

The [Cp(CO)₂Fe] (Fp) group as a donor in donor/acceptor substituted disilanes: synthesis, structure and electronic properties of Fp–Si₂Me₄–C₆H₄CH=C(CN)₂

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Abstract

UV–vis absorption spectroscopy and cyclic voltammetry are used to study electronic interactions in the donor/acceptor substituted disilane Fp–Si₂Me₄–C₆H₄CH=C(CN)₂ (Fp = η⁵-C₅H₅Fe(CO)₂) (**1**). The synthesis of **1** was achieved by a conventional chemical route, the model substances Fp–SiMe₃ (**2**), Fp–Si₂Me₅ (**3**) and Fp–Si₂Me₄C₆H₅ (**4**) were obtained by the electrolysis of Fp₂ in the presence of the appropriate chlorosilane. The structure of **1**, determined by X-ray diffraction, exhibits an all-*trans*-array of the Fe–Si–Si–C_{aryl} fragment, a basic requirement for optimal through-bond interaction. UV–vis and CV data indicate strong intramolecular donor/acceptor interaction in **1**.

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1. Introduction

There is considerable interest in the development of organic and organometallic materials showing pronounced second-order nonlinear optical properties of technological significance [1]. It is generally accepted that molecules with both large differences between ground state and excited state dipole moments and large transition dipole moments will have large second-order optical nonlinearities [2]. Pertinent studies revealed that molecular assemblies of appropriate donor and acceptor units joined together by π-bond conjugated bridges nearly perfectly fulfil these requirements. π-Bond conjugated spacers facilitate donor-to-acceptor charge transfer, their effectiveness at electronic coupling can almost readily be seen in form of completely new absorption bands, usually red shifted compared with the absorption bands of the individual donor and acceptor

chromophores, corresponding to direct transitions to highly dipolar D⁺-bridge-A[−] charge transfer states.

Intramolecular electron transfer between redox centers interconnected by various types of more or less rigid, saturated hydrocarbon bridges has also been reported [3] and it has been suggested, that through-bond interaction of the donor and the acceptor moieties via the bridge of σ-orbitals is very likely involved in mediating the electron transfer in such system. Thus, a so called σ-coupled transition with CT character and a hypsochromic shift of the local acceptor absorption band are observed in the UV absorption spectra of D/A-substituted cyclohexanes, when the geometry favors through-bond interaction between the chromophores [4]. Polymethylene-linked anthracene–dialkylaniline bi-chromophores have also been studied extensively [5]. It has been demonstrated by UV absorption and fluorescence spectroscopy, that strong electron-donor–acceptor interaction exists in the ground state of these molecules, when the energy level of the charge transfer state is lowered below that of the localized excited state by appropriate substituents. Under certain circum-

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stances, therefore, σ -bonded D-bridge-A compounds might also be suitable candidates for the synthesis of materials comprising nonlinear optical properties.

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 activity [6]. Although it is well established, that the σ -electrons in polysilanes are delocalized rather effectively along the silicon backbone resulting in unusual electronic properties like low ionization potentials of these polysilane chains [7], silicon was found to be only a weak charge transmitter when donor and acceptor moieties are connected by permethylated Si–Si-chains and the resulting optical nonlinearities are just moderate. Quite similar results independently have been obtained by Pannell et al. [8] and in our laboratories [9] for disilanes containing ferrocene as a donor and various organic acceptor groups.

The present paper describes a study on electron-donor–acceptor interactions in 1-[dicarbonyl(η^5 -cyclopentadienyl)iron]-2-[*p*-(2,2-dicyanoethenyl)phenyl]tetramethyldisilane (**1**) using UV absorption spectroscopy, cyclic voltammetry and X-ray crystallography. Because iron in **1** is bonded to silicon and, thus, directly incorporated into the conjugation path, increased interactions of the donor fragment with the polysilane chain can be expected as compared with the corresponding ferrocenyl derivative 1-ferrocenyl-2-[(2,2-dicyanoethenyl)phenyl]tetramethyldisilane. The model compounds [dicarbonyl(η^5 -cyclopentadienyl)iron]trimethylsilane (**2**), [dicarbonyl(η^5 -cyclopentadienyl)iron]pentamethyldisilane (**3**), 1-[dicarbonyl(η^5 -cyclopentadienyl)iron]-2-phenyltetramethyldisilane (**4**) and *p*-(2,2-dicyanoethenyl)phenylpentamethyldisilane (**5**) are used to describe the properties of the dicarbonylcyclopentadienyliron (Fp) donor and the (2,2-dicyanoethenyl)phenyl acceptor groups bonded to silicon in the absence of interaction.

Among many possible organometallic donors we decided to use the Fp-group in this basic study mainly because of the stability of the Fp–Si-moiety and due to its well established chemistry [10]. Fp-substituted short chain polysilanes, however, previously have been shown to be considerably photolabile [11], which strongly impedes the investigation of the nonlinear optical properties of **1** and related compounds addressed in this study. Preliminary results mainly based on UV absorption spectroscopy suggest that the photochemical decay of **1** follows a similar pathway as already described by Pannell for complexes $\text{FpSi}_2\text{Me}_4\text{C}_6\text{H}_4\text{X}$ where X is an electron withdrawing substituent [11c]. The synthesis of photolytically stable silicon-transition metal based NLO chromophores containing alternative organometallic donors currently is the matter of ongoing studies in our laboratories.

