

1,1'-Bis(dimethylvinylsilyl)ferrocene as a Two-Directional Core for the Construction of Homo- and Heterometallic Systems

Belén García,[†] Carmen M. Casado,[†] Isabel Cuadrado,^{*,†} Beatriz Alonso,[†] Moisés Morán,[†] and José Losada[†]

Departamento de Química Inorgánica, Facultad de Ciencias, Universidad Autónoma de Madrid, Cantoblanco 28049-Madrid, Spain, and Departamento de Ingeniería Química Industrial, Escuela Técnica Superior de Ingenieros Industriales, Universidad Politécnica de Madrid, 28006-Madrid, Spain

Received February 18, 1999

The divinyl derivative $\text{Fe}[(\eta^5\text{-C}_5\text{H}_4)(\text{Me}_2\text{SiCH}=\text{CH}_2)]_2$ (**1**), prepared by the low-temperature reaction of 1,1'-dilithioferrocene·TMEDA with $\text{ClSiMe}_2(\text{CH}=\text{CH}_2)$, has been used as a readily functionalizable core unit for the synthesis of multimetallic systems. The hydrosilylation reaction of **1** with Cl_2MeSiH and Ph_2MeSiH provides the tetrafunctional ferrocenes $\text{Fe}[(\eta^5\text{-C}_5\text{H}_4)(\text{SiMe}_2(\text{CH}_2)_2\text{SiMeCl}_2)]_2$ (**2**) and $\text{Fe}[(\eta^5\text{-C}_5\text{H}_4)(\text{SiMe}_2(\text{CH}_2)_2\text{SiMePh}_2)]_2$ (**5**), which after reaction with $\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{Li})(\eta^5\text{-C}_5\text{H}_5)$ and $\text{Cr}(\text{CO})_6$, respectively, afforded the pentametallic molecules $\text{Fe}[(\eta^5\text{-C}_5\text{H}_4)(\text{SiMe}_2(\text{CH}_2)_2\text{SiMeFc}_2)]_2$ (**3**) ($\text{Fc} = (\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)$) and $\text{Fe}[(\eta^5\text{-C}_5\text{H}_4)(\text{SiMe}_2(\text{CH}_2)_2\text{SiMe}\{(\eta^6\text{-C}_6\text{H}_5)\text{Cr}(\text{CO})_3\}_2)]_2$ (**6**). Characterization of the synthesized molecules by ^1H , ^{13}C , and ^{29}Si NMR and IR spectroscopy, mass spectrometry, and elemental analysis supports their assigned structures. The electrochemical behavior has been studied. While **3** contains two pairs of outer silicon-bridged ferrocenyl units, in which the iron centers interact with one another, in the related **6** the chromium tricarbonyl groups complexed to arene rings, also joined by a single silicon, are essentially noninteracting.

Introduction

Much attention has been currently devoted to the chemistry of ferrocenyl compounds because of their importance in many fields such as organic synthesis, catalysis, and materials science.¹ The ferrocene unit has proved to be a versatile building block with excellent thermal and photochemical stability. Thus, the synthesis of ferrocenes with tailor-made properties has been a goal for many synthetic chemists. In particular, the ferrocenyl unit has been successfully incorporated into polymers as a pendant group and also as an integral part of the polymer backbone.^{2–11}

Very recently, functionalized ferrocenes have become attractive units for the construction of novel organometallic molecules, in the rapidly emerging area of dendrimers.¹² The combination of the unique and valuable redox properties of ferrocene with the architectural features of dendrimers provides access to new materials with high overall symmetries, well-defined internal cavities, and nanometer dimensions together with specific physical and chemical properties which would be

* To whom correspondence should be addressed. Tel: 91-397-48-34. Fax: 91-397-48-33. E-mail: isabel.cuadrado@uam.es.

[†] Universidad Autónoma de Madrid.

[‡] Universidad Politécnica de Madrid.

(1) *Ferrocenes: Homogeneous Catalysis-Organic Synthesis-Materials Science*, Togni, A., Hayashi, T., Eds.; VCH: Weinheim, Germany, 1995.

(2) For excellent recent reviews on ferrocene-based polymers see: (a) Peckham, T. J.; Gómez-Elipé, P.; Manners, I. In *Metalloenes*; Togni, A., Halterman, R. L., Eds.; Wiley-VCH: Weinheim, Germany, 1998; Vol. 2, p 723. (b) Gonsalves, K. E.; Chen, X. Togni, A. In ref 1, p 497.

(3) For recent examples of ferrocenyl-based polymers, see refs 3–11: (a) Casado, C. M.; Cuadrado, I.; Morán, M.; Alonso, B.; Lobete, F.; Losada, J. *Organometallics* **1995**, *14*, 2618. (b) Casado, C. M.; Morán, M.; Losada, J.; Cuadrado, I. *Inorg. Chem.* **1995**, *34*, 1668. (c) Morán, M.; Casado, C. M.; Cuadrado, I.; Losada, J. *Organometallics* **1993**, *12*, 4237. (d) Casado, C. M.; Cuadrado, I.; Morán, M.; Alonso, B.; García, B.; González, B.; Losada, J. *Coord. Chem. Rev.*, in press.

(4) (a) Gómez-Elipé, P.; Resendes, R.; Macdonald, P. M.; Manners, I. *J. Am. Chem. Soc.* **1998**, *120*, 8348. (b) Jäkle, F.; Rulkens, R.; Zech, G.; Foucher, D. A. Lough, A. J.; Manners, I. *Chem. Eur. J.* **1998**, *4*, 2117. (c) Ni, Y.; Rulkens, R.; Manners, I. *J. Am. Chem. Soc.* **1996**, *118*, 4102. (d) Manners, I. *Adv. Organomet. Chem.* **1995**, *37*, 131. (e) Foucher, D. A.; Tang, B.-Z.; Manners, I. *J. Am. Chem. Soc.* **1992**, *114*, 6246.

(5) (a) Pannell, K. H.; Sharma, H. K. *Organometallics* **1997**, *16*, 3077. (b) Kapoor, R. N.; Crawford, G. M.; Mahmoud, J.; Dement'ev, V. V.; Nguyen, M. T.; Diaz, A. F.; Pannell, K. H. *Organometallics* **1995**, *14*, 4944. (c) Pannell, K. H.; Dement'ev, V. V.; Li, H.; Cervantes-Lee, F.; Nguyen, M. T.; Diaz, A. F. *Organometallics* **1994**, *13*, 3644. (d) Nguyen, M. T.; Diaz, A. F.; Dement'ev, V. V.; Pannell, K. H. *Chem. Mater.* **1994**, *6*, 952.

(6) (a) Compton, D. L.; Rauchfuss, F. *Organometallics* **1994**, *13*, 4367. (b) Brandt, P. F.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **1992**, *114*, 1926.

(7) Southard, G. E.; Curtis, M. D. *Organometallics* **1997**, *16*, 5618.

(8) Buretea, M. A.; Tilley, T. D. *Organometallics* **1997**, *16*, 1507.

(9) Hirao, T.; Kurashina, M.; Aramaki, K.; Nishihara, H. *J. Chem. Soc., Dalton Trans.* **1996**, 2929.

(10) Crumbliss, A. L.; Cooke, D.; Castillo, J.; Wisian-Neilson, P. *Inorg. Chem.* **1993**, *32*, 6088.

(11) Albagly, D.; Bazan, G.; Wrighton, M. S.; Schrock, R. R. *J. Am. Chem. Soc.* **1992**, *114*, 4150.

