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# Donor-Acceptor Substituted Cyclohexasilanes: Materials with Potential Nonlinear Optical Properties

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Summary. The dipolar cyclohexasilanes 1-ferrocenyl-4-((2,2-dicyanoethenyl)-phenyl)-decamethylcyclohexasilane (1) and 1-ferrocenyl-3-((2,2-dicyanoethenyl)-phenyl)-decamethylcyclohexasilane (2) were synthesized by conventional methods and fully characterized. Electronic absorption spectroscopic studies suggest increased  $\sigma$ - $\pi$  interactions in the cyclohexasilane derivatives when compared to their open-chained analogues. Small but noticeable electron transmission effects *via* the cyclohexasilanyl group can be derived from cyclic voltammetric data. Significantly increased values of the quadratic hyperpolarizabilities  $\beta$  in solution for 1 and 2 are shown by preliminary results of measurements using the EFISH technique.

Keywords. Polysilanes; UV spectroscopy; Cyclic voltammetry; Nonlinear optics.

# Introduction

Interactions in materials showing nonlinear optical (NLO) properties change the nature of the incident light such that new field components are produced. These materials are of technological importance in areas that utilize optical devices, with potential applications in optical signal processing, switching, and frequency generation [1]. Whereas inorganic solids such as LiNbO<sub>3</sub> and  $KH_2PO_4$  have traditionally been the NLO materials of choice, recent results suggest that molecule-based organic or organometallic materials possess superior NLO characteristics [2]. Key advantages of all organic NLO materials include the high intrinsic nonlinearities of individual organic molecules, the ability to use molecular engineering to tailor properties for specific applications, low DC dielectric constants, low temperature processing, and sometimes very fast response times. Organometallic structures additionally permit NLO responses to be tuned in ways not possible for purely organic molecules simply by variation in metal, oxidation state, ligand environment, and geometry. The search for novel organic and organometallic molecules displaying optimal nonlinear optical properties is therefore currently an intense area of research in both academia and industry.

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Quite recently, organic materials with second-order nonlinear optical properties have been the subject of intense investigation, leading to the development of certain structure/NLO property relationships. Thus, large second-order molecular hyperpolarizabilities ( $\beta$ ) are always associated with chromophores comprised of electron donors and acceptors linked by a conjugated  $\pi$ -system. The majority of systems which have been explored for second order nonlinear optics fall into the classes of donor-acceptor substituted benzenes, biphenyls, stilbenes, thiophenes, and related structures. The nonlinearity of such molecules can be enhanced by either increasing the conjugation length, thereby increasing electron delocalization, or increasing the strength of donor or acceptor groups to improve electron asymmetry within the molecule. Several reports have appeared in the recent literature quoting appreciable second-order nonlinear optical susceptibilities for organometallic chromophores containing ferrocene as a donor. Two molecules, trans-1-ferrocenyl-2-(N-methylpyridinium-4-yl)-ethylene iodide [3] and *cis*-1-ferrocenyl-2-(4-nitrophenyl)-ethylene [4] have been reported to possess rather large powder nonlinearities (220 and  $62 \times$  urea, respectively) and have sparked subsequent research activity in this area. Nowadays, ferrocene-based systems are prominent in the class of organometallic NLO compounds [2b, c], what is mainly due to attractive features like stability towards air, elevated temperatures, or light and synthetic versatility.

