMR, $^1$H-NMR: Table 1. MS (70 eV) *m*/*e* (rel. int.): 686 [$M^+$, 4], 243 (100), 186 (47), 121 (17), 73 (16).

## 3.4. *1-Ferrocenyl-4-[(2,2-dicyanoethenyl)phenyl]-decamethylcyclohexasilane (**3**)*

### 3.4.1. *1,4-bis(4-Bromophenyl)decamethylcyclohexasilane (isomeric mixture)*

The procedure followed was that used for 1,6-bis(4-bromophenyl)dodecamethylcyclohexasilane with 35 g (89.8 mmol) of 1,4-dichlorodecamethylcyclohexasilane and 276 mmol of 4-bromophenyllithium. Yield: 41 g (= 67% based on 1,4-dichlorodecamethylcyclohexasilane). $^{29}$Si-NMR (Toluol/$D_2O$, ext. $Me_4Si$, ppm): −40.81/−39.86; −41.05/−42.00. MS (70 eV) *m*/*e* (rel. int.): 630 [$M^+$, 4], 551 (11), 341 (8), 207 (100), 72 (85).

### 3.4.2. *1-Chloro-4-(4-bromophenyl)decamethylcyclohexasilane (isomeric mixture)*

The procedure followed was that used for 1-chloro-6-(4-bromophenyl)dodecamethylhexasilane with 40.6 g (64.4 mmol) of 1,4-bis(4-bromophenyl)decamethylcyclohexasilane, 5.9 ml (67.6 mmol) of triflic acid and 6.1 g (144.3 mmol) of lithium chloride. The reaction product was isolated by sublimation at 120°C and $10^{-2}$ mbar to give colorless crystals in 73% yield. $^{29}$Si-NMR (Toluol/$D_2O$, ext. $Me_4Si$, ppm): 16.72/15.50; −38.84/−39.53; −40.52/−40.59; −41.61/−42.22. MS (70 eV) *m*/*e* (rel. int.): 510 [$M^+$, 9], 429 (31), 341 (14), 215 (19), 73 (100).

### 3.4.3. *1-Ferrocenyl-4-(4-bromophenyl)-decamethylcyclohexasilane*

The procedure followed was that used for 1-ferrocenyl-6-(4-bromophenyl)dodecamethylhexasilane with 25 g (48.7 mmol) of 1-chloro-4-(4-bromophenyl)decamethylcyclohexasilane, 21 g (112.9 mmol) of ferrocene and 75 mmol of *tert*-butyllithium. Yield: 8.6 g (27%). After crystallization from hexane at −80°C orange crystals of the pure *trans*-isomer of the compound were obtained. The *cis*-isomer can be enriched in the filtrate up to 85% by removing the less soluble *trans*-isomer by repeated crystallization from hexane and is obtained as an orange oil after subsequent removal of the solvent in vacuum. $^{29}$Si-NMR (Toluol/$D_2O$, ext. $Me_4Si$, ppm):

*trans*-isomer: −40.84; −41.26; −41.34; −41.77. *cis*-isomer: −40.40; −42.02; −42.13; −42.1. MS (70 eV) *m/e* (rel. int.): 660 [$M^+$, 8], 580 (100), 243 (85), 186 (50), 135 (37), 73 (56).

