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Ferrocenylene- and Carbosiloxane-Bridged Bis(sila[1]ferrocenophanes) E[SiMe$_2$-X-SiMe*FC*]$_2$ {E = (η^5-C$_5$H$_4$)Fe(η^5-C$_5$H$_4$) or O; X = (CH$_2$)$_n$ (n = 2, 3, 6); CH=CH; *FC* = (η^5-C$_5$H$_4$)$_2$Fe}

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New **FC**[SiMe$_2$(CH$_2$)$_n$SiMe*FC*]$_2$ [**FC** = 1,1′-ferrocenylene; *FC* = 1,1′-ferrocenophane, (η^5-C$_5$H$_4$)$_2$Fe); n = 2 (**7**), 3 (**8**), 6 (**9**)] and O[SiMe$_2$-X-SiMe*FC*]$_2$ [X = (CH$_2$)$_2$ (**11**), CH=CH (**13**)] have been synthesized and characterized. The synthesis involved the reactions of **FC**Li$_2$·tmeda with **FC**[SiMe$_2$(CH$_2$)$_n$SiMeCl$_2$]$_2$ [n = 2 (**4**), 3 (**5**), 6 (**6**)] and O[SiMe$_2$-X-SiMeCl$_2$]$_2$ [X = (CH$_2$)$_2$ (**10**), CH=CH (**12**)] at −78 °C. Compounds **4**−**13** were characterized by elemental analysis, NMR spectroscopy, and for **11**, single-crystal X-ray crystallography. The cyclopentadienyl rings in the structure of **11** are tilted with a dihedral angle of 19.8°. The observed red-shift of the lowest energy transition associated with the ferrocenophanyl groups in UV/vis spectra of **7**−**9**, **11**, and **13** also confirms the ring strain. Cyclic voltammetric studies exhibited either a broad (**7**−**9**) or sharp (**11**, **13**) wave for the reversible redox process. The broadness of the band for the **FC**-bridged complexes is a composite of the two types of (η^5-C$_5$H$_4$)Fe(η^5-C$_5$H$_4$) unit, but no significant inter-*Fc* interaction could be discerned. All the new bis-ferrocenylene materials are readily ring-opened to form polymeric materials.

Introduction

Strained metallocenophanes are known for their ring-opening polymerization (ROP) chemistry,[1] and in particular sila[1]ferrocenophanes[1f] have served as monomers for a variety of polyferrocenylenesilylenes with regioregular, comb, star, and block architectures.[2] These polymers have applications such as precursors for ceramic materials,[3] conducting polymers,[4,5] and chemical sensors.[5]

A large range of sila[1]ferrocenophanes have been reported by different research groups, and representative types are depicted in Figure 1. A number of dichlorodiorganosilanes were used to prepare symmetric and unsymmetric derivatives[5b,6] [Figure 1, **A**, R^1 = R^2 = Me, Ph, Cl, ferrocenyl, O^{t}Bu, O^{i}Pr, OCH$_2$Ph; R^1 = Me, R^2 = Et, Ph, Cl, H, allyl, vinyl, n-C$_{18}$H$_{37}$, norbornyl; R^1 = Me, R^2 = (CH$_2$)$_n$Cl (n = 1−3); R^1 = Ph, R^2 = Cl]. Several cyclopentadienyl-substituted sila[1]ferrocenophanes have been reported [Figure 1, **B**, R$_x$ = Me, Me$_4$, t-Bu$_2$, Me$_3$Si, (Me$_3$Si)$_2$; R = Me, Ph],[7] and hypercoordinated sila[1]ferrocenophanes,[8] e.g., *FC*SiMeNAr (NAr = C$_6$H$_4$-2-CH$_2$NMe$_2$)[8a] have been synthesized and characterized [Figure 1, **C**].

To our knowledge 1,3-bis-ferrocenophanyl-dimethyldisiloxane, *FC*SiMeOSiMe*FC*, *FC* = (η^5-C$_5$H$_4$)$_2$Fe, represents the

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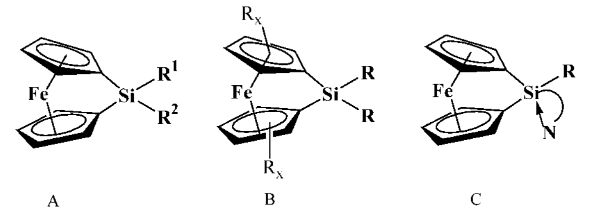


Figure 1. Schematic representation of sila[1]ferrocenophane derivatives.