(12) For recent reviews on dendrimers, see, for example: (a) Newkome, G. R.; Moorefield, C. N.; Vögtle, F. *Dendritic Molecules: Concepts, Synthesis, Perspectives*; VCH: Weinheim, Germany, 1996. (b) Newkome, G. R. *Advances in Dendritic Macromolecules*; JAI Press: Greenwich, CT, 1994–1995; Vols. 1–3. (c) Vögtle, F., Ed. *Topics in Current Chemistry*; Springer-Verlag: Berlin, 1998; Vol. 197. (d) Ardoin, N.; Astruc, D. *Bull. Soc. Chim. Fr.* **1995**, *132*, 875. (e) Gorman, C. *Adv. Mater.* **1998**, *10*, 295. (f) Frey, H.; Lach, C.; Lorenz, K. *Adv. Mater.* **1998**, *10*, 279. (g) Hearshaw, M. A.; Moss, J. R. *Chem. Commun.* **1999**, 1.

expected to differ from those of the ferrocene-based materials prepared to date.¹³

In this context, over the past few years, we and others have prepared dendrimers of different chemical nature and structure containing ferrocenyl moieties.^{13–25} In some of these dendrimers the ferrocenyl moieties are located at the periphery and behave as independent, electronically isolated units, and they can act as molecular multielectron reservoirs. Interesting applications relying upon the use of some of these ferrocenyl dendrimers as amperometric biosensors,^{15a} in molecular recognition of anions,^{13,15b,20a} as materials to modify electrode surfaces,^{13,16,17} and as multisite guests for complexation by β -cyclodextrins¹⁸ have been already recognized. In addition, we have also prepared dendrimers possessing redox-active organometallic units linked together in close proximity so that there is electronic communication between the metal sites in the dendritic structure.¹⁹

In our quest for new series of dendrimeric macromolecules possessing redox-active organometallic moieties at predetermined sites, our aim now is to use suitable polyfunctional ferrocenyl derivatives as starting cores. In particular, vinyl-functionalized molecules potentially constitute valuable building blocks in the convergent or divergent synthesis of dendrimers, as the reactive vinyl groups would allow attachment of many different groups through hydrosilylation reactions to afford the desired multimetallic systems. Hydrosilylation is one of the most versatile reactions in organosilicon chemistry.²⁶ We have previously used the hydrosilylation strategy with the following different goals: (i) to prepare novel redox-active organometallic molecules and network polymeric structures through the reactions of Si–H-functionalized tetramethylcyclotetrasiloxane and a cubic silsesquioxane with vinylferrocene, 1,1'-divinylferrocene,

and 1,1'-divinyloctamethylferrocene,^{3a,c} (ii) to grow different generations of dendrimers from tetraallylsilane^{13,14a} and tetramethylcyclotetrasiloxane^{14c} as starting cores, and (iii) to assemble ferrocenyl moieties to Si–H-functionalized silicon-based dendrimers.^{13,19,27}

This paper describes the successful use of 1,1'-bis(dimethylvinylsilyl)ferrocene as a two-directional starting core, for the synthesis of novel redox-active homo- and heterometallic pentanuclear molecules, which can be considered as first generations and useful models for dendrimers of higher nuclearity with regard to the structural and electrochemical properties.

Results and Discussion

Synthesis of the Pentaferrocenyl 3. Our first attempts to synthesize novel redox-active polymetallic molecules from a vinyl-functionalized starting core involved the reaction of 1,1'-divinylferrocene with Cl₂-MeSiH. Unfortunately, this reaction failed either completely or in large measure since it mainly afforded oxidation products of the starting ferrocene derivative, and other presumably polymeric materials, which have not been characterized. These difficulties prompted us to explore the use of a different divinyl-functionalized ferrocene as the key reactive organometallic molecule, such as 1,1'-bis(dimethylvinylsilyl)ferrocene (**1**) (Scheme 1), in which the reactive vinyl sites are separated from the cyclopentadienyl ring and protected by the SiMe₂ group. Thirty-five years ago, Greber and Hallensleben briefly described the synthesis of compound **1**, which was prepared at that time by the hydrosilylation reaction of 1,1'-bis(dimethylhydrosilyl)ferrocene with acetylene in the presence of H₂PtCl₆ as catalyst.²⁸ Only minimal characterization data (IR) were reported. In our laboratory, we have prepared and fully characterized this divinyl-functionalized ferrocenyl derivative **1**, which has now been synthesized by reaction of Fe(η^5 -C₅H₄Li)₂·TMEDA (TMEDA = *N,N,N,N*-tetramethylethylenediamine) with dimethylvinylchlorosilane in hexane at –78 °C. After appropriate workup, the crude product was purified by column chromatography on silica to afford **1**, which was isolated in a 65% overall yield as a reddish orange liquid.

The availability of the vinyl groups in the difunctional ferrocene **1** enables further functionalization with reactive SiCl groups through a hydrosilylation reaction. Thus, compound **1** was reacted with an excess of dichloromethylsilane in toluene at 40 °C in the presence of Karstedt's catalyst (divinyltetramethyldisiloxane–platinum complex) (Scheme 1). The reaction was completed in 15 min, affording in excellent yield the intermediate **2**, which was isolated as an orange oil. It is known that a critical problem in carrying out hydrosilylation reactions is the possible occurrence of Markovnikov addition, yielding the α -isomer. According to the ¹H NMR spectrum of the hydrosilylation product, only the β -isomer was formed under the described reaction conditions, which ensures a regular growth and the generation of molecules of maximum symmetry.

(13) (a) Cuadrado, I.; Morán, M.; Losada, J.; Casado, C. M.; Pascual, C.; Alonso, B.; Lobete, F. In *Advances in Dendritic Macromolecules*; Newkome, G. R., Ed.; JAI Press: Greenwich, CT, 1996; Vol. 3, p 151. (b) Cuadrado, I.; Morán, M.; Casado, C. M.; Alonso, B.; Losada, J. *Coord. Chem. Rev.*, in press.

(14) (a) Alonso, B.; Cuadrado, I.; Morán, M.; Losada, J. *J. Chem. Soc., Chem. Commun.* **1994**, 2575. (b) Cuadrado, I.; Morán, M.; Casado, C. M.; Alonso, B.; Lobete, F.; García, B.; Ibisate, M.; Losada, J. *Organometallics* **1996**, *15*, 5278. (c) Casado, C. M.; Cuadrado, I.; Morán, M.; Alonso, B.; Barranco, M.; Losada, J. *Appl. Organomet. Chem.* **1999**, *13*, 245.

(15) (a) Losada, J.; Cuadrado, I.; Morán, M.; Casado, C. M.; Alonso, B.; Barranco, M. *Anal. Chim. Acta* **1996**, *251*, 5. (b) Casado, C. M.; Cuadrado, I.; Alonso, B.; Morán, M.; Losada, J. *J. Electroanal. Chem.* **1999**, *463*, 87.

(16) Alonso, B.; Morán, M.; Casado, C. M.; Lobete, F.; Losada, J.; Cuadrado, I. *Chem. Mater.* **1995**, *7*, 1440.

(17) Takada, K.; Díaz, D. J.; Abruña, H.; Cuadrado, I.; Casado, C. M.; Alonso, B.; Morán, M.; Losada, J. *J. Am. Chem. Soc.* **1997**, *119*, 10763.

(18) Castro, R.; Cuadrado, I.; Alonso, B.; Casado, C. M.; Morán, M.; Kaifer, A. *J. Am. Chem. Soc.* **1997**, *119*, 5760.

(19) Cuadrado, I.; Casado, C. M.; Alonso, B.; Morán, M.; Losada, J.; Belsky, V. *J. Am. Chem. Soc.* **1997**, *119*, 7613.

