Functionalization of linear and cyclic siloxanes and a dendritic carbosilane with (η5-C5H5)Fe(CO)2Si(CH3)2CH=CH2 via hydrosilylation reaction

Eulalia Ramírez-Oliva [a],[1], Isabel Cuadrado [a],[*], Carmen M. Casado [a],
José Losada [b], Beatriz Alonso [a],[*]

[a] *Departamento de Química Inorgánica, Facultad de Ciencias, Universidad Autónoma de Madrid, Cantoblanco, 28049 Madrid, Spain*
[b] *Departamento de Ingeniería Química Industrial, Escuela Técnica Superior de Ingenieros Industriales, Universidad Politécnica de Madrid, 28006 Madrid, Spain*

Abstract

A series of multimetallic systems containing silicon-linked cyclopentadienyl dicarbonyl iron moieties including carbosilane dendrimers and cyclic and polymeric siloxanes have been prepared using hydrosilylation reactions. For this purpose the vinyl-substituted silyliron complex $(\eta^5\text{-}C_5H_5)Fe(CO)_2Si(CH_3)_2$ CH=CH$_2$ (**1**) was prepared by salt elimination reaction between $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ and $ClSi(CH_3)_2CH=CH_2$ and fully characterized. Hydrosilylation reaction of **1** with the appropriate Si–H functionalized molecules in the presence of Karstedt catalyst afforded the novel silyl carbonyl iron-functionalized cyclotetrasiloxane **2**, dendrimer **3** and copolymer **4**, in which the organometallic units are attached to the silicon-based frameworks through a two-methylene flexible spacer. The electrochemical behaviour of compounds **1**–**4** has been examined in dichloromethane, tetrahydrofuran and acetonitrile solutions using cyclic voltammetry.
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1. Introduction

Since the synthesis of the first silylmetal complex $(\eta^5\text{-}C_5H_5)Fe(CO)_2SiMe_3$ by Wilkinson in 1956 [1], research into the synthesis and reactivity of transition metal silyl compounds continues to develop as a significant area in organometallic chemistry because these compounds are assumed to be key intermediates in a number of important stoichiometric and catalytic transformations [2,3]. Although synthetic routes for monometallic silyl derivatives are well developed, in contrast synthetic procedures for the construction of molecules containing multiple transition metal silyl moieties are limited and only a very few attempts have been made in this direction.

In the last few years we have been exploring routes for the construction of new families of redox-active multimetallic macromolecular structures, containing organotransition metal moieties together with linear and cyclic siloxanes, cubic silsesquioxanes and silicon- and nitrogen-based dendrimers as frameworks [4–9]. One of our synthetic approaches to the synthesis of such organometallic molecules was based on hydrosilylation reactions that exploit the reactivity of metallocene derivatives containing reactive vinyl or allyl groups toward Si–H polyfunctionalized carbosilanes and siloxanes. Hydrosilylation is one of the most important reactions to form Si–C bonds in organosilicon

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[*] Corresponding authors. Tel.: +34 91 497 48 47; fax: +34 91 497 48 33.
E-mail addresses: isabel.cuadrado@uam.es (I. Cuadrado), beatriz.alonso@uam.es (B. Alonso).
[1] Present address: Facultad de Química, Universidad de Guanajuato, Guanajuato, GTO 36050, Mexico.

chemistry [10] although its use for the introduction of organometallic moieties into macromolecular structures has been much less explored.

As a continuation of our efforts towards novel multimetallic molecules, our objective now is to extend the hydrosilylation methodology to new molecules containing organometallic units having multiple iron–silicon bonds. Herein we describe the extension of this methodology to incorporate the organometallic moiety $(\eta^5\text{-}C_5H_5)\,Fe(CO)_2$-$Si(CH_3)_2CH=CH_2$ into linear and cyclic siloxanes and a dendritic carbosilane frameworks.

2. Results and discussion

Previously we have synthesized the first generation organometallic carbosilane dendrimer $Si[(CH_2)_3Si(CH_3)_2Fe$-$(CO)_2(\eta^5\text{-}C_5H_5)]_4$ (Chart 1) in which the metal atom is σ-bonded to the dendritic skeleton [11]. This compound is accessible by reaction of the carbonyl anion $Na[(\eta^5\text{-}C_5$-$H_5)Fe(CO)_2]$ with the dendritic carbosilane $Si[(CH_2)_3$-$Si(CH_3)_2Cl]_4$ via salt elimination reaction [12]. Several examples of metallocarbonyl-substituted dendrimers have been reported by Moss and coworkers [13].