### *3.4.4. 1-Ferrocenyl-4-(4-formylphenyl)-decamethylcyclohexasilane (isomeric mixture)*

The procedure followed was that used for 1-ferrocenyl-6-(4-formylphenyl)dodecamethylhexasilane with 8.6 g (13.1 mmol) of 1-ferrocenyl-4-(4-bromophenyl)-decamethylcyclohexasilane, 26.1 mmol of *tert*-butyllithium and 10.4 ml of dry DMF. Due to the sensitivity of the desired compound versus oxygen all solvents and reagents need to be carefully deoxygenated prior to use. Final purification of the reaction product was achieved by column chromatography on a silica gel column developed by a mixture of deoxygenated heptane + toluene (95:5). Yield: 4.4 g (55%) of orange–red, light and oxygen sensitive crystals. $^{29}$Si-NMR (Toluol/$D_2O$, ext. $Me_4Si$, ppm): −39.66/−40.02; −40.68/−41.44; −40.80/−41.39; −41.25/−41.63. $^1$H-NMR ($C_6D_6$, ext. $Me_4Si$, ppm, rel. int.): 9.72/9.69 (s, 1H, CHO); 7.62–7.47 (4H, phenyl); 4.21–4.00 (9H, ferrocene); 0.53–0.14 (30H, $Si(CH_3)$). MS (70 eV) *m/e* (rel. int.): 608 [$M^+$, 78], 460 (13), 243 (77), 186 (100), 121 (25), 73 (20).

### *3.4.5. 1-Ferrocenyl-4-[(2,2-dicyanoethenyl)phenyl]-decamethylcyclohexasilane*

The procedure followed was that used for 1-ferrocenyl-6-[(2,2-dicyanoethenyl)phenyl]dodecamethylhexasilane with 4.3 g (7.1 mmol) of 1-ferrocenyl-4-(4-formylphenyl)decamethylcyclohexasilane, 0.52 g (7.8 mmol) of molononitrile and two drops of piperidine. After column chromatography (silica gel) with toluene as the mobile phase and subsequent recrystallization from hexane at −80°C red crystals of the *trans* (e,e)-isomer were obtained in 35% yield. The *cis* (e,a)-isomer can be enriched in the filtrate up to 95% by removing the less soluble *trans*-isomer by repeated crystallization from hexane and is obtained as a red oil in 15% yield after removal of the solvent in vacuum. M.p. (*trans*-isomer): 152–153°C. Anal. Found: C, 54.92; H, 6.74; N, 4.22. $C_{30}H_{44}FeN_2Si_6$ (657.06) calcd.: C, 54.84; H, 6.75; N, 4.21%. $^{29}$Si-NMR, $^1$H-NMR: Table 1. MS (70 eV) *m/e* (rel. int.): 656 [$M^+$, 3], 243 (4), 186 (100), 121 (24), 66 (12), 44 (22).

## *3.5. 1-Ferrocenyl-3-[(2,2-dicyanoethenyl)phenyl]-decamethylcyclohexasilane **(4)***

### *3.5.1. 1,3-bis(4-Bromophenyl)decamethylcyclohexasilane (isomeric mixture)*

The procedure followed was that used for 1,6-bis(4-bromophenyl)dodecamethylcyclohexasilane with 35 g (89.8 mmol) of 1,3-dichlorodecamethylcyclohexasilane and 276 mmol of 4-bromophenyllithium. Yield: 45.2 g (75%). $^{29}$Si-NMR (Toluol/$D_2O$, ext. $Me_4Si$, ppm): −39.88/−40.33; −40.88/−40.99; −41.06/−41.26; −41.44/−41.44; −41.90/−41.67; −42.32/−42.06. MS (70 eV) *m/e* (rel. int.): 630 [$M^+$, 5], 551 (7), 341 (9), 215 (40), 73 (100).

### *3.5.2. 1-Chloro-3-(4-bromophenyl)decamethylcyclohexasilane (isomeric mixture)*

The procedure followed was that used for 1-chloro-4-(4-bromophenyl)decamethylcyclohexasilane with 40.6 g (64.4 mmol) of 1,3-bis(4-bromophenyl)decamethylcyclohexasilane, 10.2 g (67.6 mmol) of triflic acid and 6.1 g (144.3 mmol) of lithium chloride. Yield: 24.1 g (73%). $^{29}$Si-NMR (Toluol/$D_2O$, ext. $Me_4Si$, ppm): 16.95/15.50; −38.39/−38.47; −39.23/−39.43; −40.51/−40.66; −40.88/−40.92; −41.20/−41.86. MS (70 eV) *m/e* (rel. int.): 510 [$M^+$, 6], 429 (15), 341 (11), 215 (38), 73 (100).