(20) Valério, C.; Fillaut, J.-L.; Ruiz, J.; Guittard, J.; Blais, J.-C.; Astruc, D. *J. Am. Chem. Soc.* **1997**, *119*, 9, 2588.

(21) Cardona, C. M.; Kaifer, A. E. *J. Am. Chem. Soc.* **1998**, *120*, 4023.

(22) Köllner, C.; Pugin, B.; Togni, A. *J. Am. Chem. Soc.* **1998**, *120*, 10274.

(23) Shu, C.-F.; Shen, H.-M. *J. Mater. Chem.* **1997**, *7*, 47.

(24) Achar, S.; Immoos, C. E.; Hill, M. G.; Catalano, V. J. *Inorg. Chem.* **1997**, *36*, 2314.

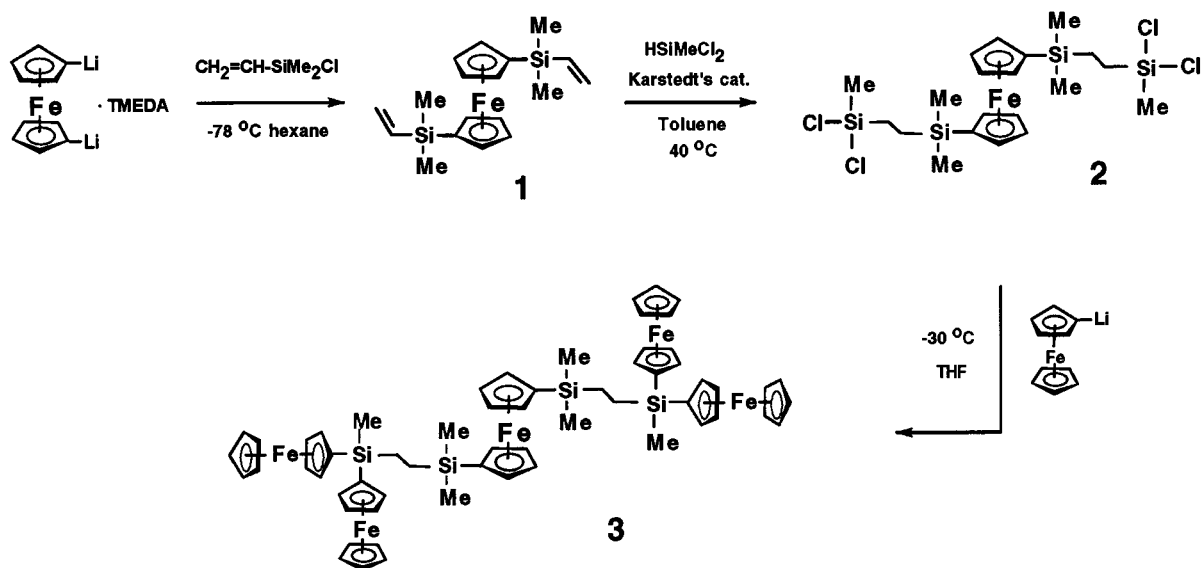
(25) Jutzi, P.; Batz, C.; Neumann, B.; Stammli, H.-G. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2118.

(26) (a) *Comprehensive Handbook on Hydrosilylation*; Marciniak, B., Ed.; Pergamon Press: Oxford, U.K., 1992. (b) Ojima, I. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappaport, Z., Eds.; Wiley: New York, 1989; Part 2, p 1479.

(27) Alonso, B. Ph.D. Thesis, Universidad Autónoma de Madrid, 1997.

(28) Greber, V. G.; Hallensleben, M. L. *Makromol. Chem.* **1965**, *83*, 148.

Scheme 1



The compositions and structures of both ferrocenyl derivatives **1** and **2** were straightforwardly determined by elemental analyses, mass spectrometry (FAB-MS), and IR and ^1H , ^{13}C , and ^{29}Si NMR spectra. For example, the ^1H NMR spectrum of **1** (see Figure 1A) shows the set of resonances characteristic of the reactive vinyl groups at δ 5.77, 6.02, and 6.31 ppm in the expected integration ratio. The complete disappearance of the vinyl resonances in the spectrum of **2** (Figure 1B) provides evidence of the completeness of the hydrosilylation reaction. In the ^{29}Si NMR spectrum of **1** (Figure 1D) a single resonance at -10.05 ppm is observed,

whereas two resonances are detected in the spectrum of **2**; the interior silicon directly bonded to the ferrocenyl unit appears at 0.21 ppm, and the signal for the terminal MeSiCl_2 is shifted downfield at 33.7 ppm (Figure 1E).

The high reactivity of the tetrafunctional **2** was exploited by subsequent conversion to the pentametallic **3** by the salt-elimination reaction illustrated in Scheme 1. For this purpose (tri-*n*-butylstannyl)ferrocene was selected as the starting material, since it has proved to be an excellent precursor of pure lithioferrocene.²⁹ This is crucial, in order to exclude the formation of the

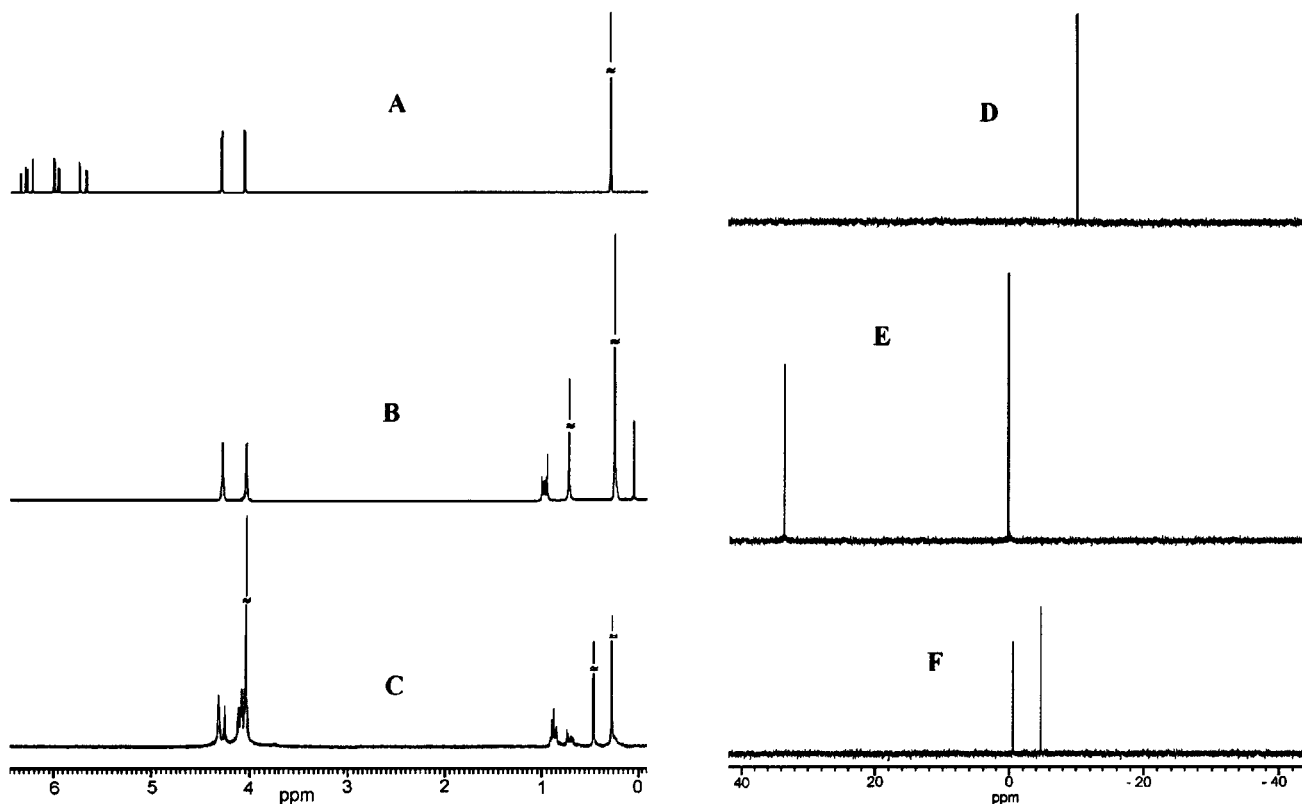


Figure 1. ^1H NMR (300 MHz, CDCl_3) spectra of **1** (A), **2** (B), and **3** (C), and $^{29}\text{Si}\{^1\text{H}\}$ NMR (59.3 MHz, CDCl_3) spectra of **1** (D), **2** (E), and **3** (F).

