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Ferrocenyl Substituted Octakis(dimethylsiloxy)octasilsesquioxanes: A New Class of Supramolecular Organometallic Compounds. Synthesis, Characterization, and Electrochemistry

Moisés Morán,* Carmen M. Casado, and Isabel Cuadrado*

Departamento de Quimica (Inorgánica), Facultad de Ciencias,
Universidad Autónoma de Madrid, Cantoblanco 28049-Madrid, Spain

José Losada*

Departamento de Ingenieria Quimica Industrial, Escuela Técnica Superior de Ingenieros
Industriales, Universidad Politécnica de Madrid, 28006-Madrid, Spain

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Ferrocenyl octa- and monosubstituted octakis(dimethylsiloxy)octasilsesquioxanes with the structures $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4CH_2CH_2Si(CH_3)_2O)]_8Si_8O_{12}$ (**2**) and $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4CH_2CH_2Si(CH_3)_2O)][HSi(CH_3)_2O]_7Si_8O_{12}$ (**3**) have been synthesized via the hydrosilylation reaction of vinylferrocene with octakis(hydrodimethylsiloxy)octasilsesquioxane (**1**), catalyzed by Karstedt's catalyst (bis(divinyltetramethyldisiloxane)platinum(0)). Hydrosilylation reactions of **1** with 1,1′-divinylferrocene and 1,1′-divinyl(octamethyl)ferrocene have proved of great utility in the preparation of polymers **4** and **5**. These synthetic routes provided access to the first examples of poly(ferrocenyl–octasilsesquioxanes). These macromolecules possess a novel backbone structure comprising ferrocene and silsesquioxane moieties. The hydrosilylation products have been characterized by ^1H, ^{13}C, and ^{29}Si NMR, infrared spectroscopy, elemental analysis, and mass spectrometry. The thermal behavior of polymers **4** and **5** was studied by using DTA, TGA, and DTG techniques. The redox properties of the synthesized compounds have been studied by conventional electrochemical techniques. Electrodes modified with electroactive films of polymer **4** have been prepared.

Introduction

Considerable current interest is focused on the development of new synthetic routes to macromolecules containing organometallic units, as a means of preparing materials with unusual and potentially useful properties.[1,2] Hydrosilylation represents an important well-established way to form Si–C bonds in organosilicon chemistry.[3] Hydrosilylation reactions of vinyl substituted organometallic monomers may also represent a versatile synthetic route for the preparation of new organometallic polymers. However, to our knowledge, to date, very few attempts to investigate this approach have been reported.

We are interested in the synthesis of new types of organometallic species with linear,[4,5] cyclic, and polyhedral siloxanes as frameworks for multimetallic compounds and polymers. Structurally well defined silsesquioxanes are a versatile class of three-dimensional oligomeric organosilicon compounds of the general formulation $(RSiO_{3/2})_n$ (n = 6, 8, 10, 12, ...). Their structures are polyhedral frameworks with various degrees of symmetry, with the silicon atoms as corners and oxygen atoms between them.[6] In the last years, these fairly stable compounds have attracted interest as they are molecular building-blocks for the synthesis of siliceous materials.[7] Most recently, they have been used in the construction of a novel class of liquid-crystalline silsesquioxane by combining mesogens with spherical silsesquioxanes.[8] In addition they are interesting due to their possible use as frameworks for building donor/acceptor systems.[9]

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[1] (a) *Metal-Containing Polymeric Systems*; Sheats, J. E., Carraher, C. E., Jr., Pittman, C. U., Jr., Eds.; Plenum Press: New York, 1985. (b) *Inorganic and Metal-Containing Polymeric Materials*; Sheats, J. E., Carraher, C. E., Jr., Pittman, C. U., Jr., Zeldin, M., Currell, B., Eds.; Plenum Press: New York, 1990. (c) *Inorganic Polymers*; Mark, J. E., Allcock, H. R., West, R., Eds.; Prentice-Hall, Inc.: Englewood Cliffs, NJ, 1992. (d) *Silicon-Based Polymer Science. A Comprehensive Resource*; Zeigler, J. M., Gordon Fearon, F. W., Eds.; Advances in Chemistry Series 224; American Chemical Society: Washington, DC, 1990. (e) *Advances in Organometallic and Inorganic Polymer Science*, Carraher, C. E., Jr., Sheats, J. E., Pittman, C. U., Jr., Eds.; Marcel Dekker, Inc.: New York, 1982. (f) *Inorganic and Organometallic Polymers*; Zeldin, M., Wynne, K. J., Allcock, H. R., Eds.; ACS Symposium Series 360; American Chemical Society: Washington, DC, 1988. (g) *Contemporary Polymer Chemistry*, 2nd ed.; Allcock, H. R., Lampe, F. W., Eds.; Prentice Hall: Englewood Cliffs, NJ, 1990.

[2] (a) Carraher, C. E., Jr. *J. Chem. Educ.* **1981**, *58*, 921. (b) Sergeev, V. A.; Vdovina, L. I. *Organomet. Chem. USSR* **1989**, *2*, 77.

[3] (a) Marciniec, B.; Gulinski, J.; Urbaniak, W.; Kronetka, Z. W. In *Comprehensive Handbook On Hydrosilylation*; Marciniec, B., Ed.; Pergamon: Oxford, U.K., 1992. (b) Marciniec, B.; Gulinski, J. *J. Organomet. Chem.* **1993**, *446*, 15. (c) Lewis, L. N.; Lewis, N.; Uriarte, R. J. In *Homogeneous Transition Metal Catalized Reactions*; Moser, W. R., Slocum, D. W., Eds.; Advances in Chemistry Series 230; American Chemical Society: Washington, DC, 1992; p 3541. (d) Ojima, I. In *The Chemistry of Organic Silicon Compounds, Part 2*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1989; p 1479. (e) Armitage, D. A. In *Comprehensive Organometallic Chemistry*; Wilkinson, G.; Stone, F. G. A.; Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1982; Vol. 2, p 117. (f) Speier, J. L.; *Adv. Organomet. Chem.* **1979**, *17*, 407.

[4] Móran, M.; Cuadrado, I.; Pascual, C.; Losada, J. *Organometallics* **1993**, *12*, 811.

[5] Morán, M.; Cuadrado, I.; Pascual, C.; Casado, C. M.; Losada, J. *Organometallics* **1992**, *11*, 1210.

[6] Voronkov, M. G.; Lavrent'yev, V. I. *Top. Curr. Chem.* **1982**, *102*, 199–236.