### *3.5.3. 1-Ferrocenyl-3-(4-bromophenyl)-decamethylcyclohexasilane*

The procedure followed was that used for 1-ferrocenyl-6-(4-bromophenyl)dodecamethylhexasilane with 25 g (48.7 mmol) of 1-chloro-3-(4-bromophenyl)decamethylcyclohexasilane, 21 g (112.9 mmol) of ferrocene and 75 mmol of *tert*-butyllithium. Yield: 9.7 g (30%). After crystallization from hexane at −80°C orange crystals of the pure *cis*-isomer of the compound are obtained. The *trans*-isomer can be enriched in the filtrate up to 85% by removing the less soluble *cis*-isomer by repeated crystallization from hexane and is isolated as an orange oil after subsequent removal of the solvent in vacuum. $^{29}$Si-NMR (Toluol/$D_2O$, ext. $Me_4Si$, ppm): *cis*-isomer: −40.19; −41.37 (int. × 2); −41.41; −41.69 (int. × 2). *trans* -isomer: −40.02; −41.47; −41.74; −42.13; −42.37 (int. × 2). MS (70 eV) *m/e* (rel. int.): 660 [$M^+$, 2], 385 (15), 243 (100), 213 (31), 73 (65).

### *3.5.4. 1-Ferrocenyl-3-(4-formylphenyl)-decamethylcyclohexasilane (isomeric mixture)*

The procedure followed was that used for (4-formylphenyl)undecamethylcyclohexasilane with 8.6 g (13.1 mmol) of 1-ferrocenyl-4-(4-bromophenyl)decamethylcyclohexasilane, 26.1 mmol of *tert*-butyllithium and 10.4 ml of dry DMF. Due to the sensitivity of the desired compound versus oxygen all solvents and reagents need to be carefully deoxygenated prior to use. Final purification of the reaction product was achieved by column chromatography on a silica gel column developed by a mixture of deoxygenated heptane + toluene (95:5). Yield: 4.8 g (60%) of orange–red, light and oxygen sensitive crystals. $^{29}$Si-NMR (Toluol/$D_2O$, ext. $Me_4Si$, ppm): −39.55; −39.98; −41.18; −41.26; −41.38 (int. x2); −41.51; −41.62; −41.70; −41.73;

− 41.91; − 42.25. $^1$H-NMR ($C_6D_6$, ext. $Me_4Si$, ppm, rel. int.): 9.71/9.70 (s, 1H, CHO); 7.59–7.38 (4H, phenyl); 4.18–3.96 (9H, ferrocene); 0.54–0.13 (30H, $Si(CH_3)$). MS (70 eV) *m*/*e* (rel. int.): 608 [$M^+$, 36], 371 (7), 243 (100), 213 (13), 163 (20), 73 (69).

### 3.5.5. *1-Ferrocenyl-3-[(2,2-dicyanoethenyl)phenyl]-decamethylcyclohexasilane*

The procedure followed was that used for 1-ferrocenyl-6-[(2,2-dicyanoethenyl)phenyl]dodecamethylhexasilane with 4.3 g (7.1 mmol) of 1-ferrocenyl-4-(4-formylphenyl)decamethylcyclohexasilane, 0.52 g (7.8 mmol) of molononitrile and 2 drops of piperidine. After column chromatography (silica gel) with toluene as the mobile phase and subsequent recrystallization from hexane at − 80°C red crystals of the *cis* (e,e)-isomer were obtained in 35% yield. The *trans* (e,a)-isomer can be enriched in the filtrate up to 95% by removing the less soluble *cis*-isomer by repeated crystallization from hexane and is obtained as a red oil in 15% yield after removal of the solvent in vacuum. M.p. (*cis*-isomer): 152°C. Anal. Found: C, 55.02; H, 6.72; N, 4.18. $C_{30}H_{44}FeN_2Si_6$ (657.06) Calc.: C, 54.84; H, 6.75; N, 4.21%. $^{29}$Si-NMR, $^1$H-NMR: Table 1. MS (70 eV) *m*/*e* (rel. int.): 656 [$M^+$, 100], 243 (34), 186 (84), 121 (20), 73 (11).