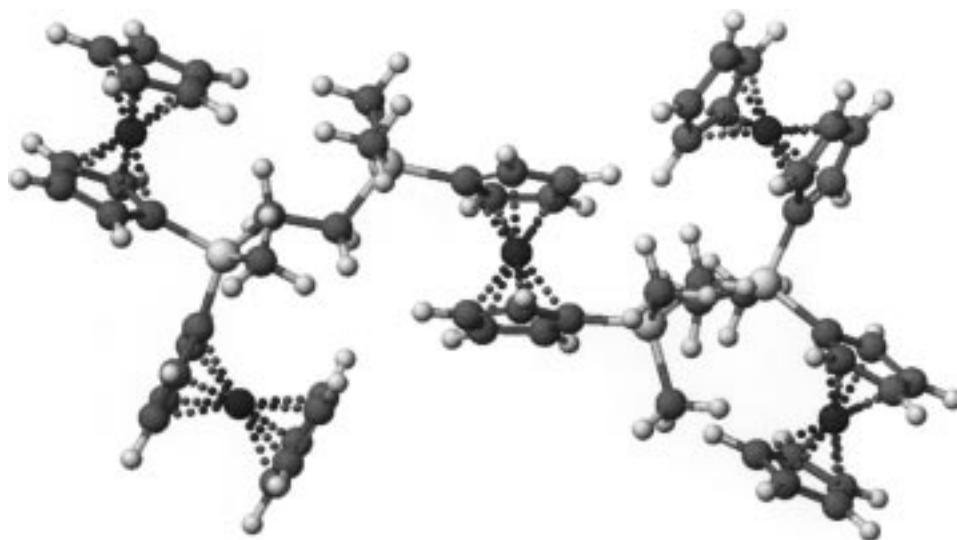


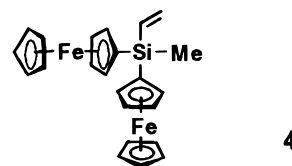
Figure 2. Structure of **3** from molecular modeling.

dimetalated ferrocene, $\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{Li})_2$, which could produce undesirable polymerization products or intramolecular side reactions. In this way, ferrocenyllithium thus generated was allowed to react with **2** in THF at -30°C . After purification by column chromatography the desired compound **3**, possessing a central ferrocene and four outer ferrocenyl units linked together in pairs through a bridging silicon atom, was isolated as an air-stable orange crystalline solid.

The pentametallic molecule **3** was fully characterized by NMR (^1H , ^{13}C , and ^{29}Si) and IR spectroscopy, mass spectrometry, and elemental analysis. As expected, only two different silicon resonances were observed in the ^{29}Si NMR (Figure 1F). The signal at $\delta -4.48$ ppm was assigned to the outer silicon atom bridging two ferrocenyl units, and the resonance at $\delta -0.32$ ppm was attributed to the inner silicon atoms linked to the disubstituted ferrocene core. In addition, in the ^1H NMR spectrum, for the five sets of different ferrocene protons, five distinguishable signals were detected with an integration ratio of 4:4:8:8:20. The singlet at $\delta 4.05$ ppm was assigned to the nonsubstituted cyclopentadienyl ring, whereas the AA'BB' systems at $\delta 4.09$ and 4.32 ppm and at $\delta 4.11$ and 4.26 ppm correspond to the outer and inner disubstituted ferrocene cyclopentadienyl rings, respectively (Figure 1C). Evidence of the pentametallic structure was also provided by mass spectrometric (EI-MS) analysis, which gave the molecular ion at 1182.3 amu as the dominant peak, as well as some informative fragmentation peaks.

Although compound **3** has been isolated as small orange crystals, unfortunately all attempts to grow crystals suitable for X-ray diffraction studies have failed so far. In the absence of the X-ray data we have used the computer-generated molecular model in order to gain insight into the structure of this pentaferrocenyl molecule. Molecular modeling calculations of **3** show that in its lowest energy conformation the four peripheral ferrocenyl units are oriented at ca. 100° relative to one another, as shown in Figure 2. This arrangement resembles that observed in the X-ray crystal structure

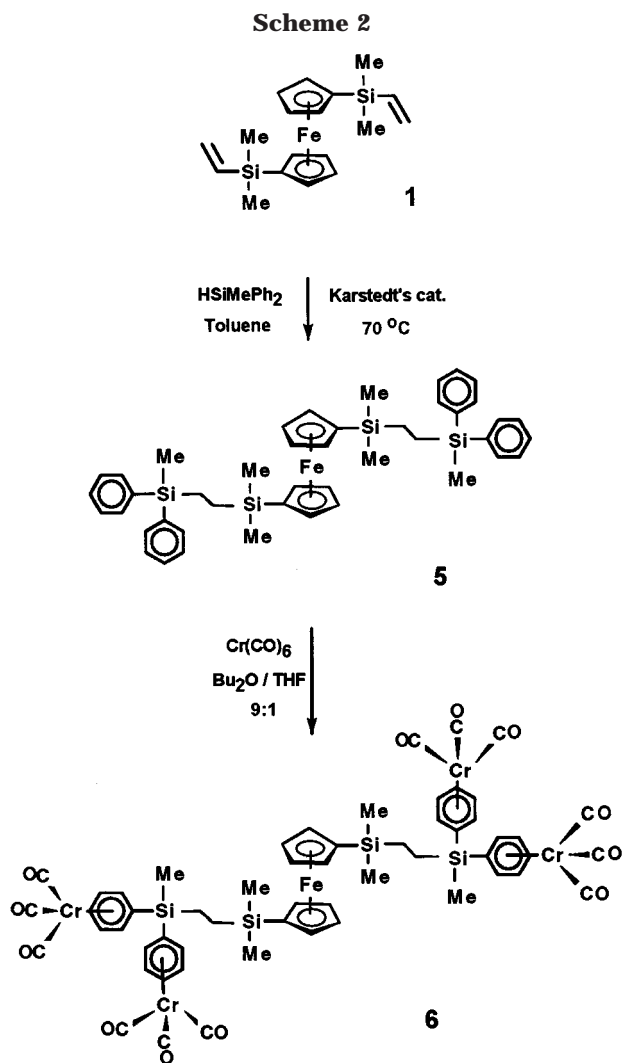
of the related silicon-bridged ferrocenyl derivative **4** previously reported.¹⁹



