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Functionalization via hydrosilylation of linear and cyclic siloxanes with appendent first generation dendrons containing electronically communicated ferrocenyl units

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Abstract

The synthesis, structural characterization and redox-properties of a new family of siloxane-based poly(ferrocenyl) dendronized molecules are described. Hydrosilylation reaction of the vinyl-functionalized silicon-bridged biferrocene, CH_2=CHSiMe[Fe(η^5-C_5H_4)(η^5-C_5H_5)]$_2$ (**1**) with Si–H-containing poly(siloxane) backbones afforded the novel copolymer **6** and homopolymer **7**. To understand the properties of these polymers more thoroughly, we also synthesized the well-defined, closely related tetraferrocenyl-functionalized disiloxane and octaferrocenyl-functionalized cyclotetrasiloxane model compounds **4** and **5**. Solution voltammetric studies of the siloxane-based poly(ferrocenyl) derivatives **4**–**7** showed two reversible redox processes with a wave separation (ΔE) of 190–160 mV, indicating that significant electronic communication exists between the ferrocenyl moieties bridged by a pendant silicon atom. The neutral cyclotetrasiloxane-based octaferrocenyl **5**, as well as polymers **6** and **7** become insoluble upon complete oxidation to the corresponding polycationic species, yielding electroactive films onto platinum and glassy-carbon electrode surfaces. The well-defined and persistent redox waves of electrode coated with these films are characteristic of electrochemically stable, surface-confined reversible redox couples. The microstructure of these multimetallic electroactive films has been analyzed by scanning electron microscopy. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Ferrocene; Hydrosilylation; Dendrimers; Polysiloxanes; Modified electrodes; Electrochemistry; Electronic communication

1. Introduction

The discovery of bis(η^5-cyclopentadienyl)iron, ferrocene in 1951 [1], and the subsequent characterization of its structure, stimulated an almost explosive research effort in organometallic chemistry. Since then, metallocenes have attracted enormous interest from both a fundamental and an applied point of view. Particularly, the chemistry of ferrocene-based structures has been receiving increasing attention because of their importance in many fields such as electrochemistry, materials science, organic synthesis and catalysis [2–5]. This is because the ferrocene unit has proved to be a versatile structural moiety with excellent thermal and photochemical stability as well as with unique and valuable redox properties. In this regard, the synthesis of ferrocene derivatives with tailor-made properties has been the goal for many synthetic chemists.

Thus, the ferrocene unit has been successfully incorporated into polymers as a pendant group and also as an integral part of the polymeric backbone [6–8]. In addition, in the last few years, ferrocene-functionalized dendrimers have gained prominence as a new generation of macromolecular materials by virtue of their fascinating structural features and advanced properties [9–22]. Thus, poly(ferrocenyl)-based macromolecules are of interest for their useful application in the chemical modification of electrodes, as electrode mediators, electrochemical sensors, as materials for the construction of liquid crystals, electronic devices, non-linear optical (NLO) systems and as chiral ligands for asymmetric catalysis.

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In this context, in the last years we have been exploring routes for the construction of new families of redox-active organometallic dendritic and polymeric structures, containing ferrocenyl moieties together with linear and cyclic siloxanes, cubic silsesquioxanes [23], and silicon- and nitrogen-based dendrimers as frameworks [9–14]. In these multimetallic systems the ferrocenyl moieties behave as independent, electronically isolated units, and the macromolecules undergo a simultaneous multielectron transfer at the same potential.

One of our synthetic approaches to the synthesis of such ferrocene – containing macromolecuar structures was based on hydrosilylation reactions that exploit the reactivity of Si–H polyfunctionalized carbosilanes and siloxanes toward suitable ferrocenyl derivatives containing reactive vinyl or allyl groups [12,13,23b,c,24]. Hydrosilylation is one of the most important reactions to form Si–C bonds in organosilicon chemistry [25] although its use for the introduction of organometallic moieties into macromolecular structures has not been explored much.

In a recent paper, we described the synthesis and redox properties of the first examples of organometallic dendrimers possessing peripheral electronically communicated ferrocenyl moieties, constructed using a convergent methodology by sequences of hydrosilylation and alkenylation reactions, from the vinyl functionalized biferrocenyl derivative **1**, therefore resulting in dendritic poly(ferrocenyl) structures such as dendron **2** and dendrimer **3** [12].

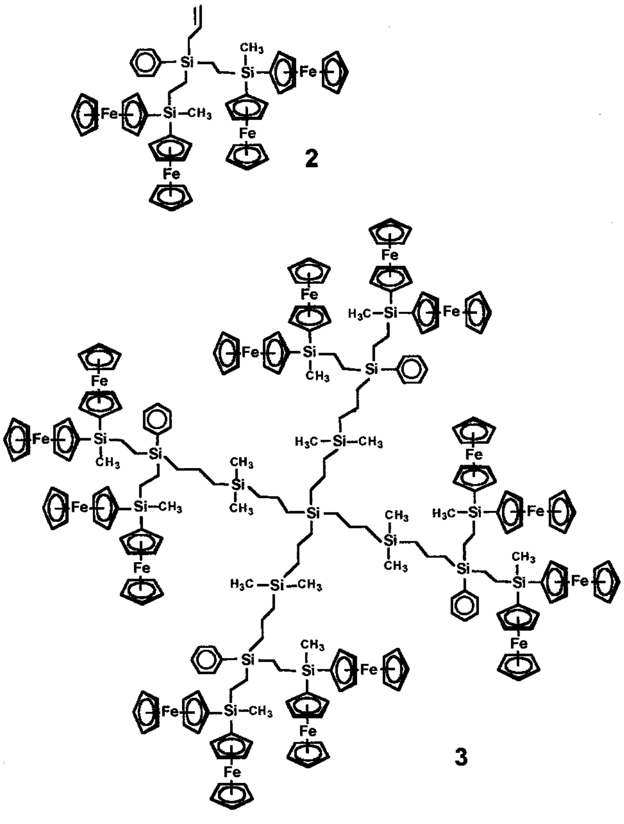


Plate 1.

