(Dimethylamino)dimethylsilyl-Substituted Dimeric and Siloxanyl Polymeric Compounds Containing $[(\eta^5\text{-}C_5R_4)Fe(CO)(\mu\text{-}CO)]_2$ (R = H, Me) Moieties. Synthesis, Characterization, and Electrochemistry

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Received August 12, 1992

Binuclear iron complexes $[\{(\eta^5\text{-}C_5R_4)Me_2Si(NMe_2)\}Fe(CO)_2]_2$ (R = H (**1**), R = Me (**2**)) have been prepared by thermal treatment of the (*N*,*N*-dimethylamino)dimethylsilyl-substituted cyclopentadiene and tetramethylcyclopentadiene with $Fe(CO)_5$. These dimers are significant because they possess two $SiNMe_2$-substituted ligands, which have been used in polymer construction. Condensation reactions of **1** and **2** with $HOSiPh_2OH$, $HOSiMe_2(1,4\text{-}C_6H_4)Me_2SiOH$, and $HOSiMe_2O(\text{–}SiMe_2O)_n\text{–}Me_2SiOH$, lead to the formation of polymers containing $[(\eta^5\text{-}C_5R_4)Fe(CO)(\mu\text{-}CO)]_2$ moieties along siloxane backbones: $[\text{–}SiMe_2(\eta^5\text{-}C_5R_4)Fe(CO)(\mu\text{-}CO)_2(CO)Fe(\eta^5\text{-}C_5R_4)Me_2SiOPh_2SiO\text{–}]_n$ (R = H (**7**), R = Me (**8**)), $[\text{–}SiMe_2(\eta^5\text{-}C_5R_4)Fe(CO)(\mu\text{-}CO)_2(CO)Fe(\eta^5\text{-}C_5R_4)Me_2SiOSiMe_2(1,4\text{-}C_6H_4)SiMe_2O\text{–}]_n$ (R = H (**9**), R = Me (**10**)), and $[\text{–}SiMe_2(\eta^5\text{-}C_5R_4)Fe(CO)(\mu\text{-}CO)_2(CO)Fe(\eta^5\text{-}C_5R_4)Me_2SiOSiMe_2O(Me_2SiO)_nSiMe_2O\text{–}]_{n'}$ (R = H (**11**), R = Me (**12**)). In order to aid to the spectroscopic characterization of the polymers, binuclear iron model complexes containing siloxane-bridged cyclopentadienyl and tetramethylcyclopentadienyl ligands, of the forms $\{SiMe_2OSiPh_2OSiMe_2\}[(\eta^5\text{-}C_5R_4)Fe(CO)_2]_2$ (R = H (**3**), R = Me (**4**)) and $\{SiMe_2OSiMe_2(1,4\text{-}C_6H_4)SiMe_2OSiMe_2\}[(\eta^5\text{-}C_5R_4)Fe(CO)_2]_2$ (R = H (**5**), R = Me (**6**)) have been prepared. In addition, the incorporation of the $(\eta^5\text{-}C_5H_4)Fe(CO)(\mu\text{-}CO)_2(CO)Fe(\eta\text{-}C_5H_4)$ moiety into polymeric supports was also effected by reacting $Fe(CO)_5$ with a preformed poly(methylsiloxane) backbone that contains pendant cyclopentadienyl rings, the polymer $[Me_3Si\text{–}O\{(\text{–}MeSiOSiMeO)(\eta^5\text{-}C_5H_4)Fe(CO)(\mu\text{-}CO)_2(CO)Fe(\eta^5\text{-}C_5H_4)\}_{n'}\text{–}SiMe_3]$ (**13**) being thus isolated. All the new compounds have been characterized by conventional spectroscopic techniques. The electrochemical oxidation and reduction of the synthesized complexes have been examined under various conditions. For the polymers **7**–**12** reversible systems corresponding to two-electron oxidation processes are observed in THF/Bu_4NPF_6. The monomeric anionic species $[\{(\eta^5\text{-}C_5R_4)Me_2Si(NMe_2)\}Fe(CO)_2]^-$ (R = H, Me) as well as the 18-electron cationic species $[\{(\eta^5\text{-}C_5R_4)Me_2Si(NMe_2)\}Fe(CO)_2(THF)]^+$ and $[\{(\eta^5\text{-}C_5R_4)Me_2Si(NMe_2)\}Fe(CO)_2(NCCH_3)]^+$ have been generated and characterized via infrared spectroelectrochemistry.

Introduction

The widespread utility of organosiloxane polymers has led to intense interest in the modification of their properties by incorporation of various organometallic moieties in the polymer chain.[1,2] In this way, a number of ferrocene-containing siloxane polymers have been prepared from monomers with functionalized cyclopentadienyl ligands.[3] However, until now no similarly constructed polymers containing Fe–Fe bonds along a siloxane support have been reported. On the other hand, while functionally-substituted cyclopentadienyl-containing organometallic compounds have been extensively used in the construction of organometallic polymers, in contrast, organometallic polymers which contain functionally-substituted permethylcyclopentadienyl ligands have been until very recently unknown.[4] However, interest in

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0276-7333/93/2312-0811$04.00/0

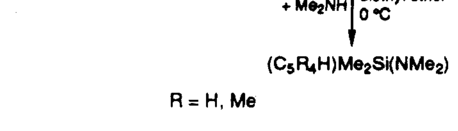
organometallic compounds with permethylcyclopentadienyl ligands has been growing in the last years because these compounds often exhibit significant differences in reactivity, stability, and other properties compared with their nonmethylated cyclopentadienyl analogues.[5]

In recent years we have been interested in the synthesis and study of new functionally-substituted organometallic compounds containing suitable reactive organosilane groups, in order to prepare organometallic siloxane polymers. Thus, we have recently reported the synthesis and characterization of some siloxane polymers with chromium tricarbonyl units.[6] Following this research, now we wish to report the synthesis of the first siloxane polymers with $(\eta^5\text{-}C_5R_4)Fe(CO)(\mu\text{-}CO)_2(CO)Fe(\eta^5\text{-}C_5R_4)$ moieties along a siloxane backbone. In this respect, we had already used siloxanyl-linked bis(cyclopentadienyl) ligands to prepare binuclear Fe–Fe-bonded carbonyliron complexes.[7] For these complexes the siloxane bridge appears to be related to the stability of the electrochemically generated species, which is different from that observed in nonbridged related dinuclear complexes.[8]

This paper describes the synthesis, spectroscopic characterization, and polymerization reactions of novel binuclear iron carbonyl complexes containing (dimethylamino)dimethylsilyl-substituted cyclopentadienyl and tetramethylcyclopentadienyl ligands, $[\{(\eta^5\text{-}C_5R_4)Me_2Si(NMe_2)\}Fe(CO)_2]_2$ (R = H, Me). These difunctionally-substituted dimers are useful in the construction of organometallic polymers via condensation reactions with disilanols. This results in polymers with silicon attached directly to the cyclopentadienyl rings. The synthesis and characterization of related siloxanyl-bridged cyclopentadienyl binuclear model complexes is also reported. The electrochemistry of the Fe–Fe-bonded dimeric and polymeric synthesized compounds has been studied in detail under a variety of conditions. In addition, through the use of infrared spectroelectrochemistry, we have been able to generate and characterize several electron-transfer products.

Results and Discussion

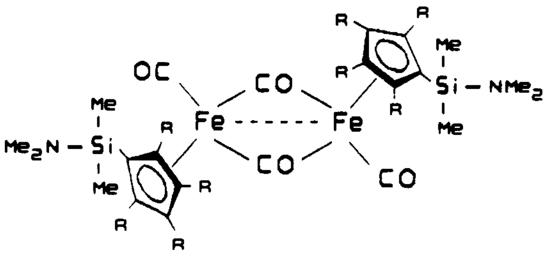
Synthesis and Characterization of Complexes $[\{(\eta^5\text{-}C_5R_4)Me_2Si(NMe_2)\}Fe(CO)_2]_2$. The starting cyclopentadienyl- and (tetramethylcyclopentadienyl)(*N*,*N*-dimethylamino)dimethylsilane ligands $(C_5R_4H)Me_2Si(NMe_2)$ (R = H, Me) are prepared according to the reactions outlined in eq 1.



(1)

Lithium cyclopentadienide and lithium tetramethylcyclopentadienide react with dichlorodimethylsilane to give the cyclopentadienyldimethylchlorosilanes $(C_5R_4H)Me_2SiCl$ (R = H, Me). Aminolysis of these chlorosilylated derivatives with dimethylamine gives $(C_5R_4H)Me_2Si(NMe_2)$ (R = H, Me) as moisture-sensitive, distillable liquids. Although these reactions have been described previously for the nonmethylated cyclopentadiene,[3] to date no analogous tetramethylated ligand had been prepared. We have been able to synthesize (tetramethylcyclopentadienyl)(dimethylamino)dimethylsilane $(C_5Me_4H)Me_2Si(NMe_2)$, which has been characterized by IR and NMR spectroscopies.

Chart I



R = H **1**

R = Me **2**

The novel binuclear complexes $[\{(\eta^5\text{-}C_5R_4)Me_2Si(NMe_2)\}Fe(CO)_2]_2$ (R = H (**1**), R = Me (**2**)) have been prepared by thermal treatment of the corresponding (dimethylamino)dimethylsilyl-substituted derivatives $(C_5R_4H)Me_2Si(NMe_2)$ (R = H, Me) with $Fe(CO)_5$, in decane at temperatures around 125–130 °C. Following the appropriate workup of the resulting materials, compounds **1** and **2** were isolated as dark-red crystalline solids. The relatively low yield (40–55%) of these preparations probably results because we avoided an excess of the $(C_5R_4H)Me_2Si(NMe_2)$ ligands to prevent their possible polymerization upon prolonged heating. Solids **1** and **2** are sufficiently air stable to be handled in air for short periods of time without the occurrence of noticeable decomposition. However, changes have been observed in the IR and NMR spectra of **1** and **2** samples exposed to air for long periods of time;[9] therefore they have been stored under a nitrogen atmosphere.

Compounds **1** and **2** were characterized by elemental analyses, IR, ^1H NMR, and electronic absorption spectroscopies. Their analytical and spectral data (Table I) are consistent with the proposed formulation as dinuclear carbonyl-bridged compounds. The solution ^1H NMR spectra of **1** and **2** exhibit a sharp single resonance near 2.5 ppm assignable to the methyl protons of the $SiNMe_2$ group. Likewise, the expected resonances due to the protons of the $\eta^5\text{-}C_5H_4$ and $\eta^5\text{-}C_5(CH_3)_4$ rings are observed in the correct regions of the spectra. In the carbonyl stretching region the terminal and bridged CO bands for complex **2** are 15–20 cm^{-1} lower in energy than those of the unmethylated analogue **1**, as a result of the enhanced electron-donating ability of the $(\eta^5\text{-}C_5Me_4)Me_2Si(NMe_2)$ ligand. IR analysis of the spectra of complex **2** in the

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[9] IR spectra of **1** and **2** solid samples exposed to air over several days show no IR bands at 1170 and 980 cm^{-1} corresponding to the $Si(NMe_2)$ group, this absence being also supported by the ^1H NMR spectra. Instead, broad IR bands around 3200 cm^{-1} along with ^1H NMR resonances assignable to the SiOH group are observed, which could result from the hydrolysis of $Si(NMe_2)$. In addition noticeable differences in the CO terminal stretching region indicate changes in the cis–trans conformation.