Fp substituted silyl compounds are most commonly made from $[\eta^5\text{-C}_5\text{H}_5]\text{Fe}(\text{CO})_2\text{Na}$ and the appropriate chlorosilane simply by salt elimination [10a]. Based on a work by Ruiz et al. [12], who synthesized Fp–SiMe₃ by the electrolysis of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ (Fp₂) in the presence of ClSiMe₃, we found electrosynthesis to be a convenient alternative avoiding the handling of rather tedious materials like mercury or sodium amalgam. Thus, we applied the electrochemical procedure developed by Ruiz et al. to mixtures of Fp₂ with ClSiMe₂–SiMe₃ or ClSiMe₂SiMe₂Cl in order to extend the scope of the method to the synthesis of the Fp-functional disilanyl derivatives **3** and **4** relevant in the course of the current study.

2. Results and discussion

2.1. Synthesis

As shown in Table 1, electrolysis is excellently suitable for the synthesis of disilanes containing the Fp substituent. High yields of the appropriate target molecules **3** and **4** were obtained using this simple method, which is fast and easy to perform. As example the electrochemical preparation of **4** is outlined in Scheme 1. Compared with the conventional multi-step chemical route described in the literature for the synthesis of **4** [11b] the procedure is simplified to a one pot reaction with an overall yield of 62% based on ClSiMe₂SiMe₂Cl (compare Scheme 1).

The mechanism proposed by Ruiz et al. for the electrochemical formation of the Si–Fe bond is depicted in Scheme 2. According to this mechanism primarily two electron reduction of the Fp dimer takes place followed by nucleophilic attack of the formed Fp[–] species on the chlorosilane.

Upon upscaling of the reaction in order to get preparative amounts of products, however, we observed, that far less than the stoichiometric amount of electrons (2 F mol^{-1}) is needed to achieve complete conversion. Monitoring of the reaction by ²⁹Si-NMR and IR (disappearance of the band corresponding to the bridging carbonyls in Fp₂ at $\nu_{\text{CO}} = 1784 \text{ cm}^{-1}$) showed, that all of the starting material is already consumed after 5 h, which means that only about 4% of the theoretically necessary charge had to be passed through the solution. Finally, we found that the reaction of chlorosilanes with Fp₂ in the presence of Mg in THF–Bu₄NBr proceeds even without electricity, although the reaction rate is very slow (several days to weeks, depending on the chlorosilane). Obviously, the reaction is catalyzed by the electrochemically induced activation of Mg. As a consequence, a mechanism involving the formation of Grignard type ‘Fp–Mg’ intermediates explains the

Table 1
Electrochemical synthesis of Fp substituted silanes

Starting silane	Reduced species	Product	Number	Percentage isolated yield
Me ₃ SiCl	Fp ₂	FpSiMe ₃	2	66
Me ₃ SiSiMe ₂ Cl	Fp ₂	FpSiMe ₂ SiMe ₃	3	51
ClSiMe ₂ SiMe ₂ Cl	PhBr	ClSiMe ₂ SiMe ₂ Ph		^a
ClSiMe ₂ SiMe ₂ Ph	Fp ₂	FpSiMe ₂ SiMe ₂ Ph	4	62 ^a

^a Based on ClSiMe₂SiMe₂Cl, ClSiMe₂SiMe₂Ph not isolated.

experimental results much better than controlled two electron reduction of Fp₂.

The difunctional derivative **1** could not be prepared electrochemically. When Fp₂ is electrolyzed together with ClSiMe₂SiMe₂-C₆H₄-CH=C(CN)₂, the activated double bond of the dicyanovinyl group reacts preferentially and a complex mixture of products is obtained. Therefore, **1** was made according to Scheme 3 starting from 1-chloro-2-(*p*-bromophenyl)tetramethyldisilane using a reaction sequence similar to the procedure already applied successfully for the preparation of the ferrocenyldisilane Fc-SiMe₂SiMe₂-Ph-CH=C(CN)₂ [8].

Moderately air-sensitive but extremely photolabile yellow crystals of **1** are obtained in an overall yield of 42%. All products were characterized by standard spectroscopic techniques (²⁹Si-, ¹³C- and ¹H-NMR, EI-MS) and elemental analysis. The results (compare Section 4) are in accordance with the proposed structures in all cases.

2.2. X-ray structure of **1**

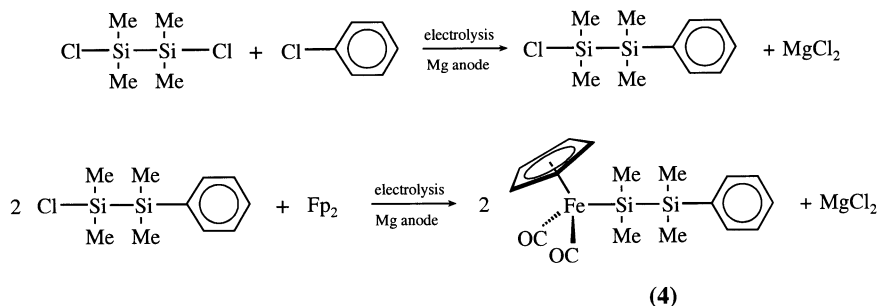
A drawing of the molecular structure of **1** with atom labeling is depicted in Fig. 1. Selected bond lengths and angles are summarized in Table 2.