Our key starting material for the synthesis of the new silane- and siloxane-containing multimetallic compounds described herein requires the preparation of an organometallic fragment containing a vinyl group. We thus prepared the vinyl-substituted organometallic fragment $(\eta^5\text{-}C_5H_5)$-$Fe(CO)_2Si(CH_3)_2CH=CH_2$ (**1**).

2.1. Synthesis and characterization of $(\eta^5\text{-}C_5H_5)Fe(CO)_2Si$-$(CH_3)_2CH=CH_2$ (1)

Compound **1** has been synthesized using a modified literature procedure [14] by the addition of one equivalent of dimethylvinylchlorosilane in hexane to a THF solution of $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ (prepared from $[(\eta^5\text{-}C_5H_5)Fe$-$(CO)_2]_2$ and a Hg/Na amalgam) at $-70\,^{\circ}C$ (Scheme 1).
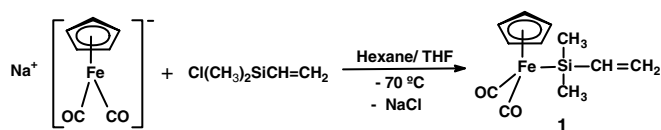
Scheme 1.

After appropriate work-up, the crude product was purified by column chromatography on silica to afford **1**, which was isolated in a 78% overall yield as a reddish-brown oil.

Compound **1** has been characterized by mass spectrometry (FAB-MS), and FTIR and ^1H, ^{13}C and ^{29}Si NMR spectroscopies. The IR spectrum of **1**, exhibits two typical $\nu(CO)$ bands at 1944 and 1996 cm^{-1} as expected for compounds of the type $(\eta^5\text{-}C_5H_5)Fe(CO)_2L$. The ^1H NMR spectrum of **1** (see Fig. 1A) shows the set of resonances characteristic of the reactive vinyl group at 5.58, 6.10 and 6.49 ppm in the expected integration ratio. The singlet at δ 4.68 ppm was assigned to the cyclopentadienyl ring, and the singlet at 0.42 ppm was assigned to the methyl groups attached to the silicon atom. As expected only one silicon resonance at 32.87 ppm was observed in the ^{29}Si NMR spectrum (see Fig. 2A). The structure of **1** was also unequivocally confirmed by the ^{13}C NMR spectrum, which displays exclusively the five resonances expected for the different carbon atoms. In the mass spectrum a molecular ion peak a 262 corresponding to M$^+$ and peaks due to the subsequent loss of CO groups are observed.

Compound **1** contains a reactive vinyl group attached to the silicon atom, which enables its incorporation in Si–H polyfunctionalized backbones via hydrosilylation reaction.

2.2. Synthesis and characterization of the tetrametallic compounds 2 and 3, and copolymer 4

The reaction of **1** with the Si–H tetrafunctionalized cyclotetrasiloxane $[SiH(CH_3)O]_4$ and carbosilane dendrimer $Si[(CH_2)_3Si(CH_3)_2H]_4$ [15], in the presence of catalytic amounts of Karstedt catalyst, in toluene solution at $45\,^{\circ}C$, afforded the desired hydrosilylated tetrametallic compounds **2** and **3**, respectively (Scheme 2). In the same way the copolymer $(Me_3SiO)(Me_2SiO)_m(MeSiHO)_n(Me_3Si)$ ($m = 70$–75%, $n = 25$–30%) was reacted with **1**. This reaction, was carried out under more forcing conditions (higher temperature and longer reaction times) than in the case of compounds **2** and **3**, in order to assure a maximum functionalization of the Si–H groups of the poly(siloxane) backbone.