Table I. IR, ^{1}H NMR, and Electronic Absorption Spectral Data for the Dimeric and Polymeric Iron Compounds

compd	IR ν(CO), cm^{-1} [a]				^{1}H NMR δ, ppm[b]	λ, nm (ϵ, L mol^{-1} cm^{-1})[c]
	solid[d]		THF		CDCl$_3$	THF
1	1999 (s)	1774 (sh)	1989 (vs)	1778 (vs)	0.45 (s, 12 H, $SiCH_3$)	348 (9190)
	1954 (s)	1771 (vs)	1950 (m)		2.48 (s, 12 H, $SiNCH_3$)	415 (1870)
	1935 (vs)	1742 (w)			4.48, 4.90 (br, 8 H, C_5H_4)	510 (570)
2	1980 (w)	1760 (vs)	1978 (w)	1758 (vs)	0.47 (s, 12 H, $SiCH_3$)	368 (10 100)
	1935 (vs)	1752 (sh)	1928 (vs)		1.65, 1.78 (s, 24 H, $C_5(CH_3)_4$)	422 (1850)
	1896 (w)	1734 (sh)			2.47 (s, 12 H, $SiNCH_3$)	537 (550)
3	1997 (vs)	1810 (w)	1991 (vs)	1779 (vs)	0.40 (s, 12 H, $SiCH_3$)	351 (9300)
	1954 (s)	1780 (vs)	1951 (s)		4.34, 4.73 (dd, 8 H, C_5H_4)	420 (1700)
					7.30, 7.50 (m, 10 H, C_6H_5)	512 (510)
4	1954 (w)	1760 (vs)	1930 (vs)	1759 (vs)	0.08 (s, 12 H, $SiCH_3$)	365 (8700)
	1931 (vs)				1.54, 1.76 (s, 24 H, $C_5(CH_3)_4$)	425 (1600)
	1891 (sh)				7.33, 7.61 (m, 10 H, C_6H_5)	520 (500)
5	1998 (vs)	1809 (w)	1992 (vs)	1780 (vs)	0.33, 0.47 (s, 24 H, $SiCH_3$)	349 (10 150)
	1954 (vs)	1775 (vs)	1951 (s)		4.43, 4.87 (m, 8 H, C_5H_4)	420 (1900)
	1936 (s)				7.53 (s, 4 H, C_6H_4)	510 (568)
6	1957 (w)	1760 (vs)	1930 (vs)	1758 (vs)	0.06, 0.32 (s, 24 H, $SiCH_3$)	364 (9500)
	1933 (vs)				1.53, 1.77 (s, 24 H, $C_5(CH_3)_4$)	428 (1730)
					7.54 (s, 4 H, C_6H_4)	535 (510)
7	1991 (vs)	1810 (w)	1991 (vs)	1780 (vs)	0.40 (s, 12 H, $SiCH_3$)	352
	1946 (s)	1773 (vs)	1951 (s)		4.36, 4.72 (br, 8 H, C_5H_4)	405
					7.32, 7.45 (m, 10 H, C_6H_5)	510
8	1931 (vs)	1758 (vs)	1930 (vs)	1758 (s)	0.08 (s, 12 H, $SiCH_3$)	370
					1.56, 1.85 (br, 24 H, $C_5(CH_3)_4$)	435
					7.28, 7.59 (m, 10 H, C_6H_5)	530
9	1995 (s)	1809 (w)	1992 (vs)	1780 (vs)	0.30, 0.43 (s, 24 H, $SiCH_3$)	350
	1952 (sh)	1770 (vs)	1952 (s)		4.42, 4.85 (br, 8 H, C_5H_4)	412
	1936 (vs)				7.48 (s, 4 H, C_6H_4)	515
10	1952 (sh)	1786 (sh)	1930 (vs)	1757 (s)	0.03, 0.50 (br, 24 H, $SiCH_3$)	368
	1931 (vs)	1759 (vs)			1.65, 1.80 (br, 24 H, $C_5(CH_3)_4$)	427
					7.54 (s, 4 H, C_6H_4)	535
11	2000 (s)	1811 (sh)	1993 (vs)	1780 (vs)	0.06 (br, n H, $SiCH_3$)	351
	1983 (m)	1786 (vs)	1952 (s)		4.46, 4.94 (br, 8 H, C_5H_4)	410
	1958 (vs)	1763 (m)				515
12	1937 (vs)	1759 (sh)	1931 (vs)	1757 (s)	0.07 (br, n H, $SiCH_3$)	364
		1748 (s)			1.57, 1.83 (br, 24 H, $C_5(CH_3)_4$)	425
						530
13	1996 (vs)	1784 (vs)	1990 (vs)	1778 (vs)	0.85 (br, n H, $SiCH_3$)	350
	1954 (s)		1949 (s)		4.45, 4.98 (br, 8 H, C_5H_4)	415
						511

[a] In CH_3CN, ν(CO): 1990 (m), 1950 (vs), 1773 (vs) for **1**; 1975 (w), 1931 (vs), 1753 (vs) for **2**. [b] Data for **2** and **5** in acetone-d_6. [c] Values for **7–13** have not been calculated. [d] In Nujol mull.

ν(CO) region revealed that they are somewhat different from those of the related pentamethylated compound $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$, in which only the centrosymmetric trans isomer is stable, in solid and in solution, at room temperature.[10] While in nonpolar solvents the two expected carbonyl bands in the bridging and terminal ν(CO) regions due to the trans isomer are observed (ν(CO) for **2** in hexane: 1936, 1760 cm^{-1}), the IR spectra of **2** exhibit an additional less intense band, at a higher energy in the ν(CO) terminal region, in both solid (1980, 1933, 1760, 1752 cm^{-1} in Nujol) and in polar solvents (1975, 1931, 1753 cm^{-1} in CH_3CN). This band is $\approx$15 cm^{-1} lower in energy than the ν(CO) band of the cis isomer of **1**, a similar shift to that observed for the trans isomers of **1** and **2**. The separation between the two terminal ν(CO) bands for complex **1** is about 40 cm^{-1} (Table I), and a similar separation is observed in the terminal bands of **2**. From these data we suggest that this higher frequency band can be reasonably assigned to the terminal ν(CO) vibration of a cis isomer of **2**. In addition, these data for **2** are close to those reported for the until not long ago unknown cis isomer of $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$, which has been detected by time-resolved IR spectroscopy in the UV flash photolysis of the trans isomer, in cyclohexane solution at room temperature.[11] The results for complex **2** are somewhat surprising considering the known steric effects of the methyl groups as well as of other substituents on the cyclopentadienyl ring.[12,13] However they could be reasoned on the basis that there is little or no kinetic barrier in the cis–trans isomerizations of $[(\eta^5\text{-}C_5R_5)Fe(CO)_2]_2$ (R = H, Me) dimers[11,14] and furthermore that it is not yet clear whether the steric or electronic effects are the most important in these isomerizations.[11]

Data in Table I indicate that the electronic spectra of **1** and **2** are similar to the spectra of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$.[15] Assignment of the intense near-UV absorption (at 348 nm for **1** and at 368 nm for **2**) to the σ_b–σ^* transition of the bridged species, associated with the Fe–Fe bond, is therefore suggested. The UV–visible spectrum of complex **2** shows a decrease in the energies of the bands, which agrees with the relative ease of electron removal from the

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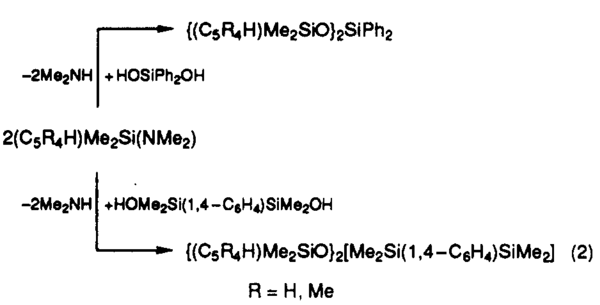
HOMO,[16] and is in accordance with the electrochemical behavior (see Electrochemical Studies). These complexes which contain Si(NMe$_2$)-substituted cyclopentadienyl and tetramethylcyclopentadienyl ligands, are suitable for use in the construction of siloxane polymers with (η^5-C$_5$R$_4$)-Fe(CO)(μ-CO)$_2$(CO)Fe(η^5-C$_5$R$_4$) moieties via condensation reactions (vide infra).

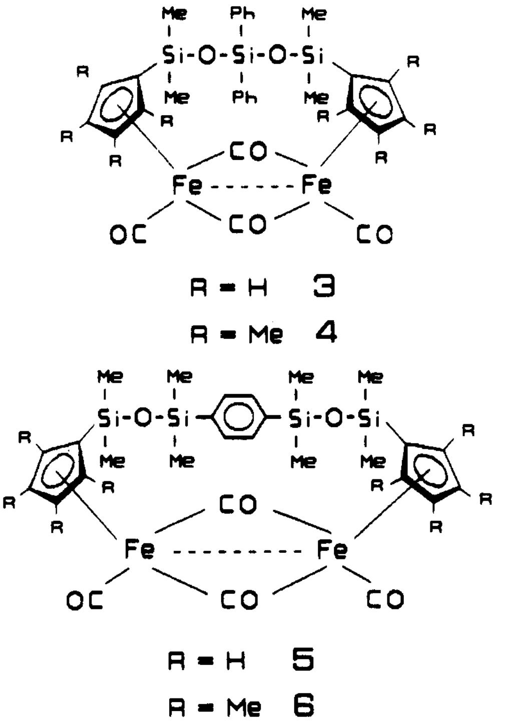
Synthesis and Characterization of Siloxanyl Polymers and Model Compounds Containing [(η^5-C$_5$R$_4$)-Fe(CO)(μ-CO)]$_2$ Moieties. Introduction of organometallic moieties into organopolysiloxane is interesting because it affects the stability of such polymers against degradation resulting from UV, heat, oxidation, etc. Consequently, this type of polymer can be employed in a variety of applications such as ultraviolet absorbers, heat age additives for organopolysiloxane compositions, and antioxidants, also being useful to enhance the lubricating characteristics of organic fluids.[1,2a] On the other hand it is remarkable that, among the wide variety of organometallic polymers, only few examples of Fe–Fe bond-containing polymers have been recently reported.[17] This is not surprising because the introduction of metal–metal bonds into polymer backbone poses several synthetic problems not normally found in polymer synthesis. Generally, these problems arise because metal–metal bonds are more reactive[17,18] than the bonds found in common polymers. Thus, under many standard polymerization reaction conditions, cleavage of the metal–metal bond would result. However, polymers with Fe–Fe bonds along polymer backbones are of considerable interest because they are potentially photochemically reactive[17,19] and have commercial uses as photodegradable materials and lithographic materials and for preparation of highly dispersed iron oxide particles within polymer films.[1b,17,20]

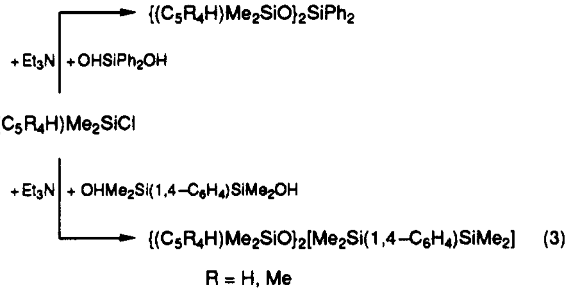
With this in mind, our route for the preparation of polymers containing Fe–Fe-bonded [(η^5-C$_5$R$_4$)Fe(CO)(μ-CO)]$_2$ molecules along a siloxane backbone consists of reactions of the dimers 1 and 2 containing Me$_2$Si(NMe$_2$)-substituted ligands with disilanols. In order to spectroscopically characterize the resulting siloxane polymers, we synthesized related model complexes. The facile condensation reaction of the SiNMe$_2$ group with silanols provides a first method to obtain siloxanyl-linked bis(cyclopentadienes), which are appropriate for use in the synthesis of the model dimers (eq 2).