Synthesis of the Heteropentametallic 6. We have also carried out the hydrosilylation reaction of **1** with Ph_2MeSiH in the presence of catalytic amounts of Karstedt's catalyst in toluene at 70°C (Scheme 2). ^1H NMR spectroscopy was used to follow the progress of the reaction, by monitoring the loss of the vinyl resonances of **1**. The reaction was completed in approximately 2 h. The resulting hydrosilylated product was purified by column chromatography using a tetrahydrofuran/hexane mixture (1/30) as eluent. The tetraphenyl-functionalized ferrocene **5** was isolated as an air-stable orange oil. It is interesting to note that this hydrosilylation reaction has been carried out under conditions more forcing (higher temperature and longer reaction times) than those used in the synthesis of **2**. This fact can be easily justified on the basis of the values of the IR stretching frequencies of the Si-H bonds for methyl-diphenylsilane ($\nu(\text{SiH})$ 2123 cm^{-1}) and methyl-dichlorosilane ($\nu(\text{SiH})$ 2215 cm^{-1}), which suggest that the electronic environment about the reacting silicon center in methyl-dichlorosilane is more suitable for hydrosilylation than in methyl-diphenylsilane. In fact, it has been well-established that electron-withdrawing substituents on the Si-H bond increase the rate of the hydrosilylation process compared to the case of more electron-donating groups.²⁶

The π -coordinating ability of the outer arene rings of **5** toward transition metals offered a good chance to gain an easy synthetic access to heterometallic molecules. Thus, the pentanuclear molecule **6** was formed by thermal treatment of **5** with an excess of $\text{Cr}(\text{CO})_6$, using an approximately 9/1 mixture (v/v) of *n*-Bu₂O and THF as solvent. After chromatographic purification, the desired **6** was isolated as a yellow solid.

(29) Guillaneux, D.; Kagan, H. B. *J. Org. Chem.* **1995**, *60*, 2502.



Several spectroscopic features were characteristic of these molecules. For example, for the heterometallic **6**, the η^6 -coordination of the Cr(CO)₃ moieties to the phenyl rings resulted in the appearance of two intense $\nu(\text{C}\equiv\text{O})$ bands at 1969 and 1893 cm^{-1} in the IR spectrum, as well as a characteristic resonance at 233 ppm due to the carbonyl carbon atoms in the ¹³C NMR spectrum. In addition, the total absence of signals in the range 7.35–7.50 ppm in the ¹H NMR spectrum of **6** provided further proof of the complete coordination of Cr(CO)₃ moieties to the four phenyl rings.

Electrochemistry of 1, 3, and 5. The cyclic voltammogram (CV) of the pentaferrocenyl molecule **3** in CH₂-Cl₂ solution containing 0.1 M [(*n*-Bu)₄N]PF₆ (TBAH) as supporting electrolyte is shown in Figure 3A. The CV exhibits two separated oxidation waves, the first one being broad and poorly resolved. In addition, a change in solubility of **3** accompanied the change in oxidation state, so that upon scan reversal after the oxidation process at a higher potential, the reduction wave was dramatically sharpened, giving rise to a cathodic stripping peak. Thus, the complete oxidation of **3** in this medium appears to result in the precipitation of the oxidized molecule onto the electrode surface, and on the reverse scan the molecule redissolves as it is reduced.

When acetonitrile is added to the CH₂Cl₂/electrolyte medium, the cathodic stripping peak disappears and the

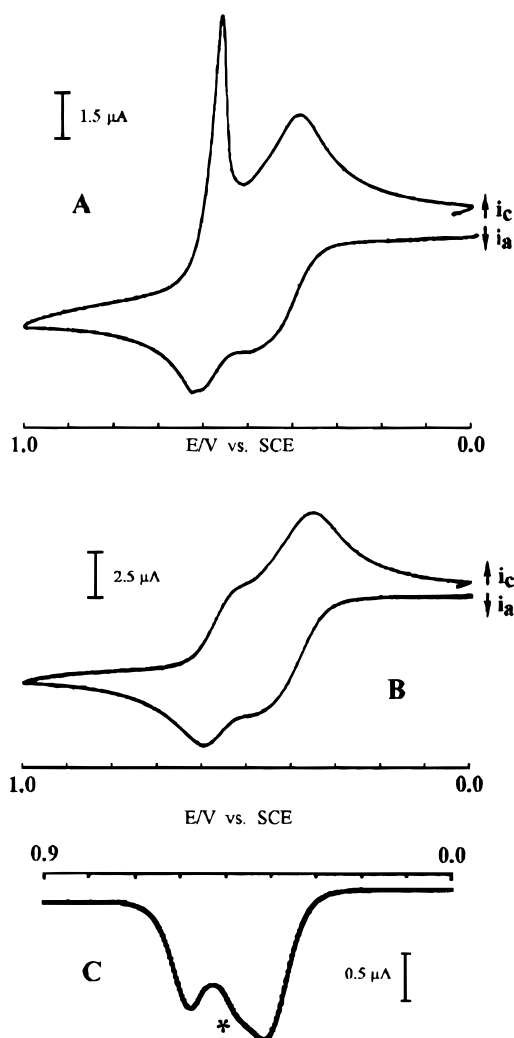


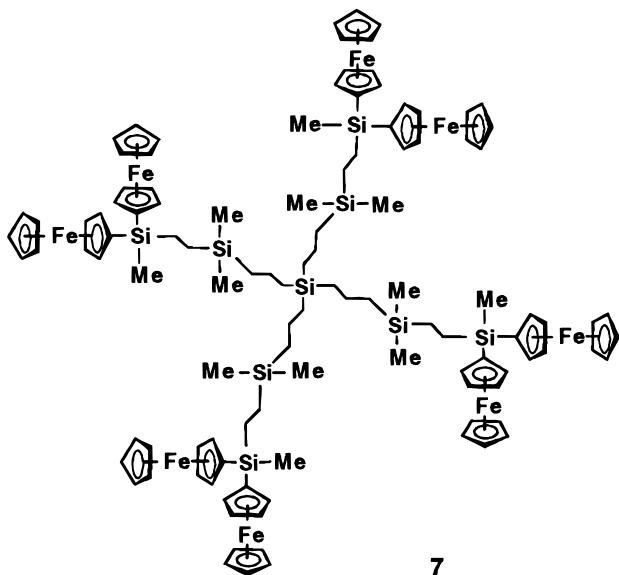
Figure 3. Cyclic voltammograms of **3** (A) in CH₂Cl₂ and (B) in CH₂Cl₂/CH₃CN (1/1 by volume) at a scan rate of 100 mV s⁻¹ and (C) a differential pulse voltammogram of **3** in CH₂Cl₂/CH₃CN (1/1 by volume) at a scan rate of 10 mV s⁻¹.

cyclic voltammogram displays the two diffusion-controlled, reversible redox processes shown in Figure 3B. The wave at the lowest potential remains broad and ill-defined. The determination of the number of electrons transferred in the complete oxidation of **3** was effected by exhaustive coulometry measurements, carried out past the anodic wave at the higher potential, resulting in the removal of 5 electrons/molecule.

The differential pulse voltammogram (DPV) of **3** (in CH₂Cl₂/CH₃CN solution) shows two peaks of different heights (Figure 3C). The first peak is broader than the second and displays a shoulder (marked in Figure 3C with an asterisk), suggesting two overlapped processes differing by approximately 70 mV in potential. Integration of the peaks areas gives a first to second wave ratio of 3:2. In the absence of any interactions between the iron centers of the pentametallic **3** one would expect two waves in a 1:4 ratio in the DPV response, corresponding to the two different ferrocene environments present in the molecule. Manners and co-workers recently found that in the DPV measurements of a related tetraferrocenylsilane the resolution of the peaks was attained if benzonitrile was used as solvent.³⁰ Unfortunately, with

our pentanuclear **3**, the use of benzonitrile as medium did not provide a higher resolution of the oxidation steps.