Compound **1** crystallizes in the centrosymmetric point group *P*2₁/*n* with four molecules in the unit cell. Most of the bond lengths and bond angles are quite unexceptional. The observed Si-Si-bond length is only slightly larger than the common value of 234 pm for disilanes bearing small substituents. The Fe-Si-distance of 232 pm appears to be significantly shorter than the value predicted for a Si-Fe-single bond [13], which is usually

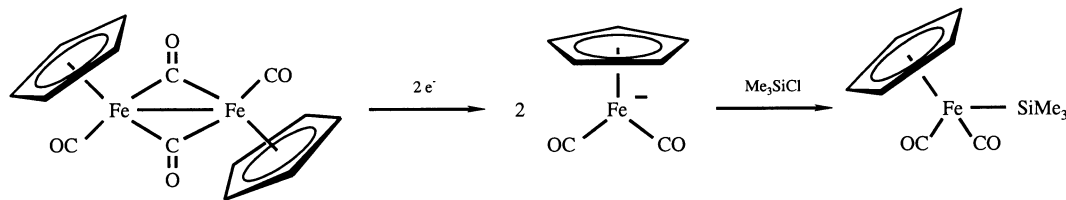
observed for Fp-Si-derivatives [14]. The geometry around the silicon atoms is approximately tetrahedral. The 2,2-(dicyanovinyl)phenyl group appears to be nearly perfectly planar (compare e.g. the dihedral angle of 178° for C(32)-C(33)-C(40)-C(41)). Compound **1** exhibits an all-*trans*-array of the Fe-Si(1)-Si(2)-C(30) fragment and a roughly perpendicular arrangement of the plane of the phenyl ring relative to the Si-Si bond with a torsional angle of 84.0° for Si(1)-Si(2)-C(30)-C(31). The molecular structure adopted by compound **1** in the solid state, therefore, provides an excellent basis for efficient through-bond interaction between the Fp- and the 2,2-(dicyanovinyl)phenyl group via the central Si-Si-bond, because optimal through-bond interaction of functional groups via an array of σ-bonds is only feasible, when the corresponding orbitals and the σ-bonds have an all-*trans* relationship [15].

2.3. UV absorption spectra

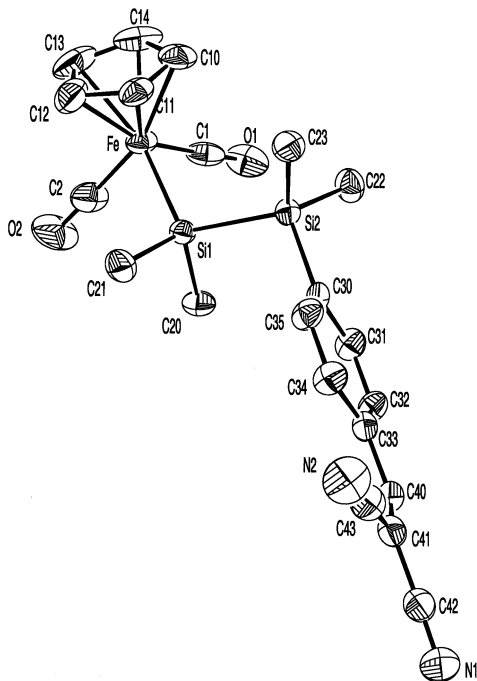
UV absorption data of compound **1** are presented in Table 3 together with data obtained for the reference compounds **2–7** which represent reasonable model systems to estimate the properties of the donor and the acceptor group in the absence of interaction. Ferrocenylpolysilanes of the general structure Fc-(Si)_{*n*}-A, where ferrocene as a donor is linked to the (2,2-dicyanoethenyl)phenyl acceptor group, where shown to exhibit only negligible intramolecular ground state donor-acceptor interactions. Thus, the UV-vis absorption spectrum of 1-ferrocenyl-2-[*p*-(2,2-dicyanoethenyl)phenyl]tetramethyldisilane fulfills the classical expectation for nonconjugatively connected



Scheme 1. Electrochemical synthesis of compound **4**.



Scheme 2. Mechanism for the electrochemical Fe–Si bond formation proposed by Ruiz et al. [12].

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

chromophores, its absorption spectrum being identical to the sum spectrum of the isolated donor and acceptor model systems ferrocenylpentamethyldisilane and *p*-(2,2-dicyanoethenyl)phenylpentamethyldisilane (Fig. 2A).

This situation, however, is quite different for compound **1** comprising two pronounced features in its absorption spectrum: (i) a hypsochromic shift combined with an intensity decrease of the band in the 320 nm region, where the isolated acceptor chromophore shows

its most intense absorption, and (ii) the appearance of a new absorption band at the long wavelength side of the spectrum centered at 360 nm (Fig. 2B). These findings strongly suggest, that **1** exhibits considerable ground state electronic interaction between the Fp and the (2,2-dicyanoethenyl)phenyl chromophores via the Si–Si bond, which is not present in the corresponding ferrocenyl derivative or D/A substituted 1,2-diphenyldisilanes studied in the literature [6]. In order to consider the possibility of intermolecular D/A interaction in compound **1** we recorded the UV spectrum of a mixture of **3** and **5**. However, as the mixture comprises exactly the same spectrum as **3** or **5** alone intermolecular interaction is rather unlikely.