The attachment of the vinyl-substituted silyliron complex **1** to the Si–H functionalised frameworks, can be easily monitored by ^1H NMR spectroscopy, in particular, by the disappearance of the Si–H resonance at 3.84 ppm in the carbosilane and at 4.72 ppm in the cyclotetrasiloxane and copolymer frameworks. After the filtration of the reaction mixture and evaporation of the solvent, the new tetra-iron compounds **2** and **3** were purified by column chromatography on silica using mixtures of hexane and THF as eluent
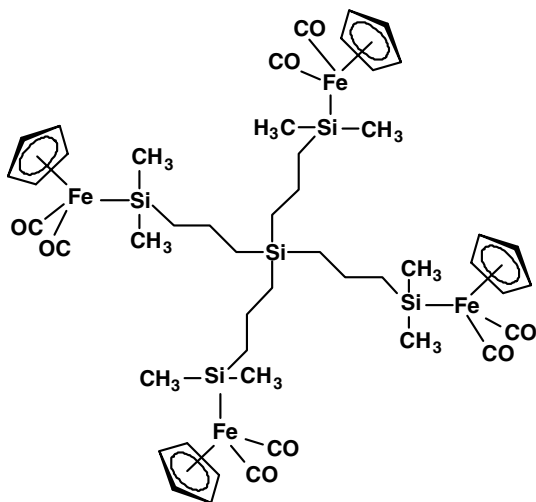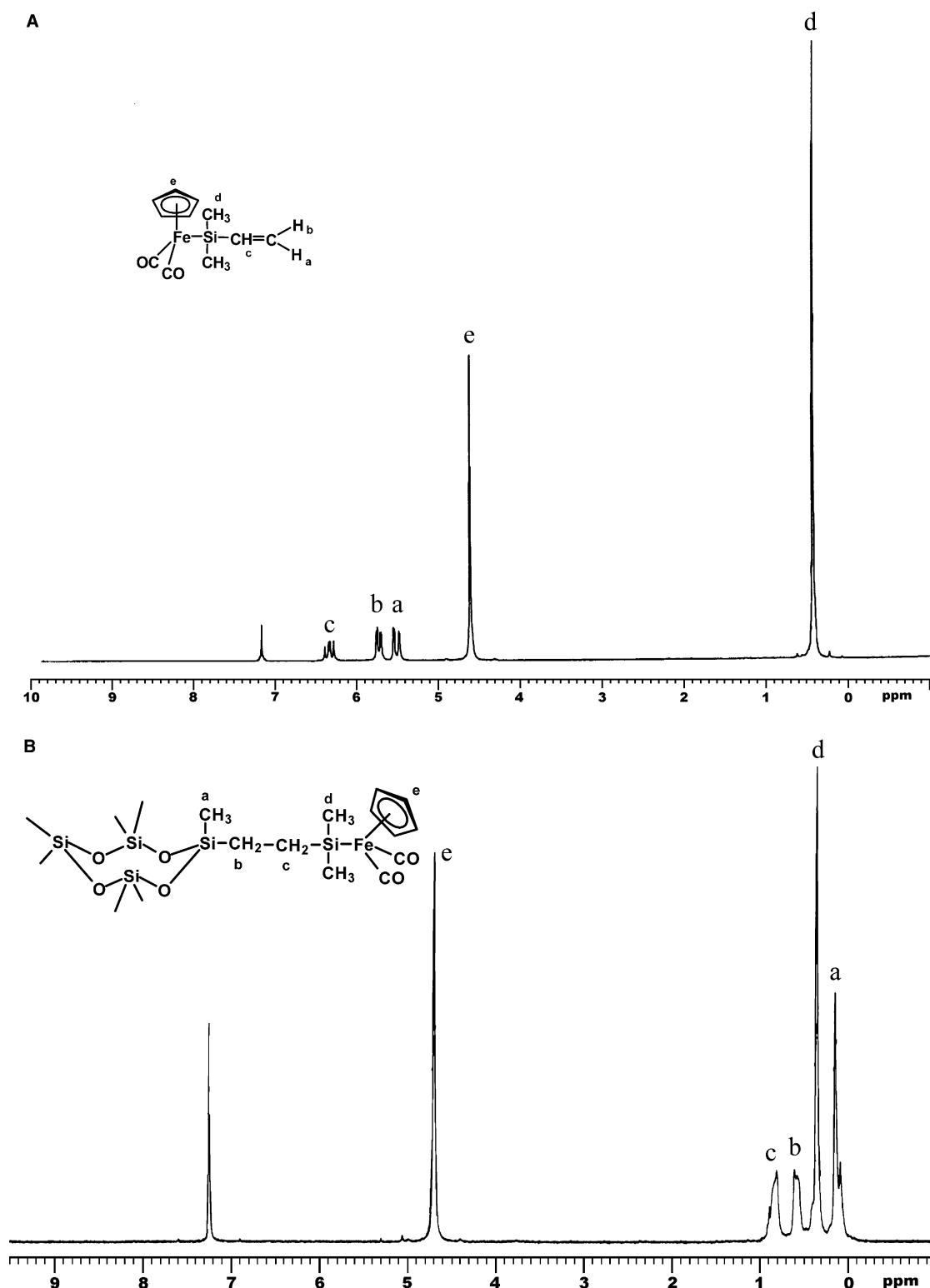

Chart 1.

Fig. 1. ^{1}H NMR (300 MHz, CDCl$_3$) spectra for **1** (A) and **2** (B).