As a continuation of our efforts toward the development of novel ferrocene-based materials, our objective now is to extend this convergent synthetic strategy to new redox-active macromolecular materials containing dendritic building-blocks with interacting ferrocenyl moieties grafted to multifunctional, flexible poly(-methylsiloxane) backbones. The combination of the unique architectural features of dendritic molecules [26] together with the electronic communication between metal centers and the well-known, remarkable features and properties of poly(siloxanes) (such as chemical stability, high permeability to gases and low toxicity) [27] is an attractive strategy for controlling the physical and redox properties of the resulting hybrid macromolecules.

We herein report the full details on the synthesis via hydrosilylation, characterization and redox properties in solution as well as confined onto electrodes, of a series of siloxane-based multimetallic compounds and polymers containing pendant dendritic wedges possessing electronically communicated ferrocenyl moieties, which represent the first members of a new family of dendronized polymers [28] and may also be useful precursors of mixed-valence compounds that are of interest for the investigation of electron-transfer processes (Chart1; Chart2).

2. Results and discussion

*2.1. Synthesis and characterization of the tetra- and octa-ferrocenyl derivatives **4** and **5***

Our key starting material for the synthesis of the new siloxane-containing multimetallic compounds described here is the bis(ferrocenyl)methylvinylsilane (**1**) that is successfully prepared by the reaction of ferrocenyllithium with vinylmethyldichlorosilane (Scheme 1) [12]. This compound contains a reactive vinyl group attached to the silicon bridge, which enables its incorporation in Si–H polyfunctionalized frameworks.

With the aim of synthesizing via hydrosilylation reactions novel siloxane-based polymers with appendent dendrons, we initially targeted two related well-defined ferrocenyl-functionalized disiloxane and cyclotetrasiloxane [29] model compounds, to facilitate the electrochemical and structural analysis of the targeted polymeric analogs.

Thus, the reaction of **1** with 1,1,3,3-tetramethyldisiloxane, and 1,3,5,7-tetramethylcyclotetrasiloxane, in the presence of catalytic amounts of Karstedt catalyst, in toluene solution at 45 °C, afforded the desired hy-

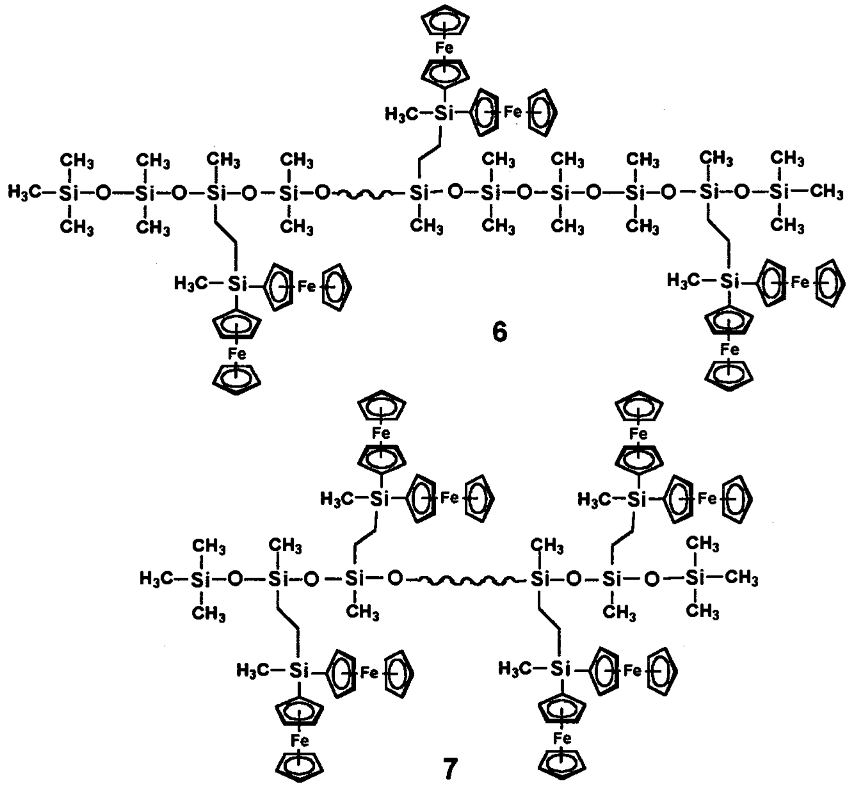


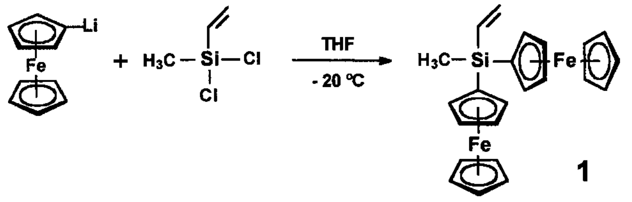
Plate 2.

drosilylated multimetallic compounds **4** and **5** (Scheme 2). ^{1}H-NMR spectroscopy was used to follow the progress of the reactions, and it was established that the complete reaction of the Si–H functionalities was achieved easily under these mild conditions. Purification of the resulting hydrosilylated products was effected by column chromatography on silica using mixtures of hexane and THF as eluent (see Section 4). The desired tetra- and octaferrocenyl compounds **4** and **5** were isolated in high yields as air stable, orange crystalline solids [30].