In addition, the high reactivity of the Si–Cl bond toward the OH in silanols also makes the chlorodimethylsilyl-substituted derivatives the reagents of choice for a different route of preparing the siloxanyl-linked bis(cyclopentadienes), as it was outlined in eq 3.

Chart II





For all reactions in eqs 2 and 3, relatively high-dilution conditions were used to avoid a possible polymerization of the substituted-cyclopentadienyl ligands. As these compounds were not easily purified, care was taken to use freshly distilled substituted cyclopentadienes and recrystallized silanols, and thus, the obtained siloxanyl-linked bis(cyclopentadienes) and bis(tetramethylcyclopentadienes) were subjected to satisfactory IR and NMR characterization. Reactions of these derivatives with Fe(CO)$_5$, in decane or xylene solution, at 125–130 °C, afforded the novel binuclear model complexes of the types {SiMe$_2$-OSiPh$_2$OSiMe$_2$}[(η^5-C$_5$R$_4$)Fe(CO)$_2$]$_2$ (R = H (**3**), R = Me (**4**)) and {SiMe$_2$OSiMe$_2$(1,4-C$_6$H$_4$)SiMe$_2$OSiMe$_2$}[(η^5-C$_5$R$_4$)-Fe(CO)$_2$]$_2$ (R = H (**5**), R = Me (**6**)). Whereas dimers **3** and **5** were obtained in relatively high yields (65–70%), the synthesis of the tetramethylated analogues **4** and **6** proved to be troublesome because a mixture of two different products was formed (see Experimental Section). This occurs probably because these reactions were slower than those of the nonethylated derivatives. The desired products **4** and **6** were therefore isolated in low yields because successive purifications were effected. The analytical and spectral data (Table I) of complexes **3**–**6** are consistent with the proposed structures. In the ^{1}H NMR spectra of

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(16) Bursten, B. E.; Cayton, R. H.; Gatter, M. G. *Organometallics* **1988**, *7*, 1342.

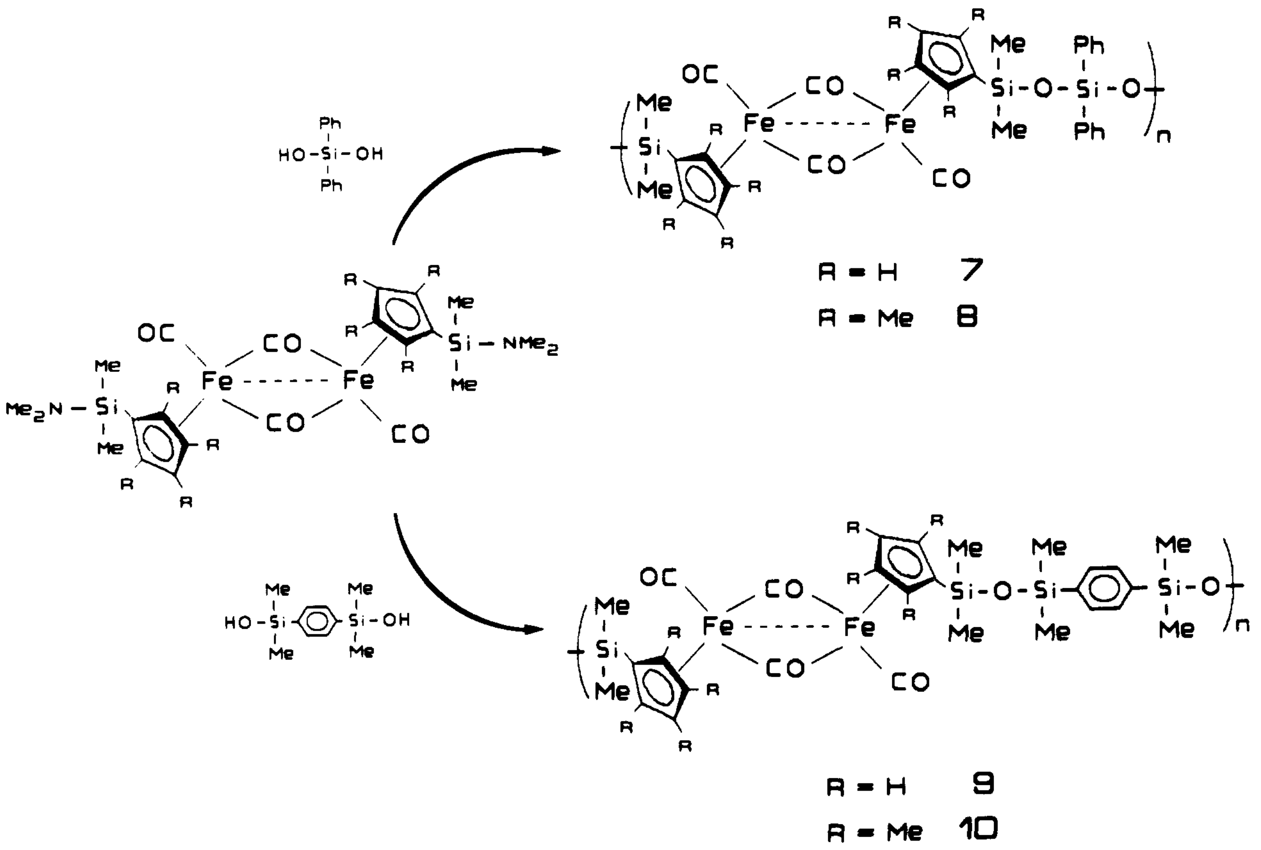
(17) (a) Tenhaeff, S. C.; Tyler, D. R. *Organometallics* **1991**, *10*, 473. (b) Tenhaeff, S. C.; Tyler, D. R. *Organometallics* **1992**, *11*, 1466.

(18) Meyer, T. J.; Caspar, J. V. *Chem. Rev.* **1985**, *85*, 187.

(19) Tenhaeff, S. C.; Tyler, D. R. *Organometallics* **1991**, *10*, 1116.

(20) (a) Pittman, C. U.; Rausch, M. D. *Pure Appl. Chem.* **1986**, *58*, 617. (b) Gonsalves, K.; Zhan-ru, L.; Rausch, M. D. *J. Am. Chem. Soc.* **1984**, *106*, 3862.

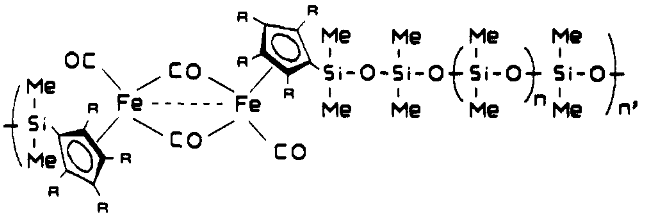
Scheme I



complexes **3** and **5** the cyclopentadienyl ring protons display resonances in an AA′BB′ pattern, as seen for other related bridged species.[21] η^5-C_5Me_4 resonances similar to those of dimer **2** were also found in complexes **4** and **6**. The IR spectra in the carbonyl stretching region as well as the electronic absorption spectra are similar to those of the dimers **1** and **2**, indicating the presence of the Fe–Fe-bonded $[(\eta^5\text{-}C_5R_4)Fe(CO)(\mu\text{-}CO)]_2$ molecules.

Siloxane polymers in which $[Fe(CO)(\mu\text{-}CO)]_2$-containing moieties are coordinated to substituted-cyclopentadienyl ligands have been prepared by polycondensation of the dinuclear Fe–Fe-bonded complexes **1** and **2** with the disilanols $HOSiPh_2OH$ and $HOSiMe_2(1,4\text{-}C_6H_4)Me_2SiOH$. These reactions were carried out in dry, degassed toluene, using the minimum volume of solvent to dilute the starting dimers **1** and **2** (ca. 5–8 mL). These high-concentration conditions were used to ensure maximization of intermolecular condensation relative to a possible competitive intramolecular cyclization process. The polymerizations were started at room temperature with subsequent slow heating to 100–110 °C. The mixtures were maintained at this temperature for 1 h and then were kept at 50–60 °C under vacuum for an additional 1 h to drive off remaining dimethylamine efficiently and complete the polymerization. After purification, the expected polymeric compounds of the types $[\text{-}SiMe_2(\eta^5\text{-}C_5R_4)Fe(CO)(\mu\text{-}CO)_2(CO)Fe(\eta^5\text{-}C_5R_4)Me_2SiOPh_2SiO\text{-}]_n$ (R = H (**7**), R = Me (**8**)) and $[\text{-}SiMe_2(\eta^5\text{-}C_5R_4)Fe(CO)(\mu\text{-}CO)_2(CO)Fe(\eta^5\text{-}C_5R_4)Me_2SiOSiMe_2(1,4\text{-}C_6H_4)SiMe_2O\text{-}]_n$ (R = H (**9**), R = Me (**10**)) were isolated as dark-red or reddish-brown solids.

Chart III



R = H **11**
R = Me **12**

These polymers can be considered as a dimethylsiloxane backbone in which a regular alternating arrangement of $[(\eta^5\text{-}C_5R_4)Fe(CO)(\mu\text{-}CO)]_2$ and either diphenylsilyl or silylphenylene units are found (Scheme I).

Related polymers containing long dimethylsiloxane chains were similarly prepared by starting from the appropriate preformed polymer, poly(dimethylsiloxane) silanol-terminated $HOSiMe_2O(\text{-}SiMe_2O)_n\text{-}Me_2SiOH$, and following the procedure previously described. In these preparations, appropriate amounts of dimers **1** or **2** and $HOSiMe_2O(\text{-}SiMe_2O)_n\text{-}Me_2SiOH$ were weighed and subsequently reacted, so that there were approximately the same number of $\text{-}SiNMe_2$ and $\text{-}SiOH$ groups. The reaction products are obtained as thick red rubberlike materials. Their spectroscopic data (Table I) are consistent with the formulation $[\text{-}SiMe_2(\eta^5\text{-}C_5R_4)Fe(CO)(\mu\text{-}CO)_2(CO)Fe(\eta^5\text{-}C_5R_4)Me_2SiOSiMe_2O(Me_2SiO)_nSiMe_2O\text{-}]_{n'}$ (R = H (**11**), R = Me (**12**)).