Formal potentials were calculated from the DPV peak potentials, and the results obtained were ${}^1E_{1/2} = 0.41$ V for the process corresponding to the first peak, ${}^2E_{1/2} = 0.48$ V for the second peak (observed as a shoulder), and ${}^3E_{1/2} = 0.59$ V for the peak at higher potential. Assignment of the formal potentials observed in the DPV of **3** to the corresponding electrochemical processes has been carried out by comparison with the redox potentials observed for the related dendritic molecule **7** previously described.¹⁹ This dendrimer, in which



ferrocenyl units are also linked together by a bridging silicon atom, serve as a valuable model, as there are significant structural and electronic similarities among the ferrocenyl moieties. The DPV of **7** shows two well-separated waves of equal intensity at $E_{1/2} = 0.41$ and 0.60 V vs SCE, indicating significant interactions between the ferrocene groups. On this basis, the first and third redox potentials of **3** can be assigned to the oxidation of the peripheral ferrocenes, as they are close to those previously observed for **7**. The redox behavior observed for these molecules can be related to that found in oligo- and polyferrocenylsilanes.^{31,32}

To assign unambiguously the second oxidation peak observed in the DPV of the pentametallc **3** at ${}^2E_{1/2} = 0.48$ V, we have also studied the electrochemical behavior of the mononuclear molecules **1** and **5**, because the environment around the ferrocenyl unit in these molecules is similar to that of the central ferrocene in **3**.

The CVs of **1** and **5** in CH_2Cl_2 solution are characteristic of a reversible oxidation process with the production of soluble stable products. Likewise, differential pulse voltammetry showed an oxidation wave at $E_{1/2} = 0.47$ V for **1** and $E_{1/2} = 0.45$ V for **5**. The less

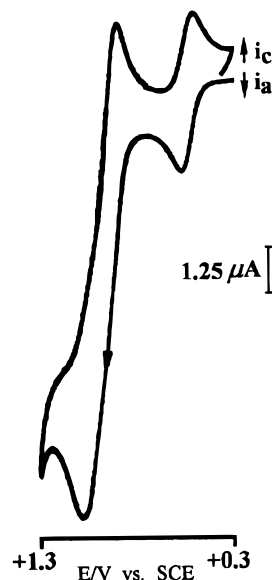


Figure 4. Cyclic voltammogram of **6** in $\text{CH}_2\text{Cl}_2/\text{TBAH}$, at a scan rate of 100 mV s^{-1} .

positive potential value determined for **1** and **5**, compared to that of the central ferrocene in **3**, indicates that in this case the removal of the electron is slightly more difficult owing to the double positive charge generated by the preceding step.

In summary, the pentametallc **3** exhibits three oxidation steps. The first two-electron step at ${}^1E_{1/2} = 0.41$ V corresponds to simultaneous electron removals from two nonadjacent outer terminal noninteracting ferrocenyl moieties. The second one-electron process at ${}^2E_{1/2} = 0.48$ V is centered on the disubstituted central ferrocene, and finally two electrons are removed from the remaining outer ferrocenyl centers neighboring those already oxidized at ${}^3E_{1/2} = 0.58$ V. The separation between the first and third waves, $\Delta E = {}^3E_{1/2} - {}^1E_{1/2}$, provides a measure of the degree of interaction between the outer iron centers. The obtained value, $\Delta E = 170$ mV, reveals significant electronic interactions between the terminal ferrocenyl moieties.

Electrochemistry of 6. The electrochemical behavior of **6** has been examined using a nonnucleophilic solvent (CH_2Cl_2) and TBAH as electrolyte. As illustrated in Figure 4 the cyclic voltammogram of compound **6** reveals two reversible oxidation waves at $E_{1/2} = 0.60$ V and $E_{1/2} = 1.05$ V vs SCE, respectively. Both oxidation processes are diffusion-controlled with the anodic current function $i/v^{1/2}$ independent of the scan rate. The ratio of the cathodic to anodic peak current is close to unity for both systems and the peak potentials separation were 60 and 160 mV, respectively.

Controlled-potential electrolysis revealed that a single electron is involved in the first oxidation step, and it can be assigned to the oxidation of the central ferrocenyl unit of **6**. The $E_{1/2}$ value of this first oxidation is appreciably higher than the $E_{1/2}$ found for the monometallic monomers **1** and **5**, and this is probably due to the electron-withdrawing nature of the four peripheral $(\eta^6\text{-C}_6\text{H}_5)\text{Cr}(\text{CO})_3$ moieties.

Analysis of the cyclic voltammogram shows that the anodic peak current of the second wave is approximately 4 times the i_p value of the first oxidation step. Therefore, this second oxidation peak can be attributed to a

(30) MacLachlan, M. J.; Lough, A. J.; Geiger, W. E.; Manners, I. *Organometallics* **1998**, *17*, 1873.

(31) (a) Rulkens, R.; Lough, A. J.; Manners, I.; Lovelace, S. R.; Grant, C.; Geiger, W. E. *J. Am. Chem. Soc.* **1996**, *118*, 12683. (b) Foucher, D. A.; Honeyman, C. H.; Nelson, J. M.; Zhong Tang, B.; Manners, I. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1709.

(32) Dement'ev, V. V.; Cervantes-Lee, F.; Parkanyi, L.; Sharma, H.; Pannell, K. H. *Organometallics* **1993**, *12*, 1983.

simultaneous multielectron transfer of four electrons removed from the four terminal chromium centers. The fact that the pentanuclear **6** exhibits this single-step oxidation process at $E_{1/2} = 1.05$ V is of relevance, as this implies that the peripheral chromium tricarbonyl moieties linked together by a silicon bridge do not essentially communicate electronically with each other. This fact contrasts interestingly with the case of **3**, in which appreciable interactions between the peripheral ferrocenyl moieties are detected. Therefore, the nature of arene rings seems to influence the degree of interaction between metallic centers.³³

Conclusions

We have established that 1,1'-bis(dimethylvinylsilyl)ferrocene can be used as an effective two-directional starting core molecule for the synthesis of homo- and heterometallic systems which are functionalized at their periphery with ferrocenyl and $(\eta^6\text{-C}_6\text{H}_5)\text{Cr}(\text{CO})_3$ moieties. The degree of interaction between the electroactive metal-based moieties linked together by a bridging silicon atom depends on their chemical nature. The extension of this synthetic methodology to the construction of higher generations of homo- and heterometallic dendrimers is currently in progress.

Experimental Section

General Data. All reactions and subsequent manipulations were carried out under an argon atmosphere by using conventional Schlenk techniques. THF was distilled from sodium benzophenone, CH_2Cl_2 and hexane were distilled from P_4O_{10} , and di-*n*-butyl ether was distilled from sodium. Dimethylvinylchlorosilane, diphenylmethylsilane, ferrocene, and *tert*-butyllithium (1.7 M solution in hexane and 1.5 M solution in pentane) were purchased from Fluka and used as received. Methylchlorosilane (Fluka) and tri-*n*-butylstannyl chloride (Aldrich) were distilled prior to use. *N*-Butyllithium (1.6 M solution in hexane) was purchased from Aldrich and used as received. Chromium hexacarbonyl (Aldrich) was sublimed prior to use. Divinyltetramethyldisiloxane-platinum complex (3–3.5% in xylene; Karstedt's catalyst), available from Petrarch Systems Inc., was used as received. (Tri-*n*-butylstannyl)ferrocene was synthesized as described in the literature.²⁹ Silica gel (70–230 mesh) and silanized silica gel (70–230 mesh) (Merck) were used for column chromatographic purifications.