[7] (a) Day, V. W.; Klemperer, W. G.; Mainz, V. V.; Millar, D. M. *J. Am. Chem. Soc.* **1985**, *107*, 8262. (b) Agaskar, P. A.; Day, V. W.; Klemperer, W. G. *J. Am. Chem. Soc.* **1987**, *109*, 5554.

[8] Kreuzer, F. H.; Maurer, R.; Spes, P. *Makromol. Chem., Macromol. Symp.* **1991**, *50*, 215.

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In this paper we describe a part of our synthetic work aimed to prepare organometallic species from vinyl substituted ferrocenes and Si–H functionalized cyclosiloxanes[10] and silsesquioxanes.[11] In contrast to the widely studied vinylferrocene derivatives, here we report an example in which the use of 1,1′-divinylferrocene and 1,1′-divinyl(octamethyl)ferrocene and a silsesquioxane as the framework leads to a new generation of presumably three-dimensional organometallic polymers. In this respect, organometallic compounds containing permethylcyclopentadienyl ligands are interesting since they often exhibit significantly different properties than their nonmethylated analogues.[12] However, organometallic polymers constructed from functionally substituted permethylcyclopentadienyl monomers have been unknown until recently.[4,13] The synthetic route described is of potentially broad applicability for designing supramolecular assemblies with silsesquioxanes as bridging components, since a similar methodology might also be successful with other organometallic monomers.

On the other hand, electroactive polymers containing ferrocene are interesting because they can be used in the chemical modification of electrodes. Electrodes thus modified have been extensively studied in recent years because of the diversity of applications in electromediation and in the construction of amperometric biosensors.[14] In this way, in addition to the study of the electrochemical properties of the synthesized compounds, we report here the preparation and characterization of electrodes modified with electroactive films of a ferrocenyl substituted octasilsesquioxane based polymer.

Results and Discussion

Our synthetic route to assemble polyhedral silsesquioxanes together with organometallic compounds containing ferrocene units consisted of exploiting the ability of vinyl substituted ferrocenes to undergo platinum-catalyzed hydrosilylation reactions. The key starting Si–H containing silsesquioxane in our work was octakis(hydrodimethylsiloxy)octasilsesquioxane $[H(CH_3)_2SiO]_8Si_8O_{12}$ (**1**). On the basis of steric and electronic reasons this silane can be suitable for hydrosilylation reactions. It has been well-established that electron-withdrawing substituents on the Si–H bond increase the rate of hydrosilylation processes compared to the case of more electron-donating groups. In this respect, values of the IR stretching frequency of the Si–H bonds can be taken as a guide to assign the relative electronegativity of silanes.[15] In this way, the ν(SiH) frequency of **1** suggests that the electronic environment about the reacting silicon centers is suitable for hydrosilylations. On the other hand, steric factors due to substituents in both silane and vinyl may also effect the rate and completeness of hydrosilylation reactions.[15a,16] In order to try addition of a functionally substituted Si–H silsesquioxane to vinylferrocene, 1,1′-divinylferrocene and 1,1′-divinyl(octamethyl)ferrocene, we reasoned that some steric hindrance could be caused by these sterically demanding organometallic moieties. Consequently, as the key starting silsesquioxane we selected **1**, in which the SiH reactive bonds were separated from the rigid cubic $[Si_8O_{12}]$ core by a dimethylsiloxy spacer.

1 was prepared according to a procedure recently described,[17] which involves the treatment of tetramethylammonium silicate with dimethylchlorosilane in a mixture of heptane and dimethylformamide as solvent. The identity of **1** was confirmed on the basis of elemental analysis, the infrared spectrum, and ^{1}H and ^{29}Si NMR data, which afforded data consistent with the assigned structure reported in the literature.

Initial attempts to hydrosilylate vinyl- and 1,1′-divinylferrocene with **1** using Speier's catalyst ($H_2PtCl_6{\cdot}6H_2O$ in *i*-PrOH) were unsuccessful,[18] and therefore, Karstedt's catalyst (bis(divinyltetramethyldisiloxane)platinum(0) in xylene, $Pt(DVTMDS)_x$), was investigated as catalyst. This was found to be an efficient hydrosilylation catalyst because it could be removed easily from the reaction products, and reactions proceeded under mild conditions and gave reproducible results. Consequently, this catalyst was further used for the remainder of our studies. Moreover, to avoid platinum coordination by solvent molecules, a nonpolar, inert solvent was chosen as the reaction medium.

Hydrosilylation reaction of **1** with 8 equiv of vinylferrocene in the presence of catalytic amounts of Karstedt's catalyst (Scheme I) was carried out in toluene at room temperature. Intentionally, aeration of the reaction mixture was effected in order to facilitate the hydrosilylation reaction and drive it to completion. In fact, it has been recently reported that aeration was critical for some platinum-catalyzed hydrosilylation reactions, as these processes are cocatalized by oxygen.[19] FTIR spectroscopy was utilized to follow the progress of the reaction, by monitoring the loss of the Si–H absorption at 2143 cm^{-1} in **1**. The reaction was completed in a few minutes. Purification of the resulting hydrosilylated product was

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(9) Herren, D.; Bürgy, H.; Calzaferri, G. *Helv. Chim. Acta* **1991**, *74*, 24.

(10) Further synthetic and electrochemical studies on related ferrocenyl substituted cyclosiloxanes will be reported.

(11) When this work was in progress an example of an organometallic monosubstituted octanuclear silsesquioxane was reported: Calzaferri, G.; Imhof, R. *J. Chem. Soc., Dalton Trans.* **1992**, 3391.

(12) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

(13) (a) Gibson, C. P.; Bem, D. S.; Falloon, S. B.; Hitchens, T. K.; Cortopassi, J. E. *Organometallics* **1992**, *11*, 1742. (b) Gibson, C. P.; Bem, D. S.; Falloon, S. B.; Cortopassi, J. E. In *Inorganic and Metal-Containing Polymeric Materials*; Sheats, J. E., Carraher, C. E., Jr., Pittman, C. U., Jr., Zeldin, M., Currell, B., Eds.; Plenum Press: New York, 1990; p 127.