An undesirable feature associated with nearly all organic and organometallic NLO materials is their often strong absorption in the visible light region, thus dramatically limiting the applicability of the corresponding materials *e.g.* for frequency doubling of the fundamental wavelength of a 820 nm laser requiring transparency at the first and second harmonic wavelengths near 800 and 400 nm. Consequently, the search for new compounds with increased transparency combined with high nonlinear efficiency remains a crucial challenge for various applications. Recently, several reports have appeared in the literature [5] concerning the synthesis and characterization of dipolar silicon compounds of the type shown below with an extended transparency range combined with interesting nonlinear optical activities.



n = 2, 3, 4, 6  $D = NMe_2$ , MeS, MeO, F, SiMe<sub>3</sub>, Si<sub>2</sub>Me<sub>5</sub>  $A = HC=C(CN)_2$ , CF<sub>3</sub>, SO<sub>2</sub>R

Connecting the donor and acceptor groups by polysilane backbones is considered to be attractive because of the following features: *i*) increased polarizability of silicon chains as compared to the carbon analogues, *ii*)  $\sigma$ - $\pi$ -interactions ( $\sigma$ (Si)- $\pi$ (C)), and *iii*) electron delocalization over the Si–Si bonds *via*  $\sigma$ -conjugation [6]. Silicon, however, was found to be only a weak charge transmitter when donor and acceptor phenyl-Si-phenyl moieties are connected in compounds of type **I**. The nonlinear optical behaviour as shown by measurements of the quadratic hyperpolarizabilities  $\beta$  using the EFISH technique easily can be accounted for by a vectorial additive model where the charge transfer interactions contributing to the overall nonlinearity are confined within the donor and the acceptor subunits. Quite similar results have been independently obtained by *Pannell et al.* [7] and in our laboratories [8] for linear polysilanes containing ferrocene as a donor and various organic acceptor groups.

In the present work the influence of the structure of the polysilane bridge on charge transfer properties in related donor-acceptor substituted organosilicon compounds is studied. In cyclic polysilanes, delocalization of  $\sigma$ (Si-Si) electrons over the ring silicon atoms gives these molecules a variety of properties resembling those of aromatic hydrocarbons [9]. Cyclopolysilanes, therefore, might be much more effective charge transmitters in dipolar structures like I compared to the open chained analogues. Thus, we report the synthesis and UV/Vis absorption spectroscopic as well as electrochemical studies of the novel cyclohexasilane derivatives 1 and 2 bearing ferrocene as a donor and the (2,2-dicyanoethenyl)-phenyl group as an acceptor.



## **Results and Discussion**

## Synthesis

The method used to prepare compounds 1 and 2 in this work mainly follows reaction sequences originally developed by *Pannell* [7] and *Mignani* [5b] for the synthesis of similar donor-acceptor substituted oligosilanes. The description of the synthesis of 1 is shown in Scheme 1. Compound 2 has been prepared analogously starting from 1,3-dichlorodecamethylcyclohexasilane. In both cases, the *E*,*E*-isomer has been isolated selectively by crystallization from hexane and used for further studies.

Closely related reaction sequences were used to prepare the reference compounds ((2,2-dicyanoethenyl)-phenyl)-undecamethylcyclohexasilane (3) and ferro-



Scheme 1. Synthesis of compound 1

cenylundecamethylcyclohexasilane (4) from chloroundecamethylcyclohexasilane and 1,4-dibromobenzene or ferrocenyllithium, respectively (Eqs. (1) and (2)).

$$\begin{array}{ccc} \text{Me}_{11}\text{Si}_{6}\text{Cl} & \xrightarrow{11 \text{ LiPhBr 2) BuLi}} & \text{Me}_{11}\text{Si}_{6}\text{PhCHO} & \xrightarrow{\text{CH}_{2}(\text{CN})_{2}} & \text{Me}_{11}\text{Si}_{6}\text{PhCH} = \text{C(CN)}_{2} & (1) \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & & \\ & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & &$$

All products were characterized by standard spectroscopic techniques (<sup>29</sup>Si, <sup>13</sup>C, and <sup>1</sup>H NMR, EI-MS) and elemental analysis. The results are in accordance with the proposed structures in all cases.