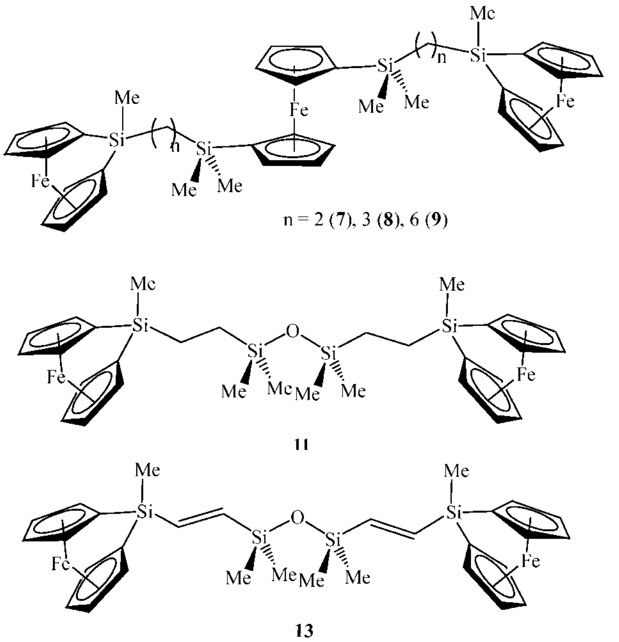


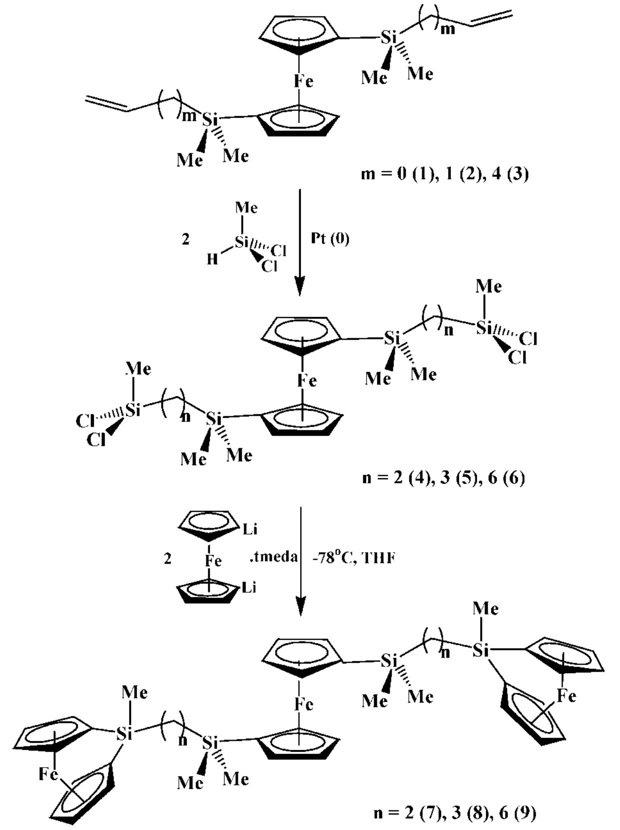
Figure 2. New bis-[sila[1]ferrocenophane] derivatives.

unique example of a molecule containing two sila[1]ferrocenophane units, but no ROP chemistry has been reported.[9] Our continuing interest in sila[1]ferrocenophanes[5,6] led us to synthesize, characterize, and preliminarily investigate a series of new bis-sila[1]ferrocenophanes bridged by carbosilylferrocenylene and carbosiloxane groups, **FC**[$SiMe_2(CH_2)_nSiMe$*FC*]$_2$ [$n = 2$ (**7**), 3 (**8**), 6 (**9**)] and O[$SiMe_2$-X-$SiMe$*FC*]$_2$ [X = $(CH_2)_2$ (**11**), CH=CH (**13**)] (Figure 2). A major interest in such monomers is due to their potential to be transformed into high molecular weight polymers; thus, the use of a bridge between two such units could be of potential to develop the chemistry of branched redox-active metal-containing polymers.

Results and Discussion

Synthesis and Characterization of (η^5-C_5H_4)Fe(η^5-C_5H_4)-[$SiMe_2(CH_2)_nSiMe$*FC*]$_2$. The overall synthetic scheme for the formation of the new ferrocenylene-bridged complexes is illustrated in Scheme 1.

Scheme 1



The starting materials for the bridges containing a central ferrocenylene unit, **FC**[$SiMe_2(CH_2)_mCH{=}CH_2$]$_2$ [$m = 0$ (**1**), 1 (**2**), 4 (**3**)], were synthesized by salt-elimination reactions of **FC**Li_2·tmeda with the corresponding commercially available chlorosilanes following the published procedures of the Cuadrado group.[10] The synthesis of the bis-dichlorosilanes (**4**−**6**) bridged by different spacer groups was effected by the Pt(0)-catalyzed hydrosilylation reactions between **1**−**3** and $MeHSiCl_2$ (2.5-fold excess) under mild conditions. These hydrosilylated products were isolated as viscous oils in 85−95% yield and characterized by elemental analysis and NMR spectroscopy and used in the following step with no further purification. The easy removal of excess $MeHSiCl_2$ from the reaction mixture *in vacuo* leads to the formation of analytically pure products in good yields.

The ^1H NMR spectra of **4**−**6** revealed the formation of the desired products as the integrated ratio of different groups is in accord with the structural composition. As expected, ^{29}Si NMR spectra exhibit two signals in each compound [^{29}Si (ppm): −0.01 (**FC**$SiMe_2$), 33.6 ($SiMeCl_2$) **4**; −2.59 (**FC**$SiMe_2$), 32.5 ($SiMeCl_2$) **5**; −2.07 (**FC**$SiMe_2$), 33.0 ($SiMeCl_2$) **6**]. The ^{13}C NMR spectra illustrate the presence of carbosilyl [$Si(CH_2)_nSi$] and [Si-CH=CH-Si] units and also rule out the presence of any unreacted olefinic or acetylenic groups of the starting material. The spectral data also suggest the regiospecific formation of the β-isomer (for **4**−**6**) since evidence for the formation of the α-isomer was not detected.

Low-temperature reactions at −78 °C between the appropriate bis-dichlorosilyl compounds **4**−**6** with **FC**Li_2·tmeda in 1:2 molar ratio in THF resulted in the high yield formation of complexes **7**−**9** as air- and moisture-sensitive orange-red materials. They have been characterized by elemental analysis and NMR spectroscopy. A long period of aerial exposure (weeks) of these molecules leads to insoluble decomposition products: however, when stored in sealed tubes in a refrigerator, these complexes are stable indefinitely. The ^{13}C NMR spectra of **7**−**9** in C_6D_6 exhibit a distinct resonance in the range of 32−34 ppm assigned to the *ipso* carbon atom of the cyclopentadienyl ring, illustrative of dihedral angle-derived ring strain typical of other such ferrocenophanes.[5−7] Their ^{29}Si NMR spectra exhibit the expected two resonances (ppm) [−1.11

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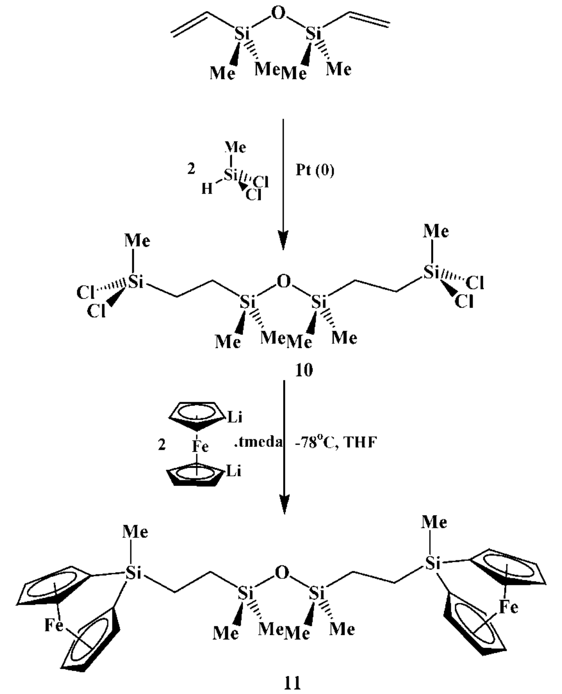
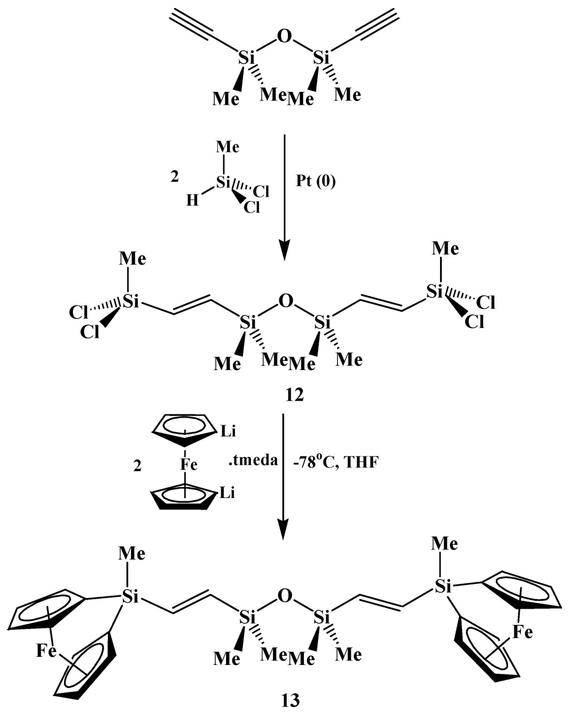
Scheme 2