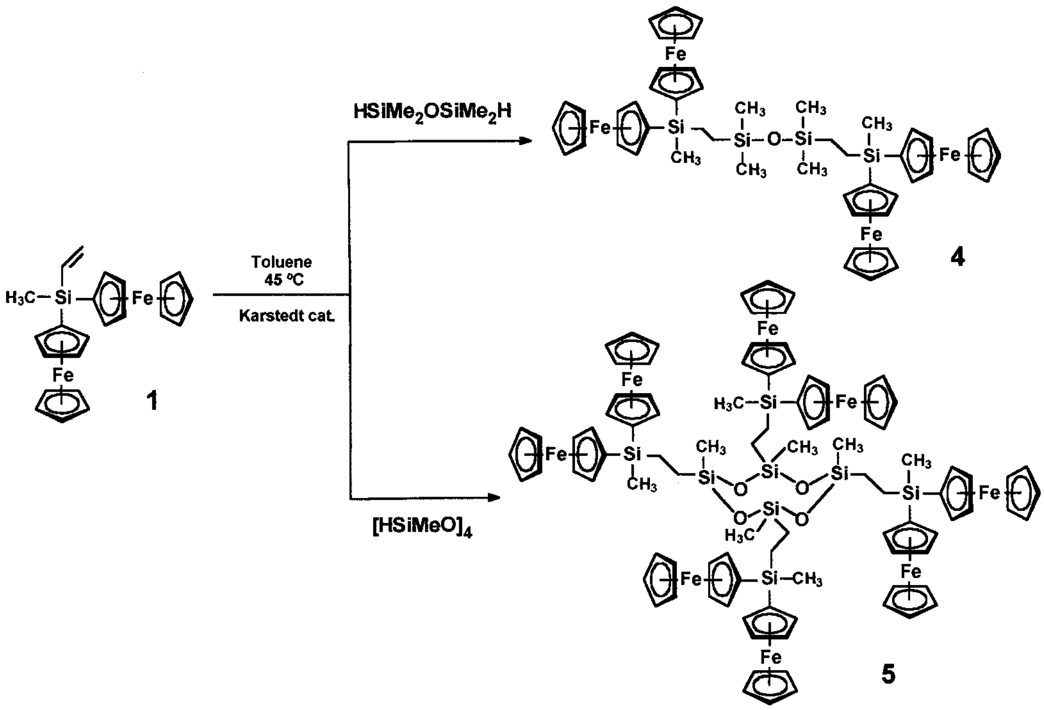
The new poly(ferrocenyl) functionalized siloxanes **4** and **5** were structurally characterized by microanalysis, IR, ^{1}H-, ^{13}C- and ^{29}Si-NMR spectroscopies and matrix-assisted laser desorption and ionization time-of-flight mass spectrometry (MALDI-TOF-MS). In the ^{1}H-NMR spectra of both new compounds, confirming the evidence of a complete functionalization of all the reactive Si–H sites in the siloxane backbone with silicon-bridged biferrocenyl moieties, is provided by the total absence of the Si–H resonance near 4.7 ppm, as well as by the expected integration of the protons corresponding to the ferrocenyl groups (which appear in the range of 4.35–4.08), the methylene units, and the methyl groups of the siloxane framework. Interestingly, ^{1}H- and ^{13}C-NMR spectra show that only the β-isomers were formed and no Markonikov addition (which would lead to α-isomers) took place, resulting in molecules with maximum symmetry. The MALDI-TOF-MS of **4** and **5** show a single signal at m/z 1014.0, and 2001.3, respectively, which in both cases correspond to the correct molecular mass (see for example Fig. 1A).

*2.2. Synthesis and characterization of copolymer **6** and homopolymer **7***

We are particularly interested in employing hydrosilylation chemistry for the construction of novel dendronized poly(siloxanes) by using wedge-shaped dendritic fragments such as **2** that contains a reactive allyl group at the focal point. In this respect, besides the application of **1** as a precursor for the well-defined tetra- and octaferrocenyl compounds **4** and **5**, the hydrosilylation of the vinyl functionalized silicon-bridged biferrocene **1** with Si–H polyfunctionalized silicones may serve as useful reference model reactions [31].



Scheme 1.



Scheme 2.

Karstedt-catalysed hydrosilylation reactions of the poly(methylhydrosiloxane)–poly(dimethylsiloxane) copolymer, $(Me_3SiO)(Me_2SiO)_m(MeSiHO)_n(Me_3Si)$ ($m = 70–75\%$, $n = 25–30\%$), and poly(methylhydrosiloxane), $(Me_3SiO)(MeSiHO)_n(Me_3Si)$ ($n \approx 35$) with **1** were carried out under more forcing conditions than in the case of the model compounds **4** and **5**, in order to assure a maximum functionalization of the Si–H groups of the poly(siloxane) backbones. In general, the reactions were run overnight, which was sufficient in both cases for complete disappearance in the IR spectrum of the ν(SiH) band, near 2155 cm^{-1}. After the filtration of the reaction mixture and evaporation of the solvent, purification of the resulting new hydrosilylated products **6** and **7** was effected by repeated dissolution in dichloromethane and precipitation with ethanol in the case of **6**, and hexane for **7**. The final compounds were isolated as air-stable materials. Compound **6** is an orange–brown tacky oil, which hardens on standing, soluble in solvents such as dichloromethane and THF. Homopolymer **7** is an orange–brown shiny solid, soluble in dichloromethane and THF and insoluble in hexane and DMF. Both polymers form amber-free standing films when cast from dichloromethane solutions.

Structural characterization of poly(ferrocenyl) polymers **6** and **7** was achieved by FTIR, and ^{1}H-, ^{13}C- and ^{29}Si-NMR spectroscopies and MALDI-TOF-MS. Significantly, IR analysis of **6** and **7** indicates a quantitative functionalization of the Si–H sites of the polymeric backbone. The ^{1}H-NMR spectra are very similar to those of the model compounds **4** and **5**, and show broad resonances for the three sets of cyclopentadienyl

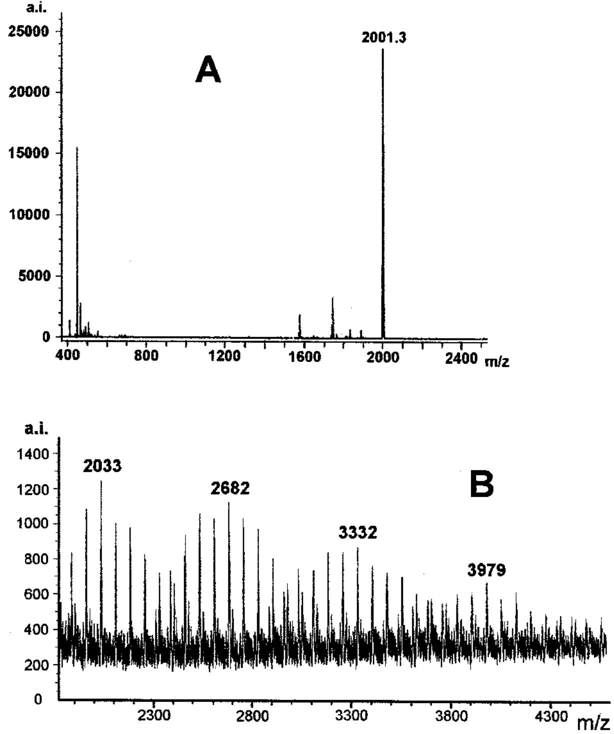


Fig. 1. MALDI-TOF-MS of: (A) the cyclotetrasiloxane-based octaferrocenyl compound **5**; and (B) copolymer **6**.