In view of the fact that intramolecular D/A-interactions were also detected in donor-bridge-acceptor compounds containing saturated hydrocarbon bridges [3] and of the electron donor/acceptor character of the substituents it seems logical to assign the 360 nm band appearing in the absorption spectrum of **1** to a transition with considerable charge-transfer character. Although a tentative assignment cannot be given at present, in particular without any fluorescence data, which are not accessible due to the photolytic sensitivity of **1**, we are quite confident to observe direct ground state EDA interaction in the absorption spectrum of the compound. Further support for this assumption is given by the cyclic voltammetry data discussed below.

2.4. Cyclic voltammetric studies

Cyclic voltammetric data of compounds **1**–**7** are presented in Table 3. Within the scan rates of 10–200 mV s^{−1} all oxidation steps display electrochemical

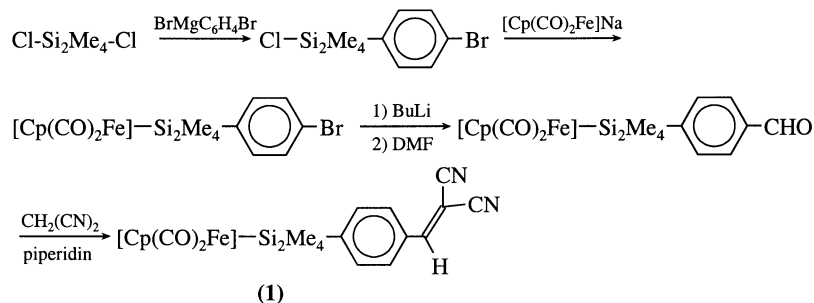
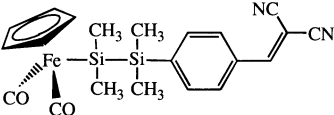
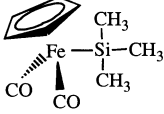
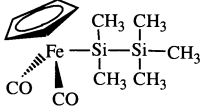
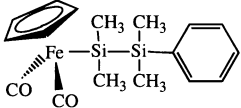
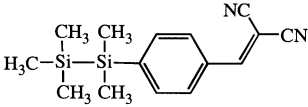
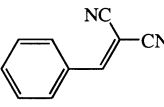
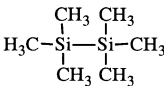
Scheme 3. Synthesis of compound **1**.

Table 2
Selected bond lengths, angles and dihedral angles for compound **1**

<i>Bond lengths</i>	
Si(1)–Si(2)	2.3543(9)
Fe–Si(1)	2.3256(8)
Si(2)–C(30)	1.892(3)
Si–C _{methyl} (mean)	1.884
<i>Bond angles</i>	
Fe–Si(1)–Si(2)	113.34(3)
Si(1)–Si(2)–C(30)	107.11(8)
C _{methyl} –Si–C _{methyl} (mean)	106.89
Si–Si–C _{methyl} (mean)	109.63
C _{cp} –C _{cp} –C _{cp} (mean)	108.00
C _{ph} –C _{ph} –C _{ph} (mean)	120.00
<i>Dihedral angles</i>	
Fe–Si(1)–Si(2)–C(30)	–176.90(8)
Si(1)–Si(2)–C(30)–C(31)	84.0(2)
C(32)–C(33)–C(40)–C(41)	178.0(3)
C(33)–C(40)–C(41)–C(42)	177.5(2)

irreversibility and can be related to the presence of the Fe–Si-skeleton. Introduction of the Fp-group into hexamethyldisilane gives rise to a tremendous decrease of the first oxidation potential (compare the values of E_{pa1} for **7** and **3** in Table 3). This finding is consistent with He(I) and He(II) photoelectron spectroscopy studies of compound **2** [16], showing the lowest valence ionizations to occur from mainly metal based orbitals and an unusually low value of the first ionization potential (7.89 eV as compared with 8.39 eV in **7** [17]). When going from **2** to **3** to **4** the observed cathodic shift increases with extension of the conjugated system. The 120 mV anodic shift observed for the first oxidation potential of **1** relative to **4** indicates the acceptor properties of the 2,2-dicyano-ethenyl group as its introduction leads to an increase of E_{pa} .

Table 3
Electrochemical data and UV absorption maxima for compounds **1–7**

Structure	No.	E_{pa1}^a [V]	E_{pa2}^a [V]	E_{pa3}^a [V]	E_{pc}^a [V]	λ_{max} [nm]	ϵ
	1	0.62	0.90	1.22	–1.64	309 360 sh	19900 12000
	2	0.64	1.24	–	–	–	–
	3	0.58	0.99	–	–	284 330sh	4700 1800
	4	0.50	0.84	1.20	–	330sh	2000
	5	1.30	–	–	–1.66	333	26400
	6	–	–	–	–1.72	225 302	10000 24000
	7	1.46	–	–	–	–	–
3 + 5		0.58	1.09 _{br}	–	–1.66	333	26200