On the other hand, an alternative method we have used for incorporating $[(\eta^5\text{-}C_5R_4)Fe(CO)(\mu\text{-}CO)]_2$ molecules along a siloxane polymer backbone involves the use of polysiloxanes containing pendant cyclopentadienyl ligands capable of reacting subsequently with $Fe(CO)_5$. In order

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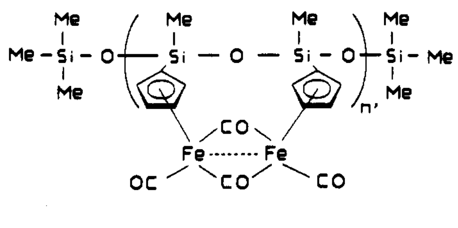
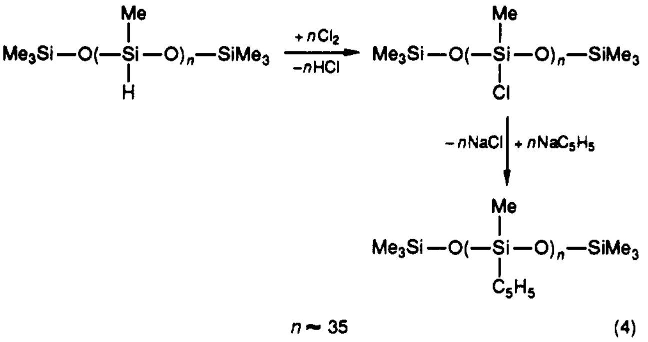
[21] (a) Wright, M. E.; Mezza, T. M.; Nelson, G. O.; Armstrong, N. R.; Day, V. W.; Thompson, M. R. *Organometallics* **1983**, *2*, 1711. (b) Janda, K. D.; McConnell, W. W.; Nelson, G. O.; Wright, M. E. *J. Organomet. Chem.* **1983**, *259*, 139. (c) Wegner, P. A.; Uski, V. A.; Kiester, R. P.; Dabestani, S.; Day, V. W. *J. Am. Chem. Soc.* **1977**, *99*, 4846.

Chart IV



13

to prepare the appropriate prepolymer support, we synthesized poly(cyclopentadienylmethylsiloxane) according to the step reactions outlined in eq 4.



$$Me_3Si{-}O({-}\underset{H}{\overset{Me}{Si}}{-}O)_n{-}SiMe_3 \xrightarrow[-nHCl]{+nCl_2} Me_3Si{-}O({-}\underset{Cl}{\overset{Me}{Si}}{-}O)_n{-}SiMe_3 \xrightarrow[-nNaCl]{+nNaC_5H_5} Me_3Si{-}O({-}\underset{C_5H_5}{\overset{Me}{Si}}{-}O)_n{-}SiMe_3 \quad n \sim 35 \qquad (4)$$

Poly(methylhydrosiloxane) was cleanly chlorinated to give the corresponding poly(methylchlorosiloxane) which reacted with sodium cyclopentadienide to form the desired poly(cyclopentadienylmethylsiloxane). This prepolymer was reacted with $Fe(CO)_5$ in decane solution, and after appropriate workup, a dark-red product was isolated, purified, and then analyzed by IR, ^1H NMR, and electronic absorption spectroscopies. The resulting data are consistent with the formulation $[Me_3Si\text{-}O\{(MeSiOSiMeO)(\eta^5\text{-}C_5H_4)Fe(CO)(\mu\text{-}CO)_2(CO)Fe(\eta^5\text{-}C_5H_4)\}_n\text{-}SiMe_3]$ (13) and with the proposed structure. The molecular weight of this polymer was not determined because of its insolubility in the appropriate organic solvents. In addition, no solution electrochemical studies could be effected due to its very low solubility in CH_2Cl_2 and THF solvents. This very insoluble nature of polymer 13 suggests a possible cross-linking, that can occur via the bonding of two cyclopentadienyl groups from different siloxane chains to the same $[Fe(CO)(\mu\text{-}CO)]_2$ moiety.

The novel organosiloxane polymers 7–12 are much less soluble in organic solvents than the precursor dimers 1 and 2 and the model complexes 3–6 but soluble enough in CH_2Cl_2, THF, $CDCl_3$, or acetone-d_6 for spectroscopic characterization and electrochemical studies. Although the solids may be handled in air without noticeable decomposition, they have been stored under an inert atmosphere. Films of polymers 7–12 could be cast from THF solutions. Spectroscopic data for 7–13 are given in Table I. In addition to the resonances due to the aromatic and methyl groups of the siloxane polymer chains, perhaps the most significant feature of the ^1H NMR spectra of compounds 7–12 was the complete lack of any resonance which could be due to methyl protons of the $SiNMe_2$ groups of unreacted starting dimers 1 or 2, which indicates that the dimers are chemically incorporated into the polymer. The electronic absorption spectra are essentially identical to those of the precursor dimers 1 and 2, an well as to those of the model complexes 3–6, indicating that the Fe–Fe bond is intact in the polymers.

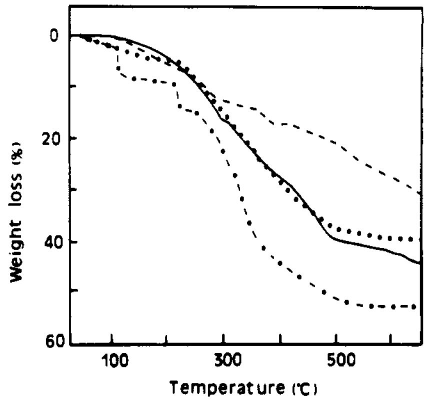


Figure 1. TGA curves for polymer 7 under atmospheres of nitrogen (—) and air (- • -) and polymer 13 under atmospheres of nitrogen (- - -) and air (···).

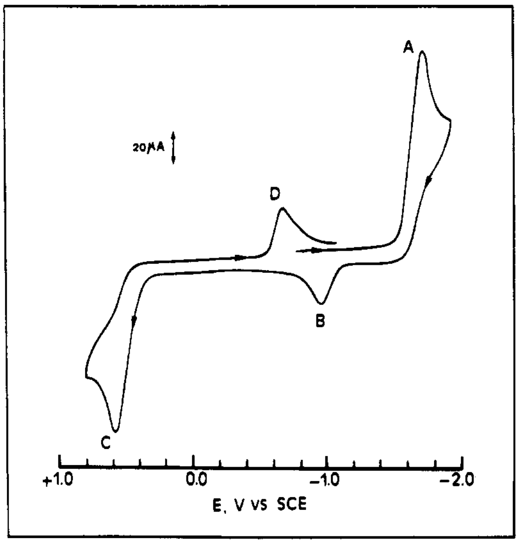


Figure 2. Cyclic voltammogram of a 1×10^{-3} M solution of $[\{(\eta^5\text{-}C_5Me_4)Me_2Si(NMe_2)\}Fe(CO)_2]_2$ (2) in 0.1 M CH_3CN/Bu_4NPF_6, at 200 mV/s.

The thermal behavior of polymers 7, 9, and 13 has been studied with the aid of differential thermal analysis (DTA), thermal gravimetric analysis (TGA), and derivative thermogravimetry (DTG), under air and nitrogen atmospheres, in the temperature range 25–650 °C. The TGA data in air showed multiple exothermic degradation processes (Figure 1). Under a nitrogen atmosphere, 7 and 9 show an initial weight loss at 300 °C of 16.4 and 16.7%, respectively, and then a sharp increase in the rate of weight loss. The initial processes correspond to carbon monoxide evolution (weight losses calculated are 16.18 and 16.43%, respectively). On the TGA plot corresponding to polymer 13, a significantly lower rate of weight loss can be appreciated and the weight loss corresponding to carbon monoxide elimination is reached at 380 °C. This apparent enhancement of overall thermal stability in polymer 13 may be related to the presence in this compound of a polysiloxane backbone with pendant cyclopentadienyl rings which could give rise to a cross-linked polymer. The DTA data recorded under a nitrogen atmosphere showed endothermic decomposition, in general agreement with the significant weight loss.

Electrochemical Studies

Voltammograms of the dimers $[\{(\eta^5\text{-}C_5R_4)Me_2Si(NMe_2)\}Fe(CO)_2]_2$ (R = H (1), R = Me (2)) in CH_3CN with 0.1 M

Table II. Peak Potentials (V, vs SCE) for Oxidation and Reduction of the Dimeric and Polymeric Iron Compounds[a]

compd	solvent	E_p(A)	E_p(B)	E_p(C)	$E°$(C/C′)	E_p(D)	E_p(E)
1	CH_2Cl_2	−1.48		0.86		−0.35	
	THF	−1.72[b]	−0.89	1.05		−0.20	
	CH_3CN	−1.55	−0.86	0.82		−0.60	
2	CH_2Cl_2	−1.85		0.64	0.58	−0.42	1.26
	THF	−2.15[c]	−1.05	0.71	0.63	−0.58	1.36
	CH_3CN	−1.70	−0.96	0.58		−0.69	
3	CH_2Cl_2	−1.68		0.82	0.76	−0.36	1.46
	THF	−1.75	−0.85	1.05	0.95[d]	−0.40	
4	CH_2Cl_2	−1.83		0.45	0.38	−0.50	0.80
	THF	−2.05	−1.10	0.69	0.57[d]	−0.58	
5	CH_2Cl_2	−1.45		0.75	0.68	−0.38	1.50
	THF	−1.70	−0.84	0.99	0.88[d]	−0.41	
6	CH_2Cl_2	−1.82		0.40	0.30	−0.50	0.80
	THF	−2.00	−1.01	0.68	0.57[d]	−0.61	
7	CH_2Cl_2	−1.64		0.85	0.78	−0.38	1.48
	THF	−1.85	−0.92	0.98	0.88[d]	−0.40	
8	CH_2Cl_2	−1.90		0.48	0.36	−0.50	1.18
	THF	−2.05	−1.00	0.58	0.47[d]	−0.56	
9	CH_2Cl_2	−1.70		0.46	0.40	−0.40	1.20
	THF	−1.83	−0.90	0.95	0.85[d]	−0.51	
10	CH_2Cl_2	−1.80		0.39	0.32	−0.40	0.98
	THF	−1.98	−1.00	0.60	0.49[d]	−0.58	
11	CH_2Cl_2	−1.75		0.65	0.59	−0.43	1.28
	THF	−1.82	−0.88	0.82	0.71[d]	−0.50	
12	CH_2Cl_2	−1.95		0.38	0.31	−0.45	0.78
	THF	−2.00	−1.03	0.68	0.58[d]	−0.58	

[a] Unless otherwise noted, scan rate v = 200 mV/s at room temperature. [b] At −60 °C $E°$(A/A′) −1.61 V. [c] At −45 °C $E°$(A/A′) −2.03 V. [d] Scan rate v = 500 mV/s.