	$\lambda_{ m max}/ m nm^a$	$\varepsilon/\mathrm{mol}^{-1}\cdot\mathrm{cm}^{-1\mathrm{a}}$	$E_{\rm f}/{ m V}^{ m b,c}$	$E_{\rm pa}/{ m V}^{\rm b}$	$E_{\rm pc}/{ m V^b}$
1	230 sh	20000			
	279	10100	0.04	0.97	-1.68
	368	17500			
2	230 sh	21000			
	281	12600	0.04	0.97	-1.67
	367	17300			
3	289	12300		1.10	-1.69
	366	23000			
4	456 <sup>d</sup>	220 <sup>d</sup>			
	328 <sup>d</sup>	160 <sup>d</sup>	0.02	0.93	
	260 sh	8500			
	225 sh	20300			

Table 1. Electronic absorption and cyclic voltammetric data for compounds 1-4

<sup>a</sup> Data measured for cyclohexane solutions of  $c = 2 \cdot 10^{-5} M$ ; <sup>b</sup> conditions: sample concentration  $10^{-3} M$ , electrolyte Bu<sub>4</sub>NBF<sub>4</sub> (0.1 *M*), CH<sub>2</sub>Cl<sub>2</sub> solution, scan rate 50 mV, potentials quoted *vs*. ferrocene/ferrocenium; <sup>c</sup>  $E_{\rm f} = (E_{\rm pa} + E_{\rm pc})/2$ ,  $\Delta E_{\rm p} = 180$  mV; <sup>d</sup> sample concentration  $4 \cdot 10^{-4} M$ 

# Electrochemical studies

To gain more insight into the electronic properties of compounds 1 and 2, we studied their redox behavior by cyclic voltammetry. The pertinent data are presented in Table 1 together with data obtained for the reference compounds 3 and 4 which represent reasonable model systems to estimate the properties of the donor and the acceptor group in the absence of interaction. The representative cyclic voltammogram of compound 1 is shown in Fig. 1.

The irreversible wave at high cathodic potential can be attributed to reduction processes of the dicyanovinyl group. The electron donating ferrocene moiety affects the reduction potentials; thus, 1 and 2 exhibit 10 and 20 mV anodic shifts, respectively, in the reduction potential relative to 4.



E/V vs. ferrocene/ferrocinium

Fig. 1. Cyclic voltammogram for 1

The first anodic wave observed in 1, 2, and 4 displays electrochemical reversibility with a peak potential  $E_{pa}$  positioned close to that of the unsubstituted ferrocene. It is therefore reasonable to assign it to the ferrocene moiety. Due to the electron withdrawing dicyanovinyl group, 1 and 2 exhibit 20 mV anodic shifts relative to 4. The  $\Delta E_p$  values ( $E_{p(anodic)} - E_{p(cathodic)}$ ) of the standard ferrocene and the compounds used in this study fall in the same range. Thus, the ferrocene oxidation may be termed as reversible or *quasi*-reversible one electron transfer. In contrast, the second oxidation step in 1, 2, and 4 (and the first one in 3) displays complete electrochemical irreversibility. Comparing the shape and maximum with unsubstituted Si<sub>6</sub>Me<sub>12</sub> ( $E_{pa} = 1.06$  V) it seems clear that this irreversible oxidation occurs in the cyclohexasilanyl part of the molecule. Including reference compounds 3 and 4, the differences in the oxidation potentials reflect the electron withdrawing or donating properties of the substituents. Thus, the cyclohexasilanyl group shows significant higher oxidation potentials in 1 and 2 than in 3, but lower ones than in 4.

Although a measuring accuracy below 10 mV seems not defendable with regard to the rather high peak separation of 180 mV for the ferrocene/ferrocenium couple, the data underline that there is a noticeable transmission effect *via* the cyclohexasilanyl group. However, it is rather small compared to that of a vinyl bridge. Cyclic voltammetric studies of 2-(4-(2-ferrocenylvinyl)-benzylidene)-malononitrile showed an anodic shift of 70 mV for the ferrocene group [10], which is about twice as much compared to **1** and **2**.