Table 1
Cyclic voltammetric data for the poly(ferrocenyl) compounds **1**–**7**

	Solution $^{1}E_{1/2}$ (V)	$^{2}E_{1/2}$ (V)	ΔE (mV)	K_c	Modified electrode $^{1}E'_{1/2}$ (V)	$^{2}E'_{1/2}$ (V)
1	0.45 [a]	0.63 [a]	180	1104		
2	0.42 [a]	0.59 [a]	170	750		
3	0.41 [b]	0.58 b	170	750	0.41	0.54
4	0.40 [a]	0.59 [a]	190	1629		
4	0.39 [b]	0.57 [b]	180	1104		
5	0.39 [b]	0.55 [b]	160	507	0.42	0.55
6	0.41 [b]	0.57 [b]	160	507	0.42	0.57
7	0.45 [c]	0.55 [c]	100		0.42	0.53

[a] CH_2Cl_2.
[b] CH_2Cl_2–CH_3CN (5:1.5).
[c] These values correspond to E_{pa}.

protons near 4.3, 4.1 and 4.07 ppm for both the polymers, together with the resonances assigned to the protons in the organic groups attached to silicon. In the ^{13}C-NMR spectra each of the observed resonances was found to agree with the different carbon atoms present in the molecules, thus providing further support for the structural assignments. The ^{29}Si-NMR spectrum of **6** consists of a single resonance at -3.96 ppm assigned to the silicon atoms bridging the two ferrocenyl units, a resonance at 7.93 ppm typical of a M-type silicon atom and two resonances detected at -21.38 and -21.69 ppm, in the region of the D-type silicon atoms [32]. For polymer **7**, resonances were observed at 7.26, -3.88 and -21.77 ppm.

The MALDI-TOF-MS of **6** (Fig. 1B) shows four major sets of peaks, each of them with a Gaussian shape, corresponding to oligomers that possess 3–6 silicon-bridged biferrocenyl units. In these sets, the peaks with the highest intensity are observed at 2033, 2682, 3332, and 3979 *m*/*z*. Each of these peaks is accompanied by several other peaks, equally spaced at 74 mass units apart, which corresponds to the mass of the Me_2SiO repeat unit. The number-average molecular weight (M_n), weight-average molecular weight (M_w) and polydispersity index (PDI $= M_w/M_n$) can be derived from the MALDI-TOF-MS [33] resulting in values of $M_n = 3080$, $M_w = 3260$ and PDI $= 1.06$. Surprisingly, all attempts to obtain a useful MALDI-TOF spectrum of polymer **7** under different experimental conditions have failed so far.

*2.3. Redox chemistry of the poly(ferrocenyl) siloxane-based model compounds **4** and **5** and polymers **6** and **7***

An important aspect of this work is to evaluate the redox properties of the newly prepared ferrocenyl-functionalized poly(methylsiloxanes), not only in homogeneous solution but also confined onto electrode surfaces (i.e. where the polymetallic molecules serve as electrode modifiers).

Solution cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were used to investigate the degree of electronic communication between the adjacent ferrocenyl moieties in the siloxane-based ferrocenyl derivatives **4**–**7**. Electrochemical data for these compounds are shown in Table 1 together with those of the related dendritic molecules **1**–**3**.

Fig. 2 compares the response of the tetraferrocenyldisiloxane **4**, with that of the octaferrocenylcyclosiloxane **5**, both with the ferrocenyl units linked together in pairs through a bridging silicon atom. As can be seen, the features of the voltammetric responses in dichloromethane solution of **4** and **5** are clearly different. In case of **4** (Fig. 2A) the CV exhibits two well-separated and reversible oxidation waves of equal intensity. For both waves, the plot of the peak current versus $v^{1/2}$ (v = scan rate) is linear, indicating diffusion controlled redox processes. Likewise, DPV measure-

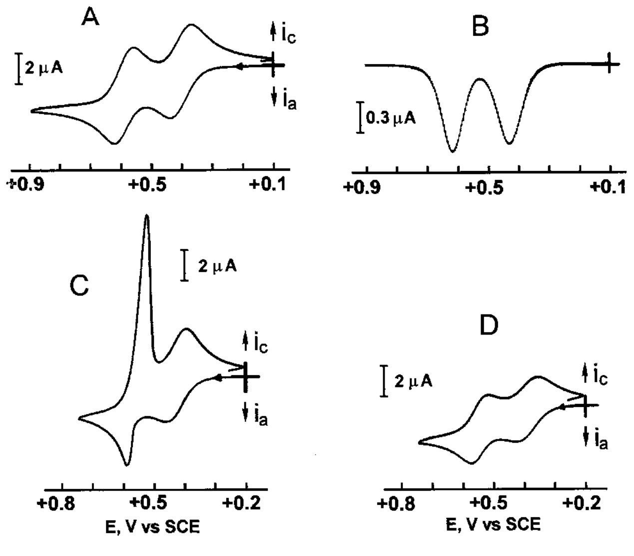


Fig. 2. (A) Cyclic voltammogram at a Pt disk electrode and scan rate of: 100 mV s^{-1} of **4** in CH_2Cl_2; (B) DPV of **4** in CH_2Cl_2; (C) CV of **5** in CH_2Cl_2; (D) CV of **5** in CH_2Cl_2–CH_3CN (5:1.5).

ments for **4** exhibited two separated oxidation waves of the same area (Fig. 2B), indicating that an equal number of electrons are transferred in both redox processes. On the other hand, controlled-potential coulometric tests performed on the tetraferrocenyl **4** show the consumption of four-electrons per molecule, after exhaustive oxidation. These results suggest that the neutral **4** undergoes two successive oxidations to yield, first the dication $\mathbf{4}^{+2}$ and then the tetracationic species $\mathbf{4}^{+4}$. This tetranuclear complex was the only one of the poly(ferrocenyl) compounds studied in this work for which oxidation and reduction does not affect the solubility of the molecule.