(see Section 4). On the other hand, purification of the new hydrosilylated product **4** was effected by repeated dissolution in hexane and precipitation with methanol. The desired tetra- and poly-silyliron compounds **2–4** were isolated in high yields as air- and moisture-sensitive, reddish-brown tacky oils.

The new multimetallic compounds **2–4** were characterized by FTIR, and ^{1}H, ^{13}C and ^{29}Si NMR spectroscopies and mass spectrometry. For example, the ^{1}H NMR spectrum of **2** (see Fig. 1B) shows two sets of multiplets due to the methylene protons at δ 0.85 and 0.59 ppm in the expected integration ratio, a singlet arising from the
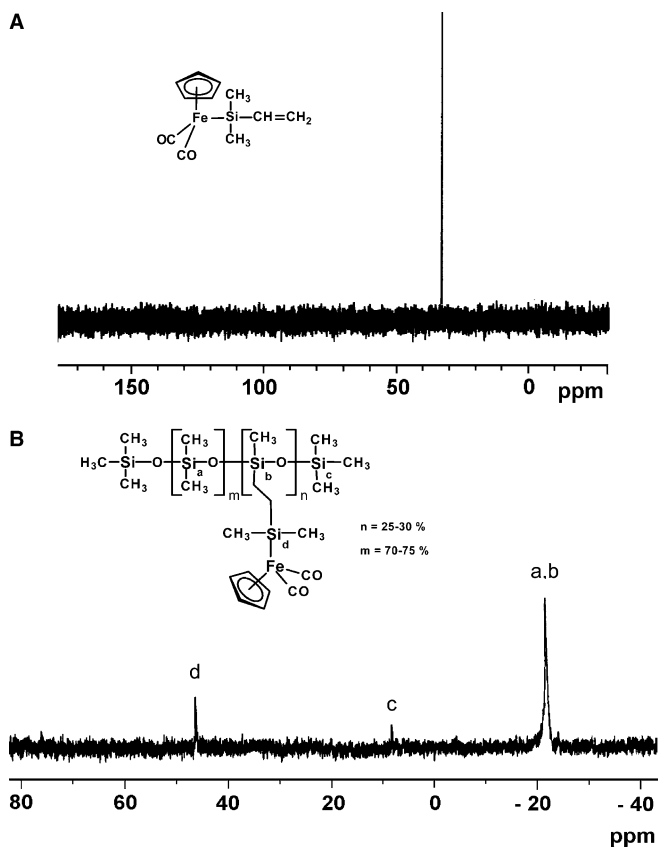
A

B

Fig. 2. ^{29}Si NMR (59.3 MHz, CDCl$_3$) spectra for **1** (A) and **4** (B).

cyclopentadienyl rings at δ 4.69 ppm and two broad singlets arising from the methyl groups. There is no significant change in ν(CO) from the precursor **1** to the resulting hydrosilylated products in the IR spectra. 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 spectra for **2**–**4** (in CDCl$_3$) display clearly separated signals for the different types of silicon atoms in the molecules, which can be easily assigned on the basis of the chemical shifts and the peak intensities (see for example Fig. 2B) [16]. Thus, the silicon atoms directly bound to the iron centres resonate at 46.62 (for **2**), 29.29 (for **3**) and 46.21 ppm (for **4**) far downfield of the remaining Si atoms. For **2** an additional resonance at -21.82 ppm was observed, which is within the range expected for a D-type silicon atom in a cyclic tetrasiloxane [17]. On the other hand, the most internal silicon atom in dendrimer **3** resonates at about 0.64 ppm upfield of the silicon atom in the dendritic branch which appear at 3.13 ppm. For copolymer **4**, a resonance at 8.10 ppm typical of a M-type silicon atom and a resonance at -21.86 ppm in the region of D-type silicon atoms were observed.

The MALDI-TOF-MS of **2** shows a signal at m/z 1288.0 which corresponds to the molecular ion M$^+$. Peaks corresponding to subsequent loss of CO groups provide further support for the formation of the tetrametallic compound.

Unfortunately, all attempts to obtain a useful MALDI-TOF spectrum of dendrimer **3** and copolymer **4** under several experimental conditions have failed so far.

2.3. Electrochemistry

The redox behaviour of compounds **1**–**4** was studied by cyclic voltammetry (CV) in CH$_2$Cl$_2$, THF and CH$_3$CN solutions containing 0.1 M [n-Bu$_4$N][PF$_6$] as supporting electrolyte at a glassy carbon disk electrode. Electrochemical parameters of the complexes are summarized in Table 1.