(14) See for example: (a) Sakamoto, K.; Nishihara, H.; Aramaki, K. *J. Chem. Soc., Dalton Trans.* **1992**, 1877. (b) Eaves, J. G.; Munro, H. S.; Parker, D. *Inorg. Chem.* **1987**, *26*, 644. (c) Jönsson, G.; Gorton, L.; Pettersson, L. *Electroanalysis* **1989**, 49. (d) Inagaki, T.; Lee, H. S.; Skotheim, T. A.; Okamoto, Y. *J. Chem. Soc., Chem. Commun.* **1989**, 1181. (e) Hale, P. D.; Lan, H. L.; Boguslavsky, L. I.; Karan, H. I.; Okamoto, Y.; Skotheim, T. A. *Anal. Chim. Acta* **1991**, *251*, 121. (f) Hale, P. D.; Boguslavsky, L. I.; Inagaki, T.; Karan, H. I.; Lee, H. S.; Skotheim, T. A.; Okamoto, Y. *Anal. Chem.* **1991**, *63*, 677. (g) Tabakovic, R.; Tabakovic, I.; Davidovic, A.; Zupan, M. *J. Electroanal. Chem.* **1992**, *332*, 297. (h) Hale, P. D.; Inagaki, T.; Karan, H. I.; Okamoto, Y.; Skotheim, T. A. *J. Chem. Soc.* **1989**, *111*, 3482. (i) Mizutani, F.; Yabuki, S.; Okuda, A.; Katsura, T. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2849.

(15) (a) Stein, J.; Lewis, L. N.; Smith, K. A.; Lettko, K. X. *J. Inorg. Organomet. Polym.* **1991**, *1*, 325. (b) Liu, H. Q.; Harrod, J. F. *Can. J. Chem.* **1990**, *68*, 1100.

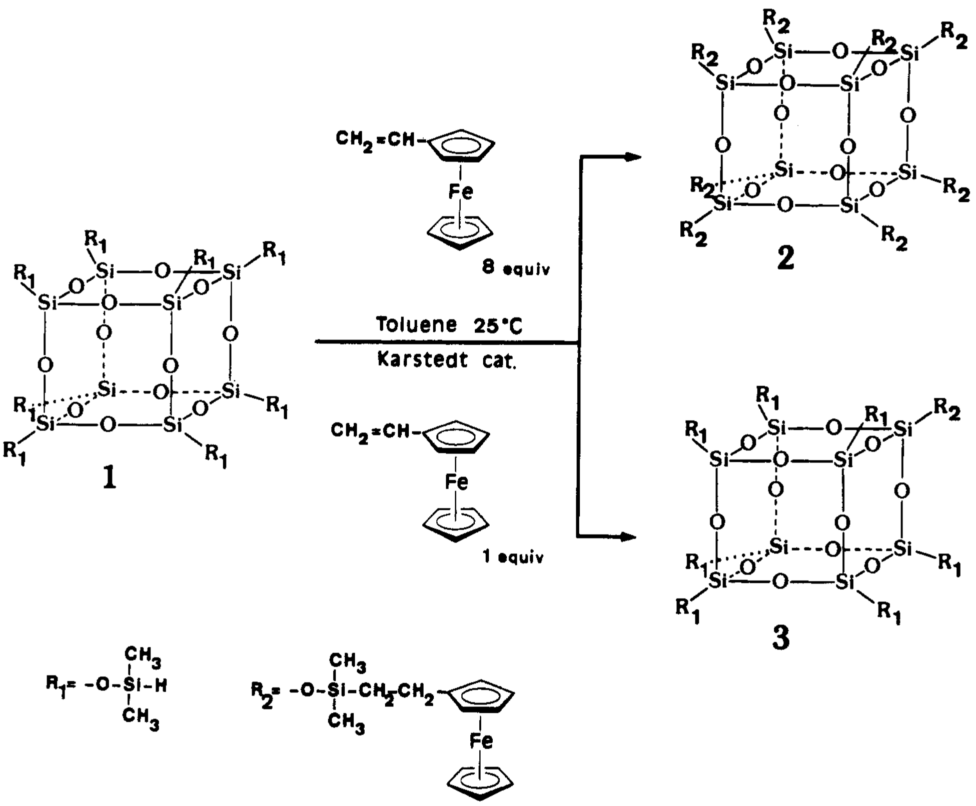
(16) (a) Puyenbroek, R.; Jekel, A. P.; van de Grampel, J. C. *J. Inorg. Organomet. Polym.* **1991**, *1*, 105. (b) Lestel, L.; Boileau, S.; Cheradame, H. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1989**, *30*, 133.

(17) (a) Akademie der Wissenschaften der DDR, Inv. EP-A 0348705, 1990; Hoebbel, D.; Pitsch, I.; Hiller, W.; Scheim, S. *Chem. Abstr.* **1990**, *113*, 125354b. (b) Wacker-Chemie GmbH, Inv. EP-A 0367222, 1990; Weidner, R.; Zeller, N.; Deubzer, B.; Frey, V. *Chem. Abstr.* **1990**, *113*, 116465m.

(18) Chloroplatinic acid has been recently reported to be unsuitable for some hydrosilylation reactions, as questionable results were obtained. See for example: (a) Allcock, H. R.; Nelson, C. J.; Coggio, W. D. *Organometallics* **1991**, *10*, 3819. (b) See also ref 16a.

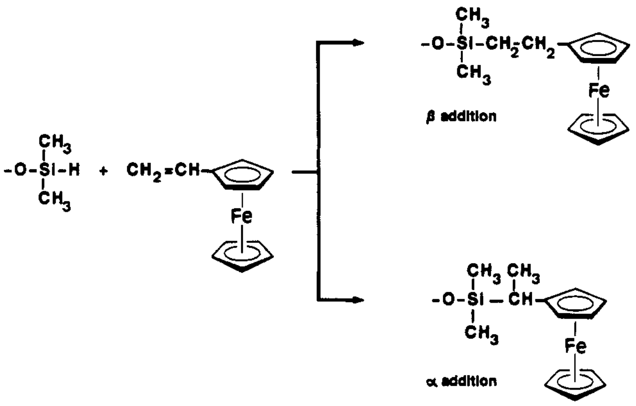
(19) The oxygen effect in hydrosilylations has been discussed in detail by L. N. Lewis. See: (a) Lewis, L. N. *J. Am. Chem. Soc.* **1990**, *112*, 5998. (b) Lewis, L. N.; Lewis, N. *Chem. Mater.* **1989**, *1*, 106. (c) Lewis, L. N.; Uriarte, R. J. *Organometallics* **1990**, *9*, 621.