In contrast, the solution electrochemical behavior of the cyclotetrasiloxane-based octaferrocenyl **5** and polymers **6** and **7**, in CH_2Cl_2 solution, is marked by the oxidation-state-dependent solubility changes, so that on scan reversal after the second oxidation process, the reduction wave was dramatically sharpened, giving rise to a cathodic stripping peak (see, e.g. Fig. 2C). Thus, the complete oxidation of **5**, **6** and **7** results in the precipitation of the oxidized polymetallic systems onto the electrode surface, and on the reverse scan these poly(ferrocenylsiloxanes) partially redissolve as they are reduced. In addition, on continuous scanning, there is an increase in the peak current with each successive scan, which indicates that the formation of an electroactive film occurs on the electrode surface. However, in the case of **5** and **6**, if a small amount of CH_3CN is added to the CH_2Cl_2 electrolyte medium, the cathodic stripping peak disappears (Fig. 2D), and the CVs become similar to that observed for the tetranuclear model complex **4** [34]. Likewise, DPV measurements for **5** and **6** in this medium exhibited two separate oxidation waves of the same area, as observed for **4**. In contrast, the homopolymer **7** undergoes oxidative deposition not only in CH_2Cl_2 but also in the CH_2Cl_2–CH_3CN mixture and in other solvents such as benzonitrile and THF, indicating that the oxidized **7** is extremely insoluble in these media. Taking into account the different behavior of copopolymer **6** and homopolymer **7**, it is clear that the solubility of these siloxane-based ferrocenyl polymers is sensitive to the number of dendritic wedges per siloxane chain. Therefore, the solubility of the homopolymer **7** is affected more by the state of charge in the ferrocene units than that of copolymer **6** which in contrast possesses additional non-redox active, solubilizing dimethylsiloxane fragments.

The presence of two well-separated oxidation waves observed for these poly(ferrocenylsiloxanes) is consistent with the existence of appreciable interactions between the two iron centers in the pendant dendritic wedge, which are linked together by a bridging silicon atom. This two-wave redox response is similar to that found in oligo- and poly(ferrocenylsilanes) reported by Manners and co-workers [35] and Pannell et al. [36], and poly(ferrocenylene persulfides) reported by Rauchfuss et al. [37] wherein, in contrast, the ferrocenyl moieties are an integral part of the main polymer chain. Thus, the initial oxidation of **4**–**7** occurs at nonadjacent ferrocene sites (see, e.g. Scheme 3), which makes the subsequent removal of electrons from the remaining ferrocenyl centers, adjacent to those already oxidized, more difficult.

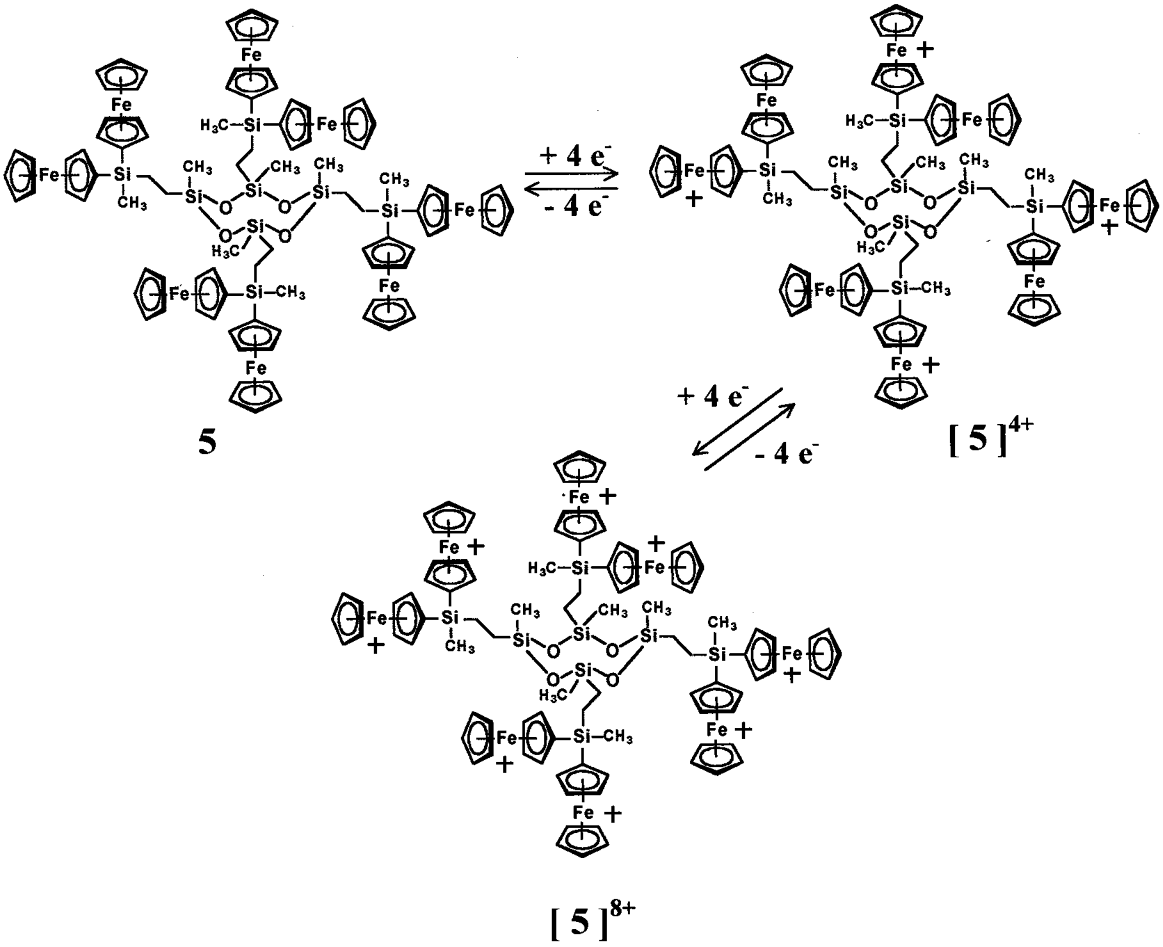
It is known that in linked metallocenes the difference in the redox potentials ($\Delta E = {}^{2}E_{1/2} - {}^{1}E_{1/2}$) observed for the two waves, is taken as a measure of the degree of electronic interaction between the two metal sites [38]. A comparison of the values of ΔE, measured in the same media, for the tetranuclear **4** (180 mV) with that for the related octaferrocenyl **5** (160 mV) (Table 1) indicates that the magnitude of the interaction between the neighboring iron sites in **4** is slightly larger than that in **5** which seems somewhat surprising. In the tetraferrocenyl **4**, after the first two electrons are removed in the first redox process, a +2 charge makes the subsequent removal of electrons more difficult. On the other hand, in **5** after the first four electrons are removed during the anodic scan (Scheme 3), a +4 charge should make it even more difficult to remove the remaining four electrons, which in turn would be reflected as a larger ΔE value for **5** than for **4**, whereas the opposite is experimentally found. In this respect, it has been found that in linked ferrocenyl systems, ΔE is not only dependent on the separation between the metal centers but also depends significantly on the nature of the bridge linking the ferrocene units [35,36,38]. In our case, the only difference among the substituents at the silicon atom bridging the ferrocenyl units in compounds **4** and **5** (i.e. the number of oxygen atoms in the silicon linked to the methylene chain adjacent to the bridging silicon atom, see Scheme 2), is substantially too far away to produce any electronic influence. Thus, an explanation for this variation in the ΔE values is likely to lie in the different charge separations in the partially oxidized species related to conformational effects, but at present we do not have a satisfactory explanation.