Scheme 3



(SiMe*FC*), 0.29 (**FC**SiMe$_2$), **7**; −3.85 (SiMe*FC*), −2.63 (**FC**-SiMe$_2$), **8**; − 3.30 (SiMe*FC*), −2.05 (**FC**SiMe$_2$), **9**].[6,7]

The synthesis of the corresponding siloxane-bridged complexes followed similar procedures outlined in Scheme 2 for the alkylsiloxane products **10** and **11**.

The alkenylsiloxane products **12** and **13** were also obtained by the same procedures using the commercially available alkynylsiloxane HC≡CMe$_2$SiOSiMe$_2$C≡CH, Scheme 3.

Spectroscopic analysis of the siloxane materials was straightforward, and all data are presented in the Experimental Section. The ^{13}C NMR spectrum for the alkenyl complex **13** shows two signals at 145.7 and 154.6 ppm for the CH=CH moiety and are assigned to the β-(E) isomer.[11] Besides the elemental and spectral analysis the bis-[silyl[1]ferrocenophane] (**11**) was also characterized by single-crystal X-ray analysis, *vide infra*.

Further evidence for the ring strain in compounds **7**−**9**, **11**, and **13** as illustrated by the ^{13}C NMR data is observed by analysis of their UV/vis spectra. All ferrocenophanyl complexes exhibit $\lambda_{\max}$ values in the range 465−478 nm, a red-shift compared to ferrocene.[1a] The bathochromic shift of the lowest energy transition arises due to the decreasing HOMO−LUMO energy gap with progressively tilting of cyclopentadienyl rings[12,13] and has been shown to depend upon the nature of the bridging atom; $\lambda_{\max}$ for ferrocene = 440 nm, *FC***Si**Me$_2$ = 478 nm, *FC***P**-Ph = 498 nm,[14] *FC***S** = 504 nm.[15]

Electrochemical studies (0.1 M TBAP/dichloromethane, GCE, with scan rates of 50 mV s^{-1}) of the ferrocenylene-bridged diferrocenophanes **7**−**9** revealed single broad reversible (i_{pa}/i_{pc} = 1) redox waves corresponding to the ferrocenyl/ferrocenium couple [E_{ox}/E_{red} (V) = 0.75/0.58 (**7**), 0.78/0.50 (**8**), 0.76/0.46 (**9**)] (Figure 6a). The broadness in these CVs of **7**−**9** is presumably due to the presence of the "extra" bridging **FC** group but illustrates an absence of a significant interferrocenylene communication.[5e,h,16] However, as expected, the siloxane-bridged bis-ferrocenophanes **11** and **13** exhibited sharp reversible waves, 0.75/0.50 (**11**) and 0.76/0.46 (**13**).

Crystal Structure of 11. Single crystals suitable for X-ray diffraction analysis of **11** were obtained from a hexane solution at 0 °C. The compound crystallized in a monoclinic crystal system with a $P2(1)/c$ space group. The molecule adopts a centrosymmetric structure, and the O atom of the siloxane unit, localized near the inversion center, was found to be disordered at two positions, Figure 3. Low-temperature data collection could not resolve this disorder. The angle Si2−O1A−Si2A of 155.8(4)° is a typical value for a disiloxane bridge.[9] As expected, the cyclopentadienyl rings are tilted with a dihedral angle (α) of 19.8°, a value in accord with those reported for *FC*SiR$_1$R$_2$ [R$_1$/R$_2$ (α) = Me/Me (20.8(5)°),[17] Ph/Ph (19.1(10)°),[18] O^{t}Bu/

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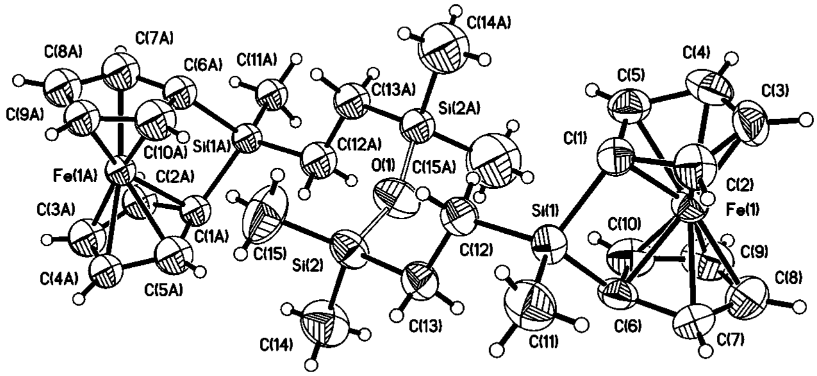

Figure 3. Molecular structure of compound **11** in the crystal. It is related by an inversion center. The ellipsoids were drawn at 40% probability. The second part of the disordered oxygen was omitted for better clarity.