# UV/Vis spectra

Solution electronic absorption spectroscopic studies of compounds designed to possess second order NLO properties are important to determine the transparency region and to study the solvatochromic behavior of the sample. Pronounced solvatochromism is generally considered as indicative of intramolecular charge transfer upon electronic excitation, what is a prerequisite for high molecular hyperpolarizabilities  $\beta$ . The electronic absorption spectra of compounds 1 and 2 were recorded in solvents of different polarity; the corresponding data are presented in Tables 1 and 2. The UV absorption spectra of 1 and 2 are displayed in Fig. 2. Figure 3 shows the spectra of the reference chromophores 3 and 4.

The spectrum of compound 4 exhibits two weak absorption maxima near 460 and 330 nm (compare Fig. 2) typical for silylated ferrocenes, which are nearly unaffected by the structure of the silyl substituent attached [11]. These bands apparently are superimposed by much stronger bands appearing around 280 and 370 nm in the spectra of 1, 2, and 3.

As shown in Fig. 2, the spectra of 1 and 2 resemble the calculated sum spectrum of the separate chromophores as represented by compounds 3 and 4. The absorption spectra of 1 and 2, therefore, seem to fulfill the classical expectation for nonconjugatively connected chromophores.

Furthermore, the solvatochromic shifts are small (<5 nm) when the solvent is changed from apolar to polar (compare Table 2). In agreement with the electrochemical studies, the above features indicate rather limited intramolecular charge



Fig. 2. Electronic absorption spectra of 1 and 2 ( $c = 2 \cdot 10^{-5} M$ ) in cyclohexane solution and calculated sum spectrum of 3 and 4

transfer from the donor to the acceptor group via the polysilanyl bridge upon electronic excitation in 1 and 2.

Most striking is the close similarity of the absorption spectra of 1, 2, and 3, regardless of the presence of ferrocene and of the relative position of the donor and the acceptor moiety at the cyclohexasilane ring in 1 and 2. The 280 nm band appearing in the spectra of 1, 2, and 3 can be assigned to the perturbed  $\sigma$ - $\sigma^*$ transition within the cyclohexasilaryl ring simply by comparison with literature values [12]. According to literature data available for linear polysilanes containing the dicyanovinyl acceptor along with various donor groups [5a,b,f], the 370 nm band can be assigned to the  $\pi$ - $\pi^*$  transition of the acceptor-containing phenyl ring. In 1, 2, and 3, however, the band appears considerably red shifted (20-30 nm) due to enhanced  $\sigma$ - $\pi$  interaction of the cyclohexasilane  $\sigma$ -(Si-Si)- and the phenyl  $\pi$ system. Compared to open chained organosilicon fragments, therefore, the cyclohexasilane ring should be markedly more effective as an electron releasing group [13]. In preliminary studies quite exceptional values of the first hyperpolarizability  $\beta$  have been measured for compounds 1 and 2 (up to 3 times that of the open chained analogues) using the EFISH technique [14]. This improved optical nonlinearity very likely may be attributed to the increased donor capacity of the cyclohexasilane ring mentioned above, hence facilitating intramolecular charge



Fig. 3. Electronic absorption spectra of 3 and 4 in cyclohexane solution

	C <sub>6</sub> H <sub>12</sub>	CH <sub>3</sub> CN	CH <sub>2</sub> Cl <sub>2</sub>
<b>1</b> <sup>a</sup>	279	281	278
	368	364	363
<b>2</b> <sup>a</sup>	281	280	279
	367	363	364
<b>3</b> <sup>a</sup>	289	292	296
	366	364	378
<b>4</b> <sup>b</sup>	328	325	325
	456	455	458

Table 2. Solvatochromic data for compounds 1-4

<sup>a</sup> Data measured for solutions of  $c = 2 \cdot 10^{-5} M$ ; <sup>b</sup> sample concentration  $10^{-3} M$ 

transfer from the Si<sub>6</sub> fragment to the dicyanovinyl acceptor *via* the aromatic ring [5a]. The question to what extent the presence of the ferrocene group is crucial for the magnitude of  $\beta$  in **1** and **2** at all is currently the matter of ongoing investigations.