Bu_4NPF_6 as supporting electrolyte show two redox processes: a two-electron reduction and a net two-electron oxidation (Figure 2 and Table II). Each process is coupled to an additional peak in the cyclic voltammogram. The peaks in Figure 2 are labeled **A**–**D** and correspond to the following general reactions:

$$[\{(\eta^5\text{-}C_5R_4)Me_2Si(NMe_2)\}Fe(CO)_2]_2 + 2e^- \xrightarrow{A} 2[\{(\eta^5\text{-}C_5R_4)Me_2Si(NMe_2)\}Fe(CO)_2]^- \quad (5)$$

$$2[\{(\eta^5\text{-}C_5R_4)Me_2Si(NMe_2)\}Fe(CO)_2]^- \xrightarrow{B} [\{(\eta^5\text{-}C_5R_4)Me_2Si(NMe_2)\}Fe(CO)_2]_2 + 2e^- \quad (6)$$

$$[\{(\eta^5\text{-}C_5R_4)Me_2Si(NMe_2)\}Fe(CO)_2]_2 \xrightarrow[CH_3CN]{C} 2[\{(\eta^5\text{-}C_5R_4)Me_2Si(NMe_2)\}Fe(CO)_2(NCCH_3)]^+ + 2e^- \quad (7)$$

$$2[\{(\eta^5\text{-}C_5R_4)Me_2Si(NMe_2)\}Fe(CO)_2(NCCH_3)]^+ + 2e^- \xrightarrow{D} [\{(\eta^5\text{-}C_5R_4)Me_2Si(NMe_2)\}Fe(CO)_2]_2 + 2CH_3CN \quad (8)$$

Potentiostatic coulometry and comparisons of the rde voltammograms with those of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ indicate that the reduction and oxidation of the dimers **1** and **2** correspond to two-electron transfers. The breadth of the oxidation peaks of **1** and **2** in acetonitrile suggests that the net two-electron oxidation of these compounds probably occurs via an ECE mechanism,[22] such as it has been proposed for related compounds.[23,24]

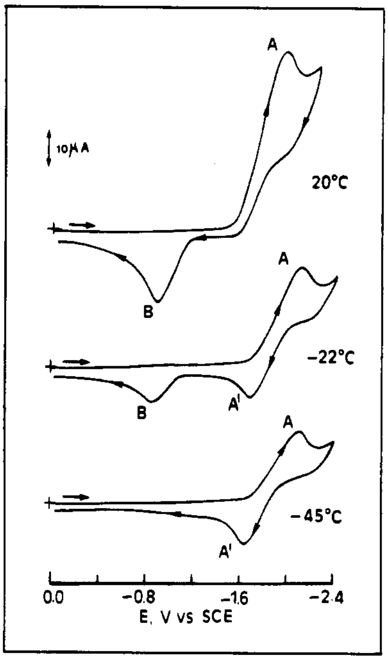


Figure 3. Cyclic voltammogram of a 1 × 10^{-3} M solution of $[\{(\eta^5\text{-}C_5Me_4)Me_2Si(NMe_2)\}Fe(CO)_2]_2$ (**2**) in 0.1 M THF/Bu_4NPF_6, at indicated temperatures (scan rate = 200 mV/s).

The electrochemical reduction of the binuclear compounds **1** and **2** in THF at room temperature is similar to that observed in CH_3CN (Figure 3). The reduction products are the anions $[\{(\eta^5\text{-}C_5R_4)Me_2Si(NMe_2)\}Fe(CO)_2]^-$ which do not contain carbonyl bridges. The formation of these species is evidenced by infrared spectroelectrochemical experiments. Figure 4 shows the spectral changes that accompany the controlled-potential reduction of **1** in THF/Bu_4NPF_6, in the thin-layer cell at room temperature. With the application of a reducing potential all the initial

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(22) (a) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706. (b) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1965**, *37*, 178.

(23) Bullock, J. P.; Palazzotto, M. C.; Mann, K. R. *Inorg. Chem.* **1991**, *30*, 1284.

(24) Kadish, K. M.; Lacombe, D. A.; Anderson, J. E. *Inorg. Chem.* **1986**, *25*, 2246.

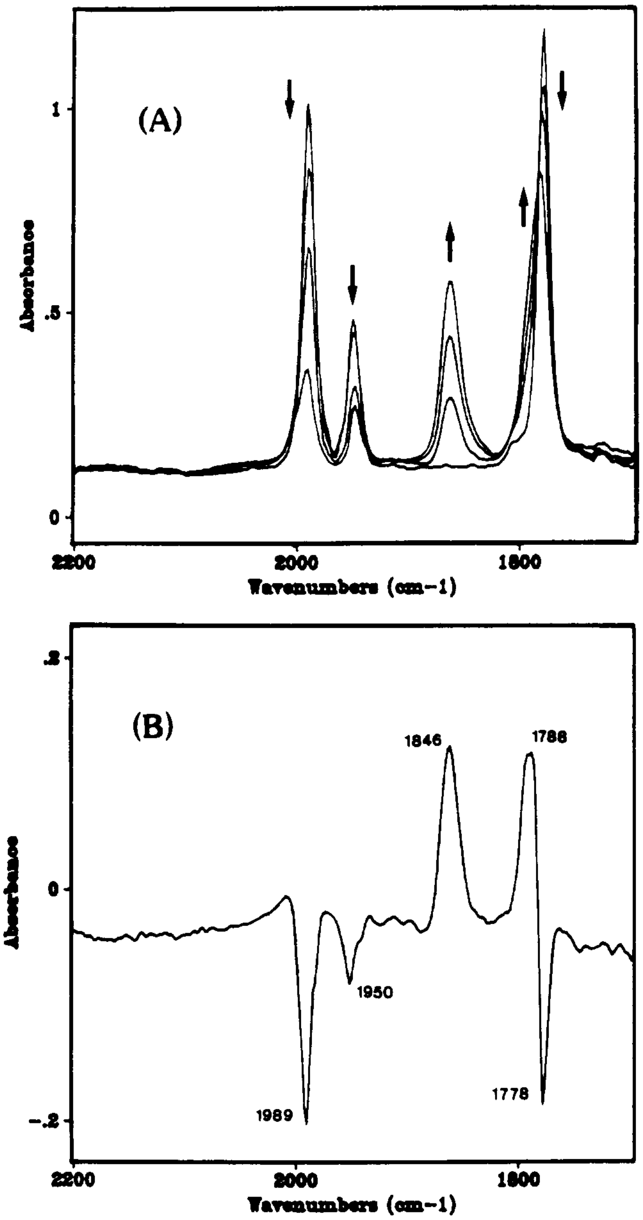

Figure 4. (A) Infrared spectral changes observed upon electroreduction of $[\{(\eta^5\text{-}C_5H_4)Me_2Si(NMe_2)\}Fe(CO)_2]_2$ (1) in THF/Bu_4NPF_6 at −2.1 V vs the Ag pseudo reference electrode in the spectroelectrochemical cell. (B) FTIR absorbance difference spectra of the starting compound and the electroreduction product.

ν(CO) carbonyl peaks at 1989, 1950, and 1778 cm^{-1}, due to the parent 1, decrease in intensity while new carbonyl bands grow at 1862 and 1788 cm^{-1}, indicating a relatively clean conversion. We assign these novel ν(CO) bands to the two-electron reduction product $[\{(\eta^5\text{-}C_5H_4)Me_2Si(NMe_2)\}Fe(CO)_2]^-$. A similar spectroelectrochemical experiment was performed with complex **2**, and the ν(CO) bands assigned to the monomeric methylated anion are indicated in Table III. The observed frequency values for these electrochemically generated anions are consistent with those observed when the reduction of dimers **1** and **2** was chemically effected in THF solution by using potassium benzophenone keyl as reducing reagent. Moreover these ν(CO) values are in agreement with those measured for the related, chemically obtained, anions $[(\eta^5\text{-}C_5H_4SiMe_2OEt)Fe(CO)_2]^-$, $[(\eta^5\text{-}C_5H_4(CH_2)_2\text{-}Si(OMe)_3)Fe(CO)_2]^-$,[8] and $[(\eta^5\text{-}C_5R_5)Fe(CO)_2]^-$ (R = H, Me).[25]

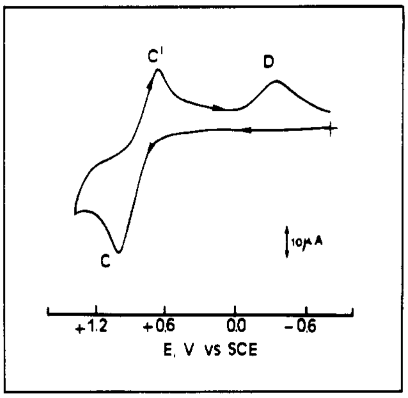

Figure 5. Cyclic voltammogram of 1 × 10^{-3} M **7** in THF/Bu_4NPF_6 at 200 mV/s.

Table III. Infrared CO Stretching Frequencies of Anionic and Cationic Species Observed by Infrared Spectroelectrochemistry[a]

compd	R = H	R = Me
$[\{(\eta^5\text{-}C_5R_4)Me_2Si(NMe_2)\}Fe(CO)_2]^{-}$ [b]	1862, 1788	1846, 1778
$[\{(\eta^5\text{-}C_5R_4)Me_2Si(NMe_2)\}Fe(CO)_2(THF)]^{+}$ [b]	2062, 2012	2038, 1990
$[\{(\eta^5\text{-}C_5R_4)Me_2Si(NMe_2)\}Fe(CO)_2(NCCH_3)]^{+}$ [c]	2065, 2020	2058, 2011

[a] Values in cm^{-1}. [b] In THF/Bu_4NPF_6. [c] In CH_3CN/Bu_4NPF.

Figure 3 also shows that in THF/Bu_4NPF_6 and at low temperature, wave **B** decreases and it is gradually replaced by an oxidation wave, **A′**, at a less positive potential, that can be assigned to the oxidation of the dimer radical-anion $[\{(\eta^5\text{-}C_5R_4)Me_2Si(NMe_2)\}Fe(CO)_2]_2^{-}$.[26] This is not stable in solution, and rapid dissociation will occur to give the mononuclear $[\{(\eta^5\text{-}C_5R_4)Me_2Si(NMe_2)\}Fe(CO)_2]^-$ anion and the 17-electron radical $[\{(\eta^5\text{-}C_5R_4)Me_2Si(NMe_2)\}\text{-}Fe(CO)_2]^\bullet$. This generated radical is electroreducible at the potential of $[\{(\eta^5\text{-}C_5R_4)Me_2Si(NMe_2)\}Fe(CO)_2]_2$ reduction, and the rapid addition of one electron will lead to a second molecule of $[\{(\eta^5\text{-}C_5R_4)Me_2Si(NMe_2)\}Fe(CO)_2]^-$, thus giving the overall two-electron reduction.[26,27] At lower temperatures, the electroreductive cleavage of dimer **2** becomes delayed, and waves **A** and **A′** correspond to one-electron reversible processes. The reduction of these dimers can be interpreted by the ECE mechanism shown in eqs 9–11.

$$[\{(\eta^5\text{-}C_5R_4)Me_2Si(NMe_2)\}Fe(CO)_2]_2 + e^- \rightleftarrows [\{(\eta^5\text{-}C_5R_4)Me_2Si(NMe_2)\}Fe(CO)_2]_2^{-} \quad (9)$$

$$[\{(\eta^5\text{-}C_5R_4)Me_2Si(NMe_2)\}Fe(CO)_2]_2^{-} \rightarrow [\{(\eta^5\text{-}C_5R_4)Me_2Si(NMe_2)\}Fe(CO)_2]^- + [\{(\eta^5\text{-}C_5R_4)Me_2Si(NMe_2)\}Fe(CO)_2]^\bullet \quad (10)$$

$$[\{(\eta^5\text{-}C_5R_4)Me_2Si(NMe_2)\}Fe(CO)_2]^\bullet + e^- \rightleftarrows [\{(\eta^5\text{-}C_5R_4)Me_2Si(NMe_2)\}Fe(CO)_2]^- \quad (11)$$

The temperature dependence of the cyclic voltammetry of compounds **1** and **2** is similar except that, for **1**, wave **A′** appears at a lower temperature (−55 °C) and that wave

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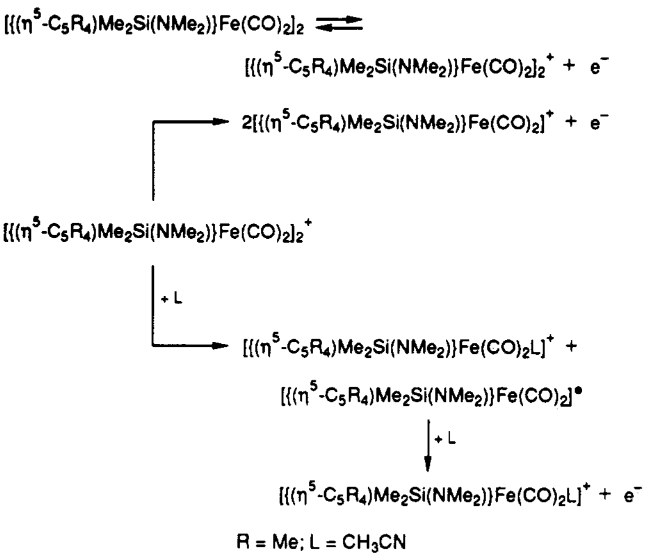
(25) (a) Catheline, D.; Astruc, D. *Organometallics* **1984**, *3*, 1094. (b) Plotkins, J. S.; Shore, S. G. *Inorg. Chem.* **1981**, *20*, 284.