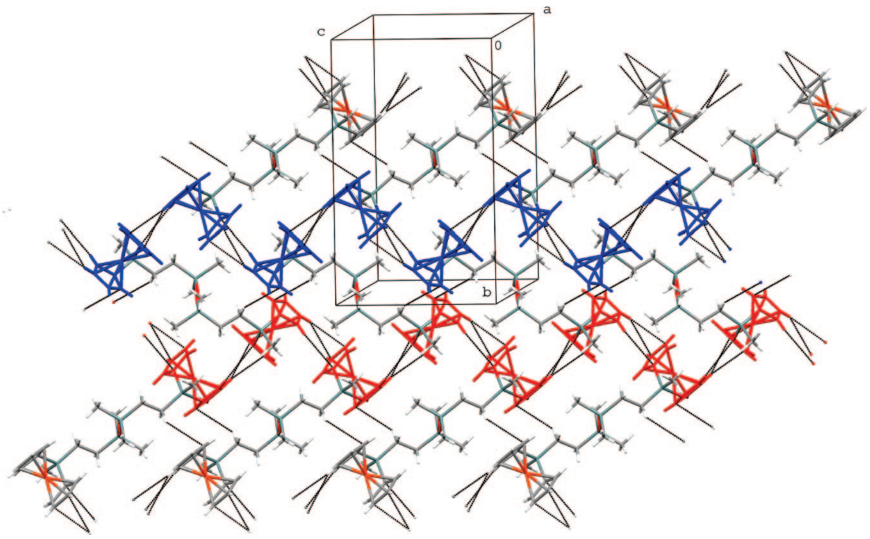

Figure 4. Crystal packing of **11** illustrating interacting chains.

O^tBu (20.7°),[6a] Cl/Cl (19.2(4)°),[19] Me/Cl (19.4(3)°),[8,9b] Me/Ph (21.0(2)°),[6e,20] ferrocenyl/Me (21.3(3)°[5b]].

The packing diagram of **11** illustrates several ferrocenylene/ferrocenylene interactions. A major component of this assembly involves a zigzag chain formed by means of T-stacked interactions Cp−H---Cp [angle Cp−H---Cp 81.50°, r(Cp---Cp) = 4.714 Å]. The separate zigzag chains are interconnected by inter CH-π interactions between the *FC*(SiMe)$\mathbf{CH_2}$ hydrogen and the Cp as a T-stacked interaction with C−H---centroid distance of ~3.66 Å (Figure 4). Together these interactions generate a network of channels along the *a* axis, which are occupied by the bridging portion of the molecule (Figure 5).

Preliminary Studies on Ring-Opening Polymerization. The ring strain in compounds **7**−**9**, **11**, and **13**, as evidenced by the spectroscopic and structural analysis above, leads to the expectation that these new systems will readily ring open to form polymeric ferrocenylenesilylene materials. Indeed facile ROP in toluene (1−2 h at room temperature in the presence of a Pt(0) catalyst) was observed, and the resulting materials, **7a**−**9a**, **11a**, and **13a**, were precipitated from the toluene solutions by addition of hexanes and isolated as brown solids with the exception of **9a**, which was isolated as a sticky gum (Scheme 4). This time period of polymerization permitted us

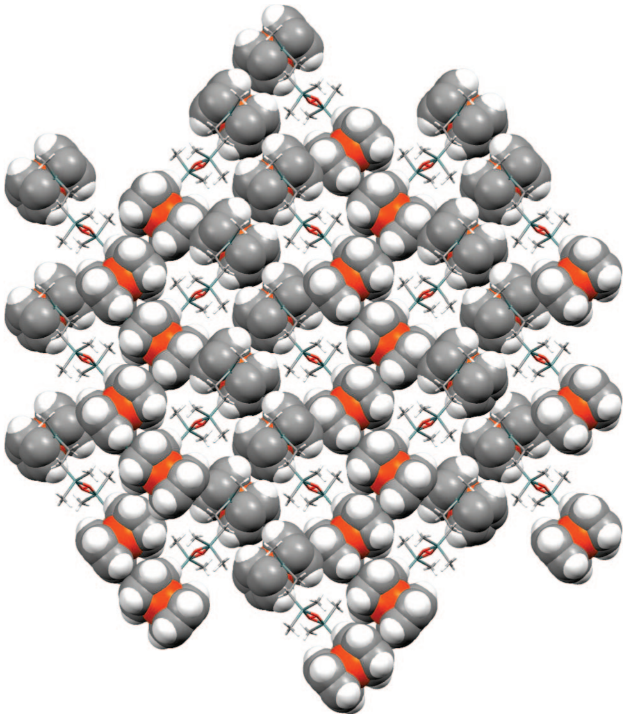

Figure 5. Crystal packing of **11** illustrating cavities containing the interferrocenophanyl bridges.

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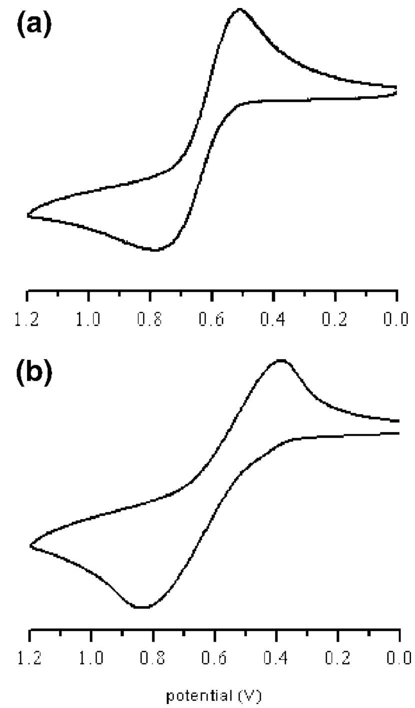


Figure 6. Cyclic voltammogram of **FC**$[SiMe_2(CH_2)_2SiMe$**FC**$]_2$ (**7**) (a) [0.1 M TBAP/DCM, GCE, Ag/AgCl] and $-\{$**FC**$[SiMe_2(CH_2)_2SiMe$**FC**$]_2\}_n-$ (**7a**) (b) [0.1 M TBAP/THF, GCE, Ag/AgCl].

to characterize the resulting polymers (**7a**−**9a**, **11a**, and **13a**) by molecular weight studies (GPC/THF) and NMR spectroscopy (THF-d_8). Longer time periods, 6−8 h, resulted in progressively more insoluble materials being precipitated from the toluene solutions. Gel permeation chromatography (GPC) data of these initially formed soluble polymers showed the formation of materials with M_w and M_n values in the range $(1.5-5.5) \times 10^5$ and, with the exception of **9a**, showed bimodal weight distribution: Polymer: M_w ($\times 10^5$); M_n ($\times 10^5$); PDI (M_w/M_n): **7a**: 5.5; 4.2; 1.30// 1.5; 1.1; 1.36; **8a**: 4.5; 3.6; 1.25. **9a**: 5.1; 4.0; 1.27// 3.7; 2.8; 1.32. **11a**: 5.4; 4.4; 1.22// 4.1; 3.2; 1.28; **13a**: 4.9; 3.5; 1.40// 3.2; 2.6; 1.23. Longer polymerization time periods led to the formation of insoluble materials.