Scheme I



effected by treatment with hexane (or CH_3CN in other attempts) and subsequent column chromatography of the insoluble oil on silanized silica using toluene or CH_2Cl_2 as eluent. The final compound $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4CH_2CH_2Si(CH_3)_2O)]_8Si_8O_{12}$ (**2**) was initially isolated as an air stable, deep orange viscous oil, which hardens and solidifies on standing. It was characterized by FTIR spectroscopy, ^1H, ^{13}C, and ^{29}Si NMR spectroscopies, mass spectrometry and elemental analysis. The ^1H NMR spectrum (C_6D_6) of the target compound **2** shows a single resonance at 4.12 ppm and a multiplet in the 4.03–4.15 ppm range, due to the cyclopentadienyl rings. In addition, the resonances observed between 1.10 and 2.54 ppm, corresponding to the bridges between the octasilsesquioxane and the ferrocene units, indicated the presence of two different, α and β, isomers.[20] These are the result of the two types of addition[3d] that can occur during the hydrosilylation process according to Scheme II. The mole ratio of α and β isomers was about 1/9, as determined from the intensities of the peaks at 2.54 and 1.53 ppm, corresponding to the methylene and methyl protons of the $C_5H_4\text{–}CH_2$ and $CH_3\text{–}CH$ groups, respectively. The total absence of the SiH resonance near 5 ppm confirmed the completeness of the hydrosilylation reaction and the total occupation of all the SiH sites of the silsesquioxane backbone. In addition, the ^{29}Si NMR spectrum of **2** (in C_6D_6) displays signals for Q- and M-type silicon atoms[21] with chemical shifts in the expected region of the spectrum,[22] which agrees with a totally substituted and symmetric structure. In this way, the resonance at −107.9 ppm was assigned to the Q-type silicon atoms in the $[Si_8O_{12}]$ framework and the resonance at 13.2 ppm can be assigned to the $M^{CH_2CH_2}$ group. In addition, elemental analysis is consistent with the incorporation of eight ferrocene units into the octa(dimethylsiloxy)octasilsesquioxane structure.

Scheme II



In order to provide additional characterization for this compound we utilized fast atom bombardment (FAB) mass spectrometry. Mass spectrometry is one of the most informative techniques for the investigation of oligosilsesquioxanes as it provides useful information, not only on the molecular mass but also on the structure of the silicon–oxygen skeleton and the nature of the substituent attached to the silicon atom. Although the natural isotopic distribution of silicon results in a multiplicity of ion peaks that in the high mass region of siloxane and silsesquioxane structures can make difficult the determination of the exact empirical formula of the resulting fragments,[22] the

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[20] In some cases formation of α and β isomers from SiH addition to vinyl derivatives has been observed: (a) Lewis, L. N.; Uriarte, R. J.; Lewis, N. *J. Catal.* **1991**, *127*, 67. (b) Aoyagi, T.; Akimoto, T.; Nagase, Y. *Makromol. Chem.* **1992**, *193*, 2821. (c) Marignan, G.; Teyssié, D.; Boileau, S.; Malthête, J.; Noël, C. *Polymer* **1988**, *29*, 1318. (d) Reference 19a.

[21] In siloxane chemistry the symbols M, D, T, and Q are used to represent framework silicon atoms which possess 3, 2, 1, and 0 organyl substituents, respectively. Superscripts are used to designate other functional groups on the silicon.

[22] *The Analytical Chemistry of Silicones*; Smith, A. L., Ed.; John Whiley & Sons, Inc.: New York, 1991.

FAB mass spectra for the synthesized compounds contained numerous informative peaks with isotopic distributions very close to calculated values. Moreover, the silsesquioxane framework is rather stable to FAB, as can be deduced from the basic lines observed in the spectra. Thus, mass spectral analysis of **2** showed a molecular ion at *m/z* 2712 at 22.75% relative abundance associated to the base peak ($M^+ + 3$) at *m/z* 2715. Apart from these lines, the only others with relative abundance >10% (but in all cases <30%) can be attributed to successive loss of different fragments from the substituents [(η^5-C_5H_5)Fe(η^5-$C_5H_4CH_2CH_2Si(CH_3)_2O$)] (see Experimental Section).

A similar reaction was performed by treatment of **1** with 1 equiv of vinylferrocene in toluene, at room temperature, in the presence of Karstedt's catalyst and it afforded a product [(η^5-C_5H_5)Fe(η^5-$C_5H_4CH_2CH_2Si(CH_3)_2O$)]-[$H(CH_3)_2SiO]_7Si_8O_{12}$ (**3**), derived from the addition of only one Si–H bond on **1** to one molecule of vinylferrocene. In this case, the progress of the reaction was followed by monitoring the loss of the vinyl absorption of the ferrocene at 1632 cm^{-1}. Compound **3** was isolated as an air stable yellow solid after repeated chromatographic purifications with hexane as eluent and was characterized by methods similar to those used for **2**. The ^1H NMR spectrum of **3** showed the cyclopentadienyl and methyl resonances in the expected 9/48 ratio. Also ^{13}C and ^{29}Si NMR spectra, the IR spectrum and mass spectrum, and elemental analysis data for **3** are consistent with the ferrocenyl monosubstituted octasilsesquioxane proposed structure (Scheme I). Both compounds **2** and **3** appear stable in solvents such as hexane, toluene, and THF. However, solutions of **2** and **3** in chlorinated solvents must be kept in the dark, because slow partial decomposition has been observed.

In order to synthesize new organometallic polymers containing skeletal ferrocene together with silsesquioxane frameworks, hydrosilylation reactions of **1** with 1,1′-divinylferrocene and 1,1′-divinyl(octamethyl)ferrocene have been explored. Reactions were carried out in toluene solution, at about 70–80 °C, and in the presence of Karstedt's catalyst. In the case of 1,1′-divinylferrocene, an infrared spectrum after 42 h showed that the hydrosilylation was essentially completed, as was suggested by the disappearance of the Si–H bonds. However with 1,1′-divinyl(octamethyl)ferrocene IR spectral analysis of the reaction mixture after the same period of time indicated that it still contained Si–H bonds. Longer reaction times and/or addition or more divinyl permethylated monomer did not show reduction of the Si–H absorptions. The polymers can be purified by repeated precipitation from CH_2Cl_2 solution by addition to a large volume of CH_3CN to remove low molecular weight components. After appropriate workup, the two expected polymeric products **4** and **5** were isolated from these reactions, as brown and yellow solids, soluble enough to be characterized. From the reaction with 1,1′-divinylferrocene another polymeric fraction was isolated as a highly insoluble shiny brown solid. Although its IR spectrum was identical to that of polymer **4**, a complete characterization of this material (which we presume to be a highly cross-linked polymeric fraction) was precluded by its insolubility in all the organic solvents tested to date.