## 3.6. *1-Ferrocenyltridecamethylhexasilane (**5**)*

### 3.6.1. *1-(4-Bromophenyl)tridecamethylhexasilane*

A total of 8.25 ml of a 1.6 M pentane solution of methyllithium (15.13 mmol) was slowly added to a solution of 8.2 g (15.13 mmol) of 1-chloro-6-(4-bromophenyl)dodecamethylhexasilane in 100 ml of toluene at − 20°C. The resulting mixture was stirred overnight. After removal of the solvent in vacuum 50 ml of petroleum ether was added and the salts were removed by filtration. Finally the solvent was stripped off again and the title compound was isolated from the resulting solid residue by Kugelrohr distillation at 150°C and $10^{-2}$ mbar. Yield 5.2 g (66%) of colorless crystals. $^{29}$Si-NMR (Toluol/$D_2O$, ext. $Me_4Si$, ppm): − 15.07; − 17.42; − 39.17; − 39.29; − 43.10; − 43.28. MS (EI, *m*/*z*, %): 519 [$M^+$, 9], 389 (22), 331 (30), 215 (32), 73 (100).

### 3.6.2. *1-Ferrocenyltridecamethylhexasilane*

A total of 0.53 ml (6.0 mmol) of triflic acid was added slowly to a solution of 3.1 g (6.0 mmol) of 1-(4-bromophenyl)tridecamethylhexasilane in 60 ml of toluene at − 20°C. The mixture was stirred at r.t. overnight. After removal of the solvent in vacuum 10 ml of THF was added. The resulting solution was treated dropwise with a THF solution of 1.2 g (6.0 mmol) of ferrocenyllithium and stirred for one hour at r.t. After aqueous workup with saturated $NH_4Cl$ solution the combined organic layers were dried over $Na_2SO_4$ and concentrated. Chromatography on a silica gel column developed by heptane affords 2.3 g (70%) of the desired compound as an orange solid. M.p.: 84–87°C. Anal. Found: C, 55.41; H, 8.91. $C_{23}H_{48}FeSi_6$ (549.0) Calc.: C, 50.32; H, 8.81%. $^{29}$Si-NMR (Toluol/$D_2O$, ext. $Me_4Si$, ppm): − 15.01, − 17.65, − 39.15, − 39.17, − 43.16, − 43.27. $^1$H-NMR ($C_6D_6$, ext. $Me_4Si$, ppm, rel. int.): 4.20 (t, 2H, ferrocene), 4.07 (s, 5H, ferrocene), 4.00 (t, 2H, ferrocene); 0.43 (s, 6H), 0.31 (s, 6H), 0.21 (s, 6H), 0.20 (s, 6H), 0.17 (s, 6H), 0.15 (s, 6H): $Si(CH_3)$. MS (70 eV) *m*/*e* (rel. int.): 548 [$M^+$, 3], 285 (4), 243 (100), 131 (5), 73 (21).