From the wave splitting (ΔE), the comproportionation constant K_c relative to the equilibrium among the three oxidation states of the two iron atoms in the dendritic wedges

$$\mathrm{Fe^{(II)}\text{-}Fe^{(II)} + Fe^{(III)}\text{-}Fe^{(III)} \rightleftarrows 2Fe^{(II)}\text{-}Fe^{(III)}}$$

was calculated according to Eq. (1) [39]. The resulting values of K_c are shown in Table 1 and indicate that the partially oxidized molecules **4**–**7** are representative mixed-valence species classified into Robin and Day class II [40].

$$K_c = \exp(F\Delta E/RT) = \exp(\Delta E/25.69) \qquad (1)$$



Scheme 3.

Undoubtedly, the most noteworthy aspect of the redox behavior of the octaferrocenyl-functionalized cyclotetrasiloxane **5** as well as of the polymers **6** and **7** is their ability to modify platinum or glassy-carbon electrode surfaces, resulting in detectable electroactive films that remain persistently attached to the electrode surface. These poly(ferrocenylsiloxanes) were electrodeposited in their oxidized forms onto electrode surfaces either by controlled potential electrolysis at + 0.9 V, or alternatively by repeated cycling between 0 and + 1.00 V potential limits. Therefore, the amount of electroactive material electro-deposited can be controlled with the electrolysis time or the number of scans. Interestingly, inspection of the electrode surfaces thus coated, after rinsing with CH_2Cl_2 to remove any adhering solution and dried in air clearly reveals the presence of an insoluble deep-blue colored film onto the electrode, which is characteristic of ferrocenium species.

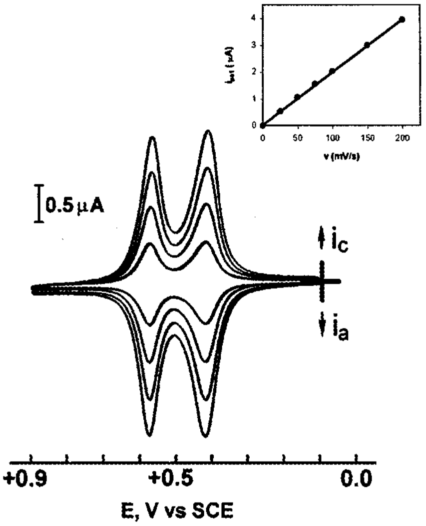


Fig. 3. Voltammetric response of a platinum-disk electrode modified with a film of poly(ferrocenylsiloxane) copolymer **6**, measured in CH_2Cl_2–0.1 M $[Bu_4N][PF_6]$. Scan rates: 25, 50, 75 and 100 mV s^{-1}. Inset: Scan rate dependence of the first anodic peak current.

The redox behavior of films of the poly(ferrocenylsiloxanes) electrodeposited onto electrode surfaces was studied by CV in fresh CH_2Cl_2 solution containing only the supporting electrolyte. The voltammetric response of a film of copolymer **6** is shown in Fig. 3 as a

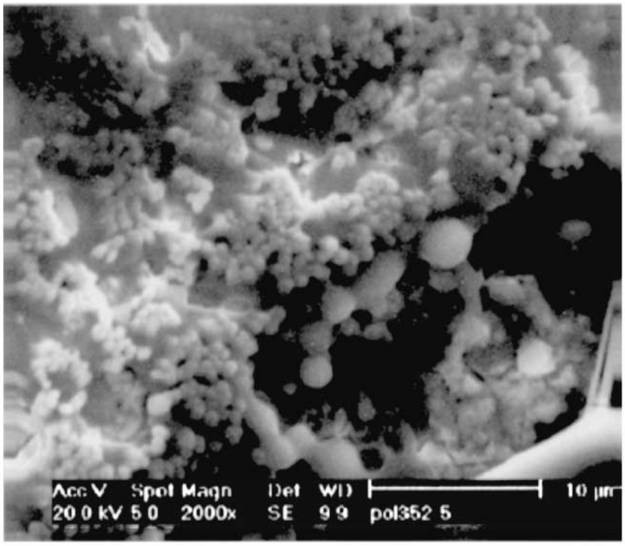


Fig. 4. Scanning electron micrograph of a film of polymer **7**, electrochemically deposited on a platinum wire electrode (0.5 mm of diameter).

representative example. Two successive well-defined, separated, symmetrical, reversible oxidation–reduction waves of equal intensity are observed, with formal potential values of ${}^1E'_{1/2} = 0.42$ and ${}^2E'_{1/2} = 0.57$ V. For both waves, a linear relationship of peak current with potential sweep rate v is observed. The peak splitting between positive and negative scans varies from ca. 0 mV at a scan rate of 25 mV s^{-1} to 10 mV at 200 mV s^{-1}, which indicates that the rate of electron transfer is rapid on the time scale. These voltammetric features unequivocally indicate the surface confined nature of the electroactive polymeric film [41]. The surface coverage of electroactive ferrocenyl sites in the film, Γ, was determined from the integrated charge of the cyclic voltammetric waves, and for the example studied shown in Fig. 3 was found to be $\Gamma = 8.9 \times 10^{-10}$ mol ferrocene cm^{-2}. Similar voltammetric responses were obtained for electrodes modified with films of **5** and **7**.