Polymers **4** and **5** were structurally characterized by FTIR spectroscopy, ^1H, ^{13}C, and ^{29}Si NMR spectroscopies, and elemental analysis and their thermal stabilities studied by thermogravimetric analysis. The ^1H NMR spectra of **4** and **5** in C_6D_6 showed broad resonances for the respective η^5-C_5H_4 and η^5-C_5Me_4 rings, in addition to the resonances assigned to the CH_2CH_2 and $SiCH_3$ groups. Most notably for the methylated compound **5** a weak absorption at 2146 cm^{-1} in the IR spectrum (in KBr) clearly shows that it contains unreacted Si–H bonds. The incompleteness of the hydrosilylation reaction can be probably due to the steric hindrance caused by the sterically demanding octamethylated ferrocene. The ^{29}Si NMR spectra of both polymers **4** and **5** consisted of two single resonances corresponding to Q- and M-type silicon atoms in the same regions of the spectrum as those observed for **2**. For polymer **5** the resonance corresponding to the $M^{CH_2CH_2}$-type silicon atoms appears slightly shifted to a high field. VPO (in THF) indicates that **4** and **5** possess an approximate number-average molecular weight ($\bar{M}_n$) of 4.3×10^4 and 3.5×10^4, respectively. Although facile formation of these polymers is possible through the described reactions, a compositionally well defined structure cannot be assigned, as the uniformity and arrangement of branching has not been determined. Polymers **4** and **5** appear stable to the atmosphere and readily form amber free-standing films when cast from solution using THF as solvent. Scanning electron microscopy (SEM) of films of **4** and **5** thus prepared revealed smooth featureless surfaces.

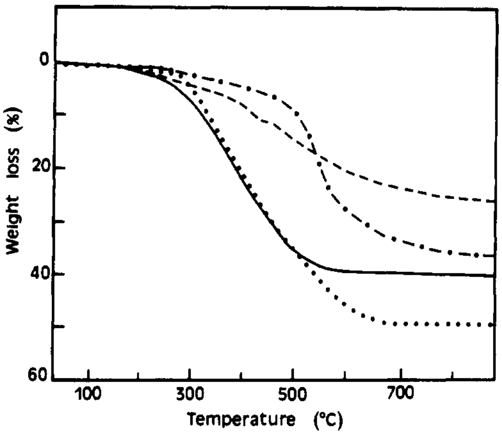

Figure 1. TGA curves for polymer **4** under atmospheres of nitrogen (- - -) and air (—) and polymer **5** under atmospheres of nitrogen (- • -) and air (···).

The thermal behavior of polymers **4** and **5** has been studied with the aid of thermal gravimetric analysis (TGA), derivative thermogravimetry (DTG), and differential thermal analysis (DTA). The samples were heated at a ramp rate of 10 °C/min, under nitrogen and air atmospheres, in the temperature range 25–850 °C. Under an inert atmosphere, the decomposition starts at about 160 °C for both polymers and beyond 800 °C a leveling off in weight loss is observed. Polymer **4** shows two endothermic effects centered at 330 and 490 °C. The weight losses recorded up to the end of these peaks are respectively 11.1% and 12.8%, and further weight loss is not observed in the temperature range studied. In the case of polymer **5** the endothermic weight loss occurs in only one step (peak at 540 °C) with a total loss percentage of 36.04%. For both compounds the resulting residue is probably a mixture of iron and silicon oxides and carbon.[23] From the TGA plots (Figure 1) a significantly lower rate of weight loss

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[23] Gonsalves, K. E.; Rausch, M. D. *J. Polym. Sci., Polym. Chem. Ed.* 1986, *24*, 1599.

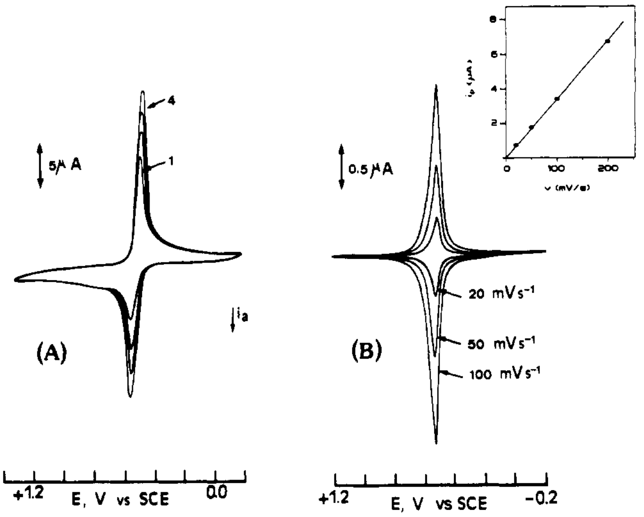

Figure 2. (A) Consecutive cyclic voltammograms of 4 at 200 mV/s at a platinum electrode in $CH_2Cl_2/0.1$ M Bu_4NPF_6. (B) Cyclic voltammograms at 20, 50, and 100 mV/s in $CH_3CN/0.1$ M Bu_4NPF_6 for a platinum electrode modified with a film of 4. Inset: plot of peak current *vs* sweep rate.

can be appreciated for polymer **5**. As can be observed, the presence of the methyl substituents in the cyclopentadienyl rings confers a higher thermal stability to the polymer. Under an air atmosphere, the TGA and DTA data show for both polymers multiple exothermic degradation processes caused by air oxygen. The weight losses are faster in air than in the nitrogen runs (Figure 1). The weight fraction of nonvolatile products (61.1% and 50.2%) indicates that the polymers are oxidized to SiO_2 and Fe_2O_3 when the temperature is raised to 600 °C, as was confirmed by the elemental analysis of the residues. A strongly exothermic process was observed for both polymers just before the onset of weight loss. This process occurred without a corresponding change in the weight of the samples, which indicates that an exothermic rearrangement of the polymers may have occurred.[6,24] We have also observed this effect in the thermoanalytical study of the related compounds **1** and **2**.

Electrochemical Studies

The electrochemical behavior of the synthesized compounds **2–5** has been studied by cyclic voltammetry in CH_2Cl_2 solution containing 0.1 M Bu_4NPF_6, at platinum and gold electrodes. Cyclic voltammograms of compounds **2** and **3** are characteristic of reversible oxidation processes with the production of soluble stable products. The peak shape was symmetrical, with the peak current i_{pa} proportional to the square root of the scan rate v. The ratio of the cathodic to anodic current, i_{pc}/i_{pa}, is essentially equal to unity and E_p was independent of the scan rate. The peak potential separation $\Delta E_p(E_{pa} - E_{pc})$ is ca. 65–80 mV (without iR compensation). Formal potential values of 0.49 and 0.45 V vs SCE, are measured for **2** and **3**, respectively. Complete electrolysis of compounds **2** and **3** carried out at potentials 100 mV more positive than the anodic potentials results in the removal of 8.0 and 1.0 electron/molecule, respectively.