## **Conclusions**

In conclusion, it has been shown by UV/Vis and electrochemical studies that the ferrocenyl donor and the (2,2-dicyanoethenyl)-phenyl acceptor group interact only weakly when linked through a cyclohexasilanyl bridge. UV/Vis absorption spectroscopy, however, provides evidence that  $\sigma$ (Si-Si)- $\pi$ (phenyl) interactions and, consequently, the electron releasing character of the polysilanyl fragment are enhanced in the cyclohexasilane derivatives investigated as compared to their open-chained analogues. Improved optical nonlinearities observed for compounds 1 and 2 in preliminary studies may be due to more facile charge transfer processes within the cyclohexasilanyl-phenyl acceptor moiety. Further studies to substantiate this assumption are currently in progress in our laboratories.

# **Experimental**

All experiments were performed under a nitrogen atmosphere using standard *Schlenk* techniques. All solvents were dried with sodium-potassium alloy 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 over 4 Å molecular sieve and distilled from CaH<sub>2</sub> prior to use. Ferrocenyllithium [15] and the starting silicon compounds 1-chloroundecamethyl-cyclohexasilane [16], 1,3-dichlorodecamethylcyclohexasilane, and 1,4-dichlorodecamethylcyclohexasilane [17, 18] were synthesized as previously reported. Cyclic voltammetric studies were performed at room temperature with a Wenking LB 95 M potentiostat and a Wenking POS 73 scan generator using a 0.1 *M* solution of Bu<sub>4</sub>NBF<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub>, a platinum disk (500 µm) microelectrode, a Pt counter electrode, and a Ag/AgCl reference electrode. The sample concentration was  $10^{-3} M$  and the scan rate 50 mV. Potentials are quoted relative to the ferrocene/ferrocinium redox couple [19].

#### 1,4-Bis-(4-bromophenyl)-decamethylcyclohexasilane

To a solution of 35.0 g (89.8 mmol) of 1,4-dichlorodecamethylcyclohexasilane in  $100 \text{ cm}^3$  diethyl ether, a  $-70^{\circ}\text{C}$  cold solution of 4-bromophenyllithium (prepared from 65.1 g, 276.1 mmol of 1,4-dibromobenzene, and 276.1 mmol of *n*-butyllithium in  $2000 \text{ cm}^3$  of diethyl ether) was added dropwise [20]. The mixture was stirred for 2 h at room temperature and subsequently refluxed for 1 h. After aqueous workup with  $50 \text{ cm}^3$  of saturated NH<sub>4</sub>Cl solution, the combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvent was stripped off in vacuum. Recrystallization of the crude product from  $200 \text{ cm}^3$  of 1-propanol affords pure white crystals of 1,4-*bis*-(4-bromophenyl)-decamethylcyclohexasilane in 65% yield.

#### 1-Chloro-4-(4-bromophenyl)-decamethylcyclohexasilane

 $5.9 \text{ cm}^3$  (67.6 mmol) of triflic acid were added to a solution of 40.6 g (64.4 mmol) of 1,4-*bis*-(4bromophenyl)-decamethylcyclohexasilane in 1000 cm<sup>3</sup> of toluene at  $-20^{\circ}$ C over a period of 7 h. The mixture was stirred at room temperature overnight, and 300 cm<sup>3</sup> of toluene were removed in vacuum and replaced by diethyl ether. 6.1 g (144.2 mmol) of anhydrous LiCl were added at 0°C, and the mixture was stirred for another 12 h at room temperature. After removal of the solvent in vacuum, 200 cm<sup>3</sup> of petroleum ether were added, and the solution was filtered. Petroleum ether was stripped off from the filtrate, and the resulting solid residue was sublimed at 120°C and 10<sup>-2</sup> mbar to give the title compound in 75% yield.