Infrared spectra were recorded on a Bomem MB-100 FT-IR spectrometer. NMR spectra were recorded on a Bruker-AMX (^1H , 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 or to residual solvent resonances for ^1H and ^{13}C NMR (CDCl_3 : ^1H , δ 7.27 ppm; ^{13}C , δ 77.0 ppm). ^{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 $\text{Cr}(\text{acac})_3$ in order to reduce T1's.

Mass spectral analyses (positive FAB and EI) were conducted on a VG Auto Spec mass spectrometer. Elemental analyses were performed by the Microanalytical Laboratory, Universidad Autónoma de Madrid, Madrid, Spain.

Molecular mechanics calculations were made using the Cache 3.11 software package for Windows. The optimized

geometry has been calculated with MM2 using MM3 parameters to an average gradient <1 . The conformation with minimized energy was obtained from the optimized molecule using the sequential search option in the software package.

Electrochemical Measurements. Cyclic voltammograms were recorded on a BAS-CV-27 potentiostat. CH_3CN and $\text{CH}_2\text{-Cl}_2$ (spectrograde) for electrochemical measurements were freshly distilled from calcium hydride under nitrogen. The supporting electrolyte was in all cases TBAH that was purchased from BAS or Strem and was purified by recrystallization from ethanol and dried under vacuum at 60 °C. The supporting electrolyte concentration was typically 0.1 M. All cyclic voltammetric experiments were performed using either a platinum-disk working electrode ($A = 0.030$ cm²) or a glassy-carbon-disk working electrode ($A = 0.070$ cm²), each of which was polished prior to use with 1 μm diamond paste (Buehler) and rinsed thoroughly with water and acetone. All potentials are referenced to the saturated calomel electrode (SCE). A coiled platinum wire was used as a counter electrode. In general the concentrations of the solutions of the redox-active molecules for cyclic voltammetry were in the range 10^{-4} – 10^{-3} M. The solutions were deoxygenated by purging with prepurified nitrogen. No *iR* compensation was used. Differential pulse voltammetry was done with a Polarecord-E-506 Metrohm, with a scan rate of 10 mV s⁻¹, a pulse height of 10–20 mV, and a duration of 60 ms. DPV were recorded using $\text{CH}_2\text{-Cl}_2/\text{CH}_3\text{CN}$ solutions of the ferrocenyl derivatives. Formal potentials were calculated from the DPV peak potentials using $E_{1/2} = E_{\text{pk}} + E_{\text{pulse}}/2$, where E_{pulse} is the pulse height. Coulometric measurements were made with a PAR-379 digital coulometer, using Pt gauze as the working electrode.

Synthesis of Compounds. Synthesis of 1. A solution of ferrocene (3.3 g, 17.8 mmol) and TMEDA (5.5 mL) in hexane was treated with *n*-butyllithium (24 mL of 1.6 M solution in hexane). An orange precipitate was formed, and the system was stirred for 18 h. The dilithium salt $\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{Li})_2\cdot\text{TMEDA}$ formed, was separated by filtration, and was washed with hexane. The resulting pale orange precipitate was slurred by addition of 50 mL of hexane and cooled to –78 °C. To this stirred system was added dropwise a 20 mL hexane solution of $\text{SiClMe}_2\text{CH}=\text{CH}_2$ (4.3 g, 35.7 mmol). After 30 min, the mixture was warmed to room temperature and stirred for an additional 10 h. The reaction mixture was filtered, and volatiles were removed under vacuum. The oily residue was subjected to column chromatography on silica using hexane as eluent. The initial yellow band corresponding to a small amount of ferrocene was discarded. A second major orange band was collected, and solvent removal afforded the target compound **1** as a reddish orange liquid. Yield: 4.1 g (65%). Anal. Calcd (found) for $\text{C}_{18}\text{H}_{26}\text{Si}_2\text{Fe}$: C, 61.04 (61.11); H, 7.34 (7.40). ^1H NMR (CDCl_3 , 300 MHz): δ 0.31 (s, 12H, $\text{Si}(\text{CH}_3)_2$), δ 4.08 (m, 4H, C_5H_4), δ 4.31 (m, 4H, C_5H_4), δ 5.77 (dd, 2H, $\text{CH}=\text{CH}_2$ (cis)), δ 6.02 (dd, 2H, $\text{CH}=\text{CH}_2$ (trans)), δ 6.31 (dd, 2H, $\text{CH}=\text{CH}_2$). ^{13}C NMR (CDCl_3 , 75.43 MHz): δ –1.98 (CH_3), δ 69.90, 71.36, 73.06 (C_5H_4), δ 131.64 (CH_2), δ 139.02 (CH). ^{29}Si NMR (CDCl_3 , 59.3 MHz): δ –10.05. IR (neat): $\nu(\text{C}=\text{C})$ 1646 cm⁻¹. MS (FAB; m/z (%)): 354.1 (M^+ , 100).

Synthesis of 2. HSiMeCl_2 (1 g, 8.7 mmol) was slowly added to a solution of **1** (1 g, 2.8 mmol) in 25 mL of toluene, containing 25 μL of Karstedt's catalyst (3–5% Pt, in xylene), and the solution was then heated to 40 °C. After the mixture was stirred for 15 min at this temperature, the complete disappearance of the vinyl resonances in the range 5.77–6.31 ppm was confirmed by ^1H NMR spectroscopy. The excess amounts of HSiMeCl_2 and toluene were removed under vacuum to afford compound **2** as a moisture-sensitive viscous orange oil, which was immediately used in the next reaction. Yield: 1.6 g (97%). Anal. Calcd (found) for $\text{C}_{20}\text{H}_{34}\text{Si}_4\text{Cl}_4\text{Fe}$: C, 41.13 (41.25); H, 5.82 (5.93). ^1H NMR (CDCl_3 , 300 MHz): δ 0.28 (s, 12H, $\text{Si}(\text{CH}_3)_2$), δ 0.75 (s, 6H, SiCl_2CH_3), δ 0.77 (m, 4H, $\text{Si}(\text{CH}_3)_2\text{CH}_2$), δ 0.98 (m, 4H, SiCl_2CH_2), δ 4.07 (m, 4H, C_5H_4), δ 4.32 (m, 4H,

(33) The lack of communication between (aryl)Cr(CO)₃ units linked by a bridging silicon atom has been also noted previously: Rieke, R. D.; Tucker, I.; Milligan, S.; Wright, D. R.; Willeford, B. R.; Radonovich, L.; Eyring, M. W. *Organometallics* **1982**, *1*, 938.

C_5H_4). ^{13}C NMR ($CDCl_3$, 75.43 MHz): δ -2.90 ($Si(CH_3)_2$), δ 4.28 ($SiCl_2CH_3$), δ 7.98 ($Si(CH_3)_2CH_2$), δ 14.66 ($SiCl_2CH_2$), δ 69.95, 71.29, 73.01 (C_5H_4). ^{29}Si NMR ($CDCl_3$, 59.3 MHz): δ 0.21 ($Si(CH_3)_2$), δ 33.7 ($SiCl_2$).