One of the most remarkable features of electrodes modified with films of **5**–**7** is that they are extremely durable and reproducible. In fact, the shape of the features in the cyclic voltammograms is independent of the scan rate from 5 to 1000 mV s^{-1}, and repeated scanning does not change the voltammograms demonstrating that films of **5**–**7** are stable to electrochemical cycling. CV scans can be carried out in CH_2Cl_2 electrolyte solutions hundreds of times, with no loss in electroactivity. Likewise, after standing in air for several weeks, the redox response was practically unchanged without any loss of the electroactive material. The high stability of these surface confined poly(ferrocenylsiloxane) films is an important observation since the applications of modified electrodes require extensive redox cycling.

In order to complete the characterization of electrodes thus modified, the microstructure of films of the ferrocenyl dendronized siloxanes electrochemically deposited on platinum wire working electrodes was examined by scanning electron microscopy (SEM). The SEM measurements can be carried out without coating with gold metal. The clear images of the SEM micrographs indicate that the polymer films are highly conductive. As can be seen from Fig. 4, a film of polymer **7** exhibits a coral-reef-like structure.

3. Conclusions

In summary, a series of siloxane-based multimetallic compounds and polymers, containing pendant, first-generation dendrons with silicon-bridged ferrocenyl moieties, have been obtained via the hydrosilylation reaction and structurally characterized. Solution voltammetric studies show two well-separated reversible redox processes, indicating the electronic communication between the metal sites in the dendritic side-chains. In addition, we have demonstrated the feasibility of modifying electrode surfaces with stable electroactive films of these siloxane-based poly(ferrocenyl) dendronized molecules. Further extensions of this synthetic strategy are in progress in order to prepare the dendronized polymers using dendritic wedges of higher nuclearity.

4. Experimental

4.1. Materials and equipment

All the reactions were performed under an inert atmosphere (prepurified Ar) using standard Schlenk techniques. Solvents were dried by standard procedures over the appropriate drying agents and distilled immediately prior to use. Compound **1** was synthesized as described in the literature [12]. The following silicon-containing products were purchased from ABCR: 1,3,5,7-tetramethylcyclotetrasiloxane, and poly(methylhydrosiloxane)(25–30%)–poly(dimethylsiloxane)(70–75%) copolymer. Poly(methylhydrosiloxane) and 1,1,3,3-tetramethyldisiloxane were obtained from Fluka and used as received. Karstedt catalyst available from Petrarch System (3–3.5% Pt in xylene) was used as received. Silica gel (70–230 mesh) was used for column chromatographic purifications. IR spectra were recorded on a Bomem MB-100 FTIR spectrometer. NMR spectra were recorded on Bruker-AMX spectrometers. Chemical shifts are reported in parts per million (δ) with reference to residual solvent resonances for ^{1}H- and ^{13}C-NMR ($CDCl_3$, ^{1}H, δ 7.27 ppm, ^{13}C, δ

77.0 ppm). ^{29}Si-NMR spectra were recorded with inverse-gated proton decoupling in order to minimize the nuclear Overhauser effects. In some cases the solutions contained 0.015 M Cr(acac)$_3$ in order to reduce T_1s. The MALDI-TOF-MS were obtained using a Reflex III (Bruker) mass spectrometer equipped with a nitrogen laser emitting at 337 nm. The matrix was ditranol. Elemental analyses were performed by the Microanalytical Laboratory, Universidad Autónoma de Madrid, Madrid, Spain.

CV experiments were performed either on a BAS CV-27 potentiostat or a BAS CV-50W potentiostat. Coulometric measurements were made with a PAR 362 potentiostat and a PAR 379 digital coulometer. Electrochemical measurements were performed in freshly distilled CH_2Cl_2 from CaH_2 under nitrogen. The supporting electrolyte was in all cases tetra-*n*-butylammonium hexafluorophosphate that was purchased from Fluka and was purified by recrystallization from EtOH and dried in vacuum at 60 °C. The supporting electrolyte concentration was typically 0.1 M. A conventional sample cell operating under an atmosphere of prepurified nitrogen was used for CV. All CV experiments were performed using either a platinum-disk working electrode ($A = 0.020$ cm^2), or a glassy carbon-disk working electrode ($A = 0.070$ cm^2) each of which was polished prior to use with either 1 μm diamond paste (Buehler) or 0.05 μm alumina–water slurry and rinsed thoroughly with purified water. All potentials are referenced to the saturated calomel electrode (SCE). A coiled platinum wire was used as a counter electrode. Solutions for CV were typically 1.0 mM in the redox active species and were deoxygenated by purging with prepurified nitrogen. DPV was performed with a Polarecord-E-506 Metrom, with a scan rate of 10 mV s^{-1}, a pulse height of 10–20 mV, and a duration of 60 ms. DPVs were recorded using CH_2Cl_2 or CH_2Cl_2–CH_3CN solutions of the ferrocenyl derivatives. The modification of electrode surfaces was effected either by controlled potential electrolysis or by repeated cycling as described in the text.