^a vs Fc/Fc⁺, in CH₂Cl₂/Bu₄NBF₄ (0.1 M), ν = 50 mV/s

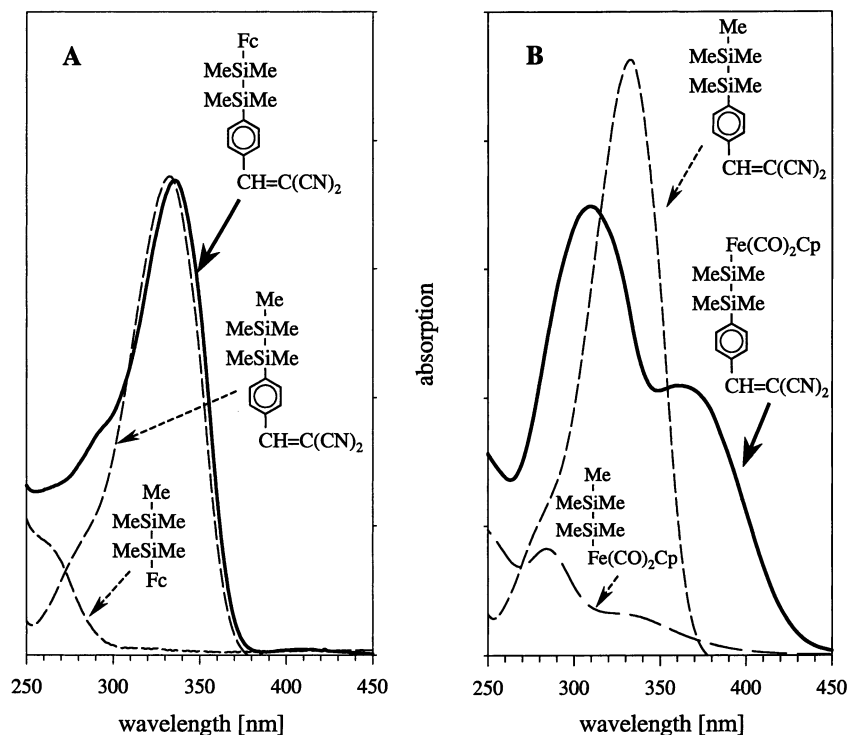


Fig. 2. UV absorption spectra of 1-ferrocenyl-(2,2-dicyanoethenyl)phenylpentamethyldisilane (A) and compound **1** (B) compared with the corresponding donor and acceptor model systems.

The irreversible wave at high cathodic potential (**1**, **5**, **6**) can be attributed to reduction processes of the dicyanovinyl group [18]. Again, the extension of the conjugated system is reflected by a shift of the redox potential; increasing the conjugation from **6** to **5** to **1** the reduction potential moves to more positive values. Thus, **1** exhibits a 80 mV anodic shift in the reduction potential relative to **6**. Intermolecular D/A interaction in **1** is also unlikely on the basis of the electrochemical data, as a mixture of **3** and **5** yielded exactly the same values for E_{pa1} and E_{pc} as **3** or **5** alone.

3. Conclusions

The all-*trans* relationship along the Fe–Si–Si–C fragment of compound **1** in the solid state provides the basis for optimal through-bond interaction between the Fp-donor and the 2,2-(dicyanovinyl)phenyl acceptor via the central Si–Si-bond. The UV absorption and cyclic voltammetry data support this assumption for solutions and indicate remarkable intramolecular electronic coupling within the molecular framework of compound **1**. They show a distinct decrease of the HOMO–LUMO gap upon introduction of the Fp group ($-E_{\text{pc}} + E_{\text{pa1}} = 2.96$ V in **5** and 2.26 V in **1**), which is consistent with the 30 nm bathochromic shift of the first UV absorption band.

4. Experimental

4.1. 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. The water content was checked by Karl Fischer titration to be below 20 ppm. Bu_4NBr and Bu_4NBF_4 (Fluka ‘puriss. electrochem. grade’) was dried in vacuum at 50 °C for 2 days. Me_3SiCl and chlorobenzene were distilled prior to use. Malononitrile and $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ were used as purchased without further purification. *N,N*-Dimethylformamide was allowed to stand on 4 Å molecular sieve and distilled from CaH_2 . $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]\text{Na}$ [19], *p*-(2,2-dicyanoethenyl)phenyl]pentamethyldisilane [20], 1-chloro-2-(*p*-bromophenyl)tetramethyldisilane [6a] and the starting silicon compounds $\text{ClMe}_2\text{SiSiMe}_3$ and $\text{ClMe}_2\text{SiSiMe}_2\text{Cl}$ [21] were synthesized as previously reported. UV–vis absorption spectra were recorded on a Perkin–Elmer Lambda 35 spectrometer in cyclohexane solution. NMR spectra were recorded on a Bruker 300-MSL spectrometer; ^1H -NMR: 300.13 MHz; ^{13}C -NMR: 75.47 MHz; ^{29}Si -NMR: 59.62 MHz. Mass spectra were run either on a HP 5971A/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.

4.2. Cyclic voltammetry

All voltammograms were run under an inert atmosphere at room temperature with a Wenking LB 95M potentiostat/Wenking POS 73 scan generator and recorded with a Kipp and Zonen BD8 flatbed recorder. The three electrode system consisted of a platinum disk microelectrode (500 μm), a Pt counter electrode and a Ag/AgCl reference electrode. 25 ml of a 0.1 M solution of Bu_4NBF_4 in CH_2Cl_2 were introduced into the cell and the silane was added in a concentration of 10^{-3} M. Ferrocene was added at the end of each experiment and used as an internal standard. Thus, all potentials are quoted relative to the ferrocene–ferrocenium redox couple [22].