(26) Dalton, E. F.; Ching, S.; Murray, R. W. *Inorg. Chem.* **1991**, *30*, 2642.

(27) Davies, S. G.; Simpson, S. J.; Parker, V. D. *J. Chem. Soc., Chem. Commun.* **1984**, 352.

Scheme II



B for the oxidation of $[\{(\eta^5\text{-}C_5H_4)Me_2Si(NMe_2)\}Fe(CO)_2]_2^-$ disappears at a lower temperature. This suggests that the radical anion of 2 is more stable than that of 1.[26] In dichloromethane solvent with 0.1 M Bu_4NPF_6 the anions of 1 and 2 are unstable (Table II).

While complex 1 exhibits net two-electron oxidations in coordinating and noncoordinating solvent–electrolyte combinations, complex 2 shows two one-electron oxidations when THF or CH_2Cl_2 is used as solvent (Table II). The first reversible process (peak C) is assigned to the oxidation of the parent to the dimer radical cation, $[\{(\eta^5\text{-}C_5Me_4)Me_2Si(NMe_2)\}Fe(CO)_2]_2^+$, and the second irreversible oxidation (peak E) can be ascribed to the direct oxidation of the radical species, to yield 2 equiv of $[\{(\eta^5\text{-}C_5Me_4)Me_2Si(NMe_2)\}Fe(CO)_2]^+$.[28] However, our attempts to electrochemically generate a bulk THF/Bu_4NPF_6 solution of the one-electron-oxidized species, in the spectroelectrochemical thin cell were unsuccessful. Instead, the monocationic THF species $[\{(\eta^5\text{-}C_5R_4)Me_2Si(NMe_2)\}Fe(CO)_2(THF)]^+$ (R = H, Me) were observed as the major oxidation products of 1 and 2 in THF (Table III). The electrochemical oxidation of 2 in different solvents in consistent with the mechanism shown in Scheme II.

When the electrochemical oxidation of 2 takes place in a noncoordinating medium, the radical-cation dimer is long-lived and can be directly oxidized at the electrode in a second one-electron process. In coordinating media as CH_3CN, the binuclear radical cation generates both $[\{(\eta^5\text{-}C_5Me_4)Me_2Si(NMe_2)\}Fe(CO)_2(NCCH_3)]^+$ and $[\{(\eta^5\text{-}C_5Me_4)Me_2Si(NMe_2)\}Fe(CO)_2]^\bullet$. The latter radical is rapidly oxidized at the electrode, and the net result is an irreversible net two-electron oxidation. The experimentally observed variation of the E_p(C) values with the scan rate and of the $[E_p - E_{p/2}]$ values for the oxidation of 2 in CH_3CN are consistent with this ECE mechanism. IR spectroelectrochemical data (Table III) that accompany the oxidation of 1 and 2 in CH_3CN/Bu_4NPF_6 clearly indicated that the monocationic acetonitrile species $[\{(\eta^5\text{-}C_5R_4)Me_2Si(NMe_2)\}Fe(CO)_2(NCCH_3)]^+$ are generated as the oxidation products of a net symmetric two-electron oxidative bond cleavage of dimers 1 and 2.[29]

The oxidation of 2 occurs in all cases at lower potentials than does that for the unmethylated 1. This can be attributed to the greater stabilization of the oxidized form of compound 2 due to the enhanced electron-donating ability of the tetramethylated ligand $(\eta^5\text{-}C_5Me_4)Me_2Si(NMe_2)$. On the other hand, the higher electron density enhances the kinetic stability of the binuclear radical-cation $[\{(\eta^5\text{-}C_5Me_4)Me_2Si(NMe_2)\}Fe(CO)_2]_2^+$ making it possible to detect it on the CV time scale in both THF and CH_2Cl_2.

Whereas the electrochemistry of the model dimers 3–6 and polymers 7–12 in dichloromethane is similar to that of the dimer 2, we observe a different electrochemical behavior for these model dimers and polymers when THF is used as solvent (Figure 5, Table II). Although chemically reversible systems can be observed, comparisons of limiting currents obtained from rotating disk electrode voltammograms indicate two-electron transfers. At lower scan rates the reversible systems disappear, irreversible processes corresponding also to two-electron transfers take place, and new reduction peaks (D) can be observed at less positive potentials. Although these results suggest that in this case the electrochemical transference takes place with the assistance of the nucleophilic attack by the solvent, the presence of the siloxane bridges permits the retention of the geometry of the complexes. In this way the iron atoms are held in a fairly close position to each other, so that the electrochemical reaction appears reversible in the CV time scale at high scan rates.

In the case of polymers 7–12 multicyclic voltammetry carried out in THF at scan rates >50 mV/s shows that these polymers are re-formed after oxidation and cleavage of the Fe–Fe bond. This fact is also explained by the presence of the siloxane chains.

Experimental Section

General Data and Materials. All reactions and subsequent manipulations were carried out under an atmosphere of dry nitrogen by using conventional Schlenk techniques.[30] Solvents were purified by distillation from appropriate drying agents under an atmosphere of dry N_2.[31] Triethylamine (Et_3N) was distilled over KOH under N_2. Anhydrous dimethylamine (Me_2NH) was purchased from Fluka. Iron pentacarbonyl and *n*-BuLi (2.5 M in hexane) were purchased from Aldrich Chemical Co. The following starting silicon compounds were purchased from Petrarch Systems Inc. and were purified as follows: dimethyldichlorosilane was distilled under N_2 just before use; 1,4-bis(hydroxydimethylsilyl)benzene and dihydroxydiphenylsilane were purified by recrystallization from CCl_4. Poly(dimethylsiloxane) silanol terminated (PS340.5) (Petrarch) and poly(methylhydrosiloxane) (Fluka) were used as received. Published methods were used to prepare 2,3,4,5-tetramethylcyclopenten-2-enone,[32,33] 1,2,3,4-tetramethylcyclopentadiene,[33] cyclopentadienyldimethylchlorosilane, and cyclopentadienyl(*N*,*N*-dimethylamino)dimethylsilane.[3] Silanized silica gel 60 (70–230 mesh)

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[28] Legzdins, P.; Wassink, B. *Organometallics* **1984**, *3*, 1811.

[29] A small amount of unknown products, probably $\{(\eta^5\text{-}C_5R_4)Me_2Si(NMe_2)\}Fe(CO)_2L$ species on the basis of the IR ν(CO) patterns, was also generated in the electrooxidations performed in THF/Bu_4NPF_6 and CH_3CN/Bu_4NPF_6, if the electrolysis times were prolonged.

[30] (a) Shriver, D. F.; Drezdron, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; John Wiley and Sons: New York, 1986. (b) *Experimental Organometallics Chemistry*; Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symposium Series 357; American Chemical Society: Washington, DC, 1987.

[31] Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon: New York, 1988.

[32] Kohl, F. X.; Jutzi, P. In *Organometallic Syntheses*; King, R. B., Eisch, J. J., Eds.; Elsevier: New York, 1986; Vol. 3.

[33] (a) Fendrick, C. M.; Schertz, L. D.; Day, V. W.; Marks, T. J. *Organometallics* **1988**, *7*, 1828. (b) Stern, D.; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 9558.

(Merck) was used for column chromatographic purifications or some filtrations. All the syntheses of the iron complexes were effected in the dark.

Infrared spectra were recorded on Bomem MB-100 and on Nicolet 5 DX Fourier transform infrared spectrometers. The solution spectra were obtained using 0.1-mm KBr solution cells. Nuclear magnetic resonance spectra were recorded on a Bruker-AMX (300 MHz, FT mode) spectrometer. The ^{1}H chemical shifts are reported in parts per million (δ) with reference to internal Me_4Si. Electronic absorption spectra were obtained with a Pye-Unicam SP8-100 spectrophotometer. Number-average molecular weights ($\bar{M}_n$) 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 650 °C.

Electrochemical Measurements. All electrochemical experiments were carried out under a blanket of dry dinitrogen saturated with the solvent in use. Dichloromethane and acetonitrile were freshly distilled under nitrogen from calcium hydride. Tetrahydrofuran (THF) was distilled under nitrogen from sodium benzophenone ketyl. Tetra-*n*-butylammonium hexafluorophosphate (Bu_4NPF_6) was purchased from BAS or Strem and purified by recrystallization from ethanol and dried in vacuo at 60 °C. All electrochemical experiments were performed at ambient temperature unless otherwise noted.

Cyclic voltammetry was performed with a PAR 362 potentiostat connected to a Nicolet 310 digital oscilloscope and to a Linseis LY-1700 X-Y recorder. The three-electrode system consisted of a glassy-carbon disk working electrode (diameter 3.0 mm), a platinum-wire counter electrode, and a silver-wire pseudo reference electrode. The working compartment of the electrochemical cell was separated from the reference compartment by a modified Luggin capillary. The potential of the silver pseudo reference electrode was stable over the duration of a given experiment and was occasionally checked vs the ferrocene(0/1+) couple. Potentials are reported vs SCE after correction with the ferrocene couple.

Bulk electrolyses were done with a PAR 362 potentiostat and a PAR 379 digital coulometer. A PAR 377A coulometry cell system fitted with platinum-gauze working electrode was used. The counter electrode was a platinum mesh, which was separated from the working electrode by a salt bridge containing the supporting electrolyte.

Spectroelectrochemical Experiments. Infrared spectral changes during thin-layer bulk electrolyses were measured by using a spectroelectrochemical cell as described previously.[6] Infrared data were collected with a Bomen MB-100 FTIR spectrometer. Bulk electrolyses were controlled by a PAR 362 potentiostat.