Figure 2 shows the cyclic voltammogram of a platinum electrode in contact with a solution of **4** in CH_2Cl_2 as the potential is scanned between −0.2 and +1.2 V. The CV curve displays a broad anodic wave and, on the reversal, a sharp cathodic wave indicating adsorption or precipitation of the oxidized polymer. The formal potential value for this reversible redox wave was 0.43 V vs SCE. Upon continuous scanning, an increase in the peak current with each successive scan was observed which indicates the formation of an electroactive polymer film occurring on the electrode surface. Au and Pt electrodes were modified with electrodeposited films of **4** by scanning the potential (at 200 mV/s) between −0.2 and +1.2 V vs SCE, in a degassed CH_2Cl_2 solution of **4** with 0.1 M Bu_4NPF_6. The electrodes thus coated were removed from the polymer-containing CH_2Cl_2 solution, rinsed with CH_2Cl_2 to remove any adhering solution, and dried in air. Their voltammetric response was examined in a fresh acetonitrile solution containing 0.1 M Bu_4NPF_6, in which both redox forms of **4** are insoluble.

The cyclic voltammogram of a platinum electrode modified with an electrodeposited film of **4** shows a single symmetrical redox wave with a formal potential $E^{\circ\prime}$ value of 0.49 V vs SCE corresponding to the ferrocene/ferrocenium couple (Figure 2B). The wave shape is characteristic of a surface-confined redox couple, with the expected linear relationship of peak current with potential sweep rate (Figure 2B inset). The peak-to-peak separation values (ΔE_p), are 20 mV at a scan rate of 20 mV/s and 35 mV at a scan rate of 100 mV/s. The surface coverage of the polymer film Γ (mol/cm^2) was determined from the integrated charge of the cyclic voltammetric wave to be 2.98×10^{-9} mol/cm^2. The coverage of the polymer films can be controlled with the scan number. The polymer film is quite stable in air, in CH_3CN, and in aqueous solution. The values of the full width at half-maximum (ΔE_{FWHM}) for the surface wave are smaller than $90.6/n$ (n = number of electrons transferred per molecule), which is the expected value for surface-confined redox species.[25,26] Thus ΔE_{FWHM} values of 40 mV for the oxidation wave and 50 mV for the reduction wave have been measured at 10 mV/s. These narrow waves can be attributed to attractive interactions between the electroactive molecules within the film.[26-28]

The microstructure of a film of polymer **4** electrochemically deposited on a platinum wire (0.25 mm of diameter) by cyclic voltammetry was examined by scanning electron microscopy. The SEM micrograph in Figure 3 shows that the film had a slightly compact structure and some porosity was observed.

In contrast to the electrochemical behavior described for **4**, polymer **5** in CH_2Cl_2 solution with 0.1 M Bu_4NPF_6 exhibits a cyclic voltammogram characteristic of a quasi-reversible system with $E_{1/2}$ value of 0.10 V vs SCE which is considerably more negative than that observed for polymer **4**. This lower redox potential for the methylated polymer **5** is due to the enhanced electron-donating ability of the permethylated cyclopentadienyl rings. The peak

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(24) Gozdz, A. S.; Reich, H. J.; Bowe, M. D. In *Silicon-Based Polymer Science. A Comprehensive Resource*; Zeigler, J. M., Gordon Fearon, F. W., Eds.; Advances in Chemistry Series 224; American Chemical Society: Washington, DC, 1990.

(25) Abruña, H. D. *Coord. Chem. Rev.* **1988**, *86*, 135.

(26) (a) Smith, D. F.; William, K.; Kuo, K.; Murray, R. M. *J. Electroanal. Chem. Interfacial Electrochem.* **1979**, *95*, 217. (b) Peerce, P. J.; Bard, A. J. *J. Electroanal. Chem. Interfacial Electrochem.* **1980**, *114*, 89.

(27) (a) Laviron, E. *J. Electroanal. Chem. Interfacial Electrochem.* **1979**, *105*, 35. (b) Laviron, E. *J. Electroanal. Chem. Interfacial Electrochem.* **1979**, *105*, 25. (c) Laviron, E. *J. Electroanal. Chem. Interfacial Electrochem.* **1979**, *100*, 263. (d) Laviron, E. *J. Electroanal. Chem. Interfacial Electrochem.* **1974**, *52*, 395.

(28) (a) Murray, R. W. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1984; Vol. 13, p 191. (b) De Long, H. C.; Butty, D. A. *Langmuir* **1990**, *6*, 1319.

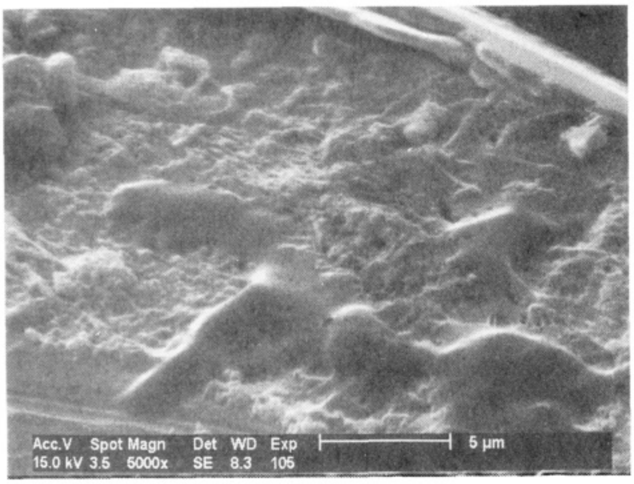

Figure 3. Scanning electron micrograph (×2705.5) of a film of 4 electrochemically deposited on a platinum electrode by cyclic voltammetry (25 cycles) from a CH_2Cl_2/0.1 M Bu_4NPF_6 solution.

potential separations ΔE_p are large (ΔE_p of ca. 170 mV was measured at 100 mV/s) and increased with increasing scan rate, implying that a kinetic limitation, e.g. slow electron transfer or slow structural changes, accompanies the charge transfer.[27] In addition no electrodeposition process was observed for this polymer by either repeated cycling or use of controlled potential electrolysis.

Experimental Section

Materials and Instrumentation. Solvents were dried over the appropriate drying agents[29] and distilled prior to use. Vinylferrocene was purchased from Aldrich and used as received. Divinylferrocene (Pluto) was sublimed prior to use. 1,1′-divinyl-(octamethyl)ferrocene was synthesized by reaction of anhydrous ferrous chloride (Aldrich) with (vinyltetramethylcyclopentadienyl)lithium.[30] Karstedt's catalyst available from Petrarch System as PC 072 (3–3.5% Pt in xylene) was used as received. Hexachloroplatinic acid hexahydrate was purchased from Strem. Tetramethylammonium hydroxide (10% aqueous solution) (Aldrich) and silicic acid (Merck) were used as received, and dimethylchlorosilane (Fluka) was distilled prior to use. Silanized silica gel 60 (70–230 mesh) (Merck) was used for column chromatographic purifications or some filtrations.