4.3. General procedure for electrolysis

Constant current supply was afforded by a Wenking STP 84 potentiostat. Electrolysis was carried out in an undivided cell equipped with a magnesium anode in the center and a cylindrical cathode, made of stainless steel, around it. Bu_4NBr was dissolved in a concentration of 0.02 mol l^{-1} in THF, and 50 ml of this solution were introduced into the cell under a dry nitrogen atmosphere. After addition of the silane and the dicarbonyl(η^5 -cyclopentadienyl)iron dimer (Fp_2), electrolysis was carried out at a constant current density of 1 mA cm^{-2} . The reaction was monitored by ^{29}Si -NMR and IR (disappearance of the band corresponding to the bridging carbonyls in Fp_2 at $\nu_{\text{CO}} = 1784 \text{ cm}^{-1}$). After removal of all volatile compounds from the resulting solution at reduced pressure, 60 ml of anhydrous pentane were added to the dark red residue. The precipitated salts were filtered off and washed with pentane twice. Subsequently, the pentane was evaporated and the crude product solved in 5 ml of toluene. After elution with toluene on a silica gel column and removal of excess toluene the pure products are obtained.

4.4. [Dicarbonyl(η^5 -cyclopentadienyl)iron]-trimethylsilane (2) [12]

Me_3SiCl (2.2 g, 20 mmol) and 3.5 g (10 mmol) of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ were electrolyzed for 5 h at 15 mA. Yield 3.3 g (66%). ^{29}Si -NMR (THF/ext. lock D_2O , ext. TMS, ppm): $\delta = 41.6$; consistent with literature [23].

4.5. [Dicarbonyl(η^5 -cyclopentadienyl)iron]-pentamethyldisilane (3)

$\text{Me}_3\text{SiSiMe}_2\text{Cl}$ (1.8 g, 10.8 mmol) and 1.9 g (5.4 mmol) of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ were electrolyzed for 5 h at 15 mA. Yield 1.7 g (51%). ^{29}Si -NMR (THF/ext. lock D_2O , ext. TMS, ppm): $\delta = 16.9$, -11.3 ; consistent with literature [24].

4.6. 1-[Dicarbonyl(η^5 -cyclopentadienyl)iron]-2-phenyltetramethyldisilane (4)

$\text{ClMe}_2\text{SiSiMe}_2\text{Cl}$ (2.5 g, 13.5 mmol) and 1.5 g (13.5 mmol) of chlorobenzene were electrolyzed at 25 mA. After 24 h all of the chlorobenzene was consumed (reaction control by GC–MS) and 2.4 g (6.8 mmol) of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ were added to the solution. After 5 h of further electrolysis the reaction was finished. Yield: 3.1 g (62%). ^{29}Si -NMR (THF/ext. lock D_2O , ext. TMS, ppm): $\delta = 16.7$, -15.2 ; consistent with literature [11b].

4.7. 1-[Dicarbonyl(cyclopentadienyl)iron]-2-(*p*-bromophenyl)tetramethyldisilane

$\text{ClSiMe}_2\text{SiMe}_2(p\text{-BrC}_6\text{H}_4)$ (3.45 g, 11.2 mmol) were dissolved in 50 ml of pentane and added dropwise to 200 ml of a THF solution of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]\text{Na}$ (prepared from 2.0 g (5.6 mmol) of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$, 0.34 g (14.8 mmol) of Na and 40 g of Hg) over a period of 30 min at 0°C . The reaction mixture was then allowed to stir at room temperature for 2 h before the solvents were stripped off in vacuum. After addition of pentane the solution was filtered, concentrated and subjected to column chromatography on a silica gel column. Elution with toluene yielded an orange band, which upon collection, removal of the solvent and recrystallization from pentane gave 4.32 g (86%) of the orange crystalline title complex.

Melting point (m.p.): $77\text{--}78^\circ\text{C}$. Anal. Found: C, 45.73; H, 4.72. Calc. for $\text{C}_{17}\text{H}_{21}\text{BrFeO}_2\text{Si}_2$: C, 45.45; H, 4.71%. IR (heptane): $\nu_{\text{CO}} = 1999, 1948 \text{ cm}^{-1}$. ^{29}Si -NMR (C_6D_6 , ext. TMS, ppm): 16.14 ($\text{Fp-Si}(\text{CH}_3)_2$); -14.83 ($p\text{-BrC}_6\text{H}_4\text{-Si}(\text{CH}_3)_2$). ^1H -NMR (C_6D_6 , ext. TMS, ppm, rel. Int.): 7.38–7.14 (AA'BB', 4H, C_6H_4); 3.94 (s, 5H, C_5H_5); 0.47 (s, 6H, $p\text{-BrC}_6\text{H}_4\text{-Si}(\text{CH}_3)_2$); 0.36 (s, 6H, $\text{Fp-Si}(\text{CH}_3)_2$). ^{13}C -NMR (C_6D_6 , ext. TMS, ppm): 216.05 (CO); 140.80, 136.10, 131.75, 123.94 (C_6H_4); 83.44 (C_5H_5); 3.94 ($\text{Fp-Si}(\text{CH}_3)_2$); -2.19 ($p\text{-BrC}_6\text{H}_4\text{-Si}(\text{CH}_3)_2$). MS (*m/e* (rel. Int.)): 448 [17, M^+]; 420 [7, $\text{M}^+ - \text{CO}$]; 392 [9, $\text{M}^+ - 2\text{CO}$]; 313 (18, $\text{CpFeSi}_2(\text{CH}_3)_4\text{C}_6\text{H}_4^+$); 271 (74, $\text{BrC}_6\text{H}_4\text{Si}_2(\text{CH}_3)_4^+$); 235 (100, $\text{Cp}(\text{CO})_2\text{FeSi}(\text{CH}_3)_2^+$); 213 (27, $\text{BrC}_6\text{H}_4\text{Si}(\text{CH}_3)_2^+$); 207 (15, $\text{Cp}(\text{CO})\text{FeSi}(\text{CH}_3)_2^+$); 193 (62, $\text{C}_6\text{H}_4\text{Si}_2(\text{CH}_3)_4^+$); 179 (16, $\text{CpFeSi}(\text{CH}_3)_2^+$); 177 (23, $\text{Cp}(\text{CO})\text{FeSi}^+$); 149 (21, CpFeSi^+); 121 (25, CpFe^+); 93 (17, CpSi^+); 73 (31, $(\text{CH}_3)_3\text{Si}^+$); 28 (9, CO^+).