The ^{13}C and ^{29}Si NMR spectra of the soluble high molecular weight materials required long collection times and exhibited broad signals. Although we cannot observe any cyclopentadienyl *ipso*-carbon resonances in the 30−40 ppm region, it is probable that not all ferrocenophane groups have ring-opened. Thus, in the early stages of the polymerization the soluble materials we obtain may contain significant non-ring-opened groups that with the longer polymerization times result in extensive cross-linking to form the insoluble materials recovered.

Due to the poor solubility of the polymers in dichloromethane, their CVs were recorded in 0.1 M TBAP/THF solution. Only broad oxidation and reduction waves [$E_{ox} = 0.75-0.85$ V, $E_{red} = 0.35-0.45$ V] were noted rather than the two distinct waves typical of ferrocenylenesilylene polymers (Figure 6b). The poor resolution due to overlapping of the two reversible waves is typical of $-[FCSiR_2]_n-$ polymers when recorded in polar solvents where the stabilization of the initial charge by the solvent restricts its capacity to be transmitted to an adjacent ferrocenylene center.[5e,h,16]

Powder diffraction X-ray analysis of **7a** and **8a** revealed their amorphous nature, while polymer **11a** showed semicrystalline behavior similar to related polymers.[2]

Experimental Procedures

All experiments were performed under an atmosphere of dry N_2 using Schlenk techniques. THF and *n*-hexanes were distilled from sodium benzophenone ketyl immediately prior to use; **FC**$(SiMe_2CH_2CH{=}CH_2)_2$ (**2**) and **FC**$[SiMe_2(CH_2)_4CH{=}CH_2]_2$ (**3**) were prepared by following the procedure reported for **FC**$(SiMe_2CH{=}CH_2)_2$[10] (**1**). Starting reagents $MeSiHCl_2$, $O(SiMe_2CH{=}CH_2)_2$, $O(SiMe_2\text{-}C{\equiv}CH)_2$, and Karstedt's catalyst were purchased from Gelest or Aldrich and used as received. Cyclic voltammetric measurements were performed using a Perkin-Elmer potentiostat/galvanostat CV (model 263A) analyzer. The electrochemical cell comprised a glassy-carbon working electrode, a silver wire reference electrode, and a silver wire counter electrode. All measurements were made in a dry N_2 atmosphere; oxidation potentials were referenced to the Ag/AgCl couple. ^1H, ^{13}C, and ^{29}Si NMR were recorded in C_6D_6 and THF-d_8 on a Bruker DPX-300 at 300, 75.4, and 59.6 MHz, respectively. Elemental analysis was performed at Galbraith Laboratories. Powder X-ray diffraction experiments were performed on an XDS 2000 Scientific Inc. USA instrument. The experiments were done in the range 5−50 θ using step size 0.020 and a scan rate of 0.01 deg/min.

Synthesis. FC$[SiMe_2(CH_2)_4CH{=}CH_2]_2$ (3). 3 was synthesized by following a procedure similar to that reported for **FC**-$[SiMe_2CH{=}CH_2]_2$ (**1**)[10] [**FC**$Li_2\cdot$tmeda, 0.011 mol; $ClSiMe_2(CH_2)_4CH{=}CH_2$, 3.88 g (0.022 mol); yield: 4.62 g (0.009 mol, 90%)]. Anal. Calcd for $C_{26}H_{42}FeSi_2$: C 66.92, H 9.07. Found: C 66.50, H 8.95.

^{1}HNMR: δ 0.34 (s, 12H, $SiMe_2$), 0.73 (4H, $SiCH_2$), 1.46 (8H, CH_2), 2.10 (4H, CH_2), 4.10 (4H, C_5H_4), 4.32 (4H, C_5H_4), 5.10 (m, 4H, $=CH_2$), 5.85 (m, 2H, $CH=$). ^{13}C NMR: δ −1.93 ($SiMe_2$), 17.1, 23.9, 33.1, 33.9 (CH_2), 68.4, 71.4, 73.2 (C_5H_4), 114.5, 139.1 ($CH{=}CH_2$). ^{29}Si NMR: δ −2.07 (**FC**$SiMe_2$).

FC$[SiMe_2(CH_2)_2SiMeCl_2]_2$ (4). To a ~20 mL toluene solution of **FC**-$[SiMe_2CH{=}CH_2]_2$ (0.35 g, 1.00 mmol) was added freshly distilled $MeSiHCl_2$ (0.28 g, 2.50 mmol) via syringe. The resulting mixture was stirred at room temperature for 5 min, and then 2−3 drops of a 7 mol % xylene solution of Karstedt's catalyst was added. The reaction mixture was refluxed for 4−6 h, and the reaction was monitored by ^{29}Si NMR spectroscopy. The solvent was evaporated after completion of the reaction, and ~10 mL of hexanes was added to the mixture. The resulting solution was filtered. The filtrate was evaporated under vacuum, and the product was isolated as a red oil in analytically pure form (0.49 g, 0.85 mmol, 85% yield). No further purification was performed. Anal. Calcd for $C_{20}H_{34}Cl_4FeSi_4$: C 41.10, H 5.86. Found: C 41.01 H 5.64. ^{1}HNMR: δ 0.30 (s, 12H, $SiMe_2$), 0.57 (s, 6H, SiMe), 0.83 (4H, CH_2), 1.03 (4H, CH_2), 4.09 (4H, C_5H_4), 4.33 (4H, C_5H_4). ^{13}C NMR: δ −2.26 ($SiMe_2$), 4.21 ($SiMeCl_2$), 8.26, 14.8 ($SiCH_2$), 69.9, 71.7, 73.3 (C_5H_4). ^{29}Si NMR: δ −0.01 (**FC**$SiMe_2$), 33.6 ($SiMeCl_2$).