Fig. 3 shows typical cyclic voltammograms at different scan rates of **1** in CH$_2$Cl$_2$. They are qualitatively the same with THF or CH$_3$CN. The cyclic voltammograms show an anodic (A) and cathodic (B) peak, but they are not associated with a reversible oxidation–reduction process. The separation of the anodic and cathodic peak potentials is very large (see Table 1) and is dependent on the scan rate; as the sweep rate is increased, all of the peaks shift (reduction peaks shift in a negative direction and oxidation peaks shift in a positive direction). These shifts in E_p and the i_{pc}/i_{pa} values (much smaller than unity), indicate that the oxidation of **1**–**4** may be followed by a rapid chemical reaction (EC mechanism). Complete electrolysis of compounds **1**–**3**, carried out at a potential 100 mV more positive than peak (A), results in the removal of 1, 4 and 4 electrons per molecule, respectively.

In view of these results, the electrochemical processes of **1**–**4** may be formulated as in Scheme 3 (for compound **1** as a representative example). The complexes are oxidized to give electron-deficient dicarbonyliron (III) species, peak (A), followed by the elimination of one CO ligand owing to decreasing π-back bonding from the Fe^{III} ion to the CO ligands. The elimination of the CO ligand is probably assisted by nucleophilic attack of the solvent, yielding solvent adducts of the electron-deficient iron (III) species. The adduct ([(η^5-C$_5$H$_5$)Fe(CO)(solvent)Si(CH$_3$)$_2$CH=CH$_2$]$^+$ for **1**) may be reduced to give the Fe^{II} monocarbonyl complexes, peak (B), ([(η^5-C$_5$H$_5$)Fe(CO)(solvent)-Si(CH$_3$)$_2$CH=CH$_2$] for **1**).

In addition, the variation of the i_{pc}/i_{pa} ratio with the scan rate is clearly indicative of the instability of the dicarboyliron (III) cation [(η^5-C$_5$H$_5$)Fe(CO)(solvent)Si(CH$_3$)$_2$-CH=CH$_2$]$^+$ (for **1**).

A similar behaviour has been reported previously in other cases and the potential value corresponding to the reduction peak of the electrogenerated species [(η^5-C$_5$H$_5$)-Fe(CO)(solvent)Si(CH$_3$)$_2$CH=CH$_2$] (for **1**) is similar to that found for analogous monocarbonyl iron (III) species [18].

3. Conclusion

The silyliron complex **1**, in which the silicon atom is directly bonded to a vinyl reactive group can be successfully attached to different Si–H polyfunctionalized frameworks resulting in a series of silane and siloxane-based multimetallic compounds.
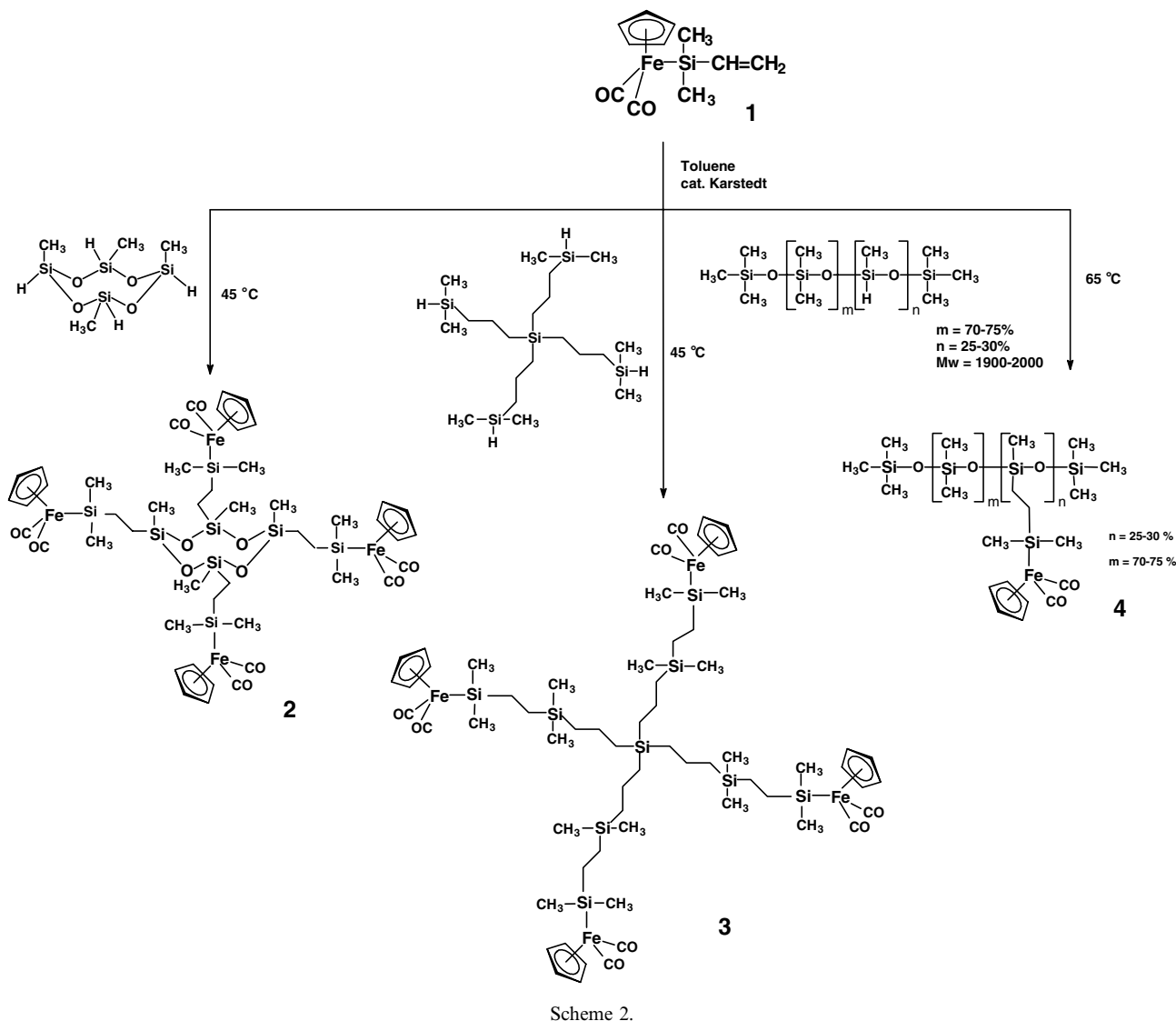
Scheme 2.