#### 1-Ferrocenyl-4-(4-bromophenyl)-decamethylcyclohexasilane

A solution of ferrocenyllithium (prepared from 21 g (113 mmol) of ferrocene and 75 mmol of *tert*butyllithium in 150 cm<sup>3</sup> of *THF*; ferrocenyllithium was crystallized by cooling the solution to  $-20^{\circ}$ C overnight, filtering and washing with cold *THF* in order to remove excess ferrocene and *tert*butyllithium) was added slowly to a stirred solution of 24.9 g (48.7 mmol) of 1-chloro-4-(4-bromophenyl)-decamethylcyclohexasilane in 50 cm<sup>3</sup> of *THF* at room temperature. The mixture was refluxed overnight. Subsequently, the solvent was stripped off, and residual ferrocene was removed by sublimation at 50°C and  $10^{-2}$  mbar. After aqueous workup of the resulting orange residue dissolved in diethyl ether with saturated NH<sub>4</sub>Cl solution, the combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. Chromatography on a silica gel column developed by a mixture of heptane/toluene (95:5) affords the desired compound in 27% yield.

#### 1-Ferrocenyl-4-(4-formylphenyl)-decamethylcyclohexasilane

To a solution of 8.62 g (13.1 mmol) of 1-ferrocenyl-4-(4-bromophenyl)-decamethylcyclohexasilane in 80 cm<sup>3</sup> of *THF* at  $-78^{\circ}$ C, a pentane solution of 26.1 mmol of *tert*-butyllithium was added slowly. The mixture was stirred for another 5 min and 10.4 cm<sup>3</sup> of dry *DMF* were added. After stirring the mixture overnight at room temperature, aqueous workup with saturated NH<sub>4</sub>Cl solution and recrystallization of the crude product from pentane afforded 1-ferrocenyl-4-(4-formylphenyl)decamethylcyclohexasilane in 55% yield.

### 1-Ferrocenyl-4-((2,2-dicyanoethenyl)-phenyl)-decamethylcyclohexasilane (1; E,E-isomer)

To a solution of 4.3 g (7.1 mmol) of 1-ferrocenyl-4-(4-formylphenyl)-decamethylcyclohexasilane dissolved in a mixture of  $15 \text{ cm}^3$  of *THF* and  $80 \text{ cm}^3$  of deoxygenated EtOH, 0.52 g (7.8 mmol) of solid malononitrile and a drop of piperidine were added. An immediate colour change from orange to dark red was observed. The mixture was stirred for 45 min (DC monitoring recommended), and the solvents were removed in vacuum. After column chromatography (silica gel) with toluene as the mobile phase and subsequent recrystallization from hexane, exclusively the *E*,*E*-isomer of the title compound was obtained in 50% yield.

M.p.: 152–153°C;  $C_{30}H_{44}FeN_2Si_6$  (657.06); found: C 54.94, H 6.81, N 4.29; calcd.: C 54.84, H 6.75, N 4.21; <sup>29</sup>Si NMR (Toluol/D<sub>2</sub>O, ext. *TMS*, 59.62 MHz):  $\delta = -39.94$ , -40.68, -41.00, -41.64 ppm; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, ext. *TMS*, 300.13 MHz):  $\delta = 7.354$  (s, 2H, phenyl), 7.151 (s, 2H, phenyl), 6.558 (s, 1H, HC=), 4.21 (t, 2H, ferrocene), 4.11 (s, 5H, ferrocene), 4.01 (t, 2H, ferrocene), 0.517 (s, 3H, Si(CH<sub>3</sub>)), 0.401 (s, 3H, Si(CH<sub>3</sub>)), 0.328 (s, 6H, Si(CH<sub>3</sub>)), 0.273 (s, 6H, Si(CH<sub>3</sub>)), 0.261 (s, 6H, Si(CH<sub>3</sub>)), 0.116 (s, 6H, Si(CH<sub>3</sub>)) ppm; <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, ext. *TMS*, 75.47 MHz):  $\delta = 159.09$  (=*C*(CN)<sub>2</sub>), 149.15, 135.73, 131.16, 129.85 (phenyl), 114.60, 113.62 (=C(CN)<sub>2</sub>), 82.80 (HC=), 73.99, 71.35, 69.00 (ferrocene), -3.57, -3.79, -4.62, -5.24, -6.20, -6.42 (Si(CH<sub>3</sub>)) ppm; MS (70 eV): m/z (%) = 656 (2.6, M<sup>+</sup>).