In a similar manner the following complexes were prepared using the amounts of reagent noted:

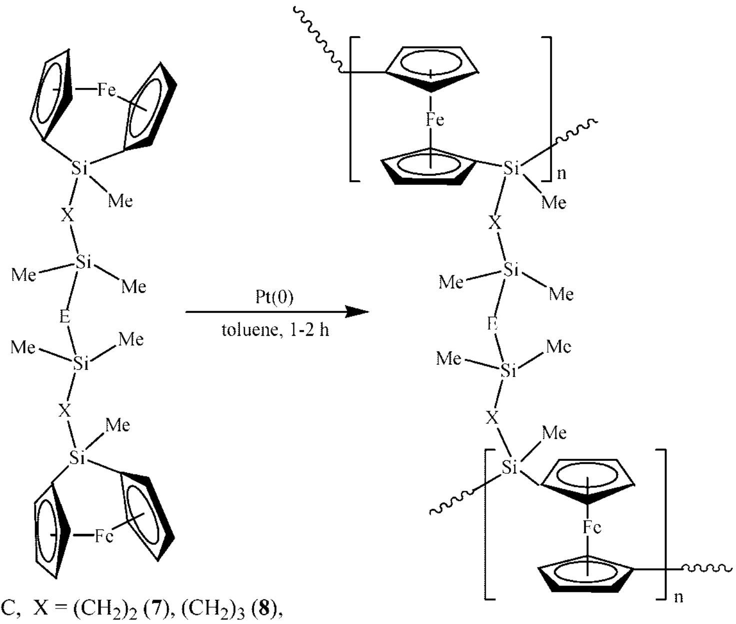
FC$[SiMe_2(CH_2)_3SiMeCl_2]_2$ (5). FC$[SiMe_2CH_2CH{=}CH_2]_2$ (0.38 g, 1.00 mmol) and $MeSiHCl_2$ (0.28 g, 2.50 mmol) were used. The product was isolated as a red oil (0.56 g, 0.92 mmol, 92%). Anal. Calcd for $C_{22}H_{38}Cl_4FeSi_4$: C 43.14, H 6.25. Found: C 43.01 H 6.12.

^1H NMR: δ 0.30 (s, 12H, $SiMe_2$), 0.52 (s, 6H, SiMe), 0.76 (4H, CH_2), 1.02 (4H, CH_2), 1.62 (4H, CH_2), 4.12 (4H, C_5H_4), 4.34 (4H, C_5H_4). ^{13}C NMR: δ −2.06 ($SiMe_2$), 5.20 ($SiMeCl_2$), 17.3, 21.4, 25.6 (CH_2), 69.2, 72.1, 73.6 (C_5H_4). ^{29}Si NMR: δ −2.59 (**FC**$SiMe_2$), 32.5 ($SiMeCl_2$).

FC$[SiMe_2(CH_2)_6SiMeCl_2]_2$ (6). FC$[SiMe_2(CH_2)_4CH{=}CH_2]_2$ (0.46 g, 1.00 mmol) and $MeSiHCl_2$ (0.28 g, 2.50 mmol) were used. The product was obtained as a red oil (0.66 g, 0.95 mmol, 95%). Anal. Calcd for $C_{28}H_{50}Cl_4FeSi_4$: C 48.27, H 7.23. Found: C 48.15, H 7.09.

^1H NMR: δ 0.36 (s, 12H, $SiMe_2$), 0.52 (s, 6H, SiMe), 0.76 (4H, $SiCH_2$), 0.91 (4H, $SiCH_2$), 1.30−1.43 (16H, CH_2), 4.13 (4H, C_5H_4),

Scheme 4



E = FC, X = $(CH_2)_2$ (**7**), $(CH_2)_3$ (**8**), $(CH_2)_6$ (**9**)
E = O, X = $(CH_2)_2$ (**11**), CH=CH (**13**)

E = FC, X = $(CH_2)_2$ (**7a**), $(CH_2)_3$ (**8a**), $(CH_2)_6$ (**9a**)
E = O, X = $(CH_2)_2$ (**11a**), CH=CH (**13a**)

Table 1. Crystal Data and Structure Refinement of $O[SiMe_2(CH_2)_2SiMeFC]_2$ (11)

formula	$C_{30}H_{42}Fe_2OSi_4$
fw	642.70
cryst syst	monoclinic
space group	$P2(1)/c$
a (Å)	8.614(5)
b (Å)	18.296(11)
c (Å)	10.853(6)
α (deg)	90
β (deg)	107.453(13)
γ (deg)	90.00
V (Å^3)	1631.7(17)
Z	2
ρ_{calc} (g cm^{-3})	1.308 Mg/m^3
μ(Mo Kα) (mm^{-1})	1.057 mm^{-1}
F(000)	676
T (K)	298(2)
$2\theta_{max}$ (deg), completeness (%)	52.6, 99.5
index ranges: $-h +h, -k +k, -l +l$	−10 9, −22 22, −13 13
total number reflns	9147
indep reflns [R_{int}]	3300 [0.0295]
refinement methods	full-matrix least-squares on F^2
data/restraints/params	3300/0/175
goodness-of-fit on F^2	1.120
R_1 [$I > 2\sigma(I)$]	0.0434
largest diff peak and hole (e·Å^{-3})	0.527 and 0.293

4.35 (4H, C_5H_4). ^{13}C NMR: δ −1.98 ($SiMe_2$), 4.90 ($SiMeCl_2$), 17.2, 21.6, 23.5, 24.2, 32.3, 33.3 (CH_2), 68.5, 71.5, 73.3 (C_5H_4). ^{29}Si NMR: δ −2.07 (**FC**$SiMe_2$), 33.0 ($SiMeCl_2$).

$O[SiMe_2(CH_2)_2SiMeCl_2]_2$ (10). $O[SiMe_2CH{=}CH_2]_2$ (0.18 g, 1.00 mmol) and $MeSiHCl_2$ (0.28 g, 2.50 mmol) were used. The product was obtained as a colorless oil (0.39 g, 0.95 mmol, 95%). Anal. Calcd for $C_{10}H_{26}Cl_4OSi_4$: C 28.84, H 6.29. Found: C 28.68, H 6.30.

^{1}H NMR: δ 0.09 (s, 12H, $SiMe_2$), 0.63 (s, 6H, SiMe), 0.99 (br, 8H, CH_2). ^{13}C NMR: δ −0.13 ($SiMe_2$), 4.31 ($SiMeCl_2$), 8.44, 14.1 ($SiCH_2$). ^{29}Si NMR: δ 8.34 (O-$SiMe_2$), 33.7 ($SiMeCl_2$).

$O[SiMe_2CH{=}CHSiMeCl_2]_2$ (12)[21]. $O[SiMe_2C{\equiv}CH]_2$ (0.18 g (1.00 mmol) and $MeSiHCl_2$ (0.28 g, 2.50 mmol) were used. The product was obtained as a colorless oil (0.37 g, 0.90 mmol, 90%). Anal. Calcd for $C_{10}H_{24}Cl_4OSi_4$: C 28.98, H 5.84. Found: C 28.80 H 5.67.