Table 1
Redox potentials (V, vs. SCE) of complexes **1–4** [a]

	E_{pA} [b]	E_{pB} [b]	E_{pA} [c]	E_{pB} [c]	E_{pA} [d]	E_{pB} [d]
1	1.14	0.30	1.04	−0.30	1.02	−0.60
2	1.24	0.30	1.07	−0.31	1.06	−0.55
3	1.17	−0.09	1.04	−0.20	1.00	−0.52
4	1.34	−0.06	1.30	−0.28	–	–

[a] At a glassy-carbon electrode, scan rate 100 mV s^{-1}.
[b] Measured in THF/[n-Bu$_4$N][PF$_6$].
[c] Measured in CH$_2$Cl$_2$/[n-Bu$_4$N][PF$_6$].
[d] Measured in CH$_3$CN/[n-Bu$_4$N][PF$_6$].

Fig. 3. Cyclic voltammograms of **1** recorded in CH$_2$Cl$_2$/0.1 M [n-Bu$_4$N][PF$_6$] using a glassy-carbon working electrode at different scan rates.

4. Experimental

4.1. Materials and equipment

All reactions and subsequent manipulations were carried out under an argon atmosphere by using conventional Schlenk techniques. Solvents were purified by distillation from appropr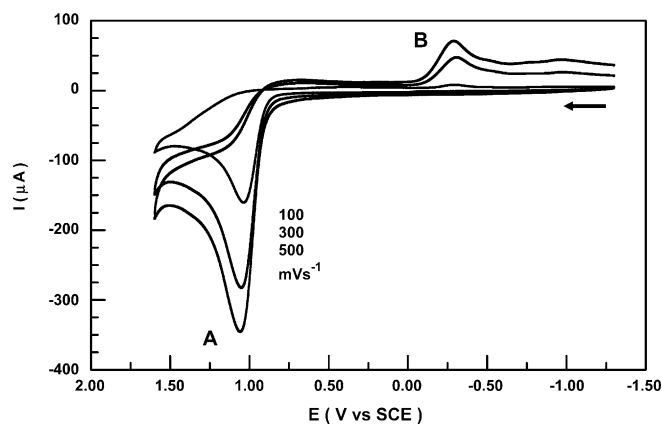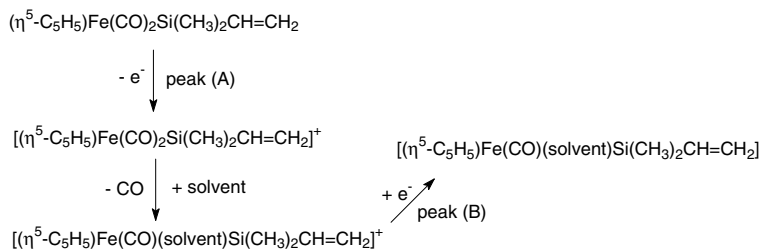iate drying agents [19] under an atmosphere of dry argon. 1,3,5,7-Tetramethylcyclotetrasiloxane, poly(methylhydrosiloxane) (25–30%) poly(dimethylsiloxane) (70–75%) copolymer, dimethylvinylchlorosilane and cyclopentadienyliron dicarbonyl dimer were purchased