#### 1-Ferrocenyl-3-((2,2-dicyanoethenyl)-phenyl)-decamethylcyclohexasilane (2; E,E-isomer)

The procedure followed was that used for 1 with 35.0 g (89.8 mmol) of 1,3-dichlorodecamethylcyclohexasilane, 65.1 g (276.1 mmol) of 1,4-dibromobenzene, and 276.1 mmol of *n*-butyllithium. The *E*,*E*-isomer was isolated by fractional crystallization from hexane in yields comparable to 1.

M.p.: 152°C;  $C_{30}H_{44}FeN_2Si_6$  (657.06); found: C 55.20, H 6.82, N 4.28; calcd.: C 54.84, H 6.75, N 4.21; <sup>29</sup>Si NMR (Toluol/D<sub>2</sub>O, ext. *TMS*, 59.62 MHz):  $\delta = -38.93$ , -40.99, -41.08, -41.19, -41.81 ppm; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, ext. *TMS*, 300.13 MHz):  $\delta = 7.30$ , 7.28, 7.25, 7.23 (4H, phenyl), 6.51 (s, 1H, HC=), 4.30–4.26 (m, 2H, ferrocene), 4.09 (s, 5H, ferrocene), 4.05–3.94 (m, 2H, ferrocene), 0.53 (s, 3H, Si(CH<sub>3</sub>)), 0.45 (s, 3H, Si(CH<sub>3</sub>)), 0.35 (s, 3H, Si(CH<sub>3</sub>)), 0.34 (s, 3H, Si(CH<sub>3</sub>)), 0.27 (s,

3H, Si(CH<sub>3</sub>)), 0.22 (s, 3H, Si(CH<sub>3</sub>)), 0.21 (s, 3H, Si(CH<sub>3</sub>)), 0.19 (s, 6H, Si(CH<sub>3</sub>)), 0.16 (s, 3H, Si(CH<sub>3</sub>)) ppm; <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, ext. *TMS*, 75.47 MHz):  $\delta = 159.13$  (=C(CN)<sub>2</sub>), 148.94, 135.93, 131.08, 129.81 (phenyl), 114.62, 113.61 (=C(CN)<sub>2</sub>), 82.66 (HC=), 74.61, 73.93, 71.64, 71.38, 70.58, 69.06, 69.00 (ferrocene), -3.43, -3.64, -3.32, -4.79, -4.85, -4.87, -5.76, -5.80, -6.78 (Si(CH<sub>3</sub>)) ppm; MS (70 eV): m/z (%) = 656 (100, M<sup>+</sup>).

#### (4-Bromophenyl)-undecamethylcyclohexasilane

The procedure followed was that used for 1,4-*bis*-(4-bromophenyl)-decamethylcyclohexasilane with 4.0 g (10.8 mmol) of chloroundecamethylcyclohexasilane, 3.7 g (16.2 mmol) of 1,4-dibromobenzene, and 16.2 mmol of *n*-butyllithium. Yield: 5 g (90% based on chloroundecamethylcyclohexasilane).