Preparation of (C_5Me_4H)Me_2Si(NMe_2). Freshly distilled tetramethylcyclopentadiene (39 g, 319.6 mmol) was dissolved in 400 mL of THF in a three-necked 1000-mL flask equipped with a dropping funnel, magnetic stirring bar, and N_2 inlet. *n*-Butyllithium (128 mL of a 2.5 M solution in hexane, 320 mmol) was syringed into the stirred and cooled (0 °C) THF solution. A milky white suspension was formed within minutes. After the reaction mixture was stirred at room temperature for 4 h, the resulting suspension was next cooled to −78 °C and Me_2SiCl_2 (64.5 g, 500 mmol) in THF (30 mL) was added rapidly with vigorous stirring. The reaction mixture was slowly warmed to room temperature and the pale yellow solution was refluxed for 16 h. The solvent and excess of Me_2SiCl_2 were removed in vacuo, and the residue was extracted with hexane. LiCl was removed by filtration through a silanized silica-packed frit, and the solvent was removed under reduced pressure. Fractional distillation at 58–60 °C/0.1 Torr yielded 46.6 g (68%) of (C_5Me_4H)Me_2SiCl as a yellow liquid.

This chlorosilane (46.6 g, 217.2 mmol) was dissolved in 400 mL of diethyl ether and transferred to a dropping funnel. Anhydrous dimethylamine (29.4 g, 652.2 mmol), previously condensed by cooling at −45 °C, was added to a three-necked 1000-mL flask equipped as above, containing 400 mL of diethyl ether which had been previously cooled to 0 °C. The (C_5Me_4H)Me_2SiCl solution was then added dropwise with stirring over a 1-h period, and the resulting mixture was warmed to room temperature and then refluxed for 1 h. The amine hydrochloride was removed by nitrogen pressure filtration. The white solid was washed with three successive 75-mL portions of diethyl ether and the filtrate was concentrated under vacuum. Fractional distillation at 52–55 °C/0.1 Torr yielded (C_5Me_4H)Me_2Si(NMe_2) as a yellow-green oily liquid (70% yield).

^{1}H NMR ($CDCl_3$): δ 0.05 (s, 6 H, $SiCH_3$), 1.81 (s, 6 H, $C_5(CH_3)_4$), 1.98 (s, 6 H, $C_5(CH_3)_4$), 2.42 (s, 6 H, $SiN(CH_3)_2$), 2.95 (s, H, $HC_5(CH_3)_4$). IR (neat, cm^{-1}): 2963 (vs), 2912 (vs), 2859 (vs), 2792 (s), 1669 (w), 1633 (m), 1448 (s), 1380 (m), 1290 (m), 1254 (vs), 1219 (m), 1179 (s), 1072 (s), 1049 (vs), 990 (vs), 951 (m), 857 (msh), 823 (vs), 799 (vs), 781 (m), 694 (s), 609 (s), 484 (s).

Preparation of [{(η^5-C_5R_4)Me_2Si(NMe_2)}$Fe(CO)_2$]$_2$ (R = H (1)). To a 250-mL flask fitted with a reflux condenser, N_2 inlet, and magnetic stir bar, 50 mL of dry-deoxygenated decane and (C_5H_5)Me_2Si(NMe_2) (12.0 g, 71.8 mmol) was added under dinitrogen. Deoxygenated and filtered $Fe(CO)_5$ (11.1 mL, 85 mmol) was then added, and the reaction mixture was slowly heated to 125–130 °C and then allowed to stir at this temperature for 24 h, under dinitrogen. The dark-red mixture was allowed to cool and filtered while slightly warm (30–40 °C) through a pad of silanized silica (3 × 3 cm) to remove small amounts of insoluble decomposition materials. The resulting dark-red solution was next cooled to −20 °C, and a red solid was formed, which was collected by filtration, washed with cold hexane, and dried in vacuo, yielding 11 g (19.8 mmol, 55%) of [{(η^5-C_5H_4)Me_2Si(NMe_2)}$Fe(CO)_2$]$_2$ (1) as an analytically pure red crystalline solid. Anal. Calcd for $C_{22}H_{32}N_2O_4Si_2Fe_2$: C, 47.51; H, 5.75; N, 5.03. Found: C, 47.60; H, 5.84; N, 5.10.

R = Me (2). This reaction was carried out in the same fashion as that used to prepare 1, starting from (C_5Me_4H)Me_2Si(NMe_2) (12 g, 53.8 mmol) and $Fe(CO)_5$ (7.8 mL, 60 mmol) in decane (50 mL). After 24 h at 130 °C, an additional 2 mL (15 mmol) of $Fe(CO)_5$ was added and the reaction mixture was allowed to stir at this temperature for an additional 24 h. The reaction mixture was filtered while slightly warm through a layer (3 × 3 cm) of silanized silica, and the solvent was removed in vacuo from the obtained red solution. The resulting red waxy material was purified chromatographically (2 × 30 cm) on silanized silica using a THF/*n*-hexane (1:3 v/v) mixture as eluent. The single red band was collected, and the solution was reduced to dryness. The residue was dissolved in THF/*n*-hexane (1:5 v/v), and the solution was stored at −30 °C to afford a solid, which was filtered under N_2 and dried in vacuo to give [{(η^5-C_5Me_4)Me_2Si(NMe_2)}$Fe(CO)_2$]$_2$ (2) as an analytically pure red solid in 40% yield (7.2 g, 10.7 mmol). Anal. Calcd for $C_{30}H_{48}N_2O_4Si_2Fe_2$: C, 53.92; H, 7.18; N, 4.19. Found: C, 54.09; H, 7.23; N, 4.25.

Preparation of {(C_5R_4H)Me_2SiO}$_2SiPh_2$ and {(C_5R_4H)Me_2SiO}$_2$[Me_2Si(1,4-C_6H_4)$SiMe_2$] (R = H, Me). These linked bis(cyclopentadienyl) ligands were prepared by the methods outlined in eqs 2 and 3. A typical procedure is illustrated for each one of these syntheses.

Method A. Recrystallized 1,4-bis(hydroxydimethylsilyl)benzene (4.7 g, 20.8 mmol) and (C_5H_5)Me_2Si(NMe_2) (6 g, 35.9 mmol) were added to a 100-mL two-necked flask containing 40 mL of toluene and equipped with magnetic stir bar, reflux condenser, and nitrogen inlet. The mixture was slowly heated to 100–110 °C for 2 h. During this time the disilanol dissolved and dimethylamine evolution was observed. The mixture was then kept under vacuo at 80 °C for 1 h, to remove the solvent and Me_2NH. To the resulting viscous mixture, an additional 15 mL of toluene was added and the solution was filtered through a layer (3 × 3 cm) of silanized silica to remove the excess silanol. The solvent was removed in vacuo, and the resulting yellow-brown oil was used without further purification. Thus, $\{(C_5H_5)Me_2SiO\}_2[Me_2Si(1,4\text{-}C_6H_4)SiMe_2]$ was isolated in 73% yield.

^{1}H NMR ($CDCl_3$): δ 0.09, 0.34 (m, 24 H, $SiCH_3$), 3.05 (s, 2 H, HC_5H_4), 6.53, 6.66 (br, 8 H, C_5H_4), 7.58 (s, 4 H, C_6H_4). IR (cm^{-1}): 3090 (m), 3050 (s), 2947 (vs), 2928 (s), 2901 (s), 2872 (m), 1616 (m), 1407 (m), 1380 (s), 1341 (m), 1256 (vs), 1138 (vs), 1061 (vs), 977 (s), 952 (s), 828 (vs), 807 (vs), 698 (s), 662 (m), 505 (s), 463 (s), 423 (m).

Similarly prepared, from the reaction of Me_2SiNMe_2-substituted cyclopentadiene and tetramethylcyclopentadiene with the corresponding disilanols, were the following:

$\{(C_5Me_4H)Me_2SiO\}_2[Me_2Si(1,4\text{-}C_6H_4)SiMe_2]$ (Yield 62%). ^{1}H NMR ($CDCl_3$): δ 0.08, 0.33 (m, 24 H, $SiCH_3$), 1.78, 1.89 (s, 24 H, $C_5(CH_3)_4$), 2.80 (s, 2 H, $HC_5(CH_3)_4$), 7.57 (s, 4 H, C_6H_4). IR (cm^{-1}): 3050 (m), 2962 (vs), 2925 (s), 2868 (s), 1632 (m), 1446 (s), 1381 (s), 1257 (vs), 1139 (vs), 1058 (vs), 907 (m), 825 (vs), 795 (vs), 730 (s), 695 (s), 659 (s), 506 (s), 464 (s).

$\{(C_5H_5)Me_2SiO\}_2SiPh_2$ (Yield 70%). ^{1}H NMR ($CDCl_3$): δ 0.01 (m, 12 H, $SiCH_3$), 2.98, (s, 2 H, HC_5H_4), 6.47, 6.61 (br, 8 H, C_5H_4), 7.37, 7.67 (m, 10 H, C_6H_5). IR (cm^{-1}): 3069 (m), 3051 (m), 2961 (vs), 2927 (s), 2872 (m), 1958 (w), 1893 (w), 1824 (w), 1592 (s), 1429 (vs), 1257 (vs), 1123 (vs), 978 (s), 952 (m), 840 (s), 805 (vs), 742 (m), 701 (vs), 512 (vs), 484 (m), 427 (m).

$\{(C_5Me_4H)Me_2SiO\}_2SiPh_2$ (Yield 58%). ^{1}H NMR ($CDCl_3$): δ 0.08 (m, 12 H, $SiCH_3$), 1.82, 1.95 (s, 24 H, $C_5(CH_3)_4$), 2.90 (s, 2 H, $HC_5(CH_3)_4$), 7.33, 7.61 (m, 10 H, C_6H_5). IR (cm^{-1}): 3075 (m), 3050 (m), 2963 (s), 2921 (s), 2862 (s), 1952 (w), 1893 (w), 1824 (w), 1633 (m), 1592 (m), 1430 (s), 1380 (m), 1256 (vs), 1219 (m), 1122 (vs), 1064 (vs), 906 (m), 834 (vs), 800 (vs), 719 (s), 700 (s), 523 (s), 488 (s).

Method B. 1,4-Bis(hydroxydimethylsilyl)benzene (4.0 g, 17.7 mmol) and freshly distilled triethylamine (5.6 g, 55.4 mmol) were suspended in 50 mL of toluene. The suspension was cooled to 0 °C and $(C_5Me_4H)Me_2SiCl$ (8 g, 37.3 mmol) was added dropwise with vigorous stirring. The reaction mixture was then allowed to warm to room temperature, subsequently heated to 80 °C for 2 h, and then left to stir at room temperature overnight. The Et_3NHCl was filtered off and washed with toluene (50 mL), and the filtrate was subjected to a further filtration over a pad of silanized silica (5 × 3 cm). The solvent was removed from the filtrate under reduced pressure to yield $\{(C_5Me_4H)Me_2SiO\}_2[Me_2Si(1,4\text{-}C_6H_4)SiMe_2]$ as a yellow-brown oil (8 g, 13.7 mmol) (74%). The related derivatives $\{(C_5H_5)Me_2SiO\}_2[Me_2Si(1,4\text{-}C_6H_4)SiMe_2]$, $\{(C_5H_5)Me_2SiO\}_2SiPh_2$, and $\{(C_5Me_4H)Me_2SiO\}_2SiPh_2$ were produced in a similar fashion in 70–93% yields.

Preparation of the Model Complexes $\{SiMe_2OSiPh_2OSiMe_2\}[(\eta^5\text{-}C_5R_4)Fe(CO)_2]_2$ and $\{SiMe_2OSiMe_2(1,4\text{-}C_6H_4)SiMe_2OSiMe_2\}[(\eta^5\text{-}C_5R_4)Fe(CO)_2]_2$ (R = H, Me). These reactions were carried out in the same fashion as that used to prepare the related complexes 1 and 2. As a representative example, a typical procedure is illustrated for the synthesis of $\{SiMe_2OSiMe_2(1,4\text{-}C_6H_4)SiMe_2OSiMe_2\}[(\eta^5\text{-}C_5H_4)Fe(CO)_2]_2$ (5).