$(\eta^5\text{-}C_5H_5)Fe(CO)_2Si(CH_3)_2CH=CH_2$

$\downarrow$ $-e^-$ | peak (A)

$[(\eta^5\text{-}C_5H_5)Fe(CO)_2Si(CH_3)_2CH=CH_2]^+$

$-CO$ | $+$ solvent $\qquad$ $[(\eta^5\text{-}C_5H_5)Fe(CO)(solvent)Si(CH_3)_2CH=CH_2]$

$[(\eta^5\text{-}C_5H_5)Fe(CO)(solvent)Si(CH_3)_2CH=CH_2]^+$ $\nearrow$ $+e^-$ peak (B)

Scheme 3.

from Fluka and used as received. Karstedt catalyst available from Petrarch System (3–3.5% in xylene) was used as received. Silica gel (70–230 mesh) (Aldrich) was used for column chromatographic purifications. IR spectra were recorded on a Bomem MB-100 FTIR spectrometer. NMR spectra were recorded at ambient temperature on a FT-Bruker-AMX spectrometer in CDCl₃ at the following frequencies: ¹H, 300 MHz; ¹³C, 73.45 MHz; ²⁹Si, 59.3 MHz. Chemical shifts are reported in parts per million (δ) with reference to residual solvent resonances for ¹H and ¹³C NMR (CDCl₃, ¹H, δ 7.27 ppm, ¹³C, δ 77.0 ppm). Matrix assisted laser desorption and ionization (MALDI) time-of-flight (TOF) mass spectrometry were conducted on a Reflex III (Bruker) mass spectrometer equipped with a nitrogen laser emitting at 337 nm. The matrix was ditranol. A VG AutoSpec mass spectrometer was used for Fast Atom Bombardment (FAB) analysis. CV experiments were performed on a BAS CV-50W pontentiostat, with a glassy carbon working electrode. Coulometric measurements were made with a PAR 362 potentiostat and a PAR 379 digital coulometer. The supporting electrolyte was in all cases [n-Bu₄N][PF₆] (purchased from Fluka) which was purified by recrystallization from EtOH and dried *in vacuum* at 60 °C. All potentials are referenced to the saturated calomel electrode (SCE) and a coiled platinum wire was used as a counter electrode.

4.2. Synthesis of 1

To a 20 ml THF solution of Na[(η^5-C₅H₅)Fe(CO)₂] (prepared from 3.0 g, 8.5 mmol of [(η^5-C₅H₅)Fe(CO)₂]₂ and a Hg/Na amalgam) was added 20 ml of a hexane solution of ClSi(CH₃)₂CH=CH₂ (1.2 g, 8.5 mmol) at −70 °C. The mixture was stirred during 16 h at room temperature and the solvent was removed in vacuum. Extraction with hexane gave an orange-brown solution. The product was purified by column chromatography on silica. An orange band was eluted with hexane. Evaporation of solvent gave a reddish-brown air-sensitive oil. Yield: 1.73 g (78%). IR ν(CO) 1996, 1944 cm⁻¹. ¹H NMR (CDCl₃, 300 MHz): δ = 4.68 (s, 5H, C₅H₅), 5.58 (dd, 1H, CH=CH₂ (cis)), 5.80 (dd, 1H, CH=CH₂, (trans)), 6.49 (dd, 1H, CH=CH₂), 0.42 (s, 6H, SiCH₃). ¹³C{¹H} NMR (CDCl₃, 75.43 MHz): δ = 215.00 (CO), 146.32 (CH), 126.58 (CH₂), 83.70 (C₅H₅), 4.53 (SiCH₃). ²⁹Si{¹H}-RMN (59.3 MHz, CDCl₃):

δ = 32.87 (SiFe). MS (FAB) m/z 262 (M⁺), 234 (M−CO⁺), 206 (M−2CO⁺).