Infrared spectra were recorded on a Bomem MB-100 FTIR spectrometer. NMR spectra were recorded on a Bruker-AMX (^{1}H, 300 MHz; ^{13}C, 75.43 MHz; ^{29}Si, 59.3 MHz) spectrometer. Chemical shifts are reported in parts per million (δ) with reference to internal $SiMe_4$ for ^{1}H and ^{13}C NMR. ^{29}Si NMR spectra, referenced externally to $SiMe_4$, were recorded with inverse-gated proton decoupling in order to minimize nuclear Overhauser effects. In some cases the solutions contained 0.015 M $Cr(acac)_3$ in order to reduce T_1's.

FAB mass spectral analyses were conducted on a VG Auto Spec mass spectrometer equipped with a cesium ion gun. 3-Nitrobenzyl alcohol was used as the matrix. Number-average molecule weights (M_n) were obtained with a Knauer vapor-pressure osmometer. Elemental analyses were performed by the Microanalytical Laboratory, Universidad Autónoma de Madrid, Madrid, Spain. Thermal analysis of the polymers was effected with a Mettler 181 thermoanalyzer. Samples (10–12 mg) were placed in platinum sample holders. The runs were performed under a nitrogen stream (50 mL/min) and under still air. The samples were heated at a ramp rate of 10 °C/min to a final temperature of 850 °C.

Cyclic voltammetric experiments were performed on either a PAR 362 potentiostat or a BAS CV-27 voltammograph. Coulometric measurements were made on a PAR 362 potentiostat and a PAR 379 digital coulometer. A PAR 377A coulometry cell system fitted with platinum-gauze working electrode was used. Electrochemical measurements were performed in acetonitrile and dichloromethane freshly distilled from CaH_2 under nitrogen. The supporting electrolyte tetra-*n*-butylammonium hexafluorophosphate (Bu_4NPF_6) was purchased from BAS or Strem and was purified by recrystallization from ethanol and dried in vacuo at 60 °C. The supporting electrolyte concentration was typically 0.10 M. All electrochemical experiments were performed using either a platinum-disk working electrode (A = 0.070 cm^2) or a gold-disk working electrode (A = 0.070 cm^2) which was polished prior to use with 1-μm diamond paste and rinsed thoroughly with water and acetone. Potentials are reported vs SCE.

The microstructure of polymer/Pt films was examined by scanning electron microscopy (SEM) on a Philips XL-30 instrument.

Synthesis of 1. Octa(hydrodimethylsiloxy)octasilsesquioxane was synthesized in a two step reaction, by following approximately literature procedures.[17]

Tetramethylammonium silicate was prepared by reaction of tetramethylammonium hydroxide (87 mL of a 10% aqueous solution) and silicic acid (5.7 g). The reaction mixture was stirred at room temperature overnight and subsequently heated to 60 °C for 10 h. The resulting colorless solution was concentrated and then cooled to 4 °C. A white solid of tetramethylammonium silicate was filtrated out and isolated (15 g).

Tetramethylammonium silicate (9.4 g) was slowly added to a mixture of heptane (200 mL), dimethylformamide (400 mL), and dimethylchlorosilane (200 mL) previously stirred for 15 min at room temperature. As it is a slightly exothermic reaction, the mixture was allowed to reach room temperature and subsequently cooled to 2 °C in an ice-water bath. Approximately 1 L of distilled water (cooled to 2 °C) was added dropwise. The organic layer was then separated from the aqueous layer and washed with water until acid free. The volatiles were removed under vacuum at 55 °C. The resulting liquid was cooled to 4 °C, and thus 1 precipitated and was isolated as a white solid (3.41 g, 85% yield) which can be recrystallized from acetone.

Spectral and Analytical data for 1. ^{1}H NMR (C_6D_6): δ 4.97 (septet, SiH), 0.17 (d, SiCH_3). ^{29}Si{^{1}H} NMR (C_6D_6): δ −0.8 (Si–H) −107.8 (SiO_4). IR ν(SiH): 2143 cm^{-1} (toluene). Anal. Calcd for $Si_{16}O_{20}H_{56}C_{16}$: C, 18.90; H, 5.56. Found: C, 18.83; H, 5.60.

Synthesis of 2. Vinylferrocene (0.7 g, 3.30 mmol) was added to a toluene solution (20 mL) containing 10 μL of a 3–3.5% solution of Karstedt's catalyst in xylene. The mixture was stirred at room temperature for approximately 1 h. A gentle stream of air was blown through the solution for a few seconds. A solution of 1 (0.42 g, 0.41 mmol) in dry toluene (20 mL) was added dropwise over a period of 1 h. During this time the original orange color of the solution darkened to orange-brown. The progress of the reaction was monitored by IR spectroscopy. After a few minutes at room temperature, no Si–H peak was detected in the IR spectrum. The reaction mixture was filtered, and the solvent was removed under vacuum. The dark brown tacky residue was treated with *n*-hexane. An insoluble oily product was formed, which was separated from the solution, redissolved in toluene, and subjected to column chromatography. Elution with toluene yielded a major brown band which was collected. Solvent removal afforded the target product as a brown viscous oil, that hardens and solidifies on standing: yield of 2 0.64 g (57%).

Spectral and Analytical data for 2. ^{1}H NMR (C_6D_6): δ 4.15–4.03 (m, C_5H_4), 4.12 (s, C_5H_5), 2.54 (m, C_5H_4-CH_2), 1.91 (q, Si–CH(CH$_3$)), 1.53 (d, Si–CH(CH_3)), 1.10 (m, Si–CH_2), 0.32 (s, SiCH_3). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 91.94 (CH$_2$–C_5H$_4$), 68.38 (C_5H$_5$), 67.57, 66.94 (C_5H$_4$), 22.634 (C$_5$H$_4$–CH$_2$), 19.00 (Si-CH$_2$), −0.14 (Si–CH$_3$). ^{29}Si{^{1}H} NMR (C_6D_6): δ 13.2 (Si–CH$_2$), −107.9 (SiO$_4$).

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(29) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon: New York, 1988.

(30) Ogasa, M.; Mallin, D. T.; Macomber, D. W.; Rausch, M. D.; Rogers, R. D.; Rollins, A. N. *J. Organomet. Chem.* **1991**, *405*, 41.