Table 2. Bond Lengths [Å] and Angles [deg] for $O[SiMe_2(CH_2)_2SiMeFC]_2$ (11)

Si(1)−C(1)	1.903(3)	Si(2)−O(1)[a]	1.657(13)
Si(1)−C(6)	1.915(3)	Si(2)−C(13)	1.870(3)
Si(1)−C(11)	1.871(4)	Si(2)−C(14)	1.872(4)
Si(1)−C(12)	1.878(3)	Si(2)−C(15)	1.865(5)
Si(2)−O(1)	1.655(13)	O(1)−Si(2A)[b]	1.657(13)
C(1)−Si(1)−C(6)	95.69(14)	C(14)−Si(2)−C(15)	109.7(2)
C(1)−Si(1)−C(11)	111.98(18)	O(1)−Si(2)−C(13)	102.4(5)
C(1)−Si(1)−C(12)	112.10(15)	O(1)[a]−Si(2)−C(13)	113.4(5)
C(6)−Si(1)−C(11)	112.41(18)	O(1)−Si(2)−C(14)	102.3(4)
C(6)−Si(1)−C(12)	110.40(16)	O(1)[a]−Si(2)−C(14)	115.4(5)
C(11)−Si(1)−C(12)	113.06(19)	O(1)−Si(2)−C(15)	121.4(3)
C(13)−C(12)−Si(1)	115.5(2)	O(1)[a]−Si(2)−C(15)	97.3(3)
C(12)−C(13)−Si(2)	114.5(2)	C(14)−Si(2)−C(13)	109.7(2)
C(13)−Si(2)−C(15)	110.34 (19)	Si(2)−O(1)−Si(2A)[b]	155.8(4)

[a] This is the disordered oxygen generated by the symmetry transformation outlined in the following footnote. [b] Symmetry transformations used to generate equivalent atoms: $-x+1, -y+1, -z+1$.

^{1}H NMR: δ 0.17 (s, 12H, $SiMe_2$), 0.63 (s, 6H, SiMe), 6.74 (4H, CH═CH). ^{13}C NMR: δ 0.09 ($SiMe_2$), 4.57 ($SiMeCl_2$), 142.8, 156.5 (CH═CH). ^{29}Si NMR: δ −2.65 ($SiMe_2$), 15.2 ($SiMeCl_2$).

FC$[SiMe_2(CH_2)_2SiMeFC]_2$ (7). To ~50 mL of a THF solution containing **FC**Li_2·tmeda (1.00 mmol) was added **FC**$[SiMe_2(CH_2)_2SiMeCl_2]_2$ (0.29 g, 0.50 mmol) at −78 °C, and the solution was allowed to warm to RT and stirred for 3 h. The THF was removed under vacuum, and the product was extracted with hexanes. The extract was filtered and dried. An orange-red solid was isolated and purified by recrystallization from a toluene/hexanes mixture and characterized as **7** (yield 0.56 g, 0.7 mmol, 70%). Anal. Calcd for $C_{40}H_{50}Fe_3Si_4$: C 59.26, H 6.22. Found: C 58.85 H 6.30.

^{1}HNMR (C_6D_6): δ 0.45 (s, 12H, $SiMe_2$), 0.51 (s, 6H, SiMe), 0.95−1.06 (8H, CH_2), 4.11- 4.52 (24H, C_5H_4). ^{13}C NMR (C_6D_6): δ −5.70 (SiMe), −2.24 ($SiMe_2$), 5.38, 7.93 ($SiCH_2$), 33.6 (*ipso*-C_5H_4), 68.4, 71.6, 73.4 ($C_5H_4SiMe_2$), 75.5, 75.9, 77.5, 77.7 ($SiMeC_5H_4$). ^{29}Si NMR (C_6D_6): δ −1.11 (SiMe*FC*), 0.29 (**FC**$SiMe_2$). UV/vis (THF): λ_{max} = 472 nm (ϵ = 260 M^{-1} cm^{-1}).

In a similar manner the following were prepared from the appropriate starting materials:

FC[SiMe$_2$(CH$_2$)$_3$SiMeFC]$_2$ (8): orange-red semisolid; yield 0.54 g (0.65 mmol, 65%). Anal. Calcd for $C_{42}H_{54}Fe_3Si_4$: C 60.14, H 6.49. Found: C 59.75 H 6.39.

^{1}HNMR (C_6D_6): δ 0.39 (s, 12H, SiMe$_2$), 0.50 (s, 6H, SiMe), 1.06−1.87 (12H, CH$_2$), 4.19−4.53 (24H, C_5H_4). ^{13}C NMR (C_6D_6): δ −4.79 (SiMe), −1.76 (SiMe$_2$), 17.6, 18.0, 21.4 (CH$_2$), 32.7 (*ipso*-C_5H_4), 68.2, 71.1, 73.2 (C_5H_4-SiMe$_2$), 75.6, 75.8, 77.5, 77.7 (SiMeC_5H_4). ^{29}Si NMR (C_6D_6): δ −3.85 (SiMeFC), −2.63 (**FC**-SiMe$_2$). UV/vis (THF): $\lambda_{max} = 470$ nm ($\epsilon = 250$ M^{-1} cm^{-1}).

FC[SiMe$_2$(CH$_2$)$_6$SiMeFC]$_2$ (9): orange-red semisolid; yield 0.59 g (0.65 mmol, 65%). Anal. Calcd for $C_{48}H_{66}Fe_3Si_4$: C 62.47, H 7.21. Found: C 62.30, H 7.25.

^{1}H NMR (C_6D_6): δ 0.40 (s, 12H, SiMe$_2$), 0.51 (s, 6H, SiMe), 0.87 (4H, SiCH$_2$), 1.03 (4H, SiCH$_2$), 1.40−1.60 (16H, CH$_2$), 4.14−4.55 (24H, C_5H_4). ^{13}C NMR (C_6D_6): δ − 2.22 (SiMe), −1.82 (SiMe$_2$), 13.9, 17.3, 23.1, 23.4, 24.4, 35.3 (CH$_2$), 33.7 (*ipso*-C_5H_4), 68.8, 71.5, 73.3 (C_5H_4-SiMe$_2$), 75.6, 75.8, 77.6, 77.8 (SiMeC_5H_4). ^{29}Si NMR (C_6D_6): δ − 3.30 (SiMe*FC*), −2.05 (**FC**SiMe$_2$). UV/vis (THF): $\lambda_{max} = 472$ nm ($\epsilon = 240$ M^{-1} cm^{-1}).

O[SiMe$_2$(CH$_2$)$_2$SiMeFC]$_2$ (11): orange-red solid; yield 0.48 g (0.75 mmol, 75%). Anal. Calcd for $C_{30}H_{42}Fe_2OSi_4$: C 56.06, H 6.59. Found: C 56.11 H 6.69.