The reaction was carried out in the same reaction vessel as that described above for dimers 1 and 2. Under nitrogen, it was charged with recently obtained $\{(C_5H_5)Me_2SiO\}_2[Me_2Si(1,4\text{-}C_6H_4)SiMe_2]$ (5 g, 10.6 mmol), filtered $Fe(CO)_5$ (5 mL, 38 mmol), and decane (40 mL). The resulting solution was deoxygenated with a nitrogen purge and then heated (120–125 °C) with stirring for 24 h. After this time the mixture, gently warmed (≈40 °C), was filtered through a pad of silanized silica. The red solution was reduced to dryness, and the residue was diluted with THF and subjected to column chromatography on silanized silica. Elution with the same solvent gave a single dark red band, which was collected, and the solvent was removed under reduced pressure, resulting in the desired product 5 as a red solid in 70% yield (5 g, 7.2 mmol). Anal. Calcd for $C_{28}H_{36}O_6Si_4Fe_2$: C, 48.58; H, 5.20. Found: C, 48.65; H, 5.29.

The related model complex $\{SiMe_2OSiPh_2OSiMe_2\}[(\eta^5\text{-}C_5H_4)Fe(CO)_2]_2$ (3) was synthesized following the above procedure from $\{(C_5H_5)Me_2SiO\}_2SiPh_2$ (4.9 g, 10.6 mmol) and $Fe(CO)_5$ (5 mL, 38 mmol), being isolated as a red waxy product in 65% yield. Anal. Calcd for $C_{30}H_{30}O_6Si_3Fe_2$: C, 52.81; H, 4.40. Found: C, 52.96; H, 4.51.

The tetramethylated complexes $\{SiMe_2OSiPh_2OSiMe_2\}[(\eta^5\text{-}C_5Me_4)Fe(CO)_2]_2$ (4) and $\{SiMe_2OSiMe_2(1,4\text{-}C_6H_4)SiMe_2OSiMe_2\}[(\eta^5\text{-}C_5Me_4)Fe(CO)_2]_2$ (6) were similarly prepared from the appropriate ligand, $\{(C_5Me_4H)Me_2SiO\}_2SiPh_2$ (5 g, 8.7 mmol) or $\{(C_5Me_4H)Me_2SiO\}_2[Me_2Si(1,4\text{-}C_6H_4)SiMe_2]$ (7 g, 8.7 mmol), and $Fe(CO)_5$ (3.5 mL, 26.6 mmol). In these cases the reaction times were prolonged up to 48 h. After filtration as above and elimination of the solvent, the IR analysis of the reaction product indicated a mixture of two different products, both with $[Fe(CO)(\mu\text{-}CO)]_2$ units on the basis of the ν(CO) pattern. These products were separated by column chromatography with THF/*n*-hexane (1:3 v/v) and by fractional crystallization. The more soluble fractions[34] contained the desired compounds, being isolated in 25–30% yields.

Anal. Calcd for $\{SiMe_2OSiPh_2OSiMe_2\}[(\eta^5\text{-}C_5Me_4)Fe(CO)_2]_2$ (4) ($C_{38}H_{46}O_6Si_3Fe_2$): C, 57.46; H, 5.79. Found: C, 57.84; H, 5.90.

Anal. Calcd for $\{SiMe_2OSiMe_2(1,4\text{-}C_6H_4)SiMe_2OSiMe_2\}[(\eta^5\text{-}C_5Me_4)Fe(CO)_2]_2$ ($C_{36}H_{52}O_6Si_4Fe_2$): C, 53.75; H, 6.47. Found: C, 53.94; H, 6.59.

Condensation Polymerizations of Complexes 1 and 2 with Disilanols. All of these condensation reactions were performed in a similar manner. The procedure for $[-SiMe_2(\eta^5\text{-}C_5H_4)Fe(CO)(\mu\text{-}CO)_2(CO)Fe(\eta^5\text{-}C_5H_4)Me_2SiOSiMe_2(1,4\text{-}C_6H_4)SiMe_2O-]_n$ (9) is described in detail as a representative example.

Dimer 1 (2 g, 3.6 mmol) was dissolved in dried deoxygenated toluene (3 mL) in a Schlenk tube fitted with a reflux condenser, nitrogen inlet, and magnetic stir bar. Recrystallized 1,4-bis(hydroxydimethylsilyl)benzene (0.8 g, 3.6 mmol) was then added along with 4 mL of toluene. A slight nitrogen stream was maintained and the mixture heated to 50 °C and stirred; at this point the disilanol dissolved and dimethylamine evolution was observed. The polymerization temperature was increased to 100 °C and held for 1 h, and next toluene was removed at reduced pressure. The resulting mixture was stirred at 60 °C under vacuo for an additional 1 h, to drive off remaining Me_2NH efficiently and complete the polymerization. The viscous dark-red mixture was dissolved in toluene (25 mL) and filtered by nitrogen pressure, and the red solution was concentrated and then added dropwise to dry deoxygenated methanol (200 mL) with vigorous stirring. The resulting red precipitate was collected by filtration under N_2 and dried in vacuo. The polymer was reprecipitated one more time from toluene with methanol and finally washed with *n*-hexane (2 × 25 mL) and then dried in vacuo for several hours (at 0.01 Torr). A total of 1.5 g of a red solid polymer was isolated. $\bar{M}_n$ (VPO, THF): 6900 ($n \approx 10$).

Similarly prepared, from the reaction of the dimers 1 and 2 with the given disilanol, and purified as we describe for 9 were the following polymers.

$[-SiMe_2(\eta^5\text{-}C_5H_4)Fe(CO)(\mu\text{-}CO)_2(CO)Fe(\eta^5\text{-}C_5H_4)Me_2SiOPh_2SiO-]_n$ (7) was synthesized from complex 1 (2 g, 3.6 mmol) and dihydroxydiphenylsilane (0.7 g, 3.6 mmol). It was isolated as a red powdery solid (1.2 g). $\bar{M}_n$ (VPO, THF): 5500 ($n \approx 8$).

$[-SiMe_2(\eta^5\text{-}C_5Me_4)Fe(CO)(\mu\text{-}CO)_2(CO)Fe(\eta^5\text{-}C_5Me_4)Me_2SiOPh_2SiO-]_n$ (8) was prepared from complex 2 (2 g, 3 mmol) and dihydroxydiphenylsilane (0.64 g, 3 mmol). A total of 0.9 g of a reddish-brown polymer was isolated. $\bar{M}_n$ (VPO, THF): 4000 ($n \approx 5$).

$[-SiMe_2(\eta^5\text{-}C_5Me_4)Fe(CO)(\mu\text{-}CO)_2(CO)Fe(\eta^5\text{-}C_5Me_4)Me_2SiOSiMe_2(1,4\text{-}C_6H_4)SiMe_2O-]_n$ (10) was synthesized from complex 2 (2 g, 3 mmol) and 1,4-bis(hydroxydimethylsilyl)benzene (0.68 g, 3 mmol); 1.8 g of a red solid was obtained. $\bar{M}_n$ (VPO, THF): 6500 ($n \approx 8$).

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[34] The IR and ^{1}H NMR spectra of the more insoluble fractions indicated that they contained a product with terminal and bridged carbonyl groups as well as $\eta^5\text{-}C_5Me_4$ ligands. These products were not obtained in an analytically pure state and were not characterized further.

[$-SiMe_2(\eta^5$-$C_5H_4)Fe(CO)(\mu$-$CO)_2(CO)Fe(\eta^5$-$C_5H_4)$-$Me_2SiOSiMe_2O(Me_2SiO)_nSiMe_2O-]_{n'}$ (11) was prepared by reacting complex 1 (2 g, 0.0072 equiv of $SiNMe_2$) and poly(dimethylsiloxane) silanol terminated (6.3 g, 0.0072 equiv of SiOH). The polymer was isolated as a red gummy materal. $\bar{M}_n$ (VPO, THF): 11 000 ($n \approx 5$).

[$-SiMe_2(\eta^5$-$C_5Me_4)Fe(CO)(\mu$-$CO)_2(CO)Fe(\eta^5$-$C_5Me_4)$-$Me_2SiOSiMe_2O(Me_2SiO)_nSiMe_2O-]_{n'}$ (12) was synthesized from complex 2 (2 g, 0.0059 equiv of $SiNMe_2$) and poly(dimethylsiloxane) silanol terminated (5.2 g, 0.0059 equiv SiOH). The polymer was isolated as a dark-red rubberlike material. $\bar{M}_n$ (VPO, THF): 13 500 ($n \approx 6$).

Preparation of [$Me_3Si-O\{(-MeSiOSiMeO)(\eta^5$-$C_5H_4)$-$Fe(CO)(\mu$-$CO)_2(CO)Fe(\eta^5$-$C_5H_4)\}_{n'}-SiMe_3$] (13). Poly(methylhydrosiloxane), $Me_3Si-O(-SiHMeO)_{\approx 35}-SiMe_3$, was chlorinated by a mixture of Cl_2 and N_2, in CCl_4 solution at 0 °C, following approximately the procedure described in ref 35. The reaction was monitored by IR spectroscopy. The chlorine–nitrogen gas mixture was passed through the solution until the ν(SiH) band (2157 cm^{-1}) had disappeared. The CCl_4 was distilled off under vacuum, and the residue was then dried under vacuum for several hours. The resulting milky viscous liquid was used, recently obtained, in the subsequent reaction. Sodium cyclopentadienide was prepared from NaH (3.4 g, 142 mmol) and 15.8 mL (12.64 g, 192 mmol) of freshly distilled cyclopentadienide, in 125 mL of THF, in a three-necked 500-mL flask, equipped with a dropping funnel, magnetic stir bar, and gas inlet. To this $NaC_5H_5{\cdot}THF$ solution, cooled at −78 °C, was added dropwise Me_3Si-O-$(ClMeSiO)_{\approx 35}-SiMe_3$ (13.8 g, 3.97 mmol), in diethyl ether (50 mL). After the addition was completed, the mixture was allowed to stir at room temperature overnight and then hydrolyzed with saturated NH_4Cl solution. The aqueous phase was washed with 50-mL portions of THF, and the resulting organic phase was dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the resulting viscous oil was characterized by IR and ^{1}H NMR spectroscopy.

To a 100-mL flask fitted with a reflux condenser, magnetic stir bar, and nitrogen inlet were added recently obtained poly(cyclopentadienylmethylsiloxane) (3 g, 0.66 mmol), $Fe(CO)_5$ (14.9 g, 2.17 mmol), and dry-deoxygenated decane (50 mL). In the dark, the mixture was heated to 110–120 °C for 30 h. After this time, the yellow fumes of $Fe(CO)_5$ were absent, indicating no unreacted iron pentacarbonyl. The red mixture was allowed to cool at −20 °C overnight and a red solid was formed, which was collected by filtration under N_2, washed with *n*-hexane, and dried in vacuo. A total of 2.2 g of polymer was isolated as a dark-red solid.

Acknowledgment. We thank the Dirección General de Investigación Cientifica y Técnica (DGICYT) (Proyect No. 90/0227) for financial support of this work.

OM920497O

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