4.2. Synthesis of **4**

1,1,3,3-Tetramethyldisiloxane (0.05 g, 0.37 mmol) in 10 ml of toluene, was added slowly to a solution of **1** (0.35 g, 0.80 mmol) in 25 ml of toluene, containing 40 μl of Karstedt catalyst (3–5% Pt, xylene), and the solution was then heated to 45 °C. After 3 h, the completeness of the reaction was confirmed by the disappearance of the resonance corresponding to the SiH group in the ^{1}H-NMR spectrum. The reaction mixture was filtered, and the solvent was removed under vacuum. The orange residue was purified by column chromatography on silica. A first orange band containing the excess of **1** was eluted with hexane. Subsequently the major red band was eluted with an *n*-hexane–THF mixture (100:1) as the eluent. Solvent removal afforded the desired product **4** as an orange air-stable crystalline solid. Yield: 0.23 g (75%). Anal. Found: C, 58.92; H, 6.02. Calc. for $C_{50}H_{62}Fe_4OSi_4$: C, 59.18; H, 6.16%. ^{1}H-NMR ($CDCl_3$, 300 MHz): $\delta = 4.35$ (m, 8H, C_5H_4), 4.14 (m, 8H, C_5H_4), 4.09 (s, 20H, C_5H_5), 0.88 (m, 4H, CH_2), 0.61 (m, 4H, CH_2), 0.47 (s, 6H, $SiCH_3$), 0.11 (s, 12H, $OSi(CH_3)_2$). $^{13}C\{^1H\}$-NMR ($CDCl_3$, 125.76 MHz): $\delta = 74.72$, 71.86 (C_5H_4), 69.50 (C_5H_5), 11.62 (CH_2), 8.47 (CH_2), 0.69 ($OSi(CH_3)_2$), -2.53 ($SiCH_3$). $^{29}Si\{^1H\}$-NMR ($CDCl_3$, 59.3 MHz,): $\delta = 8.31$ ($OSi(CH_3)_2$), -4.33 ($SiCH_3$). MALDI-TOF-MS; *m*/*z*: 1014.0.

4.3. Synthesis of **5**

This compound was prepared in a similar manner as **4**, starting from 1,3,5,7-tetramethylcyclotetrasiloxane (0.03 g, 0.13 mmol), **1** (0.35 g, 0.80 mmol), and 40 μl of Karstedt catalyst (3–5% Pt, xylene). The resulting orange residue was purified by column chromatography on silica. An orange–red band was collected using a hexane–THF mixture (20:1) as the eluent. Solvent removal afforded product **5** as an orange air-stable crystalline solid. Yield: 0.16 g (62%). Anal. Found: C, 57.28; H, 5.93. Calc. for $C_{96}H_{112}Fe_8O_4Si_8$: C, 57.61; H, 5.64%. ^{1}H-NMR ($CDCl_3$, 300 MHz): $\delta = 4.33$ (m, 16H, C_5H_4), 4.13 (m, 16H, C_5H_4), 4.08 (s, 40H, C_5H_5), 0.90 (m, 8H, CH_2), 0.67 (m, 8H, CH_2), 0.46 (m, 12H, $SiCH_3$), 0.16 (m, 12H, $OSiCH_3$). $^{13}C\{^1H\}$-NMR ($CDCl_3$, 75.43 MHz): $\delta = 73.4$, 70.55 (C_5H_4), 68.23 (C_5H_5), 9.63 (CH_2), 7.49 (CH_2), -1.19 ($OSiCH_3$), -3.21 ($SiCH_3$). $^{29}Si\{^1H\}$-NMR ($CDCl_3$, 59.3 MHz): $\delta = -4.25$ ($SiCH_3$), -19.20 (SiO). MALDI-TOF-MS; *m*/*z*: 2001.3.

4.4. Synthesis of copolymer **6**

The compound **1** (0.25 g, 0.57 mmol) was added to a toluene solution (15 ml) containing 40 μl of Karstedt catalyst (3–5% Pt, xylene). A solution of poly(methylhydrosiloxane)–poly(dimethylsiloxane) copolymer (0.10 g, ≈0.05 mmol) in dry toluene (10 ml) was added dropwise. The reaction mixture was heated to 110 °C overnight. During this time the original clear orange color of the solution darkened. The reaction completion was confirmed by the disappearance of the SiH band in the IR spectrum (2156 cm^{-1}). The reaction mixture was filtered and the solvent was removed under vacuum. The orange–brown oily residue was dissolved in CH_2Cl_2 and precipitated with cold EtOH several times. After drying under vacuum product **6** was obtained as orange–brown tacky oil. Yield: 0.11 g. ^{1}H-NMR ($CDCl_3$, 300 MHz): $\delta = 4.33$, 4.12 (br, C_5H_4), 4.07 (s, C_5H_5), 0.86 (m, CH_2), 0.58 (m, CH_2), 0.47 (s, $SiCH_3$), 0.09, 0.07 (br, OSi(CH_3)$_2$, OSi(CH_3)). $^{13}C\{^1H\}$-NMR ($CDCl_3$, 125.76 MHz): $\delta = 73.81$, 70.97 (C_5H_4), 68.63 (C_5H_5), 10.31, 7.89 (CH_2), 1.43 (OSiCH_3), -2.85 (SiCH_3). $^{29}Si\{^1H\}$-NMR ($CDCl_3$, 99.36 MHz): $\delta = 7.93$ (O*Si*(CH_3)$_3$), -3.96 (*Si*CH_3), -21.38, -21.69 (O*Si*(CH_3)$_2$O, O*Si*(CH_3)O). MALDI-TOF-MS: $M_n = 3080$, $M_w = 3260$, PDI = 1.06.

4.5. Synthesis of polymer 7

Using the same method as detailed for the preparation of polymer **6**, homopolymer **7** was synthesized starting from poly(methylhydrosiloxane) (0.042 g, $\approx$ 0.019 mmol), **1** (0.35 g, 0.80 mmol) and 40 μl of Karstedt catalyst (3–5% Pt, xylene). During heating, the original orange color of the solution darkened to orange–brown. The resulting orange–brown tacky residue was dissolved in CH_2Cl_2 and precipitated with hexane twice. Product **7** was obtained as an orange–brown shiny solid. Yield: 0.10 g. ^1H-NMR ($CDCl_3$, 300 MHz): $\delta = 4.32$, 4.12 (br, C_5H_4), 4.07 (br, C_5H_5), 0.86, 0.55 (br, CH_2), 0.47 (s, SiCH_3), 0.12 (br, OSi(CH_3)$_2$, OSi(CH_3)). $^{13}C\{^1H\}$-NMR ($CDCl_3$, 125.76 MHz): $\delta =$ 73.91, 71.10 (C_5H_4), 68.74 (C_5H_5), 10.51, 8.33 (CH_2), -0.07 (OSiCH_3), -2.59 (SiCH_3). $^{29}Si\{^1H\}$-NMR ($CDCl_3$, 99.36 MHz): $\delta = 7.26$ (O*Si*(CH_3)$_3$, -3.88 (*Si*CH_3), -21.77 (O*Si*(CH_3)O).

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