^{1}HNMR (C_6D_6): δ 0.31 (s, 12H, SiMe$_2$), 0.52 (s, 6H, SiMe), 0.94 (4H, CH$_2$), 1.13 (4H, CH$_2$), 4.16, 4.52 (16H, C_5H_4). ^{13}C NMR (C_6D_6): δ −5.73 (SiMe), 0.06 (SiMe$_2$), 4.85, 9.31 (SiCH$_2$), 33.5 (*ipso*-C_5H_4), 75.6, 76.0, 77.6, 77.8 (C_5H_4). ^{29}Si NMR (C_6D_6): δ −1.12 (SiMe*FC*), 8.65 (SiMe$_2$). UV/vis (THF): $\lambda_{max} = 470$ nm ($\epsilon = 240$ M^{-1} cm^{-1}).

O[SiMe$_2$CH═CHSiMeFC]$_2$ (13): orange-red semisolid; yield 0.43 g (0.68 mmol, 68%). Anal. Calcd for $C_{30}H_{38}Fe_2OSi_4$: C 56.42, H 6.00. Found: 55.91, H 5.92.

^{1}HNMR (C_6D_6): δ 0.41 (s, 12H, SiMe$_2$), 0.50 (s, 6H, SiMe), 4.14−4.55 (16H, C_5H_4), 6.71 (4H, CH═CH). ^{13}C NMR (C_6D_6): δ − 3.82 (SiMe), −0.76 (SiMe$_2$), 31.9 (*ipso*-C_5H_4), 72.0, 73.4, 75.9, 77.8 (SiMeC_5H_4), 145.7, 154.6 (CH═CH). ^{29}Si NMR (C_6D_6): δ −12.8 (SiMe$_2$), −3.55 (SiMe*FC*). UV/vis (THF): $\lambda_{max} = 465$ nm ($\epsilon = 230$ M^{-1} cm^{-1}).

Pt(0)-Catalyzed Polymerization. –{FC[SiMe$_2$CH$_2$CH$_2$SiMe-*FC*]$_2$}$_n$– (7a). To a ~2.0 mL toluene solution of **7** (0.11 g) in a Schlenk tube was added 2−3 drops of a 7 mol % xylene solution of Karstedt's catalyst. The solution was then stirred at room temperature for 1 h. The viscosity of the solution increased during polymerization. The polymer was then precipitated into hexanes, filtered, and washed until all the unreacted monomer washed off. The brown solid was isolated and dried under vacuum overnight and characterized as polymer **7a** (yield 45%).

^{1}H NMR (THF-*d*$_8$): δ 0.21 (s, 12H, SiMe$_2$), 0.38 (s, 6H, SiMe), 0.64 (8H, CH$_2$), 4.05- 4.22 (24H, C_5H_4). ^{13}C NMR (THF-*d*$_8$): δ − 3.87 (SiMe$_2$), −2.30 (SiMe), 8.01, 9.55 (SiCH$_2$), 67.5, 70.5, 72.3 (FC). ^{29}Si NMR (THF-*d*$_8$): δ 3.42, 9.05.

The syntheses of polymers **8a**, **9a**, **11a**, and **13a** were carried out in a similar manner, and all the products were isolated as brown solid materials in 40−50% yield.

–{FC[SiMe$_2$(CH$_2$)$_3$SiMeFC]$_2$}$_n$– (8a). ^{1}H NMR (THF-*d*$_8$): δ 0.29 (s, 12H, SiMe$_2$), 0.33 (s, 6H, SiMe), 0.82−0.94 (12H, CH$_2$), 4.08−4.28 (24H, C_5H_4). ^{13}C NMR (THF-*d*$_8$): δ −2.08 (SiMe$_2$), −1.65 (SiMe), 14.0, 18.6, 21.7 (CH$_2$), 68.5, 71.5, 73.2 (C_5H_4) ^{29}Si NMR (THF-*d*$_8$): δ − 5.65, 3.05.

–{FC[SiMe$_2$(CH$_2$)$_6$SiMeFC]$_2$}$_n$– (9a). ^{1}H NMR (THF-*d*$_8$): δ 0.28 (s, 12H, SiMe$_2$), 0.35 (s, 6H, SiMe), 0.90 (4H, SiCH$_2$), 0.99 (4H, SiCH$_2$), 1.02−1.35 (16H, CH$_2$), 4.10−4.60 (24H, C_5H_4). ^{13}C NMR (THF-*d*$_8$): δ −2.08 (SiMe), −1.21 (SiMe$_2$), 11.5, 18.7, 20.7, 22.6, 23.0, 34.9 (CH$_2$), 68.6, 71.5, 73.3 (C_5H_4). ^{29}Si NMR (THF-*d*$_8$): δ −6.60, −3.12.

–{O[SiMe$_2$CH$_2$CH$_2$SiMeFC]$_2$}$_n$– (11a). ^{1}H NMR (THF-*d*$_8$): δ −0.01 (s, 12H, SiMe$_2$), 0.02 (s, 6H, SiMe), 0.82 (4H, CH$_2$), 1.20 (4H, CH$_2$), 4.04−4.22 (16H, C_5H_4). ^{13}C NMR (THF-*d*$_8$): δ −2.70 (SiMe), −2.01 (SiMe$_2$), 8.51, 11.9 (SiCH$_2$), 68.6, 69.3, 71.6 (C_5H_4). ^{29}Si NMR (THF-*d*$_8$): δ −3.53, 8.84.

–{O[SiMe$_2$CH═CHSiMeFC]$_2$}$_n$– (13a). ^{1}H NMR (THF-*d*$_8$): δ 0.18 (s, 12H, SiMe$_2$), 0.29 (s, 6H, SiMe), 4.10−4.26 (16H, C_5H_4), 6.80 (4H, CH═CH). ^{13}C NMR (THF-*d*$_8$): δ −1.97 (SiMe), −1.34 (SiMe$_2$), 68.3, 69.8, 71.7 (C_5H_4), 147.3, 149.3 (CH═CH); ^{29}Si NMR (THF-*d*$_8$): δ − 10.5, −1.17.

X-ray Crystallography. A crystal of **11** suitable for X-ray analysis was mounted on a Bruker APEX CCD diffractometer equipped with monochromatized Mo Kα radiation. Crystallographic measurements were carried out at 296(2) K. The details of the crystal data and refinement parameters are described in Table 1, and the bond lengths and angles are listed in Table 2. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 values for all reflections using the SHELXL-97 (Sheldrick, 1997) program. All non-hydrogen atoms were assigned anisotropic displacement parameters, and hydrogen atoms were constrained to ideal geometries with fixed isotropic displacement parameters.

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Supporting Information Available: Crystallographic data in CIF format for **11** (CCDC 690523). This material is available free of charge via the Internet at http://pubs.acs.org.

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