4.8. 1-[Dicarbonyl(cyclopentadienyl)iron]-2-(*p*-formylphenyl)tetramethyldisilane

To 120 ml of a cooled (-78°C) THF solution of 4.32 g (9.6 mmol) of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{SiMe}_2\text{SiMe}_2(p\text{-BrC}_6\text{H}_4)$ was added slowly a cyclohexane solution of 9.6 mmol of *n*-butyllithium. The mixture was stirred for another 5 min followed by addition of 3.0 ml (38.9 mmol) of dry DMF. The reaction mixture was then stirred overnight at room temperature and aqueously worked up with saturated NH_4Cl solution. After extraction with diethylether the combined organic layers were dried over Na_2SO_4 and concentrated. Column chromatography (silica gel) with toluene as the mobile phase yielded 3.10 g (81%) of a yellow–brown solid.

M.p. (dec.): 39°C . Anal. Found: C, 54.26; H, 5.55. Calc. for $\text{C}_{18}\text{H}_{22}\text{FeO}_3\text{Si}_2$: C, 54.27; H, 5.57%. IR (heptane): $\nu_{\text{CO}} = 2000, 1949\text{ cm}^{-1}$, $\nu_{\text{CHO}} = 1711\text{ cm}^{-1}$. ^{29}Si -NMR (C_6D_6 , ext. TMS, ppm): 16.40 (Fp–Si(CH_3) $_2$); -14.52 (*p*-OHCC $_6\text{H}_4$ –Si(CH_3) $_2$). ^1H -NMR (C_6D_6 , ext. TMS, ppm, rel. Int.): 9.71 (s, 1H, CHO); 7.61–7.42 (AA'BB', 4H, C_6H_4); 3.93 (s, 5H, C_5H_5); 0.47

(s, 6H, *p*-OHCC $_6\text{H}_4$ –Si(CH_3) $_2$); 0.38 (s, 6H, Fp–Si(CH_3) $_2$). ^{13}C -NMR (C_6D_6 , ext. TMS, ppm): 215.99 (CO); 150.61, 137.28, 134.83, 129.16 (C_6H_4); 83.41 (C_5H_5); 3.93 (Fp–Si(CH_3) $_2$); -2.37 (*p*-OHCC $_6\text{H}_4$ –Si(CH_3) $_2$). MS (*m/e* (rel. Int.)): 398 [44, M^+]; 342 [12, $\text{M}^+ - 2\text{CO}$]; 313 (11, $\text{CpFeSi}_2(\text{CH}_3)_4\text{C}_6\text{H}_4^+$); 235 (49, $\text{Cp}(\text{CO})_2\text{FeSi}(\text{CH}_3)_2^+$); 221 (100, OHCC $_6\text{H}_4\text{Si}_2(\text{CH}_3)_4^+$); 207 (12, $\text{Cp}(\text{CO})\text{FeSi}(\text{CH}_3)_2^+$); 193 (16, $\text{C}_6\text{H}_5\text{Si}_2(\text{CH}_3)_4^+$); 186 (23, CpFeCp^+); 179 (12, $\text{CpFeSi}(\text{CH}_3)_2^+$); 163 (39, OHCC $_6\text{H}_4\text{Si}(\text{CH}_3)_2^+$); 149 (24, CpFeSi^+); 121 (32, CpFe^+); 93 (14, CpSi^+); 73 (22, $(\text{CH}_3)_3\text{Si}^+$); 28 (31, CO^+).

4.9. 1-[Dicarbonyl(cyclopentadienyl)iron]-2-[*p*-(2,2-dicyanoethenyl)phenyl]-tetramethyldisilane (**1**)

To a solution of 3.10 g (7.8 mmol) of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{SiMe}_2\text{SiMe}_2(p\text{-OHCC}_6\text{H}_4)$ in 100 ml of diethylether was added 0.53 g (8.0 mmol) of solid malonodinitrile and one drop of piperidine. In order to guarantee total conversion the mixture was allowed to stir overnight at room temperature (DC monitoring recommended). The solvent was removed under reduced pressure and the bright yellow residue purified by column chromatography (silica gel) with toluene as the mobile phase. Subsequent recrystallization from pentane at -30°C gave 2.37 g (68%) of the yellow crystalline title compound.