MS (FAB; *m/z* (%)): 2715 ($M^+ + 3$, 100), 2712 (M^+, 22.75), 2595 ($M^+ - [(\eta^5\text{-}C_5H_5)Fe] + 4$, 12.91), 2591 ($M^+ - [(\eta^5\text{-}C_5H_5)Fe]$, 10.45), 2518 ($M^+ - [(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4CH_2)] + 5$, 20.67), 2444 ($M^+ - [(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4CH_2CH_2Si(CH_3)_2)] + 3$, 15.84), 2321 ($M^+ - [(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4CH_2CH_2Si(CH_3)_2)] - [(\eta^5\text{-}C_5H_5)Fe] + 1$, 10.58), 2091 ($M^+ - 2[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4CH_2CH_2)] - [(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4CH_2)] + 4$, 27.83), 1877 ($M^+ - 3[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4CH_2CH_2)] - [(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4CH_2)] + 3$, 10.42). Anal. Calcd for $Si_{16}O_{20}H_{152}C_{112}Fe_8$: C, 49.56; H, 5.64. Found: C, 49.49; H, 5.70.

Synthesis of 3. A mixture of vinylferrocene (0.15 g, 0.70 mmol) and a catalytic amount of Karstedt's catalyst (approximately 5μL of a 3–3.5% solution in xylene) in toluene (20 mL) was stirred for 1 h at room temperature. A solution of 1 (0.72 g, 0.70 mmol) in toluene (20 mL) was then added in one fell swoop. An FTIR spectrum of the reaction mixture after a few minutes showed complete loss of the vinyl absorption at 1632 cm^{-1}. Nevertheless the mixture was stirred for several hours. The reaction mixture was filtered, and the solvent was removed under vacuum. The residue was purified by repeated column chromatographies with hexane as eluent. Solvent removal of the more soluble fraction yielded 3 as a yellow solid: yield of 3 0.16 g (18%).

Spectral and Analytical data for 3. ^1H NMR (C_6D_6): δ 4.97 (m, Si*H*), 4.19–3.99 (m, $C_5\mathit{H}_4$), 4.09 (s, $C_5\mathit{H}_5$), 2.50 (m, $C_5H_4\text{–}C\mathit{H}_2$), 1.00 (m, $Si\text{–}C\mathit{H}_2$), 0.20–0.17 (m, $SiC\mathit{H}_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 91.90 ($CH_2\text{–}\mathit{C}_5H_4$), 68.79 ($\mathit{C}_5H_5$), 67.96, 67.36 ($\mathit{C}_5H_4$), 23.08 ($C_5H_4\text{–}\mathit{C}H_2$), 19.39 ($Si\text{–}\mathit{C}H_2$), –0.01 ($Si\text{–}\mathit{C}H_3$). $^{29}Si\{^1H\}$ NMR (C_6D_6): δ 13.51 ($\mathit{Si}\text{–}CH_2$), –0.79 ($\mathit{Si}\text{–}H$), –107.77 ($\mathit{Si}O_4$). MS (FAB, *m/z* (%)): 1230 ($M^+ + 2$, 73.55), 1228 (M^+, 65.72), 1163 ($M^+ - C_5H_5$, 15.21), 1043 ($M^+ - [(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)]$, 12.00), 987 ($M^+ - [(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4CH_2CH_2)] - 2CH_3 + 2$, 59.76), 746 (32.41), 613 (100), 550 ($[(Si_8O_{20}) + 6]^+$, 89.86), 544 ($[Si_8O_{20}]^+$, 18.26). Anal. Calcd for $Si_{16}O_{20}H_{68}C_{28}Fe$: C, 27.34; H, 5.57. Found: C, 27.29; H, 5.60.

Synthesis of 4 and 5. Polymers 4 and 5 were prepared similarly to compound 2, except that 4 equiv of 1,1′-divinylferrocene and 1,1′-divinyl(octamethyl)ferrocene, respectively, were reacted with 1 equiv of 1. The reaction mixtures were heated to 70–80 °C for 42 h. FTIR spectra of the reaction mixtures showed quantitative loss of the Si–H stretch for the nonmethylated compound; however, with 1,1′-divinyl(octamethyl)ferrocene, the reaction was not completed. A 10% excess of the divinyl permethylated monomer was added and the reaction mixture was heated and stirred for an additional 12 h, but IR analysis did not show reduction of the Si–H absorption. Purification of both polymers was achieved by two successive reprecipitations from CH_2Cl_2 into CH_3CN. A dark brown insoluble solid was primarly isolated from the CH_2Cl_2 solution of polymer 4, but its high insolubility prevented its accurate characterization. 4 was isolated as a shiny brown solid and 5 as a yellow solid, in 60–65% yields.

Characterization Data for 4. ^1H NMR (C_6D_6): δ 4.12, 4.06 (br m, $C_5\mathit{H}_4$), 2.56 (br m, $C_5H_4\text{–}C\mathit{H}_2$), 1.01 (br m, $Si\text{–}C\mathit{H}_2$), 0.23 (br s, $Si\text{–}C\mathit{H}_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 92.38 ($CH_2\text{–}\mathit{C}_5H_4$), 68.52, 67.48 ($\mathit{C}_5H_4$), 22.93 ($C_5H_4\text{–}\mathit{C}H_2$), 19.99 ($Si\text{–}\mathit{C}H_2$), 0.02 ($Si\text{–}\mathit{C}H_3$). $^{29}Si\{^1H\}$ NMR (C_6D_6): δ 13.05 ($\mathit{Si}\text{–}CH_2$), –108.00 ($\mathit{Si}O_4$). Anal. Calcd for $\{Si_8O_{12}[(CH_3)_2SiO]C_{56}H_{16}Fe_4\}_n$: C, 43.90; H, 5.74. Found: C, 43.15; H, 5.69.

Characterization Data for 5. ^1H NMR (C_6D_6): δ 2.57 (br m, $C_5(CH_3)_4\text{–}C\mathit{H}_2$), 1.75 (br m, $C_5(C\mathit{H}_3)_4$), 0.74 (br m, $Si\text{–}C\mathit{H}_2$), 0.28 (br s, $Si\text{–}C\mathit{H}_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 78.77 ($\mathit{C}_5(CH_3)_4$), 9.89 ($C_5(\mathit{C}H_3)_4$), 0.15 ($Si\text{–}\mathit{C}H_3$). $^{29}Si\{^1H\}$ NMR (C_6D_6): δ 12.65 ($\mathit{Si}\text{–}CH_2$), –107.8 ($\mathit{Si}O_4$). Anal. Calcd for $\{Si_8O_{12}[(CH_3)_2SiO]C_{88}H_{128}Fe_4\}_n$: C, 51.64; H, 7.34. Found: C, 48.16; H, 7.14.

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