#### (4-Formylphenyl)-undecamethylcyclohexasilane

The procedure followed was that used for 1-ferrocenyl-4-(4-formylphenyl)-decamethylcyclohexasilane with 4.3 g (8.8 mmol) of (4-bromophenyl)-undecamethylcyclohexasilane in 50 cm<sup>3</sup> of *THF*, 17.6 mmol of *tert*-butyllithium, and 7 cm<sup>3</sup> of *DMF*. Yield: 3.5 g (91%).

#### (2,2-Dicyanoethenyl)-phenylundecamethylcyclohexasilane (3)

The procedure followed was that used for 1-ferrocenyl-3-((2,2-dicyanoethenyl)-phenyl)-decamethyl-cyclohexasilane with 3.1 g (7.1 mmol) of (4-formylphenyl)-undecamethylcyclohexasilane in 15 cm<sup>3</sup> of *THF* and 80 cm<sup>3</sup> of deoxygenated ethanol and 0.5 g (7.7 mmol) of solid molononitrile.

Yield: 2.8 g (81%); m.p.: 77–78°C;  $C_{21}H_{38}N_2Si_6$  (487.29); found: C 51.85, H 8.09; calcd.: C 51.78, H 7.86; <sup>29</sup>Si NMR (Toluol/D<sub>2</sub>O, ext. *TMS*, 59.62 MHz):  $\delta = -39.50$ , -41.08, -41.47, -41.98 ppm; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, ext. *TMS*, 300.13 MHz):  $\delta = 7.0-7.4$  (m, 4H, phenyl), 6.65 (s, 1H, HC=), 0.39 (s, 3H, Si(CH<sub>3</sub>)), 0.22 (s), 0.213 (s), 0.210 (s), 0.20 (s, 24H, Si(CH<sub>3</sub>)), 0.11 (s, 3H, Si(CH<sub>3</sub>)) ppm; <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, ext. *TMS*, 75.47 MHz):  $\delta = 159.74$  (=C(CN)<sub>2</sub>), 148.70, 135.21, 130.53, 129.29 (phenyl), 114.07, 113.05 (=C(CN)<sub>2</sub>), 82.03 (HC=), -4.68, -5.43, -6.53, -6.61, -7.21 (Si(CH<sub>3</sub>)); MS (70 eV): m/z (%) = 486 (4.5, M<sup>+</sup>).

#### Ferrocenylundecamethylcyclohexasilane (4)

The procedure followed was that used for 1-ferrocenyl-4-(4-bromophenyl)-decamethylcyclohexasilane with 5.0 g (13.5 mmol) of chloroundecamethylcyclohexasilane, 5.8 g (31.4 mmol) of ferrocene, and 9 mmol of *tert*-butyllithium in 10 cm<sup>3</sup> of *THF*.

Yield: 5.6 g (80% based on chloroundecamethylcyclohexasilane); m.p.: 118–119°C; C<sub>21</sub>H<sub>42</sub>FeSi<sub>6</sub> (518.93); found: C 48.48, H 8.31; C 48.60, H 8.15; <sup>29</sup>Si NMR (Toluol/D<sub>2</sub>O, ext. *TMS*, 59.62 MHz):  $\delta = -41.75, -41.78, -41.83, -42.20$  ppm; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, ext. *TMS*, 300.13 MHz):  $\delta = 4.18$  (2H, ferrocene), 4.09 (s, 5H, ferrocene), 4.00 (2H, ferrocene), 0.43 (s, 3H, Si(CH<sub>3</sub>)); 0.26 (s, 3H, Si(CH<sub>3</sub>)); 0.24 (s, 3H, Si(CH<sub>3</sub>)); 0.22 (s, 3H, Si(CH<sub>3</sub>)); 0.21 (s, 3H, Si(CH<sub>3</sub>)); 0.15 (s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>) ppm; <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, ext. *TMS*, 75.47 MHz):  $\delta = 73.56, 70.63, 68.40$  (ferrocene), -4.44, -5.54, -5.63, -6.38, (Si(CH<sub>3</sub>)) ppm; MS (70 eV): m/z (%) = 518 (49, M<sup>+</sup>).

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