## 3.7. *X-ray crystallography*

Suitable crystals of **3** and **4** were grown by cooling hexane solutions slowly to − 80°C. The crystals were mounted on a glass fiber. Diffraction data were collected on a Siemens SMART CCD diffractometer at 293 K using graphite monochromated Mo–$K_\alpha$ radiation ($\lambda = 0.71073$ Å), a nominal crystal-to-detector distance of 4.40 cm and 0.3° $\omega$−scan frames. Crystal data and the details of the structure determinations are given in Table 4. The data were corrected for Lorentz and polarization effects and an empirical absorption correction (SADABS [22]) was applied. Structure **3** was solved by the Patterson method while **4** was solved by direct methods (SHELXS-86 [23]). The structure refinement was performed in a full-matrix least-squares against $F^2$ (SHELXTL V5.03 [24]). All non-hydrogen atoms were refined anisotropically, all hydrogen atoms were inserted in ideal positions. The crystals obtained were not of very good quality, what is the reason for the quite high internal R values of the data sets. In structure **3** a strongly disordered solvent molecule, probably hexane, could be partly refined. However only four carbon atoms of this molecule were found and were refined anisotropically without adding hydrogen atoms. The other part of the solvent molecule is generated by the symmetry operation.

# 4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 152536 for compound **3** and 152537 for compound **4**. Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: + 44-1233-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Table 4
Crystallographic data for compounds **3** and **4**[a]

| | **3** | **4** |
|---|---|---|
| Empirical formula | $C_{30}H_{44}FeN_2Si_6C_6H_{14}$ | $C_{30}H_{44}FeN_2Si_6$ |
| Formula weight | 657.06 | 657.06 |
| Color | Red | Red |
| Crystal size (mm) | 0.36 × 0.12 × 0.10 | 0.40 × 0.14 × 0.10 |
| Crystal system | Triclinic | Monoclinic |
| Space group | $P\bar{1}$ | $P2_1/c$ |
| $a$ (Å) | 8.9262(18) | 14.04(4) |
| $b$ (Å) | 13.652(4) | 7.81(2) |
| $c$ (Å) | 17.360(4) | 33.92(11) |
| $\alpha$ (°) | 98.19(2) | 90.00 |
| $\beta$ (°) | 90.12(3) | 90.96 |
| $\gamma$ (°) | 105.00(2) | 90.00 |
| $V$ (Å$^3$) | 2020.8(9) | 3718.(19) |
| $Z$ | 2 | 4 |
| Absorption coefficient (mm$^{-1}$) | 0.575 | 0.620 |
| Detector distance (mm) | 44 | 44 |
| $\theta$ Range (°) | 2.10–20.81 | 1.20–20.90 |
| Limiting indices | $-8<h<8$, $-13<k<13$, $0<l<17$ | $-13<h<13$, $0<k<7$, $0<l<33$ |
| Reflections collected | 4201 | 3871 |
| Independent reflections | 4201 [$R_{int}=0.36$] | 3871 [$R_{int}=0.17$] |
| Observed reflections [$I>4\sigma(I)$] | 3408 | 3037 |
| Parameters/restraints | 389/0 | 353/0 |
| Final $R$ indices [$I>4\sigma(I)$] [a] | $R_1=0.0380$, $wR_2=0.0931$ | $R_1=0.0668$, $wR_2=0.1745$ |
| $R$ indices [all data] | $R_1=0.0517$, $wR_2=0.1010$ | $R_1=0.0867$, $wR_2=0.2031$ |
| Weighting scheme | $1/\sigma^2F_o+(0.0524P)^2+1.17P$;<br>$P=F_o+2F_c^2/3$ | $1/\sigma^2F_o+(0.0885P)^2+9.8161P$;<br>$P=F_o+2F_c^2/3$ |
| Goodness-of-fit on $F^2$ | 1.023 | 1.172 |
| Extinction coefficient | 0.0011(5) | 0.0003(4) |
| Max and min heights in final difference Fourier synthesis (e Å$^{-3}$) | 0.314, −0.219 | 0.420, −0.366 |

[a] $R_1=\Sigma\,||F_o|-|F_c||/\Sigma\,|F_o|$; $wR_2=[\Sigma\,w(|F_o|-|F_c|)^2/\Sigma\,wF_o^2]^{0.5}$.

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