Synthesis of 3. A solution of (tri-*n*-butylstanny)ferrocene (6.4 g, 13.5 mmol) in 25 mL of THF was cooled to $-78^\circ C$ and treated with *n*-butyllithium (8 mL, 1.6 M solution in hexane). The reaction mixture was stirred at that temperature for 90 min and then warmed to $-30^\circ C$, and a THF solution of **2** (1.6 g, 2.7 mmol) was added dropwise. The mixture was stirred for 1 h, warmed to room temperature, and stirred for a further 24 h. The solvent was removed under vacuum, and the orange residue was chromatographed on a silica gel column using hexane and a hexane/THF mixture as eluents. Elution with hexane produced a yellow band, which gave ferrocene. The orange band eluted with hexane/THF (20/1) afforded compound **3** as an orange air-stable crystalline solid. Yield: 1.43 g (45%). Anal. Calcd (found) for $C_{60}H_{70}Si_4Fe_5$: C, 60.95 (61.05); H, 5.92 (6.01). 1H NMR ($CDCl_3$, 300 MHz): δ 0.26 (s, 12H, $Si(CH_3)_2$), δ 0.45 (s, 6H, $SiF_2C_2CH_3$), δ 0.73 (m, 4H, $Si(CH_3)_2CH_2$), δ 0.84 (m, 4H, $SiF_2C_2CH_2$), δ 4.05 (s, 20H, C_5H_5), δ 4.09 (m, 8H, C_5H_4), δ 4.11 (m, 4H, C_5H_4), δ 4.26 (m, 4H, C_5H_4), δ 4.32 (m, 8H, C_5H_4). ^{13}C NMR ($CDCl_3$, 75.43 MHz): δ -3.27 ($SiF_2C_2CH_3$), δ -2.72 ($Si(CH_3)_2$), δ 8.64 ($Si(CH_3)_2CH_2$), δ 9.50 ($SiF_2C_2CH_2$), δ 68.19 (C_5H_5), δ 68.08, 71.14, 72.98 (C_5H_4/C_5H_4), δ 70.50, 70.86, 73.37 (C_5H_5/C_5H_4). ^{29}Si NMR ($CDCl_3$, 59.3 MHz): δ -0.32 ($Si(CH_3)_2$), δ -4.48 (SiF_2C_2). MS (EI; 70 eV: m/z (%)): 1182.0 (M^+ , 100), 684.0 ($[SiF_2C_2(CH_2)_3SiMeF_2]^+$, 30.2), 591.7 (M^{2+} , 18.0), 497.9 ($[SiF_2C_2(CH_2)_3SiMeF_2]^+$, 33.6), 413.0 ($[SiMeF_2]^+$, 81.3), 243.0 ($[F_2SiMe_2]^+$, 53.51).

Synthesis of 5. A mixture of 30 μL of a solution of Karstedt's catalyst (3–5% Pt in xylene) and 1 g (2.8 mmol) of **1** in toluene was stirred at room temperature for 30 min. A solution of HMeSiPh₂ (1.2 g, 6.3 mmol) in 15 mL of toluene was then added dropwise, and the reaction mixture was heated to $70^\circ C$. After 2 h, the completeness of the hydrosilylation reaction was confirmed by the disappearance of the resonances corresponding to the vinyl group in the 1H NMR spectrum. The excess amounts of HMeSiPh₂ and the solvent were removed under vacuum. The resulting orange residue was redissolved in hexane and the solution purified by column chromatography on silica. An orange band was collected using a THF/hexane mixture (1/30) as eluent. Solvent removal afforded the target product **5** as an air-stable orange oil. Yield: 1.79 g (85%). Anal. Calcd (found) for $C_{44}H_{54}Si_4Fe$: C, 70.49 (70.38); H, 7.20 (7.27). 1H NMR ($CDCl_3$, 300 MHz): δ 0.23 (s, 12H, $Si(CH_3)_2$), δ 0.54 (s, 6H, $SiCH_3$), δ 0.59 (m, 4H, $Si(CH_3)_2CH_2$), δ 0.97 (m, 4H, $SiCH_3CH_2$), δ 3.99 (m, 4H, C_5H_4),

δ 4.22 (m, 4H, C_5H_4), δ 7.35 (m, 8H, C_6H_5), δ 7.50 (m, 12H, C_6H_5). ^{13}C NMR ($CDCl_3$, 75.43 MHz): δ -2.81 ($Si(CH_3)_2$), δ -5.02 ($SiCH_3$), δ 6.41 ($Si(CH_3)_2CH_2$), δ 9.05 ($SiCH_3CH_2$), δ 68.09, 71.05, 72.98 (C_5H_4), δ 127.76, 129.04, 134.51, 137.27 (C_6H_5). ^{29}Si NMR ($CDCl_3$, 59.3 MHz): δ -0.32 (SiC_5H_4), δ -5.47 (SiC_6H_5). MS (FAB; m/z (%)): 750.4 (M^+ , 100).

Synthesis of 6. A 100 mL, two-necked round-bottomed flask equipped with a gas inlet and a straight-tube condenser topped with gas inlet and bubbler was charged with 0.88 g (4 mmol) of $Cr(CO)_6$, 0.6 g (0.8 mmol) of **5**, *n*-Bu₂O (90 mL), and THF (10 mL). The mixture was stirred and heated to a gentle reflux. The progress of the reaction was monitored by occasionally cooling a sample of the mixture to room temperature and recording the IR and 1H NMR spectra of the supernatant solution. Over the course of the reaction, new carbonyl bands at 1974 and 1904 cm^{-1} were observed to increase in intensity. Likewise, in the 1H NMR ($CDCl_3$) spectrum, the resonances in the 7.35–7.50 ppm region progressively disappeared while new resonances in the range 5.13–5.57 ppm were detected. After 48 h, the reaction mixture was cooled to room temperature and then to $-10^\circ C$ for 3 h. The suspension was filtered through a pad of silanized silica (3 \times 3 cm) to remove the small amounts of insoluble decomposition products and some unreacted $Cr(CO)_6$. From the resulting light orange solution, the solvent was removed under vacuum and the residue was purified by column chromatography (2 \times 30 cm) on silanized silica, using a CH_2Cl_2/n -hexane mixture (1/3) and pure CH_2Cl_2 as eluents. The yellow band eluted with CH_2Cl_2 was collected, and the desired product was precipitated by addition of *n*-hexane. Analytically pure **6** was isolated as a light- and air-sensitive yellow solid. Yield: 20%. Anal. Calcd (found) for $C_{56}H_{54}O_{12}Si_4FeCr_4$: C, 51.94 (51.73); H, 4.17 (4.01). 1H NMR ($CDCl_3$, 300 MHz): δ 0.28 (s, 12H, $Si(CH_3)_2$), δ 0.59 (s, 6H, $SiCH_3$), δ 0.71 (m, 4H, $Si(CH_3)_2CH_2$), δ 0.93 (m, 4H, $SiCH_3CH_2$), δ 4.07 (m, 4H, C_5H_4), δ 4.29 (m, 4H, C_5H_4), δ 5.13 (m, 8H, C_6H_5), δ 5.38 (m, 8H, C_6H_5), δ 5.57 (m, 4H, C_6H_5). ^{13}C NMR ($CDCl_3$, 75.43 MHz): δ -2.51 ($Si(CH_3)_2$), δ -3.13 ($SiCH_3$), δ 6.22 ($Si(CH_3)_2CH_2$), δ 9.11 ($SiCH_3CH_2$), δ 71.09, 72.98 (C_5H_4), δ 89.95, 96.05, 99.80 (C_6H_5), δ 232.96 (CO). IR (KBr): $\nu(C/O)$ 1969 and 1893 cm^{-1} . MS (FAB; m/z (%)): 1295.3 (M^+ , 18.9), 1211.3 ($[M - 3(CO)]^+$, 3.8).

Acknowledgment. We thank the Spanish Dirección General de Enseñanza Superior e Investigación Científica (DGES), Project PB97-0001, for the financial support of this research.

OM990109J