4.3. Synthesis of 2

1,3,5,7-Tetramethylcyclotetrasiloxane (0.2 g, 0.8 mmol) in 10 ml of toluene, was added slowly to a solution of **1** (0.9 g, 35.9 mmol) in 20 ml of toluene, containing 40 µl of Karsted catalyst, and the solution was then heated to 45 °C overnight. The completeness of the reaction was confirmed by the disappearance of the resonance corresponding to the SiH group in the ¹H NMR spectrum. The reaction mixture was filtered, and the solvent was removed under vacuum. The product was purified by column chromatography on silica. A yellow-brown band was eluted with an hexane/THF (20:8) mixture as the eluent. Evaporation of the solvent gave a reddish-brown air-sensitive oil. Yield: 0.6 g (73%). IR ν(CO) 1988, 1931 cm⁻¹. ¹H NMR (CDCl₃, 300 MHz): δ = 4.69 (s, 20H, C₅H₅), 0.85 (m, 8H, CH₂), 0.59 (m, 8H, CH₂), 0.33 (s, 24H, Si(CH₃)₂), 0.12 (s, 12H, SiCH₃). ¹³C{¹H} NMR (CDCl₃, 75.43 MHz): δ = 216.01 (CO), 83.70 (C₅H₅), 15.91, 11.90 (CH₂), 4.86 (Si(CH₃)₂), −0.90 (SiCH₃). ²⁹Si{¹H}-RMN (59.3 MHz, CDCl₃): δ = 46.62 (SiFe), −21.82 (SiO). MS (MALDI-TOF) m/z 1288 (M⁺), 1121 (M−6CO⁺), 1065 (M−8CO⁺).

4.4. Synthesis of 3

This compound was prepared in a similar manner as **2** starting from the carbosilane dendritic core Si[(CH₂ₜ)₃-Si(CH₃)₂H]₄ (0.1 g, 0.2 mmol) [15], **1** (0.25 g, 1.37 mmol), and 40 µl of Karstedt catalyst. The resulting dark-brown residue was purified by column chromatography on silica. A yellow-brown band was collected using hexane/THF mixture (80:10) as the eluent. Solvent removal afforded product **3** as a reddish-brown oil. Yield: 0.1 g (83%). IR ν(CO) 1993, 1944 cm⁻¹. ¹H NMR (CDCl₃, 300 MHz): δ = 4.69 (s, 20H, C₅H₅), 1.32 (br, 8H, CH₂CH₂CH₂), 0.85 (m, 8H, CH₂SiFe), 0.69–0.50 (br, 24H, SiCH₂), 0.33 (s, 24H, FeSi(CH₃)₂), −0.04 (s, 24H, Si(CH₃)₂). ¹³C{¹H} NMR (CDCl₃, 75.43 MHz): δ = 222.44 (CO), 83.18 (C₅H₅), 20.29, 19.70, 18.58, 17.87 (CH₂), 4.37 (FeSi(CH₃)₂), −3.78 (Si(CH₃)₂). ²⁹Si{¹H}-RMN (59.3 MHz, CDCl₃): δ = 29.29 (SiFe), 3.13 (Si(CH₃)₂), 0.64 (SiCH₂).

4.5. Synthesis of 4

Compound **1** (0.3 g, 1.4 mmol) was added to a toluene solution (20 ml) containing 40 μl of Karstedt catalyst. A solution of poly(methylhydrosiloxane)–poly(dimethylsiloxane) copolymer (0.2 g, 0.1 mmol) in dry toluene (20 ml) was added. The reaction mixture was heated to 65 °C overnight. The reaction completion 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 reddish-brown viscous residue was dissolved in hexane and precipitated with methanol several times. After drying under vacuum product **4** was obtained as a reddish-brown tacky oil. Yield: 0.1 g. IR ν(CO) 1997, 1935 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz): $\delta = 4.68$ (s, C$_5$H$_5$), 0.83 (m, CH$_2$SiFe), 0.50 (m, SiCH$_2$), 0.33 (s, FeSi(CH$_3$)$_2$), 0.08, 0.07 (br, OSi(CH$_3$)$_2$, OSi(CH$_3$)). ^{13}C{^{1}H} NMR (CDCl$_3$, 75.43 MHz): $\delta = 215.47$ (CO), 83.18 (C$_5$H$_5$), 15.47, 11.10 (CH$_2$), 4.25 Fe(Si(CH$_3$)$_2$), 1.71 (OSi(CH$_3$)), -1.15 (SiCH$_3$). ^{29}Si{^{1}H}-RMN (59.3 MHz, CDCl$_3$): $\delta = 46.21$ (SiFe), 8.10 (OSi(CH$_3$)$_3$), -21.87 (OSi(CH$_3$)$_2$O, OSi(CH$_3$)O).

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