M.p.: $128\text{--}130^{\circ}\text{C}$. Anal. Found: C, 56.81; H, 4.92. Calc. for $\text{C}_{21}\text{H}_{22}\text{N}_2\text{FeO}_2\text{Si}_2$: C, 56.50; H, 4.97%. IR (Nujol): $\nu_{\text{CN}} = 2228\text{ cm}^{-1}$, $\nu_{\text{CO}} = 1983, 1933\text{ cm}^{-1}$. ^{29}Si -NMR (C_6D_6 , ext. TMS, ppm): 16.58 (Fp–Si(CH_3) $_2$); -14.06 (*p*-(NC) $_2\text{C}=\text{CHC}_6\text{H}_4$ –Si(CH_3) $_2$). ^1H -NMR (C_6D_6 , ext. TMS, ppm, rel. Int.): 7.32–7.25 (AA'BB', 4H, C_6H_4); 6.48 (s, 1H, $\text{CH}=\text{C}(\text{CN})_2$); 3.95 (s, 5H, C_5H_5); 0.43 (s, 6H, *p*-(NC) $_2\text{C}=\text{CHC}_6\text{H}_4$ –Si(CH_3) $_2$); 0.36 (s, 6H, Fp–Si(CH_3) $_2$). ^{13}C -NMR (C_6D_6 , ext. TMS, ppm): 215.86 (CO); 159.25 ($\text{CH}=\text{C}(\text{CN})_2$); 151.70, 134.96, 131.30, 129.86 (C_6H_4); 114.59, 113.62 (CN); 83.52 (C_5H_5); 82.93 ($\text{CH}=\text{C}(\text{CN})_2$); 3.94 (Fp–Si(CH_3) $_2$); -2.47 (*p*-(NC) $_2\text{C}=\text{CHC}_6\text{H}_4$ –Si(CH_3) $_2$). MS (*m/e* (rel. Int.)): 446 [35, M^+]; 418 [15, $\text{M}^+ - \text{CO}$]; 390 [23, $\text{M}^+ - 2\text{CO}$]; 269 (49, $(\text{NC})_2\text{C}=\text{CHC}_6\text{H}_4\text{Si}_2(\text{CH}_3)_4^+$); 235 (100, $\text{Cp}(\text{CO})_2\text{FeSi}(\text{CH}_3)_2^+$); 211 (21, $(\text{NC})_2\text{C}=\text{CHC}_6\text{H}_4\text{Si}(\text{CH}_3)_2^+$); 207 (10, $\text{Cp}(\text{CO})\text{FeSi}(\text{CH}_3)_2^+$); 186 (28, CpFeCp^+); 179 (13, $\text{CpFeSi}(\text{CH}_3)_2^+$); 121 (29, CpFe^+); 93 (13, CpSi^+); 73 (24, $(\text{CH}_3)_3\text{Si}^+$); 28 (28, CO^+).

Table 4
Crystallographic data for compound **1**

<i>Crystal parameters</i>	
Empirical formula	$\text{C}_{21}\text{H}_{22}\text{FeN}_2\text{O}_2\text{Si}_2$
Formula weight	446.44
Crystal system	Monoclinic
Space group	$P2_1/n$
<i>a</i> (Å)	7.0656(1)
<i>b</i> (Å)	29.2685(1)
<i>c</i> (Å)	10.8184(2)
α (°)	90
β (°)	98.619(1)
γ (°)	90
Volume (Å 3)	2211.97(5)
<i>Z</i>	4
Absorption coefficient (mm $^{-1}$)	0.808
<i>F</i> (000)	928
<i>Data collection</i>	
θ Range (°)	1.39–26.38
Limiting indices	$-8 < h < 8, 0 < k < 36, 0 < l < 13$
Reflections collected	4513
Independent reflections	4512 [$R_{\text{int}} = 0.0476$]
Completeness to $\theta = 26.38^{\circ}$ (%)	99.6
Max and min transmission	0.9092 and 0.7707
<i>Refinement</i>	
Parameters	254
Final <i>R</i> indices	$R_1 = 0.0414, wR_2 = 0.0893$
<i>R</i> indices (all data)	$R_1 = 0.0494, wR_2 = 0.1026$
Weighting scheme	$1/\sigma^2 F_o^2 + (0.0190P)^2 + 2.28P$; $P = (F_o^2 + 2F_c^2)/3$
Goodness-of-fit on F^2	1.270
Extinction coefficient	0.0022(3)
Max and min heights in final difference Fourier synthesis (e Å $^{-3}$)	0.357 and -0.313

4.10. X-ray crystallography

Suitable crystals of **1** were grown by slow diffusion of pentane into a saturated solution of **1** in diethylether. A yellow crystal of the dimensions $0.34 \times 0.28 \times 0.12\text{ mm}$ was mounted on a glass fiber. Diffraction data were

collected on a Siemens SMART CCD diffractometer at 293 K using graphite monochromated Mo–K α radiation ($\lambda = 0.71073$ Å), a nominal crystal-to-detector distance of 4.40 cm and 0.3° ω -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 [25]) was applied. The structure was solved by direct methods (SHELXS86 [26]). The structure refinement was performed in a full-matrix least-squares method against F^2 (SHELXL-93 [27]). All non-hydrogen atoms were refined anisotropically, all hydrogen atoms were inserted in calculated positions.

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 181002, for compound 1. 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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